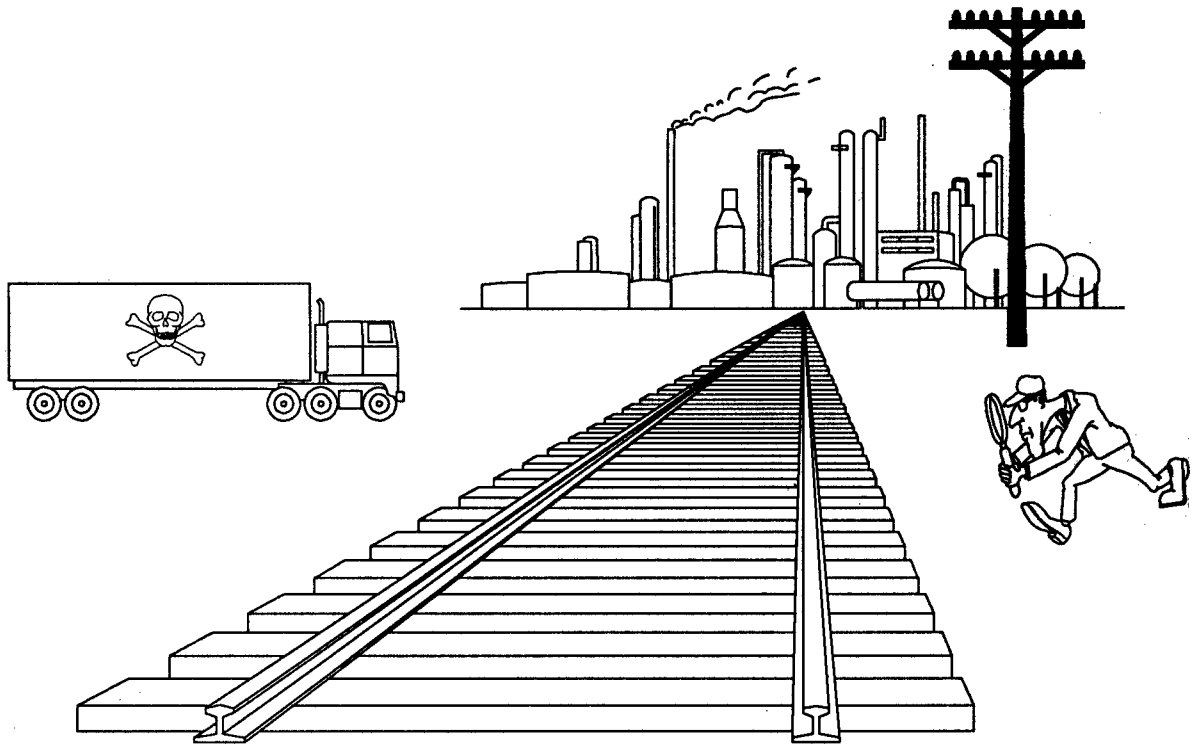
HANDBOOK OF CHEMICAL HAZARD ANALYSIS PROCEDURES



FEDERAL EMERGENCY MANAGEMENT AGENCY

U.S. DEPARTMENT OF TRANSPORTATION

U.S. ENVIRONMENTAL PROTECTION AGENCY

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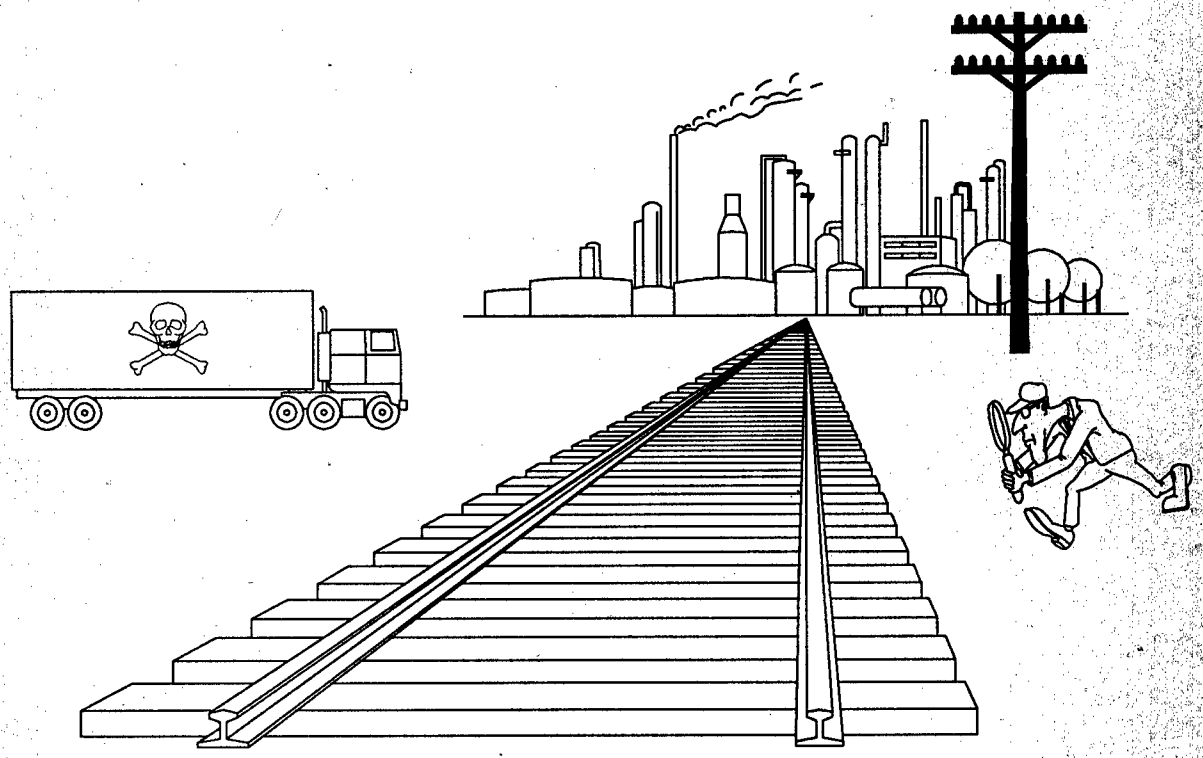

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FOREWORD

Introduction

The Federal Government has a long record of concern about hazardous materials and their potential impact on people and the environment. Over the years, several Federal agencies have provided training, technical assistance and guidance to State and local governments and industry in planning and response to emergencies involving hazardous materials. For example, the Federal Emergency Management Agency (FEMA) published the *Planning Guide and Checklist for Hazardous Materials Contingency Plans* (FEMA-10) in 1981 to assist communities developing emergency response plans. The Department of Transportation (DOT) has published several editions of the *Emergency Response Guidebook* to serve as guidance for initial action to be taken by fire fighters, police, and emergency services personnel at the scene of transportation incidents involving hazardous materials. In 1985, the Environmental Protection Agency (EPA) published *Chemical Emergency Preparedness Program* (CEPP) *Interim Guidance* to provide technical assistance for a voluntary program focusing on airborne toxic chemicals under EPA's National Strategy for Toxic Air Pollutants.

Government-wide guidance on emergency planning for hazardous material was introduced in 1987 after the passage of Title III of the Superfund Amendments and Reauthorization Act (SARA) with the publication of the National Response Team's *Hazardous Materials Emergency Planning Guide* (NRT-1). This effort to coordinate Federal planning processes concerning specific hazardous materials addressed by SARA was followed with the joint publication by EPA, FEMA and DOT of *Technical Guidance for Hazards Analysis*.

Handbook of Chemical Hazards Analysis Procedures

This *Handbook of Chemical Hazard Analysis Procedures* has several objectives one of which is to expand *NRT-1* and the *Technical Guidance on Hazards Analysis* document by including information for explosive, flammable, reactive and otherwise dangerous chemicals. Although *NRT-1* was aimed at addressing planning for all types of hazardous materials, SARA Title III required local planners to focus on a specific initial list of acutely toxic chemicals (referred to as Extremely Hazardous Substances) due to their high inhalation toxicity when airborne, and this was the primary focus of the supplemental guidance document. By introducing additional methodologies on how to plan for these and other dangerous chemicals, this handbook serves as a stepping stone from *NRT-1* and the *Technical Guidance on Hazards Analysis* to a more comprehensive approach for emergency planning. If deemed necessary and appropriate by the National Response Team after distribution and field use of this handbook by emergency planning personnel, a further enhanced hazard analysis guide may be prepared in the future.

Because this handbook provides methods to investigate local hazards in greater detail than permitted by earlier guidance, results of calculations using air dispersion models may differ. The Federal Government is continuing to evaluate these types of models and others to determine the degree of impact on calculations concerning the consequences of a chemical release. For these reasons and because this handbook requires use of the accompanying software for full utilization, users should carefully assess accident scenarios selected for evaluation to ensure that computational procedures are appropriate for the chemical being

studied. Difficulties encountered and suggestions or comments (both positive and negative) should be submitted to DOT, FEMA, and/or the EPA. Be advised that workshops are being planned by these Agencies during 1989 to address comments, gather input on the handbook and the related software, and explain their functions. Similarly, DOT, FEMA and EPA are interested in receiving information on problems and experiences associated with use of the *Technical Guidance on Hazards Analysis* document and NRT-1.

Beyond providing additional methodologies for assessing the potential impacts of hazardous material releases, this handbook also expands the three-step hazards analysis approach (hazard identification, vulnerability analysis, and risk analysis) presented in *NRT-1* and its supplement by introducing a four-step approach involving hazard identification, consequence analysis, probability analysis, and risk analysis. In addition, it provides a tutorial on hazardous chemicals, suggestions for applying hazard analysis results to writing and updating an emergency plan, and an expanded discussion of issues relating to sheltering-in-place (in-place protection) and evacuation. **Because additional projects are underway concerning these and other topics described in Chapter 14 and Appendix C of the handbook, sponsoring agencies are especially interested in comments on these sections. The workshops mentioned above will provide an opportunity for discussion and comment. General comments on the handbook, its associated computer program named ARCHIE, and earlier planning aids are highly encouraged and may also be submitted in writing to:**

Federal Emergency Management Agency
Technological Hazards Division
Federal Center Plaza
500 C Street, S.W.
Washington, DC 20472

U.S. Department of Transportation
Research and Special Programs Administration
Office of Hazardous Materials Transportation
DHM-50, 400 7th Street, S.W.
Washington, DC 20590

U.S. Environmental Protection Agency
Chemical Emergency Preparedness and Prevention Office
401 M Street, S.W., 0S-120
Washington, DC 20460

Alternatively, input to these agencies may be transmitted via use of the Hazardous Materials Information Exchange (HMIX) computerized bulletin board system operated and maintained by FEMA and the DOT. HMIX includes a Conference dedicated to ARCHIE where users may leave messages, questions or comments relating to the program or handbook, exchange viewpoints, and receive responses to inquiries. HMIX may be accessed by modem and commercial phone line at:

(312) 972-3275

An HMIX users manual and technical assistance can be obtained by calling:

1-800-PLAN-FOR Nationwide

or

1-800-367-9592 in Illinois

If you are unable to access HMIX to submit comments or questions relating specifically to the computer program, please send them in writing to:

ARCHIE Support (DHM-51/Room 8104)
Office of Hazardous Materials Transportation
Research and Special Programs Administration
U.S. Department of Transportation
400 7th Street, S.W.
Washington, D.C. 20590

Additional copies of this handbook maybe obtained by writing to:

Federal Emergency Management Agency
Publications Office
500 C Street, S.W.
Washington, D.C. 20472

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1.0 INTRODUCTION

1.1 BACKGROUND

The fact that hazardous materials pose a threat to public safety and the environment is of vital concern to industry and all levels of government, particularly in the aftermath of the tragedy in Bhophal, India, that took over 2000 lives and injured tens of thousands of others in the course of a few hours. Although the safety record of the oil and gas and chemical manufacturing and transportation industries in the United States has been excellent in recent years, and there has not been a similar catastrophic accident or incident with major loss of life in the United States in several decades, there is nevertheless a clear need for constant vigilance on the part of government agencies and those responsible for the movement and handling of hazardous materials to minimize the possibility of significant discharges to the external environment. Similarly, there is a clear and possibly even more urgent need to ensure that both government and industry are prepared to respond quickly, efficiently, and effectively in the event of an accident to reduce or prevent adverse impacts on public safety and the environment. Time is critical in the first moments of an accident. A mismanaged response due to a lack of preplanning can contribute to the causation of fatalities and injuries as well as an increase in damage to property and the environment.

The primary purpose of this handbook and its associated computer program is to provide emergency planning personnel with the resources necessary to undertake comprehensive evaluations of potentially hazardous facilities and activities within their respective jurisdictions and thereby formulate a basis for their planning efforts. Chapters 2 through 8 of the handbook discuss fundamental definitions and concepts relating to hazardous material properties and associated threats to public safety. Chapter 9 provides an *overview* of the overall hazard analysis process required to identify, characterize, and evaluate the subject threats. Chapter 10 follows with specific guidance relating to hazard identification while Chapter 11 provides assistance in evaluating the likelihood that any given accident or incident will actually occur in the foreseeable future. Chapter 12 describes and discusses the ***Automated Resource for Chemical Hazard Incident Evaluation*** (ARCHIE) computer program and how it may be used to conduct consequence analysis for postulated accident scenarios. Chapter 13 next guides the user through a simplified risk analysis procedure designed to provide a planning basis, while Chapter 14 provides guidance on how results of the overall hazard analysis process may be utilized in development of a comprehensive emergency response plan.

Several appendices to the handbook provide additional guidance and details. Appendix A is a tutorial on fundamental mathematical skills. Appendix B presents an overview of the technical basis for consequence analysis procedures, while Appendix C provides an overview of "Shelter-in-Place" concepts. Appendix D follows with the presentation of a chemical

compatibility chart for potentially reactive materials. Appendix E is a guide to installation of the ARCHIE computer program, while Appendix F ends the handbook with the basis for accident/incident probability analysis procedures.

1.2 RELATED PLANNING GUIDES AND DOCUMENTS

Multi-Agency Publications of the Federal Government

The National Response Team (NRT) is comprised of representatives of 14 federal agencies having major responsibilities for issues involving the environment, transportation, and public health and safety. It is the primary body in the United States charged with responsibility for planning, preparedness, and response actions related to spills or discharges of oil and hazardous materials into the environment.

The NRT published the Hazardous Materials Emergency Planning Guide in March 1987 as document NRT-1. This guide provides a fairly detailed overview of the efforts required for:

- Selecting and organizing an emergency planning team
- Defining the tasks of the planning team
- Developing an emergency plan and individual plan elements
- Appraising, testing, and maintaining the plan

The guide focuses on the needs and requirements of public authorities in local and state governments but also contains useful information for industrial planning personnel in terms of the basic elements of the planning process. Additionally, it provides insights into those issues of concern to public authorities and the importance of cooperation and coordination of emergency planning activities between the public and private sectors. Copies of the guide are available by writing:

Hazardous Materials Emergency Planning Guide
OS-120
401 M Street, S.W.
Washington, D.C. 20460

Subsequent to completion and distribution of NRT-1, the U.S. Environmental Protection Agency (EPA), in conjunction with the Federal Emergency Management Agency (FEMA) and the U.S. Department of Transportation (DOT), published ***Technical Guidance for Hazards Analysis -- Emergency Planning for Extremely Hazardous Substances*** to fulfill obligations mandated by the Superfund Amendments and Reauthorization Act (SARA) of 1986. Focusing primarily on the hazards associated with a specific list of highly toxic substances deemed to pose acute inhalation hazards when discharged into the atmosphere,

the guide provides simplified guidance for hazard identification, vulnerability analysis, and risk analysis of facilities subject to reporting requirements under Title III of SARA. Additionally, the document contains a simplified screening procedure for ranking the threats due to designated Extremely Hazardous Substances (EHS) in a community. Copies may be obtained by writing the same address given above for NRT-1.

Publications of the Federal Emergency Management Agency

The Federal Emergency Management Agency (FEMA) publishes the ***Guide for Development of State and Local Emergency Operations Plans*** (CPG 1-8) and the ***Guide for Review of State and Local Emergency Operations Plans*** (CPG 1-8A), which provide information to emergency management personnel and state and local government officials about FEMA's concept of planning under the Integrated Emergency Management System (IEMS). This system emphasizes integration of planning for all types of hazards that pose a threat to a community and provides extensive guidance in the coordination, development, review, validation, and revision of emergency operations plans.

The concepts if not the specific details of FEMA's guidance are applicable to individual communities and chemical facilities in that many such sites may be subject to a variety of natural and technological hazards. Under a wide variety of circumstances, a single emergency plan that provides "umbrella coverage" for a locality can ensure increased efficiency and effectiveness of a planning effort by reducing duplication of common activities.

FEMA, in conjunction with DOT and the EPA, has also published a wide variety of emergency planning guidance documents relating to emergencies involving nuclear power plants, the transportation of radioactive materials, and natural disasters. A sample of planning aids that address hazardous materials include:

- ***Hazardous Materials Contingency Planning Course (student manuals)***
- ***Disaster Planning Guidelines for Fire Chiefs***
- ***Disaster Operations: A Handbook for Local Governments***
- ***Objectives for Local Emergency Management***

Publications of the Federal Emergency Management Agency relating to a wide variety of threats to public health and safety can be obtained by writing:

Federal Emergency Management Agency
Publications Office
500 C Street, S.W.
Washington, D.C. 20472

Publications of the U.S. Department of Transportation

The U.S. Department of Transportation (DOT) has sponsored a large number of research studies and demonstration projects related to planning for transportation emergencies involving hazardous materials over the years. Appendix E of NRT-1 contains a fairly comprehensive list of resulting reports. A representative sample of current and past available titles includes:

- ***Community Teamwork: Working Together to Promote Hazardous Materials Transportation Safety -- A Guide for Local Officials***
- ***A Community Model for Handling Hazardous Materials Transportation Emergencies***
- ***Risk Assessment Users Manual for Small Communities and Rural Areas***
- ***Manual for Small Towns and Rural Areas to Develop a Hazardous Materials Emergency Plan; with an Example Application of the Methodology in Developing a Generalized Emergency Plan for Riley County, Kansas***
- ***Community Model for Handling Hazardous Material Transportation Emergencies: Executive Summaries***
- ***Hazardous Materials Demonstration Project Report: Puget Sound Region***
- ***Hazardous Materials Hazard Analysis: Portland, Oregon***
- ***Hazardous Materials Management System: A Guide for Local Emergency Managers***
- ***Lessons Learned: A Report on the Lessons Learned from State and Local Experiences in Accident Prevention and Response Planning for Hazardous Materials Transportation***

The *Community Teamwork* document may be obtained by writing to:

Office of Hazardous Materials Transportation
Attention: DHM-50
Research and Special Programs Administration
Department of Transportation
400 7th Street, S.W.
Washington, D.C. 20590

Information on the availability of the Hazardous Materials Management System Guide and other documents developed for the Portland, Oregon area can be obtained by writing:

Multinomah County Emergency Management
12240 N.E. Glizan
Portland, Oregon 97230

Most of the other publications and documents of a similar nature are available from the National Technical Information Service, 5285 Port Royal Road, Springfield, Virginia 22161 (telephone: 703-487-4650).

Publications of the U.S. Environmental Protection Agency

The EPA has published a series of documents to assist emergency planning personnel. Available titles include:

- ***Introduction to Exercises in Chemical Emergency Preparedness Programs***
- ***A Guide to Planning and Conducting Table-Top Exercises***
- ***A Guide to Planning and Conducting Field Simulation Exercises***
- ***Report of a Conference on Risk Communication and Environmental Management***
- ***Identifying Environmental Computer Systems for Planning Purposes***
- ***Chemicals in Your Community***

These documents may be obtained by writing:

Environmental Protection Agency
OS-120
401 M Street, S.W.
Washington, DC 20460

Publications of the Chemical Manufacturers Association

Even before SARA required the assignment of individual facility emergency coordinators to Local Emergency Planning Committees (LEPC's), the Chemical Manufacturers Association (CMA) established a Community Awareness and Emergency Response (CAER) program to encourage local chemical plant managers to take the initiative in cooperating with local communities in the development of integrated emergency plans for response to hazardous material incidents. The NRT guidance document cited above notes that knowledgeable chemical industry representatives can be especially helpful during the planning process and advises community planners to seek out local CMA/CAER program participants. More specifically, the document points out that many chemical plant officials are both willing and able to share equipment and personnel during emergency response operations.

The CMA publishes three documents that could prove considerably useful during the overall planning process, including:

- ***Community Awareness and Emergency Response Program Handbook***
- ***Site Emergency Response Planning***
- ***Community Emergency Response Exercise Program***

These publications are available at nominal cost from the CMA. Information on specific items can be obtained by calling (202) 887-1100 or writing:

Publications Fulfillment
Chemical Manufacturers Association
2501 M Street, N.W.
Washington, D.C. 20037

Publications of the AIChE Center for Chemical Process Safety

Established under the auspices of the American Institute of Chemical Engineers (AIChE), this being the primary professional society of chemical engineers in the United States, the Center for Chemical Process Safety has undertaken an ambitious program to promote and ensure safety at chemical plants. Initial efforts have involved the development and publication of a series of safety guideline documents. The first four titles below are complete and currently available to the public. The latter titles are expected to be published during 1989 or shortly thereafter.

- *Guidelines for Hazard Evaluation Procedures*
- *Guidelines for Safe Storage and Handling of High Toxic Hazard Materials*
- *Guidelines for Use of Vapor Cloud Dispersion Models*
- *Guidelines for Vapor Release Mitigation*
- *Guidelines for Chemical Process Quantitative Risk Assessment*
- *Guidelines for Technical Management of Chemical Process Safety*
- *Guidelines for Obtaining Process Equipment Reliability Data*
- *Guidelines for Human Reliability in Process Safety*
- *Guidelines for Process Control Safety*
- *Guidelines for Processing and Handling Reactive Chemicals*

Information on these and other AIChE publications is available from:

AIChE Publication Sales Department
345 East 47 Street
New York, NY 10017

Other Pertinent Publications

Besides the above fairly recent and generalized planning guides published by the federal government or industry trade associations, there are several other sources of general information and data available that may be helpful during the overall emergency planning process. Selected publications are listed and described in Chapter 14. Publications devoted to specific topics of possible interest to readers are referenced at appropriate locations throughout the chapters and appendices that follow.

2.0 KEY PROPERTIES OF CHEMICAL SUBSTANCES

SOLID LIQUID GAS

2.1 STATES OF MATTER

Most materials can exist in more than one physical state, a common example being ordinary water. It is well known that liquid water will freeze and become a solid at 32 degrees Fahrenheit (°F) at normal atmospheric pressure. The temperature of 32°F is known as the freezing point for this substance. Alternatively, this temperature can be referred to as its melting point. For water, both the freezing point and melting point are exactly the same and well-defined. This is true for most other substances, but there are exceptions to this general rule.

At 212°F, liquid water begins to boil at normal atmospheric pressure as it begins a transition or ***phase*** change from a liquid state to a vapor or gas. The specific temperature at which a liquid boils under a given set of environmental conditions is known as its boiling point temperature or ***boiling point*** for short. If the boiling takes place at normal atmospheric pressure, the more appropriate and accurate phrase to use is ***normal boiling point*** or boiling point at one atmosphere. The importance of qualifying the term boiling point with the words "normal" and "one atmosphere" will be discussed a bit later. For now, it is simply adequate to note that a great many materials in the environment have their own unique freezing/melting and normal boiling points which can be radically different than those of water. For example, the petroleum product known as butane, the flammable substance in most disposable lighters, has a normal boiling point of 31°F and will boil and rapidly vaporize if spilled as a liquid on a block of ice having a temperature of 32°F. A temperature of -216°F

would be required to solidify or freeze the butane to a solid, yet even this very low temperature would be insufficient to prevent boiling of such substances as liquid hydrogen, helium, nitrogen, and several others.

Not all substances, incidentally, can exist in all three states of matter in the natural environment. Some solids undergo a process called ***sublimation*** upon heating whereby the solid state directly transforms to a gaseous state without first becoming a liquid. A good example is solid carbon dioxide, also known as *"dry ice."* Carbon dioxide can only become a liquid in confinement under special conditions of storage.

2.2 DEFINITIONS OF TEMPERATURE AND HEAT

The discussion so far has demonstrated that the temperature of a substance can influence its form and properties. There is a great deal more to be said on the subject, however, so there is value in formal definition of important terms before proceeding. We start with the concept of ***temperature*** and the flow of heat and energy from one body to another.

The dictionary defines the temperature of a substance as its *"degree of hotness or coldness measured on a definite scale."* The key word here is ***scale***. In the United States, the scale with which we are most familiar is the Fahrenheit scale, and most of us are aware that most of the world uses the Celsius or Centigrade scale, this being a part of the metric system. Both of these temperature measurement systems are considered ***relative*** scales because key numbers are essentially the freezing point and boiling point of water at normal atmospheric pressure. These numbers are 32°F and 212°F respectively on the Fahrenheit scale and 0°C and 100°C on the Celsius scale. In order to convert from one scale to another, one of two common equations is used, these being:

$$\text{degrees F} = (1.8 \times \text{degrees C}) + 32$$

$$\text{degrees C} = (\text{degrees F} - 32)/1.8$$

It is also useful to know that a one degree *change* on the Celsius scale is equal to a 1.8° *change* on the Fahrenheit scale. Thus, a temperature rise of 18° on the Fahrenheit scale is equivalent to a rise of 10° on the Celsius scale.

Besides these two scales, there are two others that are commonly used in the scientific community and which are defined as ***absolute*** scales in the sense that zero degrees refers to an absolute lack of heat in the object being measured. Absolute zero is about 460° below zero on the Fahrenheit scale and about 273° below zero on the Celsius scale.

One of these absolute scales is known as the Rankine scale and is related to the Fahrenheit scale such that a temperature in degrees Rankine equals the temperature in degrees F plus 460. Thus, 100°F equals 560°R, where the R denotes use of the Rankine scale.

The second absolute scale is the Kelvin scale and is in very common use by today's engineers and scientists on a worldwide basis. It is related to the Celsius scale such that a temperature in degrees Kelvin equals the temperature expressed in degrees Celsius plus 273.15. Thus, 100°C equals 373.15°K, where the K denotes use of the Kelvin scale.

As noted before, all temperature scales are used to measure and represent the degree of hotness or coldness of a substance. In actuality, however, this is a somewhat misleading statement, because heat can be technically defined as "*energy whose interchange between a system and its surroundings takes place only by virtue of a temperature difference.*" Thus, heat is a form of energy that increases the temperature of substances and which can flow from a warm body to one which is cooler. Whenever a cold body is placed in a warm environment, there will be a temperature difference, and heat will flow from the warmer environment to the colder body. Alternatively, if the body is warmer than its surroundings, it will lose heat. Thus, when a cold liquid is spilled into a warm environment, it will experience a heat gain. Depending on the temperatures involved, this temperature may be sufficient to cause the liquid to boil (remember the boiling butane on the block of ice?). Alternatively, if the liquid was hot to begin with, it may lose sufficient heat to solidify or freeze. The importance of these concepts will become apparent as the discussion turns to the topic of how a chemical may behave when released into varying environmental conditions.

2.3 DEFINITION OF PRESSURE

The next concept to be discussed is that of pressure, which can be defined as the amount of force brought to bear on some unit area of an object. When we press our thumb down on a table, we are applying force on the table. The harder we press, the greater the force, and the greater the pressure we apply to the table surface.

As we sit here, the air in the sky above us presses down on our bodies and all objects around us with the pressure of approximately 14.7 pounds per square inch of surface area, commonly abbreviated as 14.7 psi. This pressure, essentially the average air pressure at sea level, is also known as one standard atmosphere. When one speaks of a pressure of two atmospheres as might be found in a tank, pipeline, or other container of a hazardous material, it *generally* means that 29.4 psi is present, or two times 14.7 psi.

The word *generally* is emphasized because pressure also has absolute and relative scales of measurement. The 14.7 psi of atmospheric pressure at sea level is an absolute measurement and is more properly presented in units of pounds per square inch - absolute, or ***psia*** for short. Zero psia in this case refers to a complete absence of pressure such as one might find in the perfect vacuum of outer space. The most common relative scale of measurement, this being one only used in the United States for the most part, presents numerical values in terms of ***gauge*** pressure, where a reading of zero matches an absolute pressure of one standard atmosphere. In this system, an absolute pressure of 15.7 psia would be expressed as 1.0 pound per square inch - gauge, or 1.0 ***psig*** for short. Two atmospheres of absolute pressure would be equivalent to one atmosphere gauge pressure.

There are several other systems of pressure measurement that are of an absolute nature. The most common include:

- Millimeters of mercury (mm Hg) - in which 760 mm Hg are equivalent to one standard atmosphere.
- Newtons per square meter (N/m^2) - in which 101,325 N/m^2 are equal to one standard atmosphere.
- Pascals (Pa) - which are another name for N/m^2, such that 101,325 Pa are equal to one standard atmosphere.
- Bars - in which 1.01325 bars are equal to one standard atmosphere.
- Inches of water (in H_2O) - in which 407.6 in H_2O are equal to one standard atmosphere.
- Inches of mercury (in Hg) - in which 29.9 in Hg are equal to one standard atmosphere.

The latter two sets of units are not in as common use in the scientific community as the first four but it is well to know of their existence. Those of you who pay attention to weather forecasts will recognize that meteorologists have traditionally reported current atmospheric pressures in units of inches of mercury.

2.4 VAPOR PRESSURES OF LIQUIDS AND SOLIDS

Liquids have a tendency to evaporate even at temperatures well below their boiling points. The reason for this stems from the observation that molecules of a liquid (these being the smallest parts of the liquid which retain the identity of the substance at the atomic level) have a tendency to break away from the surface of a liquid and enter the vapor state. The

speed of this process, in the absence of wind effects, is a function of temperature such that a warm liquid will evaporate more quickly than the same liquid at a cooler temperature. Note, however, that different liquids at the same temperature will evaporate at different rates depending on their particular properties.

One primary measure of a liquid's tendency to vaporize is known as its ***vapor pressure***, this being the pressure exerted by its vapors on the walls of a container which is partially full of the liquid and free of any other vapor or gas. Higher temperatures cause increases in the vapor pressure. Lower temperatures cause a decrease, and there is a direct relationship between the temperature of any given substance and its vapor pressure. Table 2.1 provides a list of vapor pressures for variety of common substances showing how they differ with respect to temperature. Note that the pressures are expressed in units of millimeters of mercury (mm Hg), this being the most common set of units used for this purpose in the United States, particularly for substances at temperatures below their normal boiling points. Note also that there are wide variations in the temperatures associated with specific vapor pressures and that even iron will have a measurable vapor pressures if heated to very high temperatures.

The substances listed in Table 2.1, and all others, exert their specific vapor pressures whether or not they are enclosed in a sealed container. When in a container, they reach a state of ***equilibrium*** such that some molecules go from the liquid state to the vapor state while others pass back from the vapor to the liquid at the same rate, and no material is lost to the outside environment. When in the open, molecules entering the vapor state mix with air and move further and further away from the liquid surface with time. As they are replaced above the surface with new molecules evaporating from the liquid, the volume of liquid is depleted. Eventually, all the liquid evaporates (be it in minutes, hours, days, or years) and the surface becomes dry.

Figure 2.1 illustrates these various phenomena. In the top diagram, we observe molecules evaporating from a pool of liquid and entering the atmosphere. Note that any type of wind or breeze blowing across the surface of the liquid would help the individual molecules in escaping and moving away from the liquid and thereby increase the overall rate of evaporation. This rate is indeed a partial function of air velocity over the surface such that higher velocities usually produce higher evaporation rates.

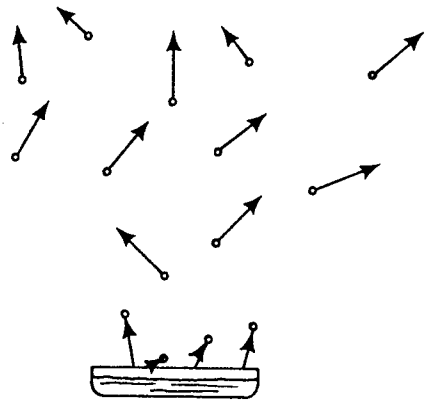
In the middle diagram of Figure 2.1, the liquid is confined within a container and the escaping vapor molecules are trapped. Eventually, as illustrated in the bottom diagram, a state of equilibrium is attained.

TABLE 2.1
VAPOR PRESSURES AS A FUNCTION OF TEMPERATURE

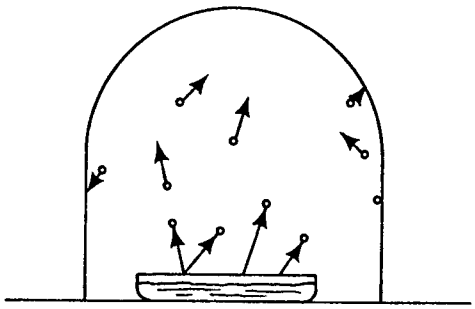
	Vapor Pressure (mm Hg)					
	1	**10**	**40**	**100**	**400**	**760**
Chemical	**Temperature (°F)**					
Benzene	-38.2	11.3	45.7	79.0	141.1	176.2
Butane	-150.7	-108.0	-74.4	-47.6	2.7	31.1
Ethyl alcohol	-24.3	27.9	66.2	94.8	146.3	173.1
Ethylene glycol	127.4	197.8	248.0	287.2	353.3	387.1
Iron	3249	3702	4035	4280	4721	4955
Methyl alcohol	-47.2	2.8	41.0	70.2	121.8	148.5
Propane	-200.0	-163.3	-134.3	-111.3	-68.1	-43.8
Water	-18*	52.3	93.3	122.3	176.5	212.0

*Approximate

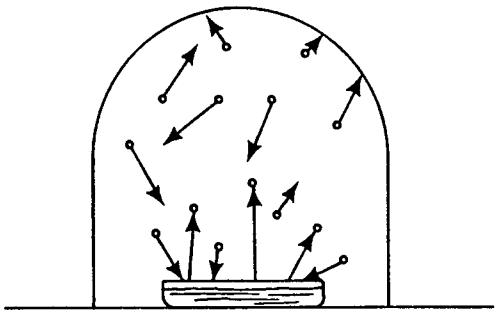
FIGURE 2.1
EVAPORATION AND VAPOR-LIQUID EQUILIBRIUM PHENOMENA



EVAPORATION: MOLECULES ESCAPING FROM
THE LIQUID TO BECOME VAPOR



EVAPORATION: MOLECULES CONFINED



VAPOR–LIQUID EQUILIBRIUM:
MOLECULES ESCAPE FROM AND
RETURN TO THE LIQUID

It should be realized that there is a direct relationship between the vapor pressure of an evaporating substance and the maximum concentration that its vapor or gas may achieve when mixed with air in the open environment. This is true because higher vapor pressures above the surface of a substance require that more molecules of the substance be physically present. Thus, if the vapor pressure of the substance is known, one can compute the approximate maximum airborne contaminant (i.e., chemical) concentration it may attain. Such concentrations are most commonly expressed in units of percent in air by volume, parts per million parts of air (ppm) by volume, parts per billion parts of air (ppb) by volume, or milligrams of chemical per cubic meter (mg/m^3) of air. The equations needed for these computations are:

$$\%\ \text{concentration} = \frac{\text{vapor pressure (mm Hg)}}{760} \times 100$$

$$\text{ppm concentration} = \frac{\text{vapor pressure (mm Hg)}}{760} \times 1{,}000{,}000$$

$$\text{ppb concentration} = \text{concentration in ppm} \times 1000$$

$$\frac{mg}{m^3}\text{concentration} = \frac{(\text{ppm concentration}) \times (\text{molecular weight})}{0.08205 \times (273.15 + {}^{o}C)}$$

A restriction to remember in using these equations is that the concentration of a gas or vapor cannot under any circumstances exceed 100% by volume or its equivalent of 1,000,000 ppm regardless of the answer obtained. An example should help the understanding of these relationships.

From Table 2.1, we find that benzene has a vapor pressure of 100 mm Hg at a temperature of 79.0°F. From earlier discussion, we also know that 79.0°F is equal to 26.1°C. Therefore:

$$\%\ \text{concentration} = \frac{100 \times 100}{760} = 13.16\%\ \text{by volume}$$

$$\text{ppm concentration} = \frac{100 \times 1{,}000{,}000}{760} = 131{,}600\ \text{ppm by volume}$$

Computation of the equivalent concentration in mg/m^3 requires not only knowledge of the temperature in degrees Celsius but of the ***molecular weight*** (m.w.) of the material, this being an atomic measure of the weight of the substance. This weight is often (but not always) listed in material safety data sheets (MSDS) and product bulletins that present data

on the physical and chemical properties of chemicals. Section 2.8 of this chapter demonstrates how to compute the molecular weight of a substance given knowledge of its chemical formula. The molecular weight of benzene is 78.1, so:

$$\frac{mg}{m^3}\text{concentration} = \frac{(131{,}600)(78.1)}{(0.08205)(273.15+26.1)} = 418{,}600 mg/m^3$$

2.5 BOILING POINTS AS A FUNCTION OF PRESSURE

It was reported earlier that a pressure of 760 mm Hg is equal to 14.7 psia or one standard atmosphere. From Table 2.1 we see that water has a vapor pressure of 760 mm Hg at a temperature of 212°F, a temperature we recognize as its normal boiling point. What is significant about this observation is that it holds true for all liquids. Any liquid will begin to boil at the temperature at which its vapor pressure equals the pressure being exerted by the environment onto the surface of the liquid. In practical terms, this means that:

- Boiling points of materials are a function of pressure.
- Liquids in sealed containers (with an exception discussed below) will remain as liquids when heated above their normal boiling points although their vapor pressures may far exceed one standard atmosphere pressure within the container.
- If heating continues and the pressure is not adequately relieved by a safety device (such as a pressure relief valve), the pressure and temperature within the tank may eventually rise to the point that some part or all of the container may burst or rupture, possibly in a violent fashion. This may also occur if the capacity of the safety device is inadequate to prevent an excessive buildup of pressure.
- Materials exposed to environmental pressures below one standard atmosphere will boil at temperatures below their normal boiling points. Thus, water will boil at a temperature below 212°F when heated on top of a high mountain. Water released into a vacuum at any temperature will almost instantly vaporize.

It is well to realize that many substances with normal boiling points far below normal ambient temperatures are shipped or stored in commerce as liquids. This is most often achieved by placing the liquid within a strong tank and permitting it to remain in the liquid state under its own vapor pressure at equilibrium conditions. Examples of the most common of these materials considered hazardous include liquid anhydrous ammonia, ethylene, chlorine, ethylene oxide, vinyl chloride, and liquefied petroleum gas (LPG) or propane. Such

substances, frequently referred to as ***compressed liquefied gases***, are particularly hazardous because: 1) leaks may result in rapid venting of gas to the atmosphere; 2) leaks may result in discharge of liquids that rapidly ***flash*** vaporize and/or boil upon exiting their containers; and 3) the flammable, toxic, or otherwise hazardous gases and vapors evolved may travel considerable distances downwind before becoming diluted with air below hazardous concentrations.

Less frequent in transportation but more common at storage and processing sites are bulk quantities of substances such as chlorine, anhydrous ammonia, or liquefied natural gas (LNG) which have been liquefied by cooling to low temperatures via the use of refrigeration systems. Although the vapor pressure of gases liquefied by refrigeration may be close to ambient pressures within storage vessels, spills into the warmer external environment will again result in boiling and the evolution of large quantities of potentially hazardous gases and vapors.

The exception to the *"rule"* that liquids in sealed containers will remain as liquids when heated above their normal boiling points involves the fact that this is true only so long as the temperature of the liquid is below what is referred to as its ***critical temperature***. The critical temperature of a substance is the temperature above which it cannot remain in the liquid state regardless of any increase in pressure. Thus, substances heated above their critical temperatures are neither liquid nor gaseous, but rather, in a state somewhere in between. Picture them as very *thick* vapors.

2.6 DEFINITIONS OF SPECIFIC GRAVITY AND DENSITY

Boiling points, vapor pressures, and melting or freezing points can tell us much about how a material will initially behave when released into the environment, but more information is needed to better define actions and behavior. This section discusses relative and absolute measures of the weights of materials, while the next discusses the degree to which one substance can mix with another.

Every solid or liquid in the environment occupies a specific volume of space and has a certain weight. Thus, we may express the weight density of a substance as its weight divided by its volume. It is well known, for example, that pure water weighs about 62.4 pounds per cubic foot (lb/ft^3) of volume, which is equivalent to 1.0 gram per cubic centimeter (g/cm^3) or 1,000 kilograms per cubic meter (kg/m^3) in the metric system. We also have observed that different substances have different weights for the same volume. One cubic foot of oil weighs about 50 pounds. A cubic foot of steel weighs about 487 pounds.

An alternative method of expressing the weight density of a solid or liquid involves use of a quantity known as the liquid or solid ***specific gravity***. Quite simply, this quantity is determined by dividing the density of a substance by the density of water. Since 62.4 divided by 62.4 has a value of 1.0, water has a specific gravity of 1.0 and serves as the reference point for all materials. The liquid specific gravity of a typical oil is 50 divided by 62.4, giving a value of 0.80. The solid specific gravity of steel is 487 divided by 62.4 and equals 7.80.

As is the case with vapor pressures, both the density and specific gravity of solids and liquids vary with temperature. Heat causes most (but not all) materials to expand in volume while cold causes them to shrink. Since the volume changes while the weight remains the same, the density of a substance generally decreases with heating and increases with cooling. This explains why most sources of information on the density of chemicals will provide the temperature at which the value was measured. In the case of specific gravities, they may list both the temperatures of the water and chemical substance used to determine the specific gravity.

Knowledge of liquid or solid specific gravities is most important when it is desired to determine how a substance will behave in the presence of water. For example, the fact that the specific gravity of a typical oil is 0.80 supports the observation that most oils are lighter than water and have an initial tendency to float. The fact that steel's specific gravity is about 7.80 explains why a block of steel will immediately sink in water.

Discussion of vapor or gas specific gravities and densities is more complicated because these properties are affected by changes in pressure as well as temperature. However, since we are primarily interested in chemical substances that escape into the natural environment, since the natural environment has a nominal atmospheric pressure of one atmosphere, and since any gas or vapor entering the atmosphere will quickly adjust its volume to achieve a total pressure of one atmosphere, it is sufficient for the purposes of this text to only consider specific gravities and densities of gases or vapors at atmospheric pressure.

The discussion begins with the observation that air has a density of 0.0763 lb/ft^3 (about 1.22 kg/m^3) at a temperature of 60°F and a pressure of one atmosphere. As in the case of other substances, higher temperatures cause a decrease in density and lower temperatures cause an increase. Similarly, there is a quantity known as the ***vapor specific gravity*** or ***vapor density*** which is a ratio of the density of a pure gas or vapor to the density of air. Found in many data sources, this specific gravity or density (the former term being used rather interchangeably with the latter) is based on the assumption that air has a value of 1.0. Thus, vapors or gases with vapor specific gravities less that 1.0 are *presumably* lighter than air in the natural environment while those with values greater than 1.0 are *presumably* heavier.

The word *presumably* is emphasized because the values for vapor specific gravities found in all too many data sources are frequently misinterpreted by their users, particularly and specifically in the case of substances below a temperature that permits them to exist as a pure vapor or gas at a pressure of one atmosphere. This can lead to incorrect conclusions about the actions of a vapor or gas upon its release to the environment.

The problem has arisen because many sources compute the vapor density of ***any*** substance by a shortcut method involving division of the molecular weight of the substance by the molecular weight of air, the latter being approximately 28.9 (as the weighted average for the mixture of gases that comprise air). Thus, since benzene has a molecular weight of 78.1, these sources will report a vapor specific gravity or density value of approximately 2.70, which to many people suggests that the vapors of benzene *in the natural environment* are always 2.70 times heavier than air, which is an absolutely untrue assumption. The misinterpretation results in the belief that benzene vapors will always hug the ground over considerable distances as they spread from the site of a release and may somehow accumulate and persist in pits, hollows, basements, or other low lying areas.

It was earlier explained that benzene has a vapor pressure of 100 mm Hg at a temperature of 79.0°F and that this vapor pressure translates into a maximum vapor concentration directly over the liquid surface of approximately 13.16% by volume. It follows that benzene cannot exist as a pure vapor at this temperature in the natural environment and that it is incorrect to assume that it is a pure vapor when estimating its vapor density relative to air (which is what is being done when a molecular weight ratio is computed). Rather, it is necessary to compare the benzene-air *mixture* density with the density of pure air to determine whether the vapors generated by the release will be heavier or lighter than air. This is accomplished in an approximate fashion via the following procedure:

Step 1: Compute the approximate density ρv of pure chemical vapor in lb/ft^3 at temperature T (in °F).

$$\rho v = \frac{1.3691 \times \text{molecular weight}}{(T + 460)}$$

Step 2: Compute the approximate density ρa of air in lb/ft^3 at ambient temperature T (in °F).

$$\rho a = \frac{39.566}{(T + 460)}$$

Step 3: Compute the relative vapor density of the chemical-air mixture.

$$\text{Relative vapor density} = \frac{\{C \times \rho v\} + \{(100 - C) \times \rho a\}}{100 \times \rho a}$$

Where C = saturated concentration of the chemical vapor in air in percent by volume.

Benzene has a molecular weight of 78.1 and a maximum vapor concentration (more precisely referred to as its ***saturated*** vapor concentration) of 13.16% in air at 79°F. Use of these values in the above equation, together with the assumption of an air temperature of 79°F, provides a true relative vapor density value of 1.22. What this means is that the benzene-air mixture **directly** above a pool of benzene at the specified temperature is only 1.22 times heavier than air and not the 2.7 times suggested by the vapor density frequently reported in the literature for this substance. Since this mixture will very quickly mix with additional air as it drifts away from the pool, it will rapidly approach the density of pure air and behave as if there were little or no difference in its density. In scientific terms, it will behave as a ***neutrally buoyant*** vapor-air mixture.

If the relative vapor density of a substance under prevailing discharge conditions exceeds 1.5 (as a general rule of thumb), then vapors or gases may indeed behave as heavier-than-air (or ***negatively buoyant***) mixtures for some distance from the source of discharge. Conversely, a relative vapor density significantly less than one suggests that a vapor-air mixture may be lighter than air (or ***positively buoyant***).

In determining or deciding whether any particular gas or vapor will be negatively, neutrally, or positively buoyant in air, it is also often necessary to consider the circumstances under which the substance may be released to the atmosphere. For example, in situations in which a compressed liquefied gas is discharged from a container, particularly when in the liquid state, the resulting vapor cloud or plume may include a considerable amount of fine liquid droplets. Although the gas or vapor mixture with air may normally be positively or neutrally buoyant, the presence of these relatively heavy droplets (also referred to as ***aerosols***) may cause the cloud or plume to behave initially in a negatively buoyant fashion.

2.7 SOLUBILITY IN WATER

All of us have observed that sugar and salt dissolve in water and seem to disappear, that our favorite alcoholic beverage can be mixed freely with water-based mixers, and that the *"fizz"* in containers of soda pop, tonic, or beer is due to carbon dioxide gas that has been dissolved in the liquid. In each case, the solid, liquid, or gas that has dissolved in water is said to be ***soluble*** in water.

An important concept to understand is that different materials have different degrees of solubility. At one extreme, there are liquids which are ***soluble in all proportions*** with water and which are also said to be ***miscible***. This means that any amount of the substance can be added to water and at no point in the process will the substance form a separate layer or phase. At the other extreme, there are substances which do not dissolve in water whatsoever and which are considered to be ***insoluble*** or ***immiscible***. A somewhat extreme example of the latter case involves stone pebbles in a glass of water. No matter how hard the pebbles are shaken or stirred, they will not dissolve or form a ***solution*** with water, this being the term used for a mixture of two liquid substances which are mutually soluble.

In between the above extremes are substances which are ***partially soluble*** in water. For example, there is only a certain amount of ordinary table salt that can be dissolved in water before any new salt added to the solution simply sinks to the bottom and is unable to dissolve. In the case of table salt, 35.7 grams of salt will dissolve in 100 grams of water at a temperature of 32°F and this will rise to about 39.8 grams (there are about 454 grams in a pound) at a temperature near 212°F. And yes, that means that solubility is also a function of temperature. Generally speaking, hot liquids can dissolve more of a partially soluble liquid or solid than cold liquids. Alternatively, because of effects involving vapor pressures and their increase with temperature, cold liquids can generally dissolve more gases and vapors than hot liquids. Increases in pressure may also increase the solubility of gases in liquids.

2.8 MOLECULAR WEIGHTS OF CHEMICAL SUBSTANCES

There are approximately 89 natural ***elements*** in the world that in various combinations make up all matter that surrounds us. In addition, a number of man-made elements have been produced under laboratory conditions involving nuclear reactions and many more have been theorized but never observed. The atoms of all elements have been assigned individual ***atomic weights*** relative to oxygen by scientists. These are listed in Table 2.2 for most common elements likely to be encountered in normal commerce and use.

Combinations of various atoms called ***molecules*** make up the smallest part of any chemical compound that retains the specific properties of the substance and have specific ***molecular weights*** that can be computed from the number of atoms of each element present in the compound, as determined by examination of the ***chemical formula*** of the substance. Such formulae are always found in material safety data sheets for pure substances and many other sources of chemical data. Examples include:

- H_2O for water
- CO_2 for carbon dioxide
- NaCl for sodium chloride

TABLE 2.2
ATOMIC WEIGHTS OF SOME COMMON ELEMENTS

Table gives chemical symbol, name, and atomic weight of each element.

Ag	Silver	107.87	Cu	Copper	63.54	P	Phosphorus	30.97
Al	Aluminum	26.98	F	Fluorine	19.00	Pb	Lead	207.19
As	Arsenic	74.92	Fe	Iron	55.85	Rb	Rubidium	85.47
B	Boron	10.81	Ga	Gallium	69.72	S	Sulfur	32.06
Ba	Barium	137.34	H	Hydrogen	1.00	Sb	Antimony	121.75
Be	Beryllium	9.01	Hg	Mercury	200.59	Se	Selenium	78.96
Bi	Bismuch	208.98	I	Iodine	126.90	Si	Silicon	28.09
Br	Bromine	79.91	Li	Lithium	6.94	Sn	Tin	118.69
C	Carbon	12.01	K	Potassium	39.10	Sr	Strontium	87.62
Ca	Calcium	40.08	Mg	Magnesium	24.31	Ta	Tantalum	180.95
Cd	Cadmium	112.40	Mn	Manganese	54.94	Ti	Titanium	47.90
Ce	Cerium	140.12	Mo	Molybdenum	95.94	U	Uranium	238.03
Cl	Chlorine	35.45	N	Nitrogen	14.01	V	Vanadium	50.94
Co	Cobalt	58.93	Na	Sodium	22.99	W	Tungsten	183.85
Cr	Chromium	52.00	Ni	Nickel	58.71	Zn	Zinc	65.37
Cs	Cesium	132.91	O	Oxygen	16.00	Zr	Zirconium	91.22

- KOH for potassium hydroxide
- CH_3NHNH_2 for methyl hydrazine
- C_6H_6 for benzene

As noted earlier, knowledge of molecular weights is required for computation of vapor concentrations in air in some cases, and indeed, knowledge of this weight is mandatory for a wide variety of calculations involving hazardous materials. Since molecular weights are not always found on materials safety data sheets, however, it is worthwhile to understand how they may be computed using the information provided in Table 2.2. This is best accomplished by an example.

From the list above we see that methyl hydrazine has a chemical formula of CH_3NHNH_2 (which may also be shown as CH_6N_2 in some references). What this means is that each molecule of this chemical consists of:

- One (1) atom of carbon represented by the symbol "C"
- Two (2) atoms of nitrogen represented by the symbol "N", and
- Six (6) atoms of hydrogen represented by the symbol "H".

From Table 2.2 we find that the atomic weights of carbon, nitrogen, and hydrogen are respectively 12.01, 14.01, and 1.00. Thus, we can compute the molecular weight of this substance by multiplying the atomic weight of each of the three elements by the number of its atoms in the molecule, and then summing the results. For methyl hydrazine, the result is:

$$\text{Molecular weight} = (1 \times 12.01) + (2 \times 14.01) + (6 \times 1.00) = 46.03$$

3.0 ACTIONS UPON RELEASE TO THE ENVIRONMENT

3.1 PHYSICAL STATE PRIOR TO RELEASE

The first step in determining how a substance will behave upon release to the environment requires knowledge of the physical state of the material within its storage or transportation container. This in turn requires knowledge of the relationship between the temperature of the material, its boiling point, and its melting point. The possibilities are:

- The temperature of the material in its container is less than its melting point, in which case the material is a solid in its container. A good example would be dry table salt in a large drum.

- The temperature is greater than the melting point of the material but less than its normal boiling point, in which case the material is a liquid and the container contents are approximately at normal atmospheric pressure. An example is water in a tank at temperatures above freezing. Such liquids, however, could also consist of substances which are normally solids but which have been melted and maintained at relatively high temperatures to keep them liquid. They could also be substances which are normally gases in the natural environment but which have been liquefied via refrigeration.

- The temperature is greater than the boiling point of the material, in which case the material is a compressed gas (gas under high pressure in a cylinder or other container) or a liquefied compressed gas (a substance that is normally a gas at normal ambient conditions but which has been turned into a liquid by subjecting it to and maintaining it at high pressures, thus raising its actual boiling point).

Table 3.1 summarizes the various possibilities in greater detail. The table requires a bit of study for complete understanding, but the effort is extremely worthwhile.

3.2 MATERIAL STATES DURING AND INITIALLY AFTER RELEASE

Once there is an understanding of the state of a hazardous material within a storage or transportation container, it is next necessary to consider how the substance will behave *initially* when discharged into an environment of normal ambient temperatures and pressures. There are 10 scenarios to consider based on the last column of Table 3.1, all of which assume that the spill or discharge does not take place during a fire or other abnormal event which would change internal and/or external temperatures.

TABLE 3-1
TYPICAL STATES OF MATERIALS IN STORAGE OR TRANSPORTATION CONTAINERS

Normal Melting or Boiling Points	Container Conditions	State of Material (Scenario #)
Melting point less than ambient T	T less than melting point and less than ambient T	Cold solid (1)
Melting point greater than ambient T	T near ambient T	Solid near ambient T (2)
Boiling point greater than ambient T	T greater than melting point, greater than ambient T, but less than boiling point	Warm or hot liquid (molten solid) (3)
Melting point less than ambient T	T greater than melting point but less than ambient T and boiling point	Cold liquid (4,5)
Boiling point greater than ambient T	T near ambient T	Liquid at ambient T (6)
	T greater than ambient T but less than boiling point	Hot liquid (7)
	T greater than boiling point and greater than ambient T	Hot or warm compressed gas or vapor over hot liquid (8)
Boiling point less than ambient T	T near ambient T	Compressed gas or compressed liquefied gas under pressure at ambient T (9, 10)
	T greater than boiling point and greater than ambient T	Hot or warm compressed gas or compressed liquefied gas under pressure at T greater than ambient (9, 10)

Notes: T = temperature within container; ambient T = temperature outdoors

Scenario #1: Cold or Refrigerated Solids

Some materials that are normally liquids or gases at ordinary temperatures or pressures are handled as solids at temperatures below their melting points and below ambient temperatures to make them easier or safer to transport or use. When exposed to a warmer environment, they will melt to become liquids, or if they are substances that pass directly from a solid to gaseous phase (i.e., substances that "sublime") they will vaporize. For example, ice spilled on the ground in summer will melt to become liquid water. Solid carbon dioxide (dry ice) will "sublime" as it warms to become carbon dioxide gas.

Scenario #2: Normally Solid Materials

Materials that are solids at ordinary ambient temperatures and which are transported or otherwise handled at such temperatures will remain as solids upon release from their containers. Dry table salt and sugar are good examples.

Scenario #3: Molten Solids

Some substances which are normally solids are melted to become liquids, since liquids are sometimes easier to handle. Indeed, for transportation, a solid may be melted and poured into a tank vehicle of some kind where it will slowly cool with time, and even possibly resolidify. When it reaches its destination, it will be pumped out if still a liquid, or first remelted (possibly using heating coils inside the tank) and then pumped out. Such substances will either be discharged as solids or as liquids that may solidify if exposed to cooler ambient temperatures during an accidental spill or discharge situation.

Scenarios #4 and #5: Cold or Refrigerated Liquids

Liquids that are handled at cold temperatures and/or which are refrigerated may have normal boiling points that are either below or above ambient temperatures. The latter substances will simply warm up when released to the environment (Scenario #4), much as cold water will heat in the sun. Those with below ambient boiling points (Scenario #5), which are typically cooled to reduce their vapor pressures in equipment or for use in air-conditioning or refrigeration systems, will warm to their normal boiling point temperatures upon release and begin to boil. Due to thermodynamic cooling effects associated with liquid evaporation or boiling, these liquids will remain at their normal boiling points. If spilled onto a surface that is a good heat insulator, the boiling may eventually slow down or stop, but the quiescent pool that remains will continue to rapidly evaporate. This evaporation process will maintain the remaining liquid near its boiling point as it picks up heat from its surroundings.

Scenario #6: Normally Liquid Materials

Materials that are normally liquids at ordinary temperatures and pressures and which are transported or otherwise handled at such temperatures will remain as liquids upon release to the environment. Good examples would be gasoline or fuel oils pouring from a hole in a storage or transportation container.

Scenarios #7 and #8: Hot Liquids

There are many cases where a substance that is a liquid at normal ambient temperatures and pressure might be heated for one purpose or another. Such liquids, if below their boiling point (Scenario #7), will cool upon release to the environment and remain as liquids. However, if they were heated above their boiling points (Scenario #8), then any space above the liquid in a container will contain gas or vapor at a pressure in excess of one atmosphere. What happens in the event of an accident or incident in this latter case will depend on what part of the container is damaged.

- If the container is punctured or otherwise damaged in the space above the liquid, vapors of the liquid will blow out (i.e., vent) from the resulting hole into the atmosphere and will continue to do so until the liquid cools below its boiling point. For example, picture steam blowing out the stack of an old-time steam locomotive.

- If the container is punctured below its liquid surface, the liquid will pour out of the hole while some amount of its "flashes" to vapor upon release. The part that remains as liquid will boil briefly and then slowly cool to ambient temperature while evaporating. As an example, picture a leak on the face of an automobile radiator with steam, a hot water mist, and hot water exiting the leak area.

Scenario #9: Compressed Liquefied Gases

Regardless of whether these liquids are at ambient or higher temperatures, they will typically be in pressure vessels designed to maintain and withstand substantial pressures. As in the prior case, what happens during an accident or incident will depend on what part of the container is damaged.

- If the container is punctured or otherwise damaged in the space above the liquid, the gas will typically vent at high velocity from the resulting hole into the atmosphere, possibly creating some amount of liquid droplets during the process. The velocity is likely to drop with time as boiling within the tank cools the mass of liquid (the tank surface may actually

become quite cold and even frost over due to thermodynamic cooling effects), but such venting of gas may continue for considerable periods of time (possibly until no more liquid is left in the tank).

- If the container is punctured below its liquid surface, the liquid may literally jet from the hole (remember the very high pressure apt to be in the vapor space over the liquid) and potentially large amounts may flash into gas or vapor. Indeed, depending on the material and the temperatures and pressures involved, the tank may blow out a large mass of vapor mixed with small liquid droplets (an ***aerosol***) to the extent that no liquid reaches the surface beneath the tank. If liquid does reach the surface, it will have a tendency to form a boiling or rapidly evaporating pool.

Scenario #10: Compressed Gases

Gases which are compressed to high pressures in a container or gas cylinder but which have not been liquefied will vent from any opening in the container at high velocity. As the gas vents, the pressure in the container will drop and the container and its contents will cool. At some point, when the pressure within the tank drops to standard atmospheric pressure, venting will cease or drop to a low rate consistent with the amount of heat that enters the container from its surroundings.

3.3 DISCHARGES ONTO LAND

Up to this point, the discussion has essentially focussed on how the boiling point and melting point of a substance may affect its actions upon release to the environment. It is now time to consider how the density and solubility of the substance impacts on where it will go once outside and how there are differences to be considered between discharges on land or water or into the air. The discussion begins with discharges onto land and again considers the physical states in which spilled substances may reach a land surface.

Cold or refrigerated solids with melting points below ambient temperature will either melt to form a liquid or sublime when spilled onto a land surface. Substances that are normally solid will remain in the solid state, while molten solids may flow for a time as liquids and eventually solidify as they cool.

Liquids with boiling points above ambient temperatures will remain as liquids and will generally cool down or heat up as necessary to approach the temperature of the ambient environment. Those with boiling points below ambient temperatures may boil on a land surface until most of the liquid has volatilized (i.e., vaporized). Alternatively, as the ground

surface cools beneath a boiling pool that has been confined by natural or man-made barriers, the boiling may cease and the remaining quiescent pool may simply evaporate at a fairly steady rate.

Gases or vapors may contaminate a land surface if they are soluble in water and either: 1) it is raining; or 2) water sprays are applied by spill response personnel to absorb, "knockdown" or otherwise accelerate the dispersion of the gas or vapor in air. The contamination occurs because the water droplets pick up some amounts of the gas or vapor and then fall to the ground.

Solids of any kind can contaminate the land surface, and are particularly of concern if they are soluble in water. In such cases, rain or other sources of water will dissolve the solids and permit them to soak deeper into the ground in a process called ***percolation***. Eventually, the dissolved chemicals may reach the water table (if any) below the land's surface and contaminate groundwater supplies serving public, private, or industrial water wells. Such contamination may pose a toxic hazard to the people, animals, and plant life that may be exposed to the soil or which use the contaminated groundwater for drinking, cooking, or crop irrigation. Similarly, the dissolved chemicals may cause undesired reactions, contamination, or corrosion of equipment upon entry to industrial processing equipment relying on well water. The situation for spilled liquids is about the same except that it must be realized that a liquid need not be soluble in water to percolate into soil or to contaminate groundwater supplies. Additionally, it must be noted that liquids are more mobile than spilled solids and do not necessarily require rain or other sources of water to assist in the spreading of contamination. The rate at which a liquid substance percolates or otherwise penetrates the ground is, of course, influenced by many factors. Penetration can be rapid in areas of extremely high permeability including limesinks, caverns, highly fractured rocks, or fractures widened by solution.

Other concerns associated with discharges of hazardous materials onto land surfaces are:

- Combustible substances may be ignited and pose a fire or explosion hazard (see Chapters 4 and 5).
- Hazardous vapors or gases may be liberated into the atmosphere from substances with significant vapor pressures at prevailing chemical or ambient temperatures (see Section 3.5 and Chapters 4 and 6).
- Solids, solids dissolved in or carried by land surface water runoff, or liquids may flow into drains or sewers leading to bodies of water or may directly contaminate such bodies (see Section 3.4).

3.4 DISCHARGES INTO WATER

Discharges of a chemical substance into a body of water may occur directly from damaged ships, barges, underwater pipelines, or railroad cars or trucks that have fallen into the water, or indirectly, as outflows from sewer or drain outfalls, runoff from spills on land, runoff of water used to control fires, or entry of contaminated groundwater into the water body. Virtually all key physical and chemical properties of hazardous materials discussed in this document play important roles in determining how a material will behave when spilled into water.

- The boiling point and vapor pressure of the material will determine whether some part of the material will boil off or otherwise vaporize upon contacting the water.

- The liquid or solid specific gravity or density of the material will determine whether it has an initial tendency to float or sink in water.

- The solubility of the material will determine whether it will dissolve in the water and the rate at which this will occur.

Table 3.2 describes the expected behavior of spills into water of materials with varying combinations of boiling point, vapor pressure, specific gravity, and solubility attributes. To be stressed is that the table describes spill behavior only in the minutes and hours directly after a release and that longer periods of time may result in different effects. For example, although it is well appreciated that oil will float on water, forming a surface slick that may foul shorelines, it is not as well known that waves, water, turbulence, and time may eventually cause a floating petroleum oil slick to emulsify (i.e., to become tiny droplets) that distribute themselves through the water column (i.e., throughout the depth of the water body), to dissolve in water to some extent, and to eventually settle on the bottom of the water body as a sludge. This sludge, in the case of petroleum oils, may mix with sand or dirt and form the "tar balls" often observed on shorelines after an offshore spill.

One special point to be made about substances often described as *insoluble* is that many of these may actually dissolve at such a slow rate in water that they are considered insoluble "*for all practical purposes.*" Given enough time or agitation, a sufficient amount may actually dissolve to cause a toxic hazard to anybody or anything exposed to the contaminated water. ***Always be wary of claims of complete insolubility when a highly toxic substance has spilled into water.***

TABLE 3.2
EXPECTED BEHAVIOR OF SPILLS INTO WATER

Boiling Point	Vapor Pressure	Specific Gravity	Solubility	Expected Behavior in Water
Below ambient	Very high	Any	Insoluble	All of the liquid will rapidly boil from the surface of the water. Underwater spills will most often result in the liquid boiling and bubbles rising to the surface.
Below ambient	Very high	Less than Water	Low or Partial	Most of the liquid will rapidly boil off but some portion will dissolve in the water. Some of the dissolved material will evaporate with time from the water. Underwater spills will result in more dissolution in water than surface spills.
Below ambient	Very high	Any	High	As much as 50% or more of the liquid may rapidly boil off the water while the rest dissolves in water. Some of the dissolved material will evaporate with time from the water. Underwater spills will result in more dissolution in water than surface spills. Indeed, little vapors may escape the surface if the discharge is sufficiently deep.
Above ambient	Any	Less than Water	Insoluble	The liquid or solid will float on water. Liquids will form surface slicks. Substances with significant vapor pressures will evaporate with time.
Above ambient	Any	Less than Water	Low or Partial	The liquid or solid will float on water as above but will dissolve over a period of time. Substances with significant vapor pressures may simultaneously evaporate with time.
Above ambient	Any	Less than Water	High	These materials will rapidly dissolve in water up to the limit (if any) of their solubility. Some evaporation of the chemical may take place from the water surface with time if its vapor pressure is significant.

TABLE 3.2 (Continued)
EXPECTED BEHAVIOR OF SPILLS INTO WATER

Boiling Point	Vapor Pressure	Specific Gravity	Solubility	Expected Behavior in Water
Above ambient	Any	Near Water	Insoluble	Difficult to assess. Since they will not dissolve, and since specific gravities are close to water, they may float on or beneath the surface of the water or disperse as blobs of liquid or solid particles throughout the water column. Some evaporation of the chemical may take place from the water surface with time if its vapor pressure is significant.
Above ambient	Any	Near Water	Low or Partial	Although a material with these properties will behave at first like materials described directly above, it will eventually dissolve in the water. Some evaporation of the chemical may take place from the water surface with time if its vapor pressure is significant.
Above ambient	Any	Any	High	These materials will rapidly dissolve in water up to the limit (if any) of their solubility. Some evaporation of the chemical may take place from the water surface with time if its vapor pressure is significant.
Above ambient	Any	Greater than Water	Insoluble	Heavier-than-water insoluble substances will sink to the bottom and stay there. Liquids may collect in deep water pockets.
Above ambient	Any	Greater than Water	Low or Partial	These materials will sink to the bottom and then dissolve over a period of time.
Above ambient	Any	Greater than Water	High	These materials will rapidly dissolve in water up to the limit (if any) of their solubility. Some evaporation of the chemical may take place from the water surface with time if its vapor pressure is significant.

A second point to be made is that concentrations of water soluble contaminants in water are typically measured or expressed in units of parts (of contaminant) per million parts (ppm) of water on a weight basis or in units of milligrams (of contaminant) per liter (mg/l) of water. These units are essentially equivalent such that one ppm equals one mg/l. When a material is dissolved in water, the mixture is often referred to as an ***aqueous*** solution of the material. Conversely, materials that do not contain water are considered to be ***anhydrous***.

Of interest with respect to the evaporation of chemicals from water is that such evaporation can take place not only from floating pools or slicks of chemicals but from the surface of solutions. It is important to realize, however, that the vapor pressure of a chemical will drop when the chemical is added to water or water is added to the chemical, and the less chemical there is in the solution, the lower its vapor pressure will be at a specific temperature. Thus, evaporation from a concentrated solution (i.e., one containing considerable chemical) near a spill site might create a downwind vapor hazard, but the hazard might be negligible some time later after the chemical has had a chance to mix with more water. Similarly, a water-soluble chemical or solution that has a flammable vapor concentration above its surface at a given temperature may often be rendered nonflammable by the addition of a sufficient quantity of water.

Besides generating flammable or toxic vapors, chemicals spilled into water or sewers can pose a variety of hazards to the public and the environment.

- Flammable chemicals or solutions can pose a fire or explosion hazard in sewers, water treatment facilities, or any other spaces they may enter when extracted from a body of contaminated water.

- Insoluble materials, particularly oils, may cause drowning of waterfowl because of loss of buoyancy, exposure due to loss of the insulating capacity of feathers, and starvation and vulnerability to predators due to lack of mobility. Coating of the gills of fish may cause death due to lack of oxygen. Coating of any life forms on the bottom of a water body can kill by smothering.

- Any insoluble or soluble toxic substance that contaminates water may poison animals (including humans) or plant life (aquatic plants or irrigated crops) exposed to the water.

- Organic substances can potentially kill fish and other aquatic life forms by lowering the oxygen content of the water via biological as well as chemical processes.

- Contaminated water drawn into industrial processes may corrode or otherwise damage or destroy equipment, and possibly cause fire or explosion hazards.

3.5 FUNDAMENTAL CONCEPTS PERTAINING TO DISCHARGES INTO AIR

Hazardous vapors or gases, i.e., those that are flammable or toxic to man or his environment, may enter the atmosphere from several sources.

- They may be vented directly into the air from a pressure relief valve, "smokestack", ruptured reaction vessel, broken pipe, or other item of equipment at a chemical plant or other fixed site facility.

- They may be vented directly from a pressure relief valve, broken valve, loose fitting, or puncture in a transportation vehicle, container, or cylinder.

- They may evolve from volatile liquids or solids discharged onto the ground or into water.

Evaluation of vapor or gas discharge hazards first requires that the duration over which the discharge takes place be characterized. It then requires assessment of how the liberated vapors or gases will mix with air over time in a process referred to as ***vapor dispersion***, and finally, requires knowledge of the specific hazards posed by exposure of people to resulting concentrations of airborne contaminants at downwind locations.

Instantaneous vs. Continuous vs. Finite Duration Discharges

The most common methods available for assessment of vapor dispersion hazards require that discharges of vapor or gases into the atmosphere be classified as either being ***instantaneous*** or ***continuous*** in duration. Instantaneous discharges are those that take place over the course of a few seconds or a minute or so and then stop for all intents and purposes. The result of such a discharge is typically a ***puff*** of vapor or gas or a distinct ***cloud.*** Continuous discharges take place over longer periods of time and produce long stretched-out ***plumes*** of gas or vapor such as those typically seen from continuously operating smokestacks. These cases represent the two extremes by which contaminant emissions may be characterized. In the real world, many discharges may be of too long a duration to be characterized as truly instantaneous, yet too short in duration to establish a continuous plume. These latter discharges are commonly said to be of ***finite duration.***

In the following, we concentrate upon describing the behavior of gases or vapors liberated from instantaneous or continuous discharges to the atmosphere, thus providing the reader an understanding of the two possible extreme cases. Realize, however, that the actual

behavior of a volume of contaminated air dispersing in the atmosphere, particularly if generated from a finite duration discharge, will behave in a manner somewhat between these two extremes.

Dispersion of Vapor Puffs or Clouds

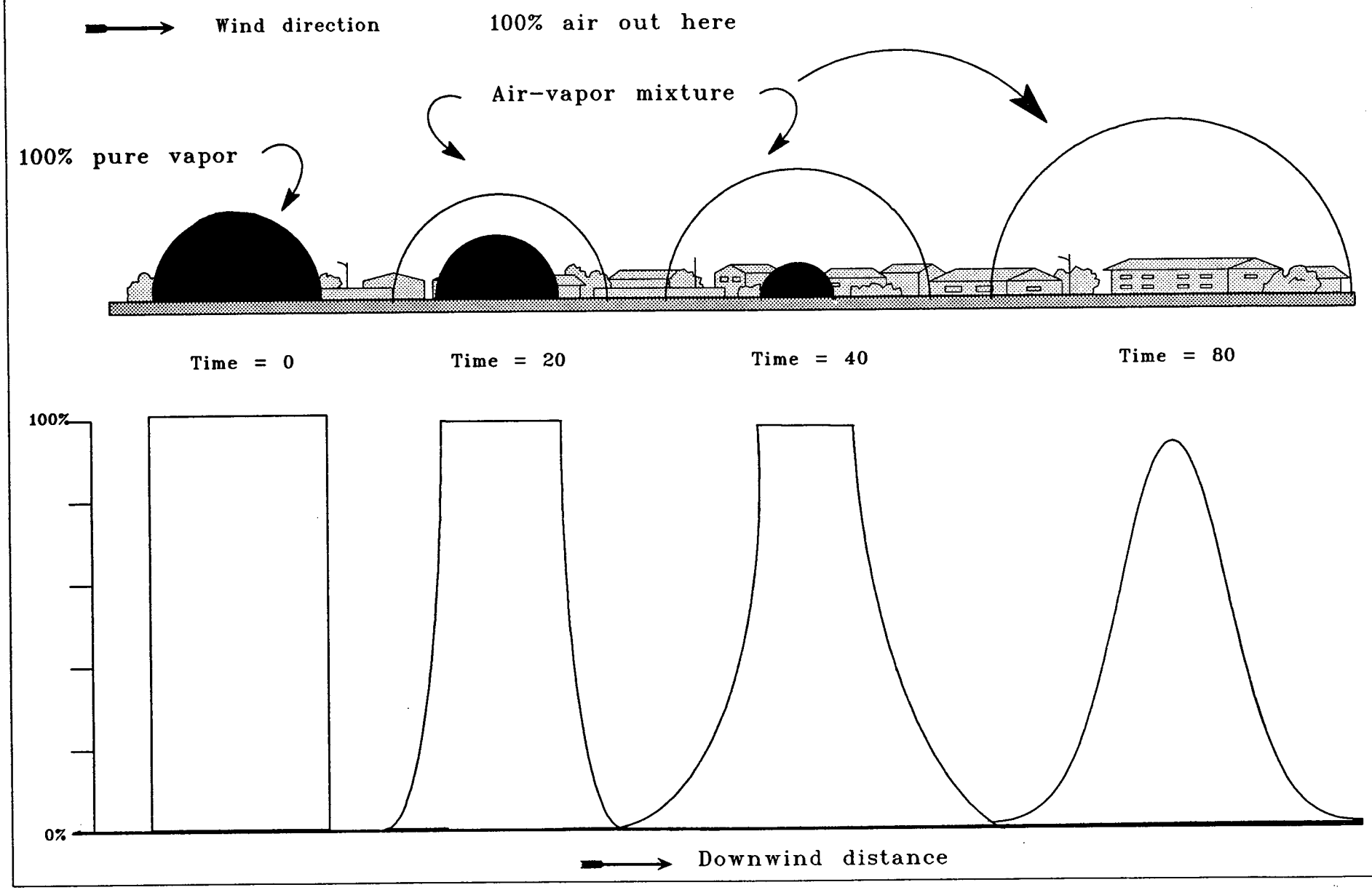
Picture if you will a large semi-spherical puff or cloud of a pure chemical vapor or gas on the ground that has somehow entered the atmosphere over the period of a few seconds and has a vapor specific gravity and vapor density similar to that of air. As the wind pushes on the puff, the puff will begin to move in the direction of the wind at a similar velocity. Simultaneously, air will begin to mix with the surface of the puff, thus diluting surface vapors. As more and more air mixes with the puff, the volume of the contaminated airspace will become larger and larger. Dilution with air, however, will cause vapor concentrations to drop with time at any point in the puff, although the central core of the puff may remain pure for a while.

What happens over time and distance as a puff disperses in air is somewhat hard to visualize with words alone, so it is worthwhile to use various illustrations and graphs in this endeavor. Figure 3.1 shows four initial stages as a puff moves downwind, each accompanied below by a graph of vapor concentration in air on the ground along a cross-section of the puff. At time equals zero, the instant the puff is formed, the concentration within the puff is close to 100% pure vapor and the air surrounding the puff is uncontaminated. At time equals 20, the puff has grown in size by mixing with air, and that portion which is still 100% pure vapor has become smaller. The vapor concentration in the remainder of the cloud ranges from 100% at the edge of the pure core of vapor to 0% at the edge of the cloud. By time equals 40, the core of 100% vapor has become even smaller, and by time equals 80, it has just disappeared. From this point onward, the peak or maximum groundlevel concentration will drop below 100% and continue to drop steadily.

Figure 3.2 continues the above sequence for a variety of later times on a single graph. What is happening is that the cloud grows larger and larger but its peak concentration, the point at its center along the ground, becomes lower and lower. At some point, this peak level will drop below whatever concentration level of the gas or vapor in air is considered hazardous. If one were to plot the groundlevel peak concentration at the center of the cloud with time or distance, it would resemble the graph in Figure 3.3.

Yet another useful way to look at cloud or puff dispersion is to look at the ground area covered by a particular preselected concentration (which could be a flammability or toxicity limit of some kind). Figure 3.4 demonstrates how this ground area changes from the point at which the puff is generated to the downwind location that every point in the puff is below the selected concentration. The view is looking down at the puff from a point up above, with

FIGURE 3.1
INITIAL STAGES OF VAPOR CLOUD OR PUFF DISPERSION



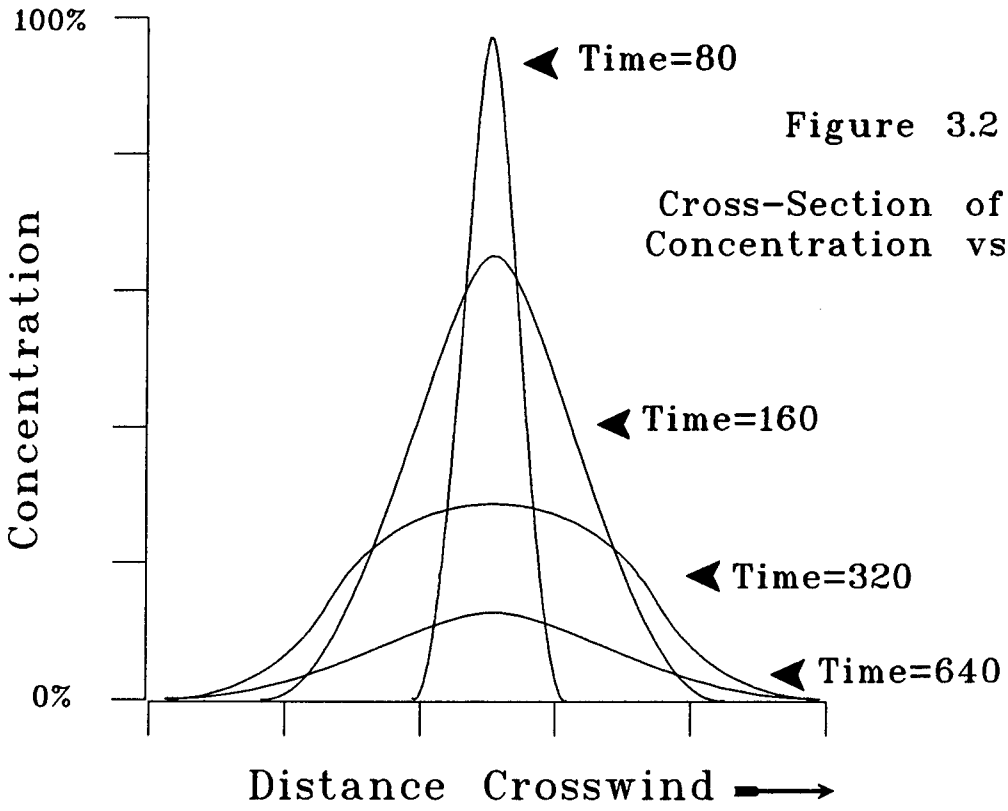


Figure 3.2

Cross-Section of Puff
Concentration vs. Time

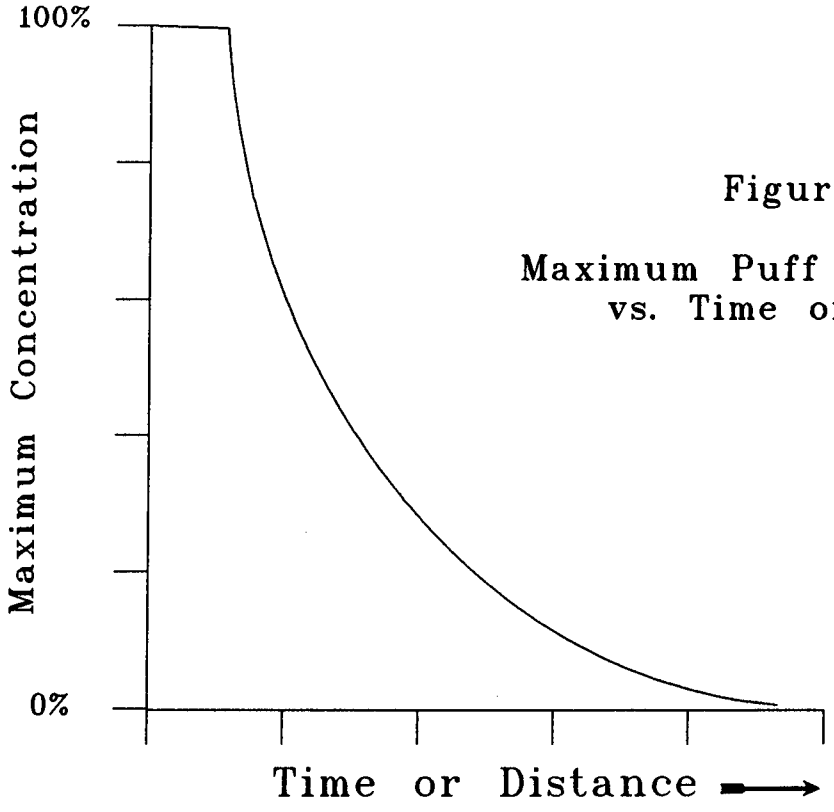


Figure 3.3

Maximum Puff Concentration
vs. Time or Distance

FIGURE 3.4
PUFF OR CLOUD ISOPLETHS AT INCREASING TIMES

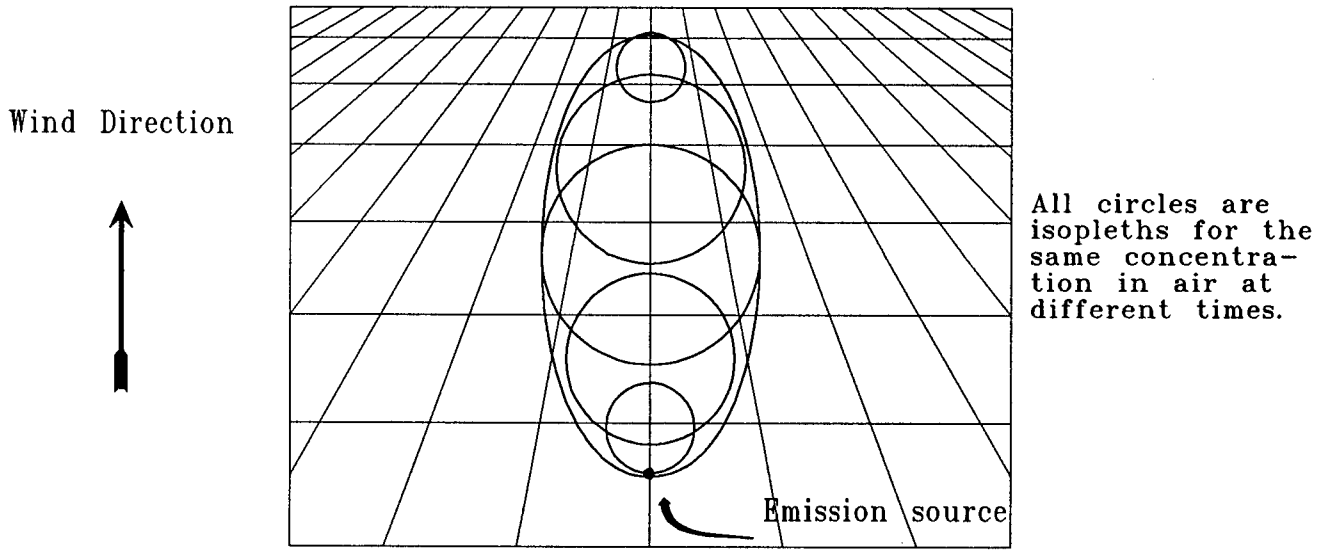
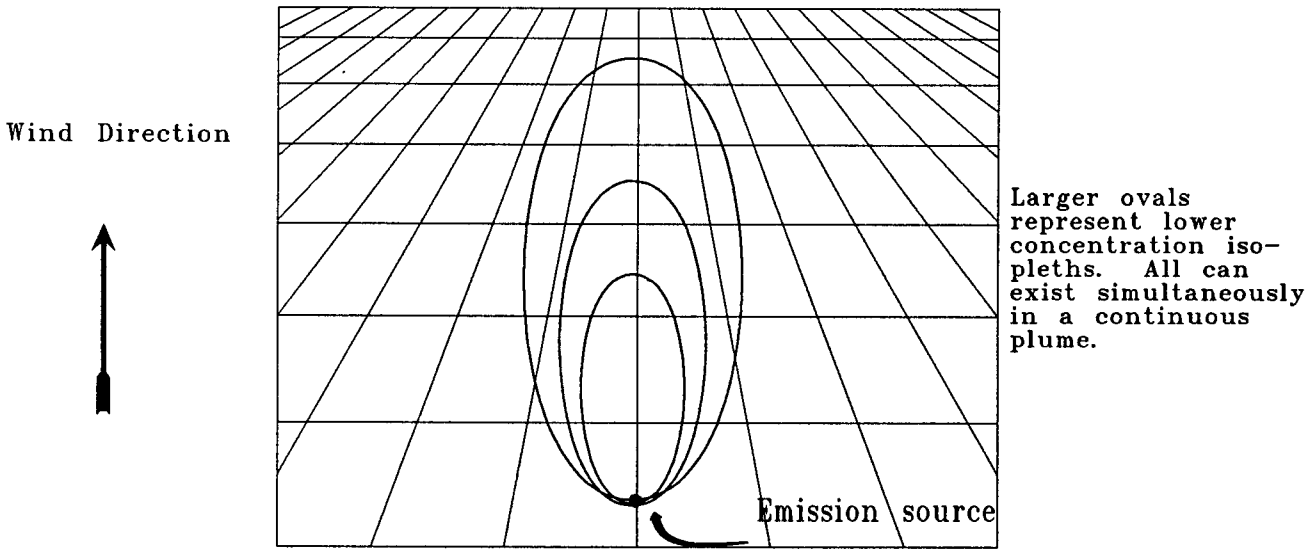


FIGURE 3.5
ISOPLETHS IN A CONTINUOUS PLUME



each circle representing a different point in time. The line around the set of circles encloses the ground area that will be subjected at some time to airborne contaminant concentrations *at or above* the preselected concentration. In somewhat technical terms, the individual circles, these being lines of constant concentration, are referred to as ***isopleths***, as is the line enclosing the entire set of circles. The latter is also sometimes referred to as the cloud's ***footprint*** on the ground for a particular hazardous concentration.

The downwind distance that any point in puff, cloud, or plume will travel within any elapsed period of time is related to the velocity of the wind *in its direct vicinity* by the relationship:

Distance = Wind Velocity x Time

Although this expression seems rather simple and straightforward, there is a "catch" to its general use. As observed above, the distance traveled is proportional to the wind velocity in the direct vicinity of the puff. Meterologists and weather stations typically report the velocity or speed of the wind as it has been measured at a point 10 meters (about 33 feet) above the ground, where the velocity is usually greater than that very close to a ground surface. Indeed, volumes of contaminated air released at groundlevel may travel as little as 50 percent of the distance given by the above relationship when the wind velocity used in the equation is measured at a 10 meter height. Clouds, puffs, or plumes liberated to the atmosphere above this height may travel faster than the reported wind velocity.

Dispersion of Continuous Plumes

As noted previously, the emission of gases or vapors to the atmosphere over an extended period of time results in establishment of a vapor or gas plume. Points downwind of the source of emissions will be exposed to a relatively constant airborne contaminant concentration for a period of time approximately equal to the duration of the emission so long as the wind direction holds steady. Note however, as is also the case in instantaneous discharges, that some amount of time will be necessary for the front edge of a cloud or plume to reach downwind locations after the initiation of a discharge and for contaminant concentrations to rise to relatively constant levels at these locations. A similar amount of time will be necessary for the trailing edge to pass downwind points after cessation of vapor or gas liberation and for contaminant concentrations to drop below levels deemed to be safe. Thus, there are different arrival and departure times associated with different downwind locations for both clouds and plumes.

Figure 3.5 shows an example of what various concentration isopleths look like through a horizontal cross-section of an established plume. The innermost isopleth encloses the area

subjected to the highest concentrations. Moving out from the innermost isopleth, each isopleth in the outer direction represents a lower concentration than the previous isopleth. As in the previous case, the view is looking down from above.

3.6 VARIABLES THAT INFLUENCE ATMOSPHERIC VAPOR DISPERSION

There are numerous factors that influence the size and shape of downwind hazard zones resulting from vapor or gas discharges into the atmosphere. The most important of these variables are discussed individually and sometimes in combination below. Since several of them interact with each other, it may be a good idea to read this section more than once to better understand various interrelationships. A solid understanding of vapor cloud and plume behavior under various conditions is an important prerequisite to proper emergency response as well as emergency planning.

Effect of Toxic or Flammable Limit Selection on Hazard Zone Size

As explained in prior discussions, the concentration of an airborne contaminant decreases with increasing distance along the downwind centerline direction of the cloud or plume path as well as in the crosswind direction. What this means in practical terms is that the choice of a higher toxic or flammable limit for definition of hazard zone boundaries during accident consequence analysis efforts will result in a smaller overall hazard zone than if a lower limit had been chosen. Conversely, lower limits will lead to larger hazard zones than higher limits.

The choice of an appropriate toxic limit, also referred to as a "level of concern" in earlier guidance documents published by the federal government, is discussed in Chapter 6. Flammable limits are discussed in Chapter 4.

Effects of Discharge Rates and Amounts on Vapor Dispersion

In the case of instantaneous discharges and others of relatively short duration, the total amount (i.e., weight) of vapor or gas released to the atmosphere has an impact on the size and shape of downwind hazard zones. All other factors being equal, larger discharge amounts will result in longer and larger downwind hazard zones. Smaller amounts will result in shorter and smaller zones.

The case with continuous releases is similar. All other factors being equal, higher discharge rates will produce longer and larger hazard zones. Lower discharge rates will produce shorter and smaller zones.

The area from which a vapor evolves is particularly important when the vapor originates from a boiling or evaporating pool of liquid. A smaller pool will usually evolve a lesser amount of vapor per unit of time than a larger pool and therefore pose less of a downwind hazard. A larger pool, having a greater surface area, will produce vapors at a higher rate and pose a greater downwind hazard. Thus, control of exposed pool surfaces can provide some degree of control over adverse downwind impacts.

Effects of Atmospheric Stability Conditions on Vapor Dispersion

The time of day, the strength of sunlight (if any) in the area, the extent of cloud cover, and the wind velocity all play major roles in determining the level of turbulence in the atmosphere and thereby the distances downwind over which airborne contaminants will remain hazardous. Meteorologists typically categorize atmospheric conditions into six ***atmospheric stability classes*** that range generally from "A" to "F". Class A represents unstable conditions under which there are strong sunlight, clear skies, and high levels of turbulence in the atmosphere, conditions which promote rapid mixing and dispersal of airborne contaminants. At the other extreme, atmospheric stability Class F represents light steady winds, nighttime skies, and low levels of turbulence. Airborne contaminants mix and disperse far less slowly with air under these conditions, which also include atmospheric ***inversions*** (when temperatures increase with altitude rather than decrease as usual), and may travel much farther downwind at hazardous concentrations than in other cases. Table 3.3 denotes the various criteria used for determination of these stability classes. Information on the percentage of time that any particular locale experiences the conditions associated with each class can be generally obtained from the nearest office of the National Weather Service, which is listed under the heading of U.S. Department of Commerce in telephone directories of major cities. Meteorologists associated with local radio and television stations or airports will also be knowledgeable of these statistics.

During an actual emergency, it will be necessary to understand that atmospheric conditions may change with time and that these changes will influence the behavior of the dispersing cloud or plume. As inspection of Table 3.3 reveals, atmospheric stability varies strongly with time of day, wind speed, extent of cloud cover, and strength of sunlight. As we are aware, these are all highly variable factors, possibly changing on an hour by hour basis in some locations during certain seasons.

Gas or Vapor Buoyancy Effects on Vapor Dispersion

The descriptions of vapor cloud and plume behavior given earlier started with the assumption that the vapor specific gravity or density of the gas or vapor being released is approximately equal to that of air. However, as also discussed earlier, certain gases or vapors and their initial mixtures with air may actually be heavier or lighter than air.

TABLE 3.3
ATMOSPHERIC STABILITY CLASS SELECTION TABLE

A -- Extremely Unstable Conditions
B -- Moderately Unstable Conditions
C -- Slightly Unstable Conditions
D -- Neutral Conditions*
E -- Slightly Stable Conditions
F -- Moderately Stable Conditions

	Daytime Conditions			Nighttime Conditions	
	Strength of sunlight				
Surface Wind Speed, mph	**Strong**	**Moderate**	**Slight**	**Thin Overcast greater than or = 4/8 Cloudiness****	**less than or = 3/8 Cloudness**
Less than 4.5	A	A - B	B	-	-
4.5 - 6.7	A - B	B	C	E	F
6.7 - 11.2	B	B - C	C	D	E
11.2 - 13.4	C	C - D	D	D	D
Greater than 13.4	C	D	D	D	D

*Applicable to heavy overcast conditions day or night
**Degree of Cloudiness = Fraction of sky above horizon covered by clouds.

In general, lighter-than-air gases, vapors, or mixtures will mix with air in the same fashion as those that are closer to the vapor specific gravity of air. Groundlevel contaminant concentrations are likely to be lower, however, because maximum concentrations along the centerline of the cloud or plume will tend to be elevated. The rate at which a cloud or plume will rise as it moves downwind will primarily be a function of the difference in vapor specific gravity between it and air and the prevailing wind speed. Lighter gases or vapors will rise faster. Strong winds will tend to keep the cloud or plume closer to the ground for longer periods of time. Figure 3.6 for distinct clouds or puffs demonstrates these concepts and the principles that also apply to plumes. In both cases, it is necessary to remember that the velocity of the wind will influence downwind travel distances within any given period of time.

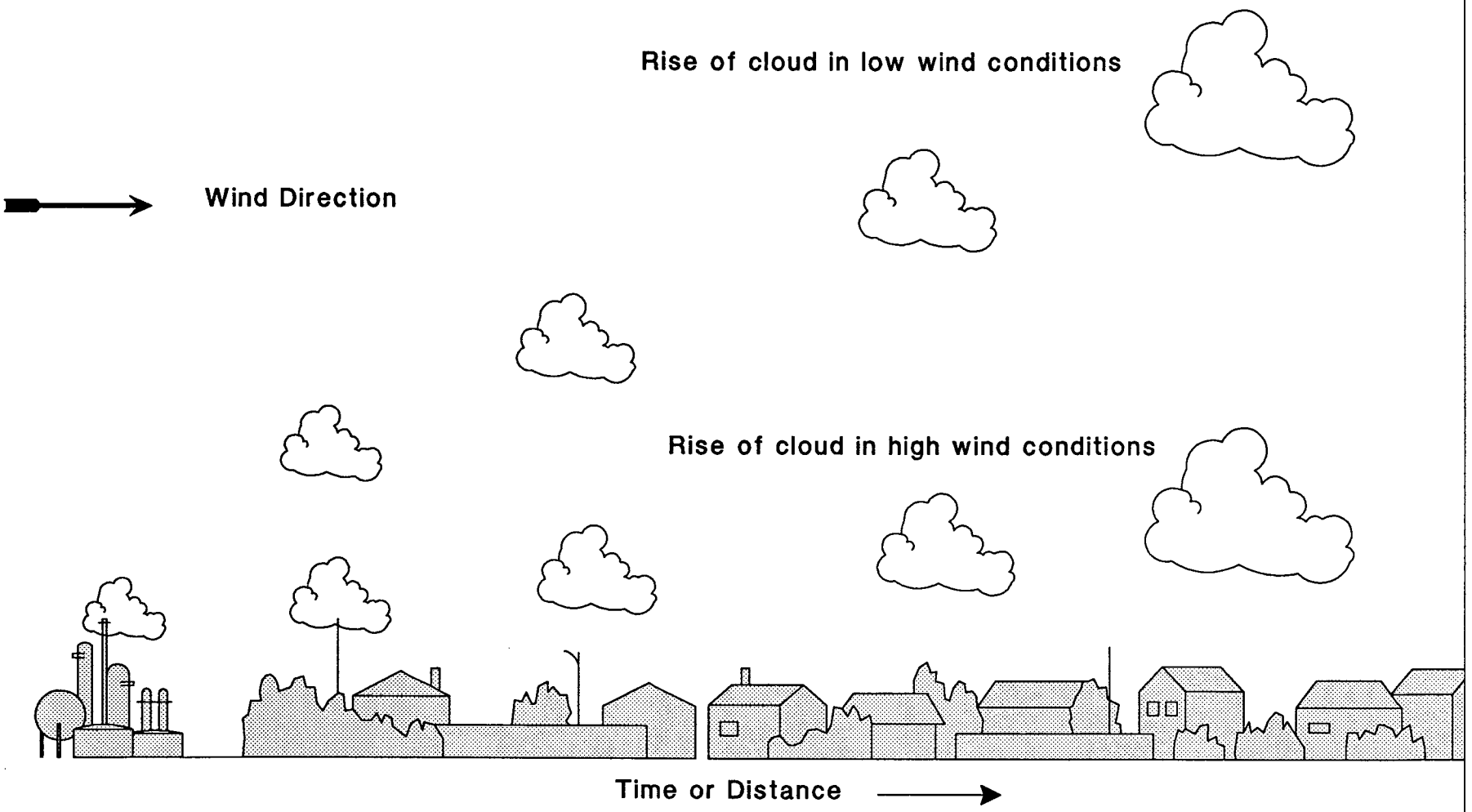
Heavier-than-air gases, vapors, or mixtures tend to hug the ground for a time when first released and may even follow terrain in directions across or against wind directions on certain boundaries. However, as these vapors and gases become more diluted with air, they will at some point begin behaving like mixtures with vapor specific gravities close to that of air. Thus, consideration of heavy gas or vapor dispersion phenomenon is more important for higher concentrations near the source (such as those associated with lower flammable limits) than for the lower concentrations typically associated with toxic limits.

The overall behavior of a heavy (negatively buoyant) cloud or plume can be very different than that of a neutrally or positively buoyant cloud or plume and the shape and dimensions of the cloud or plume can be strongly influenced by the duration of the discharge, prevailing atmospheric stability conditions, and prevailing wind velocities. For example, an instantaneous discharge of a flammable liquefied gas can result in a flammable or potentially explosive cloud that is 25 percent greater in maximum width than its length under neutral atmospheric conditions (see Table 3.3) when winds are of moderate velocity. Under more stable atmospheric conditions with lower wind speeds, the maximum width of the cloud could drop to approximately 80 percent of its length. Under specific combinations of conditions, particularly for large releases, cloud widths could be as much as 150 percent of length dimensions.

Continuous or otherwise prolonged discharges of heavy gases or vapors can behave yet differently from short-term releases. Under neutral atmospheric stability conditions, maximum plume widths typically range from 30 to 60 percent of lengths when winds are of moderate velocity. Under stable conditions, these widths can vary from 75 to 90 percent of lengths. In contrast, the maximum widths of neutrally or positively buoyant clouds or plumes are typically in the range of 40 to 50 percent of lengths.

Figure 3.6

Behavior of Lighter than Air Puffs or Clouds



Effects of Source Elevation on Vapor Dispersion

Although many discharges of gases or vapors are likely to take place at or near groundlevel, some may occur from the top of an elevated item of equipment or from a tall smokestack, pressure relief valve, or similar venting device. The principles set forth earlier with respect to post-discharge behavior of gases and vapors remain applicable in such cases, but it must be noted that groundlevel concentrations due to elevated sources may vary significantly from groundlevel concentrations due to groundlevel sources. Figure 3.7 illustrates some of the reasons for such differences.

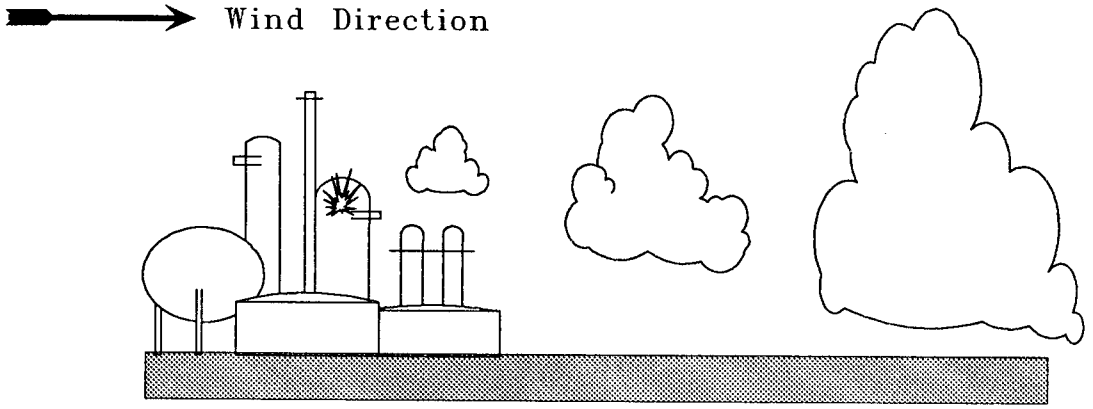
The most important concept to understand about elevated discharges is that maximum concentrations will be along the centerline path of cloud or plume travel in the downwind direction. In the case of neutrally buoyant clouds or plumes, groundlevel contaminant concentrations may be essentially zero until the bottom of the cloud or plume first touches ground. These concentrations will then rise with increasing downwind distance, reach a peak, and then drop with further distance. As demonstrated by the graph in Figure 3.3 presented earlier, this differs markedly from the variation of concentration with distance seen along the centerline path of such a cloud or plume.

When vapors or gases are lighter than air and therefore positively buoyant, the presence of harmful contaminant concentrations near groundlevel will strongly depend upon the wind velocity. As illustrated in Figure 3.6, the cloud or plume may rise quickly, slowly, and possibly not all depending on the wind speed (and the velocity with which the vapors or gases are discharged upwards into the air). Groundlevel concentrations will vary accordingly.

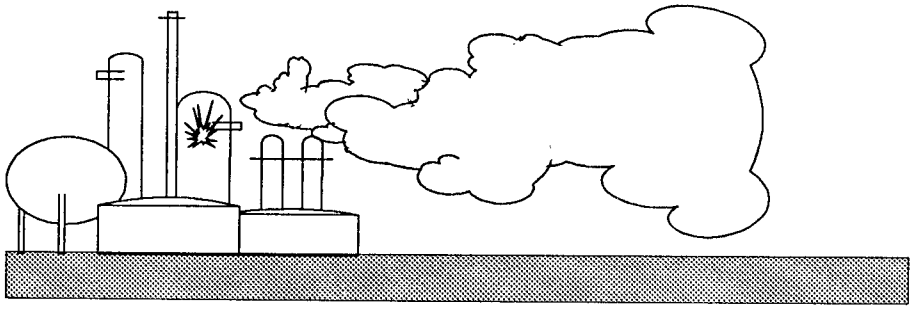
Effects on Dispersion Relating to Physical States of Contaminants

Although the discussion to this point has focused on the dispersion of gases and vapors in air, it is also important to understand that fine mists, fumes, or aerosols of liquids as well as fine dusts or powders may also be transported by the wind to downwind locations. Some discharges could involve mixtures of chemical vapors and aerosols and dusts.

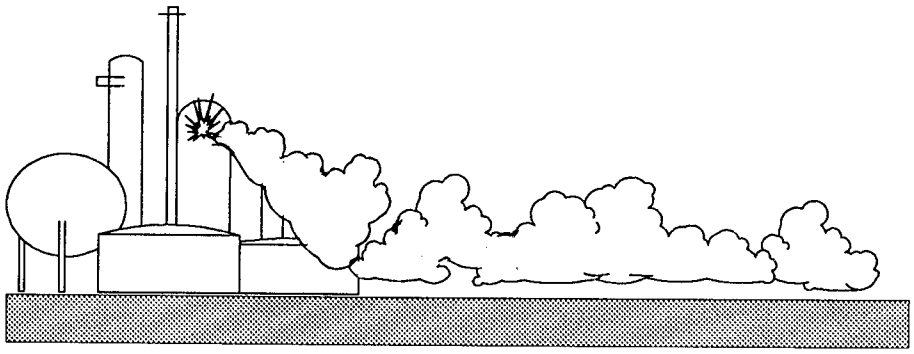
Larger and heavier droplets of liquid or particles of solids may "settle out" of the cloud or plume and drop to ground surfaces fairly close to their point of origin. Somewhat smaller particles may settle out a bit further downwind, while the smallest of all may travel as far as vapors and gases at equivalent concentrations in air. Droplets of volatile liquids may vaporize as they are carried by the wind or after they settle out of the main cloud or plume. They may also cause part or all of a cloud or plume to behave as if it is heavier than air even if the same substance in a purely gaseous state might be lighter than air or neutrally buoyant at prevailing temperatures. All of these phenomena can have an impact on groundlevel or close to groundlevel contaminant concentrations, generally resulting in levels above those



1. Puff dispersion of neutrally buoyant vapors. Groundlevel concentrations may be zero for some time until the puff first "hits" the ground. Same puff shown at different times above.



2. Continuous plume dispersion of neutrally buoyant vapors in air. Note again that some distance may be required before any contamination occurs near the ground.



3. Plume dispersion of heavy vapor. Puffs may follow a similar path during dilution with air.

Figure 3.7
Some Effects of Elevated Emissions

that would be expected in the absence of mists, fumes, aerosols, or dusts. Accurate prediction of cloud or plume behavior under these conditions is extremely complex and prone to substantial errors.

Effects of Discharge Velocities on Dispersion

Vapors or gases may be released to the atmosphere at relatively low velocities or may be vented under high pressure as a jet. There are various "jet" momentum effects that alter puff or plume behavior, particularly near the source of a discharge. A strong jet of vapor or gas will tend to entrain and mix with air rapidly at first, thus tending to reduce contaminant concentrations. These effects become less important, however, as the puff or plume moves downwind.

In the event that a high velocity high rate discharge of a heavier than air mixture of gas and liquid aerosols takes place in the downwind direction, there is a distinct possibility that downwind hazard zone lengths will be greater than those predicted by most vapor dispersion models in general use. The behavior of such highly pressurized discharges of compressed liquefied gases is a subject receiving considerable attention in scientific cicles at present, but accurate prediction of contaminant behavior under these conditions remains prone to substantial errors.

Effects of Local Terrain on Vapor Dispersion

In virtually all that has been said about atmospheric vapor dispersion phenomena up to this point, it has been tacitly assumed that the vapors or gases being discussed are dispersing over flat terrain without obstacles of any kind. In the real world, however, large portions of the country are by no means flat or devoid of hills, mountains, trees, or buildings. All of these topographical features and others influence the manner in which airborne contaminants disperse.

In most cases, a certain degree of "roughness" in the terrain is beneficial in the sense that it tends to speed up the rate at which contaminants mix with air and are thereby diluted. This is understandable if one thinks about how the wind behaves as it swirls around and over trees, hills, buildings, and other objects. There are two situations, however, in which terrain effects may cause increased hazards at or near groundlevel locations.

The first case involves situations in which contaminants are trapped within some sort of canyon, valley, or bowl-like depression in the land surface. Under these conditions, the walls or sides of these topographical features can prevent spreading of clouds or plumes and restrict dilution with air. The net result is that hazard zones might be of different size and

shape than otherwise expected. If an atmospheric inversion were to occur such that there was essentially a "cap" placed over a bowl-like depression or valley, airborne contaminants could be literally trapped for extended periods of time.

The second case involves the dispersion of gases or vapors from an elevated source when there are buildings or similar shaped features on the land in the downwind direction. As the wind passes over a building, some part of it may be drawn down into a swirling eddy pattern in a space behind the structure commonly referred to as its "wake cavity". The practical significance of this phenomenon is that contaminants liberated from elevated sources could potentially be drawn down towards groundlevel much sooner and at much shorter downwind distances than might otherwise be expected.

Readers should be advised that many of these phenomena are extremely difficult if not impossible to address in any sort of *generalized* vapor dispersion hazard prediction model or methodology regardless of its claimed level of sophistication or cost. Those who may be tempted to purchase any expensive software package to evaluate downwind vapor dispersion resulting from chemical accidents *for planning purposes* should first compare the results of the package with the results obtained from the computer program provided with this guide for several scenarios.

Effects of Wind Meandering on Evacuation or Protective Action Zones

The main reason that one would wish to determine or predict the concentration isopleths or footprints of gas or vapor clouds or plumes is to determine those downwind areas that may require public evacuation or other protective action in the event of a toxic and/or flammable vapor or gas release. It is important to realize, however, that the direction of the wind is rarely steady over any significant period of time and that the wind direction tends to shift back and forth between various directions. This shifting over time is often referred to as ***meandering***. The practical significance of wind meandering is that an area larger than that predicted by strict application of dispersion estimation methods may require evacuation or other means of public protection during an actual emergency.

The probability and extent of wind meandering in any locale is a complex function of several factors, but one of the most important involves the atmospheric stability class prevalent in the area at the time. The wind tends to meander less *on average* under stable conditions than in unstable weather.

Based on data presented on page 28 of the ***Handbook of Atmospheric Diffusion*** (U.S. Department of Energy, DOE/TIC-11223) by Hanna, Briggs, and Hosker, it has been determined that there is a 90 percent probability on average that a cloud or plume will remain within a downwind arc of 120 degrees from its point of origin under atmospheric stability class conditions A, B, and C. For more stable stability classes, the arc narrows to a 40 degree

angle. Figure 3.8 illustrates these observations, the practical significance of which is the finding that the area requiring evacuation or other protective action (such as sheltering populations in place) in the first hour of a hazardous vapor or gas release should usually be based on the above arcs and not the actual width of selected concentration isopleths. Where an evacuation is to be attempted, it is often best to start from a point nearest the emission source and work outwards towards downwind areas subject to lower concentrations. Be advised, however, that there is an exception to the above findings. When the velocity of the wind is very low under special circumstances, the direction of the wind can become very erratic. It is best to be prepared under low wind conditions for one or more sudden shifts in wind direction and the possibility that a cloud or plume may literally "hop" from one position or direction to another.

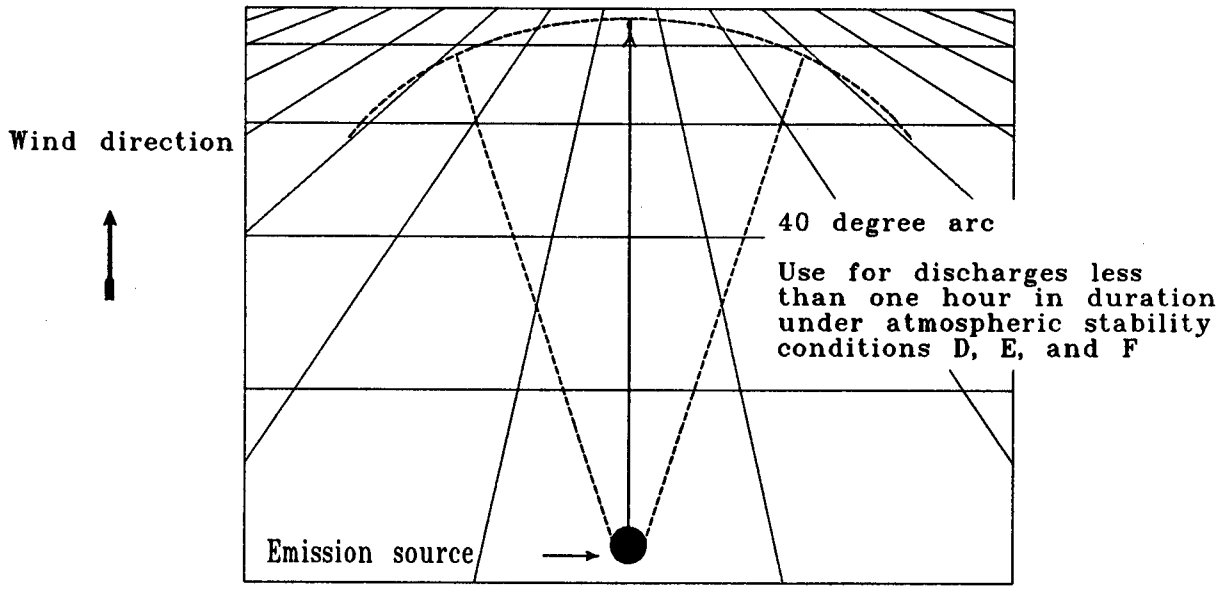
Indications of the specific areas that may require protective action in the event of specific spill or discharge situations can be obtained by drawing hazard zone boundaries on a map of the region in accordance with the "scale" shown on the map. These boundaries can be drawn for various wind directions and atmospheric stability classes to illustrate potential hazard zones under various conditions. Local census data may then be used to estimate the maximum number of people that may require protection. Note that the drawings will be most easily drawn using a ruler and protractor, keeping in mind that a full circle has 360 degrees.

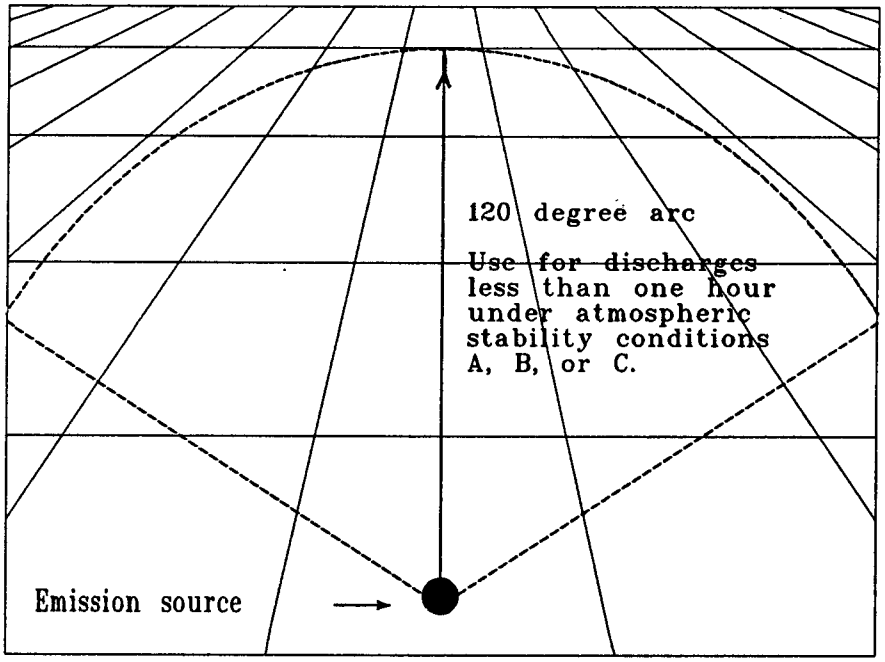
If the discharge or release may be prolonged, the probability will increase that there will be a major shift in wind direction. When and where possible, it is best to consult a meteorologist with detailed knowledge of current local conditions immediately for advice on how to expand the evacuation area as time progresses. For truly prolonged situations involving hazardous emissions, it may eventually become necessary to evacuate a full circle around the accident site out to the radial limits of the estimated hazard zone.

It is precisely because the direction of the wind during an accident cannot be predicted in advance and that the direction may shift during a hazardous event that the zone considered ***vulnerable*** around a potential accident or incident site encompasses a full circle around the site (or a "corridor" of overlapping circles if the site is along a railroad, pipeline, barge, or truck route). Although there may be many cases in which only a portion of the ***vulnerable zone*** will require protective action, public and industry officials must realize that the entire zone is at risk and will require attention during the emergency planning process, particularly with respect to populations at special risk or requiring special assistance.

The average probability of the wind being in any particular direction may be useful knowledge, particularly in locations where the wind is prone to flow in certain directions on a regular basis during various seasons. As in the case of atmospheric stability classes, the planning process can therefore benefit from consultation with a meteorologist at the nearest office of the National Weather Service or associated with a local radio or television station or

FIGURE 3.8
VAPOR DISPERSION HAZARD ZONE BOUNDARIES



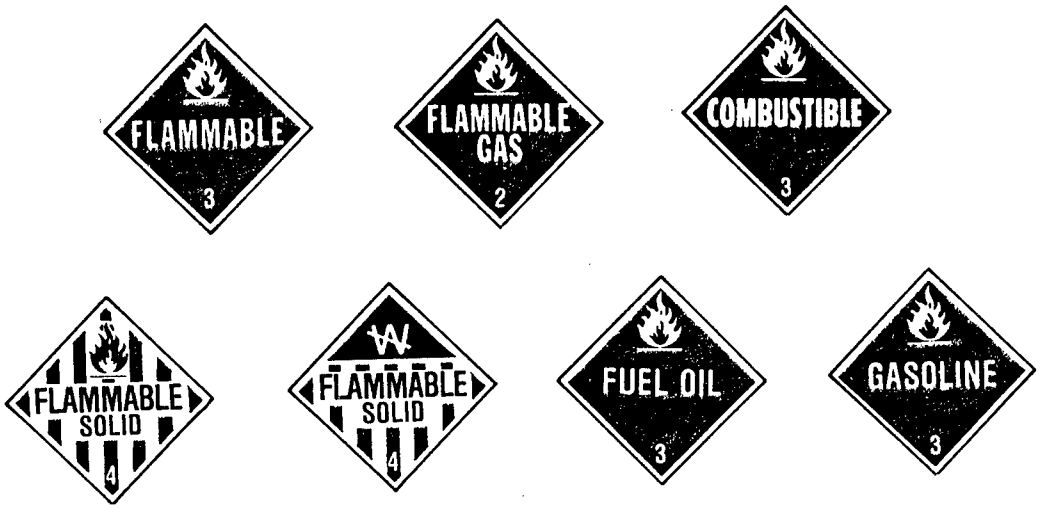


Arrows within boundaries of estimated hazard zones indicate length of downwind hazard distance in downwind centerline direction of wind.

Longer duration discharges may require up to 360 degree evacuations or protective measures if the wind direction may shift during the discharge. Consult a qualified meteorologist in actual emergencies for advice.

airport. It is common practice for these professionals to maintain or have access to detailed historical data pertaining to the frequency of various wind directions in the locale of their concern.

4.0 FIRE HAZARDS OF CHEMICAL SUBSTANCES



4.1 INTRODUCTION

When most of us think of an unwanted fire, we typically picture a burning building, a burning transport vehicle of some kind, or a burning forest with flames and smoke rising into the sky. These are clearly the most common types of fires and typically involve ordinary combustible materials such as paper, wood, cloth, plastics, and rubber. Fire departments across the nation face such fires on a daily basis and are well-equipped and trained to deal with them. Hazardous materials, however, may pose additional types of fire hazards with unusual characteristics. In the following, we first discuss measures of flammability potential, continue with a discussion of how the effects of fires may be evaluated, and finally, describe a number of "special" types of fires associated with hazardous materials.

4.2 MEASURES OF FLAMMABILITY POTENTIAL

It hardly needs saying, but most of us realize that some materials are much more easily ignited than others. Some require only a spark, such as the propane or LP-gas fuel in a gas barbecue, while others, such as a piece of granite, will not ignite even if placed under a welding torch. The most common measures of flammability potential for materials which are flammable or combustible are: 1) flash points; 2) lower flammable or lower explosive limits; 3) upper flammable or upper explosive limits; and 4) autoignition temperatures. These data are readily available in various handbooks and hazardous material data bases when known, and are commonly listed in chemical company material safety data sheets (MSDS). Fire

safety and combustion experts may also consider ignition energy requirements, fire points, flame spread rates, and heat and smoke generation rates of materials in evaluating their flammability characteristics, but knowledge of these latter attributes is not truly needed for the purposes of this document and sources of appropriate data are not readily available to the general public for a large number of subtances.

Flash Points

The ***flash point*** of a combustible substance, in simple terms, is the lowest temperature of a material at which the vapors over its liquid or solid surface will ignite and burn when exposed to a specified ignition source without necessarily causing self-sustaining combustion of the liquid or solid. Flash points vary from temperatures far *below* zero degrees Fahrenheit for flammable gases (such as natural gas, LP-gas, propane or butane), and volatile flammable liquids (such as gasoline), to hundreds of degrees *above* zero for heavy fuel oils. (Note: The temperature at which the vapors over a liquid or solid will ignite and continue to burn due to self-sustaining combustion of a liquid or solid is called its ***fire point***. These temperatures are available in the professional literature for only a relatively few materials.)

Materials with low flash points relative to temperatures in the ambient (i.e., natural) environment are usually ignited easily by a spark (be it from metal scraping metal or stone or from static electricity) or by a flame from any source. Most frequently, they are substances that are normally gaseous at ambient temperatures or liquids that readily evaporate or boil upon release. These vapors or gases can sometimes be carried by the wind to a source of ignition somewhat distant from the discharge site of the material and ***flashback*** to the spill source causing one or more of the fire hazards described later.

Substances with flash point temperatures close to ambient temperatures are also easily ignited by sparks or flames. The main difference between such materials and those described in the previous paragraph is that the ignition source must be closer to the fuel in order for ignition to take place. This follows from the observation that such materials are generally liquids of lower volatility than materials with substantially lower flash points.

The higher the flash point temperature is above ambient temperature, the more difficult it becomes to ignite a substance. Under normal circumstances, a fuel with a high flash point cannot be ignited by a spark or even a nearby flame unless: 1) the fuel is a liquid sprayed into the air as a fine mist; 2) the fuel is a finely divided solid; 3) a portion of the fuel is heated to its flash point by a nearby source of heat and then exposed to an ignition source; or 4) the fuel is heated to a temperature at or above its flash point prior to release and encounters an ignition source before cooling.

The flash point temperatures of combustible materials are determined using testing methods and equipment standardized by various organizations, with the American Society of Testing and Materials (ASTM) being the primary standard-setting body in the United States. There are two main classes of testing methods which respectively provide "open cup" or "closed cup" flash points, and each class represents more than one specific testing method. Because of differences in equipment design and testing procedure, the numerical value of closed-cup flash points is typically some 5-10° Fahrenheit lower than that of the open-cup flash point for the same substance, but the difference may be greater or less in individual cases. Due to other factors, most importantly the purity of the sample tested, it is not surprising to find a number of different closed cup or open cup flash points for any given substance, all of which differ to some extent. It is well, therefore, to consider flash point values reported in the literature as approximate rather than exact values.

Flammability and Explosivity Limits

It is rather well known that combustion cannot take place in the absence of a certain minimum amount of oxygen, be it available in air mixed with gases or vapors evolved from a combustible substance or from an internal component of the fuel. Conversely, there must be sufficient fuel vapors or gases available in a fuel-air mixture to support and sustain combustion. Thus, there are both lower and upper limits associated with fuel concentrations in air that will ignite and permit flames to spread away from the source of ignition (i.e, permit flames to ***propagate***). Fuel concentrations below the lower limit will contain insufficient fuel to ignite and propagate flame and are commonly referred to as being too ***lean*** to burn. Those above the upper limit are considered too ***rich*** to ignite; that is, they contain too much fuel and/or too little oxygen, as in the case of a "flooded" automobile engine.

The minimum concentration of a vapor or gas in air that will ignite and propagate flame is known as its ***lower flammable limit*** (LFL) concentration or its ***lower explosive limit*** (LEL) concentration and is usually expressed as a percentage by volume of fuel vapors in air. The words *flammable* and *explosive* are used interchangeably such that LFL values typically equal LEL values in the literature. The reasoning behind this is that the concentration of a fuel that will burn in air can also be expected to explode under the appropriate conditions. This supposition is only approximately true for some fuels (where precise LEL values might be slightly higher than LFL values), but it has become widely accepted over decades of use.

Similar to the above, the maximum concentration of a gas or vapor in air that will ignite and propagate flame is known as the ***upper flammable limit*** (UFL) or ***upper explosive limit*** (UEL) of the fuel. Again, the words *flammable* and *explosive* are often used in an interchangeable fashion.

LFL or LEL values are related to flash points of combustible substances in that the flash point is *theoretically* the temperature at atmospheric pressure to which a substance must be raised to produce a vapor or gas concentration over its surface equivalent to its LFL or LEL concentration. The relationship is not always observed in practice, however, because flash point measurement equipment and procedures, as discussed above, do not always produce precise values.

Flammable and explosive limits found in the literature are usually measurements made at normal atmospheric temperatures and pressures unless indicated otherwise. Be advised that there can be considerable variation in these limits at pressures or temperatures above or below normal. The general effect of an increase in temperature or pressure is to reduce the lower limit and increase the upper limit. Decreases in temperature or pressure have the opposite effect.

As a final note, it is also important to appreciate that certain solids, when dispersed in air as fine powders, may also be capable of burning or exploding upon encountering a suitable source of ignition. Some examples include coal dust produced in mining operations, grain dust produced in silos during storage or transfer operations, and flour produced in milling operations. Flammable or explosive limits for solid materials are usually expressed in units of weight of solid present in a specified volume of air.

Autoignition Temperatures

The ***ignition*** or ***autoignition temperature*** (AIT) of a substance, whether solid, liquid, or gaseous, is the minimum temperature necessary to initiate or cause self-sustaining combustion in the absence of a flame or spark. Even more so than flash points or flammable limits, these temperatures should be viewed as approximations due to the many factors that can affect testing results. Indeed, it must be noted that most values currently found in the literature were determined by testing methods that are now considered obsolete. Newer testing methods adopted by the ASTM frequently demonstrate substantially lower temperatures for the onset of combustion than older methods.

Table 4.1 provides examples of various hazardous materials and their associated flammability data. Those at or near the top of the list are extremely flammable and volatile and more likely to produce large quantities of flammable vapors or gases upon release; vapors or gases that may travel a considerable distance from the spill site and still be within flammable or explosive limit concentrations in air. Those at or near the bottom of the list are difficult to ignite without prior preheating and tend to have much lower vapor pressures (i.e., are generally of low volatility).

TABLE 4.1
EXAMPLE FLAMMABILITY CHARACTERISTICS

Substance	Closed-cup Flash Point (°F)	LFL (%)	UFL (%)	AIT (°F)
Propane	Very low	2.1	9.5	842
Gasoline	-45 to -36	1.4-1.5	7.4-7.6	536-853
Acetone	-4	2.5	13	869
Isopropyl alcohol	53	2.0	12.7 at 200°F	750
Turpentine	95	0.8	*	488
Fuel oil no. 2	126-204	*	*	494
Motor oil	275-600	*	*	325-625
Peanut oil	540	*	*	833

*Note: Flash points are often not recorded for substances that are gases at ambient temperatures because of the very low temperatures required to determine them. Similarly, flammable limits are not always available for substances with high flash points due to the high temperatures needed for ignition. Substances that are complex mixtures of a number of materials, (e.g., fuel oils) may have a range of flash points.

Sources: ***Fire Protection Guide on Hazardous Materials***, 8th ed., National Fire Protection Association, Quincy, MA, 1984.

CHRIS Hazardous Chemical Data, U.S. Coast Guard, U.S. Department of Transportation, Washington, D.C., 1978.

4.3 MEASURES OF FLAMMABILITY EFFECTS

Direct contact with a flame of any sort is obviously not a good idea for any prolonged period of time since the extreme heat may ignite combustible materials or severely burn and destroy living tissue. What may not be fully realized is that fires can also cause damage or injury from a distance via transmission of thermal radiation, not unlike the manner in which the sun warms the earth. Such radiation, which is completely different from nuclear radiation, will be strongest at the surface of a flame and will become rapidly weaker as one moves away in any direction. Consequently, during a major hazardous material release involving fire, property damage and human injuries may occur not only in burning areas, but also in a zone surrounding the fire.

Thermal radiation levels (also referred to as thermal radiation ***fluxes***) are measured and expressed in units of power per unit area of the item receiving the energy. However, since the damage or injury sustained by a receiving object is a function of the duration of exposure as well as the level, thermal radiation ***dosages*** are also of concern. These dosages are determined by combining radiation levels with exposure times and are expressed in units of energy per unit time per unit area of receiving surface. Table 4.2 lists some of the known effects of thermal radiation on bare skin as a function of exposure level and time.

4.4 TYPES OF FIRES

There are essentially six types of fires associated with hazardous material discharges, with the type of fire a function not only of the characteristics and properties of the spilled substance but the circumstances surrounding its release and/or ignition. The six types are:

- Flame jets
- Fireballs resulting from Boiling Liquid Expanding Vapor Explosions (BLEVEs)
- Vapor or dust cloud fires
- Liquid pool fires
- Fires involving flammable solids (as defined by the U.S. Department of Transportation), and
- Fires involving ordinary combustibles

TABLE 4.2
THERMAL RADIATION BURN INJURY CRITERIA

Radiation Intensity

kW/m^2	$Btu/hr\text{-}ft^2$	Time for Severe Pain (sec)	Time for 2nd Degree Burn (sec)
1	300	115	663
2	600	45	187
3	1000	27	92
4	1300	18	57
5	1600	13	40
6	1900	11	30
8	2500	7	20
10	3200	5	14
12	3800	4	11

Data sources: Buettner, K., "Effects of Extreme Heat and Cold on Human Skin, II. Surface Temperature, Pain and Heat Conductivity in Experiments with Radiant Heat," J. Ap. Phys., Vol. 3, p. 703, 1951.

Mehta, A.K., et al., "Measurement of Flammability and Burn Potential of Fabrics," Summary report to the NSF under Grant #GI-31881, Fuels Research Laboratory, Mass. Inst. of Tech., Cambridge, Mass., 1973.

Flame Jets

Transportation or storage tanks or pipelines containing gases under pressure (i.e., compressed gases) or normally gaseous substances that have been pressurized to the point they become liquids (i.e., compressed liquefied gases) may discharge gases at a high speed if somehow punctured or broken during an accident. The gas discharging or venting from the hole will form a gas jet that "blows" into the atmosphere in the direction the hole is facing, all the while entraining and mixing with air. If the gas is flammable and encounters an ignition source, a flame jet of considerable length may form (possibly hundreds of feet in length) from a hole less than a foot in diameter. Such jets pose a thermal radiation hazard to nearby people and property, and are particularly hazardous if they impinge upon the exterior of a nearby intact tank containing a flammable, volatile, and/or self-reactive hazardous material. Such events sometimes occur during multi-car train derailments or in incidents at crowded chemical plants or oil/gas processing or storage facilities. In these cases, the heat of the flame increases pressure in the intact tank while simultaneously weakening its outer wall. This may eventually cause the tank to rupture violently or explode in an event referred to as a BLEVE (see below), particularly if the flame impinges on the wall in the vapor space of the container where there is no adjacent liquid to draw heat away from the wall surface. If the contents of the intact tank are flammable, a large rising fireball may result. If the contents are nonflammable but toxic, a large amount of toxic vapors or gases may be suddenly released to the atmosphere.

Fireballs Resulting from BLEVES

Boiling Liquid Expanding Vapor Explosions (BLEVEs) are among the most feared events when sealed tanks of liquid or gaseous hazardous materials are exposed to fire. Although they are called explosions, they are not associated with strong blast waves *in many cases*. Rather, they involve the violent rupture of a container of flammable material and the rapid vaporization of the material. If the substance is flammable, a large rising fireball may form, the size of which will vary with the amount of hazardous material present, and which may be as much as 1,000 feet in diameter when involving a railroad tank car containing a flammable liquefied compressed gas like liquid propane or LPG. Although the fireball is generally of short duration, the intense thermal radiation generated can cause severe and possibly fatal burns to exposed people over relatively considerable distances in a matter of seconds. In addition, if the tank is relatively long and cylindrical in shape, part of the tank may literally "rocket" into the air, all the while spewing forth burning gases and liquids. Pieces of such tanks have been known to travel up to 5,000 feet in BLEVEs involving railroad tank cars. Fires and various impact damages have occurred at the landing points of larger pieces. (Note: Be advised that there is potential for the tank to rocket upon rupturing violently or exploding regardless of whether its contents are flammable or nonflammable.)

The phenomena leading to a BLEVE can occur with most liquids excessively heated in a closed or inadequately vented container, whether they are flammable or not, or are pure materials or mixtures, unless other circumstantial factors are considered. Two important factors are the duration of the external exposure fire and the flow capacity of any pressure relief valve if one is present. If the exposure fire is not of sufficiently long duration, or if the relief valve can vent vapor as fast as it is generated, a BLEVE will not occur. An additional factor is the availability of external cooling via fixed water spray systems, fire monitors, hose streams, etc. These can contribute to the prevention of a BLEVE either by suppressing the external fire or by cooling the heated vessel. Finally, note that the possibility of a BLEVE increases with the volatility of the hazardous material. Substances with higher vapor pressure at any given temperature are more at risk than those with lower vapor pressures.

Vapor or Dust Cloud Fires

Vapors evolved from a pool of volatile liquid or gases venting from a punctured or otherwise damaged container, if not ignited immediately, will form a plume or cloud of gas or vapor that moves in the downwind direction. If this cloud or plume contacts an ignition source at a point at which its concentration is within the range of its upper and lower flammable limits, a wall of flame may flash back towards the source of the gas or vapor, engulfing anything and everything in its path. Similarly, fires may flash through airborne clouds of finely divided combustible dusts whether or not they are formally classified as hazardous materials. People or property caught within the cloud as the flame passes may be severely injured or damaged if not protected.

Liquid Pool Fires

A liquid pool fire is defined as a fire involving a quantity of liquid fuel such as gasoline spilled on the surface of the land or water. As in prior cases, primary hazards to people and property include exposure to thermal radiation and/or toxic or corrosive products of combustion. An added complication is that the liquid fuel, depending on terrain, may flow downslope from the accident site and into sewers, drains, surface waters, and other catchments. There have been cases where such fires have ignited other combustible materials in the area or have caused BLEVEs of containers subjected to the flames. On occasion, pools of burning liquids floating on water have entered water intakes of industrial facilities and caused internal fires or explosions. Burning fuels entering sewers and drains not completely full of fluid have caused underground fires and/or threatened industrial or municipal treatment facilities at the receiving end of the sewer or drain.

Flammable Solid Fires

A ***flammable solid*** is defined by the U.S. Department of Transportation as any solid material, other than one classed as an explosive, which under conditions normally incident to transportation is liable to cause fires through friction, retained heat from manufacturing or processing, or which can be ignited readily and when ignited burns so vigorously and persistently as to create a serious transportation hazard. Included in this class are spontaneously combustible and water-reactive materials.

As the above definitions suggests, the term flammable solid encompasses materials with a wide range of hazardous properties.

- Some of these solids are considered hazardous because they can be ignited by friction, much like the head of a match.

- Some are organic materials such as charcoal, powdered coal, wet paper, and even fish scrap or fish meal which may at times internally generate heat to the point of self-ignition when improperly stored or transported.

- Some are metals in the form of powders or other small pieces which can self-ignite in prolonged contact with moisture, burn at very high temperatures, and/or be difficult if not impossible to extinguish without special techniques or materials, with aluminum and magnesium being good examples.

- Some of these materials (i.e., pyrophoric substances) may ignite if exposed to air or burn vigorously in the fashion of highway flares. Phosphorus has both of these properties and also generates large quantities of toxic and irritating smoke.

- Some have several of these properties.

Fires Involving Ordinary Combustibles

Some hazardous materials, including some of the flammable solids described above, burn with no special hazards beyond those associated with paper, wood, and other common materials of everyday life. Wet paper waste, for example, is only considered hazardous because it may ignite spontaneously (i.e., self-heat and self-ignite). Once burning, it poses no special or unusual threat. This is not meant to imply that such a fire would not be significant or important to consider in planning for emergencies, only that the nature of the threat is one encountered frequently by fire service personnel and well known to them.

4.5 PRODUCTS OF COMBUSTION

Besides evolving heat and thermal radiation, fires involving certain hazardous materials may generate smoke and gases that are more toxic than those evolved from ordinary substances. In most cases, the heat of a fire will cause these products of combustion to rise into the sky where they will become diluted with air below harmful levels before reapproaching the ground surface. On occasion, however, their toxicity level may be so high as to necessitate public evacuations until the fire has been extinguished. Indeed, a 1986 incident in Ohio involving the burning of phosphorus in a railroad car required the evacuation of at least 40,000 people due to the toxic and irritating smoke generated. This was the largest evacuation associated with a train wreck in the history of the United States.

Material safety data sheets (MSDS) and other data bases and handbooks describing individual substances will typically provide a general indication of expected products of combustion or thermal decomposition. The term "general" is used because far more often than not the discussion will be rather imprecise and unlikely to highlight more than a few rather common products of combustion or decomposition.

In the case of organic materials comprised solely of carbon, hydrogen, and oxygen, products of combustion virtually always include carbon dioxide and highly toxic carbon monoxide together with water vapor and some amounts of unburned vapors of the hazardous material. Substances of low molecular weight (i.e., simple hydrocarbons and alcohols), may indeed only generate these products of combustion when burning freely in the natural environment. More complex and heavier substances, however, may generate a complicated mixture of substances, some of which may be extremely toxic. A general rule of thumb to follow is that most strictly organic materials usually pose no more hazard when burning (although the hazard may indeed be very significant) than a burning wooden home or other building. The key exception involves fires involving organic materials of high toxicity in the unburned state, with pesticides being primary examples. Fires involving such materials may be particularly hazardous not only due to toxic combustion products but due to the potential dispersion of unburned pesticides.

One can obtain a general idea of unusual products of combustion or decomposition by looking at the chemical formula for any particular hazardous material of concern, this being an item almost always given in MSDS and other safety related publications for pure materials. Some of the more common symbols used for various individual components (i.e., elements) of chemical molecules include:

Element	Chemical Symbol
Bromine	Br
Carbon	C
Chlorine	Cl
Fluorine	F
Hydrogen	H
Lead	Pb
Mercury	Hg
Nitrogen	N
Oxygen	O
Phosphorus	P
Sulfur	S

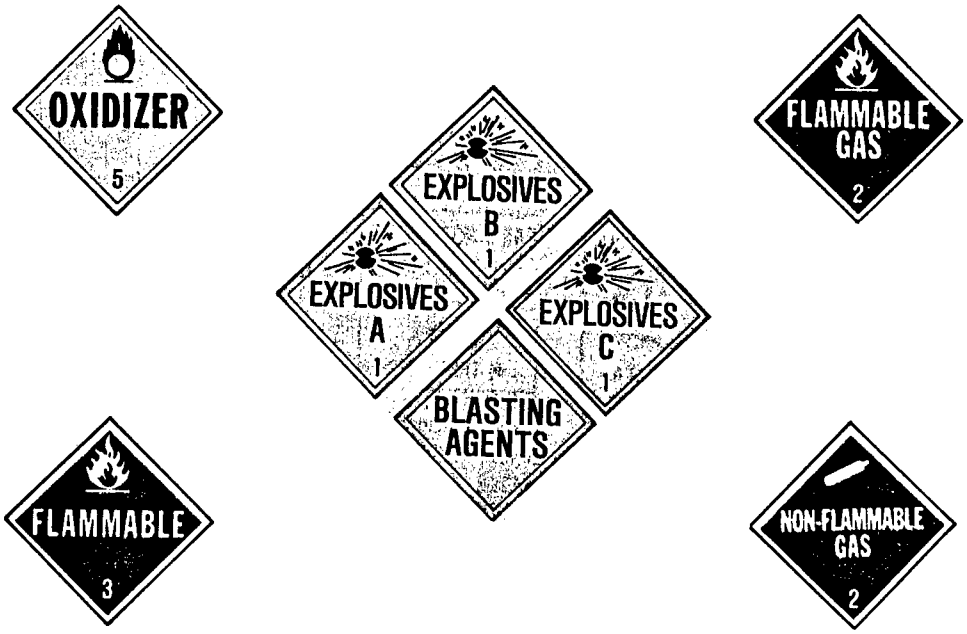
Hazardous materials containing bromine, chlorine, or fluorine, if subject to combustion or decomposition in a fire environment, may generate irritating and corrosive substances such as hydrogen bromide or hydrobromic acid, hydrogen chloride or hydrochloric acid, or hydrogen fluoride or hydrofluoric acid, and possibly gaseous bromine, chlorine or fluorine themselves. The extremely toxic substance known as phosgene may be formed in some cases when chlorine is present, particularly in combination with oxygen in the chemical molecule, so it is important to check for this possibility in MSDS and other information sources.

Both lead and mercury are well-known toxic metals that can be found as components of numerous chemical substances. Smoke or fumes from fires involving these toxic heavy metals and others (such as arsenic), must always be of concern.

Although pure nitrogen gas is non-toxic and a major component of air, chemical molecules containing nitrogen atoms may evolve toxic nitrogen oxides under fire conditions. The combination of carbon with nitrogen in a -CN group within a chemical molecule suggests that highly toxic cyanides may be generated in fires.

Dry phosphorus may ignite upon contact with air and generate thick white smoke containing phosphoric acid and phosphorus pentoxide. As noted earlier, this smoke is both highly irritating and highly toxic.

5.0 EXPLOSION HAZARDS OF CHEMICAL SUBSTANCES



5.1 DEFINITIONS

The dictionary contains two definitions of the word ***explode*** relevant to hazardous materials, these being:

- To burn suddenly so that there is violent expansion of hot gases with great disruptive force and a loud noise (in what is called a ***thermal explosion***).
- To burst violently as a result of pressure from within (in what is called a ***non-thermal explosion***).

The first definition clearly involves ignition and release of thermal energy from an explosive material or mixture while the second does not. In the following, we first discuss the conditions and factors that define the potential for both thermal and non-thermal explosions, follow with a discussion of how the effects of explosions can be measured, and then discuss the various types of explosions which meet the above criteria and which may be encountered in accidents involving hazardous materials.

5.2 FACTORS THAT INFLUENCE EXPLOSION POTENTIAL

Thermal Explosions

The definitions of lower and upper flammability limits presented earlier explained that these terms are used interchangeably with the terms lower and upper explosive limits in air. The reason for this is that a flammable mixture of a gaseous fuel in air, i.e., a mixture within the range of lower and upper flammable limit concentrations, may explode if ignited under appropriate conditions. Similarly, a cloud of combustible dust may explode if airborne concentrations are within these limits and the cloud is confined.

The set of conditions under which explosions of gases or vapors are most common involves ignition within the confined space of a building, sewer pipe, tunnel, partially empty liquid storage tank (on land or on a marine vessel), or other container. Dust explosions have frequently occurred in grain handling facilities and storage silos as well as other locations where fine combustible dusts are handled or generated.

It follows from the above that virtually all substances that are handled under conditions in which fuel-air mixtures are within explosive or flammable limits and fill a significant fraction of an enclosed space have a high probability of exploding rather than simply burning upon ignition. However, it must also be realized that gaseous mixtures may also explode at times when only partially confined or even if completely unconfined in an open environment. These latter explosions, referred to as ***unconfined vapor cloud explosions,*** often have far less power than explosions in confinement, and it has been observed that some substances have a far greater probability of exploding when unconfined than others. Nevertheless, past events have proven that unconfined explosions can occasionally cause devastating damage and widespread injuries, especially when the weight of airborne gas or vapor exceeds 1000 lbs. Below this weight, unconfined vapor cloud explosions are quite rare and typically involve a relatively few specific materials.

There also are many solids and liquids which may explode or detonate if ignited, shocked, or subjected to heat or friction, depending on their individual properties and characteristics. Some of the best known examples are TNT, dynamite, gunpowder, and nitroglycerine which may be referred to at times as ***condensed-phase*** explosives or ***high*** explosives. Determination of whether any particular liquid or solid may be explosive, and the conditions under which it may explode, requires investigation on a case-by-case basis, since there is no specific property or characteristic that sets explosives apart from other materials. Fortunately, manufacturers of these materials and hazardous material data bases and guidebooks will usually highlight the explosive properties of such materials.

The power or strength of a thermal explosion, however one wishes to express it, is a function of three primary factors:

- The amount of fuel present that is capable of exploding
- The amount of energy available in this portion of the fuel
- The fraction of the available energy (known as the ***yield***) expected to be released in the explosion process.

In simpler terms, it is understandable that two sticks of dynamite produce a larger blast than one stick, that fuel-air mixtures above or below explosive limit concentrations in air may not give additional strength to an explosion, and that some substances contain more energy per unit weight than others.

Non-thermal Explosions

The most simple type of non-thermal explosion to understand is that due to overpressurization of a sealed or inadequately vented container of some sort. Much as a balloon will burst if too much air is blown in, the walls of a sealed tank or other container may rupture violently if too much gas or liquid is forced in, if an internal chemical reaction produces excessive gases or vapors, or if a reaction or other source of heat increases the internal vapor pressure of the contents to the point that the walls are "stretched" beyond their breaking point. Since ignition and fire are not involved in the actual explosion process, these events are considered non-thermal explosions, although the contents of the container may ignite subsequent to its release if a suitable ignition source is present and the substance is flammable or combustible.

The strength of a non-thermal tank overpressurization explosion is a function of the pressure at which the walls of the container burst and the nature of the walls (i.e., whether they are ***brittle*** and will break suddenly with a "snap" or are ***ductile*** and more likely to stretch and then split or tear along some line on the surface). If the tank contains gas under pressure, the volume of the gas in the tank will also be important.

A final note is that non-thermal explosions involving compressed gases or vapors are far more likely to cause damage to distant objects than those involving liquids. This follows from the definition of shock and blast waves presented below and the relatively incompressible nature of liquids.

5.3 MEASURES OF EXPLOSION EFFECTS

When a firecracker or a stick of dynamite explodes, the violence and speed of the reactions taking place produce what is either referred to as a shock wave or a blast wave. Technically speaking, there is a difference between these two terms, but we will treat them rather interchangeably here. Either type of wave can be thought of as a thin shell of highly

compressed air and/or hot gases that rapidly expands in all directions from the point at which the explosion is initiated. Such waves can move at velocities exceeding the speed of sound in air, and, therefore, are capable of producing sonic "booms," much like those associated with supersonic aircraft. This is why significant explosions produce a loud "bang."

The damage caused by a shock or blast wave striking an object or a person is a complex function of many factors, and it is well beyond the scope of this document to attempt to describe all the complex interactions involved. Instead, we will simply refer to the wave as a rapidly expanding shell of compressed gases. The strength of the wave can then be measured in units of pressure (psi, e.g.), and the effects of ***peak overpressures*** within the wave (i.e., the maximum pressure in the wave in excess of normal atmospheric pressure) can be related to the level of property damage or personal injury likely to result.

Table 5.1 presents a list of peak overpressures and their expected effects on people and property. It is important to note that peak overpressures in a shock or blast wave are highest near the source of the explosion and decrease very rapidly with distance from the explosion site. Additionally, it must be noted that the location of the blast relative to nearby "reflecting surfaces" will influence the extent of damage incurred. For example, picture an explosion that takes place well above the surface of the ground. In this type of elevated or "free-air" event, the spherical shock wave has the opportunity to travel and dissipate in all directions simultaneously. Conversely, if the same explosion were to take place directly on the ground surface, the major portion of the energy released would only dissipate upwards and outwards. The ground surface would reflect most energy directed downward, and the net result would be a blast or shock wave with approximately twice the strength expanding from a hemi-spherical shaped volume of space situated on the ground. Hazard analysis procedures discussed in Chapter 12 and Appendix B of this guide and incorporated into the ARCHIE Computer Program therefore consider the location of an explosion relative to the ground surface. Not considered, however, are potential reflections from building walls and other surfaces that may cause actual damage patterns to be somewhat more erratic than those predicted by generalized hazard assessment methodologies for explosion events.

Beside personal injuries and property damage caused by direct exposure to peak overpressures, the blast or shock wave also has the potential to cause indirect impacts. These secondary effects of explosions include:

- Fatalities or injuries due to missiles, fragments, and environmental debris set in motion by the explosion or by the heat generated.

- Fatalities or injuries due to forcible movement of exposed people and their subsequent impact with ground surfaces, walls, or other stationary objects.

TABLE 5.1
EXPLOSION OVERPRESSURE DAMAGE ESTIMATES

Overpressure* (psig)	Expected Damage
0.03	Occasional breaking of large windows already under stress.
0.04	Loud noise (143 dB); sonic boom glass failure.
0.10	Breakage of small windows under strain.
0.15	Typical pressure for glass failure.
0.30	Some damage to house ceilings; 10% window glass breakage.
0.40	Limited minor structural damage.
0.50-1.0	Windows usually shattered; some window frame damage.
0.7	Minor damage to house structures.
1.0	Partial demolition of houses; made uninihabitable.
1.0-2.0	Corrugated metal panels fail and buckle. Housing wood panels blown in.
1.0-8.0	Range for slight to serious injuries due to skin lacerations from flying glass and other missiles.
1.3	Steel frame of clad building slightly distorted.
2.0	Partial collapse of walls and roofs of houses.
2.0-3.0	Non-reinforced concrete or cinder block walls shattered.
2.3	Lower limit of serious structural damage.
2.4-12.2	Range for 1-90% eardrum rupture among exposed populations.
2.5	50% destruction of home brickwork.
3.0	Steel frame building distorted and pulled away from foundation.
3.0-4.0	Frameless steel panel building ruined.
4.0	Cladding of light industrial buildings ruptured.
5.0	Wooded utility poles snapped.
5.0-7.0	Nearly complete destruction of houses.
7.0	Loaded train cars overturned.
7.0-8.0	8-12 in. thick non-reinforced brick fail by shearing of flexure.
9.0	Loaded train box cars demolished.
10.0	Probable total building destruction.
14.5-29.0	Range for 1-99% fatalities among exposed populations due to direct blast effects.

*These are the peak pressures formed in excess of normal atmospheric pressure by blast and shock waves.

Source:Lees,F.P, Loss Prevention in the Process Industries, Vol. 1, Butterworths, London and Boston, 1980.

The most common injuries due to missiles and the like are attributable to violent glass breakage and impact of airborne shards of glass with people. Fragments may include portions of any container that explodes and pieces of structures or equipment that are torn loose by the explosion and become airborne. Environmental debris essentially covers all else that may be forced out of place. The entire category can also be considered to encompass situations in which people are buried in the rubble of collapsed buildings or other structures.

It is very important to realize that a tank that BLEVEs or otherwise ruptures violently may break up into various fragments, one or more of which may be projected for considerable distances. Portions of cylindrical tanks have been known to literally "rocket" into the air while spewing forth burning liquids and have caused fires and impact damages upon falling back to the ground.

Where railroad tankcars or highway tank vehicles are at risk, hazardous material response guides have typically suggested that a radius of one-half mile be evacuated to prevent injuries from both fragment and thermal radiation hazards. Recent incidents have indicated, however, that individual fragments may occasionally travel as far as 4000-5000 feet from a tankcar BLEVE, and it is therefore prudent to evacuate to a radius of one mile in such cases, if this is practical. Since railroad tankcars carry 2-4 times as much cargo as typical highway tank vehicles, the one-half mile radius is ***probably*** sufficient for major truck accidents, but this is ***not*** absolutely certain for all cases.

The evacuation distances required for smaller or larger tanks than typically 3,000-12,000 gallon highway vehicles or 20,000-30,000 gallon capacity railroad tankcars will vary somewhat with the quantity of hazardous material present, but not as much as one might think. At the lower end of the scale, one major authority suggests a 1500 ft evacuation radius for situations in which an ordinary gas cylinder is involved in fire. Limited data for explosions or BLEVEs involving major stationary storage tanks do not indicate fragment hazards beyond one mile in the majority of ***known*** cases.

Where a tank or container ruptures violently due to internal overpressurization, fragment hazards are to some degree a function of whether the wall materials are brittle or ductile. Brittle materials (such as glass) may shatter into many smaller pieces. Tanks or containers made of ductile materials (such as most metals at or above relatively normal temperatures) are more likely to split or tear into a few large pieces.

Fatalities or injuries due to forcible movement of exposed people and their subsequent impact with objects quite literally involves situations in which the shock or blast wave pushes or picks up and throws bodies against obstacles.

5.4 TYPES OF EXPLOSIONS

Many of the basic types of explosions have already been described, but there are benefits in listing them again and providing more formal definitions of terms.

Container or Tank Overpressurization Explosions

As noted earlier, these events are a result of excessive pressure within a sealed tank or other container and are deemed to be non-thermal explosions. They occur when excessive pressure causes the walls of a tank or container to rupture violently, much as a balloon "pops" when too much air is blown in.

Dust Explosions

A cloud of combustible dust that is airborne and has concentrations within its upper and lower explosive limits may explode when ignited. Explosions usually occur when the dust fills most of an enclosed space of some kind.

An earlier discussion of fire hazards described how non-exploding clouds of dust in air may simply burn in a dust cloud fire that can also be referred to as a ***deflagration***. It is important to realize that there is no fine line between a deflagration and an explosion, since deflagrations are also capable of producing shock waves with measurable peak overpressures. It is usually when these overpressures become significant to the point of causing damage or injury that the event is called an explosion. It is when the shock or blast wave moves at a velocity greater than the speed of sound under the conditions present, thus being capable of causing maximum damage, that the event may be called a ***detonation***.

Gas or Vapor Explosions

As in the case of airborne dusts, a gas or vapor within flammable or explosive limit concentrations may cause a deflagration, explosion, or detonation upon ignition. These events can occur when the fuel-air mixture is confined, partially confined, or completely unconfined, but confinement of the mixture most definitely increases the probability of significant personal injury or property damage. Note that the gas or vapor may be directly released to the vulnerable environment or may evolve from evaporating or boiling liquids that have entered the area.

Condensed-Phase Explosions or Detonations

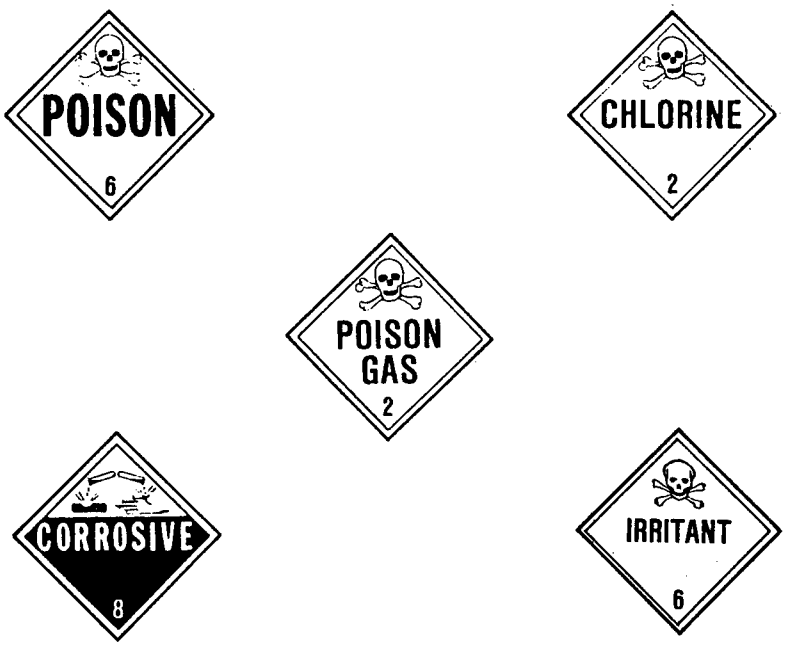
As noted above, when the substance that explodes or detonates is a liquid or a solid, the event is often called a condensed-phase explosion or detonation. Those who use this term may be prone to call events involving gases or vapors in air as ***diffuse-phase*** or ***gas-phase*** explosions or detonations.

Boiling Liquid Expanding Vapor Explosions (BLEVEs)

BLEVEs were described in some detail in the prior section discussing fire hazards of concern, where it was stated that they are not associated with strong shock or blast waves *in many cases*. Obviously, this also means that shock or blast waves with sufficient power to cause injury or damage may indeed occur at times.

Although some experts may disagree with the fine points of what is being said, BLEVEs can also be described as a combination of other types of fires and explosions. Indeed, bursting of a tank of liquid or compressed liquefied gas due to overheating is related to tank or container overpressurization explosions. Subsequent ignition of expanding gases, which may result in a large fireball, can be thought of as resulting in one type of gas or vapor cloud deflagration.

6.0 TOXICITY HAZARDS OF CHEMICAL SUBSTANCES



6.1 INTRODUCTION

Although hazardous materials can pose both short-term and possibly long-term toxicological threats to terrestrial and aquatic wildlife and plants, the immediate concern during significant discharges is protection of human life and health. Consequently, this section addresses the toxicity and toxic hazards posed to the public by chemical substances. It must be noted, however, that much of what will be presented can also be applied to understanding toxicological hazards to plants and animals.

6.2 ROUTES OF ENTRY

Toxic materials, be they solids, liquids, or gases/vapors, can affect living creatures via three primary ***routes of entry***.

- Inhalation -- the process by which irritants or toxins enter the body via the lungs as a result of the respiratory process
- Ingestion -- the process of consuming contaminated food or water or otherwise permitting oral intake of irritants or toxins

- Direct contact with skin or eyes -- the process by which hazardous materials cause injury to bodily tissues via direct contact or cause poisoning via absorption through the skin or other external tissues. Also included in this category is the passage of toxic materials into the body via puncture wounds or other breaks in the skin.

Inhalation exposures may result from breathing gases vented from containers, vapors generated from evaporating liquids (on land or in water), liquid aerosols generated during venting of pressurized liquids, fumes generated from spilled acids, gases or fumes generated by chemical reactions, dusts that become airborne due to an explosion or due to wind forces, the products of combustion of a burning hazardous material, or a variety of other mechanisms.

Ingestion (i.e., oral) exposures may follow from poor hygiene practices after handling of contaminated materials or from ingestion of contaminated food or water. Ingestion may also occur following inhalation of insoluble particles that become trapped in mucous membranes and swallowed after being cleared from the respiratory tract.

Direct contact may result from exposures to hazardous gases, liquids or solids in the environment, either on land, in the air, or in water. Effects may be local and involve irritation or burns of the skin or eyes or involve poisoning via absorption through external bodily tissues.

The fact that a toxic chemical can cause harm by inhalation, ingestion, or irritation or burning of the skin or eyes is probably well appreciated by most people. Poisoning due to absorption through external bodily tissues, however, is not as well known a hazard and benefits from further explanation.

In simple terms, there are various specific gases, liquids, and even solid materials which have the capability of passing through the skin or tissues of the eyes at various rates upon contact. Those that are highly toxic and which penetrate the body rapidly are the most hazardous. Those that penetrate slowly or which are of relatively low toxicity may require long term contact with large parts of the body to cause significant effects. Although some materials may give some warning that contact has occurred by causing some sort of burning sensation, others may give little or no warning to the victim.

While on this topic, it is also worthwhile to consider the commonly accepted meaning of phrases like ***high toxicity*** and ***low toxicity***. When one speaks of a material that is of high toxicity, it generally means that relatively small quantities may cause significant health effects upon inhalation, ingestion, and/or direct contact. Conversely, a low toxicity substance generally requires larger amounts to be inhaled, ingested, or contacted for an equally significant adverse health effect. It is therefore well to always remember that a large quantity

of a low toxicity material may present the same or greater ***toxic hazard*** to a community or individual than a much smaller quantity of a highly toxic material. It is also necessary to understand that the toxicity of a material is only one of several factors to be considered in determining the toxic hazard posed by the material. These concepts are reiterated and discussed in further detail in a later section.

6.3 TYPES OF TOXIC EFFECTS

Most toxic substances can be classified as irritants, asphyxiants, anesthetics and narcotics, systemic poisons, sensitizers, carcinogens, mutagens, and/or teratogenic substances. Systemic poisons may be further disaggregated into the categories of hepatotoxic agents, nephrotoxic agents, neurotoxic agents, agents which act on the blood or hematopoietic system, and agents which damage the lung.

Many of these terms may be unfamiliar because they are mostly used in the medical/public health community and among toxicologists. Fortunately, they need not all be memorized because most hazardous material data bases and guides, material safety data sheets, and manufacturers' product bulletins generally "translate" the effects of toxic materials upon the body into more common language. There are, however, certain terms and expressions that appear frequently and which can be helpful in understanding the most common effects of toxic materials upon the body.

Irritants

Irritants are substances with the ability to cause inflammation or chemical burns of the eyes, skin, nose, throat, lungs, and other tissues of the body in which they may come in contact. Some substances such as strong acids (e.g., sulfuric acid, oleum, chlorosulfonic acid, hydrochloric acid, hydrofluoric acid, or nitric acid) may be irritating to the point of being corrosive when concentrated, and may quickly cause second or third degree chemical burns upon contact with the skin or eyes. If inhaled as a gas, vapor, fume, mist, or dust, they may cause severe lung injury, and if ingested, can seriously damage the mouth, throat, stomach, and/or intestinal tract. Yet other irritants may have milder effects and may only cause reddening of the skin or eyes after contact.

Some of the most common irritants are organic solvents or hydrocarbon fuels which can dissolve natural oils in the skin and cause ***dermatitis***. After repeated or prolonged contact, these will dry the skin to the point that it may become cracked, inflamed and possibly infected. These same materials often cause irritation of the eyes and possibly loss upon contact of the corneal epithelium, a clear thin membrane that covers the surface of the cornea. Although the effect is temporary, since the epithelium will usually regrow in a few days, some data sources may refer to the effect as a "corneal burn."

Entry into the lungs of many liquid hydrocarbons and some organic liquids that are irritants may cause chemical ***pneumonia*** or ***pneumonitis*** together with ***pulmonary edema*** (filling of the lungs with fluid), hemorrhage, and tissue ***necrosis*** (i.e., death of living tissue). Since entry of liquids into the lungs usually involves ***aspiration*** when a victim who has accidentally ingested the substance vomits, the first aid instructions for such substances typically recommend against intentional inducement of vomiting. They also are likely to mention that the effects of aspiration into the lungs may not appear for several hours or even days after the exposure has taken place.

Asphyxiants

Simple asphyxiants are typically non-toxic gases that may cause injury by inhalation only if they are present in air in such high concentrations that they displace and exclude the oxygen needed to maintain consciousness and life. A good example is nitrogen, a gas that makes up about 78% of the air we breathe and which is perfectly harmless at this level as a component of air. If additional nitrogen or another such simple asphyxiant were added to the air to the point that the normal oxygen concentration of approximately 21 percent by volume was significantly reduced, however, the situation could become life-threatening. Tables 6.1 and 6.2 illustrate the effects of oxygen depletion on the body and the four stages of asphyxiation.

Chemical asphyxiants are substances that in one way or another prevent the body from using the oxygen it takes in and are often highly toxic substances. One classic example is carbon monoxide which combines with and "ties up" the component of blood (hemoglobin) that transports oxygen from our lungs to other organs. If too much of the hemoglobin becomes unavailable for carrying oxygen, a person may pass out and eventually die. Other examples are among the family of cyanides (i.e., substances which have a -CN, carbon-nitrogen, combination in their molecule and which somewhere in their names have the word "cyanide" or the letter combinations "cyan" or "nitrile"). These act by interfering with the action of the enzymes necessary for living tissues to use available oxygen, thus resulting in a condition referred to as ***cyanosis***.

Anesthetics and Narcotics

Numerous hydrocarbon and organic compounds classified as hazardous materials, including some alcohols, act on the body by ***depressing*** the ***central nervous system*** (CNS). Early symptoms of exposure to these substances include dizziness, drowsiness, weakness, fatigue, and incoordination. Severe exposures may lead to unconsciousness, paralysis of the respiratory system, and possibly death.

TABLE 6.1 EFFECTS OF OXYGEN DEPLETION	
Percent of Oxygen In Air	**Symptoms**
20	Normal
17	Respiration volume increases, muscular coordination diminishes, attention and clear-thinking requires more effort.
12 to 15	Shortness of breath, headache, dizziness, quickened pulse, efforts fatigue quickly, muscular coordination for skilled movements lost.
10 to 12	Nausea and vomiting, exertion impossible, paralysis of motion.
6 to 8	Collapse and unconsciousness occurs.
6 or below	Death in 6 to 8 minutes.

Source: Kimmerle, George, "Aspects and Methodology for the Evalution of Toxicological Parameters During Fire Exposure," ***JFF/Combustion Toxicology***, Vol. 1, February, 1974.

TABLE 6.2 FOUR STAGES OF ASPHYXIATION	
1st Stage:	21-14% oxygen by volume, increased pulse and breathing rate with disturbed muscular coordination.
2nd Stage:	14-10% oxygen by volume, faulty judgment, rapid fatigue, and insensitivity to pain.
3rd Stage:	10-6% oxygen by volume,nausea and vomiting, collapse,and permanent brain damage.
4th Stage:	Less than 6% by volume, convulsion, breathing stopped, and death.

Source: Cryogenics Safety Manual, British Cryogenics Council, London, 1970

Sensitizers

A few hazardous materials are ***sensitizers*** and cause ***sensitization***. What this means is that some people who are exposed to one of these materials may not be abnormally affected the first time, but may experience significant and possibly dangerous effects even in the presence of very low levels of the contaminant if ever exposed again. In simple terms, victims become extremely allergic to the material and possibly others of a similar nature.

Other Types of Toxic Agents

- ***Hepatotoxic agents*** are materials that cause liver damage.
- ***Nephrotoxic agents*** are materials that cause kidney damage.
- ***Neurotoxic agents*** are substances that in one way or another impact the nervous system and possibly cause neurological damage.
- ***Carcinogens*** are substances that may incite or produce cancer within some part of the body.
- ***Mutagens*** can produce changes in the genetic material of cells.
- ***Teratogenic materials*** may have adverse effects on sperm, ova, and/or fetal tissue.

Note: Besides the chemical asphyxiants described above, there are other substances that in one way or another act on the blood or the hematopoietic system (i.e., bone marrow). Inhalation of free silica or asbestos over a period of time can cause changes in lung tissue with serious health consequences. Yet other toxic substances also have unusual or unique effects on human health.

6.4 ACUTE VS. CHRONIC HAZARDS

The majority of industries and many common daily activities of life utilize equipment, processes, and materials that continuously or intermittently discharge toxic materials into the occupational and/or natural environment. Some workers may be exposed to such materials 8 hours per day, 5 days per week or so, over a large part of their careers. Similarly, the general public may be exposed to various contaminants continuously or intermittently. Such exposures are said to be of a ***chronic*** nature and usually but not always involve low concentrations of contaminants in air, food, water, and/or soil.

When a major accident or other rare event causes a significant spill or discharge of a toxic material into the environment, the general public or nearby workers may be exposed to relatively high levels of one or more toxic contaminants until such time as they escape or are rescued from contaminated locations or the contaminant becomes diluted below hazardous levels. These short-term, rare exposures (in the sense there will be long periods of time between repeated exposures if they reoccur at all) are referred to as ***acute*** exposures. Not all acute exposures, of course, need involve high concentrations of toxic materials. A small spill or discharge may produce low levels of contamination yet still be of an acute nature.

To be noted is that many chemicals will not persist for long periods of time in the environment, or at least in those parts of the environment of concern, while others may remain present for weeks, months, or even years. The former materials include substances that may be digested by bacteria (i.e., which are ***biodegradable***), substances that will undergo various reactions with materials in the environment that render them harmless, or those that become so diluted in air or water that they no longer present a hazard. Examples are simple alcohols that may be digested by bacteria in soil or water much as humans drink and digest alcoholic beverages, as well as volatile materials which evaporate and are swept away into the vast ocean of air above us. Such materials are unlikely to pose long-term chronic hazards in the event of a major spill or discharge in most cases. Alternatively, toxic substances which are relatively inert and which do not degrade, react, vaporize, or dissolve freely may pose health hazards for extended periods of time within a localized environment and may require additional planning to address long-term ***chronic*** exposure hazards to the public. Examples include heavy metals and various chlorinated hydrocarbons such as DDT, trichloroethylene, and PCBs.

6.5 IMPORTANCE OF EXPOSURE LEVEL AND DURATION

In considering the effects of toxic exposures, it is necessary to understand that the duration of an exposure can be as important as the level of exposure in determining the outcome. This follows from the observations that:

- The body has a capacity to cope with the intake of many contaminants at a certain rate. Below a certain *threshold* rate of intake or absorption which can be counterbalanced by the body's ability to excrete or somehow convert the contaminant to a harmless substance, toxic effects may be minimal or non-existent. For example, note that arsenic is commonly found in all human bodies at low levels. It is only when the level exceeds the safe threshold due to excessive intake that symptoms of toxicity become apparent.

- The rate at which a contaminant enters the body by inhalation is a function of the concentration of the contaminant in the air being breathed, the rate of breathing, the length of time the body remains within a volume of contaminated air, and the specific properties of the contaminant. Higher concentrations in air obviously lead to higher rates of intake or absorption into bodily tissues.

- The potential for toxic effects via skin absorption is a function of the amount of toxic material that contacts the body, the properties of the material, and the length of time it is permitted to remain in contact.

- Toxic effects via ingestion can also be a function of the amount or rate of intake over a period of time. Small doses of certain poisons ingested hours or days apart may not be harmful, but taking the total amount all at once may be deadly. Other poisons may accumulate in the body such that small doses taken over time may buildup to a fatal dose.

The reason that chronic exposure to low levels of toxic materials commonly found in the environment does not often cause widespread health problems is that the rate of intake is below the *threshold* at which health effects become apparent. Conversely, major spills or discharges of toxic materials may pose a significant threat to public health because the resulting contaminant concentrations in the local area may be so high that only a moment or two of exposure is sufficient to produce severe health problems due to an excessive ***body burden*** of contamination. This is particularly true where large amounts of toxic gases or vapors are released into the air. Relatively few members of the general public are ever harmed by direct contact with toxic materials, since most individuals have the common sense not to touch or go walking through spilled chemicals and will cleanse themselves promptly if such contact is made. Similarly, few people are likely to drink potentially contaminated water or eat contaminated food once warned of the possibility of contamination. Most at risk in such situations are emergency response personnel who enter contaminated areas without adequate personnel protective clothing and respiratory devices in attempts to contain or otherwise mitigate the impacts of the spill.

6.6 TOXICITY VS. TOXIC HAZARD

The observations above naturally lead to a further discussion of the difference between the ***toxicity*** of a substance and the ***toxic hazard*** it poses to the public. This is an extremely important concept because materials of high toxicity are often assumed to pose a severe toxic hazard regardless of the other properties of the material and the circumstances surrounding its spillage.

Imagine a one ton discharge of two different materials. The first is an extremely toxic, non-volatile solid material that has spilled in the middle of a street in a densely populated metropolis. The material is so extremely toxic that only 10 pounds would be sufficient to kill 100,000 people by ingestion if somehow introduced into their food in equal portions. The second discharge involves an overturned tank truck on the same street that has just released a very common compressed liquefied gas that is considered to be of moderate toxicity. As it boils and vaporizes upon release, the ton of liquid may become as much as 30,000 cubic feet or more of pure gas. If it were to mix uniformly with air and happened to be deadly in very short-term exposures at a concentration of 5,000 ppm in air, the potentially lethal cloud spreading over the city would conceivably have a total volume of 6 million cubic feet.

On a strictly weight basis, the solid material may be many thousands of times more toxic than the gas, but is unlikely to poison members of the public just a short distance away because it lacks mobility. Thus, the solid must be carefully handled and removed from the scene, but actually poses a relatively low toxic hazard to the public. Authorities may wish to evacuate the immediate spill area and cover the solid with plastic sheeting to prevent any dust from becoming airborne until its careful recovery, but the risk of fatalities among the general public will be low in most cases.

The situation with the lower toxicity liquefied gas poses a greater toxic hazard because the gas will quickly spread over downwind areas. The gas may prove rapidly fatal to people near the spill site and cause toxic effects among many hundreds or thousands of others in the downwind direction.

The *moral* of this story is that the toxic hazard posed by a material is not a sole function of its toxicity. One must always consider the amount of material present or spilled, the properties of the substance, and the opportunity it has to affect the population in its vicinity.

6.7 RECOGNIZED EXPOSURE LIMITS FOR AIRBORNE CONTAMINANTS

It should be fairly clear by this point that discharges of gases and vapors into the atmosphere generally pose greater toxic hazards to people than discharges of non-volatile materials. As is widely appreciated, one of the key tasks in planning for hazardous materials emergencies involves preparations for identifying, notifying, evacuating, sheltering, or otherwise protecting populations that may be exposed to such gases and vapors.

Achievement of the above goal requires planning personnel to select the airborne concentration in air that can be tolerated by exposed populations while toxic vapors or gases remain in the immediate area, since it is this concentration that will determine the boundaries of the hazard zone. This, in turn, requires knowledge of the source and nature of commonly

available and accepted exposure limits for airborne contaminants as well as their various advantages and disadvantages for the intended use. Primary data sources to be considered include:

- ACGIH Threshold Limit Values (TLVs)
- OSHA Permissible Exposure Limits (PELs)
- AIHA Workplace Environmental Exposure Limits (WEELs)
- NIOSH Immediately Dangerous to Life or Health Levels (IDLHs)
- AIHA Emergency Response Planning Guidelines (ERPGs)
- NAS/NRC Emergency Exposure Guidance Levels (EEGLs) and Short-term Public Emergency Guidance Levels (SPEGLs)

ACGIH TLVs

The American Conference of Governmental Industrial Hygienists (ACGIH) formed a committee in 1941 to review available data on toxic compounds and to establish exposure limits for employees working in the presence of airborne toxic agents. The committee continues to this day to publish an annual list of several hundred compounds and recommended exposure limits in a booklet titled ***Threshold Limit Values and Biological Exposure Indices***. Copies of the latest edition were available for $5 in late 1988 from the ACGIH at 6500 Glenway Ave., Bldg D-7, Cincinnati, Ohio 45211 or (513) 661-7881.

The primary purpose of the exposure limits adopted by the ACGIH is to protect healthy male workers in ***chronic*** exposure situations and the ACGIH specifically notes that "*These limits are **not** fine lines between safe and dangerous concentrations nor are they a relative index of toxicity, and **should not** be used by anyone untrained in the discipline of industrial hygiene.*" Nevertheless, the information provides valuable guideposts for identifying exposure limits that will usually be decidedly safe for short-term acute exposures.

Exposure limits established and published by the ACGIH are of several different types and include:

- ***Threshold Limit Value - Time Weighted Average*** (TLV-TWA): The time weighted average concentration for a normal 8-hour workday and a 40-hour workweek, to which nearly all workers may be repeatedly exposed, day after day, without adverse effect.

- ***Threshold Limit Value-Short Term Exposure Limit*** (TLV-STEL): A time-weighted average concentration to which workers *should not* be exposed for longer than 15 minutes and which should not be repeated more than four times per day, with at least 60 minutes between successive exposures. This limit supplements the TLV-TWA where there are recognized acute effects from a substance whose toxic effects are primarily of a chronic nature. STELs are recommended only where toxic effects have been reported from high short-term exposures in either humans or animals.

- ***Threshold Limit Value-Ceiling*** (TLV-C): The concentration in air that should not be exceeded during any part of the working exposure. Ceiling limits may supplement other limits or stand alone.

In addition to the above limits, the ACGIH occasionally enters the notation "skin" after listed substances. This notation indicates the potential for absorption of the substance through the skin, eyes, or other membranes and the possibility that such absorption may contribute to the overall exposure. An excessive amount of absorption may invalidate any TLV limit; a high potential for direct contact with the substance may suggest the need for special protective measures.

For many of the materials with an assigned TLV-TWA, the ACGIH could not find sufficient toxicological data to establish a TLV-STEL. For these substances, it recommends "*Short-term exposures should exceed three times the TLV-TWA for no more than a total of 30 minutes during a work day and under no circumstances should they exceed five times the TLV-TWA, provided that the TLV-TWA is not exceeded*" for the 8-hour workday. The airborne concentrations derived from this recommendation are referred to as ***excursion limits.***

OSHA PELs

The Occupational Safety and Health Administration (OSHA) within the U.S. Department of Labor is responsible for the adoption and enforcement of standards for safe and healthful working conditions for men and women employed in any business engaged in commerce in the United States. When first established in the early 1970's, OSHA essentially adopted the then current ACGIH TLV-TWAs and TLV-Cs as occupational exposure limits and made them official federal standards. Instead of calling the limits Threshold Limit Values, however, it referred to them as ***Permissible Exposure Limits*** (PELs). As in the case of TLVs, there are both time-weighted average (TWA) and ceiling (C) values for various materials as well as occasional peak values for shorter time periods. While the ACGIH reviews and frequently revises its TLVs on an annual basis, OSHA did not similarly update

its PELs except for a relatively small number of individual substances until early 1989 when it lowered the PELs for 212 widely used chemicals, adopted new PELs for 164 substances not previously regulated, and reaffirmed the PELs for 52 materials.

PELs are formally listed in Title 29 of the Code of Federal Regulations (CFR), Part 1910, Subpart Z, General Industry Standards for Toxic and Hazardous Substances. An inexpensive and valuable source of current PELs and much other information on chemical hazards is the ***NIOSH Pocket Guide to Chemical Hazards*** published by the National Institute for Occupational Safety and Health, a part of the U.S. Department of Health and Human Services. When in stock, single copies may be available at no cost from NIOSH Publications, 4676 Columbia Parkway, Cincinnati, Ohio 45226 (Telephone: 513-533-8287). Copies are otherwise available at nominal cost as DHHS (NIOSH) Publication No. 85-114 from the Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402 or one of the many regional branches of the GPO. Be advised, however, that it may take some time for NIOSH to update the currently available guide with the new PELs.

Besides PELs and a wide variety of other valuable information, the pocket guide includes the IDLH values described below.

AIHA WEELs

The American Industrial Hygiene Association (AIHA) has established a committee to develop ***Workplace Environmental Exposure Levels*** (WEELs) for toxic agents which have no current exposure guidelines established by other organizations. Essentially, the committee is attempting to establish occupational exposure limits for materials not addressed by the ACGIH or OSHA but of interest to various segments of industry. A separate guide providing documentation is being prepared for each substance.

There are two WEEL limits for most materials. The first is an 8-hour TWA value similar in concept to ACGIH TLV-TWA values. The second, which is only available in a limited number of cases, is a short-term TWA for exposures of either 1- or 15-minute duration. As of October of 1988, WEELs were available for 33 materials. Non-members prices were $5 for each individual guide and $125 for the entire set (plus shipping and handling).

The WEEL guides are available from AIHA Publications, 475 Wolf Ledges Parkway, Akron, Ohio, 44311-1087 (Telephone: 216-762-7294). A price list and order form are available at no charge.

NIOSH IDLHs

NIOSH defines ***Immediately Dangerous to Life or Health*** (IDLH) levels as the maximum airborne contaminant concentrations "*from which one could escape within 30 minutes without any escape-impairing symptoms or any irreversible health effects.*" Not surprisingly, given that these limits are for 30-minute exposures under what are essentially emergency conditions, IDLH values generally far exceed corresponding TLVs or PELs. They are available in the pocket guide referenced above for most substances currently regulated by OSHA.

NAS/NRC EEGLs and SPEGLs

The Committee on Toxicology of the National Research Council (NRC), an operating arm of the National Academy of Sciences (NAS), has published a list of ***Emergency Exposure Guidance Limits*** (EEGLs) and ***Short-term Public Emergency Guidance Levels*** (SPEGLs) as guidance in advance planning for the management of emergencies. Although the Committee has been adding toxic substances to the list on a periodic basis, the careful attention to detail and thoroughness of its work has resulted in EEGLs being established for relatively few materials to date. Table 6.3 lists those available as of late 1988.

SPEGLs are concentrations whose occurrence is expected to be rare in the lifetime of any one individual. These values, of which there are only four in the table, "*reflect an acceptance of the statistical likelihood of a nonincapacitating reversible effect in an exposed population while avoiding significant decrements in performance*". They are concentrations considered acceptable for public exposures during emergencies.

EEGLs differ from SPEGLs in that they are intended to apply to defined occupational groups such as military or space personnel rather than the general public. Because these groups are typically younger and healthier, the EEGL for any particular substance may differ substantially from the SPEGL.

Further information on these exposure limits and levels may be obtained by writing the National Academy of Sciences, Committee on Toxicology, 2101 Constitution Avenue, Washington, D.C., 20418 to the attention of Dr. Bakshi. Note that the Committee plans to have completed work on trichloroethylene and lithium chromate by early 1989 if not sooner.

AIHA ERPGs

Several major chemical companies formed a task force in 1986 to develop ***Emergency Response Planning Guidelines*** (ERPG) values for selected toxic materials. The results of their joint efforts are being published by the AIHA and are available from the publication office cited earlier. As of late 1988, guidelines had been completed for 10 substances

TABLE 6.3
SUMMARY OF EMERGENCY EXPOSURE GUIDANCE LEVELS
FROM THE NATIONAL RESEARCH COUNCIL

Chemical	60-Minute EEGL (ppm)	Chemical	60-Minute EEGL (ppm)
Acetone	8,500	Dichlorofluoromethane (Freon-21)	100
Acrolein	0.05	Dichlorotetrafluoromethane (Freon-114)	10,000
Aluminum oxide	15 mg/m³	1,1-Dimethylhydrazine	0.24*
Ammonia	100	Ethanolamine	50
Arsine	1.0	Ethylene oxide	20 (proposed)
Benzene	1000 (proposed)	Ethylene glycol	40
Bromotrifluoromethane	25,000	Fluorine	7.5
Carbon disulfide	50	Hydrazine	0.12
Carbon monoxide	400	Hydrogen chloride	20
Chlorine	3	Hydrogen chloride	1*
Chlorine trifluoride	1	Hydrogen sulfide	10 (24 hr)
Chloroform	100	Isopropyl alcohol	400
Dichlorodifluoromethane (Freon-12)	10,000	Lithium bromide	15 mg/m³

Note: Units in parts per million by volume in air unless otherwise stated.
*SPEGL (Short-term Public Emergency Guidance Levels)

TABLE 6.3 (Continued)
SUMMARY OF EMERGENCY EXPOSURE GUIDANCE LEVELS
FROM THE NATIONAL RESEARCH COUNCIL

Chemical	60-Minute EEGL (ppm)	Chemical	60-Minute EEGL (ppm)
Mercury vapor	0.2 mg/m³ (24 hr)	Sodium Hydroxide	2 mg/m³
Methane	5,000 (24 hr)	Sulfur dioxide	10
Methanol	200	Sulfuric acid	1 mg/m³
Monomethyl hydrazine	0.24*	Toluene	200
Nitrogen dioxide	1*	Trichlorofluoromethane (Freon-11)	1,500
Nitrous oxide	10,000	Trichlorotrifluoroethane (Freon-113)	1,500
Ozone	1	Vinylidene chloride	10 (24 hr)
Phosgene	0.2	Xylene	200

Note: Units in parts per million by volume in air unless otherwise stated.
*SPEGL (Short-term Public Emergency Guidance Levels)

including ammonia, chlorine, chloroacetyl chloride, chloropicrin, crotonaldehyde, diketene, formaldelhyde, hydrogen fluoride, perfluoroisobutylene, and phosphorous pentoxide. Published in two sets of five, the first set costs $7 while the second is priced at $11.

As in the case of NAS/NRC efforts, the task force is attempting to define toxic exposure limits suitable for use in advance planning for emergencies. It ultimately wishes, however, to address a much greater number of chemicals than those considered to date by the NAS/NRC.

The task force intends to establish three limits for each material, these being:

- **ERPG-3**: The maximum airborne concentration below which, it is believed, nearly all individuals could be exposed for up to one hour without experiencing or developing life threatening health effects.

- **ERPG-2**: The maximum airborne concentration below which, it is believed, nearly all individuals could be exposed for up to one hour with out experiencing or developing irreversible adverse or other serious health effects or symptoms which could impair an individual's ability to take protective action. This particular limit is being developed using criteria similiar to those applied by the NAS/NRC.

- **ERPG-1**: The maximum airborne concentration to which nearly all individuals could be exposed for up to one hour without experiencing or developing health effects more severe than sensory perception or mild irritation, if relevant.

6.8 ADVANTAGES AND DISADVANTAGES OF VARIOUS LIMITS

A key problem of using TLV, PEL, or WEEL values in the course of evacuation planning or hazard assessment is that they are intended for use in the occupational environment where presumably healthy workers are exposed to concentrations near these limits day after day throughout their careers. This, and the desire to prevent health effects associated with both acute and chronic exposures, means that these values are often (but not always) much lower than what they need be to protect the public from exposures associated with rare or infrequent spills of brief duration. Consequently, use of a TLV, PEL, or WEEL value, although decidedly safe in the vast majority of cases, could conceivably result in major overprediction of downwind evacuation or hazard zones in many situations. Key exceptions involve materials such as chlorine, acids, caustics, and other generally corrosive materials for which limits are based on irritant rather than toxic effects and for which applied safety factors may be minimal.

NIOSH IDLH limits are considerably higher, are defined for an exposure duration closer to what would be expected in many actual short-term spill emergencies, and are closer to the borderline between levels that are barely tolerable and those that may cause significant injury. The problem is that "barely tolerable" contaminant concentrations may have the potential to cause considerable irritation or other distress, possibly to the point of prompting large numbers of people to seek medical assistance. Also, since NIOSH is again assuming that healthy workers are being exposed, IDLH concentrations may have the potential to cause significant injury to young children, the elderly, or individuals with preexisting health problems. Consequently, it is apparent that a safety factor must be applied if the IDLH is used in any way for protection of the general public, especially if exposures exceed 30 minutes in duration.

The NAS/NRC SPEGLSs and AIHA ERPG-2 values are possibly the best choice among currently available guidelines for protection of the public during relatively short-term events given the objectives of their respective developers. Unfortunately, only a small number of hazardous materials have been addressed to date.

Overall, the above discussion might seem to suggest there is no widely accepted method available for selection of an appropriate exposure limit for general populations subjected to toxic vapors or gases, particularly where the exposure limit is to be used for public emergency planning purposes. That is indeed (and unfortunately) an accurate appraisal of the current situation. So what should you do? Some *options*, in order of decreasing preference, and by no means mandatory for use, are as follows:

- Use the NAS/NRC SPEGL or the AIHA ERPG-2 value for the material if one has been established.

- Consult a toxicologist or similarly qualified individual for advice based on a formal review of the toxicity of the material of concern.

- Use the highest value among the following:

  - IDLH value divided by 10 (with "10" being a safety factor)
  - TLV-STEL
  - TLV-TWA multiplied by 3 (if a TLV-STEL does not exist)
  - TLV-C

- If the evacuation of additional areas is not a problem, or the exposure may be prolonged beyond one hour, use the TLV-TWA or the TLV-C value or apply an additional safety factor to other selections.

The above suggestions should not be considered more than rough guidelines that will generally lead to an adequately "safe" answer for most members of a community. There is, however, one more problem to consider.

The chronic exposure limits for substances known or suspected to be carcinogens are usually set at very low levels to protect workers from developing cancer during their lifetimes. Such values are generally many times (possibly several hundred times) lower than the limits enforced for the same materials prior to the discovery of a potential cancer threat. For example, the TLV-TWA for vinyl chloride is now 5 ppm whereas it was 200 ppm for many years, yet even 200 ppm is well below any concentration causing observable health effects in short-term *acute* exposures. Obviously, the size of the evacuation or hazard zone for a 5 ppm limit would be many times larger than a zone with boundaries of 200 ppm. The difference in the numbers of people that may require evacuation or other protective action may differ by thousands if not tens of thousands in urban areas.

There is no hard evidence that a single exposure to a substance such as vinyl chloride will cause excess cancers in a population of exposed humans. However, some scientists are of the opinion that *any* exposure might lead to at least a minor increased risk of such cancers, and this belief poses a dilemma during planning for evacuations, especially given the public fears that may naturally accompany the announcement that a cancer-causing agent has been released into the atmosphere. It is therefore necessary for government and industry to consider cases involving carcinogens carefully and on a case-by-case basis, giving full attention to the safety issues involving large-scale evacuations as well as the potential long-term health, political, and legal implications of their decisions.

6.9 RELATIONSHIP OF RECOMMENDATIONS TO EPA LOCs

Under the Superfund Amendments and Reauthorization (SARA) Act of 1986, the U.S. Environmental Protection Agency (EPA) established a list of several hundred Extremely Hazardous Substances (EHS) subject to emergency planning, community right-to-know, hazardous emissions reporting, and emergency notification requirements. In providing guidance to planning personnel for screening and prioritizing threats posed by EHS, the EPA made a first attempt at specifying what it termed Levels of Concern (LOCs) for these substances, essentially adopting portions of the approach recommended above.

For the 390 or so substances for which NIOSH has established IDLH levels, the EPA set LOCs to one-tenth of available IDLHs until such time as industry and government develop more appropriate exposure limits for protection of the public during episodic short-term emergencies. For substances for which IDLHs had not been established, the EPA developed a highly approximate procedure to estimate LOCs comparable to IDLHs. Essentially, IDLHs were estimated for new substances via use of data obtained from

laboratory experiments involving acute exposures of animals to toxic substances. Inhalation data were used in preference to data for other routes of exposure when available, but data for other routes of exposure were indeed used when necessary. The following equations were then applied to convert available data to airborne concentrations presumably comparable to IDLHs.

1) Estimated IDLH = LC_{50} x 0.1
2) Estimated IDLH = LCLo
3) Estimated IDLH = LD_{50} x 0.01
4) Estimated IDLH = LDLo x 0.1

The abbreviations used above for lethal concentrations and dosages are defined and described in Section 6.12 of this chapter. Please note that the above discussion only provides a general overview of the EPA's general approach and should not be applied in an indiscriminate fashion.

6.10 CONSIDERATION OF MIXTURES OF HARMFUL GASES AND VAPORS

Preceding discussions have focused on relatively pure substances. As is well appreciated, however, many materials handled by industry are multi-component mixtures. It is well therefore to discuss how to determine appropriate toxic limits for mixtures via a review of *traditional* guidance found in the literature.

The ACGIH, in an appendix to its TLV booklet, reports that one of the first tasks in looking at mixtures is a determination of whether mixture components have ***additive*** or ***independent*** effects on the human body. In other words, when two or more toxic agents in a mixture act upon the same organ system, it is their combined or additive effect rather than their individual effects that should be given primary consideration, and indeed, this is the preferred approach in the absence of specific information to the contrary. Where toxicological data firmly support a finding that the chief effects of the different substances are not in fact additive (in the sense that they produce purely local effects or affect different organs of the body), it is only then acceptable to assume that adverse effects are independent.

Where effects are evaluated as being additive, the ACGIH suggests that the sum of the following fraction be computed:

$$\text{Sum} = \frac{C_1}{T_1} + \frac{C_2}{T_2} \cdots \frac{C_n}{T_n}$$

where: C_n indicates the measured or predicted atmospheric concentration, T_n indicates the corresponding toxic limit in the same units as C_n, and there are "n" number of toxic substances in the mixture.

When the **Sum** of the fractions equals 1.0 or less, then the vapor mixture is considered to be at or below the toxic limit. In those cases where all components of a mixture are deemed to produce independent effects, the toxic limit is considered to be exceeded only when one or more of the individual C_n / T_n fractions has a value greater than one.

To be noted is that ***synergistic*** action or ***potentiation*** may occur with some combinations of toxic agents: these being cases in which the combined effect of the mixture actually exceeds the impact indicated by assumption of additive effects. Such cases, which are fortunately rather rare, must be considered on a case-by-case basis.

When the source of airborne contamination is a liquid mixture, the ACGIH suggests (to its typical audience of industrial hygienists and other occupational health personnel) that the composition of the airborne mixture be assumed similar to the composition of the original liquid mixture. In effect, this results in the further assumption that all components of the mixture will evaporate at a constant rate in direct proportion to their concentration in the liquid mixture. The assumption has merit when one in interested in evaluation of a relatively long-term time-weighted average exposure resulting from a mixture that will eventually evaporate in its entirety, but has severe limitations when applied to the assessment of acute exposures resulting from accidental and episodic events. It is well, nevertheless, to present the ACGIH's general methodology for estimating the toxic limit of a liquid mixture of this type, this being:

$$\text{Toxic Limit (mixture)} = \frac{1.0}{\frac{F_1}{C_1} + \frac{F_2}{C_2} \cdots \frac{F_n}{C_n}}$$

where: F_n indicates the weight fractions of individual components in the liquid mixture, and C_n indicates the corresponding toxic limits in units of mg/m^3.

A more formal approach to determining the airborne mixture toxic limit for evaporating or boiling pools of liquid requires consideration of vapor-equilibrium factors beyond the scope of this text. Nevertheless, where needs for a more precise limit are critical, it is desirable to apply more sophisticated analytical procedures to evaluate vapor compositions above liquid mixtures or to make direct measurements of representative samples. The procedures for such efforts are well within the state of the art of engineering practice and entail fundamental principles of thermodynamics.

6.11 EXPOSURE LIMITS FOR CONTAMINATED WATER

The U.S. Environmental Protection Agency (EPA) has established or recommended water quality criteria for a variety of water uses and a relatively large number of chemicals. Advice from their personnel as to what concentrations of any particular chemical are tolerable in any given situation may be available with only a telephone call to one of the EPA's 10 regional offices.

Among the various standards and guidelines developed by the EPA for protection of water quality are:

- National Drinking Water Standards: The maximum contaminant levels (MCLs) for selected heavy metals, pesticides, radioactive substances, and other water quality characteristics permitted by law in water destined for human consumption. Listed in Parts 141 and 143 of Title 40 of the Code of Federal Regulations (CFR).

- Drinking Water Health Advisories (HAs) -- previously called Suggested No Adverse Response Levels (SNARLS): Human health effects advisories for unregulated drinking water contaminants commonly found in potable water supplies. HAs are somewhat unique in that they provide guidance for short-term exposure as well as the long-term chronic exposures typically of interest to the EPA.

- Maximum Contaminant Level Goals (MCLGs) -- formerly known as Recommended Maximum Contaminant Levels (RMCLs): Published in the Federal Register of June 12, 1984, the EPA proposed zero contamination limits for six halogenated hydrocarbons and benzene. Low levels of contamination were permitted for two other halogenated hydrocarbons (i.e., 1,1,1-trichloroethane and 1,4-dichlorobenzene). MCLGs were recently proposed for several additional contaminants.

- Federal Water Quality Criteria: Criteria for acute and chronic exposure of freshwater and saltwater aquatic life and human health based on long-term consumption of drinking water and contaminated fish or shellfish. Available for a relatively long list of substances.

Spills of toxic materials into a body of surface water differ from discharges of toxic vapors or gases into the air in that a large number of people are unlikely to suffer toxic effects before authorities have a chance to restrict water use. Indeed, response planning for the spill of any hazardous material into water more typically involves preparations to:

- Alert proper state and federal authorities.
- Warn public, industrial, agricultural, and recreational users of the water on as prompt a basis as possible of the contamination.
- Attempt to limit the degree of contamination or the amount of water affected.
- Attempt to remove as much of the contaminating substance as possible from the water (possibly employing a contractor with specialized expertise and equipment).
- Analyze the water to determine the extent of contamination.
- Consult with proper authorities as to whether the water is fit for use or whether other remedial actions are first necessary; and
- Prepare for the eventuality that a particular water supply may become unavailable for use for a time.

6.12 UNDERSTANDING TOXICOLOGICAL DATA IN THE LITERATURE

Toxicologists have a number of "short-hand" methods of expressing the toxicity of hazardous materials by various routes of entry. An understanding of some of the more common abbreviations used can lead to a greater understanding of how the toxicities of various materials can be assessed, particularly when these abbreviations are encountered in hazardous material data bases or the safety related literature of chemical manufacturers that address the effects of acute exposures.

The easiest way to learn the abbreviations is to look at a few examples and then discuss their meaning:

- The orl rat LD_{50} for Chemical A is 200 mg/kg.
- The ihl LC_{50} for the mus or gpg is 800 ppm/4 hrs. The TCLo is 100 ppm/4 hrs.
- The rbt skn LD_{67} is 50 mg/kg.

LD in the above examples is an abbreviation for ***lethal dose*** while LC stands for ***lethal concentration.*** TC is short for ***toxic concentration*** while TD means ***toxic dose.*** There are other similar abbreviations but these are by far the most common.

Each of the LD or LC notations are followed by a number that is usually a subscript. A "50" means that 50% of the test population of animals were killed under stated test conditions, a "67" means 67% were killed and so forth. The letters "Lo" instead of a number mean this is the lowest *reported* level having the stated effect.

In order for one of the above notations to have meaning, both the species of animal tested and the route of entry must be specified. Typical abbreviations are:

Species of Animal	Route of Entry
Rat = rat	**Oral = orl**
Mouse = mus	**Skin application = skn**
Guinea pig = gpg	**Inhalation = ihl**
Rabbit = rbt	
Human = hmn	
Mammal = mam	
Monkey = mky	

Both oral and skin application dosages are typically expressed in units of milligrams of chemical applied per kilogram of the animal's body weight, or ***mg/kg*** for short. The actual total amount of a toxic material necessary to cause the stated effect is determined by multiplying the dose in units of mg/kg by the weight of the animal species expressed in units of kilograms (1 kg = approximately 2.2 lb).

Inhalation data must include the concentration in air to which the animal species was subjected as well as the duration of exposure. Concentrations in air are typically expressed in units of ppm (by volume) or mg/m^3. Times are typically given in minutes or hours. ***Be advised that any airborne concentration not accompanied by an indication of the duration of exposure should be considered a useless and thoroughly meaningless item of information.***

One of the most comprehensive compilations of toxicological data is a multi-volume set of documents titled ***Registry of Toxic Effects of Chemical Substances***. The 1985-1986 edition, published in April 1987, is available for a cost close to $100 from the Superintendent of Documents, U.S. Government Printing Office, Washington, D.C., 20402, or one of the

many regional offices of the GPO, as Stock No. 17-33-00431-5. Developed jointly by the U.S. Public Health Service, Centers for Disease Control and NIOSH, the set is also listed as DHHS (NIOSH) Publication No. 87-114.

7.0 REACTIVITY HAZARDS OF CHEMICAL SUBSTANCES

7.1 INTRODUCTION

It has up to this point been assumed that the hazardous materials being discharged or spilled do not in any way react with or chemically transform due to contact with water, air, other common materials in the environment, or other chemicals that may be present in the vicinity. It has also assumed that these materials are not ***self-reactive*** under conditions that may be encountered. Although the overall topic of chemical reactivity hazards is extremely complex, it is necessary to at least briefly outline some of the more common and/or dangerous types of reactions and how they may pose a threat to nearby populations. With due apologies to chemists, chemical engineers, and others with a knowledge of these topics, it is acknowledged that some liberties are taken in this process to ensure that various concepts are more easily understood by non-technical audiences.

7.2 EXOTHERMIC REACTIONS

When one substance is brought together or mixed with another and the resulting interaction evolves or generates heat, the process is referred to as an ***exothermic reaction.*** Alternatively, if no reaction will take place unless heat is continuously added to the combination of ***reactants***, the interaction resulting from the provision of heat is called an ***endothermic reaction.*** However, it is important to understand that some exothermic reactions may require heating just to get started, and will then proceed on their own.

Exothermic reactions pose special hazards whether occurring in the open environment or within a closed container. In the open, the heat evolved will raise the temperature of the reactants, of any products of the reaction, and of surrounding materials. Since several properties of all substances are a function of temperature, the resulting higher temperatures may affect how the materials involved may behave in the environment. Of key importance is the realization that heat will increase the vapor pressures of hazardous materials and the rate at which they vaporize. If very high temperatures are achieved, nearby combustible materials may ignite. Explosive materials, be they the reactants or products of the reaction, may explode upon ignition or excessive heating.

Similar hazards are associated with exothermic reactions taking place in closed containers. In this case, however, increasing internal temperatures as well as the evolution of gases from the reaction may increase internal pressures to the point that the tank or container ruptures violently in an overpressurization explosion, thus suddenly releasing large amounts of possibly flammable and/or toxic gases or vapors into the atmosphere. Such gases or vapors may also be released through ruptured pipes, opened pressure relief devices, or any other paths to the external environment.

Reactions with Water or Air

Some of the most basic types of exothermic reactions (which are barely "reactions" in the true sense of the term) occur when certain materials are dissolved in water. Such substances have what is called a positive ***heat of solution***. They do not transform to a different material, but simply generate heat while mixing. Some examples are sodium hydroxide (also called caustic soda) and sulfuric acid, which generates considerable heat to the point of causing some degree of "violence" when concentrated or pure materials are spilled into water. Yet other materials may ignite, evolve flammable gases, or otherwise react violently when in contact with water. Knowledge of the reactivity of any substance with water is especially important when water is present in the spill area or a fire takes place and firefighters do not wish to make the situation worse by applying water to the flames or chemicals.

While discussing such substances, it is well to add that several of the strong acids and related substances in this category of materials may evolve *large* amounts of ***fumes*** when in contact with water or moisture in the air. These fumes, which may consist of a mixture of fine droplets of acid in air and acid vapors, are usually highly irritating, corrosive, and heavier than air.

Many substances referred to as being ***pyrophoric*** will react violently or exothermically with air and are likely to ignite in a spontaneous fashion. Such substances (such as phosphorus) are commonly transported or stored in a manner that prevents exposure to air,

often submerged in water or some type of compatible oil. Note that the fact that a substance can be safely stored under water in no way suggests that it may also be safely submerged in oil. Nor may submersion in water be safe for a substance usually maintained under some type of oil.

Reactions with Combustible Organic Materials

Certain chemicals are known as strong ***oxidizing agents*** or ***oxidizers***. They have the common characteristic of being able to decompose or oxidize organic materials and react with a variety of inorganic materials while generating heat, oxygen, flammable gases, and possibly toxic gases. If the heat generated is sufficient to ignite a combustible or flammable material, a fire or explosion may occur.

Another group of chemicals are referred to as strong ***reducing agents***. These substances may evolve hydrogen upon reaction with many other chemicals, may evolve other flammable or toxic gases, and like oxidizing agents, may generate heat. As above, a fire or explosion may result if sufficient heat is generated to ignite a combustible or flammable substance. Strong reducing agents and oxidizing agents should never be allowed to make contact without appropriate safeguards since they represent opposite extremes of chemical reactivity.

Exothermic Polymerization Reactions

A few of the more common plastics in use on a widespread basis are polyethylene, polypropylene, polystyrene, and polyvinyl chloride (PVC). Although all are manufactured from liquids or gases, they are typically solids in their final form.

The above plastics are respectively manufactured from ethylene, propylene, styrene, and vinyl chloride by means of a ***polymerization*** reaction in which molecules of these materials are linked together into long chains of molecules. As the chains become longer and begin connecting to each other, thus greatly increasing the molecular weight of individual molecules, a solid plastic is formed.

Some chemicals capable of being polymerized have a strong tendency to do so even under normal ambient conditions and are especially prone to polymerize if heated above a certain temperature or if contaminated by a ***catalyst*** or ***polymerization initiator***, which in some cases might be a rather common substance such as water or rust. Once polymerization starts, an exothermic chain reaction may occur that develops high temperatures and pressures within containers and which can lead to possible explosion or violent rupture of the container and/or discharge of flammable and/or toxic gases if safety and control systems malfunction or are lacking. The incident in Bhopal, India partially involved this type of reaction when a container of methyl isocyanate contaminated with water and chloroform began polymerizing.

The heat of the runaway (i.e., out of control) reaction caused a large portion of the highly toxic isocyanate to vaporize into the air through a pressure relief system before it had a chance to polymerize.

Quite often, substances with the above tendency to ***self-polymerize*** or to undergo ***autocatalytic*** polymerization are transported or stored only while containing an amount of a substance called an ***inhibitor***. As their name implies, inhibitors act to inhibit, slow, or interfere with the chemical processes that can lead to a runaway uncontrolled polymerization reaction under *normal* conditions of transportation or storage. Inadvertent contamination or excessive heat, however, may overpower the inhibitor and allow the reaction to proceed. Thus, an inhibited cargo should not be considered safe if there is a possibility of it being overheated or contaminated with those substances that may initiate polymerization. The very fact that a substance needs an inhibitor for safe storage is in many cases (but by no means all) a sign of potential hazardous instability.

Exothermic Decomposition Reactions

Much as some chemical molecules can join together to form larger molecules via exothermic polymerization, others are unstable and can break apart in a runaway exothermic reaction once the process is initiated. Again, inhibitors may be used to slow the process down or to prevent its occurrence and various contaminants or heat may overcome the inhibitors or otherwise start a reaction. Containers may explode, rupture, and/or vent various flammable and/or toxic gases to the atmosphere.

Incidentally, the above decomposition and polymerization reactions are hazardous only if they somehow become uncontrolled and start a chain reaction that cannot be stopped with available equipment, materials, or safety systems. They are widely and safely conducted in chemical and other manufacturing plants across the nation on a daily basis without incident. It is only when control or safety systems break down or people make mistakes that problems begin.

7.3 NEUTRALIZATION REACTIONS

Spill response guides often suggest consideration of ***neutralization*** as a way in which a hazardous substance can be converted via a chemical reaction to one or more substances that pose lesser threats to the public health or the environment. It is therefore worthwhile to say a few words on the topic.

In the traditional sense of the word, neutralization typically refers to the combination of an acid and a base or alkaline material to form some sort of salt. A good example involves the careful combination of sodium hydroxide (caustic soda -- NaOH) with hydrochloric acid (muriatic acid -- HCl in water). This reaction, which may proceed violently for a time,

generate heat and gases, and cause boiling and spattering of acid if not properly controlled, results in the combination of sodium (Na) atoms with chlorine (Cl) atoms to form sodium chloride (NaCl), which is ordinary table salt. The remaining hydrogen (H) atoms and hydroxide (OH) molecules combine to form ordinary water (H_2O). Thus, one strongly corrosive and hazardous substance is used to convert another to a solution of ordinary salt and water.

When used in the spill response community, neutralization refers to the general use of one or more chemicals or other substances to render another less harmful. The term need not solely apply to acid-base reactions.

7.4 CORROSIVITY HAZARDS

The process by which a chemical gradually erodes or dissolves another material is often referred to as ***corrosion***. The process represents yet another type of chemical reactivity that must be considered in assessing the hazards of any given material, and is particularly important when: 1) choosing materials of construction for container walls or linings, piping, pumps, valves, seals, gaskets, and so forth; and 2) assuring that equipment and materials used during response to emergencies will not be damaged or destroyed by contact with the spilled material during their period of use. The word ***corrosive*** is also used descriptively to indicate that a substance may cause chemical burns of the skin, eyes, or other bodily tissues upon contact.

In evaluating whether one material is corrosive to another via reference to material safety data sheets, chemical company product bulletins, hazardous material data bases, or other reference sources, it is often important to place the time frame and rate of corrosion into the proper context. For example, certain reference sources may state that one substance is unacceptably corrosive to a particular material of construction because long term (i.e., 10 to 20 years) exposure will result in failure of the material prior to the desired lifetime of the equipment. Yet other reference sources may discuss the issue in terms of short term resistance of equipment or clothing construction materials to chemical attack, particularly if addressing use under emergency conditions. This distinction is not always clear in the literature.

Finally, note that some of the most corrosive substances to common metals include strong acids of one type or another. Not only may the "wrong" acid in contact with the "wrong" metal cause rapid corrosion of the metal, but the process may generate flammable and potentially explosive hydrogen gas.

7.5 OTHER HAZARDOUS RESULTS OR PRODUCTS OF REACTIONS

The above discussions have really only scratched the surface of the overall topic of hazardous chemical reactions. It is also necessary to point out that:

- The combination of various chemicals may produce new chemicals with hazards quite different and possibly more severe than those associated with the original materials.

- Some combinations may result in spontaneous fires; spontaneous explosions; formation of substances which will ignite or explode if shocked, heated or subjected to friction; generation of toxic gases, liquids or solids; or generation of flammable gases, liquids, or solids.

- It is necessary to look at hazardous materials on a fairly specific case-by-case basis to determine their reactivity hazards.

7.6 SOURCES OF CHEMICAL REACTIVITY DATA

There are numerous sources of chemical reactivity data that address the topic somewhat superficially and several that are highly technical and somewhat beyond the perceived "needs" of the audience to which this document is directed. The following three sources provide an excellent balance between completeness, precision, specificity, and common availability.

- ***Fire Protection Guide on Hazardous Materials***, containing "Manual of Hazardous Chemical Reactions," NFPA 491M-1986, National Fire Protection Association, Batterymarch Park, Quincy, MA 02269 (Telephone 1-800-344-3555 for orders).

- Bretherick, L., ***Handbook of Reactive Chemical Hazards***, 3rd edition, Butterworths, London and Boston, 1985. Available through libraries and bookstores serving the scientific community.

- Hatayama, H.K., et al., ***A Method for Determining the Compatibility of Hazardous Wastes***, EPA Report No. EPA-600/2-80-076, Municipal Environmental Research Laboratory, U.S. Environmental Protection Agency, Cincinnati, Ohio, April 1980. Available as publication PB80-221005 from the National Technical Information Service, Springfield, Virginia 22161.

The NFPA Fire Protection Guide on Hazardous Materials contains the described manual of chemical reactions as well as considerable additional information and data on hazardous materials. Found in the libraries of numerous fire departments, it was available in 1988 at a cost of approximately $49 to non-members. Although the section on hazardous chemical reactions has not truly been updated since 1975, and is not nearly as extensive as the work by Bretherick, the guide remains an excellent source for a broad range of specific information. Major sections of the guide can also be found in the NFPA National Fire Codes as Sections 325M, 49, 491M, and 704.

The handbook by Bretherick covers approximately 9000 compounds versus the 1600-1700 found in the NFPA guide. It is a major and somewhat unique work in the field which retails for $110.

The report prepared by Hatayama and his co-workers under the sponsorship of the EPA is an excellent supplement to either of the above sources of information. Those above mostly list and describe the specific hazardous consequences of combining various sets of chemicals, *as reported in the general literature.* Since there are many tens of thousands of known chemicals, and since only a small fraction of the possible combinations have been reported upon, neither of these sources can even begin to claim that combinations not listed are safe. The work by Hatayama et al. attempts to fill the gaps by providing a *general* indication of the *typical* effects of mixing a substance from one chemical *family* with a substance from another *family* via a single chemical compatibility chart. The title of the work suggests it only considers hazardous waste materials, but that in no way affects the validity of the information for hazardous materials in general. Appendix D to this guide contains a copy of the chart as well as additional explanatory information.

It is also necessary to note that many of the product bulletins and safety-related documents available free from most chemical manufacturers can be excellent sources of information when one is concerned with the reactivity hazards of a relatively small number of materials. The problem is that collection of such publications for a large number of materials can be a burdensome and lengthy process.

Chemical company literature, however, can be a great source of information on the compatibility of common materials of equipment construction with specific chemicals. Alternatives include some of the better hazardous materials data bases, books devoted to this topic, and more widely available handbooks in the fields of chemical and mechanical engineering. Many of these same sources address the compatibility of materials used for chemical protective clothing, and substantial information is available from the manufacturers of such clothing. One excellent source of information on protective clothing that deserves special notice is:

- Schwope, A.D., et al., ***Guidelines for the Selection of Chemical Protective Clothing***, 3rd edition, 1987; sponsored by the EPA and USCG and available for approximately $35 from the ACGIH Publications Section, 6500 Glenway Ave, Bldg D-7, Cincinnati, Ohio 45211 (Telephone 513-661-7881).

8.0 HAZARDOUS MATERIAL CLASSIFICATION SYSTEMS

8.1 INTRODUCTION

Various organizations in the United States have established or defined classes or lists of hazardous materials for regulatory purposes or for the purpose of providing rapid indication of the hazards associated with individual substances. An awareness and knowledge of these classification systems can assist emergency preparedness personnel in identifying those materials that may pose a potential threat to their respective jurisdictions.

8.2 U.S. DEPARTMENT OF TRANSPORTATION CLASSIFICATIONS

As the primary regulatory agency concerned with the safe transportation of hazardous materials in interstate commerce, the U.S Department of Transportation (DOT) has established definitions of various classes of hazardous materials, established placarding and marking requirements for containers and packages, and adopted an international cargo commodity numbering system. Each of these topics is individually discussed in the following. Further details are available in 49 CFR 171-179.

Material Classification Definitions

The DOT classifies hazardous materials in transportation into one or more of the following categories.

An ***explosive*** is defined as "*any chemical compound, mixture, or device, the primary or common purpose of which is to function by explosion, i.e., with substantially instantaneous release of gas and heat...*" within certain limitations noted in DOT regulations. The overall category of explosives is further broken down into Class A, Class B, and Class C explosives. ***Class A*** materials are among the most powerful and include bombs, mines, torpedoes, and ammunition used by the military; various high explosives like nitroglycerin and dynamite; blasting caps, detonating fuzes, and powerful rocket propellants. ***Class B*** substances and devices are generally less powerful and typically (not always) function by rapid combustion rather than detonation. The class includes special fireworks, flash powders, some pyrotechnic signal devices, liquid or solid propellants, some smokeless powders, and certain types of ammunition. ***Class C*** explosives are manufactured articles which contain Class A or B materials, or both, as components in strictly restricted quantities. The class also includes certain types of fireworks.

A ***blasting agent*** is a material designed for blasting which has been tested in accordance with DOT regulations and "*found to be so insensitive that there is very little probability of accidental initiation to explosion or of transition from deflagration to detonation.*" In other words, the material is capable of exploding under very special conditions, but these conditions are unlikely to occur in transportation, even in the event of an accident involving fire or impact.

Flammable liquid refers to any liquid, within certain limitations and exceptions, that has a "closed-cup" flash point below 100°F (37.8°C). Similarly, ***combustible liquid*** refers to any liquid that has a flash point of 100°F or more but no higher than 200°F. A ***pyrophoric liquid*** is any liquid that ignites spontaneously in dry or moist air at or below 130°F (54.5°C).

Flammable solids are "*any solid material, other than one classed as an explosive, which, under conditions normally incident to transportation is liable to cause fires through friction, retained heat from manufacturing or processing, or which can be ignited readily and when ignited burn so vigorously and persistently as to create a serious transportation hazard. Included in this class are spontaneously combustible and water-reactive materials.*"

An ***oxidizer***, according to DOT regulations, "*is a substance such as a chlorate, permanganate, inorganic peroxide, or a nitrate, that yields oxygen readily to stimulate the combustion of organic matter.*" The key hazard associated with oxidizing agents or materials is that contact with a combustible substance, particularly organic materials, may cause the substance to ignite and possibly even explode.

An ***organic peroxide*** is essentially a derivative of hydrogen peroxide (H_2O_2) where one or more of the hydrogen atoms have been replaced by molecular chains containing carbon

and hydrogen atoms. The substances in this category do not meet the definitions of Class A or B explosives but may be capable of exploding under certain conditions. They may also have the hazards associated with oxidizers.

DOT defines a ***corrosive*** material as "*a liquid or solid that causes visible destruction or irreversible alterations in human skin tissue at the site of contact, or in the case of leakage from its packaging, a liquid that has a severe corrosion rate on steel.*" A liquid is considered to have a severe corrosion rate if it "eats away" more than 0.25 inch of a certain type of steel at 130°F over the course of one year.

A ***compressed gas*** is defined as any material or mixture with an absolute pressure in a container of:

- More than 40 psia at 70°F
- More than 104 psia at 130°F
- If the substance is flammable and in the liquid state, more than 40 psia at 100°F.

A ***flammable compressed gas*** is a compressed gas that has a lower flammable limit (LFL) concentration of 13% or less by volume in air, or which has a flammable range (i.e., the difference between the LFL and UFL) of greater than 12%, or which behaves in a prespecified manner in a flammability testing apparatus. A ***liquefied compressed gas*** is a gas which is partially a liquid under the pressure in the container at 70°F. A ***non-liquefied compressed gas*** is a substance which is entirely gaseous at a temperature of 70°F.

Poisonous materials are divided into three groups in DOT regulations according to their degree of hazard in transportation. ***Poison A*** substances are "*poisonous gases or liquids of such a nature that a very small amount of the gas, or vapor of the liquid, mixed with air is dangerous to life.*" ***Poison B*** materials are liquids or solids, other than Class A poisons or irritating materials, "which are known to be so toxic to man as to afford a hazard to health during transportation; or which, in the absence of adequate data on human toxicity, are presumed to be toxic to man" because they meet certain criteria for inhalation, ingestion, or skin exposures when tested on laboratory animals. ***Irritating materials*** are liquid or solid substances "*which upon contact with fire or when exposed to air give off dangerous or intensely irritating fumes.*"

In the aftermath of the Bhopal incident, DOT rules were modified to require special marking of packages or containers of volatile toxic liquids which had previously escaped classification as poisons. After adopting a new set of special criteria for inhalation toxicity hazards, the DOT required that packages containing more than one liter and no more than

110 gallons of these materials be marked ***Inhalation Hazard.*** Poison placards were required in addition to other required placards for trucks, rail cars or containers carrying any amount of these materials. Shipping papers for containers holding more than one liter were required to include the statement ***Poison - Inhalation Hazard.***

An ***etiologic agent*** is "*a viable microorganism, or its toxin, which causes or may cause human disease.*" For the most part, such agents include potentially infected living tissue and bacteriological materials.

Radioactive materials are substances that give off potentially harmful nuclear radiation, and are classed in three groups according to the controls needed to provide "nuclear criticality safety" during transportation. ***Fissile Class I*** materials are among the safest of these substances, do not require nuclear criticality safety controls during transportation, and may be shipped together in an unlimited number of packages. ***Fissile Class II*** substances are somewhat more dangerous and can only be shipped in limited amounts when packages are shipped together. ***Fissile Class III*** do not meet the requirements of the other classes and must be controlled to provide nuclear criticality safety in transportation by special arrangement between the shipper and the carrier.

Finally the DOT has a category called ***Other Regulated Material*** (ORM) for a wide variety of hazardous materials shipped in limited quantities and in certain kinds of packaging. There are five classes of such cargos with the designations ORM-A, ORM-B, ORM-C, ORM-D, and ORM-E.

Identification Numbers

The DOT has assigned a four-digit identification to each of the hazardous materials regulated in transportation. When appearing in documentation, these numbers are preceded by the letters "UN" or "NA". The UN numbers, such as UN1203 for gasoline, were assigned in cooperation with the United Nations and are used on an international basis. The NA numbers are not recognized in international transportation except to and from Canada.

Most of the numbers and the material shipping names to which they are assigned represent very specific materials. It is well to recognize, however, that the DOT also permits some cargos to be identified in a rather generic fashion. For example, the identification number UNl993 applies to *flammable liquid, n.o.s.*. The last three letters are an abbreviation for *not otherwise specified,* so the number does not permit identification of the specific material in the container.

Placards and Labels

The DOT has numerous regulations dealing with the placards and labels that must appear respectively on bulk containers and packages of hazardous materials. Figure 8.1 illustrates the required placards, these being the fairly large signs that must appear on railroad tankcars, highway tank trucks, and other large transport vehicles. Labels are fairly similar and any differences are rather self-explanatory.

Special Notes

Before continuing, it is necessary to make two important observations about DOT classification systems and placarding and labeling requirements. The first is that these systems and requirements are modified on a frequent basis and there has been considerable activity to improve them in the aftermath of the Bhopal incident. Although the material presented herein is of a fairly general nature, some items may become outdated with time. Indeed, even as this document was being prepared, the DOT was in the process of finalizing new regulations in this area.

Secondly, and most importantly, be intensely aware that the **current** DOT material classification system has weaknesses that prompted the above activities. Furthermore, the current system is primarily designed to denote the perceived primary hazard of a material as determined by application of rigorous classification criteria. ***Do not under any circumstances assume that the hazard indicated by a warning label or placard attached to a container is the only hazard associated with the material found therein.***

8.3 U.S. ENVIRONMENTAL PROTECTION AGENCY CLASSIFICATIONS

The EPA has developed several lists of chemicals and chemical wastes that may be broadly categorized as"hazardous substances." Besides the water pollutants discussed earlier in Chapter 6, they include:

- A list of specific ***hazardous wastes*** and criteria for designating other materials as wastes under the Resource Conservation and Recovery Act (RCRA) of 1976 and subsequent amendments. See Title 40, Part 261 of the Code of Federal Regulations (40 CFR 261) for details.

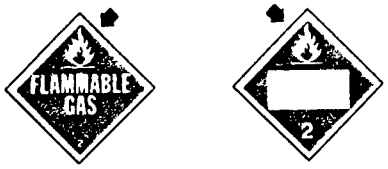
- A list of ***hazardous substances*** developed under Section 311 (b) (2) (A) of the Clean Water Act of 1977. See 40 CFR 112-114 for details.

- Chemicals listed as ***toxic pollutants*** under Sections 307(a) and 307(c) of the Clean Water Act. See 40 CFR 116-117 for details.

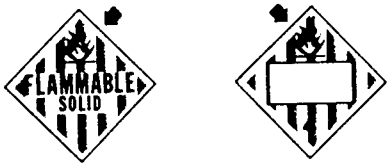
FIGURE 8.1
U.S. D.O.T. PLACARDS

The alternate display incorporating the UN/NA 4-digit number appears to the right of the placard.

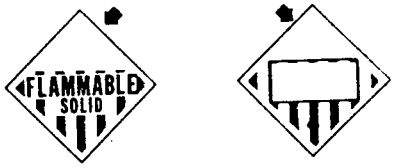
FLAMMABLE GAS



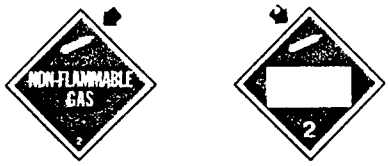
FLAMMABLE SOLID



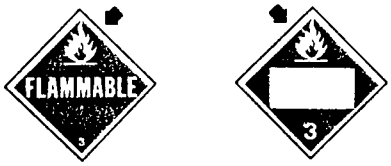
FLAMMABLE SOLID



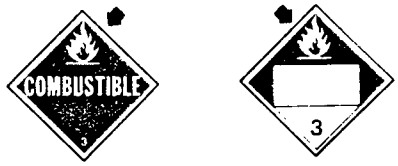
NON-FLAMMABLE GAS



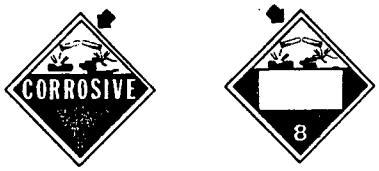
FLAMMABLE



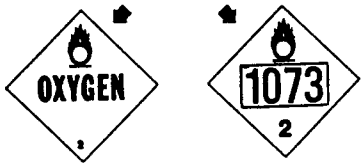
COMBUSTIBLE



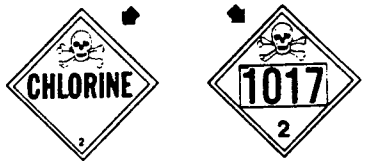
CORROSIVE



OXYGEN

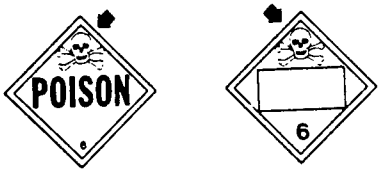


CHLORINE



EXPLOSIVES

POISON



RADIOACTIVE

EXPLOSIVES

POISON GAS

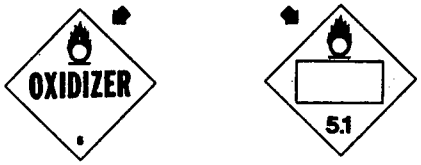
NOTE: No alternate display is permitted for EXPLOSIVES A, POISON GAS, and RADIOACTIVE materials

NOTE

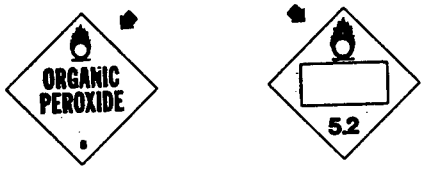
Hazard Class Numbers

1 Explosives
2 Compressed gases
3 Flammable/Combustible Liquids
4 Flammable solids
5.1 Oxidizers
5.2 Organic peroxides
6 Poisons
7 Radioactive materials
8 Corrosives

OXIDIZERS



ORGANIC PEROXIDES



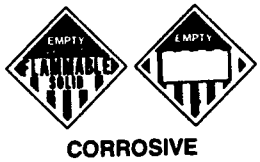
PLACARDED EMPTY TANK CARS

FLAMMABLE GAS

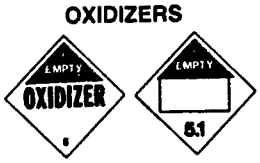
NON-FLAMMABLE GAS

FLAMMABLE

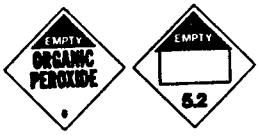
FLAMMABLE SOLIDS



OXIDIZERS

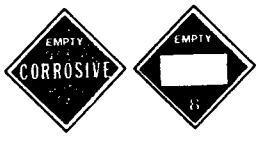


ORGANIC PEROXIDES



POISON

CORROSIVE



1075

When required on tank cars, portable tanks or cargo tanks, identification numbers, as specified in §172.101 or §172.102, shall be display on an orange panel or placard. §172.332
An identification number may not be displayed on a Poison Gas, Radioactive or Explosives placard. §172.334(a); but if a tank car, portable tank or cargo tank carrying such a commodity requires an identification number, it must be displayed on an orange panel. §172

- A list of materials deemed to be ***Extremely Hazardous Substances*** (EHS) by virtue of their acute inhalation toxicity in air. Established under Title III, section 302(a) of the Superfund Amendments and Reuthorization Act of 1986, this list has been subject to frequent changes. It may be expanded in the future to include materials with other hazardous characteristics.

- A list of hazardous substances established under the 1980 Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), also known as Superfund. The list is comprised of chemicals listed under RCRA, the Clean Air Act, and/or the Clean Water Act. See 40 CFR 302 for details. Extremely Hazardous Substances are also to be included in this list.

- A list of toxic chemicals established under section 313 of SARA Title III for emissions reporting. See 40 CFR 372 for details.

The hazardous substances listed under CERCLA have been assigned ***reportable quantities*** by the EPA. These are the amounts that must be spilled within a specified period of time before the party responsible for the spill or discharge is ***required*** to report the spill to federal, state, and local governments. They range from one pound for materials considered to be extremely harmful to the environment (plus some chemicals which are under review and have not yet been assigned more appropriate reportable quantities) to 5000 lbs for those substances considered to pose significant but comparatively moderate environmental hazards. It is well to recognize that:

- The current EPA CERCLA hazardous substance list mostly includes substances that were identified as a result of their long-term environmental and public health hazards. There are many significant hazardous materials which do not appear in the list.

- Reportable quantities (RQs) were generally derived from an evaluation of the long-term health and environmental hazards of the listed chemicals. RQ values represent a relative ranking of the chemicals vis-a-vis each other and are not absolute indicators of risk. Due to the criteria by which they were derived, RQs should not be used to rank substances for planning or emergency response activities involving episodic spills or discharges of hazardous materials posing acute threats to the public.

Each Extremely Hazardous Substance designated by the EPA has been assigned a ***Threshold Planning Quantity*** (TPQ) which triggers various reporting, community right-to-know, and emergency planning requirements. Please note that:

- The list of Extremely Hazardous Substances was prepared quickly after the Bhopal incident as an attempt to denote those materials which pose a high acute toxicity hazard to the public when discharged into the environment. The list contains several substances that are highly toxic but lack mobility under ordinary spill conditions.

- Although Threshold Planning Quantities have an important role in defining regulatory requirements, there is no guarantee that lesser quantities of a designated EHS will not pose threats to public health and safety under all accident conditions.

8.4 NATIONAL FIRE PROTECTION ASSOCIATION HAZARD RANKINGS

In an attempt to provide fire service personnel a rapid means of assessing the dangers of hazardous materials, the National Fire Protection Association (NFPA) has developed a ranking system that assigns separate values in the range of zero to four to the health, flammability, and reactivity hazards of individual materials. A fourth category for "special" hazards uses the following symbols among occasional others:

- "**W**" to denote unusual reactivity with water

- "**OX**" to denote that the material has oxidizing properties

- "**COR**" to denote that the material is corrosive to living tissue

- The standard radioactivity symbol to denote radioactivity hazards

Table 8.1 defines the rankings specified by the NFPA for health, flammability, and reactivity. Although the individual rankings are often simply listed by category in NFPA documents and many chemical company material safety data sheets, they may also be seen within a diamond-shaped sign with blue, red, yellow, and white squares containing the respective rankings for health (blue), fire (red), reactivity (yellow) and other (white).

8.5 INTERNATIONAL MARITIME ORGANIZATION CLASSIFICATION

Under the auspices of the United Nations, the International Maritime Organization (IMO) has developed and continues to refine its International Maritime Dangerous Goods Code (IMDG) to facilitate and ensure the safety of international shipments of hazardous materials. The DOT has adopted and/or permits use of IMDG requirements under numerous circumstances, and it is very common to see references to these requirements in MSDS and

TABLE 8.1
NFPA HAZARD RANKINGS

Identification of Health Hazard Color Code: BLUE		Identification of Flammability Color Code: RED		Identification of Reactivity (Stability) Color Code: YELLOW	
	Type of Possible Injury	Susceptibility of Materials to Burning		Susceptibility to Release of Energy	
Signal		Signal		Signal	
4	Materials which on very short exposure could cause death or major residual injury even though prompt medical treatment were given.	4	Materials which will rapidly or completely vaporize at atmospheric pressure and normal ambient temperature, or which are readily dispersed in air and which will burn readily.	4	Materials which in themselves are readily capable of detonation or of explosive decomposition or reaction at normal temperatures and pressures.
3	Materials which on short exposure could cause serious temporary or residual injury even though prompt medical treatment were given.	3	Liquids and solids that can be ignited under almost all ambient temperature conditions.	3	Materials which in themselves are capable of detonation or explosive reaction but require a strong initiating source or which must be heated under confinement before initiation or which react explosively with water.
2	Materials which on intense or continued exposure could cause temporary incapacitation or possible residual injury unless prompt medical treatment is given.	2	Materials that must be moderately heated or exposed to relatively high ambient temperatures before ignition can occur.	2	Materials which in themselves are normally unstable and readily undergo violent chemical change but do not detonate. Also materials which may react violently with water or which may form potentially explosive mixtures with water.
1	Materials which on exposure would cause irritation but only minor residual injury even if no treatment is given.	1	Materials that must be preheated before ignition can occur.	1	Materials which in themselves are normally stable, but which can become unstable at elevated temperatures and pressures or which may react with water with some release of energy but not violently.
0	Materials which on exposure under fire conditions would offer no hazard beyond that of ordinary combustible material.	0	Materials that will not burn.	0	Materials which in themselves are normally stable, even under fire exposure conditions, and which are not reactive with water.

other hazardous material publications. Indeed, the DOT has proposed to adopt IMDG performance oriented packaging requirements in their entirety for implementation in the United States.

The IMO has categorized its overall list of hazardous materials into nine major classes, many of which are further broken down into two or more divisions. Table 8.2 lists and describes the basic definitions of IMO classes and divisions. Detailed definitions, including more specific breakdowns for explosives, are provided in the text of the IMDG code.

TABLE 8.2
BASIC IMO MATERIAL CLASSES AND DIVISIONS

Class 1 -- Explosives

Division 1.1 Substances and articles which have a mass explosion hazard. *Explosive A*

Division 1.2 Substances and articles which have a projection hazard but not a mass explosion hazard. *Explosive A or B*

Division 1.3 Substances and articles which have a fire hazard and either a minor blast hazard or a minor projection hazard or both, but not a mass explosion hazard. *Explosive B*

Division 1.4 Substances and articles which present no significant hazard. *Explosive C*

Division 1.5 Very insensitive substances. *Blasting Agent*

Class 2 -- Gases (compressed, liquelified or dissolved under pressure)

Division 2.1 Flammable gases. *Flammable gas*

Division 2.2 Nonflammable gases. *Nonflammable gas*

Division 2.3 Poison gases. *Poison A* and other poison gas

Class 3 -- Flammable liquids

Division 3.1 Low flash point group (liquids with flash points below 0°F). *Flammable liquid*

Division 3.2 Intermediate flash point group (liquids with flash points of 0°F or above but less than 73°F). *Flammable liquid*

Division 3.2 High flash point group (liquids with flash points of 73°F or above up to and including 141°F). *Flammable liquid or Combustible liquid*

Class 4 -- Flammable solids or substances

Division 4.1 Flammable solids. *Flammable solid*

Division 4.2 Substances liable to spontaneous combustion. *Flammable solid* or, for pyrophoric liquids, *Flammable liquid*

Division 4.3 Substances emitting flammable gases when wet. *Flammable solid*

Class 5 -- Oxidizing substances

Division 5.1 Oxidizing substances or agents. *Oxidizer*

Division 5.2 Organic peroxides. *Organic peroxide*

Class 6 -- Poisonous substances and infectious substances

Division 6.1 Poisonous substances. *Poison B*

Division 6.2 Infectious substances. *Etiologic agent*

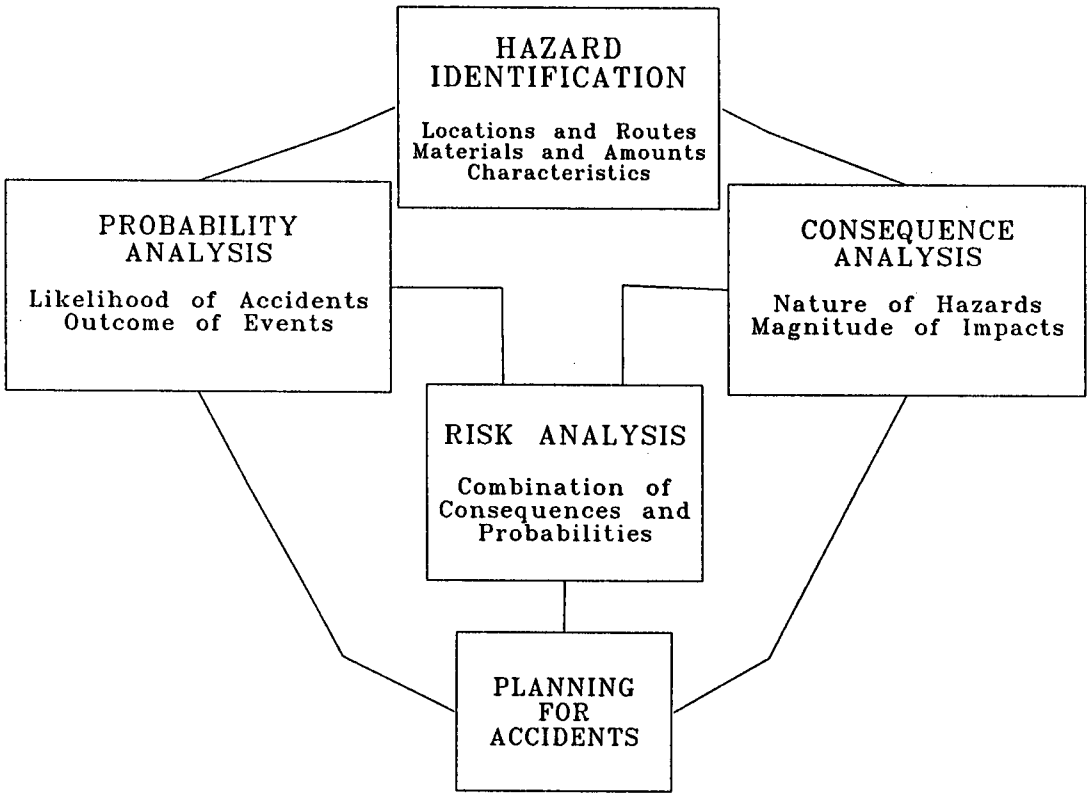
Class 7 -- Radioactive substances. *Radioactive material*

Class 8 -- Corrosives. *Corrosive material*

Class 9 -- Miscellaneous dangerous substances. *Other regulated material*

Note: Corresponding DOT classes are shown in italics following IMO classes and divisions.

9.0 OVERVIEW OF THE HAZARD ANALYSIS PROCESS



9.1 INTRODUCTION

Chapter 1 to this document reported that recent guidance manuals published by the federal government have used the term *hazard analysis* to describe the overall procedure for evaluating the hazards, consequences, vulnerabilities, probabilities, and risks associated with the presence of hazardous materials within any given locality or jurisdiction. This term will also be used herein for the sake of consistency with earlier publications, although it is recognized that *hazard analysis* is often applied in a somewhat different context within government and industry.

There are four basic steps presented in this guide for the conduct of a hazard analysis, and a related fifth step that takes advantage of the knowledge gained during the effort to develop a comprehensive emergency plan for hazardous materials that focuses attention on the known threats to a community or facility while maintaining sufficient flexibility to deal effectively and efficiently with unforeseen events. These steps include:

- Location, identification, and characterization of potential spill sources and accident sites in the jurisdiction or locality of concern in a process referred to as ***hazard identification.*** This step essentially concludes with the identification

and/or postulation of fundamental accident scenarios requiring further consideration and analysis. Results from the probability analysis step which follows can often help in further refining these scenarios.

- Evaluation of the likelihood of individual accident scenarios in a process called ***probability analysis.*** This step permits examination and/or prioritization of potential accident scenarios in terms of their probability of occurrence.

- Evaluation of the consequences and impacts associated with the occurrence of postulated accident scenarios in a process that is referred to as ***consequence analysis.*** This step provides an understanding of the nature and outcome of an accident and permits examination and/or prioritization of scenarios in terms of their potential impact on people and property.

- Combination of results from the accident probability and consequence analysis efforts to provide a measure of overall risk associated with the specific activity or activities being studied in a process referred to as ***risk analysis***. The effort permits examination and/or prioritization of scenarios in terms of *overall* "risk".

- Use of the results of the above activities (which in aggregate provide a ***planning basis*** for emergency preparedness personnel) during actual development and preparation of an emergency plan.

It is the express purpose of this chapter to introduce and describe these various steps further and to set the stage for accomplishment of necessary efforts via use of the data, information, analysis procedures and computational methods presented in subsequent chapters of this guide.

Note that the various steps of the overall hazard analysis need not be performed in precisely the order shown for all postulated accident scenarios. Indeed, as descriptions of the various steps are read, keep in mind that:

- Some users of this guide may wish to employ all steps outlined to one postulated accident sceneario at a time, starting with the scenario they *perceive* as posing the greatest threat to their jurisdiction and then working down their "list".

- Some users may wish to perform one step at a time for all postulated accident scenarios.

- Some users may wish to ignore the probability analysis step for one or more postulated accident scenarios if they perceive or determine that the consequences of an accident would be major or catastrophic and wish to plan for them

regardless of their likelihood of occurrence. Such decisions are specifically supported by guidance provided below and in Chapter 13. Although the most severe yet credible accidents that can be foreseen in any jurisdiction or locality are most likely to have low probabilities of occurrence, the very fact that consequences may be catastrophic or major is usually sufficient justification for consideration of the scenario during the emergency planning process.

- Some users may wish to skip the assessment of accident impacts and consequences for scenarios that are determined to be highly unlikely and are also known to pose comparatively low threats to the public due to the quantity and/or characteristics of the materials involved.

- Some users may wish to perform a "quick and dirty" assessment of potential accident probabilities and/or consequences using readily available information and assuming "worst case" conditions for unknown data or parameters. The answers obtained could then be used to prioritize more formal analyses of important accident scenarios.

9.2 STEP 1: HAZARD IDENTIFICATION

Hazard identification involves delineation and specification of those facilities and transportation modes that handle hazardous materials within the locality or jurisdiction of concern. In other words, it requires that planning personnel determine where and how hazardous materials are stored, handled, or processed in their locality; how and by what routes they are transported to and from these facilities; and where and how hazardous materials may pass through the area on their way to other destinations via rail, highway, marine, or pipeline transportation routes.

A directly related and important activity involves characterization of each potential spill or accident site in sufficient detail to formulate potential accident scenarios and to permit subsequent evaluation of accident probability, likely spill amount, and nature and magnitude of resulting impacts. In other words, once detective work has discovered where hazardous materials are located, this step involves gathering the data and information necessary to eventually postulate the circumstances under which accidents may occur and to evaluate the approximate hazards and risks that these accidents may pose to surrounding populations.

Specific guidance and advice pertaining to the conduct of a hazard identification effort follow in Chapter 10 of this guide.

9.3 STEP 2: PROBABILITY ANALYSIS

With all the media attention given to the topic on a national as well as international basis in recent times, one might easily come to believe that a major disaster involving hazardous materials is bound to occur within the foreseeable future wherever such materials are handled, stored, processed, or transported. Indeed, a survey of public authorities a few years ago placed such events at the top of a list of concerns for conceivable emergencies in their respective jurisdictions. Fortunately, however, catastrophic spills or discharges, i.e., those that actually kill or significantly injure more than a few people at a time, are actually rare events in our large and heavily industrialized nation, although accidents in general involving hazardous materials are very common. The vastly increased attention given to chemical safety in recent times by industry and government alike should serve to further improve overall safety performance in the future. Better preparedness to respond to accidents should serve to reduce overall risks to society by helping to reduce or limit adverse impacts once an accident has occurred.

The probability analysis step may be considered optional where community leaders or facility owners wish to prepare for every conceivable accident regardless of its probability of occurrence and have the time, manpower, and resources to achieve their goals. More often than not, however, emergency planners will find that time and resources are limited, that other threats to the community or public needs compete for attention, and that there is value in conducting a probability analysis. Prioritization of chemical related threats in terms of probability permits attention to these threats in an orderly fashion and reduces the chance that time and resources will be expended on scenarios of exceedingly low credibility or significance.

The task of evaluating the potential for a hazardous material emergency in any locality or jurisdiction involves use of historical accident data in conjunction with local factors (to the extent possible) to predict the frequency of future accidents, and to some extent, the general consequences of these events. Prediction of the future, of course, is an inexact science, but probabilistic accident assessment methods can provide approximate indications of the number and nature of accidents expected *on average* in a given locale within a specified period of time, and can therefore provide valuable guideposts for decision-making purposes.

There are many localities where the total traffic and use of hazardous materials pose a clear threat to public health and safety and which are generally aware of the need for comprehensive emergency planning. These localities could benefit from a probabilistic assessment of accident potential which permits the various threats to be ranked and prioritized, thus ensuring that the most important and serious threats receive the full attention they deserve and that available resources are wisely allocated. (Note: At least one instance is known where a city purchased a set of expensive chemical protective clothing -- fully encapsulating suits

resembling space suits -- and stored them away after allowing its hazmat response team members to try them on once. The suits eventually mildewed and rotted from lack of need and attention.)

At the opposite end of the spectrum are localities which face relatively few hazardous material threats and which may be unsure whether the risk of an accident warrants extensive expenditures of time and resources for emergency preparedness. A probabilistic assessment of accident potential, coupled with the results of a consequence analysis, can assist these localities in deciding upon the appropriate level of planning and preparedness. Together with assessments of other natural and man-made threats to the locality, priorities can be set for allocating time and resources to threats with the highest potential for harming the public. Efforts can be initiated for sharing response capabilities and resources among neighboring jurisdictions where the chances of a significant accident in a region encompassing several jurisdictions are considerable, but the chance that the accident will occur in any specific locale within the region is comparatively low.

Guidelines and methods for probabilistic assessment of hazardous materials emergencies are presented in Chapter 11 of this guide.

9.4 STEP 3: CONSEQUENCE ANALYSIS

Probabilistic assessment of accident potential can provide a good idea of the likelihood that a potential accident will actually take place. It must be realized, however, that the most frequent types of spills or discharges have relatively minor consequences, and that more serious accidents will generally have lower probabilities of occurrence. Thus, a full understanding of the *risks* faced by any specific locale requires knowledge not only of the probabilities associated with different types of accidents, but also the expected impacts and consequences of these events.

Estimation of potential accident impacts and consequences can be accomplished via a variety of consequence, vulnerability, and hazard assessment methodologies described in Chapter 12 of this guide and incorporated within the computer program named ARCHIE that is an integral part of this document.

9.5 STEP 4: RISK ANALYSIS

The risk analysis step is also somewhat optional in the sense that it relies upon the results of the accident probability analysis for completion. It entails combination of the probability or likelihood of an accident occurring with a measure of the predicted consequences of the accident to provide an overall measure of ***risk*** that can be used for threat prioritization and planning purposes.

Readers should be aware that the term *risk* is often misused by society. Being usually defined as a *combined* measure of the probability and severity of potential threats, it is possible for a threat with low probability of occurrence and relatively high potential severity to pose a comparable level of risk to a community (from a planning perspective) as a threat with a higher probability of occurrence but lower severity. Thus, the performance of a risk analysis permits all threats to be viewed from a perspective that is not biased by consideration of either probabilities or consequences alone.

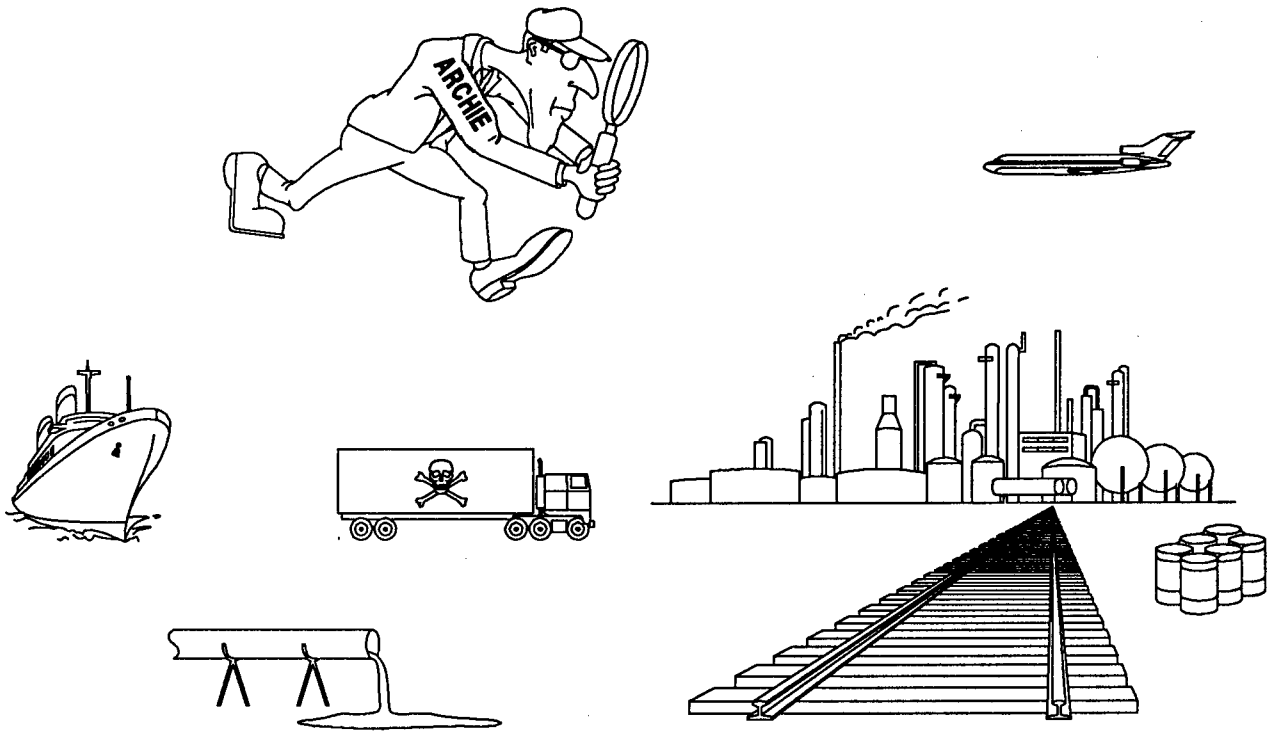
Chapter 13 provides guidance on how the accident scenarios evaluated in Steps 2 and 3 may be evaluated in terms of risk. It also contains a discussion of how the risks associated with hazardous materials compare with more common threats to life and property. The latter topic is considered important because the hazardous materials accident problem has several emotional and political aspects that sometimes tend to distort the truth.

9.6 STEP 5: USE OF HAZARD ANALYSIS RESULTS IN EMERGENCY PLANNING

The scenarios resulting from the overall hazard analysis process will hopefully represent the full range of *significant* hazardous material emergencies that have a reasonable likelihood of occurring in the foreseeable future within any given locality. It remains to consider how these scenarios and related analysis results may be used to focus an emergency response plan on credible threats to the locality of concern and to ensure that the emergency plan provides for efficient, rapid, and comprehensive mitigation of adverse impacts.

Chapter 14 of the guide discusses the planning ramifications associated with individual accident scenarios in some detail and serves as a guide for the use of these scenarios during emergency planning. Note that each scenario deemed credible and worthy of consideration gives planning personnel the opportunity to sit back under non-emergency conditions, identify steps that must be taken to protect the public, and ensure that response personnel will have the necessary organization, communications systems, equipment, materials, manpower, sources of assistance, and training to cope with the situation and minimize casualties, property damage, and environmental pollution.

10.0 HAZARD IDENTIFICATION GUIDELINES



10.1 INTRODUCTION

The purpose of this chapter is to assist planning personnel in identifying and characterizing potential sources and locations of hazardous material spills within their jurisdiction. It is primarily directed to local and county governments, but broad application of its guidance also permits use at the state level and within industry.

The chapter outlines a variety of methods to obtain the desired information. It is left to individual localities or jurisdictions to select the method or combination of methods best suited to local conditions.

10.2 REASON FOR THE DESIRED INFORMATION

There are three fundamental and *interrelated* reasons why a town, city, county, or state government should have knowledge of the identity, location, and characteristics of hazardous materials and related processes within its boundaries.

1. **For hazard assessment purposes:** The desired information, together with identified accident scenarios and the use of consequence analysis procedures presented in this guide, can provide emergency command personnel with an

indication of the potential nature and magnitude of hazardous material threats facing a community. This knowledge in turn can facilitate decisions concerning protection of the public and on-scene response personnel in the event of an actual emergency.

2. **For emergency planning purposes:** It can be difficult and extremely inefficient to plan *and* prepare for *every* conceivable emergency situation. The desired information, together with the probability analysis and consequence analysis procedures presented in this guide, permit emergency plans to be "tailored" to the specific threats facing a community.

3. **For actual response purposes:** Hazardous material spills are often confusing and dangerous situations in their initial stages, especially if responding emergency personnel do not have a good idea of the nature and quantities of the substances that may be involved upon arriving at the accident scene. The hazard identification process permits compilation of a centralized data base that can be accessed upon first notification of an emergency to determine (or at least limit) the overall range of possibilities.

10.3 SUGGESTED SCOPE OF THE EFFORT

The guidance that follows may suggest to some readers that the collection and compilation of the desired data will require a major effort on the part of planning personnel. This will be true to some degree in highly industrialized communities, but the effort can be made manageable by keeping certain thoughts and concepts in mind.

- Small amounts of hazardous materials (unless they have unusual and extremely dangerous properties) are generally likely to cause problems in only a very localized area. Data collection efforts can be greatly minimized by concentrating efforts on transportation routes and facilities that handle or store significant quantities of hazardous materials.

- Industrial concerns that manufacture or use large amounts of hazardous materials are likely to employ or have access to technical personnel with expertise in chemical safety and will be well aware in most cases of their liabilities for any deaths, injuries, or property damages caused by an accident. Some facilities, particularly those associated with major corporations, may be willing to compile the desired data and even perform the analyses described in Chapters 11, 12, and 13 of this guide if asked to do so at the appropriate level of management. These firms have a clear and vested interest in ensuring that the local community is well prepared to protect the health and property of the public in the event of an accident. Many of them, especially since the Bhopal

tragedy and its attendant litigation, have already taken steps to assess and reduce the risks that their chemical-related activities may pose to nearby populations and the continued viability of their business operations in the event of a major accident.

- Major accidents are fairly rare events, particularly when one focuses on any relatively small part of the nation, as is the case with the 4000 or so local emergency planning committees (LEPCs) that have been established in response to federal laws and regulations relating to the Superfund Amendments and Reauthorization Act (SARA) of 1986. The detailed and time-consuming work can be spread out over some reasonable period of time once minimum planning requirements mandated by SARA have been fulfilled.

- Everyone has a stake in hazardous materials safety. Civic-minded citizens, business organizations, and individual companies may be willing to volunteer time and resources to the overall effort. The fact that LEPCs have been established across the nation has set the stage for, should facilitate, and should indeed encourage planning efforts that transcend the limitations of mandatory planning requirements.

- Neighboring communities and jurisdictions will need much of the same data and information, not only on hazardous material transportation traffic, but also with respect to facilities that may pose a threat across jurisdictional boundaries in the event of an accident. Cooperation and integration of activities on a regional basis may not only reduce the workload for all parties, but result in cooperative agreements that may increase the effectiveness and efficiency of emergency response actions during actual emergencies. Fire departments across the nation, for example, have long appreciated the value of regional mutual aid systems. This concept can be extended in a variety of ways for response to hazardous material related accidents, thus reducing the burden on individual jurisdictions.

- Many of the efforts and tasks described in this and the following chapters appear more complex when first looked over than they really are. The work will go much more smoothly and quickly as experience is gained in applying suggested methods and interpreting their results.

- Most importantly, federal laws and regulations require many (though not all) facilities that utilize hazardous materials to provide LEPC's all information needed (with certain exemptions related to *trade secrets*) for preparation of emergency plans. Those facilities that store quantities of Extremely Hazardous Substances (EHSs) in excess of designated Threshold Planning

Quantities (TPQs) are required to appoint a *facility emergency coordinator* to assist the LEPC in its planning efforts. Other facilities may also be required by SERCs to participate in the planning process under Title III of SARA.

10.4 NATURE OF DESIRED INFORMATION

Table 10.1 briefly summarizes the types of information generally needed for various transportation modes and stationary facilities, while subsequent discussions provide further descriptions of data requirements. Both the table and associated discussions are somewhat general because the specific details needed are not only a function of the properties of the hazardous materials being handled, but the circumstances under which they are transported, stored, transferred, or processed, and the degree of detail that emergency planning personnel wish to include in their overall effort. It is therefore strongly recommended that Chapters 11 and 12 of this guide be carefully studied and that examples be worked out so that data collection personnel will have (or can be given) specific guidance with respect to the detailed information desired in any given situation or jurisdiction.

Rail Transportation

If the locality of interest has one or more railroad right-of-ways, it is first necessary to determine whether these tracks are used for shipments of hazardous materials. Any track segments used for this purpose should then be characterized in terms of specific location and length. Special attention should be given to identifying track segments that pass over or along the side of bodies of water. For subsequent response planning purposes, particularly in rural areas, some thought should be given to how various portions of the route may be accessed or approached by emergency response personnel and vehicles. Any information collected on these topics can best be shown on maps of the area, which may also be modified to highlight population centers and special occupancies such as schools, hospitals, prisons, and nursing homes -- not just for railroad accident purposes, but for all credible accident scenarios.

There are major railroad corridors in the United States that provide passage for a wide variety of hazardous materials, and there are numerous routes that only have limited traffic to specific destinations. Some part of this traffic may consist of regularly scheduled shipments (e.g., weekly or monthly shipments from a particular shipper to a particular receiver), another part may consist of non-regular but recurrent shipments, and a smaller part may consist of unique, non-recurrent shipments. Ideally, it is desired that planning and emergency response personnel obtain as complete a picture as possible of the specific hazardous cargos handled over the course of a recent 6-12 month period, the types and capacities of their containers, the general frequency of individual shipments, and the frequency of trains (called "consists" in the railroad industry) which haul hazardous cargos. Such data are best obtained by initiating direct contact with personnel within the safety department(s) of the railroad(s) that use the

TABLE 10.1
SPILL SOURCE CHARACTERIZATION FACTORS

Rail Transportation

- Route(s) and associated mileage through locality
- Classifications of track
- Location and layout of railroad yards
- Specific hazardous cargos
  - Number of cars passing through and length of stay in yards
  - Types and capacities of containers

Highway Transportation

- Route(s) through locality
- Nature and length of roads by segment
- Location and layout of local terminals
- Specific hazardous cargos
  - Number of trucks passing through and length of stay
  - Types and capacities of containers

Water Transportation

- Route(s) through locality
- Mileage of route(s)
- Nature and characteristics of waterway(s)
- Location and layout of moorings and anchorages
- Specific hazardous cargos
  - Number of ships or barges passing through and length of stay
  - Types and capacities of vessels and containers

Pipeline Transportation

- Pipeline route(s)
- Mileage of route(s) through locality
- Contents of pipeline(s)
- Pressure and temperature of pipeline(s)
- Flowrate through pipeline(s)
- Overall length and diameter of line(s)
- Characteristics of leak detection and shutdown system(s) (if any)

TABLE 10.1 (Cont.)
SPILL SOURCE CHARACTERIZATION FACTORS

Chemical and Petroleum Bulk Processing Facilities

- Location and layout of overall facility
- Location, type, dimensions, capacity, venting systems, contents, pressure, and temperature of chemical reactors, storage tanks, holding tanks, and other vessels.
- Route, length, diameter, flowrate, pressure, temperature, and contents of major intraplant pipelines, together with information on leak detection and shutdown systems.
- Location and nature of bulk cargo loading and unloading facilities and frequency of transfer operations.
- Location, size, and layout of secondary containment systems such as sumps, trenches, dikes, or barriers around potential spill locations.
- Location, layout, and destination of sewer and drainage systems.

Chemical and Petroleum Bulk Storage Facilities

- Location and layout of overall facility.
- Location, type, dimensions, capacity, pressure, temperature, venting systems, and contents of bulk storage tanks.
- Route, length, diameter, flowrate, pressure, temperature, contents, and frequency of use of major intrafacility pipelines together with information on leak detection and shutdown systems.
- Location and nature of bulk cargo loading and unloading facilities and frequency of transfer operations.
- Location, size, and layout of secondary containment systems, as above.
- Location, layout, and destination of sewer and drainage systems.

Pesticide and Other Packaged Chemical Warehouses

- Location and layout of overall facility.
- List of products stored in facility together with data on storage locations.
- Fire protection systems in the facility.
- Location, layout, and destination of sewer and drainage systems in area.
- Location, size, nature, and layout for secondary containment of spilled chemicals or contaminated water used for firefighting.

track(s) in question. Although these individuals may refer you elsewhere within their organizations for the desired data, contact with them can also be beneficial because they will have knowledge of the plans and preparations undertaken by the railroad to respond to emergencies involving hazardous commodities along their routes -- information which will be highly useful during the community emergency planning process. (Note: Railroads are *common carriers*, as are many trucking firms and marine shipping operations. Although such carriers do not own the cargos they transport, and very often do not own the vehicles in which the cargo is placed, they are legally and financially responsible for the damages resulting from any accidents that occur while a hazardous commodity is in their possession. As common carriers, they in most cases have little choice but to transport any commodity placed in their custody in accordance with current federal regulations.)

If the locality includes a railroad terminal or yard that transfers cars with hazardous cargos between trains heading to different destinations and/or which stores them for a time (which could be days or more) before they move on, a map should be obtained of the specific location and layout of the facility. In addition, if hazardous material cars are in any way segregated or sorted into special holding areas, these areas should be identified. As in the case of moving traffic, as much information as possible should be obtained as to the identities, quantities, frequency, and length of residence of individual cargos over a representative period of time. Employees at the facility are the best initial source of information. Be sure to ask if they have prepared an emergency plan for the facility and if they are willing to integrate and/or coordinate this plan with the general community planning effort.

Highway Transportation

Much of the information desired for railroad carriers of hazardous materials is also desired for over-the-road carriers. Specific needs include identification of major traffic corridors; specification of the location, length, and nature of roads; characterization of hazardous cargos, shipment frequencies, container types, and container capacities; and characterization (as in the case of railroads) of any local terminals or other gathering areas for hazardous material transport vehicles such as truck stops, weigh stations, motels, and so forth. It may also be beneficial to compile data on any travel and route restrictions in effect in the region.

Water Transportation

Those localities on the coastline of the United States, bordering inland waterways, or home to a port or harbor must be concerned with haulage of hazardous materials by ship or barge. Although relating to the marine environment, the desired information is similar to that discussed above for railroad and highway transport.

Pipeline Transportation

Most major cross-country pipelines in the United States convey natural gas, crude oil, LPG, refined petroleum products or anhydrous ammonia, but one may occasionally encounter more exotic commodities being transferred between specific sites (e.g., between the manufacturer and a major user of a particular chemical). Besides the specific route of a pipeline and its length through the jurisdiction of concern, it is desirable to determine pipeline contents, pressure, temperature, typical and maximum flowrate, diameter, and overall length, as well as characteristics of any leak detection and shutdown systems. The effort should probably include high pressure natural gas transmission lines and larger distribution lines, but not the smaller low pressure pipelines serving individual buildings and neighborhoods.

Bulk Chemical and Petroleum Processing Facilities

This category includes a variety of chemical manufacturing plants, oil refineries, and facilities which use large quantities (i.e., bulk quantities) of hazardous materials during the manufacture of their products. In order to make the information gathering task more manageable at large and complex facilities, it may be necessary to screen chemical handling areas and focus on those that utilize the largest quantities of the most hazardous materials, keeping in mind the difference between the toxicity of a substance and the toxic hazard presented to the public. Plant personnel, if cooperative, can be of invaluable assistance in this task. Screening can also be facilitated by asking plant personnel for a list of hazardous materials used at the facility together with typical quantities on hand.

Of key importance is the need to obtain a plot plan of the facility showing the location of hazardous material stores (tanks, loading racks, pipelines, etc.) as well as the identity and amount of chemicals present. This information is useful for actual emergency response as well as planning purposes. Aerial photographs can also be valuable.

It is next prudent to focus on any storage tanks of chemicals or large containers used for mixing or reacting chemicals. Desired information includes type and location of the tank or container, working capacity, dimensions, maximum potential pressure and temperature of contents, identity of contents, the discharge orifice size of any emergency pressure relief vents, and any systems installed to capture, recover, or destroy flammable and/or toxic gases that may be released under emergency conditions. While looking at such tanks, it is also important to determine if the contents have the ability to undergo any type of runaway exothermic polymerization or decomposition reaction, or if they are subject to any other hazardous reaction in the event of equipment failure, human operator error, or inadvertent contamination by materials available in the general area of the tank or container (particularly

those that are somehow linked to the tank by a pipeline system). Make note also of the diameters of pipelines and various pipes that exit each tank and which could discharge the contents of the tank or container in the event of a break or rupture.

While on the subject of intraplant pipelines, note that such facilities may have literally miles of relatively small pipes linking items of equipment together and possibly a limited number of intraplant lines of large capacity. It is well to gather the list of information under *Pipeline Transportation* above for the larger lines conveying hazardous materials.

Facilities that handle large volumes of chemicals are also likely to ship and/or receive hazardous materials by rail, highway or water transportation modes, thus necessitating cargo loading and unloading facilities. Details of interest at these sites include identity, frequency, and volume of individual shipments, diameter and type of loading/unloading hoses or arms, normal pumping rates of cargos through hoses or arms, time required to observe any tank overflows and to shutdown pumps, type and capacity of transport vehicles, and the number, contents, and duration of stay of railcars, trucks, or marine vessels serving the facility.

Many facilities have installed *secondary containment systems* around storage tanks, process areas, and loading/unloading areas to collect and contain any spilled materials, typically in the form of dikes, curbs, or other barriers surrounding items of equipment or pits or sumps to which spilled cargo will flow and collect. Since the total rate at which vapors or gases will evolve from a pool of boiling or evaporating liquid is a function of the surface area of the pool, and since the size of a liquid pool fire is also a function of pool dimensions, the dimensions of diked areas or sumps provide highly useful information. For response planning purposes, information is desirable on plant fire protection systems and emergency spill response capabilities.

Finally, it is also desirable to determine whether spilled materials have the opportunity to enter underground sewer or drain pipes and where these pipes lead. Flammable liquids in pipes that are not full and exposed to a source of air can evolve vapors that might explode violently if ignited. Either flammable or toxic substances might pose problems at the end of the pipe, be it a river, lake, or water treatment facility.

Chemical and Petroleum Bulk Storage Facilities

There are various bulk storage facilities across the United States that receive bulk quantities of chemical and petroleum products, including liquefied energy gases such as LPG and LNG, by one or more modes of transportation, store them for a time, and then load them onto other transport vehicles for distribution to buyers and users of the products.

The information desired about such facilities is the same as that needed for the portions of bulk chemical and petroleum processing facilities that store and transfer products. Refer to the previous section for a discussion of specific items.

Pesticide and Other Packaged Chemical Warehouses or Distribution Centers

Numerous types of common businesses store hazardous materials in bottles, drums, boxes, cylinders, and other packaging materials. Although the amount in any given package might be relatively small, the facility may store a large number of such packages in some sort of warehouse facility or even on the shelves of a store of some kind. Some materials may be in small containers simply because buyers do not need or want larger quantities at any given time. Others may be in such packages, particularly at laboratory supply companies, because DOT regulations prohibit transportation of bulk quantities due to their special hazards.

As in prior cases, it is desired to obtain information on the location and layout of the overall facility, the products typically stored therein, their usual storage locations, sewer and drainage systems in the area, secondary containment systems, and fire protection systems. The latter two topics are particularly important for this category, because one of the more worrisome scenarios involves fire. Serious environmental impacts may occur if large amounts of water applied to burning chemicals cause contaminated runoff into sewers or drains leading to bodies of water or treatment plants. Indeed, some fire departments have prefire plans, particularly for warehouses storing toxic pesticides, that call for allowing the facility to burn while only protecting surrounding buildings with water until all chemicals are consumed, thus avoiding a water contamination problem. Although the building may be a total loss, and populations subject to smoke exposure may require evacuation or other protective action, savings may actually be realized because of the expenditures that would otherwise be necessary to decontaminate land and water bodies polluted by contaminated runoff.

Miscellaneous Facilities

Besides the large number of facilities and transportation modes that are commonly associated with the chemical and petroleum industries, there are many other common types of businesses and facilities that are apt to use or store hazardous materials and which should not be overlooked. Some possibilities are listed in Table 10.2 but are only a sampling of the many types of facilities likely to store and use hazardous materials in some significant quantity.

TABLE 10.2
MISCELLANEOUS POTENTIAL SPILL SOURCES

Airport and marine fuel depots - gasolines and fuel oils

Breweries and distilleries - alcohols

Compressed gas suppliers - medical and industrial gases

Construction firms and sites - explosives, compressed gases, fuels

Dry cleaners - cleaning solvents, perchloroethylene

Electronic circuit makers - acids

Embalming supply houses - formaldehyde

Farm/garden supply shops - pesticides, fertilizers, herbicides

Fireworks manufacturers - explosives, pyrotechnics

Food stores or warehouses - ammonia (in refrigeration systems), combustible dusts

Foundries - resins, other chemicals

Fuel oil companies - fuel oils

Furniture stripping operations - solvents

Gasoline stations - gasoline

Gun and ammo shops - ammunition, explosives

Hazardous waste disposal facilities - virtually anything

Hospitals - compressed gases, medicines, radioactive materials, etiologic agents

Laboratories, chemical and biological - various chemicals, etiologic agents

Lawn fertilizer companies - pesticides, herbicides, fertilizers

Leather tanners - various chemicals

LP-gas or propane suppliers - liquefied flammable gases

Paint, varnish, and lacquer makers and wholesalers - resins, solvents, chemical pigments and additives

Pest control companies - pesticides, poisons

Plastic and rubber makers - solvents, additives, bulk chemicals

Plating shops - acids, cyanides

Pulp and paper mills - bleaches, caustics, acids, sulfur compounds, and others

School and university chemical laboratories - various chemicals

Swimming pools (public) - liquefied chlorine

Swimming pool supply houses - oxidizers (calcium hypochlorite), hydrochloric acid, algaecides

Steel mills - acids, degreasers

Textile and fiber manufacturers - solvents, dyes, resins, various other bulk chemicals

Water treatment facilities - liquefied chlorine, acids

Welding shops - compressed gases

Welding supply shops - compressed gases

10.5 AVAILABLE METHODOLOGIES TO COMPILE DESIRED INFORMATION

Previous sections have discussed the primary reasons for identifying and characterizing potential spill sources and accident sites, and briefly described the information and data desired for hazard identification and analysis purposes. It is now time to briefly review some of the methods available for fulfilling these information needs. In reviewing this material, keep in mind that major potential spill sources outside the the community of interest may also have the capability to impact residents and their property in the event of an accident. It may not be enough to only study facilities that lie within the precise boundaries of the community or jurisdiction of concern.

Enforcement of Right-to-Know Laws

Right-to-Know laws or regulations, be they of federal, state or local origin, typically require that manufacturers and users of specified hazardous materials provide material safety data sheets (MSDS) or lists of available MSDS for the substances handled on their respective sites to employees, community leaders, fire departments, state emergency planning groups, and/or members of the general public. The various laws and regulations enacted or promulgated over the years have differed in several important aspects, but all, in some fashion or another, have had the potential to facilitate identification of facilities which handle or otherwise utilize specified hazardous materials.

Although Right-to-Know laws were enacted in more than 25 states in recent years, recently revised federal laws and regulations have essentially preempted most of these legislative initiatives. The new laws and regulations are *very* comprehensive and have the net objective of ensuring that State Emergency Response Commissions (SERCs) and LEPCs will be automatically informed of the presence of *most* hazardous materials present at facilities within their respective jurisdictions. ***Indeed, enforcement of right-to-know laws and regulations is the most direct and efficient method available to LEPCs for the identification of facilities that manufacture, store, process, or otherwise use hazardous materials that may pose a threat to community health and safety.*** In most cases, enforcement may require little more than informing these facilities, either individually or via a general public relations campaign, that they are subject to these laws and regulations. Although progress is being made in this area, there remain many facilities and businesses, particularly those that do not consider themselves part of the chemical industry, who have been slow to realize or recognize that they are fully subject to the mandates of these laws and regulations regardless of the nature of their operations.

The specific reporting requirements originally mandated by SARA are summarized within Appendix A of the ***Hazardous Materials Emergency Planning Guide*** (NRT-1) cited in Chapter 1 of this document. Stated quite briefly, SARA requires that facilities storing or using EHSs in excess of TPQs must notify the local SERC and LEPC, appoint a facility

emergency coordinator to assist the LEPC in emergency planning and to provide any additional information and data required during the planning process. In addition, any facility subject to the the ***Hazard Communication Standard*** (29 CFR 1910.1200) of the Occupational Safety and Health Administration (OSHA) must submit a list of the hazardous chemicals on its site or a set of material safety data sheets for these materials to the state emergency response commission (SERC), local emergency planning committee (LEPC), and local fire department. These organizations are also to be provided annual reports of hazardous material inventories grouped by hazard category. **Because SARA Title III makes planning for EHS's a mandatory effort, hazard identification should begin with these materials.**

A very significant and somewhat recent development (late 1988) is that OSHA succeeded, after a battle in the courts, to expand coverage of its hazard communication standard from a very specific and somewhat limited set of industries to all employers except those in the construction industry. Thus, many loopholes (though not all) that would otherwise have complicated the hazard identification efforts of LEPCs have now been closed by the federal government.

The various laws and regulations discussed above are being frequently modified and/or expanded in coverage in a concerted attempt to further facilitate the work of local emergency planning personnel. Current information on federal initiatives under the Resource Conservation and Recovery Act and Superfund law may be obtained by calling the RCRA/Superfund Hotline at 800-424-9346 or 202-383-3000. Current information on the specific regulations prompted by Title III of SARA can be obtained by calling the Emergency Planning and Community Right-to-Know Hotline at 800-535-0202 or 202-479-2449. Both hotlines have been established by the federal government and are operational from 8:30 am to 7:30 pm EST during the normal work week.

NOTE WELL: Although the above laws and regulations will greatly help community emergency planning personnel in identifying fixed-site facilities that handle hazardous materials, they are not necessarily all inclusive and encompassing. There will still be many cases in which hazardous materials are handled at a facility but insufficient data will be made automatically available to LEPCs to permit the performance of a comprehensive hazard analysis. Additionally, the fact that reporting requirements do not apply to transportation modes conveying hazardous materials through individual jurisdictions is highly significant and important, as is the fact that many fities and businesses are not yet aware of their specific responsibilities. **Consequently, comprehensive planning for hazardous materials emergencies, although not fully mandated by law, requires a concerted effort on the part of LEPCs to identify and characterize potential threats that have in one way or another escaped mandatory reporting and planning assistance requirements.**

Use of Fire Department and Building Inspection Records

Over the years, local fire departments may have accumulated substantial data on the businesses and facilities within their jurisdiction as a part of fire hazard surveys, inspections associated with regulatory or insurance requirements, response to accidents, and preplanning for fire emergencies. It follows that fire department records and personnel can be a key source of desired information in many communities and counties. Similarly, building inspection departments of local governmental entities may have useful records and knowledgeable personnel. And last but not least, note that local police departments will have considerable general knowledge of the businesses that operate in their respective jurisdictions. Law enforcement personnel patrol the streets on a 24-hour basis and will often have first hand knowledge of many of the potentially hazardous activities of concern.

Use of Industry Questionnaires

A reasonably detailed questionnaire mailed to all businesses which may handle hazardous materials, particularly if accompanied by a letter from the mayor, town or city council, or local fire chief, can provide valuable information on a significant fraction of the facilities contacted. It is a good idea to call first to determine to whom the questionnaire should be directed, and also, to determine who can be called for follow-up questions. Alternatively, a self-addressed, stamped postcard can be inserted in the package with a request that the person given responsibility for completing the document list his or her name and telephone number on the card and drop it in the mail. A news release to local media about the effort can alert the business community as to the arrival of the questionnaire and alert the public about the planning effort being undertaken. In all cases, be sure to stress the fact that the information is solely desired for emergency response planning purposes. As discussed later, be sensitive to the possible need to maintain the confidentiality of certain data.

Meetings with Business Organizations and Trade Groups

Many businesses throughout the country are members of local Chambers of Commerce or mutual aid groups (i.e., groups of companies in the same industry that have agreed to help each other as best they can in time of emergency). Presentation of community emergency response planning information needs during a general meeting of such a group has the potential to obtain publicity for the effort, to obtain assistance and cooperation from the local business community, and most importantly, to obtain formal endorsement of the organization for the effort, thus encouraging individual members to cooperate fully with public authorities.

Meetings with Individual Business Personnel

Where the effort is within reason, planning personnel assigned this task may choose to meet with key personnel within the individual companies or organizations handling hazardous materials, explain the benefits of cooperation to both the community and the business, and request a tour of facilities. Necessary details of operations can be obtained during these meetings and tours, or questionnaire forms may be left behind for later completion.

It is well to keep in mind during such meetings or other contacts that many companies have undertaken intensive efforts to determine the hazards and risks faced by the community and themselves due to the storage and use of hazardous materials, especially in the aftermath of the Bhopal incident. Requests for the results of such analyses might lead to the receipt of much desired information. Given that the Chemical Manufacturers Association is actively encouraging such efforts among the entire chemical industry under its Community Awareness and Emergency Response (CAER) Program (see Chapter 1), a request may even provide impetus for initiating such work, which could ultimately save community planning personnel considerable effort.

It is also desirable to ask if the facility has a contingency plan for dealing with on-site emergencies and whether any attempt has been made to coordinate and integrate the plan with community efforts. This can prompt some thought on preparing a facility plan where none exists, lead to obtaining a copy of the plan (which is bound to contain useful information), and/or initiate a useful and continuing dialog between company and public emergency preparedness personnel.

As noted earlier, it is important during such meetings to stress that the ultimate objective of the community is to ensure it is prepared to protect the public during potential hazardous material emergencies and to lend appropriate assistance to the responsible party (i.e., the company or firm that owns and/or has custody of the materials in question) in mitigating damages resulting from an accident. It is also important, however, to be sensitive to the fact that the success and commercial viability of some businesses may depend on proprietary technology or processes that cannot fully be protected with patents or copyrights. Indeed, one or more products of any chemical-related business may be based on "secret recipes" that would hurt the company if disclosed to competitors. Do not be surprised, therefore, if there is reluctance at times to discuss certain details of company operations.

The right-to-know laws and regulations discussed above have specific provisions relating to claims of *trade secrets* by facilities and these provisions should be followed when applicable. When not applicable, there are essentially two methods to approach the problem when there is an acknowledged or known threat to the community and issues of confidentiality that hamper planning efforts. The first involves a formal agreement between the company

and the community to use any information provided solely for emergency planning purposes and not to disclose the information to any third parties. This places a substantial legal burden on the community and requires active management of sensitive data, but potentially serves the needs of both parties. The other approach necessitates that the company itself undertake the analysis procedures outlined in Chapters 11 and 12 and provide planning personnel with only the final results and a promise to disclose the identity of any discharged or spilled materials immediately in the event of an accident. The effort may be facilitated on the part of the company by the employment of independent consultants or contractors.

Queries of Rail, Marine, and Pipeline Transportation Companies

One of the more difficult tasks in some localities will involve compilation of sufficient data on transportation of hazardous commodities in the area, particularly if these cargos do not have a specific destination in the locality that can be identified and queried but are simply passing through. The survey methods to be considered vary with the mode of transportation being utilized.

As note above, the best source of railroad traffic data is the railroad company that owns and operates any specific track segment of interest. Many will have computerized records of train movementss and the cargos carried. Others might be willing to compile the desired data over a specific period of time to assist the data collection effort. Companies that receive or ship hazardous materials and which have facilities in the area can provide data on the portion and nature of the traffic for which they are responsible if cooperative. They can also act to inform emergency planners of the specific transportation companies that they employ for potentially hazardous cargo movement.

Pipeline routes, particularly those conveying hazardous commodities, are often clearly marked and known to public authorities, particularly those who may have issued a permit for the route at some time in the past. Substantial information may be readily available from "digsafe" program offices in many areas of the country that maintain records of buried pipelines and cables. Local utilities will know of such programs, as will construction companies, and a hotline number for the local digsafe program is likely to be prominently displayed in the local telephone directory. Contact with the owner of any pipeline is likely to provide current operating conditions, specific route of the pipeline, and any emergency response preparations that have been undertaken in anticipation of a future accident.

Sources of information in ports and harbors include the port or harbor master, the companies that offload, ship, or receive hazardous cargos, the public commission or council (if any) that operates or has regulatory or oversight responsibility for the waterfront, the marine transportation companies that operate in the area, and any local or regional offices of

the U.S. Coast Guard or U.S. Army Corps of Engineers. The best approach is to locate a person who knows how the port or harbor operates and how records are kept, and ask his or her advice on how best to proceed.

Truck Traffic Surveys

By their very nature, trains, pipelines, and marine vessels follow routes that are fixed in location, readily identifiable, and utilized by a comparatively small number of transportation companies. This is not true in the case of truck traffic which may be found on a wide variety of roads and highways and potentially involve a large number of different carriers. The task of characterizing truck traffic and its routes will therefore be substantially more time-consuming in many jurisdictions but can be accomplished to a large extent using the following methods and procedures.

Almost all jurisdictions are served by firms that provide fuels such as gasoline, fuel oil, and LP-gas (LPG) or propane to industry and the public. These should never be overlooked. Trucks conveying gasoline are known to be involved in more serious accidents than those transporting any other hazardous material in the United States due to the flammable and explosive properties of the substance and its extremely widespread use and distribution. LP-gas and liquefied propane, which are also used in large quantities in most parts of the country, are highly flammable compressed liquefied gases that may fuel pool fires, flame jets, BLEVEs, vapor cloud deflagrations, and confined and unconfined vapor cloud explosions if discharged to the external environment. Fortunately, the vast majority of firms that receive, sell, and deliver these commodities will be readily identifiable. Those companies that serve commercial accounts or the general public usually advertise frequently to gain new customers and will be easily found in the "yellow pages" of local or regional telephone companies, as will product wholesalers or distribution companies. Discussions with the operators of a sample of local gasoline stations can also be helpful.

The shippers and receivers of other hazardous materials in the locality of concern are one good source of information about the nature and frequency of over-the-road shipments. Routing and additional shipment information can be obtained from the trucking firms that deliver or pick-up cargos.

Most large trucking companies have established terminals at various locations across the country. Although these terminals may be located outside the locale of concern, company management, safety or dispatch personnel may be able to provide substantial information on the cargos routed through the subject jurisdiction. They may also have a good idea of the operations of other carriers that function in the area, since keeping track of the activities and operations of competitors is often good business practice. Similarly, smaller companies in the region, particularly those that specialize in carriage of hazardous materials, can be a useful source of information.

Finally, when all else fails to provide a reasonably complete overview of hazardous materials traffic by highway, there is always the possibility of conducting a roadside traffic survey. One form of survey involves stationing observers along highways at key locations of interest, such as major intersections or entrances into the jurisdiction for a period of time and making counts of traffic. The placards and other signs on individual vehicles (see Chapter 8 for descriptions) will provide a general if not specific indication of the nature of any hazardous cargos being carried. The names of transportation firms on vehicles can provide leads to sources of more detailed information when needed.

The task can be somewhat facilitated for major highway traffic if there is a truck weighing station on the route and observers are positioned at these locations. Similarly, survey activities may be coordinated at times with roadside safety inspections conducted by the highway patrol, state police and/or department of motor vehicles. Police forces may also be asked to make note of hazardous materials traffic at all times during routine duties on a periodic basis, as may collection personnel at toll booths.

Although much of the information of interest for planning purposes has been provided above, it is well to note that the U.S. Department of Transportation and the U.S. Department of Energy jointly sponsored a study to identify and characterize methods by which information may be obtained on hazardous material shipments at the local level. The resulting report is:

- Overcast, T.D, and Dively, D.D., ***Options for Gathering Information About Shipments of Radioactive and Other Hazardous Materials,*** DOT Report DOT/RSPA/DHM-61-86-2, 1987, available from the National Technical Information Service, Springfield, VA 22161.

Use of Permit Records

Companies that handle hazardous materials typically require a variety of permits and licenses to build their facilities, to handle or store flammable materials, chemicals or wastes, and to discharge pollutants into the air or water. These permits and licenses are issued by a variety of local, state, and federal authorities and may provide a reasonably efficient means to identify these facilities in some jurisdictions. Organizations with possibly useful records include fire and police departments, building inspection agencies, zoning boards, public or occupational health and safety departments, state and federal environmental protection agencies, water and sewer commissions, the U.S. Army Corps of Engineers, and the U.S. Coast Guard, among others.

Use of the "Yellow Pages"

The local telephone company "yellow pages" directory can be of major assistance in identifying all types of firms that potentially store, handle, or transport significant quantities of hazardous materials. Better yet, it can provide their addresses and telephone numbers.

Access to Detailed Chemical Property Data and Hazard Information

As readers will realize, industry is generally required to provide emergency planning personnel with material safety data sheets (MSDS) or information similar to that found on such sheets. It is important to note that this information and data, although of considerable value in many respects, is not always adequate for a full and complete understanding of the hazards and properties of individual hazardous materials. Indeed, it is not uncommon to review several MSDS for the same material, each prepared by a different manufacturer, and to find numerous subtle and sometimes major inconsistencies in their contents.

Quite frankly, MSDS with different origins and authors often vary greatly in both accuracy and completeness, although the situation has improved vastly in recent years. Even the best available MSDS, however, provide but a simplified overview of material hazards, appropriate first aid measures, suggested emergency response actions, and so forth. It is often best, therefore, to use MSDS as a screening tool to identify those materials that clearly pose the greatest hazards to a jurisdiction, and then to make an additional effort to compile more complete information on these substances. Realize also, however, that some manufacturers have a tendency to exaggerate hazards of their products to avoid the possibility that they will be found negligent in warning customers of possible dangers in the event of an accident. Conversely, though this is not nearly as common as it once was, and may simply have been due to a lack of knowledge or expertise, some firms have been known to downplay the hazards of their products in the past.

There are essentially three available methods to obtain more detailed information on a specific hazardous material. The first involves access and study of the numerous hazardous material data bases, handbooks, and guides available in the marketplace. The best of these contain considerable useful and accurate data on the common and sometimes rare chemical products and fuels used in industry. The worst, however, can be a considerable waste of funds, so it is wise to purchase these documents or computer programs with care. (*Note: Some computerized data bases, in particular, have absurdly high prices given the nature and quality of the data they provide. In many cases, the authors have simply copied data that is available in hardcopy documents selling for a tiny fraction of the computer program price.)*

The name and addresses of chemical manufacturers and distributors, together with indexed lists of their products, can be found in several chemical buying guides. Potential sources of these guides include major public and university libraries, the purchasing

departments of companies that buy chemicals, and even individual chemists and chemical engineers in the community. The second approach involves identification of the manufacturers of materials of special concern and the mailing of requests for detailed product information bulletins and safety handling guides. Most large corporations will honor such requests at no cost.

The third approach, which is best suited to identifying a source of detailed information for an unusual hazardous material, involves calling the Chemical Referral Center in Washington, D.C. This Center was established by the Chemical Manufacturers Association (CMA) in late 1985 to assist callers in contacting sources of information on over 250,000 chemical products and basic chemicals on a non-emergency basis. The center operates from 8 a.m. to 9 p.m. (EST) Monday through Friday and may be reached toll-free from the continental United States and Hawaii at 800-CMA-8200. Callers in the District of Columbia and Alaska may telephone 202-887-1315 on a collect basis.

10.6 SOURCES OF ADDITIONAL HAZARD IDENTIFICATION GUIDANCE

The U.S. Department of Transportation and the Federal Emergency Management Agency have sponsored numerous demonstration projects associated with hazardous materials safety and emergency response planning. The experiences of the local, county, and state authorities involved in these projects, as documented in the reports they have prepared on their activities, can provide additional ideas and insights on how best to conduct a hazard identification survey in any given locale. Most of these reports are listed and referenced in Appendix E of the ***Hazardous Materials Emergency Planning Guide*** (NRT-1).

10.7 FORMULATION OF CREDIBLE ACCIDENT SCENARIOS FOR PLANNING PURPOSES

As noted earlier, it is not sufficient to determine the locations and characteristics of the sites and hazardous materials that may become involved in a future accident; it is also necessary to gain an understanding of the potential nature and outcome of potential accidents for comprehensive planning purposes. An important step in this process is the formulation or postulation of credible accident scenarios based on the information obtained during hazard identification activities. These scenarios can then be evaluated with respect to specific probabilities of occurrence, consequences, and/or risks to the community via the procedures respectively described in Chapters 11, 12, and 13 of this guide.

Chapter 11, in particular, describes, discusses, and enables probability analysis for credible accidents at fixed site facilities and in transportation. Although the probability analysis step itself is considered optional, planning personnel should nevertheless refer to Chapter 11 for assistance in the definition of accident scenarios in their respective jurisdictions based upon results of the hazard identification procedures. They may choose to

select several scenarios for each hazardous activity (ranging from low to high severity) for further analysis, or to simplify matters by only selecting worst case scenarios (i.e., those posing the greatest threats to the community.)

10.8 ORGANIZATION OF THE DATA

As noted previously, the information compiled during the hazard identification and characterization task is not only useful for planning and hazard analysis purposes, but can also be valuable during actual emergency response if readily accessible in a centralized data base. It is therefore a good idea to organize the information and data in a filing system of your choosing, and/or to enter the most important facts into a data management system installed on a personal computer. If placed in a location that is manned on a 24-hour basis, such as police or fire department dispatch offices or a designated emergency operations center, response personnel can be briefed on potential hazards by radio while en route to an accident site and be given answers to specific questions that may arise upon their arrival at the scene.

11.0 PROBABILITY ANALYSIS PROCEDURES

11.1 INTRODUCTION

The transportation and use of hazardous materials poses threats that are of concern to society, but which are not always fully understood in terms of their likelihood of occurrence or viewed in perspective with regard to their relation to other threats. The purpose of this chapter is to provide emergency planning personnel with the basic information, data, and procedures necessary to refine and evaluate individual hazardous material accident scenarios in terms of their annual probability or frequency of occurrence on at least an order of magnitude basis.

As noted earlier in Chapter 9, this probability analysis step may be considered optional where community leaders (or individual facility operators) wish to prepare for every conceivable accident regardless of its likelihood of occurrence and have the time, manpower, and resources to achieve their goals. More often than not, however, these individuals will find that time and resources are limited and that other threats or needs compete for attention. Prioritization of potential accidents in terms of annual probability as well as severity will permit attention to these threats (and it is eventually hoped all threats to public health and safety) in a logical and orderly fashion and thereby reduce the chance that time and resources will be expended on emergency scenarios of exceedingly low credibility or significance. Note, however, that assessment of hazardous material accidents or any other threats on a probabilitistic basis does *not* guarantee that all such hazards will be identified or that less likely events will not occur.

The chapter addresses seven primary activities associated with hazardous materials, each with the potential to result in public emergencies. These include:

- Bulk transportation by truck
- Bulk transportation by rail
- Bulk transportation by barge or other marine vessel
- Transportation by pipeline
- Bulk storage, processing, or handling at fixed facilities
- Transportation of packages
- Transportation by air

The overall approach presented in this chapter involves use of average national accident rates determined from historical records and relevant exposure data. While such rates may overestimate or underestimate average annual accident probabilities for any specific facility or transportation activity, they are not expected to be vastly in error in aggregate for any jurisdiction or facility. The ultimate goal, after all, is not exact estimation of accident probabilities, but their approximation at a level of accuracy sufficient for

emergency planning purposes. Appendix F to this guide presents the basis and rationale for the recommendations and procedures that follow, and additionally, discusses the use of local and other data and information (where available) to further refine estimates where this may be desireable.

The actual computation of the annual accident probability associated with any specific activity involves using the frequency with which such accidents are known to occur in combination with a measure of the "exposure" of the community or other jurisdiction to the potentially hazardous activity. For most transportation modes, for example, historical accident rates are presented in terms of the number of accidents expected per mile of travel and exposures are expressed in terms of the number of trips made per year and the mileage of routes within the locality. Simple multiplication of these values provides the expected number of accidents per year involving the activity being considered. Further multiplication of this result by such factors as the fraction of accidents that result in loss of cargo to the environment and the fraction of accidents that result in a prespecified amount of cargo loss permits greater specificity in predictions. Worksheets for each activity facilitate computations, and are provided in lieu of tabulated or generalized categorizations of accident probabilities to provide planning personnel with the option of using local data for greater accuracy. Planning personnel may use the predicted accident frequencies to determine an appropriate "accident probability category" during the risk analysis step described in Chapter 13 of this guide.

An important point to be made is that the analysis methods presented herein provide their users with the annual accident probability expected for the entire area of concern and not for specific locations or subregions within the locality. Should it be desired to determine the probability of a release near a specific populated area, a specific body of water, or a specific environmentally sensitive habitat, it will be necessary for users to determine that fraction of the overall community or facility exposure associated with this special area and to adjust overall accident frequency predictions in an appropriate fashion.

Special Notes

Wherever the term "spill" is used in the discussions that follow, readers are advised to interpret the term as referring to any release or discharge of a hazardous material in a manner capable of posing a threat to the public or the environment.

The procedures that follow permit the user to estimate the number of "spills/year" expected on average from individual activities or operations involving hazardous materials. The average reoccurrence interval for a specific spill scenario can be determined by dividing the number "1.0" by the predicted frequency of spills per year. Thus, a spill frequency of 2×10^{-2} spills per year can be translated to mean that a spill can be expected to occur once every

50 years on average. Where desired, readers may also sum the spill frequencies derived for similar individual activities and then determine the reoccurrence interval associated with the combination using the same methodology.

Throughout this chapter, historical accident rates and other data are frequently presented in "scientific notation". Readers unfamilar with this method of representing very small (or very large) numbers are referred to Appendix A for guidance.

11.2 GENERAL SEVERITY OF ACCIDENTS CONSIDERED

The types of accident scenarios that could theoretically be covered in this chapter range from minor spills of gasoline at service stations to major catastrophes that occur once every 10 or 20 years on average on a worldwide basis. The primary focus, however, is somewhere between these extremes, and on the types of events which occur somewhere in the United States every week or month, but for which the risks to any one specific community might be low but nevertheless significant. In other words, we are not highly concerned with routine and common spills and discharges of relatively minor significance. Nor are we overly concerned with extremely rare events.

For a general perspective on hazardous materials accidents, consider that there are many thousands of hazardous materials releases which occur each year in transportation and at fixed facilities, yet the vast majority are of very limited consequence. Tables 11.1 to 11.3 give some idea of the total numbers of accidents reported each year and the relative contribution made by various activities. More specifically, Table 11.1 addresses the number of evacuations in recent years that were of sufficient magnitude to warrant reporting. Table 11.2 provides an estimate of the total number of accidents over a ten year period involving hazardous material releases from transportation activities, while Table 11.3 focuses on major events by type of activity. Although the data presented in the latter table are somewhat dated, they are nevertheless sufficient to demonstrate that only a small fraction of all accidents result in major consequences.

11.3 BULK TRANSPORTATION OF HAZARDOUS MATERIALS BY HIGHWAY

Bulk transportation of hazardous materials by highway involves the use of tank trucks or trailers and certain types of more specialized bulk cargo vehicles. In all, trucks transport more than sixty percent of the hazardous materials not carried by pipelines, with just under fifty percent of this material being gasoline (OTA, July 1986). Average trip lengths are 28 miles for gasoline trucks and 260 miles for chemical trucks, implying that most gasoline shipments are very localized while chemical shipments may be regional or interstate. Since trucks carry hazardous materials the greatest number of miles near populated areas, and are also responsible for the largest number of shipments, it is not surprising that this mode of transportation is also responsible for the greatest number of accidents.

TABLE 11.1
CHEMICAL ACCIDENTS REQUIRING EVACUATIONS

Type of Accident	1980-1984	1984
Train derailment	55	8
Railcar spill/fire	23	5
Truck accident	35	5
Truck spill/fire	32	7
Chemical plant release	43	5
Industrial plant release	78	24
Pipeline	4	0
Ship incident	4	1
Waste site accident	7	1
Other*	14	1
TOTAL	295	57

*Includes helicopter crash, plane crash, sewer gas episode, oil well explosion, swimming pool chlorine accident, pesticide spill in retail store, mine fire, two military missile silo accidents, and two electrical transformer leaks.

Source: Sorensen, 1986

TABLE 11.2
HAZARDOUS MATERIAL TRANSPORTATION ACCIDENTS

Mode	Number of Accidents Per Year[1]	1973-1983 Average[2]
Highway	10,000 - 15,000	10,289
Rail	1,000	975
Air	200	150
Water	20	26

Source: [1]Materials Transportation Bureau, 1983 and Cheok et al, 1985
[2]OTA, March, 1986

TABLE 11.3
MAJOR HAZARDOUS MATERIALS ACCIDENTS*

Activity	1964-1973	1953-1973
Chemical plants	6	12
Oil refineries and storage	10	13
Gas storage tanks	1	2
Oil drilling rigs	2	2
Pipelines	1	1
Fireworks plants	0	2
Marine tankers, barges	8	15
Railroad tank cars	5	8
Trucks	3	8
TOTAL	36	63

*10 or more fatalities, 30 or more injuries, $3,000,000 or more in property damage

Source: Office of Radiation Programs, 1980

Tank trucks are usually tractor-semitrailer vehicles or smaller bobtail-type units. The tanks themselves are usually constructed of steel or an aluminum alloy, but may also be stainless steel, nickel and other materials. Capacities are usually in the range of 3000-10,000 gallons, although slightly smaller and larger units are available. Intermodal tanks which consist of a tank within a protective rigid framework, one-ton tanks which are lifted on and off the transporting vehicle, and large gas cylinder bundles are also commonly used for bulk transport by highway.

Commodity breakdowns for trucks, as described in various data sources are not considered very accurate and vary widely. However, a one-month survey of cargoes in Virginia found a fairly close match (by percentage) to the average distribution of commodities involved in accidents. The comparison for commodities involved in accidents in Virginia also matched national accident breakdowns fairly well (Urbanek and Barber, 1980). National involvement in accidents by type of commodity for the time period July 1973-December 1978 was:

Flammable liquids	60.5%
Combustible liquids	16.3%
Corrosives	11.6%
Flammable compressed gases	3.2%
Oxidizers	2.1%
Poisons (liquid or solid)	2.1%
Nonflammable compressed gases	1.9%
Explosives	1.5%
Radioactive materials	0.5%
Flammable solids	0.3%

Causes and Examples of Past Accidents

Truck accidents on roadways, regardless of the cargo involved, are generally due to:

- Collisions with other vehicles
- Collisions with fixed objects such as bridges or overpass supports
- Running off the road
- Overturns due to excessive speed on curves

These four events are most likely to result in a release of large quantities of hazardous materials, and are predominantly the result of human error. Smaller releases may arise due to defective or loose valves, fittings or couplings; weld failures; and various other structural defects. (Note: Loading or unloading spills are considered separately in the category of *fixed facilities* below and actually result in the majority of overall releases involving trucks.)

The severity and consequences of discharges resulting from truck accidents can vary widely. Some examples include:

- A tank truck carrying 11,000 gallons of gasoline blew a tire, struck a cement barrier which ripped open the side of the tank, and then burst into flames on Interstate 95 near Peabody, Massachusetts. State troopers closed down the highway while an emergency crew from Logan International Airport spread foam on the wreckage. The highway remained partially closed for several days, since one section had melted and needed to be replaced. There were no injuries or deaths. (December 3, 1985)

- Littleton, New Hampshire, was spared a potentially catastrophic accident when a tank trailer loaded with 9,200 gallons of liquefied propane jack-knifed on an icy hill and tipped on its side about 75 yards from a large storage tank of liquid propane and less than 100 yards from large fuel oil storage tanks. No propane leaked from the truck, but a diesel fuel tank was ruptured; 1500 people residing within a half mile radius were evacuated until the propane was safely transferred to another vehicle the next day. (February 11, 1982)

- A truck pulling two tank trailers loaded with molten sulphur collided with a highway barrier on a toll bridge and burst into flames taking two lives and injuring twenty-six. Firemen encountered difficulty extinguishing the fire and rescuing victims. Visibility at the time was poor due to fog and the spilled sulfur had burned through water supply lines. (January 19, 1986)

- In Houston, a tank truck carrying liquefied anhydrous ammonia collided with a car and fell from an elevated highway to a busy freeway. The truck exploded violently on impact releasing billowing clouds of ammonia. Four persons (including the truck driver) were killed, dozens of motorists were overcome by the fumes in a three-mile area, and at least 100 were treated at area hospitals. The vapors and fumes were so thick that police helicopters were initially repelled. The city was forced to use all available ambulances and privately-owned hearses to transport the injured. (May 12, 1976)

- Although certain details are unclear, a tank truck carrying liquid propylene sprang a leak in the vicinity of a crowded campsite in Spain. Flammable gases spread from the truck, encountered a source of ignition, flashed back to the vehicle, and caused a BLEVE with a large fireball. The death toll from burns was approximately 170. Numerous other people suffered moderate to severe burns but otherwise survived. (July 11, 1978)

Suggested Approach for Assessment of Accident Potential

Since we are concerned with accidents with the potential to cause major problems for a community or other jurisdiction and not those which are handled on a routine basis, it is best to focus on vehicular accidents rather than relatively minor leaks from valves, fittings, or open relief valves. Based on the information discussed in Appendix F, an average accident rate of 2×10^{-6} accidents/mile is considered representative of the general experience of trucks carrying bulk quantities of hazardous materials. If adequate local/state data are available for determination of individual accident rates for divided and undivided roadways, their use is recommended because the resulting rates will more accurately reflect accident probabilities under local conditions.

With respect to the fraction of truck accidents that result in a spill or discharge, the available data suggest a consensus opinion on the order of 0.50 (50%) if all spills including very minor valve and fitting leaks are considered. Omitting these, a spill appears to result from an accident in about 0.15 - 0.20 (15% - 20%) of accidents. A value of 0.20 (20%) is therefore adopted for use for the sake of conservatism.

Based upon available spill size distributions, and considering the likely causes of accidents, the following distribution is suggested for general use:

- 10% cargo loss (thru 1" hole) ***or*** 1000 gal --- 60% of the time
- 30% cargo loss (thru 2" hole) ***or*** 3000 gal --- 20% of the time
- 100% cargo loss (instantly) ***or*** 10,000 gal --- 20% of the time

These values cover the range of significant releases. If desired, a two-point distribution assuming that 3000-gallon spills occur 80% of the time and 10,000-gallon spills occur 20% of the time may be used to simplify consequence analysis procedures.

The suggested accident rates and other factors for truck accidents are summarized in Table 11.4. Worksheet 11.1 presents a simplified format for computing the annual average probabilities of truck accidents resulting in spills of various amounts. A copy of the worksheet should be completed for each hazardous material transported in bulk by truck within or through the community, or (if desired) groups of chemicals or materials posing similar threats in the event of a release may be analyzed together. Local information needed for the task includes:

- Material(s) of concern
- Annual number of shipments
- Total capacity per shipment

TABLE 11.4
SUGGESTED FIGURES FOR TRUCK TRANSPORTATION

Accident Rate:	2×10^{-6} accidents/mile
Conditional Spill Probability	0.2 for significant spills
Spill Size Distribution:	0.60 for 10% loss of cargo through 1" hole, or 1,000 gal
	0.20 for 30% of cargo through 2" hole, or 3,000 gal
	0.20 for 100% of cargo, or 10,000 gal

Note: Worksheet 11.1 demonstrates how these figures can be used to estimate annual accident probabilities and associated spill volumes for truck transportation.

WORKSHEET 11.1

ESTIMATING BULK TRUCK TRANSPORTATION RELEASE FREQUENCIES

Hazardous Material(s): _____

Total Number of Annual Shipments: A = _____
(loaded trucks only)

Length of Route of Concern: B = _____
(miles within jurisdiction)

Total Number of Miles Per Year*: C = A x B = _____

Accident Frequency: D = C x 2 x 10^{-6} = _____(accidents/year)

Spill Frequency: E = D x 0.2 = _____(spills/year)

Spills by Size+

10% loss of cargo (1" hole) ***or*** 1,000 gal: E x 0.6 = _____(spills/year)

30% loss of cargo (2" hole) ***or*** 3,000 gal: E x 0.2 = _____(spills/year)

100% loss of cargo ***or*** 10,000 gal: E x 0.2 = _____(spills/year)

Notes:

*If there are a number of different routes with varying numbers of shipments, multiply the number of shipments by the route length for each route individually and then sum. For example, 100 shipments of 15 miles and 50 shipments of 7 miles would give (100 x 15) + (50 x 7) = 1850 total miles.

+ The user may consider all three scenarios for consequence modelling and planning purposes or just the largest spill.

- Total length of route within community

- Type of roadways travelled (if specific rates by type of highway are available)

Note that it may be necessary in some cases to combine the number of shipments with the length of route within the community to compute total mileage because there may be several routes for the same material. A prime example is for gasoline which may be delivered to several locations within any community or jurisdiction as well as driven through the locality. Worksheet 11.1 provides further information on how this may be accomplished.

Additional Data/Methodologies

Should more precise methodologies be desired or should special circumstances warrant attention, the reader can consider one of the techniques listed below. First efforts should be directed at obtaining more precise data either on a local, county, state or regional basis. The data specific to one carrier should not be broadly applied, however, as there can be major differences between carriers - even when they operate in the same area. This may occur due to differences in truck design and upkeep, characteristics of the cargo, training of the drivers, enforcement of speed restrictions, and other factors.

More detailed methodologies which take into account specific accident situations include:

- Separate models to predict accidents on interstates, rural highways or urban arterials as a function of several input variables (Urbanek and Barber, 1980).

- Analyses of rail/highway grade crossing accidents (National Transportation Safety Board, 1981). Note: There are only 60 or so of these each year, nationwide, on average. They usually involve trucks carrying petroleum products and occur close to distribution/storage terminals, with very localized impacts.

- Breakdowns of rates by rural, urban, suburban and number of lanes (Smith and Wilmot, 1982).

- Risk assessments of transportation through tunnels (Considine, 1986).

- Detailed considerations of the severities of various types of accidents for particular vehicle configurations (Clarke et al, 1976).

Use of Results in Consequence Analysis

Each of the three accident scenarios denoted and evaluated above actually provides the user with two options, the first being assumption of a certain percentage of cargo loss through an orifice of a given size, and the second being assumption of a specific total amount of cargo loss. For example, in the first scenario considered, the user can assume that 10% of the total cargo of the vehicle is discharged through a hole having a diameter of one inch, or alternatively, simply assume that 1000 gallons of presumably liquid cargo are released before the discharge is terminated for one reason or another under average accident conditions. These results are based on *generalized* historical records of past accidents and provide one way in which the ultimate consequences of an incident can be evaluated by use of the analysis procedures discussed in Chapter 12 of this guide. Conversely, depending upon the type of hazardous material involved and the desires of the user, these scenarios can be further refined for consequence analysis purposes, taking better advantage of locally available information.

Where the user wishes to assume a fixed percentage of cargo loss (this requiring knowledge of total cargo amounts) or a fixed amount of spillage for liquid cargos, the spill can be assumed to take place *instantaneously*, thus obviating need for use of discharge rate and duration estimation methods discussed in Chapter 12 and available in the computer program provided with this guide. It is cautioned, however, that the assumption of an instantaneous release in such situations may greatly overestimate resulting hazard zones from evolution of toxic or flammable vapors, fires, or explosions. Spill amounts presented in units of gallons of liquid can be converted to the units of pounds required by the computer program by use of the following expression:

Amount in pounds = 8.34 x Amount in gallons x Liquid specific gravity

Where a hole size is specified and cargo tank or compartment dimensions are known, it is alternatively possible (*and recommended*) to utilize available discharge rate and duration estimation procedures to obtain an ultimately more realistic indication of accident consequences. This is *particularly* advisable when the cargo is a compressed gas, a liquefied compressed gas, or an otherwise highly volatile material. The suggested percentage of cargo loss, when less than 100%, can be ignored, if necessary, in deference to the results obtained from the discharge models. (This is due to the fact that the hazard zone will be primarily determined by the release rate and the first ten or so minutes of the release; the ultimate release quantity is less significant.)

11.4 BULK TRANSPORTATION HAZARDOUS MATERIALS BY RAIL

According to recent statistics, about 80 million tons of hazardous materials are shipped annually by rail in the U.S. (OTA, March 1986). The majority of these shipments are in a single tank permanently mounted on a rail car. Exceptions include multi-tank tank cars (the units are usually ton containers), seamless steel cylinders (as for very high pressure service), and compartmented tank cars in which each compartment is treated as a separate tank. The sizes of these will range from a few hundred gallons in the case of a ton container to 45,000 gallons in so-called jumbo tank cars. Since 1970, however, the capacity of new tank cars has been limited to 34,500 gallons. There is also occasional use of intermodal tanks, as mentioned under truck transportation.

The design, construction, inspection, and use of tank cars are regulated by both the American Association of Railroads (AAR) and the Federal Railroad Administration (FRA) within the U.S. Department of Transportation (USDOT). Carbon steel is used to construct over 90% of the tanks, with aluminum for most but not all of the remainder. Nickel or nickel alloy is found in acid service, and there are a small number of stainless steel cars (Wright and Student, 1985). Safety relief valves (and vents) are required, unless otherwise specified. Cars are usually classified into the categories of pressure tank cars, non-pressure tank cars, cryogenic liquid tank cars, and miscellaneous tank cars. Tanks may be lined, insulated, and possibly fitted with heating coils. Some may have special thermal protection to prevent BLEVEs or other explosions in the event of exposures to pool fires or flame jets. Relatively recent regulations have required shelf couplers - which limit potential for the puncturing adjacent cars in the event of a derailment or collision - for all new and old cars. Cars carrying liquefied flammable gases or ammonia have been required to have head shields to further limit puncture potential, and new housings for bottom outlets have also been adopted.

It has been estimated that 35% of all freight trains carry hazardous materials, but that only 7.5% of railroad accidents involve trains carrying these materials (von Herberg, 1979). This figure corresponds to the percentage of all cars which carry chemicals and allied products or petroleum products versus the total number of cars on an annual basis (AAR, 1985).

A fairly extensive data base on commodity flows is available for railroads. The July 1986 OTA report provides the following breakdown on a tonnage basis:

Flammable liquids	26%
Corrosive materials	25%
Combustible liquids/ nonflammable compressed gases	22% (less than 12% each)
Flammable compressed gases	12%

Poison B	3%
Poison A	0.1%
Radioactive materials	0.03%

Detailed breakdowns by state, railroad company, and other divisions are also available from various sources described in the OTA report.

Data on rail yards shows that the number of hazardous materials cars handled by each ranges from 1-15 percent of the total throughput (Chemical and Engineering News, July 29, 1985). In one study, based on data through 1977, it was found that 36% of derailments and 73% of collisions occurred in such yards (Nayak et al, 1983).

Causes and Examples of Past Accidents

For releases of hazardous materials from rail accidents, there are two types of events of concern. The most important for this analysis is the accident that involves a collision or a derailment, since these typically involve the largest spills or discharges. However, there is a second class of releases which may arise from fitting or seal leaks, relief valve leaks, and other releases associated with improper tightening of closures or defective equipment. Harvey et al (1987) estimate that these account for 70% of the roughly 1000 releases each year. Rail accidents, like those for trucks, can result in virtually no adverse consequences up to very large losses of life, depending on the materials involved and the circumstances of the accident. Many of the more severe accidents occur in yards and on sidings (Wolfe, 1984). As for truck transportation, incidents arising during loading or unloading operations are addressed under fixed facilities.

AAR data (Wolfe, 1984) showed that the materials most often involved in accidents with more than $100,000 of damage in 1981 were:

- LPG
- Acrylonitrile
- Fuel oil
- Vinyl chloride
- Anhydrous ammonia

The same source found that there were less than 30 accidents each year with this level of damage.

Examples of past accidents involving the rail transportation of hazardous materials are given below. These particular incidents include some of the most severe that have occurred in recent times.

- In Waverly, Tennessee the derailment of two propane cars was treated rather casually as crews worked to clear the track and right the cars. As this was being done, some 40 hours after the derailment, propane began leaking from one car, reached a source of ignition, flashed back to the car, and caused an explosion and fireball. The town center looked like a battle scene after the explosion with 16 dead, 54 requiring hospitalization for burns, and 42 requiring outpatient care. (February 24, 1978)

- Over 240,000 people were evacuated for all or part of a week in Mississauga, Canada after a derailment involving 11 propane cars, 1 chlorine car and 10 cars loaded with other chemicals. The wreckage produced a series of explosions, launched missiles more than half a mile, and prompted fears of a massive chlorine release. No fatalities or major injuries occurred partly due to the quick accident response of authorities, a well executed emergency evacuation plan, and various fortuitous circumstances. (November 10, 1979)

- A white cloud of toxic smoke towered a thousand feet over the community of Miamisburg, Ohio and covered an area about a mile wide and 10-15 miles long at one point after a derailment caused a car containing white phosphorus to fail and ignite. The intense heat and difficulties in controlling the fire forced authorities to wait four days for the blaze to burn itself out. Eleven persons were hospitalized after exposure to the toxic smoke, with a total of 273 being treated for skin, eye, and lung irritations. The 40,000 (or more) evacuees were the largest number ever resulting from a train accident in the U.S. (July 8, 1986)

Suggested Approach for Assessment of Accident Potential

Based on the data presented in Appendix F, it is suggested that an accident rate of 3×10^{-6} per train-mile be used for mainline track. To convert this to a per car-mile basis, it is assumed that 0.20 (20%) of the cars will be damaged in an accident (based upon data presented in Nayak, 1979). The overall rate therefore becomes $0.2 \times 3 \times 10^{-6}$/ train-miles or about 6×10^{-7} per car-mile.

The accident rate for rail yards is obtained by taking 1.3×10^{-5} accidents per train-mile and a 20% damage estimate to obtain about 3×10^{-6}/car-mile for the track in yards. Sidings also pose a risk, but these risks are considered herein to be overshadowed by those associated with mainline and yard track.

It is suggested that 0.15 (15%) of accidents be assumed as resulting in a spill for both mainline and yard accidents, as no data are available to permit distinctions between these events.

With respect to the distributions of spill amounts in accidents, the available data suggest use of:

- 3,000 gallons ***or*** 10% of cargo (thru 2" hole) - 50% of the time
- 10,000 gallons ***or*** 30% of cargo (thru 2" hole) - 20% of the time
- 30,000 gallons ***or*** 100% loss of cargo - 30% of the time

The higher weighting of the last category partially accounts for the potential for more than one car to release part of its contents in an accident.

Table 11.5 summarizes the accident rates and other factors suggested for use, while Worksheet 11.2 outlines the procedure for determining the annual average probability of an accident involving spills of various amounts. A copy of the worksheet should be completed for each hazardous material transported in bulk by rail within or through the community. (As for trucks, groups of chemicals posing similar hazards may be considered together.) Local information that will be required to accomplish the effort includes:

- Material(s) of concern
- Annual number of cars
- Total capacity per car
- Total miles of mainline track within community
- Total miles of yard track travelled by a typical car

Railcar trips and associated mileage involving loaded vehicles are of primary concern as these pose the greatest risk. Nevertheless, it is important to realize that the residual materials within tank vehicles considered "empty" can also pose a hazard under certain circumstances. If local data on accident rates or spill frequencies are available, they can be directly substituted for the rates and other factors listed in Table 11.5.

Additional Data/Methodologies

Should a more detailed evaluation be desired or required, readers can consider use one of the techniques listed below. However, any effort to improve the specificity of accident predictions should probably first involve the determination and use of individual state or railroad company accident rates for specific routes.

More detailed evaluations of rail transportation can also include consideration of several different factors (alone or in combination) in the analysis. Examples of these include:

- Detailed review of accident severity to determine the overall likelihood of puncture, crush, impact and fire scenarios (Clarke et al, 1976)

TABLE 11.5
SUGGESTED FIGURES FOR RAIL TRANSPORTATION

Mainline accident:	6×10^{-7}/car-mile
Yard accident rate:	3×10^{-6}/car-mile
Spill size distribution:	0.5 for 10% cargo loss through a 2" hole, or 3,000 gallons
	0.2 for 30% cargo loss through a 2" hole, or 10,000 gallons
	0.3 for complete loss of a cargo load, or about 30,000 gallons on average

Note: Worksheet 11.2 demonstrates how these figures can be used to estimate annual accident probabilities and associated spill probabilities for rail transportation.

WORKSHEET 11.2

ESTIMATING BULK RAIL TRANSPORTATION RELEASE FREQUENCIES

Hazardous Material(s): _____

Number of Cars Per Year: A = _____
(loaded cars only)

Number of Car-Miles in Yards: B = _____
(miles per trip in jurisdiction)

Number of Car-Miles on Mainline: C = _____
(miles per trip in jurisdiction)

Accident Frequency: $D = (A \times B \times 3 \times 10^{-6}) + (A \times C \times 6 \times 10^{-7}) =$ _____(accidents/year)

Spill Frequency: $E = D \times 0.15 =$ _____(spills/year)

Spills by Size*

10% loss of cargo (2" hole) ***or*** 3,000 gal: $E \times 0.5 =$ _____(spills/year)

30% loss of cargo (2" hole) ***or*** 10,000 gal: $E \times 0.2 =$ _____(spills/year)

100% loss of cargo ***or*** 30,000 gal: $E \times 0.3 =$ _____(spills/year)

Notes:

*The user may consider all three scenarios for consequence modelling and planning purposes or just the largest spill.

- Detailed consideration of specific types of accidents and associated leak sizes. (Note: One study in Finland considered 14 types of accidents and four categories of leaks, including valve leaks, broken valves, moderate breaks and punctures, and large breaks.) (Lautkaski et al, 1979)

- Separate consideration of different classes or quality of track (FRA, 1988, gives some the additional information needed for this type of evaluation)

- Separate consideration of mainline, yard, and sidings

Use of Results in Consequence Analysis

Each of the three accident scenarios denoted and evaluated above actually provides the user with two options, the first being assumption of a certain percentage of cargo loss through an orifice of a given size, and the second being assumption of a specific total amount of cargo loss. For example, in the first scenario considered, the user can assume that 10% of the total cargo of the vehicle is discharged through a hole having a diameter of two inches, or alternatively, simply assume that 3000 gallons of presumably liquid cargo are released before the discharge is terminated for one reason or another under average accident conditions. These results are based on *generalized* historical records of past accidents and provide one way in which the ultimate consequences of an incident can be evaluated by use of the analysis procedures discussed in Chapter 12 of this guide. Conversely, depending upon the type of hazardous material involved and the desires of the user, these scenarios can be further refined for consequence analysis purposes, taking better advantage of locally available information.

Where the user wishes to assume a fixed percentage of cargo loss (this requiring knowledge of total cargo amounts) or a fixed amount of spillage for liquid cargos, the spill can be assumed to take place *instantaneously*, thus obviating need for use of discharge rate and duration estimation methods discussed in Chapter 12 and available in the computer program provided with this guide. It is cautioned, however, that the assumption of an instantaneous release in such situations may greatly overestimate resulting hazard zones from evolution of toxic or flammable vapors, fires, or explosions. Spill amounts presented in units of gallons of liquid can be converted to the units of pounds required by the computer program by use of the following expression:

Amount in pounds = 8.34 x Amount in gallons x Liquid specific gravity

Where a hole size is specified and cargo tank or compartment dimensions are known, it is alternatively possible (*and recommended*) to utilize available discharge rate and duration estimation procedures to obtain an ultimately more realistic indication of accident consequences. This is *particularly* advisable when the cargo is a compressed gas, a liquefied

compressed gas, or an otherwise highly volatile material. The suggested percentage of cargo loss, when less than 100%, can be ignored, if necessary, in deference to the results obtained from the discharge models.

11.5 BULK TRANSPORTATION OF HAZARDOUS MATERIALS BY MARINE VESSELS

A large portion (about 550 million tons in 1982 according to the OTA) of the hazardous materials shipped annually in the United States is transported by barge or other marine vessel on coastal and inland waterways. Extensive regulations cover safety procedures, cargo documentation, vessel construction and certification, hazardous material transfers, and the handling of explosives or dangerous cargos within or near waterfront facilities. Individual shipments can be vastly larger than those conveyed by rail or truck due to the size differences among these conveyences.

The primary types of marine vessels used for bulk transportation of hazardous goods are bulk liquefied gas carriers, chemical tankers, oil tankers and tank barges, but bulk cargos may also be found in smaller tanks placed on the decks of vessels or in standard intermodal cargo containers. Some barges are self-propelled but most are designed to be pushed by a tugboat singly or in arrays called "tows". Marine transportation generally involves volumes of 300-600 thousand gallons in barges, though some such vessels are of far larger capacity. Tank ships can have capacities that are ten times or more greater (OTA, July 1986).

Commodity flow data are compiled fairly rigorously for marine transportation. Crude petroleum, petroleum products, and chemicals and liquefied gases constitute a large fraction of all shipments in and out of most major ports. Petroleum products include alcohols, crude oil, refined fuels, solvents and residuals. Typical chemicals include sulfuric acid, benzene, toluene, sodium hydroxide, inorganic speciality products, and fertilizers. The most frequently transported liquefied gases are propane and butane, but anhydrous ammonia, chlorine, propylene, butylene and butadiene are also frequently transported by water, as are many other bulk commodities.

Causes and Examples of Past Accidents

Marine transportation is generally at slow speeds and involves many precautions and traffic controls. Hence, it has the lowest accident rate per ton-mile and the lowest number of accidents. However, the large energies involved when these massive vessels strike each other or other objects can result in severe consequences at times in terms of cargo loss. As with other modes of transport, small releases can result from problems with gaskets, flanges, valves or even the tanks themselves. The separation from population limits the consequences of small releases, however.

A few examples of accidents involving marine transportation of hazardous materials include:

- A total of 23,000 gallons of leaded and unleaded gasoline spilled into the southern approach to Cape Cod Canal when a barge ran aground. The Army Corps of Engineers and the Coast Guard responded with divers and marine safety personnel to assess the damage after the tugboat called for assistance. The Coast Guard expected the sea current to dissipate the spill. Environmental damage was said to be minimal. There were no deaths or injuries. (August 18, 1986)

- A collision in the Houston Ship Channel between a tug and barges and a grain ship resulted in an explosion and fire involving one 33,000 gallon tank of butadiene. Two burning barges were towed to sea where they burned for five days. (August 7, 1980)

- A 565-foot long tanker carrying two million gallons of gasoline rammed an unlighted oil drilling rig in the Gulf of Mexico. The tanker caught fire and had to be abandoned. (August 21, 1980).

- A barge carrying 400,000 gallons of acrylonitrile struck the Galveston Causeway railroad bridge and ignited. Resultant explosion caused one end of the barge to sink and release an unknown amount of chemical into the water. (January 3, 1982)

- Up to 40,000 pounds of hydrobromic acid spilled into the Mississippi waterway after a collision between two ships. Violent reactions between the acid and water required evacuation of 3000 people on the adjacent shore. (July 22, 1980)

Suggested Approach for Assessment of Accident Potential

Based upon the information and data presented in Appendix F, and given the understanding that harbors and inland waterbodies are of greater concern than shipping activities on the open ocean and/or otherwise distant from coastlines (in terms of the distances typically associated with spill effects that may pose a threat to human life and health), accident rates and other spill characterization factors are presented below for:

- Collisions in lakes, rivers, and intercoastal waterways
- Groundings in lakes, rivers, and intercoastal waterways
- Collisions and groundings in harbors and bays
- Collisions/casualties while vessels are moored/docked

An accident rate of 10^{-5}/mile of travel is suggested for use for collisions in the first category to cover both the lower expected accident rates on certain slow speed waterways and the higher ones for congested, highly utilized routes. Based on Gulf Intercoastal Waterway (ICWW) statistics, a grounding casualty rate of 5×10^{-6}/ mile is suggested for the serious type of grounding which could lead to a release. Note that this is also a "per mile" rate. The harbor/bay area grounding and collision rate given below is "per transit", while the moored collision rate is "per port call." (There are two transits per port call.) The suggested rate for groundings and collisions in a harbor area is 10^{-3}/transit, while the suggested casualty rate for moored or docked vessels is 2×10^{-4} per port call.

If no distinction is being made with regard to vessel type and construction, it should be assumed that 0.15 (15%) of accidents result in actual loss of cargo to the environment. Alternatively, it can be assumed that accidents involving single-hulled vessels result in cargo loss 0.25 (25%) of the time and that accidents involving double-hulled and bottomed watercraft result in cargo loss 0.05 (5%) of the time.

The recommended distribution of spill amounts is:

- 10% loss of cargo in one tank/compartment -- 35% of the time
- 30% loss of cargo in one tank/compartment -- 35% of the time
- Full loss of cargo in one tank/compartment -- 30% of the time

This distribution is weighted toward more severe events than the spill distributions presented earlier, because the earlier distributions are heavily influenced by minor fitting leaks.

Table 11.6 summarizes the accident rates and other factors suggested for use, while Worksheet 11.3 outlines the procedure for determining the annual average probability of an accident involving spills of various amounts. A copy of the worksheet should be completed for each hazardous material or group of similar materials transported in bulk by waterborne vessels through the community or other jurisdiction of concern. Local information that will be required to accomplish the effort includes:

- Material(s) of concern
- Maximum tank capacity of vessels carrying this material
- Total number of lake, river, or intercoastal waterway miles in the area,
- Total ships traveling this route in a year,
- Total cargo barges/tankers entering and exiting the bay area or harbor,
- Total barge/tanker port calls,

TABLE 11.6
SUGGESTED FIGURES FOR MARINE TRANSPORTATION

Accident Rates:	10^{-5}/mile for collision on lakes, rivers and inter-coastal waterways
	5×10^{-6}/mile for groundings on same
	10^{-3}/transit for collisions and groundings in harbors/bays
	2×10^{-4}/port call for collisions/casualties while moored
Conditional Spill Probabilities:	0.15 if using one rate regardless of vessel
	0.05 for double-hulled/double-bottomed vessels
	0.25 for single-hulled vessels
Spill Size Distribution:	0.35 for 10% loss of one tank or compartment
	0.35 for 30% loss of one tank or compartment
	0.30 for 100% loss of one tank or compartment

Note: Worksheet 11.3 demonstrates how these figures can be used to estimate annual accident probabilities and associated spill probabilities for marine transportation.

WORKSHEET 11.3

ESTIMATING BULK MARINE TRANSPORTATION RELEASE FREQUENCIES

Hazardous Material(s): _____

Length of Lake, River, ICWW Route*: A = _____ (miles within jurisdiction)

Annual Number of Trips on Route*: B = _____ (loaded trips only)

Annual Number of Transits of Harbor/Bay*: C = _____ (loaded transits only)

Annual Number of Dockings*: D = _____ (loaded dockings only)

Accident Frequency: $E = (A \times B \times 1.5 \times 10^{-5}) + (C \times 10^{-3}) + (D \times 2 \times 10^{-4}) =$ _____ (accidents/year)

Spill Frequency+:

F = E x 0.15 = _____ (spills/year)
(all vessels)

OR

F = E x 0.25 = _____ (spills/year)
(single hull)

F = E x 0.05 = _____ (spills/year)
(double hull)

Spills by Size°

10% loss of one tank or compartment: F x 0.35 = _____ (spills/year)

30% loss of one tank or compartment: F x 0.35 = _____ (spills/year)

100% loss of one tank or compartment: F x 0.3 = _____ (spills/year)

Notes:

*If applicable
+If it is known how many vessels are single-hulled and how many are double hulled, this worksheet can be completed twice; the first time for single-hulled vessels and the second for double-hulled.
° The user may consider all three scenarios for consequence modelling and planning purposes or just the largest spill.

- Total river miles in the area,
- Number of barges/tankers traveling the river route in a year.

When totaling barge/tanker port calls or harbor transits, remember to count only those involving actual carriage of hazardous materials. Empty vessels may pose some risk of fire or explosion, but are not as important as loaded vessels. Also, note that all of the data listed above may not be needed for every location. For example, a community located on a river and not having a harbor or bay area only needs the total river miles and number of ships traveling the river. In this case, only moving collisions and river groundings would be of interest.

Nonimpact casualties, such as fire/explosions, hull and machinery damage or breakdowns, and structural failture have a very low likelihood of occurrence. It is not considered necessary to include them in the analysis.

Additional Data/Methodologies

A more detailed and accurate analysis may be performed if one chooses to derive the appropriate casualty rates and conditional probabilities for a specific harbor or water route using local data. An accident rate may be derived by combining a measure of vessel movements with the number of past accidents reported for the type of movement being looked at. The movement measure may consist of: 1) the total waterbody, river, or waterway miles traveled; 2) the total port calls made; or 3) the total harbor transits. Counts should be made only for loaded hazardous material tankers and barges. The number of accidents is then divided by the total number of transits or miles, as appropriate, for a similar period of time to determine the accident rate.

Conditional spill probabilities and spill distributions are derived in a similar fashion. The probability of a spill is obtained by dividing the number of spill accidents by the total number of accidents that occurred for a specific type of movement. A spill amount distribution from local or national data can then be applied to determine the percentage of the spills expected in various size ranges.

Several other means exist for estimating the probability of marine casualties and spills but they are generally highly technical, time-consuming, and occasionally quite expensive. The reader is directed to the reference list at the end of the chapter for further information.

Use of Results in Consequence Analysis

Due to the special nature of the discharges from marine vessels, and difficulties in estimating discharge rates and durations when there is water outside the cargo tank rather than air, it is recommended (in the absence of more specific information or assumptions) that all discharges be assumed to take place *instantaneously* for emergency planning purposes. Spill amounts available in units of gallons of liquid can be converted to units of pounds by use of the following expression:

Amount in pounds = 8.34 x Amount in gallons x Liquid specific gravity

11.6 TRANSPORTATION OF HAZARDOUS MATERIALS BY PIPELINE

Pipelines in the United States primarily carry petroleum liquids, such as crude oil, gasoline and natural gas liquids, and energy gases which include natural gas and liquefied petroleum gas (LPG). To a much smaller extent, pipelines also transport ethane, ethylene, liquefied natural gas (LNG), anhydrous ammonia, carbon monoxide, sour (hydrogen sulfide containing) gas, and many other chemicals. The majority of these pipelines are between a limited number of suppliers and users, as opposed to natural gas transmission lines. Low pressure gas distribution lines found within many cities and towns are not the focus of this section.

Pipelines are generally constructed out of steel, although some cast iron is still in use and plastic, nickel alloys, stainless steel, carbon steel and other materials are also used. Diameters also vary tremendously, from 2 to 4 inches to 36 inches and over. The more hazardous materials tend to be conveyed in lines at the smaller end of the size range. Pressures also span a wide range, and can be several thousands of pounds per square inch or more in the highest pressure lines encountered.

In order to reduce failures caused by corrosion, pipelines are frequently coated and/or cathodically protected. Lines may also be insulated, heated, double-piped for additional protection and control, and protected with leak detection and shutdown systems.

Causes and Examples of Past Accidents

Pipeline failures may be a result of:

- Internal corrosion -- especially on two-phase flow lines and those in sour service
- External corrosion -- from defects in protective systems, in cased crossings beneath roads and railway lines

- External impact -- due to farm or construction machinery
- Structural failures or mechanical defects -- as a result of defective seams or welds
- Natural hazards -- from seismic events, subsidence, etc.

Operating errors and construction defects are also potential causes of pipeline incidents. Leaks may also occur at valves and pump stations.

While there are over a thousand leaks reported each year, many of these are very small and have minor or no consequences to the public. For instance, 1984 data show the following number of incidents and deaths resulting from pipeline failures (Transportation Systems Center, 1985):

	No. of failures	No. of deaths
Gas pipelines	967	35
Liquid pipelines	188	0

These rates are not particularly consistent from year to year. In 1983, there were 1575 gas pipeline failures, but only 12 deaths resulted. There were also 6 deaths from liquid pipeline failures.

The following three examples illustrate typical accidents involving pipeline transport of propane and natural gas. No injuries occurred in these accidents because of their remote locations.

- In Port Hudson, Missouri, propane escaped from a pipeline, flowed into a sparsely inhabited valley, ignited, and exploded with a blast equivalent to 50 tons of TNT. No fatalities or injuries occurred because the area was so sparsely inhabited. (September 12, 1977)
- In Prattville, Alabama, a natural gas pipeline exploded into two fireballs, and shot flames 600 feet high. Two houses were scorched; 200 people were evacuated, but no one was hurt. (July 12, 1986)
- A natural gas pipeline explosion ignited a 200-ft flame jet and left a huge crater: 60 ft across and 20 ft deep. No one was injured but an unmanned metering station at the accident site was destroyed. (November 2, 1985)

Another typical pipeline accident did not have so fortunate an outcome as the above three.

- In Jackson, Louisiana, a natural gas pipeline explosion resulted in 50-foot high flames. The blaze was battled by firefighters for several hours. The five dead and twenty injured were gas company employees repairing the pipeline. (November 26, 1984)

Suggested Approach for Assessment of Accident Potential

Based on the information presented in Appendix F, an accident rate of 1.5×10^{-3}/mi-yr is suggested for lines of unknown size or lines less than 20" in diameter. For pipelines with diameters greater than or equal to 20", a rate of 5×10^{-4}/mi-yr is proposed.

The following spill size distribution, incorporating the limited data available , is suggested for analyzing pipeline releases of hazardous materials:

- For liquid pipelines: discharge computed using consequence analysis procedures of Chapter 12 assuming a complete line break along the route of the pipeline - - - 20% of the time

- For gas pipelines: discharge computed using consequence analysis procedures of Chapter 12 assuming complete line break along the route of the pipeline - - - 20% of the time

- For either gas or liquid pipelines: 1 hour release through 1" hole - - - 80% of the time

Table 11.7 summarizes these rates, and Worksheet 11.4 demonstrates the procedures for their use.

The application of this material requires local information on:

- Material of concern
- Length of pipeline within jurisdiction
- Pipeline diameter
- Flow rate (capacity) of pipeline
- Presence (or not) of a leak detection and emergency shutdown system

Should a pipeline be a very short segment between two facilities, it is possible to include it with one of the facilities, rather than analyzing it separately.

TABLE 11.7
SUGGESTED FIGURES FOR PIPELINE TRANSPORTATION

Accident Rates:	1.5×10^{-3}/mi-yr with diameters less than 20" of if diameter is not known
	5.0×10^{-4}/mi-yr lines with diameters greater than or equal to 20"
Spill Size Distribution:	0.20 for 15 min. (or 1 hour if no emergency shutdown) at the capacity flow rate through an orifice equal to the pipe size
	0.80 for 1 hour release through 1" hole

Note: Worksheet 11.4 provides guidance on how to utilize these rates and probabilities for estimating releases of hazardous materials from pipelines.

WORKSHEET 11.4

ESTIMATING PIPELINE RELEASE FREQUENCIES

Hazardous Material(s): _____

Length of Pipeline of Unspecified Diameter: A = _____ (miles in jurisdiction)

Length of Pipeline < 20" in Diameter: B = _____ (miles in jurisdiction)

Length of Pipeline ≥ 20" in Diameter: C = _____ (miles in jurisdiction)

Spill Frequency: $D = (A \times 1.5 \times 10^{-3}) + (B \times 1.5 \times 10^{-3}) + (C \times 5 \times 10^{-4}) =$ _____(spills/year)

Spills by Size*

1 hour release through 1" hole: D x 0.8 = _____(spills/year)

Complete line break calculated according to procedures given in Chapter 12: D x 0.2 = _____(spills/year)

Note:

*The user may consider both scenarios for consequence modelling and planning purposes or just the scenario posing the greatest threat to public safety. If several pipelines have been grouped by diameter, the line posing the greatest threat should not automatically be assumed to be the line with the largest diameter within any group. Rather, the various pipelines should be individually evaluated using the consequence analysis procedures described in Chapter 12 to determine the actual worst case scenario, if this is desired.

Additional Data/Methodologies

The main alternative to the approach given above is the specific consideration of pipeline design and the operating environment to more precisely determine the failure rate associated with each potential cause of failure (Technica, 1983).

Use of Results in Consequence Analysis

For pipelines conveying compressed (but *not* liquefied gas), the consequence analysis procedures described in Chapter 12 and incorporated into its associated computer program are fully capable of estimating the rate and duration of gas release from either full line breaks or smaller leaks.

Due to the complexity of the problem, the computer program's liquid pipeline discharge model is only capable of addressing full line breaks. It will be necessary to consult with the pipeline owner or operator for assistance in estimating discharge rates and durations for outflows from one inch diameter holes if these scenarios are considered worthy of analysis.

11.7 HANDLING AND TRANSFER OF HAZARDOUS MATERIALS AT FIXED FACILITIES

A broad range of facilities may pose potential risks associated with the release of hazardous materials. These can include: large refineries, chemical plants, and storage terminals; more moderately sized industrial users, warehouses, and isolated storage tanks for water treatment; small quantity users/storage as may be found in high school and college laboratories, florists, greenhouses, hardware and automotive stores, paint stores, etc.

As a result of this broad spectrum of potential spill sources, virtually no accurate data exists to determine the magnitude of this problem. Marine terminals and loading/unloading activities for rail cars and trucks are somewhat more widely reported and are considered within this overall category.

FEMA has a database that identifies the number of chemical and petroleum facilities by county. These facilities are broken down into chemical and allied products, petroleum and coal products, and rubber and miscellaneous plastic products. No accident information is maintained, however. As of 1981, there were 16,000 chemical process industry plants with 20 or more employees and 6,000 plants with 100 or more employees. Los Angeles and Cook (Illinois) counties each have over 200 plants. The number of counties with between 11 and 50 plants is 160; all the rest have ten or fewer plants. About 50% of all the counties in the U.S. have no chemical process industry plants (Cheok et al, 1985). (This is not to say that

there are no facilities handling hazardous materials in these counties.) McGraw Hill has published a map of the plant locations and a booklet entitled "Census of the Chemical Process Industries."

Causes and Examples of Past Accidents

Releases from fixed facilities may arise from: storage tank or container ruptures or leaks, piping ruptures or leaks, releases through safety and relief valves, fire-induced releases, other equipment failures, malicious or deliberate actions, overfills and overflows of storage tanks, human errors, open valves, failed loading hoses, or improper hose connections. These may generally be grouped into three categories for large facilities:

- Transfer, loading and unloading activities
- Processing activities
- Storage tanks and their spill control systems

Smaller facilities may not have any processing activities.

Transfer areas include pipelines, pumps, valves, and control instrumentation needed to achieve the movement of material within a facility. The loading/unloading area involves the most handling operations and the largest potential for human error in most facilities. This is where the raw materials are brought in and products and by-products are removed, and temporary connections are frequently used. The storage area may be for raw materials, intermediates, products, or by-products. The greatest volumes are contained here, so spill sizes can be quite large. The processing area has equipment for raw material conversion into products. This is the area that will only be found in a plant, while handling and storage activities may take place at warehouses, water treatment facilities, greenhouses, and numerous other types of miscellaneous facilities.

Examples of a broad spectrum of accidents are given below. These cover events which start with a release of hazardous materials, as well as those where a fire propagates into a hazardous materials release.

- A natural gas pipeline rupture at a Texas refinery caused a series of explosions and fires. Two hundred firefighters worked nearly six hours to control the blaze fed by three other propane pipelines. Two refinery workers were killed; a town of 1,200 people was evacuated. Damage to the complex was predicted "into the millions." At least three similar explosions had occurred in the area in the prior five years.

- Lightning struck a power pole in a chemical plant, then jumped to a tank of dilute hydrochloric acid, damaging a tank valve. A cloud of gas floated across several nearby neighborhoods. Hundreds of residents were forced to evacuate their homes; three plant workers were injured. (August 1, 1980)

- A refrigeration line at an ice cream plant in Burbank, California ruptured spilling 300 gallons of anhydrous ammonia. Firefighters sprayed water to control the fumes until the main valve could be shut off and the leak stopped. Eleven people were hospitalized and 60 residents were forced to leave the surrounding area. (November 13, 1984)

- In Covington, Kentucky a chlorine gas cylinder ruptured at a swimming pool jammed with about 300 swimmers. More than 140 people were hospitalized; no serious injuries were reported. (June 21, 1981)

- At least 11 people were injured and 100 persons evacuated from a one-square mile area East Los Angeles after 100 gallons of chlorine overflowed from a storage tank. (March 1, 1982)

- A 25,000 ton storage tank in Portland, Oregon, discharged 3-5 tons of anhydrous ammonia due to a valve malfunction. An area three miles downwind was evacuated while response personnel used water fog to knock down vapors and had the spill vacuumed. (February 5, 1982)

- Falling equipment sheared off a pipe leading to a tank of hydrofluoric acid. There were 66 serious injuries and roughly 3000 people were evacuated around the Texas City oil refinery. Water fog was used to help control the vapor cloud and the tank contents were transferred to adjacent rail cars. (October 31, 1987)

- More than 16,000 south Chicago residents were evacuated from the vicinity of a bulk storage and terminal when a silicon tetrachloride storage tank sprang a leak. The escaping liquid, on the order of 150,000 gallons, reacted with the moisture in the air to form hydrogen chloride, resulting in a dense, corrosive, choking plume that stretched 5-10 miles downwind at times. It required 8 days for authorities to stop the leak, neutralize the spillage, and transfer remaining tank contents to other containers. Approximately 100 people were hospitalized during the incident. (April 26, 1974)

- A truck driver delivering sodium hydrosulfide to a Chicago leather company was directed to the wrong valve and began unloading the sodium hydrosulfide cargo into a tank of chromic acid. The reaction of the two chemicals released a deadly gas, hydrogen sulfide. Over 170 persons working inside the four-story tannery were overcome by the gas; a total of eight died and twenty-nine were injured. (February 14, 1978)

There is one last type of accident that merits special attention for fixed facilities, whether they be small or large. This is the potential for external events to cause releases, with earthquakes being of particular concern. Any natural disaster can cause releases as well as affect responses. For instance, transportation and access to the facility may be restricted, water lines for fire protection may be broken, and resources may not be adequate to cover all situations simultaneously. Within any one site, an earthquake may impair the integrity of containment (e.g., dikes) and/or may cause multiple containers/tanks to fail, thereby exceeding the capacity of dikes, curbs, or other types of containment. Jurisdictions particularly prone to such natural events as major earthquakes and floods should consider a more formal analysis of facility risks, taking into account the presence or lack thereof of appropriate protective measures for these threats.

Suggested Approach for Assessment of Accident Potential

Based upon the information presented in Appendix F, the approach suggested for getting a handle on fixed facility accident scenarios is to consider three basic types of release events for plants; one or two release scenarios for facilities such as water treatment plants, laboratories and industrial facilities; and one release scenario for warehouses and other facilities storing hazardous materials. It has been shown that very little specific historical information exists upon which to base accident rates. Hence, the best general approach is to look at equipment failure rates. The increasing use of physical barriers to limit spills, drainage systems to channel spills, and venting and scrubbing systems to control releases all help to render this simplified accident estimation procedure more meaningful.

For example, a large facility may be coarsely modelled as having storage operations, loading/unloading operations, and processing operations. These can respectively be represented by storage tank failures and leaks, hose failures, and piping and process vessel failures. The rates suggested for each of these are:

Storage tank - double walled	10^{-6}/tank-year
Storage tank - single walled	10^{-4}/tank-year
Pressure vessels	10^{-4}/vessel-year
Inplant piping	1.5×10^{-6}/ft-year

Loading hoses	10^{-4}/operation or 10^{-2}/hose-year

While these certainly do not cover all potential release scenarios, they do capture some of the more likely ways to lose large volumes of material. The only piping of prime concern is that of relatively large diameter and long segments. In other words, a 100-foot expanse of 8" pipe should be counted during assessment of failure potential if it contains hazardous materials, but not 10 or 20 foot sections between vessels. As shown in Table 11.8, the spill size is generally taken to be a function of the specific release scenario.

For the middle category of industrial users, water treatment plants, laboratories, etc., the main focus should be on storage tank or container failures. Piping failures or loading hose failures may be considered if there is a significant amount of piping (say over 100 feet) or if there are frequent loading/unloading operations (say 10 or more per year). The rates to be used are the same as those listed above and summarized in Table 11.8.

Storage of hazardous materials, such as in warehouses or greenhouses, may also result in failures of storage containers, but the greater threat here is probably from a fire which spreads to the storage area and results in release, ignition, explosion, and/or combustion of stored materials (with attendant evolution of potentially toxic smoke). The occurrence rate of such fires is suggested to be 10^{-3}/yr resulting in a release of 10% to 100% of the stored volume of hazardous materials -- as summarized in Table 11.8. This is one area in which more specific local data and information would be particularly helpful for better definition of scenarios and estimation of their likelihood. Worksheet 11.5 summarizes the overall recommended procedure recommended for analysis of fixed facilities.

The data required for an analysis that generally focuses on the larger and/or more likely (yet significant) events at fixed facilities are:

- Material(s) of concern
- Number, dimensions, capacities, and contents of storage containers or tanks
- Number, dimensions, capacities, and contents of other vessels with large inventories of hazardous material (such as columns, separators, reaction vessels)
- Size, length, and operating conditions of piping systems
- Number of unloading and loading operations per year, materials involved, and transfer flowrates

TABLE 11.8
SUGGESTED FIGURES FOR FIXED FACILITIES

ITEM	ACCIDENT RATE	SPILL SIZE
Chemical Plants		
Double-walled storage tank	1.0×10^{-6}/tank-year	100% of time -- total amount of typical contents released instantaneously
Single-walled storage tank or pressure vessel	1.0×10^{-4}/tank-year	90% of time -- release of contents through 1" hole until leak can be plugged or otherwise terminated
		10% of time -- total contents released instantaneously
Piping	1.5×10^{-6}/foot-year	90% of time -- release through 1" hole in wall of pipe until leak can be plugged or otherwise terminated
		10% of time -- complete rupture of pipe
Loading hose	10^{-4}/loading or unloading or 10^{-2}/hose-year	100% of time -- release through full hose diamete at loading/unloading rate until flow can be terminated
Industrial Users, Laboratories, Water Treatment Plants		
Storage tank/container	1.0×10^{-4}/tank-year	90% of time -- as above for single-walled storage tank or vessel
		10% of time -- as above for single-walled storage tank or vessel
Piping (if more than 100 ft)	1.5×10^{-6}/foot-year	90% of time -- release through 1" hole in wall of pipe until leak can be plugged or otherwise terminated
		10% of time -- complete rupture of pipe
Loading hose (if used more than 10 times/yr)	10^{-4}/operation or 10^{-2}/hose-year	100% of time -- release through full hose diamete at loading/unloading rate until flow can be terminated
Warehouses and Other Storage Facilities		
Storage containers (drums, cylinders, etc.)	10^{-3}/year	90% of time -- release of 10% of total stored volume
		10% of time -- 100% loss of total stored volume (i.e., all containers combined)

WORKSHEET 11.5
ESTIMATING FIXED FACILITY RELEASE FREQUENCIES

Hazardous Material(s): _____

Number of Process Vessels/Single-Wall Storage Tanks: A = _____

Number of Double-Walled Storage Tanks: B = _____

Length of Pipe: C = _____ (feet)

Annual Number of Loadings/Unloadings: D1 = _____

(or number of hoses) D2 = _____

Spill Frequencies*

Process Vessels/Storage Tanks: $E = A \times 10^{-4}$ = _____ (spills/year)

Double-Walled Storage Tanks: $F = B \times 10^{-6}$ = _____ (spills/year)

Piping: $G = C \times 1.5 \times 10^{-6}$ = _____ (spills/year)

Loading/Unloading Hoses: $H = D1 \times 10^{-4}$ = _____ (spills/year)
OR
$H = D2 \times 10^{-2}$ = _____ (spills/year)

Spills by Size*+

Process Vessels/Storage Tanks
10% of contents (1" hole): E x 0.9 = _____ (spills/year)

100% of contents: (E x 0.1) + F = _____ (spills/year)

Piping
release through 1" hole: G x 0.9 = _____ (spills/year)

release through full pipe diameter for time needed for shutdown or until associated tank is emptied: G x 0.1 = _____ (spills/year)

Loading/Unloading Hoses
release through full hose diameter at transfer rate for time needed for shutdown: H = _____ (spills/year)

Notes:

*Assumes that the consequences of releases will be based on the tanks, piping and loading hoses which give the worst consequences. If desired, individual components or smaller groupings may be evaluated by completing the worksheet separately for each grouping.

+The user may consider all these scenarios for consequence modelling and planning purposes, or just the largest spill in each category.

The more of this data available, the better. A first cut analysis could start with just the storage tanks/containers and any other large vessels, adding loading activities and piping only if the more information is desired or needed. Tanks of similar size and contents may be grouped together for probability analysis purposes, as may pipelines.

Additional Data/Methodologies

In addition to the multi-tiered approach discussed above, there are a number of more detailed analysis procedures that are appropriate for fixed facilities. These generally require more complete risk assessments which can be time consuming and expensive, and which mandate the complete cooperation of plant/facility management in order to obtain accurate and complete results. Numerous data sources discuss the merits and requirements of such analyses. Some starting points might include CONCAWE: 1982, Atherton et al: 1980, Simmons: 1974, COVO: 1982, and literally dozens of other reports and hundreds of articles.

Use of Results in Consequence Analysis

The choice of consequence procedures to be utilized for any given potential source of hazardous material discharge or spillage depends on the type of container or tank involved and the nature of the particular hazardous material contained therein. Although Chapter 12 of this guide and its related computer program provide a wide variety of analysis tools to assist users in evaluating individual accident scenarios, the large number of diverse situations that may be encountered at many fixed facilities does not permit the provision of detailed guidance for each and every case. Rather, emergency planning personnel need to apply the following guidelines with some degree of flexibility and common sense.

The first objective of a consequence analysis for a fixed facility should be evaluation of threats posed by storage tanks or process vessels that contain significant amounts of hazardous materials. Releases from short lengths (10-20 feet) of piping attached to these containers are included in the vessel failure rates. Each container of this type should be evaluated individually. If a length of piping between containers can result in simultaneous discharges from more than one container, this fact should be considered in the analysis. To the extent possible, the analysis should utilize available information on the operating conditions of each vessel in terms of typical and maximum amount of contents, operating temperature, pressure, and so forth. Any container of a substance with the potential for runaway polymerization, decomposition, or other unusual reactivity hazard should be given special consideration and attention. (However, the frequency of such events cannot be estimated using general historical data.)

Most intraplant or facility piping systems will be attached to one or more storage or process vessels and should consider the amount of contents of such vessels. In addition, larger lines of significant diameter and length may require analysis via use of pipeline discharge models to the extent that is feasible, or alternatively, the use of tank discharge models. Although the procedures of Chapter 12 permit evaluation of full line breaks and leaks from small holes in compressed gas pipelines, only full line breaks can be considered for liquid pipelines. Consequently, assistance will be required from facility owners or operators for analysis of smaller liquid leaks if this lower consequence but higher probability scenario is to be addressed. If shutdown capability is not known, a reasonable release duration may be assumed to be 15 minutes.

Loading hose failures commonly involve transfers to and from transportation vehicles. It will be necessary in many (but not all) such cases to assume a discharge rate equivalent to the cargo transfer rate through the hose, though the actual rate of discharge may be somewhat higher (especially initially). The potential duration of discharge should be determined by investigation of the presence of emergency shutdown systems, available response forces, and the likely time needed for them to terminate the release by various means at their disposal. In no case, however, should the total amount of discharge exceed the total contents of the storage tank and the transportation vehicle. While evaluating such situations, pay special attention to situations in which manually activated emergency shutdown systems may be present but not approachable due to the hazardous properties of the material being released. Obviously, a truck driver may be reluctant or unable to approach a vehicle to pull an emergency shutoff valve lever if his vehicle is venting large amounts of a highly toxic, flammable, and/or explosive gas or liquid. In the absence of such information, a recommended release duration is 5 minutes.

Evaluation of consequences from small containers or cylinders stored in warehouses, laboratories, and a wide variety of other commercial or public facilities will require consideration on a case by case basis where greater specificity is desired than that given in Table 11.8 and Worksheet 11.5, giving due consideration to the nature of potential accidents and their likely outcome. Gas cylinder leaks can generally be evaluated in a direct and straightforward manner using the procedures of Chapter 12 and its related computer program. Note, however, that one of the most common major problems in this general type of facility is not leakage from one or more containers but a fire in the facility that involves the hazardous materials stored therein and produces large quantities of toxic smoke that may adversely impact downwind areas. Given the diversity of substances that may be involved, there is no simple manner in which the downwind area possibly requiring evacuation or other protective action can be precisely estimated in such events. Rather the general emergency plan must be sufficiently flexible to permit on scene decisions during an actual emergency and the rapid initiation of evacuation or protective action activities.

11.8 TRANSPORTATION OF PACKAGED HAZARDOUS MATERIALS

It has been estimated that there are up to 700,000 vehicles and vessels used to carry hazardous materials in small packages in the United States (OTA, March 1986). Such packages may be cylinders, drums, barrels, cans, boxes, casks, bottles, or other similar containers, and are defined as having a capacity of less than 110 gallons or 1000 pounds. They may be transported by air, water, rail (usually in box cars), truck or van. Non-bulk transportation of hazardous goods is estimated to represent 50% of the total tons shipped by truck and 80% of the total truck spills (OTA, July 1986). Up to 8% of the marine transportation of hazardous materials involves dry cargo barges carrying portable tanks or drums.

Commodity flow information for such shipments is very limited due to the large number and variety of shipments that take place and a lack of reporting requirements. Thus, there is also a lack of accident rates or spill amount distributions which can be applied on a general basis. But the small amounts of materials involved usually (not always) imply limited consequences in the event of a release.

Causes and Examples of Past Accidents

The causes of releases from small packages include:

- Improperly tightened or faulty fittings, valves, and closures
- Dropping packages (while loading/unloading or in transit)
- Puncturing packages (again while handling or in transit)
- Improper blocking and bracing which allows packages to move, fall or fail from impact or crushing while in a vehicle
- Fires
- Freezing, getting wet, or other severe environmental exposure

Examples of some incidents involving small packages are given below. These particular examples cover transportion as well as loading and unloading incidents.

- Ten employees were treated and released when a container of arsenic trichloride was found ruptured as a truck was being unloaded. (July 19, 1985)

- A drum loaded with pesticide began leaking its contents as it was being transported on a flatbed truck near Cologne, Germany. The small spill formed a large gas cloud which was toxic and corrosive. Traffic had to be halted for a considerable time to allow clean-up crews to neutralize the situation. (May 15, 1985)

- A container loaded with drums of phosphorous was being lifted by crane from a barge to the dock when it ignited after an adjacent obstruction punctured a drum through the container walls. The crane driver submerged the entire container in the water away from the barge. The phosphorous reignited when the container was placed on the dock; by then the fire department had arrived and extinguished the fire with dry powder. No deaths or injuries resulted. (May 15, 1986)

- In a Houston port, a freight container explosion from improperly packaged aluminum phosphide killed a dock worker. When inspectors from the Marine Safety Office opened the container, boxes of high explosives were found, even though the aluminum phosphide had warning labels marked, "Do not store with high explosives." (January 20, 1986)

- Amid heavy tourist traffic, a truck driver noticed that water was leaking from his cargo, drums containing nuclear reactor sludge. Further inspection at a busy truck stop showed that the hole in the drum had been patched with electrician's tape. (November 14, 1979)

Suggested Approach for Assessment of Accident Potential

The available accident data covers accidents per unit of handling for a package (without designation of spill or nonspill events) (Kloeber et al, 1979), and there are a few data sources (ICF, 1984) which give release fractions for transit as well as at associated terminals. The methods needed to take advantage of these data, however, require more information than can be obtained by emergency planning personnel with a reasonable amount of effort in the vast majority of cases.

The approach suggested is to identify particular shipments of concern which were discovered during initial data collection efforts and to only analyze those selected materials/shipments which involve sufficient volumes of materials to pose major hazards. The basic approach is to then utilize the basic accident rates for rail, marine, or highway transport as dictated by the type of transportation taking place, and to combine the resulting annual accident rate with the fraction of accidents expected to result in a spill or discharge. As a first pass on estimating the spill size distribution, consider using:

- Loss of one container (or group of containers, such as 12 bottles in a box) --- 90% of the time

- Full loss of cargo (all containers) --- 10% of the time

Additional Data/Methodologies

Should more precise estimates be needed, one of the more detailed methodologies should be utilized (for example, see ICF, 1984, and the references contained therein).

Use of Results in Consequence Analysis

Given the relatively small amounts of hazardous materials transported in individual packages and the manner in which most fail, the best course of action for consequence analysis purposes is to assume that the amount of cargo specified directly above is released instantaneously to the environment.

11.9 TRANSPORTATION OF HAZARDOUS MATERIALS BY AIR

The transportation of hazardous materials by air is generally limited to small packages, but this category of accidents also applies to crop dusters applying pesticides. The materials transported by air are usually of high value or of high priority time-wise. The annual tonnage shipped is between 200 and 300 thousand tons, but this involves a very large number of shipments. One study (OTA, March 1986) reports that in an evaluation of the air cargo packages at 39 major airports, 5% involved hazardous materials.

As demonstrated at the beginning of this chapter, there are relatively few hazardous materials incidents each year involving this mode of transportation. One source (Hazardous Materials Intelligence Report, May 31, 1985) found that there were only 6 incidents in 1984 which resulted in death, injury or more than $25,000 of property damage on a nationwide basis. The accidents tend to concentrate in the vicinity of airports, as might be expected.

There are numerous regulations covering the transportation of hazardous goods by air, including quantity restrictions and detailed regulations involving packaging. Many incidents which occur have been shown upon investigation to involve violations of these regulations.

In terms of emergency response planning, there is little that can be done to accurately determine a community's potential vulnerability to this type of accident, and admittedly, there is a question of whether planning should go beyond the development of communications links with airport facilities that handle hazardous materials, and the identification of

those locations where hazardous materials may be found on airport property. This observation follows from both the very low frequency of serious incidents and the extremely incomplete data available on commodity flows.

Crop dusters present a special case. Although accident rates and specific consequences cannot be predicted in advance due again to a rarity of serious incidents, it is a good idea for jurisdictions in which these aircraft work to give some thought to how to respond to a crash. Note that these planes usually carry pesticides and herbicides that may be highly toxic when concentrated. The crash site and surrounding areas may be highly contaminated. Crashes in or near bodies of water may threaten water supplies or cause environmental damage.

11.10 SUMMARY

The preceding sections have presented methodologies for estimating the annual probability of hazardous material releases from fixed facilities and transportation systems. Individual worksheets have been provided for truck, rail, marine, pipeline and fixed facility activities and operations. At the very least, a separate worksheet will need to be completed for each material or group of materials of concern and/or each facility of concern. Even if accident probabilities are not computed, the worksheets and related text can be valuable for the identification and refinement of individual accident scenarios.

The most critical local information needed for completion of worksheets involves exposure data -- i.e., the number and length of shipments, the number and capacity of storage tanks or process vessels, and so forth. When obtaining this information, it is usually sufficient to obtain the correct order of magnitude -- great expenditures of resources or very precise counts are not warranted. Should information be unavailable, it may be necessary to make a best estimate, with advice from other knowledgeable individuals. This is surely better than eliminating any potentially significant accident scenario from consideration.

Another important point is that no one event can result in all possible potential consequences simultaneously. In other words, if a rail car or tank truck experiences a BLEVE, it cannot then also have major downwind toxic vapor dispersion hazards as these require non-ignition of the cloud. Also, not all ignitions of flammable vapors result in explosions. The percentage of events which result in various consequences is very dependent on the material involved, the quantity released, and the reason for the release. General percentage breakdowns cannot be given.

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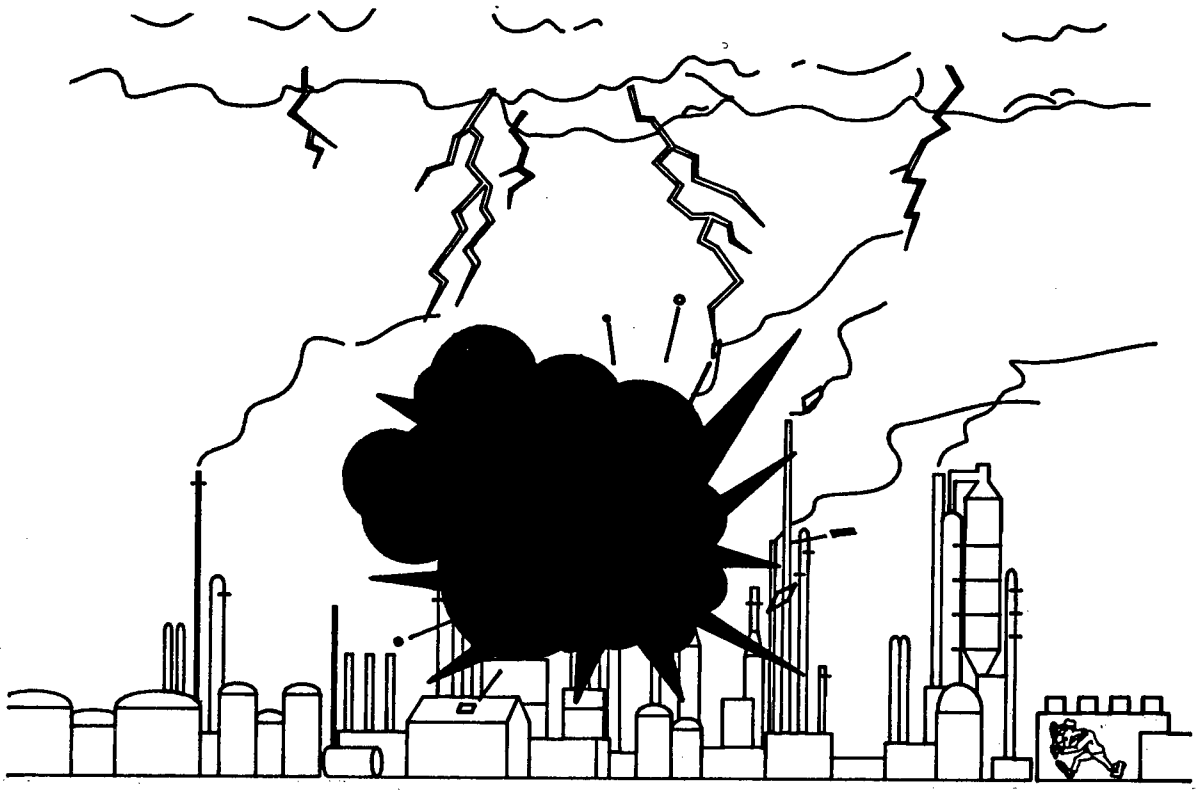
12.0 CONSEQUENCE ANALYSIS PROCEDURES



12.1 INTRODUCTION TO ARCHIE

With the wide proliferation of personal computers throughout the United States in recent years, particularly of IBM™ PC and fully compatible systems, it is now possible to provide emergency preparedness personnel at all levels of government and industry with relatively sophisticated computational tools to evaluate the nature and magnitude of threats facing individual jurisdictions. To facilitate what would otherwise be a difficult, time consuming, and expensive (if not impossible) task in many cases, the majority of accident hazard assessment and consequence analysis procedures required for a comprehensive hazard analysis have been incorporated into a single software program titled Automated Resource for Chemical Hazard Incident Evaluation (ARCHIE). A copy of Version 1.0 of the program has been provided together with this guide. Future efforts being considered by the federal government to further refine ARCHIE include installation of a data base of chemical and physical properties for a large number of hazardous materials, installation of more sophisticated analysis procedures enabled by availability of a database, and development of a version that will function on Apple™ Macintosh computers. Whether or not these enhancements are undertaken will depend upon the acceptance of ARCHIE by emergency preparedness personnel and feedback received by the government on the usefulness of the program to their individual planning efforts.

Due to the length of this chapter and the likelihood that users will refer to it often, Table 12.1 provides a special index to the following sections.

Purpose and Objectives of ARCHIE

The primary purpose of ARCHIE is to provide emergency preparedness personnel with several integrated estimation methods that may be used to assess the vapor dispersion, fire, and explosion impacts associated with episodic discharges of hazardous materials into the terrestial (i.e., land) environment. The program is also intended to facilitate a better understanding of the nature and sequence of events that may follow an accident and their resulting consequences.

Be advised that the detailed site-specific modeling techniques incorporated within ARCHIE differ from the more simplistic approaches in *Technical Guidance for Hazard Analysis* and are likely to produce different results. In addition, ARCHIE permits assessments for numerous types of hazards not addressed in the earlier guide.

General Features of the Program

The core of the ARCHIE computer program is a set of hazard assessment procedures and models that can be sequentially utilized to evaluate consequences of potential discharges of hazardous materials and thereby assist in the development of a *basis* for emergency planning. In other words, ARCHIE can help emergency planning personnel understand: 1) the nature and magnitude of hazards posing a threat to their jurisdictions; 2) the sequence of events that must take place for these threats to be realized; and ultimately 3) the nature of response actions that may be necessary in the event of an emergency to mitigate adverse impacts upon the public and its property. Among the models or calculation procedures incorporated into Version 1.0 of ARCHIE are:

- Nine methods for estimating the discharge rate and duration of a gas or liquid release from a tank or pipeline.
- Seven methods to help the user estimate the size of any liquid pools that may form on the ground.
- Two methods to estimate the rate at which a liquid pool will evaporate or boil and the duration of these phenomena until the point in time that the pool is depleted.
- A method to estimate the size of the downwind hazard zone that may require evacuation or other public protective action due to the release of a toxic gas or vapor into the atmosphere.

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- A method to evaluate the thermal radiation hazards resulting from the ignition of a flammable or combustible pool of liquid.

- Two methods to evaluate the size of the downwind area that may be subjected to flammable or explosive concentrations of gases or vapors in air due to the release of a flammable or explosive gas or vapor -- together with the maximum weight of potentially explosive gas or vapor in air that occurs during the incident.

- A method to evaluate the consequences of an unconfined vapor cloud explosion if the flammable gas or vapor in air should explode upon ignition.

- A method to evaluate the consequences of an explosion arising from the internal overpressurization of a sealed or inadequately vented tank due to external heating or internal reaction.

- A method to evaluate the consequences of an explosion arising from ignition of a true explosive material in the solid or liquid state.

An overview of technical details for individual models and the assumptions applied during their development are supplied in Appendix B for those who wish to review these aspects of the models. This chapter provides generalized discussions more suitable to the average user.

Given a potential accident scenario defined during the Hazard Identification and/or Probability Analysis portions of the overall hazard analysis, the program user is expected to select the appropriate sequence of calculation procedures to be utilized (generally starting from the top of the above list and working down). At the conclusion of the process, when the user is satisfied that the scenario has been properly represented, the user may then ask for a printed summary of the accident scenario evaluation results for future reference. Subsequent sections of this chapter will provide greater details on these topics.

To facilitate conduct of accident scenario evaluations and organization or results, assessment of each new scenario begins with the creation of what is referred to as an *Accident Scenario File* (ASF). This is a computer data file that automatically stores both the input data provided by the user and the results of all computations. For convenience, the user may assign any name to the file so long as the name is no longer than eight alphanumeric characters. Files are automatically assigned the name extension ".ASF" to differentiate them from others on the computer. Each is intended to consider a single specific accident scenario involving a specific hazardous material. The files are stored and retrived from the disk drive and directory specified by the user during the system initialization step described below.

Please note that users should never rename an ASF file using DOS commands outside the ARCHIE operating environment. Any such attempt will result in the file becoming unusable until its original name is restored.

Once an ASF file has been created, it may be recalled, revised, and placed back in storage under its original name, or it may be copied to an ASF file with a new name. This provides a great deal of flexibility to the ARCHIE program because:

- Users that are unsure of the validity of any particular input parameter value during initial evaluation of a scenario may provide an estimate, determine the proper value at their convenience, recall and correct the value in the ASF file without having to start from scratch, and rerun the various models as necessary to finalize the overall evaluation.

- Users who wish to evaluate a series of scenarios that differ only slightly from one another may recall the first file created, rename it, change the input values associated with scenario differences, and rerun the appropriate models with the new values. This procedure automatically creates a new ASF file with minimal effort while leaving the original file unchanged.

Accuracy and Limitations of Hazard Evaluation Methodologies

Several comments are in order with respect to the accuracy and other features of the consequence modelling and hazard assessment procedures found in ARCHIE. These procedures are in many cases simplified versions of more sophisticated methods developed by and/or available to professionals in the field. ARCHIE is intended to provide approximate answers for general emergency planning purposes. It will in most cases produce results that overestimate rather than underestimate threats to a community, but occasional exceptions are both **possible** and **likely**. Application of safety factors by users is both encouraged and recommended.

Although ARCHIE has the ability to address a wide variety of common accident scenarios in a fairly comprehensive manner, it is not capable of addressing several potentially hazardous phenomena that may result from accidents and which may therefore require special consideration by emergency planning personnel. These limitations are common to most if not all programs of this type and include inabilities to address:

- Downwind public exposures to toxic combustion products from fires.

- Damages to people or property from impact by high velocity fragments produced in explosions.

- Damages and injuries resulting from liquid superheat explosions or significant explosions taking place inside a building or other structure.

- Damages to property caused by exposure to thermal radiation or corrosive substances.

- Unusual threats or phenomena associated with hazardous chemical reactions.

Be sure to carefully evaluate the accident scenario you select and ensure that it applies to the hazardous material being studied.

Use of ARCHIE for Mixtures of Hazardous Materials

The hazard evaluation methodologies in ARCHIE are primarily designed to address spills or discharges of relatively pure substances. Mixtures can *only* be handled by knowledgeable users in certain *special* cases by provision of the physical and chemical properties of the mixture where and when such properties are requested by the program.

Inconsistent or Inappropriate Use of Models

A great deal of effort was devoted during development of ARCHIE to ensure that users do not apply hazard evaluation methodologies in an inconsistent and/or inappropriate fashion. Although anyone who attempts to use the program in such a fashion will find a large number of checks and balances in the system to prevent misuse, the complexity of the processes and phenomena being considered did not permit development of a fully foolproof program. It is therefore necessary for users to apply common sense at each stage of an analysis to ensure that the input data and information provided to the program are reasonable. For example, it is obviously inappropriate to attempt to force the program to utilize one of the fire or explosion models for a substance that is not inherently flammable, combustible, or explosive. Postulation of accident scenarios that are beyond the realm of reasonable credibility should be avoided to prevent unreasonable assessment results.

12.2 INSTALLATION OF THE ARCHIE COMPUTER PROGRAM

Detailed instructions for installation of the computer program on a variety of IBM™ PC and fully compatible personal computer systems are presented in Appendix E to this guide. ***Please refer to Appendix E and follow its instructions exactly prior to any attempt to run the program.*** Although you are unlikely to harm the program diskette, it is also unlikely that the program will operate as desired without reference to these instructions.

12.3 GENERAL NOTES ON RESPONDING TO QUESTIONS FROM THE PROGRAM

Throughout program use, the user will be required to answer numerous questions of various types. These typically involve:

- Input of ***yes*** or ***no*** in response to simple questions
- Input of ***letters*** or ***numbers*** for selection of menu options
- Input of ***numbers*** for measurable quantities

Response to Yes or No Questions

Whenever a question requires a simple *yes* or *no* answer, the query will generally end with one of the following three phrases in parentheses. Note that the key that must be pressed after any entry to the program is variously referred to as the CARRIAGE RETURN, RETURN, or ENTER key. Although the program uses the abbreviation "<cr>" to represent this key on screen displays, the following text will refer to this key as the ENTER key.

- (Y or <cr>/N) -- means that the program will accept either a "***Y***" or "***y***" followed by a press of the ENTER key, or simply a press of the ENTER key *alone*, to indicate a *yes* answer. A "***N***" or "***n***" followed by a press of the ENTER key is required to indicate a *no* answer.

- (Y/N or <cr>) -- means that the program will only accept "***Y***" or "***y***" followed by a press of the ENTER key as meaning *yes*. A "***N***" or "***n***" followed by a press of the ENTER key, or simply a press of the ENTER key *alone*, indicates a *no* answer.

- (Y/N) -- means that entry of an upper or lower case "***y***" or "***n***" followed by a press of the ENTER key are the only acceptable responses.

The choice of which of these options appears at the end of every question was made on the basis of which answer is most likely to be provided by the user in any given situation. Thus, although the program asks the user numerous questions during an accident scenario evaluation, a great many of them can be quickly answered by simply keeping the "little" finger of the right hand close to the ENTER key on the keyboard.

Selection of Menu Options

All primary menus in ARCHIE present a list of options with each line item preceded by a lower case letter. Selection of any specific option is accomplished by typing the appropriate letter (either lower or upper case letters are acceptable) and following the entry with a press of the ENTER key.

Several shorter menus displayed during use of various hazard assessment models typically denote available options with a number instead of a letter. As in the prior case, selection of an option is accomplished by entry of the appropriate number followed by a press of the ENTER key.

Entry of Required Input Parameter Data

During the course of an accident scenario evaluation, the user will be asked to provide a variety of numerical input data about the hazardous material involved and the circumstances under which it may pose a hazard to the public. Each time that the computer program requires a particular data item not previously provided by the program user, it will display a custom tailored parameter input screen. These screens define and describe the data item, the units in which the value is desired, and the range of values considered reasonable. Each screen also provides an opportunity for the user to confirm that the proper value has been entered, and several will ask if the user desires assistance in estimating an appropriate value. A *yes* answer to one of these questions will activate one of several *help* sections of the program. These ranges from one or two screens of text that provide guidance to major subprograms that provide assistance in estimating the vapor pressures of hazardous materials at various temperatures from minimal input data or which assist the user in characterizing the tank or container in which the hazardous material resides and the physical states, weights, and volumes of container contents.

Once a user provides an input value to a model at the request of the program, that value is immediately stored in the ASF file. If the same value is required by a subsequent hazard assessment model, the value is shown in a list of previously stored data (applicable to the model being used) together with a query as to whether the user wishes to change any value before continuing. It is ***VITALLY*** important to realize that changing one of these values ***AFTER*** earlier use may invalidate results of a prior model. Consequently, if a parameter value is changed, it may become necessary to return to and rerun any prior models that used this value to ensure that the entire sequence of computations is based upon a consistent set of input data.

Of particular interest is that ARCHIE generally requires no more data about a hazardous material than can usually be found on a well written and complete material safety data sheet (MSDS). Nevertheless, users with access to more detailed knowledge of material characteristics and properties are in several cases given the opportunity to improve the overall accuracy of scenario evaluation results by providing more exact input data. This is especially true in those cases where ARCHIE suggests use of typical values for needed data not found on a MSDS.

12.4 INITIALIZATION OF PROGRAM CONFIGURATION SETTINGS

Once the program is properly installed, it can be started by simply typing ARCHIE followed by a press of the ENTER key at the appropriate system prompt. A few seconds will be required while the computer reads the program into memory from its storage location. Indeed, such waits of a several seconds in duration for the reading and writing of program and data files from disk storage locations are common during use of the computer program and are no cause for concern.

The first time that the program is executed, it will begin with a series of two to four questions. The answers to these questions will tell the program about the video display attached to the system and the locations where you wish to store and retrieve data from Accident Scenario Files (ASF).

The ***first question*** is straightforward and simply asks if a color computer video monitor is attached to the system. Although there are programming techniques available to determine whether the computer contains a video adapter card *capable* of displaying color, no such method exists to determine if the card is actually attached to a color monitor. (Note: Some of you with monochrome monitors may wish to experiment with telling the program you have a color monitor, simply to learn if you prefer the screen displays generated to the more simple screens that will otherwise appear.)

The ***second question*** only appears if you answered *yes* to the first question and may be a bit difficult to answer if you have limited knowledge of the computer system you are using. The question itself is "*Is an EGA card installed and operating in the EGA mode?*" EGA is an abbreviation for Enhanced Graphics Adapter, a video display board option for computers that permits higher resolution graphics than the more typical boards found in older and/or less expensive systems. The presence of an operational EGA requires special program instructions to set the colors of screen borders. Do not be concerned whatsoever if you do not know the answer to the question. Just answer *no* and continue. The absolute worst that can happen is that some screens will have a black border in place of the more colorful border that would otherwise appear. Indeed, the very fact that black borders appear consistently is a good clue that you should change your answer at some point in the future. (Note: We tell you below how to change your answers to any of these questions once the program is running. Nothing is cast in stone!)

The ***third question*** (which could be the second at times) requests the letter of the disk drive on which you wish to store and retrieve Accident Scenario File data. Most of you should not have any problem deciding where you wish these files to be stored. For the rest of you, until you can obtain assistance for a more experienced computer user, here is some simple advice that will keep you out of trouble.

- If you are running the program from two floppy diskettes and there are two floppy drive slots in the front of the computer, place a blank or semi-blank but formatted diskette in the drive on the right (if the drives are side by side) or lower right (if one drive is on top of the other), close the door of the drive by twisting the lever, and **then** answer B to the question.

- If you are running the program from two diskettes, but there is only one floppy drive in the system, answer C for the time being. This will result in storage of ASF files in the *root directory* of the hard drive or card installed in your system.

- If the entire program fits on one diskette and you are using a floppy, just answer A to the question for now.

- If the program is installed on a fixed or hard drive within the computer, just press ENTER.

The ***last question*** only appears when you have installed the program on a fixed or hard drive within the computer. If you do not understand the question, simply press ENTER to continue and all will be well.

The program will save the answers to these questions and use them automatically next time you use the system. As noted above, however, you can change your answers quite easily. If you are within the program, choose Option E from the Main Task Selection Menu (see below) to restart the initialization procedure. If you are outside the program, you can force an automatic initialization the next time the program is used by erasing the file named ARCHIE.INI on your program disk.

12.5 DISPLAY OF THE PROGRAM TITLE SCREEN

The title screen for the program is simply that. Give it a look and press ENTER to continue. This screen will be the first to appear in systems that were initialized during prior use of the program. Otherwise, it will follow the questions described above.

12.6 INTRODUCTION TO OPTIONS ON THE MAIN TASK SELECTION MENU

The title screen is followed by the Main Task Selection Menu reproduced in Table 12.2, this being the place where you decide which major task you wish to accomplish. There are six options available lettered "a" to "f". These are discussed in the following, but not quite in the order that you might expect, primarily because your needs the first time or two you use the program will be different than your needs at later times.

TABLE 12.2
MAIN TASK SELECTION MENU

MAIN TASK SELECTION MENU	
a	Start assessment procedure for a new hazardous material accident scenario.
b	Recall and modify data for previously considered accident scenario.
c	Print summary of accident scenario hazard evaluation after completion.
d	Proceed to system description menu.
e	Reset system configuration settings.
f	Terminate session.
ENTER LETTER OF SELECTED OPTION (a-f):	

TABLE 12.3
SYSTEM DESCRIPTION AND USE INSTRUCTIONS
TASK SELECTION MENU

SYSTEM DESCRIPTION AND USE INSTRUCTIONS TASK SELECTION MENU	
a	Program purpose and objectives.
b	Suggested sequence of model use.
c	Creation and use of accident scenario files.
d	Recall and modification of previously created accident scenario files.
e	Printout of accident scenario hazard evaluation summaries.
f	Sources of assistance.
g	Return to main menu.
ENTER LETTER OF SELECTED OPTION (a-g):	

Option D: Proceed to System Description Menu

Selection of Option D results in the appearance of the System Description and Use Instruction Task Selection Menu which is reproduced in Table 12.3 and which has seven options lettered "a" to "g". This part of the program provides brief descriptions of various program features and objectives as well as other general information about the program. It is included primarily for users who ignore printed manuals or program instructions or who may receive the program without a printed copy of this guide. It can also help users who may not have used the program for a time and simply need their memory to be refreshed. Selection of any option but the last will display one or more screens of information about the program and then return you to this menu. Selection of the last option will return you to the Main Task Selection Menu.

Option E: Reset System Configuration Settings

Remember the questions discussed concerning initialization of the program? This option on the Main Task Selection Menu permits you to change any of your previous answers by restarting the initialization process.

Option F: Terminate Session

Simply stated, selection of this option from the Main Task Selection Menu says "goodbye" and ends the program.

Option A: Start Assessment for a New Hazardous Material Accident Scenario

When Option A is chosen from the Main Task Selection Menu, the program begins the process of creating a new Accident Scenario File (ASF). As reported earlier, this is a data file that automatically stores both the input data provided by the user as well as results of all computations. Initial file creation steps entail answers by the user to several questions, these involving:

- The name to be assigned to the ASF file (mandatory).
- The name of the hazardous material of concern (optional).
- The name, location, or address of the facility or transportation route where the postulated accident may occur (optional).
- The geographical latitude of the potential accident location (optional).
- The geographical longitude of the potential accident location (optional).

- The date on which the scenario was evaluated (optional).
- A one to three line textual description of the accident scenario being evaluated (optional).
- An indication of whether or not the hazardous material of interest is flammable or combustible (mandatory).

The program will prompt the user for necessary information at each step of the ASF file initialization process and provide opportunities to change or modify user responses to the above queries. When this process is complete, the program will proceed to the Hazard Assessment Model Selection Menu described further below.

Option B: Recall and Modify Data for Previously Considered Accident Scenario

Once an Accident Scenario File has been created via use of Option A on the menu, it may be recalled, copied and renamed (this is optional), modified, and eventually placed back into storage by selection of Option B on the menu.

Prior to display of the Hazard Assessment Model Selection Menu, the program provides opportunities to:

- View the names of all ASF files stored at the location specified during *program* initialization.
- Specify the name of the file that is to be retrieved.
- Indicate whether he or she wishes to copy the data in the named file to a new file with a different name, and
- Review and revise the file initialization data provided when Option A was used to create the file.

Option C: Print Summary of Accident Scenario Hazard Evaluation After Completion

Option C of the Main Task Selection Menu permits the user to obtain a printed summary of the overall results of the accident scenario evaluation for any scenario previously analyzed using ARCHIE. This printout will be two to seven pages in length depending on which evaluation procedures were used and the number of tables that were generated.

The printouts are formatted using standard commands of the BASIC program language and should therefore print without problem on a wide variety of computer printers. It cannot be guaranteed, however, that all output devices will behave as desired, particularly in the

case of laser printers. Many brands of these devices require individual special software "drivers" that are normally only provided with specific types of commercial word processing and graphics generation programs. In some cases, the presence of a "print spooler" may cause problems during printing.

While on the topic of printed output, it is also well to note that a printout of most individual program screens can often be obtained by pressing the *PrtSc, Print Scrn,* or similar key on the keyboard. Some earlier keyboards, particularly those provided with the first generation of personal computers, may require simultaneous pressing of the *Shift* and *PrtSc* keys. As in the case of scenario evaluation summaries, be advised of the possibility that this method may not work with some laser printers.

12.7 INTRODUCTION TO THE HAZARD ASSESSMENT MODEL SELECTION MENU

The hazard assessment models incorporated into the computer program are made available to the user as options on the Hazard Assessment Model Selection Menu reproduced in Table 12.4. The menu has 14 options lettered "a" to "n".

The first major step in use of the computer program to evaluate a specific accident scenario requires selection of appropriate models from the model selection menu. To facilitate this task, Figure 12.1 provides a logic diagram pertaining to the most common spill hazards associated with episodic discharges of hazardous materials. Figure 12.2 is a related directory of the models available in ARCHIE to evaluate these hazards. As noted on the diagrams in this figure, letters in parentheses within individual blocks refer to options available on the Hazard Assessment Model Selection Menu. ***In all cases, it is best to start at the top of one of the charts shown in the figure and work downwards towards the conclusion of each threat scenario.*** Note that the model selection charts can be viewed from within the computer program by selection of Option M from the subject menu.

The second step in most accident scenario evaluations in which fairly detailed information is available with regards to the tank, pipeline, or other container that may discharge its contents will usually involve use of a discharge rate and duration estimation model. Table 12.5 reproduces the separate menu for these models that will appear when Option A is chosen from the Hazard Assessment Model Selection Menu.

The first four options (a through d) on the Discharge Model Selection Menu are intended for use when the temperature of a liquid chemical within a tank or other container is at or below its boiling point temperature, with the choice of any particular option depending on the general shape of the container. Containers are assumed to be non-pressurized because the vapor pressure of their liquid contents will be at or below ambient atmospheric pressure.

TABLE 12.4
HAZARD ASSESSMENT MODEL SELECTION MENU

HAZARD ASSESSMENT MODEL SELECTION MENU	
a	Estimate discharge rate of liquid or gas.
b	Estimate area of liquid pool.
c	Estimate vaporization rate of liquid pool.
d	Evaluate toxic vapor dispersion hazards.
e	Evaluate pool fire radiation hazards.
f	Evaluate fireball radiation hazards.
g	Evaluate flame jet hazards.
h	Evaluate vapor cloud/plume fire hazards.
i	Evaluate vapor cloud explosion hazards.
j	Evaluate tank overpressurization rupture hazard.
k	Evaluate solid/liquid explosion hazard.
l	Review model descriptions.
m	Review model selection charts.
n	Return to main menu.
ENTER LETTER OF SELECTED OPTION (a-n):	

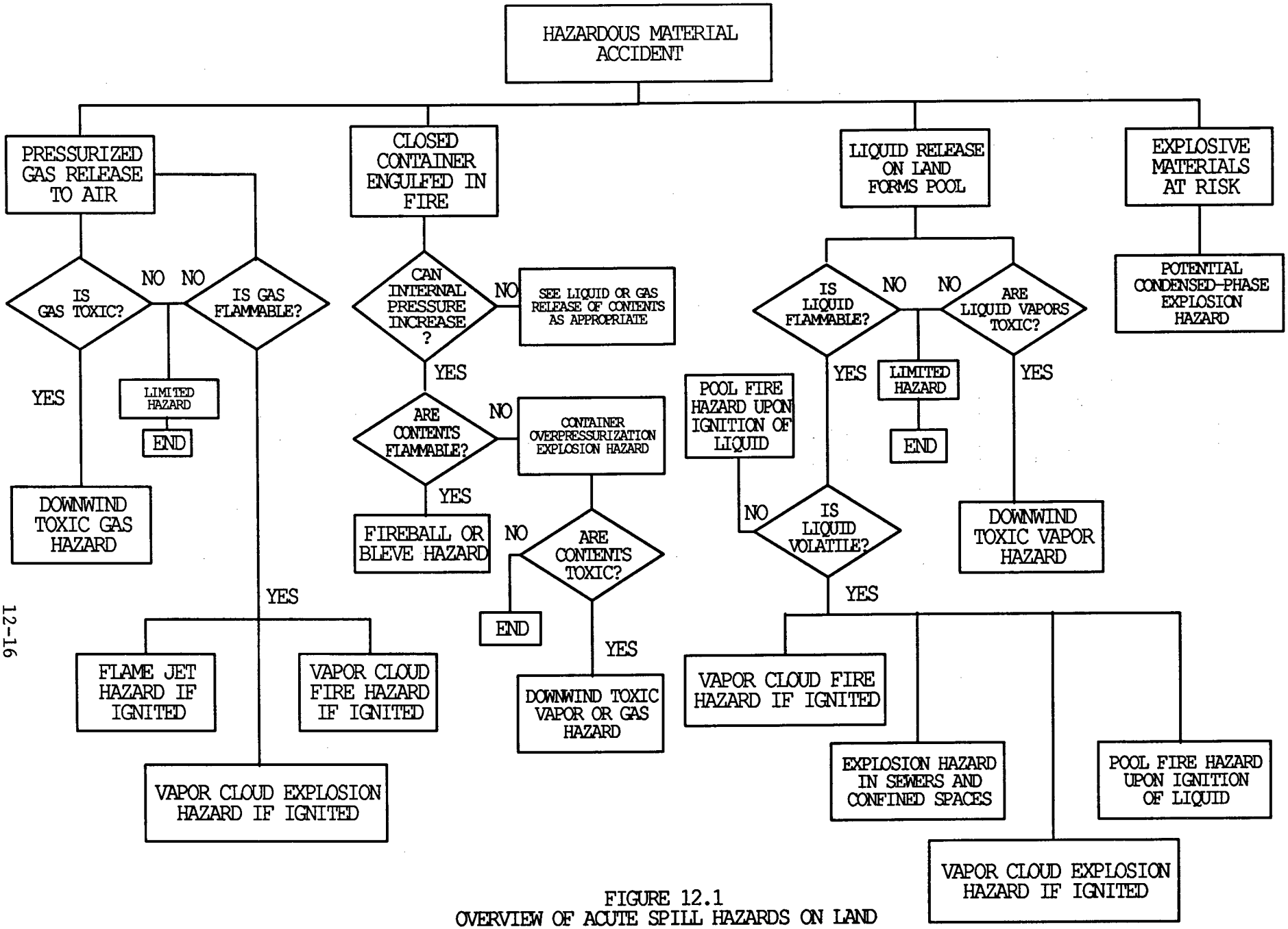
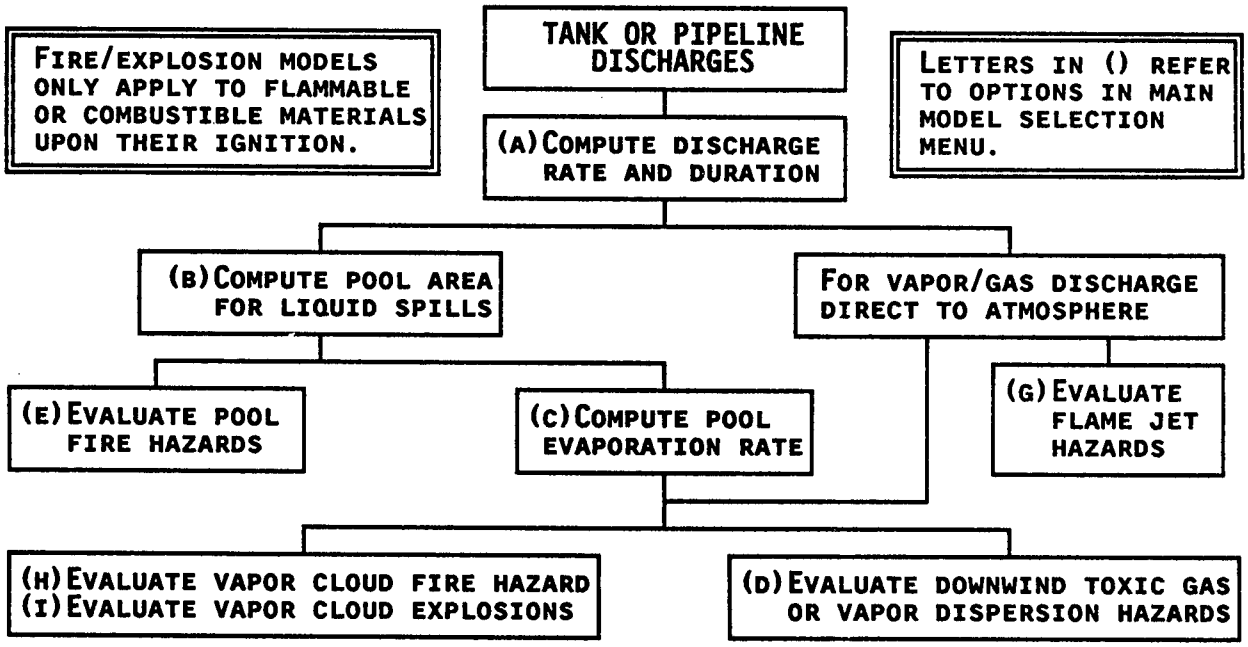
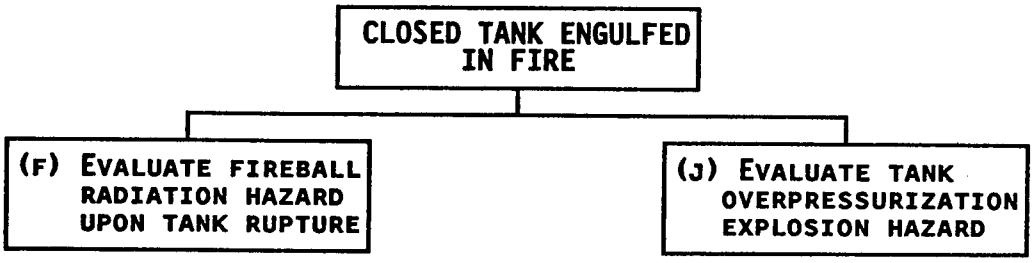


FIGURE 12.1
OVERVIEW OF ACUTE SPILL HAZARDS ON LAND

FIGURE 12.2
MODEL SELECTION CHARTS





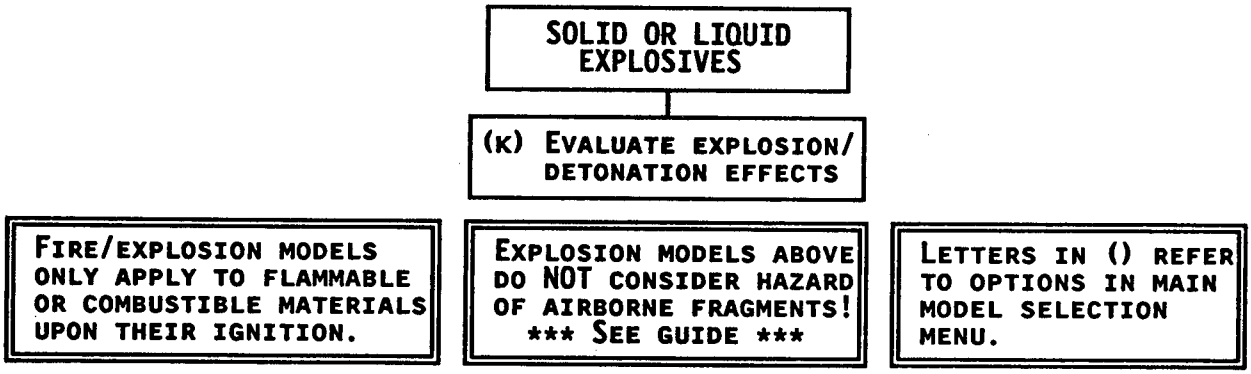


TABLE 12.5
DISCHARGE MODEL SELECTION MENU

DISCHARGE MODEL SELECTION MENU
NON-PRESSURIZED TANKS CONTAINING LIQUID
a Rectangular tank
b Spherical tank
c Vertl cylindrical tank
d Horzl cylindrical tank
PRESSURIZED TANKS CONTAINING GAS AND/OR LIQUID
e Liquid discharge from tank when hole/pipe end 4 inches or less from tank.
f Liquid discharge from tank when hole/pipe end more than 4 inches from tank.
g Gas discharge from any tank.
RELEASE FROM A LONG PIPELINE
h Pipeline containing liquid under pressure.
i Pipeline containing gas under pressure.
j Return to main model selection
ENTER LETTER OF SELECTED OPTION (a-j):

Options "e" and "f" pertain to tanks or other containers of compressed liquefied gases, and are generally applicable to situations in which the temperature of the liquid is above its normal boiling point. Option "e" should be used when the location from which the liquid is expected to exit is four inches or less from the internal wall surface of the tank. Option "f" is more appropriate when the discharge outlet may be more than four inches from the internal wall, as may occur when a pipe directly connected to a container breaks or ruptures some distance from the vessel. Option "g" on the menu is intended for use when the tank or container (excluding long pipelines) only stores a compressed gas.

Options "h" or "i" on the menu should be used to evaluate discharges from long pipelines. The first applies to lines solely containing some type of liquid. The second applies to lines solely containing compressed gases.

The next nine sections of this chapter provide information on use of the nine discharge models listed under Options A to I on the Discharge Model Selection Menu. The tenth option of this particular menu (this being Option J) will return the user to the Hazard Assessment Model Selection Menu. The nine sections pertaining to discharge models each have titles that begin with the prefix "*12.XX Discharge Menu Option X:*".

The discharge model descriptions are followed by descriptions of the remaining model options available from the Hazard Assessment Selection Menu. Each of these sections has a title that begins with the prefix "*12.XX Hazard Model Menu Option X:*". Subsequent sections discuss and describe non-model related options available from this menu, special subprograms, and utilities available to assist the user in describing and defining input parameter values necessary for model use. A final section of the chapter provides information about related computer programs that have been developed under sponsorship of the federal government.

Be advised that each of the model descriptions was *intentionally* written to stand alone to the maximum extent possible, thus facilitating future reference to these discussions. It is for this reason that there is a considerable degree of redundancy within the sections that follow.

As a final note before individual model selection options are introduced and discussed, emergency planning personnel should realize that the most common hazardous material likely to be encountered is automative gasoline, yet specific properties of this material are generally difficult to locate in the literature. Based upon an evaluation of the 24 most common components of a typical fresh unleaded gasoline blend, key properties that should be provided to ARCHIE in the absence of more precise data, include:

- Molecular weight = 90.9
- Normal boiling point = 114.9°F
- Specific Gravity = 0.64 at 68°F
- Vapor pressure = 82 mm Hg at 0°F
- Vapor pressure = 343 mm Hg at 68°F
- Vapor pressure = 595 mm Hg at 100°F
- Lower flammable limit = 1.4%
- Heat of combustion = 18,570 Btu/lb

12.8 DISCHARGE MENU OPTION A: NON-PRESSURIZED RECTANGULAR TANK OF LIQUID

Purpose of Model

Intended for use with liquids having temperatures *at* or *below* their respective normal boiling points, this model is used to estimate the duration and average rate of liquid discharge from a punctured or otherwise leaking *rectangular* tank or container. A container should be classified as rectangular if it resembles a box of tissues or a shoebox in general shape.

Required Input Data

The following input parameter values and information may be requested during use of this model.

- Normal boiling point of the liquid (°F)
- Temperature of the liquid in the tank or container (°F)
- Ambient environmental temperature (°F)
- Weight of liquid in the container (lbs)
- Indication of whether or not an instantaneous spill is to assumed
- Length of the rectangular tank or container (ft)
- Width of the rectangular tank or container (ft)
- Height of liquid in the container as measured from its bottom (ft)
- Diameter of the hole from which liquid will discharge (inches)
- Discharge coefficient of the hole
- Specific gravity of the liquid

As discussed in Chapter 2 of this guide, many properties of hazardous materials are a function of temperature, with one of the most important being the vapor pressure of the substance (since this property will ultimately have a major effect on the magnitude of toxic or flammable vapor dispersion threats). Consequently, for planning purposes, it is desireable to select both tank and ambient environmental temperatures among the highest that may be experienced during a typical year. In selecting these temperatures, note that the temperature

of the contents inside a metal tank can often (not always) be 20°F or more higher than the ambient air temperature on a sunny day. Even when not higher in the container, the temperature of the liquid may increase upon spillage onto a hot surface or when exposed to the sun (particularly when the vapor pressure of the material is relatively low and evaporative cooling does not play a major role).

Prior to asking the user to provide the weight of liquid in the tank, an input parameter value that would otherwise require several manual computations, the program asks if the user desires assistance in characterizing the volume of the container and the weights, volumes, and physical states of its contents. Further details on the *Tank and Container Contents Characterization Subprogram* and its general data requirements are provided in Section 12.29 of this chapter. Use of the subprogram may result in requests for a few informational items not listed above but is nevertheless highly recommended.

Hazard evaluations for emergency planning purposes should strive to assume the worse credible conditions under which an accident may take place. In the case of the amount of liquid in the tank or container, guidance should be obtained from the owner or operator of the vessel with respect to the largest amounts that may be expected to be present. In the case of transportation vehicles, it is usually sufficient to assume that the container is at least 90% full unless other information is available.

There may be situations envisioned in which the tank or container of interest may be expected to fail in a very quick and catastrophic fashion; for example, in the event of its exposure to a major explosion or collapse due to severe structural failure. Consequently, after the user has supplied the weight of liquid in the tank, the program asks if the user wishes to assume that the spill or discharge should be assumed as being essentially instantaneous. A *yes* answer to this question will halt use of the model and result in the assumption that the entire contents of the container will be released to the environment in one minute and that the average rate of discharge will be the weight of tank contents per minute. A *no* answer will result in normal continuation of model use.

The program inherently assumes that the discharge outlet is circular in shape. In those instances where the expected shape is not expected to be circular it will be necessary to: 1) determine or estimate the area of the expected outlet in units of square inches; and 2) compute the diameter of the equivalent circle having this area. Appendix A to this guide provides assistance in this task for those who require further guidance.

The discharge coefficient of the hole is a measure of its edge characteristics that has a major and direct influence on the rate of discharge. The input parameter screen for the data item will provide guidance in selection of an appropriate value.

The specific gravity of the liquid should ideally be the value associated with the liquid at its temperature in the container or tank of concern. Note, however, that this value varies very little with changes in temperature for the vast majority of liquids for which this model is applicable. The specific gravity given at a temperature of 68°F (20°C) on a typical material safety data sheet (MSDS) will be of more than acceptable accuracy in most cases.

Model Results and Usage

Results of the model include the average rate of liquid discharge in pounds/minute, the duration of discharge in minutes, the total weight of contents discharged in pounds, and the physical state of the discharged material (which will always be *liquid* when this particular discharge model is used).

Results of the model are typically utilized by the program as input parameters to the pool area estimation methods (Hazard Model Menu Option B) available from the Hazard Assessment Model Selection Menu.

Major Assumptions of the Methodology

The model assumes that the hole or other discharge outlet from which the liquid is being released is at or near the bottom of the tank for initial calculation purposes, thus resulting in a further assumption of complete loss of liquid contents. Note, however, that an opportunity is given at the end of the procedure, prior to the point in time that results are stored in the ASF file, to replace the computed duration of discharge with a shorter time. This is one way in which users can adjust discharge model results to account for situations in which the discharge outlet being considered is actually above the bottom portion of the tank or container. An alternative approach would be to specify a height of liquid measured upward from the location of the expected discharge outlet and not from the bottom of the tank or container.

Another major assumption is that there is an opening somewhere in the top portion of the tank or container that permits entry of air to fill the volume previously taken by liquid discharged to the enviroment. This assumption will be valid for any container that has some sort of pressure equalization system to maintain standard atmospheric pressure above the liquid surface while liquid is being pumped in or drawn out of the container. In cases where no such system exists or is operational, it is well to recognize that the model will estimate a much shorter discharge time duration and much higher average discharge rate than would be expected in the real world. The reason for this is that the flow of liquid will be periodically interrupted as air enters through the discharge outlet to fill the new vapor space created above the liquid surface. The situation will in many respects resemble that which occurs when a bottle or can of a soft drink is turned upside down and the liquid exits in a series of spurts rather than in a continuous and smooth flow pattern.

A final and relatively minor assumption is that the discharge outlet, be it a hole in the side of the tank or a broken pipe attached to the container, is relatively close to the container. This assumption can lead to underprediction of discharge durations and overprediction of discharge rates in cases when the discharge outlet is at the end of a complicated and/or lengthy piping system attached to the container since such piping systems produce friction that can slightly slow the flow of liquid and hence reduce the discharge rate.

12.9 DISCHARGE MENU OPTION B: NON-PRESSURIZED SPHERICAL TANK OF LIQUID

Purpose of Model

Intended for use with liquids stored at temperatures *at* or *below* their respective normal boiling points, this model is used to estimate the duration and average rate of liquid discharge from a punctured or otherwise leaking *spherical* tank or container resembling a ball of some kind in general shape.

Required Input Data

The following input parameter values and information may be requested during use of this model.

- Normal boiling point of the liquid (°F)
- Temperature of the liquid in the tank or container (°F)
- Ambient environmental temperature (°F)
- Weight of liquid in the tank or container (lbs)
- Indication of whether or not an instantaneous spill is to assumed
- Diameter of the spherical tank or container (ft)
- Height of liquid in the container as measured from its bottom (ft)
- Diameter of the hole from which liquid will discharge (inches)
- Discharge coefficient of the hole
- Specific gravity of the liquid

As discussed in Chapter 2 of this guide, many properties of hazardous materials are a function of temperature, with one of the most important being the vapor pressure of the substance (since this property will ultimately have a major effect on the magnitude of toxic or flammable vapor dispersion threats). Consequently, for planning purposes, it is desireable to select both tank and ambient environmental temperatures among the highest that may be experienced during a typical year. In selecting these temperatures, note that the temperature of the contents inside a metal tank can often (not always) be 20°F or more higher than the ambient air temperature on a sunny day. Even when not higher in the container, the

temperature of the liquid may increase upon spillage onto a hot surface or when exposed to the sun (particularly when the vapor pressure of the material is relatively low and evaporative cooling does not play a major role).

Prior to asking the user to provide the weight of liquid in the tank, an input parameter value that would otherwise require several manual computations, the program asks if the user desires assistance in characterizing the volume of the container and the weights, volumes, and physical states of its contents. Further details on the *Tank and Container Contents Characterization Subprogram* and its general data requirements are provided in Section 12.29 of this chapter. Use of the subprogram may result in requests for a few informational items not listed above but is nevertheless highly recommended.

Hazard evaluations for emergency planning purposes should strive to assume the worse credible conditions under which an accident may take place. In the case of the amount of liquid in the tank or container, guidance should be obtained from the owner or operator of the vessel with respect to the largest amounts that may be expected to be present. In the case of transportation vehicles, it is usually sufficient to assume that the container is at least 90% full unless other information is available.

There may be situations envisioned in which the tank or container of interest may be expected to fail in a very quick and catastrophic fashion; for example, in the event of its exposure to a major explosion or collapse due to severe structural failure. Consequently, after the user has supplied the weight of liquid in the tank, the program asks if the user wishes to assume that the spill or discharge should be assumed as being essentially instantaneous. A *yes* answer to this question will halt use of the model and result in the assumption that the entire contents of the container will be released to the environment in one minute and that the average rate of discharge will be the weight of tank contents per minute. A *no* answer will result in normal continuation of model use.

The program inherently assumes that the discharge outlet is circular in shape. In those instances where the expected shape is not expected to be circular it will be necessary to: 1) determine or estimate the area of the expected outlet in units of square inches; and 2) compute the diameter of the equivalent circle having this area. Appendix A to this guide provides assistance in this task for those who may require guidance.

The discharge coefficient of the hole is a measure of its edge characteristics that has a major and direct influence on the rate of discharge. The input parameter screen for the data item will provide guidance in selection of an appropriate value.

The specific gravity of the liquid should ideally be the value associated with the liquid at its temperature in the container or tank of concern. Note, however, that this value varies very little with changes in temperature for the vast majority of liquids for which this model is applicable. The specific gravity given at a temperature of 68°F (20°C) on a typical material safety data sheet (MSDS) will be of more than acceptable accuracy in most cases.

Model Results and Usage

Results of the model include the average rate of liquid discharge in pounds/minute, the duration of discharge in minutes, the total weight of contents discharged in pounds, and the physical state of the discharged material (which will always be *liquid* when this particular discharge model is used).

Results of the model are typically utilized by the program as input parameters to the pool area estimation methods (Hazard Model Menu Option B) available from the Hazard Assessment Model Selection Menu.

Major Assumptions of the Methodology

The model assumes that the hole or other discharge outlet from which the liquid is being released is at or near the bottom of the tank for initial calculation purposes, thus resulting in a further assumption of complete loss of liquid contents. Note, however, that an opportunity is given at the end of the procedure, prior to the point in time that results are stored in the ASF file, to replace the computed duration of discharge with a shorter time. This is one way in which users can adjust discharge model results to account for situations in which the discharge outlet being considered is actually above the bottom portion of the tank or container. An alternative approach would be to specify a height of liquid measured upward from the location of the expected discharge outlet and not from the bottom of the tank or container.

Another major assumption is that there is an opening somewhere in the top portion of the tank or container that permits entry of air to fill the volume previously taken by liquid discharged to the enviroment. This assumption will be valid for any container that has some sort of pressure equalization system to maintain standard atmospheric pressure above the liquid surface while liquid is being pumped in or drawn out of the container. In cases where no such system exists or is operational, it is well to recognize that the model will estimate a much shorter discharge time duration and much higher average discharge rate than would be expected in the real world. The reason for this is that the flow of liquid will be periodically interrupted as air enters through the discharge outlet to fill the new vapor space created above the liquid surface. The situation will in many respects resemble that which occurs when a bottle or can of a soft drink is turned upside down and the liquid exits in a series of spurts rather than in a continuous and smooth flow pattern.

A final and relatively minor assumption is that the discharge outlet, be it a hole in the side of the tank or a broken pipe attached to the container, is relatively close to the container. This assumption can lead to underprediction of discharge durations and overprediction of discharge rates in cases when the discharge outlet is at the end of a complicated and/or lengthy piping system attached to the container since such piping systems produce friction that can slightly slow the flow of liquid and hence reduce the discharge rate.

12.10 DISCHARGE MENU OPTION C: NON-PRESSURIZED VERTICAL CYLINDER OF LIQUID

Purpose of Model

Intended for use with liquids stored at temperatures *at* or *below* their respective normal boiling points, this model is used to estimate the duration and average rate of liquid discharge from a punctured or otherwise leaking *vertical cylindrical* tank or container. A tank or container that would be classified as a vertical cylinder would resemble (in general shape) a can of tuna fish or a can of soft drink sitting upright on a table. Such tanks are the most typical containers seen at facilities that store gasoline and/or fuel oils in above ground vessels.

Required Input Data

The following input parameter values and information may be requested during use of this model.

- Normal boiling point of the liquid (°F)
- Temperature of the liquid in the tank or container (°F)
- Ambient environmental temperature (°F)
- Weight of liquid in the tank or container (lbs)
- Indication of whether or not an instantaneous spill is to assumed
- Diameter of the vertical cylindrical tank or container (ft)
- Height of liquid in the container as measured from its bottom (ft)
- Diameter of the hole from which liquid will discharge (inches)
- Discharge coefficient of the hole
- Specific gravity of the liquid

As discussed in Chapter 2 of this guide, many properties of hazardous materials are a function of temperature, with one of the most important being the vapor pressure of the substance (since this property will ultimately have a major effect on the magnitude of toxic or flammable vapor dispersion threats). Consequently, for planning purposes, it is desireable to select both tank and ambient environmental temperatures among the highest that may be experienced during a typical year. In selecting these temperatures, note that the temperature

of the contents inside a metal tank can often (not always) be 20°F or more higher than the ambient air temperature on a sunny day. Even when not higher in the container, the temperature of the liquid may increase upon spillage onto a hot surface or when exposed to the sun (particularly when the vapor pressure of the material is relatively low and evaporative cooling does not play a major role).

Prior to asking the user to provide the weight of liquid in the tank, an input parameter value that would otherwise require several manual computations, the program asks if the user desires assistance in characterizing the volume of the container and the weights, volumes, and physical states of its contents. Further details on the *Tank and Container Contents Characterization Subprogram* and its general data requirements are provided in Section 12.29 of this chapter. Use of the subprogram may result in requests for a few informational items not listed above but is nevertheless highly recommended.

Hazard evaluations for emergency planning purposes should strive to assume the worse credible conditions under which an accident may take place. In the case of the amount of liquid in the tank or container, guidance should be obtained from the owner or operator of the vessel with respect to the largest amounts that may be expected to be present. In the case of transportation vehicles, it is usually sufficient to assume that the container is at least 90% full unless other information is available.

There may be situations envisioned in which the tank or container of interest may be expected to fail in a very quick and catastrophic fashion; for example, in the event of its exposure to a major explosion or collapse due to severe structural failure. Consequently, after the user has supplied the weight of liquid in the tank, the program asks if the user wishes to assume that the spill or discharge should be assumed as being essentially instantaneous. A *yes* answer to this question will halt use of the model and result in the assumption that the entire contents of the container will be released to the environment in one minute and that the average rate of discharge will be the weight of tank contents per minute. A *no* answer will result in normal continuation of model use.

The program inherently assumes that the discharge outlet is circular in shape. In those instances where the expected shape is not expected to be circular it will be necessary to: 1) determine or estimate the area of the expected outlet in units of square inches; and 2) compute the diameter of the equivalent circle having this area. Appendix A to this guide provides assistance in this task for those who may require guidance.

The discharge coefficient of the hole is a measure of its edge characteristics that has a major and direct influence on the rate of discharge. The input parameter screen for the data item will provide guidance in selection of an appropriate value.

The specific gravity of the liquid should ideally be the value associated with the liquid at its temperature in the container or tank of concern. Note, however, that this value varies very little with changes in temperature for the vast majority of liquids for which this model is applicable. The specific gravity given at a temperature of 68°F (20°C) on a typical material safety data sheet (MSDS) will be of more than acceptable accuracy in most cases.

Model Results and Usage

Results of the model include the average rate of liquid discharge in pounds/minute, the duration of discharge in minutes, the total weight of contents discharged in pounds, and the physical state of the discharged material (which will always be *liquid* when this particular discharge model is used).

Results of the model are typically utilized by the program as input parameters to the pool area estimation methods (Hazard Model Menu Option B) available from the Hazard Assessment Model Selection Menu.

Major Assumptions of the Methodology

The model assumes that the hole or other discharge outlet from which the liquid is being released is at or near the bottom of the tank for initial calculation purposes, thus resulting in a further assumption of complete loss of liquid contents. Note, however, that an opportunity is given at the end of the procedure, prior to the point in time that results are stored in the ASF file, to replace the computed duration of discharge with a shorter time. This is one way in which users can adjust discharge model results to account for situations in which the discharge outlet being considered is actually above the bottom portion of the tank or container. An alternative approach would be to specify a height of liquid measured upward from the location of the expected discharge outlet and not from the bottom of the tank or container.

Another major assumption is that there is an opening somewhere in the top portion of the tank or container that permits entry of air to fill the volume previously taken by liquid discharged to the enviroment. This assumption will be valid for any container that has some sort of pressure equalization system to maintain standard atmospheric pressure above the liquid surface while liquid is being pumped in or drawn out of the container. In cases where no such system exists or is operational, it is well to recognize that the model will estimate a much shorter discharge time duration and much higher average discharge rate than would be expected in the real world. The reason for this is that the flow of liquid will be periodically interrupted as air enters through the discharge outlet to fill the new vapor space created above the liquid surface. The situation will in many respects resemble that which occurs when a bottle or can of a soft drink is turned upside down and the liquid exits in a series of spurts rather than in a continuous and smooth flow pattern.

A final and relatively minor assumption is that the discharge outlet, be it a hole in the side of the tank or a broken pipe attached to the container, is relatively close to the container. This assumption can lead to underprediction of discharge durations and overprediction of discharge rates in cases when the discharge outlet is at the end of a complicated and/or lengthy piping system attached to the container since such piping systems produce friction that can slightly slow the flow of liquid and hence reduce the discharge rate.

12.11 DISCHARGE MENU OPTION D: NON-PRESSURIZED HORIZONTAL CYLINDER OF LIQUID

Purpose of Model

Intended for use with liquids stored at temperatures *at* or *below* their respective normal boiling points, this model is used to estimate the duration and average rate of liquid discharge from a punctured or otherwise leaking *horizontal cylindrical* tank or container. A container classified as being a horizontal cylinder would resemble the tank seen on the back of a typical gasoline truck in general shape.

Required Input Data

The following input parameter values and information may be requested during use of this model.

- Normal boiling point of the liquid (°F)
- Temperature of the liquid in the tank or container (°F)
- Ambient environmental temperature (°F)
- Weight of liquid in the tank or container (lbs)
- Indication of whether or not an instantaneous spill is to assumed
- Diameter of the horizontal cylindrical tank or container (ft)
- Length of the horizontal cylindrical tank or container (ft)
- Height of liquid in the container measured from its bottom (ft)
- Diameter of the hole from which liquid will discharge (inches)
- Discharge coefficient of the hole
- Specific gravity of the liquid

As discussed in Chapter 2 of this guide, many properties of hazardous materials are a function of temperature, with one of the most important being the vapor pressure of the substance (since this property will ultimately have a major effect on the magnitude of toxic or flammable vapor dispersion threats). Consequently, for planning purposes, it is desireable to select both tank and ambient environmental temperatures among the highest that may be experienced during a typical year. In selecting these temperatures, note that the temperature of the contents inside a metal tank can often (not always) be 20°F or more higher than the

ambient air temperature on a sunny day. Even when not higher in the container, the temperature of the liquid may increase upon spillage onto a hot surface or when exposed to the sun (particularly when the vapor pressure of the material is relatively low and evaporative cooling does not play a major role).

Prior to asking the user to provide the weight of liquid in the tank, an input parameter value that would otherwise require several manual computations, the program asks if the user desires assistance in characterizing the volume of the container and the weights, volumes, and physical states of its contents. Further details on the *Tank and Container Contents Characterization Subprogram* and its general data requirements are provided in Section 12.29 of this chapter. Use of the subprogram may result in requests for a few informational items not listed above but is nevertheless highly recommended.

Hazard evaluations for emergency planning purposes should strive to assume the worse credible conditions under which an accident may take place. In the case of the amount of liquid in the tank or container, guidance should be obtained from the owner or operator of the vessel with respect to the largest amounts that may be expected to be present. In the case of transportation vehicles, it is usually sufficient to assume that the container is at least 90% full unless other information is available.

There may be situations envisioned in which the tank or container of interest may be expected to fail in a very quick and catastrophic fashion; for example, in the event of its exposure to a major explosion or collapse due to severe structural failure. Consequently, after the user has supplied the weight of liquid in the tank, the program asks if the user wishes to assume that the spill or discharge should be assumed as being essentially instantaneous. A *yes* answer to this question will halt use of the model and result in the assumption that the entire contents of the container will be released to the environment in one minute and that the average rate of discharge will be the weight of tank contents per minute. A *no* answer will result in normal continuation of model use.

It should be recognized that not all horizontal cylindrical tanks have circular cross-sections or flat ends as inherently assumed by the model. Where the tank cross-section is more of an oval, set the requested diameter equal to either the widest part of the tank (or to the average of the narrowest and widest sections if somewhat greater accuracy is desired). It is always safe to set the length of the tank to its longest dimension regardless whether its ends are hemispherical, dished, or flat. The errors introduced will be relatively minor.

The program inherently assumes that the discharge outlet is circular in shape. In those instances where the expected shape is not expected to be circular it will be necessary to: 1)

determine or estimate the area of the expected outlet in units of square inches; and 2) compute the diameter of the equivalent circle having this area. Appendix A to this guide provides assistance in this task for those who may require guidance.

The discharge coefficient of the hole is a measure of its edge characteristics that has a major and direct influence on the rate of discharge. The input parameter screen for the data item will provide guidance in selection of an appropriate value.

The specific gravity of the liquid should ideally be the value associated with the liquid at its temperature in the container or tank of concern. Note, however, that this value varies very little with changes in temperature for the vast majority of liquids for which this model is applicable. The specific gravity given at a temperature of 68°F (20°C) on a typical material safety data sheet (MSDS) will be of more than acceptable accuracy in most cases.

Model Results and Usage

Results of the model include the average rate of liquid discharge in pounds/minute, the duration of discharge in minutes, the total weight of contents discharged in pounds, and the physical state of the discharged material (which will always be *liquid* when this particular discharge model is used).

Results of the model are typically utilized by the program as input parameters to the pool area estimation methods (Hazard Model Menu Option B) available from the Hazard Assessment Model Selection Menu.

Major Assumptions of the Methodology

The model assumes that the hole or other discharge outlet from which the liquid is being released is at or near the bottom of the tank for initial calculation purposes, thus resulting in a further assumption of complete loss of liquid contents. Note, however, that an opportunity is given at the end of the procedure, prior to the point in time that results are stored in the ASF file, to replace the computed duration of discharge with a shorter time. This is one way in which users can adjust discharge model results to account for situations in which the discharge outlet being considered is actually above the bottom portion of the tank or container. An alternative approach would be to specify a height of liquid measured upward from the location of the expected discharge outlet and not from the bottom of the tank or container.

Another major assumption is that there is an opening somewhere in the top portion of the tank or container that permits entry of air to fill the volume previously taken by liquid discharged to the enviroment. This assumption will be valid for any container that has some sort of pressure equalization system to maintain standard atmospheric pressure above the

liquid surface while liquid is being pumped in or drawn out of the container. In cases where no such system exists or is operational, it is well to recognize that the model will estimate a much shorter discharge time duration and much higher average discharge rate than would be expected in the real world. The reason for this is that the flow of liquid will be periodically interrupted as air enters through the discharge outlet to fill the new vapor space created above the liquid surface. The situation will in many respects resemble that which occurs when a bottle or can of a soft drink is turned upside down and the liquid exits in a series of spurts rather than in a continuous and smooth flow pattern.

A final and relatively minor assumption is that the discharge outlet, be it a hole in the side of the tank or a broken pipe attached to the container, is relatively close to the container. This assumption can lead to underprediction of discharge durations and overprediction of discharge rates in cases when the discharge outlet is at the end of a complicated and/or lengthy piping system attached to the container since such piping systems produce friction that can slightly slow the flow of liquid and hence reduce the discharge rate.

12.12 DISCHARGE MENU OPTION E: PRESSURIZED LIQUID WHEN DISCHARGE LOCATION IS 4 INCHES OR LESS FROM THE TANK SURFACE

Purpose of Model

Intended for use with liquids stored at temperatures *above* their respective normal boiling points, this model estimates the *peak* rate of discharge and duration of discharge from a punctured or otherwise leaking tank or container of what must be considered a compressed liquefied gas under the specified conditions of storage. A special qualification is that the model is only appropriate for use when the discharge outlet or hole is four inches or less from the inner wall surface of the tank or container. The discharge model described under Option F below should be used if the discharge location is more than four inches distant.

Required Input Data

Primary data requirements for use of the model include:

- Normal boiling point of the liquid (°F)
- Temperature of the liquid in the tank or container (°F)
- Ambient environmental temperature (°F)
- Weight of liquid in the tank or container (lbs)
- Indication of whether or not an instantaneous spill is to assumed
- Diameter of the horizontal cylindrical tank or container (ft)
- Length of the horizontal cylindrical tank or container (ft)
- Height of liquid in the container measured from its bottom (ft)

- Diameter of the hole from which liquid will discharge (inches)
- Discharge coefficient of the hole
- Specific gravity of the liquid

As discussed in Chapter 2 of this guide, many properties of hazardous materials are a function of temperature, with one of the most important being the vapor pressure of the substance (since this property will ultimately have a major effect on the magnitude of toxic or flammable vapor dispersion threats). Consequently, for planning purposes, it is desireable to select both tank and ambient environmental temperatures among the highest that may be experienced during a typical year. In selecting these temperatures, note that the temperature of the contents inside a metal tank can often (not always) be 20°F or more higher than the ambient air temperature on a sunny day.

Prior to asking the user to provide the weight of liquid in the tank, an input parameter value that would otherwise require several manual computations, the program asks if the user desires assistance in characterizing the volume of the container and the weights, volumes, and physical states of its contents. Further details on the *Tank and Container Contents Characterization Subprogram* and its general data requirements are provided in Section 12.29 of this chapter. Use of the subprogram may result in requests for a few informational items not listed above but is nevertheless highly recommended.

Hazard evaluations for emergency planning purposes should strive to assume the worse credible conditions under which an accident may take place. In the case of the amount of liquid in the tank or container, guidance should be obtained from the owner or operator of the vessel with respect to the largest amounts that may be expected to be present. In the case of transportation vehicles, it is usually sufficient to assume that the container is at least 90% full unless other information is available.

The user may request assistance in determining the vapor pressure of the liquid at the point in time that the program asks for this parameter value. See Section 12.28 below for a description of the *Vapor Pressure Input Assistance Subprogram.*

There may be situations envisioned in which the tank or container of interest may be expected to fail in a very quick and catastrophic fashion; for example, in the event of its exposure to a major explosion or collapse due to severe structural failure. Consequently, after the user has supplied the weight of liquid in the tank, the program asks if the user wishes to assume that the spill or discharge should be assumed as being essentially instantaneous. A *yes* answer to this question will halt use of the model and result in the assumption that the entire contents of the container will be released to the environment in one minute and that the average rate of discharge will be the weight of tank contents per minute. A *no* answer will result in normal continuation of model use.

The program inherently assumes that the discharge outlet is circular in shape. In those instances where the expected shape is not expected to be circular it will be necessary to: 1) determine or estimate the area of the expected outlet in units of square inches; and 2) compute the diameter of the equivalent circle having this area. Appendix A to this guide provides assistance in this task for those who may require guidance.

The discharge coefficient of the hole is a measure of its edge characteristics that has a major and direct influence on the rate of discharge. The input parameter screen for the data item will provide guidance in selection of an appropriate value.

The specific gravity of the liquid should ideally be the value associated with the liquid at its temperature in the container or tank of concern. Note, however, that this value varies little with changes in temperature for many liquids for which this model is applicable. The specific gravity given at a temperature of 68°F (20°C) on a typical material safety data sheet will be of acceptable accuracy in most cases.

Model Results and Usage

Results of the model include the *peak* rate of liquid discharge in pounds/minute, the duration of discharge in minutes based on the peak rate, the total weight of contents discharged in pounds, and an indication of the expected physical state of the discharged material. Depending upon the material, environmental, and normal boiling point temperatures involved, the model may indicate that either an airborne mixture of gas and liquid droplets (i.e., aerosols) or liquid is being discharged.

In the case of *liquid* discharges from the container, results of the model are normally utilized by the program as input parameters to the pool area estimation methods (Hazard Model Menu Option B) available from the Hazard Assessment Model Selection Menu. In the case of airborne gas and aerosol mixture discharges from the container, the results may be utilized as necessary for input to the toxic vapor dispersion model (Hazard Model Menu Option D) and/or the vapor cloud or plume fire hazard model (Hazard Model Menu Option H) on the menu. In addition, the duration of gaseous discharge may be utilized by the flame jet model (Hazard Model Menu Option F).

Major Assumptions of the Methodology

The model assumes that the hole or other discharge outlet from which the liquid is being released in at or near the bottom of the tank for initial calculation purposes, thus resulting in a further assumption of complete loss of liquid contents. Note, however, that an opportunity is given to the user at the end of the procedure, prior to the point in time that results are stored in the ASF file, to replace the computed duration of discharge with a shorter time. This is one way in which users can adjust discharge model results to account

for situations in which the discharge outlet being considered is actually above the bottom portion of the tank or container. An alternative approach would be to specify a height of liquid measured upward from the location of the expected discharge outlet and not from the bottom of the tank or container. It is necessary to stress, however, that either of these modifications to normal program use will result in a situation in which any gas exiting the discharge outlet after completion of liquid discharge will not be accounted for in model results. This discharge of gas, which will quickly drop from a high to low rate when the tank or container is not being heated or somehow internally generating heat, will pose a downwind toxic or flammable gas hazard for a period of time that may be greater than that estimated for the liquid discharge. If the remaining liquid in the tank or container is indeed being heated, the flow of gas could be of considerable rate and duration yet incapable of being estimated via use of ARCHIE. It is for this reason that the model inherently assumes that the entire tank will empty quickly and at a high rate to provide a conservative basis for emergency planning purposes.

A second assumption is that vaporization of liquid in the tank or container to generate vapor or gas to fill the void left by escaping liquid will not result in a major thermodynamic cooling effect. A significant cooling effect would tend to lower the estimated rate of discharge and increase its duration, but this phenomena usually plays only a minor role in influencing discharge rate and duration estimates. The rate is primarily controlled by the height of the liquid in the tank above the discharge outlet location and the specific gravity of the substance.

The decision as to whether the discharged material will be a mixture of gas and aerosols or a liquid depends upon the temperature of the hazardous material in its container and the normal boiling point of the substance. An airborne mixture of gas and aerosols is assumed whenever the container content temperature exceeds the normal boiling point by 10.8°F (6°C) as a general rule of thumb. The assumption is conservative in that it may at times indicate that no liquid will reach the ground although this may indeed occur to some degree. More precise assessment of the physical characteristics of the discharged material requires knowledge of physical property data not expected to be readily available to the average user of Version 1.0 of ARCHIE and must therefore await installation of a database in this program.

12.13 *DISCHARGE MENU OPTION F: PRESSURIZED LIQUID WHEN DISCHARGE LOCATION IS MORE THAN 4 INCHES FROM THE TANK SURFACE*

Purpose of Model

Intended for use with liquids stored at temperatures *above* their respective normal boiling points, this model estimates the *peak* rate of discharge and duration of discharge at this rate from a punctured or otherwise leaking tank or container of a compressed liquefied gas. A special qualification is that the model is only appropriate for use when the discharge outlet or hole is more than four inches from the intarnal wall surface of the tank or container. The discharge model described under Option E should be used if the discharge location is four inches or less distant from the wall.

Required Input Data

Primary data requirements for use of the model include:

- Normal boiling point of the liquid (°F)
- Temperature of the liquid in the tank or container (°F)
- Ambient environmental temperature (°F)
- Weight of liquid in the tank or container (lbs)
- Indication of whether or not an instantaneous spill is to assumed
- Diameter of the horizontal cylindrical tank or container (ft)
- Length of the horizontal cylindrical tank or container (ft)
- Height of liquid in the container measured from its bottom (ft)
- Diameter of the hole from which liquid will discharge (inches)
- Discharge coefficient of the hole
- Specific gravity of the liquid

As discussed in Chapter 2 of this guide, many properties of hazardous materials are a function of temperature, with one of the most important being the vapor pressure of the substance (since this property will ultimately have a major effect on the magnitude of toxic or flammable vapor dispersion threats). Consequently, for planning purposes, it is desireable to select both tank and ambient environmental temperatures among the highest that may be experienced during a typical year. In selecting these temperatures, note that the temperature of the contents inside a metal tank can often (not always) be 20°F or more higher than the ambient air temperature on a sunny day.

The user may request assistance in determining the vapor pressure of the liquid at the point in time that the program asks for this parameter value. See Section 12.28 below for a description of the *Vapor Pressure Input Assistance Subprogram.*

Prior to asking the user to provide the weight of liquid in the tank, an input parameter value that would otherwise require several manual computations, the program asks if the user desires assistance in characterizing the volume of the container and the weights, volumes, and physical states of its contents. Further details on the *Tank and Container Contents Characterization Subprogram* and its general data requirements are provided in Section 12.29 of this chapter. Use of the subprogram may result in requests for a few informational items not listed above but is nevertheless highly recommended.

Hazard evaluations for emergency planning purposes should strive to assume the worse credible conditions under which an accident may take place. In the case of the amount of liquid in the tank or container, guidance should be obtained from the owner or operator of the vessel with respect to the largest amounts that may be expected to be present. In the case of transportation vehicles, it is usually sufficient to assume that the container is at least 90% full unless other information is available.

There may be situations envisioned in which the tank or container of interest may be expected to fail in a very quick and catastrophic fashion; for example, in the event of its exposure to a major explosion or collapse due to severe structural failure. Consequently, after the user has supplied the weight of liquid in the tank, the program asks if the user wishes to assume that the spill or discharge should be assumed as being essentially instantaneous. A *yes* answer to this question will halt use of the model and result in the assumption that the entire contents of the container will be released to the environment in one minute and that the average rate of discharge will be the weight of tank contents per minute. A *no* answer will result in normal continuation of model use.

The program inherently assumes that the discharge outlet is circular in shape. In those instances where the expected shape is not expected to be circular it will be necessary to: 1) determine or estimate the area of the expected outlet in units of square inches; and 2) compute the diameter of the equivalent circle having this area. Appendix A to this guide provides assistance in this task for those who may require guidance.

The discharge coefficient of the hole is a measure of its edge characteristics that has a major and direct influence on the rate of discharge. The input parameter screen for the data item will provide guidance in selection of an appropriate value.

The specific gravity of the liquid should ideally be the value associated with the liquid at its temperature in the container or tank of concern. Note, however, that this value varies very little with changes in temperature for many liquids for which this model is applicable. The specific gravity given at a temperature of 68°F (20°C) on a typical material safety data sheet will be of acceptable accuracy in most cases.

The specific heat capacity of the liquid is a measure of the heat necessary to raise the temperature of a unit weight of the material by one degree. Prior to request of this value, the program will provide the user an opportunity to request assistance in selection of an appropriate heat capacity value using several generalized rules-of-thumb (reproduced in Table 12.6) that require user knowledge of the chemical formula of the hazardous material being evaluated. Although the accuracy of model answers would be improved by provision of a more precise value for the substance at or near the temperature in its container, errors introduced by use of an estimation method presented by the program should not be highly significant in most (but not all) cases. Note that liquid heat capacity values provided in units of calories/gram-°C in various data bases and technical handbooks are *numerically* equivalent to values expressed in units of Btu/lb-°F.

Model Results and Usage

Results of the model include the *peak* rate of liquid discharge in pounds/minute, the duration of discharge in minutes, the total weight of contents discharged in pounds, and an indication of the expected physical state of the discharged material. Depending upon the material, environmental, and normal boiling point temperatures involved, the model may indicate that either an airborne mixture of gas and liquid droplets (i.e., aerosols) or a liquid is being discharged.

In the case of *liquid* discharges from the container, results of the model are normally utilized by the program as input parameters to the pool area estimation methods (Hazard Model Menu Option B) available from the Hazard Assessment Model Selection Menu. In the case of airborne gas and aerosol discharges from the container, the results may be utilized as necessary for input to the toxic vapor dispersion model (Hazard Model Menu Option D) and/or the vapor cloud or plume fire hazard model (Hazard Model Menu Option H) on the menu. In addition, the duration of gaseous discharge may be utilized by the flame jet model (Hazard Model Menu Option F).

Major Assumptions of the Methodology

The model assumes that the hole or other discharge outlet from which the liquid is being released is at or near the bottom of the tank for initial calculation purposes, thus resulting in a further assumption of complete loss of liquid contents. Note, however, that an opportunity is given at the end of the procedure, prior to the point in time that results are stored in the ASF file, to replace the computed duration of discharge with a shorter time. This is one way in which users can adjust discharge model results to account for situations in which the discharge outlet being considered is actually above the bottom portion of the tank or container. An alternative approach would be to specify a height of liquid measured upward from the location of the expected discharge outlet and not from the bottom of the

TABLE 12.6
ASSISTANCE DISPLAY FOR LIQUID SPECIFIC HEAT

LIQUID SPECIFIC HEAT SELECTION ASSISTANCE
• For organic materials predominantly consisting of carbon (C), hydrogen (H), oxygen (O), nitrogen (N), and/or sulfur (S), values range from 0.30 to 0.80. A value of 0.30 will usually give a conservative result and is suggested for use in the absence of better data.
• For materials containing chlorine (Cl), fluorine (F), or silicon (Si), values typically range from 0.20 to 0.40. A value of 0.20 will usually give a conservative result and is suggested for use in the absence of better data.
• For materials containing bromine (Br) or iodine (I), or organic compounds containing one or more metals such as nickel (Ni), iron (Fe), magnesium (Mg), cadmium (Cd), tin (Sn), zinc (Zn), vanadium (Vd), or titanium (Ti), values typically range from 0.10 to 0.20. A value of 0.10 will usually give an acceptable result and is suggested for use in the absence of better data.

TABLE 12.7
ASSISTANCE DISPLAY FOR VAPOR/GAS SPECIFIC HEAT RATIO

SPECIFIC HEAT RATIO SELECTION ASSISTANCE FOR GASES
• Monatomic gases are substances such as argon, neon, xenon, krypton, or helium. Such gases have only one atom in each molecule when in the gaseous state. An approximate specific heat ratio of 1.67 may be used for such gases when more precise values are not readily available.
• Diatomic gases are substances with two atoms in each molecule when in the gaseous state. Examples include oxygen (0_2), nitrogen (N_2), hydrogen (H_2), chlorine (Cl_2), and carbon monoxide (CO). An approximate specific heat ratio of 1.40 may be used when more precise values are not readily available for such gases.
• Polyatomic gases have more than two atoms in each molecule when in the gaseous state. Examples include ammonia (NH_3), propane (C_3H_8), and methyl bromide (CH_3Br). An approximate specific heat ratio of 1.30 may be used for such gases if more precise values are not readily available.

tank or container. It is necessary to stress, however, that either of these modifications to normal program use will result in a situation in which any gas exiting the discharge outlet after completion of liquid discharge will not be accounted for in model results. This discharge of gas, which will quickly drop from a high to low rate when the tank or container is not being heated or somehow internally generating heat, will pose a downwind toxic or flammable gas hazard for a period of time that may be greater than that estimated for the liquid discharge. If the remaining liquid in the tank or container is indeed being heated, the flow of gas could be of considerable rate and duration yet incapable of being estimated via this first version of ARCHIE. It is for this reason that the model inherently assumes that the entire tank will empty quickly and at a high rate to provide a conservative basis for emergency planning purposes.

A second assumption is that vaporization of liquid in the tank or container to generate vapor or gas to fill the void left by escaping liquid will not result in a major thermodynamic cooling effect. A significant cooling effect would tend to lower the estimated rate of discharge and increase its duration, but this phenomena usually plays only a minor role in influencing discharge rate and duration estimates. The rate is primarily controlled by the height of the liquid in the tank above the discharge outlet location and the specific gravity of the substance.

The decision as to whether the discharged material will be a mixture of gas and aerosols or a liquid depends upon the temperature of the hazardous material in its container and the normal boiling point of the substance. An airborne mixture of gas and aerosols is assumed whenever the container content temperature exceeds the normal boiling point by 10.8°F (6°C) as a general rule of thumb. The assumption is conservative in that it may at times indicate that no liquid will reach the ground although this may indeed occur to some degree. More precise assessment of the physical characteristics of the discharged material requires knowledge of physical property data not expected to be readily available to the average user of Version 1.0 of ARCHIE and must therefore await installation of a database in this program.

12.14 DISCHARGE MENU OPTION G: PRESSURIZED GAS RELEASE FROM ANY CONTAINER

Purpose of Model

The primary purpose of this model is to estimate the *peak* rate of discharge and duration of discharge at this rate when a compressed gas is being released to the atmosphere from a tank or other container that is not a long distance pipeline.

The model may be used in a very approximate fashion to evaluate gas or vapor discharge rates and durations when a runaway exothermic chemical reaction of some kind takes place in the container. Use of the model for the latter purpose requires that the user provide the program with suitably high values for the pressure and temperature in the tank (accuracy in providing these values is not extremely important) and an appropriate molecular weight and ratio of specific heats for the gas *actually* being discharged. If the reaction involves polymerization of one or more substances, some thought should be given to reducing the weight of hazardous material(s) presumed to be in the tank by at least 10 to 33% since the portion that polymerizes during the reaction is unlikely to be discharged to the atmosphere as a gas or vapor.

Required Input Data

Primary data requirements for use of the model include:

- Normal boiling point of the liquid (°F)
- Temperature of the gas and/or liquid in the container (°F)
- Ambient environmental temperature (°F)
- Pressure of the gas in the container (psia)
- Weight of hazardous material in the container (lbs)
- Indication of whether or not an instantaneous spill is to assumed
- Diameter of the hole from which gas will discharge (inches)
- Discharge coefficient of the hole
- Ratio of specific heats (C_p/C_v) for the gas
- Height of liquid in the container measured from its bottom (ft)
- Molecular weight of the gas and/or liquid

As discussed in Chapter 2 of this guide, many properties of hazardous materials are a function of temperature, with one of the most important being the vapor pressure of the substance (since this property will ultimately have a major effect on the magnitude of toxic or flammable vapor dispersion threats). Consequently, for planning purposes, it is desireable to select both tank and ambient environmental temperatures among the highest that may be experienced during a typical year. In selecting these temperatures, note that the temperature of the contents inside a metal tank can often (not always) be 20°F or more higher than the ambient air temperature on a sunny day.

The user may request assistance in determining the pressure of the gas at the point in time that the program asks for this parameter value. See Section 12.28 below for a description of the *Vapor Pressure Input Assistance Subprogram.* Note, however, that some compressed gas containers may normally be at temperatures in excess of the *critical temperature* of the gas. This is a temperature above which the substance cannot exist in a

liquid state regardless of the pressure applied. Consequently, the term *vapor pressure* no longer has meaning when a material is at a temperature above its critical temperature, the vapor pressure input assistance subprogram is no longer applicable, and it is necessary for the user to specify any required pressures.

Prior to asking the user to provide the weight of hazardous material in the tank, an input parameter value that would otherwise require several manual computations, the program asks if the user desires assistance in characterizing the volume of the container and the weights, volumes, and physical states of its contents. Further details on the *Tank and Container Contents Characterization Subprogram* and its general data requirements are provided in Section 12.29 of this chapter. Use of the subprogram may result in requests for a few informational items not listed above but is nevertheless highly recommended.

Hazard evaluations for emergency planning purposes should strive to assume the worse reasonable and credible conditions under which an accident may take place. In the case of the amount of liquid in the tank or container, guidance should be obtained from the owner or operator of the vessel with respect to the largest amounts that may be expected to be present. In the case of transportation vehicles, it is usually sufficient to assume that the container is at least 90% full unless other information is available.

There may be situations envisioned in which the tank or container of interest may be expected to fail in a very quick and catastrophic fashion; for example, in the event of its exposure to a major explosion or collapse due to severe structural failure. Consequently, after the user has supplied the weight of liquid in the tank, the program asks if the user wishes to assume that the spill or discharge should be assumed as being essentially instantaneous. A *yes* answer to this question will halt use of the model and result in the assumption that the entire contents of the container will be released to the environment in one minute and that the average rate of discharge will be the weight of tank contents per minute. A *no* answer will result in normal continuation of model use.

The program inherently assumes that the discharge outlet is circular in shape. In those instances where the expected shape is not expected to be circular it will be necessary to: 1) determine or estimate the area of the expected outlet in units of square inches; and 2) compute the diameter of the equivalent circle having this area. Appendix A to this guide provides assistance in this task for those who may require guidance.

The discharge coefficient of the hole is a measure of its edge characteristics that has a major and direct influence on the rate of discharge. The input parameter screen for the data item will provide guidance in selection of an appropriate value.

The ratio of specific heats for the compressed gas or vapor is a thermodynamic property related to the amount of heat necessary to increase the temperature of a unit weight of gas or vapor by one degree under specified conditions. Prior to request of this value, the program will provide the user an opportunity to request assistance in selection of an appropriate specific heat ratio using several generalized rules-of-thumb (reproduced in Table 12.7) that require user knowledge of the chemical formula of the hazardous material being evaluated. Although the accuracy of model answers would be improved by provision of a more precise value for the substance at or near the temperature in its container, errors introduced by use of the property estimation methods provided by the program should not be highly significant in most (but not all) cases.

The program provides assistance (upon request of the user) in computing the molecular weight of the discharged substance from its chemical formula via a procedure similar to that described in Section 2.8 of the guide.

Model Results and Usage

Results of the model include the *peak* dicharge rate of compressed gas or vapor discharge in pounds/minute, the duration of discharge in minutes *at this peak rate*, the total weight of contents discharged in pounds, and the physical state of the discharged material (which will always be *gas* when this particular discharge model is used). It is vital that the user read and understand the assumptions made during formulation and use of this model.

Results may be utilized as necessary for input to the toxic vapor dispersion model (Hazard Model Menu Option D) and/or the vapor cloud or plume fire hazard model (Hazard Model Menu Option H) on the menu. In addition, the duration of gas discharge may be utilized by the flame jet model (Hazard Model Menu Option F).

Major Assumptions of the Methodology

As a compressed gas or vapor is discharged from a tank or other container *only* containing the material in its gaseous state, the loss of gas to the atmosphere together with thermodynamic cooling effects associated with gas expansion will typically result in a rapid decrease of the discharge rate with time. Since this model bases its results solely on the initial peak discharge rate of the gas or vapor, it will consistently overestimate the discharge rate and underestimate the duration of discharge. The overestimation of discharge rate may result in overestimation of downwind toxic or flammable gas hazard zones (which is not bad for emergency planning purposes) and underestimation of hazard durations (which must be kept clearly in mind) when Options D and H are respectively chosen from the Hazard Assessment Model Selection Menu. Similarly, the flame jet model available as Option G on the menu may underestimate the time duration of the flame jet on occasion.

When the tank contains a liquefied compressed gas and the gas discharge model is being used to evaluate a discharge of gas or vapor from the *head* space of the tank (i.e., the volume above the liquid surface), there is a excellent chance that the computed peak discharge rate will vary even more significantly from the actual average discharge rate, primarily because the model assumes that all of the tank or container contents, *including the liquid portion*, will discharge at the computed peak *gas* discharge rate. In actuality, there may be cases when thermodynamic cooling effects will rapidly cool the liquid to a temperature near its boiling point, at which time flow from the tank will greatly decrease and even possibly stop while the tank still contains a considerable amount of hazardous material.

The assumptions described above can be restated in a different fashion by noting that the model formulation inherently assumes that sufficient heat is entering the tank or container from the external environment, or is being internally generated due to an internal chemical reaction of some kind, to offset any thermodynamic cooling effects and to maintain the gas discharge rate near its peak value. Since this model may be used at times to evaluate discharge rates and durations under these "worst case" conditions, and any number of accident scenarios may involve the potential for exposure of the tank or container to an external fire or an internal exothermic chemical reaction, the assumptions clearly have advantages as well as disadvantages.

The primary reason why it was necessary to provide a model that may provide inaccurate results at times (*but results that tend more often than not to overestimate the hazards of the release*) is that a more rigorous and formal analysis procedure would necessitate a substantially larger program and chemical physical property data not readily available to the expected average user of Version 1.0 of ARCHIE.

12.15 DISCHARGE MENU OPTION H: RELEASE FROM A PRESSURIZED LIQUID PIPELINE

Purpose of Model

This *highly simplified* model is intended to provide an estimate of the discharge rate and duration expected when a long distance pipeline *totally filled with liquid* completely ruptures at some point along its route. No distinction is made between liquids that are below or above their respective normal boiling points. Since the topography of the land surface over the pipeline route will greatly influence model results, and since the topography is likely to vary over the route, it may be necessary to use this model several times for any given pipeline, each time assuming a different pipeline break location near sensitive environmental areas or population zones.

Required Input Data

Data requirements of the model include the following input parameter values, some of which are unusual. The program makes a special attempt to assist the user in selecting a value wherever an unusual item of information is required, but does expect the user to have a rather complete understanding of pipeline, pipeline contents, and pipeline route characteristics. Note, however, that the relatively uninformed user should not hesitate to use the model. Input parameter values not known can be guessed at and modified at a later time. An opportunity is always provided to discard the results of any analysis when it is completed.

- Normal boiling point of the liquid (°F)
- Temperature of the liquid in the pipeline (°F)
- Ambient environmental temperature (°F)
- Molecular weight of the liquid
- Specific gravity of the liquid
- Vapor pressure of the liquid in the pipeline (psia)
- Length of pipeline that will empty in the event of a rupture (ft)
- Diameter of the pipeline (inches or feet)
- Maximum height of the liquid column in the line that will empty (ft)
- Total pressure of the liquid in the pipeline (psia)
- Pipeline shutdown time if a discharge is detected (minutes)
- Indication of whether line breaks at one end or along route
- Pumping rate of liquid through the pipeline (lbs/minute)
- Discharge coefficient of the hole

As discussed in Chapter 2 of this guide, many properties of hazardous materials are a function of temperature, with one of the most important being the vapor pressure of the substance (since this property will ultimately have a major effect on the magnitude of toxic or flammable vapor dispersion threats). Consequently, for planning purposes, it is desireable to select both pipeline and ambient environmental temperatures among the highest that may be experienced during a typical year.

The program provides assistance (upon request of the user) in computing the molecular weight of the discharged substance from its chemical formula via a procedure similar to that described in Section 2.8 of the guide.

The specific gravity of the liquid should ideally be the value associated with the liquid at its temperature in the container or tank of concern. Note, however, that this value varies very little with changes in temperature for the vast majority of liquids for which this model is applicable. The specific gravity given on a typical material safety data sheet (MSDS) will be acceptable in most cases.

The user may request assistance in determining the vapor pressure of the liquid at the point in time that the program asks for this parameter value. See Section 12.28 below for a description of the *Vapor Pressure Input Assistance Subprogram.*

The question regarding the length of the pipeline that will empty in the event of a rupture can be rather tricky when the line travels up and down various hills and valleys. The length that empties will not necessarily be the total length of the pipeline from its beginning to its end.

Picture a pipeline that starts at the top of one hill, travels down to the floor of a valley, and then travels up the side of another hill to its top. If the pipeline breaks *at the top* of either hill, and we assume there is no pressure in the line for the moment, then it can be understood that little if any of the pipeline contents will escape to the environment. Alternatively, picture what would happen if the pipeline were to break *on the floor* of the valley. In this case, all contents of both resulting pipeline sections from the top of one hill to the top of the second will empty onto the valley floor. Thus, it is important to carefully consider the topography of the land and specific potential accident sites when dealing with long pipelines. A tracing of the route on a topographical map of the area can be invaluable in estimating appropriate pipeline lengths. It is prudent, however, to first ask the pipeline owner or operator if a discharge volume analysis of any kind was conducted prior to installation of the line since these analyses are sometimes necessary for compliance with environmental impact reporting requirements associated with the obtainment of permits from regulatory authorities.

A question related to the desired length of pipeline asks the user for the maximum height of the liquid column in the pipeline that will empty upon pipeline rupture. This is the maximum vertical height between the assumed point of discharge and the highest point within the pipeline from which liquid is expected to empty. In the second example presented above, it would be the vertical height from the top of the highest hill to the floor of valley where the pipeline rupture is expected. A highly accurate estimate is not necessary.

The next question essentially requests the user to provide the total pressure of the liquid in the pipeline. Provision of an answer requires the user to realize that the force that moves the liquid from one end of the pipeline to the other is the pressure mechanically provided by various pumping stations along the route. This pressure can be considerable and far above the simple vapor pressure of the liquid as it is *pushed* up various hills. Although the program uses this pressure in units of psia, the user is given five sets of units to choose among while providing an answer to the question.

Many pipeline systems have sensors and alarms that alert operators to the fact that the pipeline has developed a major leak and permit them to shutdown pumping stations manually, while others have systems that act automatically to shutdown pumps. Quicker

shutdowns obviously result in less loss of pipeline contents since the pumps will cease to push the liquid through the line. Thus, even a rough estimate of how long it will require the owner or operator of the line to detect and act upon a major pipeline break will help improve the accuracy of analysis results. This information should be readily available from pipeline owners or operators.

If a pipeline breaks or ruptures at one end, then the liquid will be released from one open end of the line. Conversely, if the line breaks along its travel path, there could conceivably be two open ends of the line from which liquid will flow, thus increasing the discharge rate and reducing the duration of discharge. It follows that the program requires some indication of whether the discharge will involve one or two ends of the pipeline.

During the elapsed time between the instant that the pipeline breaks or ruptures and the pumps are shut down, there will be some period of time in which liquid continues to spill from the line due to continued pumping. Consequently, the program asks the user for the normal flowrate of liquid through the line under normal operating conditions. This also is an item of information that should be readily available from the owner or operator of the line. Although the program will use this rate internally in units of pounds per minute, the user is given a choice of five sets of units in which to provide an answer.

The discharge coefficient of the hole is a measure of its edge characteristics that has a major and direct influence on the rate of discharge. The input parameter screen for the data item will provide guidance in selection of an appropriate value. The proper value for pipeline breaks will usually be 0.62.

Model Results and Usage

In cases where the pumping shutdown time is specified as zero, the program will provide the average discharge rate in pounds per minute, the duration of discharge in minutes, the total weight of discharged material in pounds, and an indication of whether the pipeline contents will be discharged as an airborne mixture of gas and small liquid droplets (i.e., aerosols) or as a liquid. When the pumping shutdown time is greater than zero, a brief paragraph will describe the discharge rates and times associated with various time periods and provide an overall average rate and duration of discharge for use by subsequent models.

In the case of *liquid* discharges from the pipeline, results of the model are normally utilized by the program as input parameters to the pool area estimation methods (Hazard Model Menu Option B) available from the Hazard Assessment Model Selection Menu. In the case of gas and airborne aerosol discharges from the container, the results may be utilized as necessary for input to the toxic vapor dispersion model (Hazard Model Menu Option D)

and/or the vapor cloud or plume fire hazard model (Hazard Model Menu Option H) on the menu. In addition, the duration of gaseous discharge may be utilized by the flame jet model (Hazard Model Menu Option F).

Major Assumptions of the Methodology

As noted earlier, this is a highly simplified model for estimating discharge rates and durations from liquid pipelines.

The first simplifying assumption made, one that is *not* highly consequential, is that the liquid experiences no friction as it flows through the pipeline. In reality, the walls of the line will produce friction that will tend to slow the outward flow of liquid when a break occurs. Inclusion of friction into the model, however, would not produce significantly decreased discharge rates except under very unusual circumstances for the types of full line break scenarios being considered.

A major assumption that can indeed adversely affect the accuracy of results involves the inherent assumption that the liquid in the pipeline does not contain a dissolved gas under high pressure and is not itself a liquefied compressed gas. Liquids with dissolved gases under pressure (such as a crude oil pipeline containing significant amounts of dissolved natural gas) will experience what is sometimes referred to as a "champagne" effect upon rupture. In other words, expansion of the dissolved gases when the pressure is relieved may cause a gushing forth of pipeline contents to the extent that the total amount of liquid discharged will be greater than that normally predicted by the model. Similarly, liquefied compressed gases may erupt from the pipeline in a manner not fully considered by the model.

The decision as to whether the discharged material will be a mixture of gas and aerosols or a liquid depends upon the temperature of the hazardous material in its container and the normal boiling point of the substance. An airborne mixture of gas and aerosols is assumed whenever the container content temperature exceeds the normal boiling point by 10.8°F (6°C) as a general rule of thumb. The assumption is conservative in that it may at times indicate that no liquid will reach the ground although this may indeed occur to some degree. More precise assessment of the physical characteristics of the discharged material requires knowledge of physical property data not expected to be readily available to the average user of Version 1.0 of ARCHIE and must therefore await installation of a database in this program.

12.16 *DISCHARGE MENU OPTION I: RELEASE FROM A PRESSURIZED GAS PIPELINE*

Purpose of Model

This model is intended to provide an estimate of the discharge rate and duration expected when a pressurized long distance pipeline *totally filled with a gaseous substance* develops a leak or completely ruptures at some point along its route. The model cannot be used for pipelines containing both liquid and gas.

Required Input Data

Data requirements of the model include the following input parameter values:

- Normal boiling point of the substance (°F)
- Temperature of the gas in the pipeline (°F)
- Ambient environmental temperature (°F)
- Vapor pressure of the gas in the pipeline (psia)
- Molecular weight of the gas
- Length of the pipeline from beginning to end (ft)
- Diameter of the pipeline (inches or feet)
- Actual pressure of the gas in the pipeline where applicable (psia)
- Indication of whether small hole or full rupture occurs in line
- Diameter of the hole from which gas will discharge (inches)
- Discharge coefficient of the hole
- Ratio of specific heats (C_p/C_v) for the gas

As discussed in Chapter 2 of this guide, many properties of hazardous materials are a function of temperature, with one of the most important being the vapor pressure of the substance (since this property will ultimately have a major effect on the magnitude of toxic or flammable vapor dispersion threats). Consequently, for planning purposes, it is desireable to select both pipeline and ambient environmental temperatures among the highest that may be experienced during a typical year.

The user may request assistance in determining the vapor pressure of the gas at the point in time that the program asks for this parameter value. See Section 12.28 below for a description of the *Vapor Pressure Input Assistance Subprogram.* Note, however, that many gas pipelines, especially those conveying fuel gases with low normal boiling points, typically operate at temperatures in excess of the *critical temperature* of the gas. This is a temperature at or above which the substance cannot exist in a liquid state regardless of the pressure applied and permits pipeline operators to compress the gas to high pressures without causing liquefication. Consequently, the term *vapor pressure* no longer has meaning when a material

is at a temperature above its critical temperature, the vapor pressure input assistance subprogram is no longer applicable, and it is necessary for the user to specify the pressure in the pipeline using information obtained from the pipeline owner or operator. For purposes of checking whether or not the temperature of the gas in the pipeline is above or below the critical temperature, without actually asking for this value, the program estimates the critical temperature of the gas as being 1.8 times the normal boiling point temperature of the substance expressed in degrees Kelvin. (Technically oriented users may remember that the rather common rule-of-thumb being applied typically uses a multiplication factor of 1.65 instead of 1.8. The higher factor was chosen to prevent the program from erroneously assuming the critical temperature has been exceeded when the actual temperature is somewhat greater than the value estimated when a factor of 1.65 is applied.)

In those cases in which the critical temperature of the gas has *not* been exceeded, there is a possibility that the pipeline might be operated at a pressure below the vapor pressure of the material being transported. Although this is not likely, the user is given the opportunity to specify the actual pressure in the pipeline. Be advised that input of a pressure that exceeds the vapor pressure of the pipeline gas at its specified temperature will result in a warning message to the user to the effect that the pipeline contains liquid. Since the model is only applicable when there is no liquid in the line, it will be necessary for the user to either revise the pipeline pressure to an acceptable value (i.e., one at or below the specified vapor pressure) or to choose the liquid pipeline model for use (Discharge Menu Option H). As noted above, neither of the available pipeline models can cope with a situation in which the pipeline contains both gas and liquid.

The program provides assistance (upon request of the user) in computing the molecular weight of the discharged substance from its chemical formula via a procedure similar to that described in Section 2.8 of the guide.

The program gives the user the option of specifying that: 1) a relatively small hole should be assumed to occur in the pipeline; 2) the line should be assumed to break completely at one end; or 3) the line should be assumed to break completely at some point along its route of travel. The diameter of the discharge outlet hole will only be requested if the first option is chosen.

The program inherently assumes that the discharge outlet is circular in shape. In those instances where the expected shape is not expected to be circular it will be necessary to: 1) determine or estimate the area of the expected outlet in units of square inches; and 2) compute the diameter of the equivalent circle having this area. Appendix A to this guide provides assistance in this task for those who may require guidance.

The discharge coefficient of the hole is a measure of its edge characteristics that has a major and direct influence on the rate of discharge. The input parameter screen for the data item will provide guidance in selection of an appropriate value. The proper value will usually be 0.62 for a leaking or ruptured pipeline.

The ratio of specific heats for the compressed gas or vapor is a thermodynamic property related to the amount of heat necessary to increase the temperature of a unit weight of gas or vapor by one degree under specified conditions. Prior to request of this value, the program will provide the user an opportunity to request assistance in selection of an appropriate specific heat ratio using several generalized rules-of-thumb (reproduced in Table 12.7) that require user knowledge of the chemical formula of the hazardous material being evaluated. Although the accuracy of model answers would be improved by provision of a more precise value for the substance at or near the temperature in its container, errors introduced by use of the property estimation methods provided by the program should not be highly significant in most (but not all) cases.

Model Results and Usage

Results of the model include the *peak* rate of gas discharge in pounds/minute (adjusted in the case of full line break scenarios), the duration of discharge in minutes at the computed rate of discharge, the total weight of contents discharged in pounds, and the physical state of the discharged material (which will always be *gas* when this particular discharge model is used).

To be realized is that the initial peak rate of gas discharge will drop in magnitude *extremely* rapidly in any scenario involving a full break or rupture of the pipeline. In order to avoid *gross* overestimation of the discharge rate and underestimation of the discharge duration in such cases, the model provides a rate of discharge that is 75% of the initial peak discharge rate. The impact of the adjustment should not be cause for concern since the model will in all likelihood continue to overestimate the discharge rate and this is not undesireable for emergency planning purposes.

Results of the model may be utilized as necessary for input to the toxic vapor dispersion model (Hazard Model Menu Option D) and/or the vapor cloud or plume fire hazard model (Hazard Model Menu Option H) on the menu. In addition, the duration of gas discharge may be utilized by the flame jet model (Hazard Model Menu Option F).

Major Assumptions of the Methodology

The first simplifying assumption made, one that is *not* highly consequential, is that the flow of gas is not hindered by friction. In reality, the walls of the pipeline will produce some degree of friction that will tend to slow the discharge rate.

A second assumption is that the model assumes that thermodynamic cooling effects will also not reduce the discharge rate of gas.

12.17 HAZARD MODEL MENU OPTION B: POOL AREA ESTIMATION METHODS

Purpose of Methods

In the event of a discharge that results in formation of a pool of liquid on the ground, it is necessary to obtain an estimate of the area of the pool. This estimate is required by the pool evaporation (Hazard Model Menu Option C) that estimates the rate of vapor evolution to the atmosphere and by the liquid pool fire model (Hazard Model Menu Option E) that estimates the height of the flame and surrounding hazard zones.

Required Input Data

Use of the model requires the following information.

- Molecular weight of the liquid
- Specific gravity of the liquid
- Discharge rate of the liquid from its container (lbs/minute)
- Duration of liquid discharge (minutes)
- Normal boiling point of the liquid (°F)
- Temperature of the liquid in its container (°F)
- Ambient environmental temperature (°F)
- Wind velocity (mph)
- Vapor pressure of the liquid at ambient temperature (mm Hg)
- Area to which the liquid may be restricted if a secondary containment system is present (ft^2)
- Other input parameter values discussed below

The program provides assistance (upon request of the user) in computing the molecular weight of the discharged substance from its chemical formula via a procedure similar to that described in Section 2.8 of the guide.

The specific gravity of the liquid should ideally be the value associated with the liquid at its temperature in the container or tank of concern. Note, however, that this value varies very little with changes in temperature for the vast majority of liquids for which this model is applicable. The specific gravity given on a typical material safety data sheet (MSDS) will be acceptable in most cases.

The liquid discharge rate and duration of discharge are usually computed via use of an appropriate model from the Discharge Model Selection Menu. Any attempt to estimate pool areas before these input parameters have been computed will result in a warning to the user and a question as to whether he or she wishes to continue the analysis.

As discussed in Chapter 2 of this guide, many properties of hazardous materials are a function of temperature, with one of the most important being the vapor pressure of the substance (since this property will ultimately have a major effect on the magnitude of toxic or flammable vapor dispersion threats). Consequently, for planning purposes, it is desireable to select both tank and ambient environmental temperatures among the highest that may be experienced during a typical year. In selecting these temperatures, note that the temperature of the contents inside a metal tank can often (not always) be 20°F or more higher than the ambient air temperature on a sunny day. Even when not higher in the container, the temperature of the liquid may increase upon spillage onto a hot surface or when exposed to the sun (particularly when the vapor pressure of the material is relatively low and evaporative cooling does not play a major role).

Assistance in selection of a wind velocity that is consistent with the atmospheric stability class specification that will be required by one or more subsequent models is provided during model use (upon request of the user) by display of the class selection chart (reproduced here in Table 12.8). The longest downwind hazard distances along the centerline of the wind direction are usually obtained when stability class F is specified, and this is usually a good choice for general emergency planning purposes -- as is a wind velocity specification of 4.5 mph. However, be advised that there may be exceptions to this general rule when an evaporating liquid pool is the source of hazardous vapor emissions. Higher wind velocities typically produce greater evaporation rates, yet are usually associated with atmospheric stability classes other than F. Thus, the actual *worse case* for toxic vapor dispersion hazard assessments may involve a different combination than suggested above for some materials. In the absence of more precise historical meterological data for the region of concern, an atmospheric stability class of D together with a wind velocity of about 10 mph can be assumed to evaluate threats under more typical atmospheric conditions. (Note: The wind velocity and atmospheric stability class are not always used by these models but are always requested. They will definitely be needed by subsequent models so this poses no additional burden on the user.)

The user may request assistance in determining the vapor pressure of the liquid at the point in time that the program asks for this parameter value. See Section 12.28 below for a description of the *Vapor Pressure Input Assistance Subprogram.*

TABLE 12.8
ATMOSPHERIC STABILITY CLASS SELECTION TABLE

A -- Extremely Unstable Conditions
B -- Moderately Unstable Conditions
C -- Slightly Unstable Conditions
D -- Neutral Conditions*
E -- Slightly Stable Conditions
F -- Moderately Stable Conditions

	Daytime Conditions			Nighttime Conditions	
	Strength of sunlight				
Surface Wind Speed, mph	**Strong**	**Moderate**	**Slight**	**Thin Overcast > or = 4/8 Cloudiness****	**< or = 3/8 Cloudness**
Less than 4.5	A	A - B	B	-	-
4.5 - 6.7	A - B	B	C	E	F
6.7 - 11.2	B	B - C	C	D	E
13.4	C	C - D	D	D	D
Greater than 13.4	C	D	D	D	D

*Applicable to heavy overcast conditions day or night

**Degree of Cloudiness = Fraction of sky above horizon covered by clouds.

Many facilities install secondary containment systems in the form of dikes, curbs, sumps, or pits designed to restrict and contain the spreading of discharged liquids in the event of an accidental spill. The program will ask if such a system is present. If the answer is *yes*, the program will next ask the user to provide an estimate of the area to which liquid spreading will be restricted.

In the event that the program decides it best to assume that the liquid will boil upon its release to the environment, it will directly compute the area of the boiling pool. In all other cases, the program will first estimate the maximum credible pool area for non-boiling but potentially volatile liquid pools based on the information provided. It will then proceed to a menu that provides the user with a variety of options for specifying or estimating the expected pool area.

Once the area of the evaporating or potentially boiling pool has been determined, it next becomes necessary (*only* in the case of combustible or flammable liquids) to estimate the area of the burning pool that will occur if the liquid is ignited. This first involves a question to the user as to whether he or she wishes to assume the liquid is ignited immediately upon release or after the pool has attained its maximum size, with the latter choice resulting in the larger and more hazardous fire. The program will then proceed to estimate the area of the resulting burning pool.

Model Results and Usage

Use of the model provides two results. The first is the approximate area of the expected boiling or evaporating liquid pool. The second, *only* provided in the case of combustible or flammable liquids, is the estimated area of the burning pool.

The boiling or evaporating pool area is typically utilized as an input parameter to the liquid pool evaporation rate and duration estimation model (Hazard Model Menu Option C). In addition, this area is used to adjust estimated initial evacuation zone widths resulting from use of the toxic vapor dispersion model (Hazard Model Menu Option D). The estimated area of the burning pool is normally utilized as an input parameter to the liquid pool fire model (Hazard Model Menu Option E).

Major Assumptions of the Methodologies

Estimation of pool areas resulting from liquid spills is one of the most difficult and error prone aspects of accident scenario evaluations for hazardous materials, except in those cases in which the discharge source is confined by a secondary containment system of known dimensions and the liquid will cover the the bottom of the confinement area. Unconfined spills rarely occur in a location where the ground surface is flat and impermeable to liquids. Rather, in the real world, and particularly in transportation accidents, the spilled liquid will

usually follow rainwater drainage paths while simultaneously vaporizing, burning, and/or soaking into the ground. Thus, this model is actually comprised of a number of different estimation procedures, all designed to ease the task of the program user in obtaining a reasonable though not always highly accurate answer.

In the case of liquids that are expected to boil upon release to the environment, the program uses a relatively simple and crude methodology to estimate the rate at which the liquid will vaporize. It then uses this rate in conjunction with a liquid spreading model to estimate the desired pool area. Various assumptions made are described in Appendix B.

For non-boiling liquids, the program first uses an evaporation rate model in conjunction with a pool spreading model to estimate the pool area that would be necessary in order for the total vaporization rate of the spilled liquid to approximate the discharge rate of the liquid from its tank or other container. The result is a maximum credible pool area that provides an upper bound that cannot be exceeded. The program then provides the user various options for estimation of a more accurate pool area. Assumptions of these procedures are again of a rather technical nature and require reference to Appendix B of this guide.

Burning pool areas are determined in a fashion similar to that used for boiling pools with the exception that the vaporization rate of the pool is replaced with an estimate of the rate at which the liquid will burn.

12.18 HAZARD MODEL MENU OPTION C: POOL EVAPORATION RATE AND DURATION ESTIMATES

Purpose of Methods

Once the area of a boiling or evaporating pool of liquid has been estimated by the above model or provided by the user, it next becomes necessary to obtain an estimate of the total rate at which at which potentially hazardous vapors will evolve from the pool and the duration of vapor evolution.

Required Input Data

Input parameter values that are most commonly requested by the program are listed below. If the liquid is among a small group of substances with an extremely low normal boiling point, only the boiling point, the discharge rate of the liquid in pounds per minute, and the duration of discharge in minutes will be requested.

- Normal boiling point of the liquid (°F)
- Molecular weight of the liquid
- Specific gravity of the liquid

- Temperature of the liquid in its container (°F)
- Ambient environmental temperature (°F)
- Vapor pressure of the liquid at ambient temperature (mm Hg)
- Area of the evaporating or boiling pool of liquid (ft^2)
- Total weight of discharged liquid (lbs)
- Atmospheric stability class (A to F)
- Wind velocity (mph)

The program provides assistance (upon request of the user) in computing the molecular weight of the discharged substance from its chemical formula via a procedure similar to that described in Section 2.8 of the guide.

The specific gravity of the liquid should ideally be the value associated with the liquid at its temperature in the container or tank of concern. Note, however, that this value varies very little with changes in temperature for the vast majority of liquids for which this model is applicable. The specific gravity given on a typical material safety data sheet (MSDS) will be acceptable in most cases.

As discussed in Chapter 2 of this guide, many properties of hazardous materials are a function of temperature, with one of the most important being the vapor pressure of the substance (since this property will ultimately have a major effect on the magnitude of toxic or flammable vapor dispersion threats). Consequently, for planning purposes, it is desireable to select both tank and ambient environmental temperatures among the highest that may be experienced during a typical year. In selecting these temperatures, note that the temperature of the contents inside a metal tank can often (not always) be 20°F or more higher than the ambient air temperature on a sunny day. Even when not higher in the container, the temperature of the liquid may increase upon spillage onto a hot surface or when exposed to the sun (particularly when the vapor pressure of the material is relatively low and evaporative cooling does not play a major role).

The user may request assistance in determining the vapor pressure of the liquid at the point in time that the program asks for this parameter value. See Section 12.28 below for a description of the *Vapor Pressure Input Assistance Subprogram.*

The area of the evaporating or boiling pool is usually computed via use of the pool area estimation method listed as Option B on the Hazard Assessment Model Selection Menu. The total weight of spilled liquid is usually determined via use of one of the models available from the Discharge Model Selection Menu. Any attempt to use this model before these parameters have been estimated by a prior model will result in a warning to the user and a question as to whether he or she wishes to continue the analysis.

Assistance in selection of the appropriate atmospheric stability class and a wind velocity consistent with this class is provided (upon request of the user) by reproduction of the class selection chart (reproduced here in Table 12.8). The longest downwind hazard distances along the centerline of the wind direction are usually obtained when stability class F is specified, and this is usually a good choice for general emergency planning purposes -- as is a wind velocity specification of 4.5 mph. However, be advised that there may be exceptions to this general rule when an evaporating liquid pool is the source of hazardous vapor emissions. Higher wind velocities typically produce greater evaporation rates, yet are usually associated with atmospheric stability classes other than F. Thus, the actual *worst case* for toxic vapor dispersion hazard assessments may involve a different combination than suggested above for some materials. In the absence of more precise historical meterological data for the region of concern, an atmospheric stability class of D together with a wind velocity of about 10 mph can be assumed to evaluate threats under more typical atmospheric conditions. (Note: The wind velocity and atmospheric stability class are not always used by this model but are always requested. They will definitely be needed by subsequent models so this poses no additional burden on the user.)

Model Results and Usage

Results of the model include the rate of vapor evolution into the atmosphere in pounds per minute and the duration of vapor evolution in minutes. These results are typically utilized as necessary as input parameter values to the toxic vapor dispersion model (Hazard Model Menu Option D) and/or the vapor cloud or plume fire hazard model (Hazard Model Menu Option H).

Major Assumptions of the Methodologies

As in the case of pool area estimation, estimation of pool vaporization rates and durations from liquid spills is one of the most difficult and error prone aspects of accident scenario evaluations for hazardous materials. Although relatively sophisticated and accurate estimation methods have been developed and validated in recent years, they unfortunately require knowledge of chemical property data that are not always readily available and/or entail complex algorithms that demand excessive computation times on typical personal computers. Appendix B describes the rather unusual and relatively simple and crude methodology employed by ARCHIE. Be advised that answers will not be highly accurate but will be in the correct "ballpark" for most cases. Only occasionally should vaporization rates be underestimated.

12.19 HAZARD MODEL MENU OPTION D: TOXIC VAPOR DISPERSION MODEL

Purpose of Model

The discharge, emission, or release of a toxic gas or vapor to the atmosphere has the potential to pose an inhalation hazard to downwind populations under a wide variety of circumstances. The purpose of this model is to provide an estimate of the dimensions and characteristics of the initial downwind zone that may require protective action in the event of a hazardous material discharge.

Although primarily designed for gas or vapor releases, the model can be used in a very approximate fashion for discharges of fine dusts or powders to the atmosphere. In such cases, the user will be required to estimate and provide the program with the rate at which these materials are emitted to the atmosphere and the duration of this emission.

Required Input Data

The model requires eight input parameter values, these being:

- Molecular weight of the toxic substance
- Toxic vapor limit selected by the user (ppm, mg/m^3, or gm/m^3)
- Discharge height of the vapor or gas above groundlevel (ft)
- Atmospheric stability class (A to F)
- Wind velocity (mph)
- Temperature of the toxic substance in its container (°F)
- Ambient environmental temperature (°F)
- Vapor/gas emission rate (lbs/minute)
- Duration of vapor/gas emission (minutes)

The program provides assistance (upon request of the user) in computing the molecular weight of the discharged substance from its chemical formula via a procedure similar to that described in Section 2.8 of the guide.

Selection of an appropriate toxic vapor limit is discussed in Chapter 6. Note that the program will provide you with a choice of units in which this toxic limit may be expressed. All subsequent presentations of results, however, will utilize units of parts per million (ppm) by volume in air.

Assistance in selection of the appropriate atmospheric stability class and a wind velocity consistent with this class is provided (upon request of the user) by reproduction of the class selection chart (reproduced here in Table 12.8). The longest downwind hazard distances along the centerline of the wind direction are usually obtained when stability class

F is specified, and this is usually a good choice for general emergency planning purposes -- as is a wind velocity specification of 4.5 mph. However, be advised that there may be exceptions to this general rule when an evaporating liquid pool is the source of hazardous vapor emissions. Higher wind velocities typically produce greater evaporation rates, yet are usually associated with atmospheric stability classes other than F. Thus, the actual *worst case* for toxic vapor dispersion hazard assessments may involve a different combination than suggested above for some materials. In the absence of more precise historical meterological data for the region of concern, an atmospheric stability class of D together with a wind velocity of about 10 mph can be assumed to evaluate threats under more typical atmospheric conditions.

As discussed in Chapter 2 of this guide, many properties of hazardous materials are a function of temperature, with one of the most important being the vapor pressure of the substance (since this property will ultimately have a major effect on the magnitude of toxic or flammable vapor dispersion threats). Consequently, for planning purposes, it is desireable to select both tank and ambient environmental temperatures among the highest that may be experienced during a typical year. In selecting these temperatures, note that the temperature of the contents inside a metal tank can often (not always) be 20°F or more higher than the ambient air temperature on a sunny day.

The vapor or gas emission rate to the atmosphere and the duration of the emission are usually computed by one or more of the preceding models on the Hazard Assessment Model Selection Menu. Any attempt to use the toxic vapor dispersion model before these parameters have been computed will result in a warning to the user and a question as to whether he or she wishes to continue the analysis.

Model Results and Usage

Estimation of hazard zone dimensions and characteristics requires a complex iterative procedure that literally *searches* in the downwind direction for distances associated with the user specified toxic limit concentration. The program displays the results of this search as it proceeds to find the downwind length of the hazard zone at the discharge height of the vapor or gas, the peak concentration expected at groundlevel together with the location of this peak for elevated sources, and the downwind length of the hazard zone at groundlevel. It then provides a summary report of distances appropriate for the scenario being evaluated.

Two tables provide groundlevel concentrations, source height concentrations, recommended initial evacuation zone widths, contaminant arrival times, and contaminant departure times as a function of downwind distance.

Due to the numerous uncertainties associated with even the most sophisticated vapor dispersion modeling procedures, emergency planners should use the results of this model only as guideposts in decisions regarding necessary protective action in the event of an actual emergency. The prime value of the model is in its ability to provide a rough estimate of the magnitude of downwind areas that will be at risk, and in no way should model results be expected to be either highly accurate or precise. Indeed, be advised that many professionals consider the answers produced by a vapor dispersion model to be of acceptable accuracy if they are correct within a factor of two in 50% or more of trials.

A special note is necessary with respect to the procedures used to estimate contaminant arrival and departure times at downwind locations. Since the velocity of the wind generally increases with height, and since the wind velocity reported by meteorologists is usually the velocity measured at a height of 10 meters (about 33 feet) above the ground surface, estimation of these times is at best highly approximate, particularly if the source of toxic gas or vapor emissions is elevated above the ground. The model will generally underestimate rather than overestimate contaminant arrival times, but exceptions to this general rule are distinctly possible. Similarly, the model will generally overestimate rather than underestimate contaminant departure times, but exceptions to this general rule are again possible under certain circumstances. See Appendix B for details of the computation procedures.

Yet another special note is necessary with respect to the evacuation zone widths predicted by the model when the wind velocities in the hazard zone are very low. Under such conditions, the direction of the wind can become very erratic, and it may not always be wise to fully trust the results of the analysis in terms of its high probability that the wind will not change direction within the first hour of the release. Be prepared at any time under low wind conditions for one or more sudden shifts in wind direction and the possibility that the cloud or plume of vapor or gas may literally "hop" from one position or direction to another. Also, always remember that the evacuation zone widths are based on a *probabilistic* evaluation of wind direction shifts. Many a favorite race horse at the track has lost its event by a wide margin. Longshots actually win at times.

Use of model results are rather self-evident. They provide emergency planning personnel with an indication of the land area and thus populations subject to inhalation exposures at or above the specified toxic limit concentration in the event of an accident. In addition, they provide an estimate of the duration of the toxic vapor or gas hazard. These items of information, in turn, permit estimation of the number of people in the jurisdiction of concern that may require notification, protective action, transportation, shelter, medical care, and so forth.

Major Assumptions of the Methodology

The particular vapor dispersion model being utilized for toxic vapors primarily assumes:

- The discharge is of finite duration.
- All vapors or gases are discharged from a single point.
- The vapors or gases are neutrally buoyant.
- The ground surface is flat and generally free of obstacles.
- Atmospheric conditions remain constant during the discharge.
- The emission rate to the atmosphere is a constant during the release.
- The gas or vapor enters the atmosphere at a low velocity.
- Only gases or vapors are being released to the atmosphere.

Because of the importance of this topic, Sections 3.5 and 3.6 of the guide are devoted to a description and discussion of fundamental vapor dispersion phenomena and the factors that influence the size and characteristics of downwind hazard zones. Please refer to these sections for an understanding of the significance of these assumptions. Also note that Appendix B of the guide provides additional discussion of model assumptions, albeit in more technical terms.

Be advised and stay aware that there is at least one special case in which the type of dispersion model(s) being employed by ARCHIE may underestimate downwind hazard zone lengths. This involves scenarios in which a compressed liquefied gas under very high pressure in its container vents a high velocity jet of gas and liquid aerosols at a high rate in the downwind direction. When the jet is forceful and the gas and aerosol mixture is heavier-than-air, actual downwind travel distances to given concentrations in air may at times exceed those predicted by ARCHIE.

Due to the possibility that airborne contaminants released well above the ground surface may be forced by local terrain effects to drop to groundlevel locations sooner than would be expected, it is worthy to highlight the fact that evacuation zone width estimates are based on the assumption that all discharges occur at groudlevel. In other words, populations residing *under* a cloud or plume of airborne contaminants are always assumed to be at risk regardless of the fact that there may be times when the cloud or plume may harmlessly pass over them.

12.20 HAZARD MODEL MENU OPTION E: LIQUID POOL FIRE MODEL

Purpose of Model

The purpose of the liquid pool fire model is to compute the radius of the circular zone around a fire in which unprotected and/or unsheltered people may experience lethal burns due to thermal radiation exposures. Additionally, the model computes the radius of the zone in which second degree burns and/or severe pain may be experienced by exposed individuals.

Required Input Data

The model requires four input parameter values, these being:

- Molecular weight of the liquid
- Specific gravity of the liquid
- Normal boiling point temperature of the liquid (degrees F)
- Area of the burning pool (ft^2)

The program provides assistance (upon request of the user) in computing the molecular weight of the discharged substance from its chemical formula via a procedure similar to that described in Section 2.8 of the guide.

The specific gravity of the liquid should ideally be the value associated with the liquid at its temperature in the container or tank of concern. Note, however, that this value varies little with changes in temperature for the vast majority of liquids for which this model is applicable. The specific gravity given on a typical material safety data sheet (MSDS) will be acceptable in most cases.

The area of the burning pool is typically estimated using one of the pool area estimation procedures available when Option B is selected from the Hazard Assessment Model Selection Menu. An attempt to use this model before this area has been computed will result in a warning to the user and a question as to whether he or she wishes to continue the analysis.

Model Results and Usage

The model provides the radius of the burning pool, the height of the expected flame, the radius from the center of the pool in which exposed people may be fatality burned, and the radius from the center of the pool in which exposed people may experience second degree burns or severe pain.

These results are useful to emergency planning personnel for estimating the number of people that may require rescue and medical care, and for giving fire departments an indication of the size and nature of the fire they must be prepared to confront. They are also potentially useful for identifying other containers or stores of hazardous materials in the area that may be subject to fire or thermal radiation exposures, possibly resulting in a tank overpressurization explosion, a massive discharge of toxic gas, formation of a fireball, and/or the high velocity dissemination of container fragments that may damage more distant containers or populations.

Major Assumptions of the Methodology

The model assumes that the wind velocity in the burning pool area will be insufficient to tilt the flame in the direction of the wind to a significant degree, thus resulting in circular hazard zone estimates. In the event the wind does indeed cause tilting of the flame, hazard zones will be more of an oval shape and have a somewhat greater radius from the flame in the downwind direction. The radii of the respective zones will be somewhat smaller in the upwind direction.

The model assumes that people in direct view of the flame and in the open will have exposed skin. In other words, their skin will not be protected completely from the effects of thermal radiation by any clothing being worn.

Hazard zone estimates are based on the assumption that the base of the flame will be fairly circular in shape. Any major deviation from such a shape may invalidate model results, but these results are likely to remain conservative.

The model assumes that neither carbon dioxide or water vapor in the air will absorb any of the thermal radiation impinging on exposed people.

Based on experimental data, a radiation intensity of 5 kW/m^2 (1600 $Btu/hr\text{-}ft^2$) was selected for the purpose of defining injury zones since this incident flux will cause second degree burn injuries on bare skin within 45 seconds. An incident flux level of 10 kW/m^2 (3200 $Btu/hr\text{-}ft^2$) was chosen as the level capable of causing fatalities among exposed people since it can be expected to quickly cause third degree burns leading to potential fatalities.

12.21 HAZARD MODEL MENU OPTION F: FLAME JET MODEL

Purpose of Model

The flame jet model has the purpose of estimating the length of the flame and the zone around it that may be subjected to harmful levels of thermal radiation when a flammable gas discharges from its container at high speed and is ignited. Due to special properties of the

material, be advised that the model may greatly overpredict flame jet lengths associated with discharges of hydrogen but is expected to produce relatively accurate estimates for other substances.

Required Input Data

The model requires eight input parameter values, these being:

- Normal boiling point of the material (°F)
- Temperature of the material in its container (°F)
- Ambient environmental temperature (°F)
- Pressure of the flammable gas in the container (psia)
- Ratio of specific heats (C_p/C_v) for the gas
- Molecular weight of the gas
- Lower flammable limit of the gas (volume %)
- Diameter of the hole from which the gas is venting (inches)

As discussed in Chapter 2 of this guide, many properties of hazardous materials are a function of temperature, with one of the most important being the vapor pressure of the substance (since this property will ultimately have a major effect on the magnitude of toxic or flammable vapor dispersion threats). Consequently, for planning purposes, it is desireable to select both tank and ambient environmental temperatures among the highest that may be experienced during a typical year. In selecting these temperatures, note that the temperature of the contents inside a metal tank can often (not always) be 20°F or more higher than the ambient air temperature on a sunny day.

The user may request assistance in determining the pressure of the gas or vapor in the container at the point in time that the program asks for this parameter value. See Section 12.28 below for a description of the *Vapor Pressure Input Assistance Subprogram.*

The ratio of specific heats for the compressed gas or vapor is a thermodynamic property related to the amount of heat necessary to increase the temperature of a unit weight of gas or vapor by one degree under specified conditions. Prior to request of this value, the program will provide the user an opportunity to request assistance in selection of an appropriate specific heat ratio using several generalized rules-of-thumb (reproduced in Table 12.7) that require user knowledge of the chemical formula of the hazardous material being evaluated. Although the accuracy of model answers would be improved by provision of a more precise value for the substance at or near the temperature in its container, errors introduced by use of the property estimation methods provided by the program should not be highly significant in most (but not all) cases.

The program provides assistance (upon request of the user) in computing the molecular weight of the discharged substance from its chemical formula via a procedure similar to that described in Section 2.8 of the guide.

The lower flammable limit (LFL) of a gas or vapor was defined in Chapter 4 of this guide. Values are always listed on material safety data sheets (MSDS) when appropriate and available for the material of concern.

The program inherently assumes that the discharge outlet is circular in shape. In those instances where the expected shape is not expected to be circular it will be necessary to: 1) determine or estimate the area of the expected outlet in units of square inches; and 2) compute the diameter of the equivalent circle having this area. Appendix A to this guide provides assistance in this task for those who may require guidance.

Model Results and Usage

The model estimates the length of the expected flame jet and a safe separation distance from the flame, both in units of feet. If a gas discharge model providing a duration of discharge has been used previously, the model will also display the expected duration of the flame jet in minutes.

The length of the flame jet and its surrounding hazard zone radius are useful to emergency planning personnel not only in estimating the number of people that may subject to injury from the fire, but perhaps more importantly, the number and characteristics of other containers or stores of hazardous materials at industrial sites that may be adversely impacted by the fire. Of special concern is that a flame jet involving one storage or transportation container may impinge on another container, thus possibly causing a tank overpressurization explosion, a massive discharge of toxic gas, formation of a fireball, and/or the high velocity dissemination of container fragments that may damage more distant containers or populations.

Major Assumptions of Methodology

The model assumes that the pressurized gas or vapor will discharge at sufficient velocity to form a lengthy flame jet resembling a large *torch*. In the event that this condition is not satisfied, the flame exiting from the discharge outlet is likely to be shorter and to curve upwards. In technical terms, this model is said to address turbulent or momemtum dominated flame jets. If flow velocity criteria are not fulfilled, the flame will be buoyancy dominated.

Due to the complexities involved in estimating safe separation distances from flame jets that may have a wide variety of orientations with respect to the person or persons at risk of receiving burn injuries, the safe separation distance provided by the model is simply twice the length of the flame. This is considered to be a conservative estimate based on evaluations conducted with more sophisticated models of flame jet phenomena.

12.22 HAZARD MODEL MENU OPTION G: FIREBALL THERMAL RADIATION MODEL

Purpose of Model

This model characterizes the fireball and associated thermal radiation hazard zones resulting from exposure of a sealed or inadequately vented container of a flammable liquid or liquefied compressed gas to an external fire or other source of excessive heat sufficient to cause explosion or violent rupture of the container. The model may also be used in an approximate fashion for containers of flammable compressed gas.

Required Input Data

The model only requires the user to provide the weight in pounds of the flammable material in the container at the point in time that it explodes or ruptures. The most conservative course of action is to simply assume that the container will explode or rupture when it is full. Realize, however, that many Boiling Liquid Expanding Vapor Explosions (BLEVES) occur when flame weakens the wall of the vapor or head space of the container. If the tank is fairly full to begin with and is fitted with a pressure relief device, it may vent a considerable portion of its contents before occurrence of a BLEVE.

Model Results and Usage

The fireball that results from rupture of a tank or container and subsequent ignition of its contents will quickly rise while growing in size and then burn out. Results of the model include estimates of the:

- Maximum diameter of the fireball (ft)
- Maximum expected height of the fireball (ft)
- Estimated duration of the fireball (seconds)
- Distance (radius) from the container in which fatalities may be expected due to thermal radiation burns (ft)

- Distance (radius) from the container in which significant burn injuries may be expected due to thermal radiation (ft)

Output of the model during the accident scenario evaluation session always stresses that *"Boiling Liquid Expanding Vapor Explosions (BLEVES) may cause high velocity tank fragments to travel considerable distances. Some tanks, especially horizontal cylindrical types, may rocket while spewing forth flames"*. See Chapter 5 for a more complete description and discussion of potential fragment hazards.

Results of the model are useful to emergency planning personnel in defining safe separation zones in situations where there is a potential for fireball formation and fragment impact hazards. Additionally, where the event may occur without time for protective actions to be taken, the results can help planners estimate the number of people that may be killed or injured. Although specific characteristics and potential damages cannot be predetermined, the fact that container fragments may disperse at high velocity can help identify other containers or stores of hazardous materials that may be impacted by the accident and pose additional threats to the public.

Major Assumptions of the Methodology

Key assumptions of the model include:

- No thermal radiation will be absorbed by water vapor or carbon dioxide gas present in the atmosphere.
- All flammable materials of interest are similar in characteristics to liquefied compressed propane.
- Both the container and exposed people are on or near the ground.
- The burn severity depends upon the amout of energy absorbed by the skin after a surface temperature of 55°C is achieved. See Appendix B for additional information.

12.23 HAZARD MODEL MENU OPTION H: VAPOR CLOUD OR PLUME FIRE MODEL

Purpose of Model

A plume or cloud of flammable vapor or gas has the potential to either burn or burn and then explode upon encountering a suitable source of ignition. The purpose of this model is to estimate the dimensions of the downwind area that may be subjected to flammable and

potentially explosive vapors or gases in the event of an accidental discharge. In addition, the model estimates the maximum weight of flammable of explosive gas that may be airborne at any time during dispersion of the cloud or plume.

Required Input Data

The model requires the following input parameter values:

- Molecular weight of the substance
- Normal boiling point of the discharged material (°F)
- Temperature of the substance in its container (°F)
- Ambient environmental temperature (°F)
- Vapor pressure of the substance after spill (mm Hg)
- Lower flammable limit of the gas or vapor (volume %)
- Atmospheric stability class (A to F)
- Wind velocity (mph)
- Vapor/gas emission rate (lbs/minute)
- Duration of vapor/gas emission (minutes)

The program provides assistance (upon request of the user) in computing the molecular weight of the discharged substance from its chemical formula via a procedure similar to that described in Section 2.8 of the guide.

As discussed in Chapter 2 of this guide, many properties of hazardous materials are a function of temperature, with one of the most important being the vapor pressure of the substance (since this property will ultimately have a major effect on the magnitude of toxic or flammable vapor dispersion threats). Consequently, for planning purposes, it is desireable to select both tank and ambient environmental temperatures among the highest that may be experienced during a typical year. In selecting these temperatures, note that the temperature of the contents inside a metal tank can often (not always) be 20°F or more higher than the ambient air temperature on a sunny day.

The user may request assistance in determining the vapor pressure of the discharged substance at the point in time that the program asks for this parameter value. See Section 12.28 below for a description of the *Vapor Pressure Input Assistance Subprogram.* The model uses the vapor pressure in this case simply to confirm that flammable vapors can be generated at specified temperatures in the external environment. Thus, if the vapor pressure of the gas or vapor is above one atmosphere (equivalent to 760 mm Hg), the value displayed will be limited to a maximum vapor pressure of 760 mm Hg.

The lower flammable limit (LFL) of a gas or vapor was defined in Chapter 4 of this guide. Values are always listed on material safety data sheets (MSDS) when appropriate and available for the material of concern.

Assistance in selection of the appropriate atmospheric stability class and a wind velocity consistent with this class is provided (upon request of the user) by reproduction of the class selection chart (reproduced here in Table 12.8). The longest downwind hazard distances along the centerline of the wind direction are usually obtained when stability class F is specified, and this is usually a good choice for general emergency planning purposes -- as is a wind velocity specification of 4.5 mph. However, be advised that there may be exceptions to this general rule when an evaporating liquid pool is the source of hazardous vapor emissions. Higher wind velocities typically produce greater evaporation rates, yet are usually associated with atmospheric stability classes other than F. Thus, the actual *worst case* for toxic vapor dispersion hazard assessments may involve a different combination than suggested above for some materials. In the absence of more precise historical meterological data for the region of concern, an atmospheric stability class of D together with a wind velocity of about 10 mph can be assumed to evaluate threats under more typical atmospheric conditions.

The vapor or gas emission rate to the atmosphere as well as the duration of the emission is usually computed by one or more of the preceding models on the Hazard Assessment Model Selection Menu. Any attempt to use the toxic vapor dispersion model before these parameters have been computed will result in a warning to the user and a question as to whether he or she wishes to continue the analysis.

Model Results and Usage

Output of the model includes:

- Downwind hazard distance (feet)
- Maximum downwind hazard zone width (feet)
- Maximum weight of airborne gas (lbs)
- Initial relative vapor/air density
- Type of model used for analysis

Two sets of results are provided for the first four items in the above list. The first set is based on a concentration that is 50% of the specified lower flammable limit (LFL) for the gas or vapor in air. The second is based on the full value of the LFL.

The concentration of a gas or vapor at any specific point downwind will fluctuate about an average value due to atmospheric turbulence even if all other factors that can influence vapor dispersion phenomena remain unchanged. Vapor dispersion models, including the models in ARCHIE, are usually formulated to provide this average value as a function of downwind location, which is perfectly acceptable for consideration of toxic gas or vapor dispersion hazards. In the case of flammable gases or vapors, however, it is necessary to make a distinction between that portion of a cloud or plume that can burn and that portion that may explode, and this requires consideration of peak to average concentrations at downwind locations. Without getting into more technical details, suffice it to say that a cloud or plume has the potential to burn out to the boundaries of the area encompassed by a gas or vapor concentration that is approximately one-half the LFL. The area subject to explosion, however, is better estimated via use of the actual LFL value.

This procedure in ARCHIE actually consists of two separate and distinct models. If the program decides that the gases or vapors released to the atmosphere are best treated as being neutrally buoyant, it uses elements of the toxic vapor dispersion model to provide desired results. Conversely, if the vapors are deemed to be best treated as being negatively buoyant in air, it uses a specially formulated and simplified *heavy gas* model.

Results of the model primarily provide emergency planning personnel with an indication of the size of the hazard zone that may be subject to a vapor or gas cloud or plume deflagration, and thus, indications of the number of people that may be killed or severely injured, and the number and characteristics of buildings and other resources that may be exposed to the flame. The maximum weight of potentially explosive airborne gas or vapor estimated by the model is typically utilized as an input parameter to the unconfined vapor cloud or plume explosion model (Hazard Model Menu Option I).

Major Assumptions of the Methodology

Assumptions associated with use of the vapor dispersion model for neutrally buoyant vapors or gases are discussed in Section 12.19 above. Technical details and assumptions of the heavy gas model are provided in Appendix B to this guide.

The decision as to which of the two models is to be used is based on a computation of the ratio of the vapor-air mixture density to the density of pure air. The computation procedure leading to this relative vapor density is presented in Section 2.6 of the guide. The concentration of gas or vapor in air is taken to be 100% by volume in the event of pressurized gas releases.

The program assumes that the vapor or gas is best treated as being neutrally buoyant if its initial relative vapor density has a value of 1.5 or below. Values above 1.5 lead to use of the heavy gas model for negatively buoyant gases or vapors. Note that this version of ARCHIE is incapable of taking the presence of airborne liquid aerosols into account and may therefore occasionally err during this process.

Be advised and stay aware that there is at least one special case in which the type of dispersion model(s) being employed by ARCHIE may underestimate downwind hazard zone lengths. This involves scenarios in which a compressed liquefied gas under very high pressure in its container vents a high velocity jet of gas and liquid aerosols at a high rate in the downwind direction. When the jet is forceful and the gas and aerosol mixture is heavier-than-air, actual downwind travel distances to given concentrations in air may at times exceed those predicted by ARCHIE.

12.24 HAZARD MODEL MENU OPTION I: UNCONFINED VAPOR CLOUD EXPLOSION MODEL

Purpose of Model

Although some flammable and therefore potentially explosive gases and vapors have a greater propensity to explode than others upon ignition when at or above their respective lower flammable limit (LFL) concentrations in the open environment, the threat of such an explosion exists with a large number of hazardous materials. This threat increases for most materials as the degree of confinement is increased.

The purpose of this particular model in ARCHIE is to evaluate the impacts of an explosion involving an unconfined (or even partially confined) gas or vapor cloud or plume in air.

Required Input Data

Input data and information required by the model include:

- Lower heat of combustion of the gas or vapor (Btu/lb)
- Yield factor for the explosion
- Weight of airborne flammable gas or vapor (lbs)
- Location of the explosion relative to the ground surface

The heat of combustion of a material is the amount of heat generated when a unit weight of the substance is burned under specified conditions. The *lower* heat of combustion ideally desired for model use is the amount of heat liberated when the material is burned in oxygen at a temperature of 25°C (77°F) and the products of combustion, including any water

that may form, remain as gases. The input screen for the parameter provides guidance for selecting a value when more precise data are unavailable. For informational purposes, it is noted that the ***CHRIS Hazardous Chemical Data*** manual available at a cost of $41 in late 1988 from branches of the Government Printing Office contains the desired value for over 1200 hazardous materials. This manual is widely used by fire service and other emergency response personnel across the country and is very likely to be locally available. No hazardous materials library would be complete without the document.

When a volume of gas or vapor in air burns and explodes, only a small fraction of the energy in the cloud or plume actually contributes to the formation of shock or blast waves that can damage people and property. This fraction is referred to as the *yield factor* and varies for different materials. Upon request of the user, the program will provide guidance for selection of an appropriate yield factor for the substance of concern when it is completely unconfined in the environment. This guidance is reproduced in Table 12.9. Pay special attention to the fact that the guidance only applies to situations in which the gas or vapor cloud or plume is completely unconfined. Yield factors can increase substantially when there is a significant degree of confinement.

The weight of flammable gas or vapor in air is usually computed by the vapor cloud or plume fire model described above (Hazard Model Menu Option H). Any attempt to use the unconfined vapor cloud explosion model before this weight has been computed will result in a warning to the user and a question as to whether he or she wishes to continue the analysis. In addition, the user will be warned if the weight provided is less than 1000 pounds, since the probability of a completely unconfined vapor cloud explosion (based on historical data) is very low in such cases, except for a very few reactive substances and for situations in which there is some degree of confinement prior to ignition.

As discussed in Chapter 5 of this guide, an explosion centered near the ground can behave quite differently than an explosion at some point well above the ground surface (a so called *free air* blast). Thus, the program asks the user whether a ground or elevated location should be assumed. Be advised that the damages caused by a groundlevel explosion will be greater than those caused by a free air blast when all other factors are equal.

Model Results and Usage

The model produces a table which lists distances from the explosion center associated with various degrees of injury and damage to people and property. *It is important to realize in the case of unconfined vapor cloud explosions that the center of the explosion could be anywhere within the area subjected to gas or vapor concentrations at or above the LFL for the material of concern.* This area is usually defined by use of the vapor cloud or plume fire model described in Section 12.23 (Hazard Model Menu Option H).

TABLE 12.9
ASSISTANCE DISPLAY FOR EXPLOSION YIELD FACTOR

YIELD FACTOR SELECTION ASSISTANCE FOR COMPLETELY UNCONFINED CLOUDS			
EXAMPLES OF SUBSTANCES WITH YF = 0.03			
Acetaldehyde	Dimenthyl sulfide	Isopropyl alcohol	Propanol
Acetone	Ethane	Methane	Proprionaldehyde
Acrylonitrile	Ethanol	Methanol	Propyl acetate
Amyl acetate	Ethyl acetate	Methyl acetate	Propylene
Amyl alcohol	Ethyl amine	Methyl amine	Propylene dichloride
Benzene	Ethyl benzene	Methyl butyl ketone	Styrene
Butadiene	Ethyl chloride	Methyl chloride	Tetrafluoroethylene
Butane	Ethyl formate	Methyl ethyl ketone	Toluene
Butene	Ethyl proprionate	Methyl formate	Vinyl acetate
Butyl acetate	Furfural alcohol	Methyl mercaptan	Vinyl chloride
Carbon monoxide	Heptane	Methyl propyl ketone	Vinylidene chloride
Cyanogen	Hexane	Naphthalene	Water gas
Cymene	Hydrocyanic acid	iso - Octane	Xylene
Decane	Hydrogen	Pentane	
Dichlorobenzene	Hydrogen sulfide	Petroleum ether	
Dichloroethane	Isobutyl alcohol	Phthalic anhydride	
Dimethyl ether	Isobutylene	Propane	

EXAMPLES OF SUBSTANCES WITH YF = 0.06	
Acrolein	Ethylene
Carbon disulfide	Ethyl nitrite
Cyclohexane	Methyl vinyl ether
Diethyl ether	Propylene oxide
Divinyl ether	

EXAMPLES OF SUBSTANCES WITH YF = 0.19	
Acetylene	Isopropyl nitrate
Ethylene oxide	Methyl acetylene
Ethyl nitrate	Nitromethane
Hydrazine	Vinyl acetylene

Each of the hazard zone distances estimated by the program is associated with a specific peak overpressure in the shock or blast wave and these in turn are related to specific levels of expected damage using the information tabulated in Table 5.1 of this guide. Table 12.10 illustrates the format of the general results obtained from ARCHIE but shows the peak overpressures associated with each level of damage or injury instead of a specific distance.

Results of the model provide emergency planning personnel with an indication of the radii of the circular zones around the center of the explosion that may be subject to explosion impacts of various levels of severity, thus additionally providing indications of the number of people that may be killed or severly injured, and the number, characteristics, and level of damage that may be sustained by buildings, homes, and other resources that may be exposed to the shock or blast wave.

Major Assumptions of the Methodology

Be advised that model results assume the surrounding area is essentially flat and without obstacles. In actuality, potential reflections of the blast or shock wave from building walls or the sides of other obstacles and surfaces may cause actual damage patterns to be somewhat more erratic than those predicted by this generalized hazard assessment methodology.

12.25 HAZARD MODEL MENU OPTION J: TANK OVERPRESSURIZATION EXPLOSION MODEL

Purpose of Model

The tank overpressurization explosion model is used to evaluate the hazards resulting from cases in which a sealed or inadequately vented tank or container may be internally overpressurized by a gas or vapor to the point of violent rupture. This type of explosion is described and discussed more fully in Chapter 5.

Required Input Data

The model requires knowledge of:

- The shape of the tank or container
- Pressure at which the tank or container will rupture (psia)
- Gas or vapor volume in the tank (ft^3)
- Ratio of specific heats (C_p/C_v) for the gas or vapor
- Ambient environmental temperature (°F)
- Temperature of the gas or vapor in the tank (°F)

TABLE 12.10
EXAMPLE OUTPUT FROM EXPLOSION MODELS

Peak Overpressure (psia)	EXPECTED DAMAGE
0.03	Occasional breakage of large windows under stress.
0.30	Some damage to home ceilings; 10% window breakage.
1.00 - 0.50	Windows usually shattered; some frame damage.
1.00	Partial demolition of homes; made uninhabitable.
8.00 - 1.00	Range serious/slight injuries from flying glass/objects.
2.00	Partial collapse of home walls/roofs.
3.00 - 2.00	Non-reinforced concrete/cinder block walls shattered.
12.2 - 2.40	Range 90-1% cardrum rupture among exposed population.
2.50	50% destruction of home brickwork.
4.00 - 3.00	Frameless steel panel buildings ruined.
5.00	Wooden utility poles snapped.
7.00 - 5.00	Nearly complete destruction of houses.
10.0	Probable total building destruction.
29.0 - 14.5	Range for 99-1% fatalities among exposed populations due to direct blast effects.

Note: Output from the computer program shows Distance from Explosion in feet in place of Peak Overpressures shown here for reference purposes. See Table 5.1 of guide for additional information.

The first question asked by the program in cases where the answer has not been previously specified is the shape of the tank or other container. Valid choices are rectangular tank, horizontal cylindrical tank, vertical cylindrical tank, and spherical tank. This particular model cannot be used for pipelines.

Knowledge of the pressure at which the tank will rupture when overpressurized will require some detective work since tank construction standards vary widely for different types of hazardous materials. The best bet is to query the owner or operator of the tank, and if necessary, the company that initially constructed the vessel for this information.

Prior to asking the user to provide the volume of the tank or other container that contains compressed gas or vapor, an input parameter value that would otherwise require several manual computations, the program asks if the user desires assistance in characterizing the volume of the container and the weights, volumes, and physical states of its contents. Further details on the *Tank and Container Contents Characterization Subprogram* and its general data requirements are provided in Section 12.29 of this chapter. Use of the subprogram may result in requests for a few informational items not listed above.

The ratio of specific heats for the compressed gas or vapor is a thermodynamic property related to the amount of heat necessary to increase the temperature of a unit weight of gas or vapor by one degree under specified conditions. Prior to request of this value, the program will provide the user an opportunity to request assistance in selection of an appropriate specific heat ratio using several generalized rules-of-thumb (reproduced in Table 12.7) that require user knowledge of the chemical formula of the hazardous material being evaluated. Be advised that the results of this particular model are sensitive to the value provided by the user. Accuracy of model results can and will be improved by provision of a more precise value for the substance at or near the temperature in its container, but this is by no means mandatory.

As discussed in Chapter 2 of this guide, many properties of hazardous materials are a function of temperature, with one of the most important being the vapor pressure of the substance (since this property will ultimately have a major effect on the magnitude of toxic or flammable vapor dispersion threats). Consequently, for planning purposes, it is desireable to select both tank and ambient environmental temperatures among the highest that may be experienced during a typical year. In selecting these temperatures, note that the temperature of the contents inside a metal tank can easily be 20°F or more higher than the ambient air temperature on a sunny day.

Model Results and Usage

The tank overpressurization explosion model produces a table which lists distances from the explosion center associated with various degrees of injury and damage to people and property. Each of the hazard zone distances estimated by the model is associated with a specific peak overpressure in the shock or blast wave and these in turn are related to specific levels of expected damage using the information tabulated in Table 5.1 of this guide. Table 12.10 illustrates the format of the general results obtained from ARCHIE, but shows the peak overpressures associated with each level of damage or injury instead of a specific distance. Note that the model does not fully address the potential dispersion of high velocity tank or container fragments that may result from the explosion and pose a threat to other containers or stores of hazardous materials or other vulnerable resources.

Results of the model provide emergency planning personnel with an indication of the radii of the circular zones around the center of the explosion that may be subject to explosion impacts of various levels of severity, thus additionally providing indications of the number of people that may be killed or severely injured, and the number, characteristics, and level of damage that may be sustained by buildings, homes, and other resources that may be exposed to the shock or blast wave.

Major Assumptions of the Methodology

Be advised that model results assume the surrounding area is essentially flat and without obstacles. In actuality, potential reflections of the blast or shock wave from building walls or the sides of other obstacles and surfaces may cause actual damage patterns to be somewhat more erratic than those predicted by this generalized hazard assessment methodology.

Since most tanks or containers subject to this type of violent explosion or rupture are likely to be on or near the ground, the model assumes this location for the explosion in all cases. See Chapter 5 for a discussion of the difference between groundlevel and *free air* explosions. The latter type of event will typically produce specified damages over lesser distances than those predicted for groundlevel explosions.

12.26 HAZARD MODEL MENU OPTION K: CONDENSED-PHASE EXPLOSION MODEL

Purpose of Model

This model is used to evaluate the hazards of solid or liquid explosive materials such as nitroglycerine, TNT, dynamite, and a wide variety of lesser known substances with true explosive properties. This type of detonation or explosion is more fully described and discussed in Chapter 5.

Substances most likely capable of detonation will be classified as ***explosives*** by the DOT. Explosives for which the model is applicable may also be formed at times during the reaction of two or more substances which are not individually considered to have explosive characteristics (see Chapter 7).

Be advised that substances classified as ***blasting agents*** by the DOT, despite their name, are considered to have a much lower likelihood of exploding, even in accidents involving fire or impact. See Chapter 8 for formal DOT definitions of blasting agents and designated explosive materials.

Required Input Data

The model requires only two input values, these being:

- Heat of combustion of the explosive material (Btu/lb)
- Weight of material at risk of exploding (lbs)

The heat of combustion of a material is the amount of heat generated when a unit weight of the substance is burned under specified conditions. The *lower* heat of combustion ideally desired for model use is the amount of heat liberated when the material is burned in oxygen at a temperature of 25°C (77°F) and the products of combustion, including any water that may form, remain as gases. The input screen for the parameter provides guidance for selecting a value when more precise data are unavailable. For informational purposes, it is noted that the ***CHRIS Hazardous Chemical Data*** manual available at a cost of $41 from branches of the Government Printing Office contains the desired value for over 1200 hazardous materials. This manual is widely used by fire service and other emergency response personnel across the country and is very likely to be locally available. No hazardous materials library would be complete without the document.

Model Results and Usage

The model produces a table which lists distances from the explosion center associated with various degrees of injury and damage to people and property. Each of the hazard zone distances estimated by the program is associated with a specific peak overpressure in the shock or blast wave and these in turn are related to specific levels of expected damage using the information tabulated in Table 5.1 of this guide. Table 12.10 illustrates the format of the general results obtained from ARCHIE but shows the peak overpressures associated with each level of damage or injury instead of a specific distance.

Results of the model provide emergency planning personnel with an indication of the radii of the circular zones around the potential explosion site that may be subject to explosion impacts of various levels of severity, thus additionally providing indications of the

number of people that may be killed or severly injured, and the number, characteristics, and level of damage that may be sustained by buildings, homes, and other resources that may be exposed to the shock wave.

Major Assumptions of the Methodology

The model is the traditional *TNT-equivalent* procedure widely used for many years for evaluation of high explosive detonation hazards. A primary assumption, which is usually quite valid for the types of explosives being considered, is that the blast or shock wave produced by the explosion will dissipate in the same fashion as the explosion that would occur if a weight of TNT having the same total energy of combustion were detonated.

Since the explosive material is most likely to be on or near the ground surface when the explosion occurs, the procedure assumes this location for the explosion in all cases. See Chapter 5 for a discussion of the difference between groundlevel and *free air* explosions. The latter type of event will typically produce specified damages over lesser distances than those predicted for groundlevel explosions.

As in the case of the other types of explosions, be advised that model results assume the surrounding area is essentially flat and without obstacles. In actuality, potential reflections of the blast or shock wave from building walls or the sides of other obstacles and surfaces may cause actual damage patterns to be somewhat more erratic than those predicted by this generalized hazard assessment methodology.

12.27 REMAINING OPTIONS ON THE HAZARD ASSESSMENT MODEL SELECTION MENU

Option L: Review of Model Descriptions

Selection of this option permits the user to view several screens of text containing brief descriptions of the models available from the Hazard Assessment Model Selection Menu.

Option M: Review of Model Selection Charts

This option permits the user to view the model selection charts that were previously presented in Figure 12.2.

Option N: Return to Main Menu

As the title suggests, selection of this option returns the user to the Main Task Selection Menu. Be advised that a return to this menu will "close" the Accident Scenario File (ASF)

being worked on while the Hazard Assessment Model Selection Menu is in use. In order to make this ASF file active again, it will be necessary to select Option B from the Main Task Selection Menu and recall the file into active service.

12.28 USE OF THE VAPOR PRESSURE INPUT ASSISTANCE SUBPROGRAM

Knowledge of the vapor pressure of a hazardous substance as a function of temperature is an important prerequisite to an adequate evaluation of accident scenario results in most cases. There are likely to be many situations, even when some vapor pressure data points are available for specific temperatures, however, when these data will be for temperatures other that those needed by the program. Thus, the vapor pressure input assistance subprogram is designed to facilitate characterization of the vapor pressure versus temperature relationship for a hazardous substance regardless of whether detailed data are available or whether only the data on a material safety data sheet are at hand. Upon a request of assistance from the user at one of the points in the program that vapor pressures are requested for specific temperatures, the program will respond with a short menu offering ***three options***, these being:

1. The user provides the vapor pressures at these temperatures.

2. The user can provide whatever vapor pressure and other data are available and permit the program to estimate the vapor pressures at the desired temperatures.

3. If available, the user can provide the coefficients for the Antoine equation for the substance. Further information is given when this option is selected.

The ***first option*** is simply an escape mechanism for the user who arrives at this menu unintentionally, and also, for the user who chooses one of the two following options, is not satisfied with the results of the vapor pressure input assistance procedures, and desires to exit the assistance subprogram.

The ***second option*** takes advantage of any and all available vapor pressure data sets (where a *set* is defined to be a specific vapor pressure and related temperature) for the substance of interest. Selection of this option results in a series of questions to the user alternated with information screens. The general order of events is:

1. The user is asked if he or she has the vapor pressure for the material at a temperature of 68°F (20°C), this being a vapor pressure available on material safety data sheets for most volatile substances. If the user answers *yes*, he or she is next asked to choose the units in which the vapor pressure will be provided. Choices include pounds per square inch - absolute (psia) ,

atmospheres (atm) , millimeters of mercury (mm Hg), Pascals (Pa), Newtons per square meter (N/m^2), and Bars. *(Note: Definitions of these units appear in Chapter 2 of this guide.)* Once the value has been input in the specified set of units, the program lists the vapor pressure provided in all sets of available units and asks the user to confirm that the value was entered properly.

2. The vapor pressure of any substance, as noted in Chapter 2, is always 760 mm Hg or the equivalent at its normal boiling point temperature at one standard atmosphere. The program will report this fact to the user simply for informational purposes.

3. The subprogram will now have a least one data set and possibly two. Although the subprogram can generate a curve of vapor pressure versus temperature from two points, the curve would not be very accurate. Thus, the subprogram continues with a question asking if the user has a vapor pressure at another temperature. A *yes* answer from the user will result in a choice of units for the vapor pressure, a request for input of the vapor pressure value, a choice of units for the related temperature, a request for input of this temperature, and a screen seeking confirmation that the data has been entered properly. If three data sets are now available, the subprogram will skip to item 5 below. Otherwise, it will repeat this step until it receives a *no* answer to its initial query.

4. If only one or two data sets are available at this point, the subprogram will ask the user if the substance is flammable or combustible. A *yes* answer will result in requests for the lower flammable limit (LFL) of the substance in volume percent and its flash point (closed cup preferred) in degrees Fahrenheit if they are available. These data will be used to generate a data set based on the assumption that the flash point of a substance is theoretically equivalent to the temperature at which its vapor pressure provides a vapor concentration equivalent to its LFL.

5. If only one data set is available after all of the above steps, the subprogram will inform the user that available data are insufficient and return him or her to the opening menu of the subprogram. If two data sets are available, the user will be warned of the potential inaccuracy of vapor pressure estimates and will be shown vapor pressure predictions for the normal boiling point temperature of the hazardous material, the temperature of the material in its tank or other container, and the ambient environmental temperature. A final question will ask if the predictions appear to be of acceptable

accuracy. If three data sets are available, the subprogram will directly proceed to a display of the above predictions and ask if results are acceptable. If they are, it will then display the Antoine equation coefficients derived from the input data and the temperature bounds in which the equation should produce fairly accurate results.

Several excellent reference sources of chemical property data contain tables of vapor pressure versus temperature for literally hundreds of substances, as well as a wide variety of other data useful for hazard assessment purposes. Among the more readily available of these references in libraries and often in the possession of local chemical engineers and chemists (including possibly the local high school chemistry teacher) are:

- ***Perry's Chemical Engineers' Handbook***, McGraw-Hill Book Company, New York, NY (various editions have different editors and publication dates).

- Weast, R.C., et al., ed.'s, ***CRC Handbook of Chemistry and Physics***, CRC Press, Boca Raton, FL (various editions have different publication dates).

The ***third option*** on the opening menu to the subprogram, as noted above, asks if the user has access to the Antoine equation coefficients for the hazardous material of interest. For those who may not be familiar with this equation, be advised that it is a commonly used equation with three coefficients. When provided a temperature within the range of temperatures for which it is applicable, it predicts the vapor pressure associated with this temperature. Each hazardous material has its own relatively unique set of coefficients that can be found in various data sources. Two excellent sources of Antoine coefficients and considerable other data for a large number of chemicals include:

- Reid, R.C., et al., ***The Properties of Gases & Liquids***, McGraw-Hill Book Company, New York, NY

- Dean, J.A., ed., ***Lange's Handbook of Chemistry***, McGraw-Hill Book Company, New York, NY.

Various editions of both of these books have differents publication dates, but all contain valuable data and information. The first book lists Antoine coefficients for almost 600 materials in its 4th edition. The second has coefficients listed for over 900 substances in its most recent editions.

The general form of the Antoine equation is:

$$\log(P) \text{ or } \ln(P) = A - (B / (T + C))$$

where A, B, and C are the three coefficients, T is the temperature at which the vapor pressure is desired, and P is the vapor pressure (shown on the left side of the equal sign as the log or natural log of the pressure).

Different reference sources use different units for the various coefficients and other parameters associated with the equation, so the subprogram begins with a series of question designed to determine the specific units for which the coefficients on hand are valid. These initial questions request:

- An indication of whether the left side of the equation provides the log or natural log of the vapor pressure (P).
- An indication of whether the equation uses temperatures (T) in units of degrees Celsius or Kelvin.
- An indication of whether the vapor pressure predicted is in units of millimeters of mercury (mm Hg), Pascals (Pa), Newtons per square meter (N/m^2), or Bars.
- An optional specification of the temperature range over which the equation is valid.

Once the program has confirmed that the user has entered this information as he or she intended, it proceeds to request the three equation coefficients. It then predicts vapor pressures for the normal boiling point temperature of the hazardous material, the temperature of the material in its tank or other container, and the ambient environmental temperature. A final question asks if the predictions appear to be of acceptable accuracy.

12.29 USE OF THE TANK AND CONTAINER CONTENTS CHARACTERIZATION SUBPROGRAM

A user of ARCHIE will very often have knowledge of the dimensions of a tank or other container of the hazardous material of concern, the temperature and pressure of its contents, and some idea of how full it might be on average or when in peak use. The tank and container contents characterization subprogram helps the user in translating this information into the weights, volumes, and other characteristics of the container and its contents that are required by ARCHIE, thus reducing or eliminating the need for a variety of manual calculations. The subprogram is available from any input parameter screen in ARCHIE that requests the weight of the hazardous material in the tank or the volume of the tank that contains a compressed gas. Be advised that use of the subprogram is highly recommended since denial of this offer of assistance creates a situation in which ARCHIE must accept input data from the user without being able to ensure that all data are consistent.

Use of the subprogram is very straightforward. First, it asks for several but not necessarily all of the following input parameter values if these have not previously been provided, including the:

- Shape of the tank or other container
- Length, width, height, and/or diameter of the tank as needed
- Molecular weight of the contents
- Normal boiling point temperature of the contents (°F)
- Vapor pressure of the material in the container (psia)
- Temperature of the material in the container (°F)
- Ambient environmental temperature (°F)
- An indication of whether or not the tank contains any liquid
- Specific gravity of the liquid, if applicable

Once the above list of information has been obtained, the subprogram follows with what might be the most important question of all (presuming the user has earlier indicated there is liquid in the tank), this being *"Which of the following do you know about the tank contents?"*.

1. Amount of liquid in the container in gallons
2. Amount of liquid in the container in pounds
3. Amount of liquid in the container in cubic feet
4. Height of liquid in the container as measured from its bottom
5. Percentage of container filled with liquid
6. None of the above

Selection of one of these options and input of the appropriate answer leads to a screen in which the dimensions of the tank and the characteristics of its contents are listed. A final question asks if the user wishes to repeat the procedure (in case some item or another looks in error). A *yes* answer leads to a screen summarizing user input values and asking which ones should be changed. A *no* answer takes the user back to where he or she was in ARCHIE prior to entering this subprogram.

12.30 OTHER COMPUTER PROGRAMS

There are a number of other computer programs that may be of interest to emergency planning and response personnel. The EPA document entitled ***Identifying Environmental Computer Systems for Planning Purposes*** (Preparedness and Prevention Technical Assistance Bulletin #5) provides a checklist of computer system needs related to hazard analysis and information on other available systems applicable to local planning efforts. The checklist addresses a variety of systems for air dispersion and other environmental modeling, for access to chemical properties data, and for emergency response planning. Note that

different systems, particularly those associated with consequence analysis, may provide differring results due to varying assumptions made during model formulation by system developers.

13.0 FORMULATION OF A PLANNING BASIS

13.1 INTRODUCTION

Chapter 10 of this guide provides guidance pertaining to the identification and characterization of those activities or operations within a specific community or jurisdiction that involve the use, storage, or transportation of hazardous materials and which therefore pose some degree of hazard or risk to the public. Chapter 11 of the guide provides the data, methods, and procedures necessary to estimate the probability of an accident associated with each of these activities or operations. In addition, the chapter provides an opportunity in many cases to assess the probabilities associated with different levels of accident severity and discusses how to analyze scenarios with consequence analysis procedures. Chapter 12 continues with a discussion of the ARCHIE program and its individual models that may be used to evaluate many of the specific consequences of a spill, discharge, fire, or explosion involving hazardous materials.

Planning personnel who apply the procedures presented in the referenced chapters will obtain a great deal of knowledge and insight into the specific threats facing their jurisdiction from hazardous materials. Some may wish to use this knowledge directly in an attempt to plan for all possible scenarios, and are not discouraged from doing so if the time and resources available are sufficient for this endeavor. For all intents and purposes, the entire set of accident scenarios identified and considered during the hazard analysis will in aggregate become the basis for their planning effort and they may proceed to Chapter 14.

Those who do not have the resources available to plan for every possible contingency, or who have other threats competing for attention, may wish to limit their planning efforts for hazardous materials by focusing on the most important situations. This can be accomplished by screening accident scenarios to identify those that have a reasonable likelihood of occurrence in the foreseeable future and/or which may have significant consequences in the absence of an organized, rapid, and effective response effort. It is the purpose of Chapter 13 to assist these latter personnel in such a screening effort via a simplified risk analysis process. The set of scenarios that remain after this process will then provide a planning basis for their jurisdiction.

13.2 DEFINITION OF ANNUAL ACCIDENT PROBABILITY CATEGORIES

Each of the accident scenarios identified during prior efforts should first be classified into five categories based on the annual probability determined for the scenario using the methods described in Chapter 11 of this guide. The categories of interest include:

- Common accidents,
- Likely accidents,
- Reasonably likely accidents,
- Unlikely accidents, and
- Very unlikely accidents

Common accidents are defined herein as events expected to occur one or more times each year on average. Such incidents have occurred in the locality of concern in the past and are likely to reoccur with some regularity.

Likely accidents are defined herein as events expected to occur at least once every 10 years on average according to available statistics. Given the rapid increase in production and usage of hazardous materials in the last 10 to 20 years, this type of accident is not one that has necessarily occurred in the past in any given community, yet there is a 10% or greater chance that it can occur in any given future year based on current levels of activity.

Reasonably likely accidents are events predicted to occur between once every 10 years and once every 100 years on average. There is somewhere between a 1% and 10% chance of such an event occurring in the locality of concern in any given year for the identified scenario. In that similar scenarios involving different materials may also occur, the overall likelihood of an event requiring a certain type of emergency response could be much higher. (Note: This is equally true for the other categories.)

Unlikely accidents are events predicted to occur between once every 100 years and once every 1000 years on average in a specific locale. They are unlikely to occur within the foreseeable future or during the lifetime of current inhabitants. Chances of their occurring in any given future year are less than 1% and possibly as low as 0.1% for each specific scenario.

Very unlikely accidents are events predicted to occur less than once in 1000 years. The odds are at least 100 to 1 *against* such an event occurring in the next 10 years in a specific locale. The chances of one occurring in any particular future year are less than one in a thousand.

If one is only evaluating releases qualitatively, common and likely accidents may be equated to "high", reasonably likely and unlikely accidents to "medium", and very unlikely accidents to "low" probability categories.

13.3 DEFINITION OF ACCIDENT SEVERITY CATEGORIES

It is also necessary to classify accident scenarios according to their severity as defined via application of consequence analysis procedures. To assist in this effort, accident consequences are classified into the four categories defined below, these being:

- Minor accidents,
- Accidents of moderate severity,
- Major accidents, and
- Catastrophic accidents

Minor accidents are specified herein as those with the potential to have one or more of the following features:

- Low potential for serious human injuries.
- No potential for human fatalities.
- No need for a formal evacuation, although the public may be cleared from the immediate area of the spill or discharge.
- Localized, non-severe contamination of the environment which does not require costly cleanup and recovery efforts.
- No need for resources beyond those normally and currently available to local response forces.

Accidents are specified herein as of moderate severity when they have the potential to have one or more of the following features:

- Up to 10 potential human fatalities.
- Up to 100 potential human injuries requiring medical treatment or observation.
- Evacuation of up to 2000 people.
- Localized contamination of the environment requiring a formal but quickly accomplished cleanup effort.
- Possible assistance needed from county and state authorities.

- Only limited need for specialized equipment, services, or materials for a rapid and effective response.

Major accidents are specified herein as those with the potential to have one or more the following features:

- Up to 100 potential human fatalities.
- Up to several hundred potential human injuries requiring medical treatment or observation.
- Evacuation of up to 20,000 people.
- Significant contamination of the environment requiring a formal and somewhat prolonged cleanup effort.
- Assistance needed from county, state, and possibly federal authorities.
- Significant need for specialized equipment, services, or materials for a rapid and effective response.

Catastrophic accidents are defined as those having the potential to have one or more of the following features:

- More than 100 potential human fatalities.
- More than 300 potential human injuries requiring formal medical treatment.
- Evacuation of more than 20,000 people.
- Significant contamination of the environment requiring a formal, prolonged, and expensive cleanup effort to protect human health and the environment.
- Assistance needed from county, state, and federal authorities.
- Significant need for specialized equipment, services, or materials for a rapid and effective response.

Which category a given scenario falls into can be determined by considering consequence analysis results along with local maps and population data.

There are two points to be made about the accident severity categories defined above. The first is that they do not represent hard and fast rules. What some people may perceive as a minor or routine incident may seem to be a major event to others. Do not hesitate, therefore, to make any changes to the procedure if some point or another makes you uncomfortable. After all, the authorities in a major city are likely to deal with loss of life and serious injuries due to various "non-natural" causes on almost a daily basis. It is understandable that they may have a different perspective on such events than the authorities of a small and quiet town in a rural part of the country.

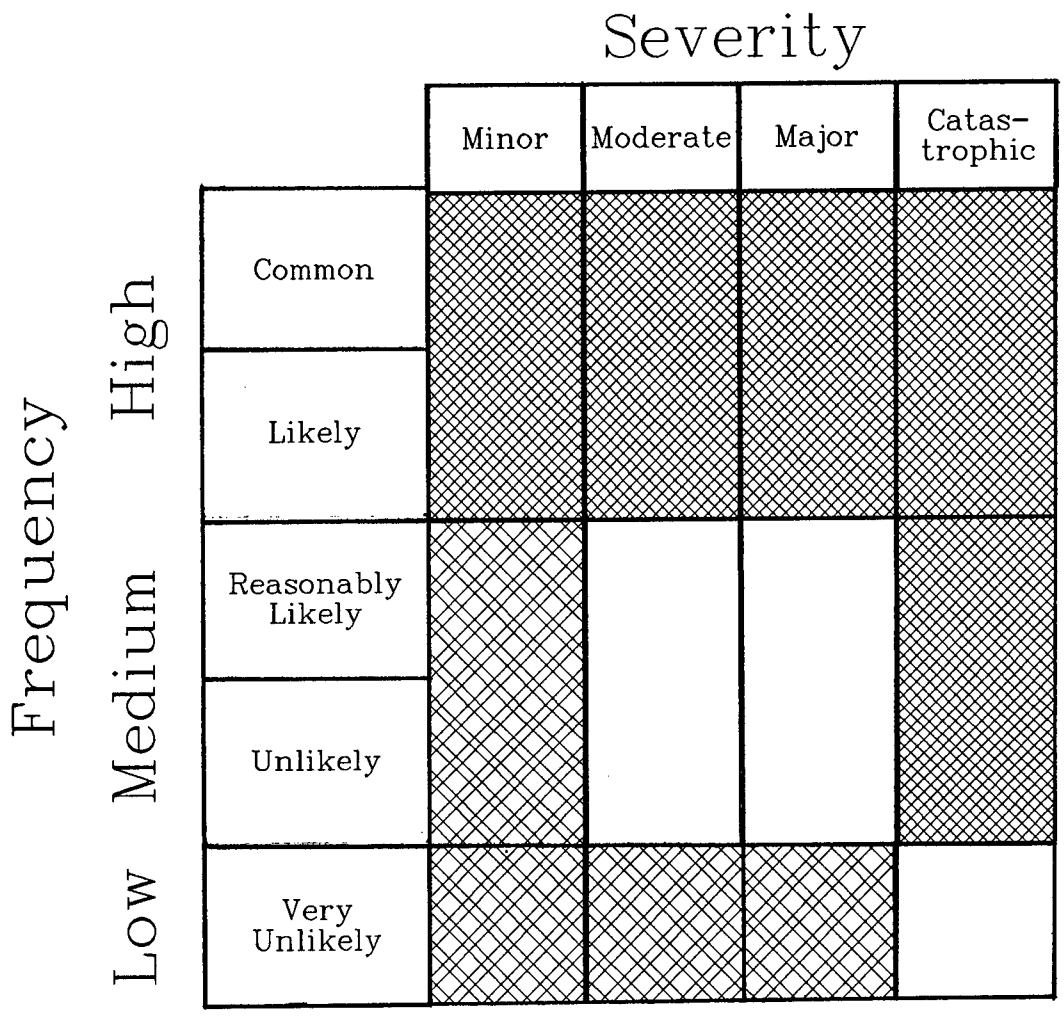
The second point to be made is that the accident severity categories above are partially defined in terms of *potential* deaths and injuries. It must be realized that consequence analysis procedures essentially provide estimates of the *area* or *zone* that may be subjected to harmful levels of airborne contaminants, thermal radiation, and/or explosion overpressure. Although people within such an area will have a definite potential to be killed or injured, a large fraction may actually escape unharmed. Reasons for this are varied and complex, but think about how many times the evening news has shown a community devastated by a tornado, with dozens of buildings and homes knocked flat, and only reported a death or two (if any) and a handful of injuries.

13.4 APPLICATION OF SCREENING GUIDELINES

Figure 13.1 presents a matrix of accident probability categories versus accident severity classes. Each block of the matrix *suggests* a planning approach to be taken for accident groups that meet criteria associated with the block. *These approaches are only suggestions and should be treated as such.* Special circumstances may require special consideration on a case by case basis. Specific guidelines should be worked out by each locale to best represent the resources and relationships between organizations applicable to that community.

The matrix should be applied only at the level of government or industry that identified and analyzed the planning basis scenarios for a particular locale or jurisdiction. The reason for this stems from the fact that levels of authority above the local level typically have responsibility for several individual jurisdictions. Since there is a higher probability that a particular type of accident will take place within a large jurisdiction than in a specific smaller one within its borders (e.g., a county vs. a town), a higher level of authority may find it necessary to plan for accidents that are too rare to worry about at a lower level. This does not mean, however, that all jurisdictions should not work together in coordinating their response to rare events. Rather, it means that the higher level authority should probably take a leadership role in such instances.

FIGURE 13.1
ACCIDENT FREQUENCY/SEVERITY SCREENING MATRIX



Comprehensive planning and preparedness are essentially mandatory at the appropriate levels of government or industry.

Comprehensive planning is optional and does not necessarily warrant any major efforts or costs. Give consideration to sharing any necessary special response resources on a regional basis.

Comprehensive planning may be unwarranted and unnecessary.

The frequency (annual probability) has been reduced to three categories to reflect the fact that the treatment of individual scenarios may produce low annual probabilities, yet the chance of a similar accident involving one of a number of different hazardous materials may be much higher. The original five categories may be used to prioritize accident scenarios more precisely within the broader categories.

13.5 MOTIVATION FOR CONTINUED PLANNING

The EPA recently sponsored an intensive effort to determine the number and severity of accidents involving hazardous material releases in the six-year period of 1980-1985. The total number of deaths recorded was 138, for an average of 23.0 per year, for the entire United States. The annual average expected for any jurisdiction of 100,000 people can therefore be computed as being on the order of 0.01 per year. Given that the identification of deaths due to all episodic hazardous material accidents is difficult due to current reporting requirements, it is likely that the EPA underestimated the true extent of the problem. Nevertheless, the fatality rate would still be relatively minor even if multiplied by 10 or even 100.

These figures can be compared to annual mortality statistics in the United States to put the overall problem of hazardous materials into the proper perspective. To help do this, Table 13.1 presents annual mortality rates for a variety of natural and accidental causes of death using statistics for recent years. The actual number of deaths that may be expected each year *on average* due to any specific cause in any particular jurisdiction can be obtained by multiplying the annual mortality rate for that cause by the population of concern.

Given the above findings one might wonder why there is such widespread concern about the dangers of hazardous materials. The answer to this question is actually quite complex. Part of it involves the fact that recent major accidents in *other* countries have demonstrated the *potential* for a *single* accident to cause hundreds if not thousands of deaths and injuries. Although the safety record of the U.S. chemical industry has generally been excellent, in terms of loss of life, people here (including government agencies) have naturally felt a need to reassess safety standards and ensure our country is prepared to deal with future emergencies. Yet another part of the answer involves the realization that hazardous material accidents differ greatly from more typical accidents and require special preparations for an effective response. Indeed, it is precisely a lack of knowledge about chemical threats facing a community, and a lack of specific preparations to counter these threats, that can lead to a disaster that may otherwise have been prevented.

Finally, it must be appreciated that the general public has a greater fear of threats that can cause multiple fatalities, threats they may not fully understand or have any control over, and threats due to activities that do not provide a direct benefit on an individual basis. The

TABLE 13.1

ANNUAL INDIVIDUAL MORTALITY RATES FOR NATURAL AND ACCIDENTAL CAUSES OF DEATH

Cause of Fatality	Risk of Fatality (per 100,000 people)
All Diseases	830
Heart Disease	320
Cancer	190
Cerebrovascular Disease	64
Pneumonia	28.3
Diabetes	15.5
All Accidents	39
Motor Vehicles	19
Falls	5.0
Drowning	2.2
Fires, Burns	2.1
Natural Hazards and Environmental Factors	0.8
Cataclysm (tornado, flood, earthquake, etc.)	0.09
Excessive Heat	0.09
Excessive Cold	0.40
Lightning	0.04

Source: *Accident Facts*, 1988 Edition, National Safety Council

reasons why tens of thousands of highway deaths are tolerated each year partially stem from the facts that they usually occur one or two at time, individuals have control over whether they drive or ride in automobiles, and because automobiles are perceived to provide a substantial benefit to each individual.

14.0 USE OF HAZARD ANALYSIS RESULTS IN EMERGENCY PLANNING

14.1 INTRODUCTION

Planning personnel who have followed the preceding guidance of this document should have gained considerable insight into the true problems and risks associated with hazardous materials in their respective jurisdictions. Additionally, they should have an understanding of the probability, nature, and likely consequences of potential accidents. It remains to discuss how this knowledge can be best utilized during plan preparation to ensure prompt, efficient, and effective response to actual emergencies.

The discussions that follow are intended to ***supplement*** guidance provided by the National Response Team in the ***Hazardous Materials Emergency Planning Guide*** (NRT-1). That particular publication discusses how to organize the overall emergency planning process and provides a suggested outline for the resulting plan, *an outline that contains numerous important topics not directly associated with hazard analysis results but vital to the completion of a comprehensive emergency plan.* In contrast, this chapter mostly limits itself to planning issues directly related to findings of a hazard analysis and has the objectives of 1) providing more detailed guidance in this topical area than found in NRT-1; and 2) bridging the gap between this guide to hazard analysis and other more comprehensive publications devoted to emergency planning and/or emergency response to emergencies.

Readers are advised that this chapter focuses on planning for *significant* incidents involving spillage or discharge of a hazardous material and not the minor types of spills or leaks that are relatively common and of a routine nature. In addition, it should be noted that chapter contents are only intended to give readers a strong *push* in the right direction. Decisions will be necessary on a case by case basis as to whether any particular planning activity is desired or considered warranted by local conditions. Special or unique circumstances may require planning efforts and activities not addressed by this chapter.

Finally, be advised that the chapter is directed to planning personnel in state and local governmental agencies. Although much of the guidance and discussion presented in the chapter is also applicable to emergency planning for specific industrial sites, such sites are likely to have additional planning needs not addressed herein. For the benefit of industrial planning personnel, a later section of the chapter references specific publications better suited to the needs of industry for development of in-plant emergency response plans.

14.2 ORGANIZATION OF THE CHAPTER

Chapter 14 addresses 43 separate topics associated with emergency response planning in 12 subject areas, with Table 14.1 serving as an overall index. These topics are assigned unique "item" numbers for reference and organization purposes.

Each topic is presented and discussed in an individual section of the chapter using a standardized format. Each of these sections denotes the circumstances under which the planning item is applicable, states the planning goal to be achieved, suggests one or more action items for accomplishment of this goal, and ends with a brief discussion of the overall topic. Planning personnel should refer to the ***Hazardous Material Emergency Planning Guide*** for advice on how to organize results of their planning activities into their final written plan.

14.3 ADDITIONAL SOURCES OF PLANNING GUIDANCE AND INFORMATION

Additional details on what to plan for, how to plan, and how to manage response to an overall incident involving spillage or discharge of a hazardous material can be found in numerous other publications.

Publications of the Federal Emergency Management Agency

Given that FEMA is the primary agency of the federal government having responsibility for planning for *all* types of emergencies with the potential to threaten public health and safety in the United States, and that the agency employs numerous personnel who are experts in this field, it is not surprising to find that FEMA has published several documents that can be *extremely useful* to state and local planning agencies as well as industrial facilities. Indeed, it is ***strongly*** recommended that planning personnel obtain, review, and make use of *at least* the following three documents while planning for emergencies related to non-radioactive hazardous materials. Chapter 1 provides information on how these documents may be obtained, though it is highly likely that most governmental emergency preparedness organizations (particularly civil defense agencies) will already have copies of the first two publications on hand.

- ***Guide for Development of State and Local Emergency Operations Plans***
- ***Guide for the Review of State and Local Emergency Operations Plans***
- ***Hazardous Materials Contingency Planning Course*** (student manuals)

The planning course is designed to be presented by a trained instructor and involves the viewing of several video tapes in the classroom. Nevertheless, several of the nine separate student reference manuals contain truly excellent and highly detailed information and guidance on important topics that could only be allocated a few paragraphs of general discussion in this chapter.

Publications of the Disaster Research Center

Individuals wishing to obtain a more formal and indepth "education" with respect to problems and issues associated with emergency planning and response are advised to request a publication list from the Disaster Research Center, University of Delaware, Newark, Delaware, 19716 (telephone 302-451-6618). A representative sample of some excellent books, reports, and articles of potential value to both public and industrial planning personnel includes:

- Tierney, K.J., ***A Primer for Preparedness for Acute Chemical Emergencies,*** Book and Monograph #14, 1980.

- Quarantelli, E.L., ***Organizational Behavior in Disasters and Implications for Disaster Planning,*** Report Series #18, 1985.

- Quarantelli, E.L., and Gray, J., ***First Responders and Their Initial Behavior in Hazardous Chemical Transportation Accidents,*** Preliminary Paper #96, 1985.

- Gray, J., ***Three Case Studies of Organized Responses to Chemical Disasters,*** Misc. Report #29, 1981.

- Quarantelli, E.L., ***People's Reactions to Emergency Warnings,*** Article #170, 1983.

- Quarantelli, E.L., et al., ***Evacuation Behavior and Problems: Findings and Implications from the Research Literature,*** Book and Monograph Series #18, 1984.

- Quarantelli, E.L., et al., ***Evacuation Behavior: Case Study of the Taft, Louisiana Chemical Tank Explosion Incident,*** Misc. Report #34, 1983.

Publications Oriented Towards Industrial Emergency Planning

Guidance documents particularly suited to the task of emergency planning for the protection of employees and property within the boundaries of individual industrial facilities include:

- ***Site Emergency Response Planning***, Chemical Manufacturers Association, 1986. See Chapter 1 for information on obtaining publications of this organization.

- Newton, J.E., ***A Practical Guide to Emergency Response Planning***, Pudvan Publishing Co., 1935 Shermer Road, Northbrook, Illinois, 60062, 1987 (telephone 312-498-9840).

Other Books and Reports

Dozens of books and manuals pertaining to planning or management of hazardous material emergencies have been written over the years, with literally a flood of such publications (some good, some not so good) appearing in the aftermath of the Bhopal tragedy. A *sample* of publications worthy of special mention (who due apologies to authors whose works were not identified or reviewed) includes:

- American Petroleum Institute, ***Developing a Highway Emergency Response Plan for Incidents Involving Hazardous Materials***, API Recommended Practice 1112, available from the API, 1220 L Street Northwest, Washington, D.C., 20005, November 1984.

- Bennett, G.F., et al., ***Hazardous Materials Spills Handbook,*** McGraw-Hill Book Company, New York, 1982.

- Cashman, J.R., ***Hazardous Materials Emergencies Response and Control,*** TECHNOMIC Publishing Company, 851 New Holland Avenue, Box 3535, Lancaster, Pennsylvania 17604, 1983.

- International Association of Fire Chiefs, ***Fire Service Emergency Management Handbook,*** available from IAFC Foundation, 101 E. Holly Ave. - Unit 10B, Sterling, VA 22170, January 1985.

- Omohundro, J.T., ***Oil Spills: A Public Official's Handbook,*** Report No. PB80-184351, prepared for the National Oceanic and Atmospheric Administration, available from the National Technical Information Service, Springfield, VA 22151, March 1980.

- Shaver, D.K., and Berkowitz, R.L., ***Guidelines Manual: Post Accident Procedures for Chemicals and Propellants,*** Report No. AFRPL TR-82-077, prepared for the Air Force Rocket Propulsion Laboratory and the U.S. Department of Transportation, available from the National Technical Information Service, Springfield, VA 22151, January 1983.

- Shaver, D.K., Berkowitz, R.L., and Washburne, P.V., ***Accident Management Orientation Guide,*** Report No. AFRPL TR-82-075, prepared for the Air Force Rocket Propulsion Laboratory and the U.S. Department of Transportation, available from the National Technical Information Service, Springfield, VA 22151, October 1983.

- Smith, A.J., Jr., ***Managing Hazardous Substance Accidents,*** McGraw-Hill Book Company, New York, 1981.

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ITEM #N1

Topic: ***Initial Notification of Spills***

When/Where Applicable: Any locale with hazardous material spill or discharge potential.

Planning Goal: Establishment of central contact point(s) for initial notification of spills to facilitate response plan activation.

Action Items:

- Identify the 24-hour telephone number(s) that is (are) to be called by members of the public, industry personnel, and government employees to report a spill or discharge or any situation that could result in such an event in the near future.

- Identify and list the information that should be requested from the caller to facilitate initial assessment of the gravity of the situation.

- Ensure that all parties have been advised of reporting procedures.

Discussion:

Ordinary citizens are likely to call local police or fire departments if they observe an accident, and it is reasonable to assume that most jurisdictions will not discourage the practice. This does not mean, however, that one of these organizations must always serve as the central point of contact for coordinating communications during hazardous material emergencies. A better choice in some jurisdictions may be a predesignated emergency command post or emergency operations center at either the local or county level that has regular telephone, "hot" line, and/or radio communications links with response forces, public authorities, and major industrial complexes.

In localities with major fixed-site potential spill sources, it is vital that all facility operators know exactly when and where to call to report an incident to local government authorities, and that all public officials in the area are in agreement as to required notification procedures. Bluntly stated, the planning group should make every effort to resolve "turf battles" and interagency squabbles as well as the real (yet sometimes political) needs of elected officials.

ITEM #N2

Topic: ***Notification of Response Organizations and Public Authorities***

When/Where Applicable: Any locale with hazardous material spill or discharge potential.

Planning Goal: Rapid activation of emergency response forces at a level consistent with the known gravity of the situation.

Action Items:

- Provide the central contact point(s) with instructions and procedures relating to alert or call-out of response forces, including the individual or his/her alternates with command responsibility for spill response in the jurisdiction of concern.

Discussion:

The watch-stander or dispatcher who first receives notification of an accident involving hazardous materials should have fairly detailed instructions with respect to who should be notified of the event and/or who should be asked to respond. Minor incidents may simply require dispatch of a fire department to the scene. More significant events may necessitate call-out of additional forces and notification of county, state, and federal authorities. In any case, it should be clear to all as to who will be alerted under varying circumstances and who will be in charge of response actions during various phases of an emergency situation.

Communities that frequently experience hazardous material emergencies of a minor nature but are only rarely faced with more significant events may wish to consider a staged response. For example, depending on the severity of the situation as described by the initial caller, various levels of response might be established, thus avoiding the immediate need to call out forces in strength for all incidents. Personnel arriving at the scene could, of course, request additional assistance and thereby raise the level or stage of response, much as additional alarms might be sounded during major fires or the threat thereof.

One strategy to be considered for establishing levels of response classifies responses into three levels as follows:

Level 1: An incident which can be controlled by the first response agencies and does not require evacuation of other than the involved structure or the immediate outdoor area. The incident is confined to a small area and does not pose an immediate threat to life or property.

Level 2: An incident involving a greater hazard or larger area which poses a potential threat to life or property and which may require a limited evacuation of the surrounding area.

Level 3: An incident involving a severe hazard or a large area which poses an extreme threat to life and property and will probably require a large scale evacuation; or an incident requiring the expertise or resources of county, state, federal, or private agencies/organizations.

If military explosives can be found in the region of concern at times, the plan should identify the nearest military base that can provide assistance with these materials. Similarly, where radioactive materials may pose a threat, it should identify the nearest radiological emergency assistance team established by the Department of Energy or the state (see NRT-1 for DOE regional contacts). Where etiologic materials (those posing biological or biomedical hazards) may be encountered, it is well to list the emergency information telephone number for the Director of the Center of Disease Control in Atlanta, Georgia, this being 404-633-5313. Other important telephone numbers at the national level include:

- National Response Center: 800-424-8802 (202-426-2675 or 202-267-2675 in Washington, DC area), for notification, information, and assistance involving agencies of the federal government.

- Chemical Transportation Emergency Center (CHEMTREC): 800-424-9300, for information and assistance from industry as coordinated by the Chemical Manufacturers Association.

ITEM #N3

Topic: ***Facilities Requiring Special Notification***

When/Where Applicable: Where a major incident may occur in a location that threatens schools, day care centers, hospitals, nursing homes, universities, prisons, and similar facilities serving large groups of people with needs for special transportation, protection, or handling.

Planning Goal: To ensure that the above facilities receive the earliest possible notification of the need to shelter-in-place or evacuate their inhabitants.

Action Items:

- Identify and obtain the telephone numbers and names of key supervisory personnel in facilities that meet the above criteria.
- Ensure that the emergency response plan provides for direct notification of these facilities on a prompt basis.
- Ensure that the emergency response plan contains a procedure for notification of these facilities during periods of interrupted telephone service.
- Encourage facility operators to establish emergency evacuation plans coordinated with those of the community.
- Ensure that the person(s) responsible for notification of these facilities document their actions during an emergency.

Discussion:

Time can be critical during some hazardous material emergencies. The above action items ensure that facilities requiring special attention are notified at the earliest possible indication of a threat, thus permitting them an early start to evacuating or otherwise protecting their inhabitants.

ITEM #N4

Topic: ***Notification of Water Users***

When/Where Applicable: Any locale that may experience a spill of a hazardous material into a body of water.

Planning Goal: To ensure that industrial, agricultural, public water supply, and other users of water resources are quickly notified of potential water contamination in the aftermath of a spill.

Action Items:

- Compile a list of those companies or facilities that extract water from water bodies in the area of concern, together with a list of appropriate contacts and telephone numbers at these facilities.
- Establish a mechanism by which these facilities may be quickly informed of potential water contamination in the event of an upstream hazardous material spill.

Discussion:

Numerous facilities intake water from nearby water bodies for industrial or food processing purposes, farm irrigation, drinking supplies, and so forth. Entry of a toxic, flammable, or corrosive material into their water intakes can contaminate food or drinking water, damage equipment, ruin products, and possibly even cause a fire or explosion.

These facilities may be identified during the survey process discussed in Chapter 10, by a special survey of facilities along the "waterfront", or possibly, by a search of local, state, or federal permit records (presuming some sort of permit was required for them to intake water from the water bodies in question).

Note that it may not be necessary for public authorities to call a long list of facilities themselves. It is entirely feasible to establish a "waterway warning network" in which each person receiving a call on behalf of a facility is given responsibility to call two or more other facilities in the downstream direction. This would mean that public officials would only have to make one or two telephone calls to start the process.

In undertaking this planning task, realize that spills with the potential to adversely impact water quality, particularly spills into rivers, need not actually occur in the jurisdiction of concern. Indeed, they could occur at locations many miles upstream from jurisdictional boundaries.

ITEM #N5

Topic: ***Notification of Water Treatment Plants***

When/Where Applicable: Where spillage of a hazardous material may enter a sewage or drainage system leading to a municipal treatment plant.

Planning Goal: To ensure that the treatment plant is warned as soon as possible of the event.

Action Items:

- Identify the 24-hour telephone numbers and names of key supervisory personnel in the subject facilities.
- Plan to have these personnel notified immediately if hazardous materials enter the waste streams to their plant.
- Identify sewer shut-off points for the containment of hazardous materials that may leak or flow into sanitary and storm sewers.

Discussion:

The sudden appearance of a toxic or flammable substance can cause many problems and serious hazards at a treatment plant. Early notification may help prevent or mitigate adverse impacts.

A study sponsored by the EPA may be of use to biological wastewater treatment plants in assessing the effects of potential hazardous materials spills and developing emergency plans. The reference is:

> Brinsko, G.A., et al., ***Hazardous Material Spills and Responses for Municipalities***, Report No. PB 80214141, available from the National Technical Information Service, Springfield, VA 22161, July 1980.

Note that this report is solely devoted to wastewater treatment plant problems. Its title is somewhat misleading in that it suggests broader coverage of spills and related response actions.

See Item #SC3 for additional information and discussion of problems associated with entry of flammable liquids into storm drains.

ITEM #N6

Topic: ***Notification and Shutdown of Electric and Gas Utilities***

When/Where Applicable: Wherever a large explosion or potential explosion may necessitate shutdown of electric power or natural gas distribution systems in an area.

Planning Goal: To identify who and where to call to have the above utilities shutdown on a rapid basis.

Action Items:

- Contact local utility companies and establish a mechanism to accomplish the planning goal.

Discussion:

Major explosions may be caused by or may themselves cause leaks or ruptures of natural gas distribution systems. Additionally, they can cause breaking of power lines and an electrocution hazard to those who might make contact with any "downed" lines. In either case, there may be circumstances in which it is desired to shutdown natural gas or electric power systems rapidly in an area.

ITEM #N7

Topic: ***Notification and Control of Air, Rail and Waterborne Traffic***

When/Where Applicable: Any locale in which a hazardous material accident may threaten airplanes, helicopters, trains, barges, ships, recreational boaters, and other non-highway traffic not normally aware of local conditions.

Planning Goal: To identify the means to warn aircraft, trains, and waterborne traffic of a hazard and to keep them away from the hazard zone.

Action Items:

- Identify air traffic control facilities, railroad dispatchers, and Coast Guard or harbor master facilities that have the ability to warn and control the movement of the subject traffic in the area or jurisdiction of concern.

Discussion:

The planning goal and action items are mostly self-explanatory. It is only necessary to add that a train accident on a heavily travelled segment of track may require immediate dispatch of personnel to locations where they can attempt to flag down and stop other trains approaching the accident site. Overflight of any incident site should be prohibited except with permission from the Federal Aviation Administration (FAA) and on-scene authorities. Where available, helicopters having public address systems can facilitate warning of traffic and even the general public.

ITEM #CC1

Topic: ***Establishment and Staffing of Command Posts***

When/Where Applicable: Wherever a coordinated, large-scale response may become necessary due to a major spill or discharge of hazardous materials.

Planning Goal: To quickly establish one or more command posts from which the emergency response may be directed and coordinated.

Action Items:

- Select an appropriate location (and possible alternate) for rapid establishment of a primary command post or emergency operations center.
- Plan for a field command post near the site of the emergency from which spill containment and countermeasure operations may be conducted when necessary.
- Designate the individuals who should immediately report to each site in the event of a major emergency.
- Establish a "check-in" location where key officials can be "logged in" and their movements tracked once they appear on the scene.
- Establish an ID system to control and track entry and movement of public authorities and emergency crews.
- Equip sites with the office equipment, maps, data sources, communication systems, and other supplies and resources necessary for command and control of response activities.
- Provide security and access control at vital sites such as the emergency operations center, communications center, media center, emergency supply center or depot, and the incident site itself.

Discussion:

A complex emergency requires coordination of numerous activities beyond spill containment and countermeasure efforts. There can therefore be benefits to establishment of both central and field command posts. The former, while in close communication with the field site, can handle relations with the press, evacuation operations, contacts with the public and outside government agencies, procurement of necessary supplies and resources, and a variety of other details. The field site can then concentrate on its own key mission of directing hazard containment and control operations.

The central command post should ideally be assigned representatives of all agencies and organizations with a role in emergency response, as well as support personnel including secretaries, clerks, radio operators, messengers, and so forth. This will facilitate communications, decision-making, and conduct of necessary efforts.

Serious consideration should be given to establishing a "check-in" location at each command post, for requiring all individuals to "sign in" and "sign out" (particularly at the incident site), and to issuing ID cards and/or badges to personnel authorized to pass through roadblocks and enter controlled areas. Color-coded badges or items of clothing may be used to designate different levels of access and/or on-scene authority.

Note that the establishment of a local command organization for management of emergencies is a related prerequisite more fully discussed in the ***Hazardous Materials Emergency Planning Guide*** and the ***Hazardous Materials Contingency Planning Course*** manuals referenced earlier in this document. Emergency plans should contain a clear and concise summary of primary and support responsibilities for: Command and Control, Alerting and Notification, Communications, Public Information, Accident Assessment, Public Health and Sanitation, Social Services, Fire and Rescue, Traffic Control, Emergency Medical Services, Law Enforcement, Transportation, Public Protective Actions, Exposure Control, and Public Works functions, among others. Block diagrams should illustrate the relationships among the various response groups, each of which may require assignment of a specific manager under the overall direction of an individual assigned overall responsibility and authority for command of emergency operations. The command and control team and its written plan must provide a capability for 24 hour protracted operations (requiring the establishment of work shifts), definition of decision-making processes in at least general terms, availability of sources of assistance (including specialized experts) to aid decision-making, and establishment of a means to determine operational readiness. Possible staging areas should be identified for gathering and dispatch of response forces as necessary. One or means must be available to obtain detailed and accurate information on the hazards and properties of any and all chemicals involved in an accident on a rapid basis.

Keep in mind during planning for the above activities that areas outside established hazard zones will continue to require some degree of police, fire, rescue, ambulance, health care, and public works services.

Give consideration to identifying sources of video and telephoto equipment that can be used to view particularly hazardous accident sites from a safe distance on a continuous basis at command, control, and media centers. A closeup view of the site on a television screen can be extremely helpful to all parties to the response action in evaluating and choosing the appropriate course of action, as well as satisfy media requests for photo coverage and many of the information needs of government officials on scene. It also enables experts to provide guidance to response personnel approaching the site to undertake fire control, leak plugging, spill containment, and/or spill cleanup efforts.

One of the first steps of a response action must be restriction of access to the spill site and other hazardous areas. There is a not-so-old saying that states "if you want to draw a very large crowd instantly, in the middle of nowhere, dump something lethal on the ground and set it on fire." Experienced emergency coordinators will attest to the validity of this observation.

ITEM #CC2

Topic: ***Establishment of Emergency Communication Systems***

When/Where Applicable: Wherever a coordinated, large-scale response may become necessary due to a major spill or discharge of a hazardous material.

Planning Goal: To quickly establish secure communication links between all major parties to a response action.

Action Items:

- Designate the primary and alternate individuals responsible for communication links at important locations.
- Survey the kinds and types of communication systems used by various agencies and organizations with a major role in emergency response, particularly with respect to radio-communications equipment.
- Work out (at the very least) a system whereby the central command post can communicate with all key parties to an incident and relay messages between them regardless of the possible overloading of normal communication channels.
- Where necessary, have telephones with "unlisted" numbers installed at key locations.
- Where necessary, determine the procedure necessary to request the installation of new or additional telephone lines by the local telephone company at various locations on an emergency basis.

Discussion:

Good communications are critical to a successfully orchestrated response action, particularly if a number of different agencies or organizations at the local, county, state, and even federal level have important roles. Unfortunately, however, radio systems are unlikely to be compatible among all parties, thus complicating overall coordination of activities. Field personnel may not have ready access to telephones at all times. Incoming calls from members of the public, news reporters, and a wide variety of others seeking information, can tie up or slow available telephone service to emergency operations centers, police departments, fire departments, and offices of public officials, if not throughout the entire community.

Where current radio systems are incompatible and there is limited opportunity to replace or supplement existing units with compatible devices, the problem can be solved in a fashion by planning to have each key responding agency or organization dispatch a radio-equipped vehicle and driver to the central command post parking lot. If the command post itself has radios compatible with one or more of the mobile units, messages can be relayed between various systems by drivers of the vehicles.

Incidents that are obviously going to require long-term response activities and/or evacuations (i.e., more than a day or two) may necessitate the installation of temporary telephone lines at various centers of activity (including the field command post). It is well to know beforehand how to request such emergency service from the local telephone company. Alternatively, vehicles with cellular telephones may be stationed at the site.

There are definite benefits for all emergency operation centers (including those at major industrial facilities) to have several phone lines with unlisted and confidential telephone numbers. These can provide open lines of communications when all others are tied up.

With respect to the overall use of telephones, take special precautions where an explosion or fire at some critical location may destroy vital communication links or services.

Give serious thought to organizing and taking advantage of the capabilities of local ham radio operators in the area where and when their services may be necessary. Many of these individuals take their hobby very seriously, are likely to have fixed station and portable equipment that not only equals but exceeds the capabilities of local authorities (since most ham radio operators truly enjoy attempting to contact distant states, countries, and even continents with high power equipment), and will be more than willing to lend a helping hand during an actual emergency.

It can also be prudent to establish a system for tracking, documenting, and prioritizing messages, to test all vital communication links on a periodic basis, to inventory equipment every so often, and to ensure vital equipment is properly maintained (and replaced with alternate systems while undergoing repair).

ITEM #CC3

Topic: ***Formulation of Response Objectives and Strategy***

When/Where Applicable: Wherever a spill, leak, fire, or potential explosion incident involving hazardous materials may occur.

Planning Goal: To Establish procedures for formulating response objectives and strategies, and to identify emergency situations in which response personnel should limit their activities until the situation has "stabilized" or until further information or expert assistance has been obtained.

Action Items:

- Use the results of the hazard analysis to identify situations in which response personnel should not intervene or should limit or restrict their response actions.

- Establish procedures for evaluating hazards, risks, and site conditions so that response objectives and strategy can be properly formulated at the scene of an incident or accident.

Discussion:

Spill response guides published by industry and government alike often contain phrases like "do not extinguish burning cargo unless the flow can be stopped safely." Additionally, they almost universally advise response personnel to withdraw in the event of any sign that a tank may explode (such as discoloration of the tank or rising sound from a venting pressure relief device) or if the fire cannot be controlled by unmanned devices. More than one fire department has planned to allow certain buildings (such as pesticide warehouses) to burn while only protecting adjacent structures with water, thus preventing serious pollution problems from chemically-contaminated runoff.

It follows from the above that there are potential accident scenarios in which the risks associated with certain types of response activities may exceed any benefits to be realized, thus providing ample reason to only undertake protective and containment actions from a safe distance until the situation has stabilized or expert assistance has been obtained. General examples of situations in which the best course of action may be to hold back from a direct "attack" include:

- When a major release takes place that poses unknown hazards or hazards for which response personnel are not equipped or prepared.

- When a flammable gas or liquid is on fire and extinguishment could lead to release of toxic or flammable vapors or gases, and possibly, explosive reignition.

- When there are no endangered persons or structures nearby and the container(s) and/or hazardous materials present significant hazards to response personnel.

- When the addition of water to a fire may serve to spread highly toxic contaminants into the environment, thus causing a pollution problem that may cost much more to resolve than the value of the burning materials, vehicles, or buildings.

Due to the possibility of such situations, response personnel should assess each particular incident before taking action and formulate realistic response objectives. The assessment should be based on:

- Pre-incident plans and/or standard operating procedures

- Information that has been obtained regarding:

  - Material(s) involved
  - Container(s) involved
  - Vehicle(s) and/or structures involved
  - Atmospheric conditions affecting the incident

- Environmental monitoring and sampling data, if available

- Public protective actions that have or have not been initiated

- Resource requirements (i.e., trained personnel, specialized protective gear, other equipment, etc.)

- Hazards and risks posed to humans, animals, property, and the environment.

Upon completion of the incident assessment, command personnel will be in a better position to determine whether their response strategy should be defensive or offensive in nature. A defensive posture is best taken when intervention may ***not*** favorably affect the outcome of the incident, will likely place emergency response personnel in significant danger, and/or may possibly cause more harm than good. An offensive posture (i.e., one requiring response personnel to work well within the boundaries of hazard zones) is best taken when intervention is likely to result in a favorable outcome without exposing personnel to undue danger and without causing new and potentially more severe problems. In all cases, of course, actions to protect the public and environment outside the immediate spill or discharge area and/or to contain the hazard from a safe distance can be initiated regardless of whether a defensive or offensive response strategy is chosen at the actual incident site.

ITEM #CC4

Topic: ***Ensuring Health and Safety at Incident Scenes***

When/Where Applicable: Wherever a coordinated response may be necessary due to a significant spill or discharge of hazardous materials.

Planning Goal: To establish procedures for assuring the health and safety of response personnel operating at hazardous material incidents.

Action Items:

- Use the results of the hazard analysis to identify situations in which response personnel may be exposed to chemical or physical hazards at an incident scene.

- Establish standard operating procedures for a site safety and health program that addresses:

  - Establishment of hazard control zones
  - Positioning of personnel, apparatus, and equipment
  - Selection and use of personal protective gear
  - Safe operating practices
  - Medical surveillance and care
  - Decontamination of protective gear and equipment
  - Decontamination of response personnel
  - Maintenance of field personnel

- Identify equipment and materials that may be needed to support the site safety and health program.

- Establish procedures for obtaining any equipment and materials that may be needed to support the site safety and health program.

Discussion:

A system must be established to ensure the health and safety of emergency response personnel. The responsibility of establishing and managing the safety and health program should be assigned to a predesignated Safety Officer and an alternate, who may also be assigned one or more assistants.

An important component of the safety program will involve establishment of hazard control zones at the incident scene to limit the number of people in the most hazardous areas. The exact size and configuration of these hazard control zones must be determined and visually differentiated at each particular incident based on incident-specific factors and situations and may include the following:

- "Hot Zone" - Area of maximum hazard surrounding the damaged container(s) or fire area which may only be entered by specially equipped and trained response personnel.

- "Warm Zone" - Area of moderate hazard outside the Hot Zone in which properly equipped and trained backup crews standby and decontamination takes place.

- "Cold Zone" - Area outside the Warm Zone that poses minimal or negligible hazards to emergency personnel. The command post, most of the deployed apparatus, and the resource staging area should be located in the Cold Zone.

Safe operating procedures to be established and enforced by the Site Safety and Health Officer include but are not limited to:

- The use of appropriate protective gear and equipment (see Items #PP1 and #PP2 that follow).

- Limiting the number of personnel in the "Hot" and "Warm" hazard control zones.

- Utilizing the most experienced personnel for the most hazardous tasks.

- Positioning a backup team in the "Warm Zone" in case it is needed to assist or rescue personnel in the "Hot Zone".

- Providing medical surveillance for personnel before and after "Hot" and "Warm" Zone operations.

- Monitoring (visually and through communications contact) the welfare of personnel operating within the "Hot" and "Warm" Zones.

- Ensuring that all personnel understand their assignments.

- Ensuring that responders do not ingest contaminants through eating, drinking, or smoking.

- Enforcing a "No Smoking" policy at incidents involving flammable or combustible materials.

- Decontamination of protective gear and response equipment (see Item #PP3 that follows).

- Replacing fatigued personnel with "fresh" personnel.

- Adjusting hazard control zones to reflect changing conditions.

Where deemed necessary, properly equipped medical personnel and one or more ambulances should be available to check and (if necessary) treat injured or contaminated response personnel as necessary. These personnel should check the vital signs and general health of all personnel who will don specialized protective gear and enter "Hot" or "Warm" Zones, particularly where fully encapsulating protective suits are being used, since non-cooled suits can be very stressful to the wearer. The health of potentially exposed response workers should be rechecked as appropriate and deemed necessary upon completion of their duties.

Readers should be advised that the Occupational Safety and Health Administration (OSHA) has developed ***interim*** regulations for protection of workers at hazardous waste and emergency spill sites. Covering all hazmat teams, local fire and police departments, and emergency medical services, these regulations provide far more details than that provided herein on how to go about meeting site safety and health requirements. Planning personnel should therefore obtain the latest version of these requirements (see 29 CFR 1910.120) and ensure they are prepared to comply with their provisions. Final rules on this topic are expected during 1989.

The interim regulations currently in force reference several publications that provide guidance on establishing safe operating procedures. A sample of these and others of potential interest include:

- ***Standard Operating Safety Guidelines***, U.S. EPA Office of Emergency and Remedial Response, Hazardous Response Support Division, December 1984.

- ***The Decontamination of Response Personnel***, Field Standard Operating Procedures #7, available from same EPA office cited above, December 1984.

- ***Preparation of a Site Safety Plan***, Field Standard Operating Procedures #9, available from same EPA office cited above, April 1985.

- ***Work Zones***, Field Standard Operating Procedures #6, available from same EPA office cited above.

- ***Personal Protective Equipment for Hazardous Materials Incidents***: A Selection Guide, U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, October 1984 (see Items #PP1 and #PP2 also).

ITEM #EV1

Topic: ***Designation of Decision Responsibility for Public Protective Actions***

When/Where Applicable: Wherever public evacuations or other protective actions may become necessary due to hazardous material spills or discharges.

Planning Goal: To ensure the emergency plan denotes the specific individual(s) with authority to initiate and later terminate an evacuation or other protective action under varying circumstances.

Action Items:

- Check local and state laws and regulations to determine who has responsibility for evacuation or "shelter-in-place" decisions.
- Ensure that this individual is aware of the responsibility and prepared to act in a timely fashion.

Discussion:

Laws designating authority for public evacuations, activation of the Emergency Broadcast System (EBS), or activation of other means to alert or notify the public of an emergency vary from state to state and even possibly at the local level. Since time is critical during the initial stages of a real or potential emergency, it is necessary to know who has authority to make evacuation and similar decisions. In addition, it is necessary to ensure that this (these) individual(s) will be contacted promptly, will be given the information needed to make proper decisions, and will be capable of acting quickly and decisively.

Where these decisions are the responsibility of elected officials such as the governor of the state or local mayors, it may be prudent to ask these individuals to delegate the responsibility to the person(s) given overall command of response activities, particularly if these latter personnel are better qualified to assess the nature and magnitude of the threat.

Once the emergency is over, a person in authority must give approval to permit reentry of evacuated areas or to give an "all clear" signal. The response plan should also identify this individual.

ITEM #EV2

Topic: ***Criteria for Evacuation and Shelter-in-Place Decisions***

When/Where Applicable: Wherever public evacuations or other protective actions may become necessary due to hazardous material spills or discharges.

Planning Goal: To give command personnel guidelines with respect to: 1) the circumstances under which the public should be evacuated or instructed to shelter-in-place; and 2) the size and shape of the areas that should be considered vulnerable during various types of emergency situations.

Action Items:

- Make policy decisions with respect to levels of toxic agents, thermal radiation, and explosion overpressures which may be tolerable by the public.
- Compile data on the size and shape of potential hazard zones.
- Develop criteria for evacuation and shelter-in-place decisions.

Discussion:

This is not a topic commonly suggested for inclusion in hazardous materials emergency response plans but is one that definitely warrants attention. Time can be critical in situations that may require public evacuations or related protective actions and may not permit lengthy discussions or deliberations as to whether an evacuation is warranted or how large an area should be considered at risk. Predetermined criteria for decision-making can therefore greatly facilitate the process.

The accident scenarios developed via use of this guide, as well as the computational methods described in Chapter 12, can be a key source of information for evacuation planning where specific facilities or hazardous material shipments are known to pose a threat. These threats can be quantified via use of this guide and tabulated within the emergency response plan. Separate tabulations can be prepared for toxic vapor clouds or plumes, liquid pool fires, flame jets, potential BLEVEs, and the other specific hazards addressed by Chapter 12. Where alternative guidance is lacking, and the incident scenario is not one that was considered during the planning process, some thought may be given to the suggestion that the methods of Chapter 12 be applied on a real-time basis during emergencies to evaluate hazard zones.

The ***1987 Emergency Response Guidebook*** (DOT P 5800.4) contains guidance from the U.S. Department of Transportation (DOT) with respect to recommended evacuation distances for potential BLEVEs and vapor or gas hazards involving rail or highway vehicle accidents. The list of hazardous materials considered for gas or vapor hazard purposes (in an appendix to the DOT guide) is relatively short but includes those highly volatile substances most commonly transported in commerce.

This same section of the emergency plan should also give some guidance as to whether the public should be evacuated from a toxic vapor hazard zone or told to shelter-in-place -- or whether both protective measures should be considered for use in different portions of the zone (i.e., evacuation close in to the vapor source where concentrations are higher; shelter-in-place at further distances). See Appendix C to this document for further information on evaluation and implementation of the shelter-in-place option.

In all cases, remember that hazardous material spills can be "dynamic" events in the sense that incident conditions, the weather, and the wind direction can change with time. Guidance obtained from consequence analysis procedures provided in this document or other sources should only be considered a starting point for the decision process. In an actual emergency, evacuation area and/or hazard zone assessment must be a continuous activity.

ITEM #EV3

Topic: ***Public Alert/Notification/Instruction Procedures***

When/Where Applicable: Wherever public evacuations or shelter-in-place decisions may become necessary due to hazardous materials spills or discharges.

Planning Goal: To plan for and specify the methods and procedures by which the public will be alerted of an emergency situation and given instructions on what to do.

Action Items:

- Identify available alert and notification methods and practices.
- Specify which are to be used, who will use them, and when and how they are to be activated.
- Have lists of suitable shelter facilities available and procedures specified for assigning different groups of people to these various locations.
- Specify evacuation routes for all areas at risk based on results of the hazard analysis.
- Prepare sample messages for various situations.
- Establish a procedure to obtain and distribute appropriate protective equipment to personnel who may experience prolonged or excessive exposures to toxic contaminants while performing notification or evacuation operations. Provide training in use of this equipment as necessary.

Discussion:

Public authorities require the means to alert the public of an emergency situation and to give instructions to those individuals within a hazard zone or approaching such a zone.

Options for alerting the public include community or industrial facility horns or sirens, use of the Emergency Broadcast System (EBS), broadcasts by individual radio and television stations (including cable TV), use of police or fire department vehicles with public address systems, door-to-door coverage of neighborhoods by knocking on doors, use of an "all-call" system which rings all telephones in the area and repeats a recorded message, use of helicopters with public address systems, and various combinations of the above. Be advised that the public must be instructed *before* an actual emergency as to the meaning of warnings provided by horns or sirens via a public education program. Emergency planning requires knowledge of the specific procedures and access codes for utilization of the EBS and radio and television station resources. As an evacuation progresses, police, fire, public works,

and/or other government employees (depending on who might be the most readily available and free of other important duties at the time) may have to go door-to-door to ensure that all residents have been alerted and to provide assistance to the elderly, physically handicapped or hearing impaired. It is a good idea for these personnel to be equipped with appropriate personal protective equipment when necessary and a supply of chalk or colorful tags that can be used respectively to mark doorsteps or place on door knobs to indicate that the building has indeed been evacuated. Note that evacuation of people in individual residences who require special notification or assistance can be facilitated if public officials have compiled a list of those homes requiring special attention.

In designating evacuation routes, keep in mind that major roads are most desirable, but may not always be available. Since the direction of the wind at the time of a hazardous gas or vapor release cannot be predetermined, and since the direction may change with time, emergency personnel may require more than one option for any given hazard zone. As soon as an evacuation has been declared, police and auxiliary personnel should be prepared to control traffic on evacuation routes, to keep non-evacuation related traffic off these roads, and to remove any vehicles that breakdown and cause a slowdown of movement. These activities may in turn require the ready availability of tow trucks and portable roadblock materials (barricades, cones, signs, etc.). Additionally, thought should be given to removing impediments to traffic flow caused by excessive precipitation (rain or snow), fallen trees, crossing trains, and so forth.

Standard message formats for use in radio and television broadcasts can facilitate and reduce the time necessary to alert the public of a problem and inform them of the protective actions to be taken. The overall planning process must consider designation of evacuation routes and these routes should be identified in public warning messages, as should the location of shelters to which people with automobiles should proceed, the locations where people without automobiles should gather for pick up by buses or vans (see item #EV4), and what actions should be taken by people with children at school in a potential hazard zone. These messages should instruct people to bring any prescription medicines and special personal care items with them. See item #EV7 for a discussion of what to do about pets. The ***Hazardous Materials Contingency Planning Course*** manuals referenced in Chapter 1 provide several sample messages for consideration in accomplishing this objective. Keep in mind that messages may have to be broadcast in languages other than English in communities with concentrations of ethnic minorities.

Incidentally, be advised that there are likely to be people who for one reason or another may resist instructions to evacuate, even when confronted face-to-face with a police officer. Officers sent to persuade the last few families or individuals who refused to evacuate in a major 1986 evacuation in Miamisburg, Ohio, achieved considerable success by asking these people to provide information on their "next of kin" for use in the event of their demise. The holdouts, to the last person, got the message and cooperated with the evacuation order.

ITEM #EV4

Topic: ***Transportation Functions***

When/Where Applicable: Wherever public evacuations may become necessary due to hazardous material spills or discharges and public authorities find it necessary to provide transportation for evacuees.

Planning Goal(s): To plan for the availability of buses, vans, ambulances, and other vehicles to transport general members of the public without automobiles, school children, residents of hospitals and nursing homes, and possibly even prison populations to safe shelters.

Action Items:

- Assign one or more persons responsibility for coordination of transportation activities during an emergency.
- Establish agreements with public and private bus companies and ambulance services for provision of vehicles and drivers under emergency conditions.
- Develop evacuation plans for special occupancies such as schools, day care centers, hospitals, nursing homes, and prisons and the like, possibly coordinating efforts with similar facilities in some sort of mutual aid program.
- Develop communications, dispatch, and command/coordination systems for control of the vehicle fleet.
- Brief drivers on procedures periodically.
- Establish a procedure to obtain and distribute appropriate protective equipment to personnel who may experience prolonged or excessive exposures to toxic contaminants while performing notification or evacuation operations.
- Consider giving training to at least a portion of the drivers in the use of self-contained breathing apparatus (SCBA) if entry might be necessary or may unexpectedly occur (due to wind direction shifts or other factors) to zones with toxic air contamination.
- Select safe locations (to the extent possible) at which the public should assemble in their respective neighborhoods for pick-up by transport vehicles.

- Where large areas may be at risk (based upon results of the hazard analysis), plan for a staged evacuation with zones at highest risk being first evacuated, followed by zones with lesser risks.

Discussion:

The action items are self-explanatory. Note that a good evacuation plan is not only useful for hazardous material emergencies but any other emergency situation that may require relocation of the public. The presence of hospitals, large schools, nursing homes, and/or prison facilities can require detailed planning and preparedness to facilitate what will be a monumental task under the best of circumstances.

The individual given responsibility for transportation operations might also be given responsibility for ensuring that any needed response equipment, materials, and personnel are delivered promptly to the scene of an accident and for ensuring an adequate state of operational readiness, thus consolidating the management of all transportation related activities.

ITEM #EV5

Topic: ***Care and Shelter of Evacuees***

When/Where Applicable: Where public authorities may find it necessary to provide shelter for large numbers of evacuees.

Planning Goal(s): To provide safe and comfortable shelters for relocated populations.

Action Items:

- Use hazard analysis results to estimate the maximum number of people for which shelter might need to be provided and the possible duration of a major evacuation, taking into account those families and individuals that might stay with friends or relatives or prefer to check into hotels and motels.
- Coordinate shelter planning efforts with the American Red Cross and ensure that the local chapter can cope with the number of potential evacuees.
- Have lists of shelters and route maps readily available for use in giving instructions to evacuees and vehicle drivers.
- Where necessary, ensure plans are in place for populations needing special care.

Discussion:

High schools with showers and cafeteria facilities are probably the best choices for use as temporary shelters, with large churches having function halls a viable alternative in most communities. During vacation seasons, universities or other schools with dormitory facilities should be considered. Not to be forgotten are any nearby military bases with excess or temporary housing facilities and overnight summer camps for youngsters in the off-season.

The American Red Cross has long established methods and procedures for sheltering evacuees. Determine its capabilities in the locale or jurisdiction of concern, consider its needs in overall emergency planning, and plan to provide any assistance required to achieve the stated planning goal. Helpful hint: Work with the local chapter in developing evacuation instructions to be broadcast to the public, particularly with respect to the clothing, bedding, medicines, and other supplies the Red Cross may wish the public to bring with them.

Once evacuees reach a shelter, people will want to report "missing" persons or to determine if their friends, family members, relatives, or neighbors are "lost" or at another shelter. Response to these queries, as well as identification of persons legitimately missing, will require registration of people upon entry and communications between shelters. Where

the evacuation may be prolonged, and vehicles are available for use after the primary evacuation has been completed, a mechanism should be established for reunion of separated families, relatives, and close friends that can provide a mutual support system under adverse circumstances.

Shelters should be assigned medical teams to care for people who become ill during the evacuation or at later times. These medical personnel should be alerted to the signs and symptoms of exposure to the hazardous material(s) involved in the incident so that they may identify victims and provide necessary care. Contaminated individuals (those having contaminant residues on their persons or clothing) should be segregated from unexposed people until decontaminated. (Note: Significant contamination is unlikely to be of concern except where highly toxic aerosols, mists, or dusts have entered the atmosphere or where individuals were in the immediate vicinity of the spill or discharge.) Facilities should also be available for care of the handicapped or elderly.

Thought should be given as to how best to manage any pets brought along by evacuees. Human services personnel may be necessary to fulfill counseling, recreational, and other needs of confined populations. Quite obviously, shelters will require initial and periodic supplies of food, water, and all other personal need items of inhabitants.

ITEM #EV6

Topic: ***Security of Evacuated Hazard Zones***

When/Where Applicable: Wherever large areas may require evacuation due to hazardous material spills or discharges.

Planning Goal: To ensure that private and public property is safe-guarded during evacuations and that unauthorized individuals do not enter hazard zones.

Action Items:

- Plan to provide police and/or other forces to man roadblocks on routes to potential hazard zones.
- Plan for ground and possibly aerial patrols of evacuated areas.
- Establish procedures to provide personnel with appropriate personal protective devices and training in their use where changing accident or environmental conditions may suddenly change the boundaries of hazardous areas.

Discussion:

Personnel and vehicles should be available to establish and maintain roadblocks on the boundaries of hazardous areas. One reason for this is to prevent uninformed or curious members of the public from entering hazardous locations. Another involves prevention of entry by those who may wish to take unlawful advantage of the fact that some part of the community has been temporarily abandoned.

Where and when it is safe to do so and deemed necessary, patrols of evacuated areas can enhance security while double-checking that all members of the public have left designated areas. Aerial patrols during daylight hours can provide a better "picture" of what is happening on the ground, while helicopters can help ferry critical personnel and supplies. Helpful hint: Helicopters may be available from the state police, local charter services, local radio and television stations, and nearby military posts.

ITEM #EV7

Topic: ***Movement and Care of Livestock and Pets***

When/Where Applicable: Wherever evacuations may become necessary due to hazardous material spills or discharges.

Planning Goal: To plan for and specify the methods and procedures by which domestic or other captive livestock may be moved to a safe location and properly cared for when the potential arises for a major toxic gas or vapor release to the environment and time permits this action. Also, to give some thought to tending pets left behind in an evacuation or brought to shelters by evacuees.

Action Items:

- Use the results of the planning basis development process to determine if a large number of valuable livestock might be threatened by a major spill or discharge.
- Decide whether resources and time might be available for this activity or whether it is only practical to protect human populations.
- If desired and necessary, plan for the movement and care of livestock with local resources.
- Establish procedures for handling household pets during evacuations.

Discussion:

Movement and care of domestic livestock is likely to be most applicable in rural areas with large populations of valuable animals and relatively few people. It may not be worthy of consideration in other circumstances unless a zoo containing extremely valuable or rare animals may be at risk.

The subject of household pets may seem rather trivial at first, but it is well to remember that *many* people care deeply for their animal friends, and the issue of pets has caused problems in past accidents. Planning personnel will have to decide whether to permit evacuees to bring their pets with them to shelters or to mandate that they be left behind, with the knowledge that both options are surely to cause difficulties of one kind or another.

As time passes during an evacuation in which pets have been left behind, and the evacuation was ordered because of the threat of a release rather than an actual discharge, people will ask questions about what is being done to feed their animals and/or may attempt to enter evacuated areas to care for them. One way to handle the problem for pets left outdoors is to assign someone the responsibility of leaving supplies of water and pet foods at various locations on a daily basis when and where it is safe to do so. People who are forced

to leave pets indoors can be told to set out several days of food and water before leaving home. Keep in mind that pets exposed to toxic agents may be injured or killed and that hazard zone reentry activities after the threat has abated should include procedures to collect, care for, and possibly dispose of these animals as necessary and appropriate.

Even if evacuees are told to leave pets behind and not bring them to shelters, emergency preparedness personnel should expect and plan for the fact that some people will indeed bring their pets with them and should have procedures worked out on how to handle these situations.

ITEM #FF1

Topic: ***Special Firefighting Equipment and Materials***

When/Where Applicable: Any locale in which a fire involving hazardous materials may require special equipment or extinguishing agents for control and/or extinguishment.

Planning Goal: To ensure that the fire service has rapid access to any special equipment and materials it may need in the event of an unusual fire situation.

Action Items:

- Use the results of the hazard analysis to identify those sites or spill scenarios that appear to present unusual fire hazards in the sense that specialized equipment and/or supplies may be required for response.
- Identify sources of needed firefighting equipment or supplies that may be called upon in an emergency.

Discussion:

Public fire departments primarily rely upon water for fire control and extinguishment, but are well aware that water can be ineffective on some types of fires and may actually be counterproductive or dangerous for use in other cases. Nevertheless, since water is usually adequate for most large fires encountered, these departments rarely stock more than a limited number of portable dry chemical or carbon dioxide extinguishers and possibly a small amount of foam concentrate. These supplies of auxiliary agents may not be adequate for major chemical or petroleum product fires or fires involving combustible metals. Thus, where the hazard analysis has identified scenarios requiring unavailable resources, the fire department should be assisted in identifying sources of additional supplies and equipment for use in emergencies.

Airports comprise one potential source of assistance. Military airports are likely to have crash/rescue vehicles with significant foam generation and dispensing capabilities. They are also likely to have large capacity units for discharging carbon dioxide, halons, and possibly dry chemicals. Civilian airports are likely to have large foam trucks and/or dry chemical trucks, and wheeled-portable dry chemical units. Both types of airports may have supplies of special agents for combustible metal fires.

Chemical and petroleum processing facilities with internal fire brigades are another potential source of supplies. They may also have special portable equipment for fighting storage tank fires.

ITEM #FF2

Topic: ***Identification of Water Sources in Rural Areas***

When/Where Applicable: Where an accident requiring large amounts of water for response takes place in an area distant from hydrant or other water supply systems.

Planning Goal: To identify sources of water in areas not served by a central water supply system.

Action Items:

- Use hazard analysis results to identify potential incident locations distant from water systems.
- Compile a list of rivers, streams, lakes, ponds, reservoirs, wells, farm holding tanks, other water tanks, and swimming pools that can be used to supply water to an accident scene or to refill water trucks.
- Establish procedures for coordinating and implementing water supply operations.

Discussion:

The planning goal and action items are self-explanatory.

ITEM #HC1

Topic: ***Establishment of Special Rescue Squads***

When/Where Applicable: Wherever response personnel or members of the public may be disabled or trapped due to a spillage, fire, or explosion involving hazardous materials.

Planning Goal: To have two or more special teams available who can safely enter hazardous environments to rescue injured or trapped individuals.

Action Items:

- Assign responsibility for special rescue operations to specific teams.
- Use the planning basis scenarios to identify potential situations requiring special clothing or equipment for safe rescue operations.
- Ensure that trained rescue personnel have or can quickly obtain self-contained breathing apparatus (SCBA) and any required chemical protective clothing.
- Ensure that spare breathing apparatus is available for use by those being rescued where necessary.

Discussion:

There are a variety of scenarios under which workers at chemical facilities or members of the public near or downwind of a hazardous material release may be overcome by toxic vapors or gases, exposed to high levels of thermal radiation, or injured due to the effects of an explosion. Fire departments are usually well-prepared and experienced in rescuing people from fire and explosion situations, and will in many cases not require any new or additional planning to meet these responsibilities. The situation can be quite different, however, where toxic or corrosive chemicals may have been released to the environment or continue to be released.

Chapter 6 explained that some chemicals can be readily absorbed through the skin to cause toxic effects and that others can have a corrosive action on bodily tissues. A problem arises when: 1) such materials are on the ground, must be walked through to reach victims, and are incompatible with the usual footwear of rescue personnel, thus possibly allowing contamination of the feet; or 2) high concentrations of such substances in air can penetrate the normal clothing of rescue personnel. In either case, rescue workers may need special chemical protective clothing, together with a self-contained breathing apparatus (SCBA), to carry out their mission without themselves falling victim. There are benefits, therefore, in

assigning these unusual rescue missions to special teams that are trained and properly equipped for the duty. More on the topic can be found in items relating to personal protection.

The purpose of suggesting the availability of spare SCBA units is actually two-fold. Not only might people trapped in hazardous area require them to escape, rescue workers may need extra air supplies to accomplish lengthy rescues. Even the best SCBA units rarely provide air to the wearer for more than 30-60 minutes. Heavy exertion while wearing these units can significantly shorten their duration of effective operation.

Rescue teams operating in hazardous environments should work in at least pairs. This is a common safety practice, as is the practice of having a backup team ready for action if a problem should develop.

Rescue teams of a different nature and with different equipment requirements may be necessary when buildings have collapsed due to an explosion and people are trapped under the rubble.

ITEM #HC2

Topic: ***Provision of Ambulance Services for Victims***

When/Where Applicable: Wherever the number of casualties due to a hazardous material spill or discharge may exceed the normal capacity of available ambulance services.

Planning Goal: To ensure that sufficient ambulances and EMTs are available for mass casualty situations (in addition to units that may be needed for evacuation of health care facilities).

Action Items:

- Use hazard analysis results to determine worst case ambulance service needs.
- Establish mutual aid systems with services in neighboring communities and regions as needed.
- Determine procedures for requesting military medical assistance if major bases are nearby.
- Establish procedures that may be required by EMTs in treatment and decontamination of victims exposed to chemical contaminants, including the administration of special antidotes that may be necessary in the event of poisoning by certain highly toxic substances.
- Establish procedures for obtaining and distributing potentially required personal protective clothing and devices to ambulance personnel; provide necessary training for their use.
- Ensure that any decontamination and/or treatment supplies required by ambulance personnel will be readily available in an actual emergency.

Discussion:

The action items are self-explanatory. While undertaking planning activities, keep in mind that populations normally residing outside the established hazard zone will continue to require access to emergency ambulance services. With respect to the potential problem involving contamination of victims and vehicles by chemical residues, be advised that this will usually only be of concern for relatively few hazardous materials released into the atmosphere as aerosols or dusts (when the victims have not been in the immediate vicinity of the spill or discharge). The vast majority of airborne gases or vapor will not "stick" to a person or his/her clothing in any significant fashion. See Item #HC3 for contamination problems in health care facilities and Item #PP3 for decontamination of protective clothing and other response equipment for additional information.

ITEM #HC3

Topic: ***Establishment of a Mass Casualty Plan***

When/Where Applicable: Wherever mass public casualties are likely in the event of a disaster.

Planning Goal: To ensure that area hospitals and health care facilities are prepared to handle mass casualty situations, including those due to spills or discharges of hazardous materials.

Action Items:

- Use the hazard analysis results to determine which hazardous materials accidents could cause mass public casualties.
- Ensure that area hospitals and health care facilities have a coordinated plan for handling mass casualty situations *in general.*
- Ensure that necessary advice for medical treatment of chemical exposures is readily available.
- Ensure that means exist to rapidly obtain any special antidotes or medical supplies that might be needed on short notice and in large quantities.
- Work with the American Red Cross, the Salvation Army, and members of the local clergy in developing procedures for notification of next of kin in the event of fatalities or serious injuries.

Discussion:

This item pertains to those emergency situations which have the potential to kill or injure dozens, hundreds, or possibly thousands of individuals over a short period of time. Its intent is to ensure that medical care providers can cope with the problem as efficiently and effectively as possible. Fortunately, many hospitals and clinics across the country already have such plans for non-chemical related emergencies and therefore have the basic elements of a plan that can be expanded to cope with hazardous material emergencies. There are, however, five special topics to consider.

First of all, it is necessary in ***all*** chemical exposure situations, not just those involving large numbers of people, to have information readily available on: 1) the toxic effects of the substance(s) of concern by all likely routes of exposure; 2) the observable symptoms of human exposures; 3) the special medical tests (if any) that may be advisable to assess the extent of injury; 4) the need to observe victims for delayed effects; and 5) the treatment methods or protocols recommended for various types and levels of exposure. Public authorities should ***never*** assume that physicians or hospitals have this information on hand.

Nor should they assume that the basic first aid and health effect data given in typical material safety data sheets will be adequate for all eventualities. Options to identify or obtain more comprehensive information include:

1) Compile or arrange rapid access to a library of detailed chemical toxicology guides and handbooks.

2) Arrange access to computerized on-line toxicology data banks such as the major system operated by the National Library of Medicine.

3) Rely on CHEMTREC to identify appropriate information sources at chemical manufacturing companies in the aftermath of a spill or discharge.

4) Request that industrial complexes handling hazardous materials prepare a medical response plan for chemical emergencies and appoint one or more liaisons to area medical facilities, preferably selected from their internal medical department staffs.

5) Make contact with local Poison Control Centers to determine their capabilities.

Mass casualty situations may require establishment of field hospitals to care for the injured and to identify, stabilize, and transport more serious cases to hospitals. Some consideration should be given to preselection of sites to which the public can be directed in the aftermath of a spill emergency where this action is warranted. Outside and local medical care personnel should be informed of their responsibilities in staffing and equipping such facilities on a rapid basis. Emergency plans should consider the need for accurate accounting of patients and their destinations after triage. The onscene medical command post should be under the direction of a single individual and an alternate in charge of all medical operations. A supplement to the ***Guide for Development of State and Local Emergency Operations Plans*** referenced in Chapter 1 of this guide and dated March 18, 1987, provides extensive guidance on planning for this contingency and is highly recommended. FEMA's document designation for this supplement is *CPG 1-8, CHG 1.*

Some chemical exposures that can poison the body are best treated with *specific antidotes* or *special equipment.* Medical response plans should identify and ensure availability of any such special supplies. This does not necessarily mean that large stocks must be purchased and stockpiled, only that sources be identified and a mechanism be established for their rapid procurement. Helpful hint: Ask the medical departments of local industries handling toxic chemicals whether they stock or see a need to stock special supplies or antidotes for chemical exposures.

Be aware that victims of a chemical-related emergency may be contaminated in the sense that their skin, hair, or clothes may have residues of chemicals under several envisionable accident scenarios, particularly if they have been in the immediate vicinity of the spill or discharge or exposed to airborne aerosols or dusts. There have been cases where

medical personnel have had to decontaminate victims and have needed protective clothing (at least gloves and masks) to protect themselves from potential toxic exposures. Medical response plans should take such possibilities into account.

Finally, besides the possible need for a temporary morgue and large-scale mortuary services, note that next of kin must be promptly notified of fatalities or severe injuries carefully and in a sensitive and supportive fashion. As noted elsewhere, this activity should be discussed with the American Red Cross and Salvation Army and coordinated with members of the local clergy.

ITEM #PP1

Topic: ***Availability of Respiratory Protective Devices***

When/Where Applicable: Any locale that may experience a major release of irritating or toxic airborne contaminants.

Planning Goal: To ensure both initial and continued availability of a sufficient number of self-contained breathing supply apparatus (SCBA) during emergency situations.

Action Items:

- Inventory the number and types of units currently available to local fire departments.
- Determine the circumstances under which available equipment can be used safely and ensure that all limitations on use are clearly understood.
- Determine local capabilities for refilling of air supply tanks.
- Attempt to estimate the need for such units under worst case conditions determined during the hazard analysis process.
- If a shortage may develop, identify sources of additional equipment and refilling capabilities that may be called upon in an emergency.

Discussion:

Fire departments will in most cases have a sufficient number of self-contained breathing supply units and refilling systems to meet the initial needs of their own personnel in chemical related emergencies. There may be situations involving major discharges of airborne contaminants, however, where an insufficient number of units are readily available to meet the potential needs of police officers, ambulance personnel, spill containment and cleanup personnel, public authorities and officials at the scene of the incident, and others who may need to function in an area that could be suddenly exposed to hazardous vapors, gases, or aerosols in the event a container fails or the wind shifts direction. It is therefore important that this topic be given special attention during the overall emergency response planning process.

The need for training in the use of these devices is addressed in Item #TR1. Keep in mind that it is difficult or impossible to wear a self-contained breathing unit while driving or riding in many types of vehicles. This should be given consideration during the planning process.

Expert guidance on selection and use of personal respiratory protective devices can be found in the ***NIOSH Guide to Industrial Respiratory Protection***, available from Publications Dissemination, DSDTT, National Institute for Occupational Safety and Health, 4676 Columbia Parkway, Cincinnati, Ohio, 45226 (telephone 513-841-4287). Additional information may be found in publications cited in Item #PP2.

ITEM #PP2

Topic: ***Availability of Special Protective Clothing***

When/Where Applicable: Any time that rescue, leak plugging, spill containment, or other response activities may directly expose individuals to sudden fires or corrosive, irritating, or toxic solids, liquids, gases, vapors or fumes that may harm the individual via direct contact with the skin or eyes.

Planning Goal: To ensure the ready availability of any special chemical or thermal protective clothing that might be needed by response forces, particularly during the initial phases of a response action.

Action Items:

- Use the results of the hazard analysis to determine the spill scenarios and related chemicals that may require local forces to enter highly contaminated and/or fire prone environments.
- Determine the *types* of protective clothing that may be required to permit response workers to enter these environments.
- Determine which clothing *materials* are appropriate for the expected exposures.
- Arrange for rapid availability of appropriate protective clothing in the event of an emergency.

Discussion:

The normal turnout clothing of fire service personnel may be fully adequate to protect these individuals in a wide variety of fire and/or spill situations. But there may also be cases where rescue teams or individuals who desire to enter the immediate spill area for leak plugging or spill containment purposes might be exposed to corrosive substances or toxic substances that might be absorbed through the skin. Such situations may require more complete protection of the body by clothing that is resistant to the damaging effects of the spilled substance. The clothing itself may range from boots, gloves, or disposable suits made of chemical resistant materials to air-tight fully encapsulating "astronaut" suits that offer complete protection of the body from spilled substances on the ground or in high concentrations in the air. Where fires may occur, appropriate thermal protection may be additionally necessary.

The first action item takes advantage of the information gathered during the hazard analysis process to identify the hazardous substances and related spill scenarios that may require the availability of specialized clothing. The second action item indicates that emergency planners should determine the types of specialized clothing that may be necessary (i.e., gloves, boots, aprons, face shields, splash suits, astronaut-type suits, etc.), while the third notes it is necessary to ensure that the materials from which the clothing is constructed will not be penetrated by the spilled substance. Finally, the last item suggests that a mechanism be established to ensure that the necessary clothing is readily available when needed.

Several guides to the selection of protective clothing for spill response are:

- ***Guidelines for the Selection of Chemical Protective Clothing***, sponsored by the EPA and available from the ACGIH Publications Section, 6500 Glenway Avenue, Bldg. D-7, Cincinnati, Ohio 45211, or (513) 661-7881.

- ***Occupational Safety and Health Guidance Manual for Hazardous Waste Site Activities***, prepared jointly by NIOSH, USCG, and EPA and available as DHHS (NIOSH) Publication No. 85-115 from the U.S. Government Printing Office.

- ***Personal Protective Equipment for Hazardous Material Incidents: A Selection Guide***, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 84-114, available as document PB 85-222-230 from the National Technical Information Service, Springfield, VA 22161.

Note that it may not be cost effective for every community to purchase every possible type of protective clothing that may become necessary. There are advantages to cooperative agreements on a county or regional basis (with industry or government institutions) that permit individual communities or firms to draw upon a central stockpile. There are also advantages to giving consideration to the likelihood that an accident requiring certain clothing will actually take place in the foreseeable future. It does not necessarily make sense to purchase something with a shelf-life of 5-10 years at high cost if probability analysis procedures have indicated a potential need once every 200 years or so on average.

ITEM #PP3

Topic: ***Decontamination of Exposed Protective Clothing and Other Response Equipment.***

When/Where Applicable: Wherever a spill situation may contaminate the protective clothing of response personnel or other items of equipment.

Planning Goal: To ensure that response personnel are not contaminated with corrosive or toxic materials while removing protective clothing worn in a contaminated environment; similarly, to prevent injury of people later using items of contaminated equipment.

Action Items:

- Establish decontamination procedures for clothing and equipment in the emergency response plan.
- Assign responsibility for clothing and equipment decontamination to a qualified individual.

Discussion:

Clothing and equipment used in a contaminated environment may itself become contaminated. Clothing must be decontaminated before it can be safely removed by its wearer. Contaminated equipment may need careful decontamination before being safe to touch or use in the aftermath of an incident.

In many instances, it will be sufficient to merely wash the clothing or equipment down with strong water sprays or large amounts of water. Several manufacturers market decontamination showers for wearers of protective clothing, these consisting of a framework of water piping with numerous water spray nozzles surrounding an open space the size of a shower stall. Fire hoses and possibly even garden hoses can be used to wash down most equipment as well.

There are two potential complications to be considered. First of all, it must be realized that the water and/or other solutions used to decontaminate the clothing or equipment may contain some amount of the contaminant. It must be decided on a case-by-case basis whether this water should be contained, collected, treated, and/or sent to an appropriate wastewater disposal facility, or whether it can simply be released to the environment. Secondly, it must be realized that not all contaminants may be completely washed off by water alone. Final decontamination may require the careful use of various solvents or cleaning compounds. These may range from ordinary soap to specialized chemicals designed to neutralize remaining residues.

ITEM #PR1

Topic: ***Public Relations in Emergency Situations***

When/Where Applicable: Any locale subject to a significant hazardous material incident.

Planning Goal: Preparations for keeping the public informed of continuing developments via newspaper and broadcast media while minimizing rumors, conflicting reports, confusion, and unnecessary interference with the activities of key response personnel -- and while also coordinating media relation efforts with those of other agencies or parties to the response.

Action Items:

- Designate one specific individual and an alternate press officer to join the team of press officers that may be formed from representatives of all major parties to an emergency response operation (be they from local, state or federal government agencies, or the company responsible for the accident).
- Compile a list of telephone numbers of local radio and television station personnel who can initiate special "on air" announcements.
- Provide designated press officers with secretarial support, photocopy machines, and a means of communications with the overall commander of the response operation.
- Select a site, preferably but not necessarily near the central emergency operations center, where the press can convene and be briefed by the press officer team. This site should ideally have telephones, electrical outlets, restrooms, and other facilities that media personnel may require.
- Establish a firm policy among all local officials and response personnel as to who should or should not speak to media personnel.
- Ensure that key emergency response personnel understand the need to relay up-to-date "status reports" to press officers on a regular basis.

Discussion:

The public needs to be informed accurately and rapidly as to what is happening during an emergency situation. Significant incidents may result in a large number of reporters arriving on scene and attempting to interview anybody and everybody. The above action items will help to reduce confusion, facilitate information transfer, reduce problems that might be otherwise caused by a lack of organization, and reduce the incidence of unfounded rumors.

The book by A.J. Smith, Jr., referenced at the beginning of this chapter, has an excellent section addressed to public officials on the subject of dealing with the media which discusses many "do's" and "don'ts". These mostly pertain to the actions of press officers for government agencies, and include:

THINGS TO DO

1. Accommodate the media as much as possible; make the news available to them.

2. Schedule news conferences and avoid written releases.

3. Be direct and specific.

4. Always, *always* tell the truth, don't hedge.

5. Hold public hearings at least twice during a week-long event and invite the press.

6. Have news conferences immediately after any meeting from which the media or public have been barred.

7. Send a press representative to the command post.

8. Ensure that the team of press officers is in contact with the command post at all times.

9. If safety permits, allow the media to take pictures of the accident site.

THINGS NOT TO DO

1. Do not permit arguments among public officials or press officers from different organizations in front of the press. Do, however, permit statements of dissenting opinions.

2. Avoid giving gut opinions or conjecturing.

3. Do not be evasive. If the answer to a question is not known, refer the question to someone who has the appropriate answer.

4. Do not be critical in a personal manner; i.e., avoid personal remarks about other people at the accident scene.

5. Do not be philosophical. These kinds of discussions are extremely susceptible to being quoted out of context.

6. Do not make off-the-record comments. They may end up in print with later retractions buried in the back pages.

7. Avoid friendly chats with media people. Casual comments may appear in print.

8. Avoid bad or foul language.

9. Do not hide from the media. They can sense this and form an unfavorable opinion of the press officer(s) as a credible source of news.

10. Do not answer questions beyond personal knowledge or expertise.

11. Do not permit media persons to attend emergency response team meetings. These are likely to be technical meetings with lively discussions that may last forever if people are *performing* rather than dealing with the problem at hand.

Reasons for planning for and controlling statements made during a severe emergency go beyond a simple desire to ensure orderly and accurate dissemination of information. One of the groups showing up more frequently at hazardous materials accidents are lawyers representing a wide variety of interests. It should be remembered that good lawyers will remember everything they see and hear. A thoughtless comment or statement can surface months later in a courtroom. Placements of blame, criticisms of response actions, airing of dirty laundry in public, and similar statements can result in lengthy and messy legal battles over comments or charges made in the heat of a very hectic moment.

ITEM #SC1

Topic: ***Plugging/Stopping of Leaks***

When/Where Applicable: Any locale in which an industrial or transportation accident may result in a leak or puncture of a tank, pipeline, or other container.

Planning Goal: To ensure the jurisdiction of concern has at least a basic capability of plugging or stopping leaks in tanks, pipelines, or other containers.

Action Items:

- Assign responsibility to one or more individuals for identifying methods of plugging or stopping leaks, assembling the materials and supplies necessary for this task, and training for their use under emergency conditions.

- Alternatively, identify and arrange for the rapid provision of the above services on an emergency basis by an experienced and qualified private contractor.

Discussion:

Small leaks left unattended for extended periods of time can cause large losses of chemicals to the environment and much more severe effects than would occur if the leak was somehow completely or partially plugged on a prompt basis or some other means were employed to reduce outflow of the hazardous material. There are great benefits, therefore, in having access to one or more individuals with the basic tools and knowledge needed to limit losses from punctured or leaking tanks or pipelines.

The most widely available means for plugging holes or leaks in equipment involves use of conical, cylindrical, square or wedge shaped pieces of wood, rubber or metal sheets, inflatable pipe plugs, pneumatic leak sealing "bandages", special patching compounds, clamps of various types, and a number of other items. The plugs alone, if available in a variety of sizes, can be jammed into holes and greatly reduce the open area from which the contents of the tank or pipeline can escape; assuming, of course, that it is safe for individuals to approach the leak area. The book by J.R. Cashman listed at the beginning of this chapter is especially enlightening on this topic. Several vendors market special leak plugging and patching kits. Innovative response personnel may be able to fashion their own devices.

Where a tank vehicle is losing liquid cargo, it may be worthwhile to have the means available to turn the body of the vehicle over such that the point of leakage rises. This will lessen the total amount of cargo than can escape before the liquid level in the tank drops below the height of the hole. Be advised, however, that this may require special equipment, trained personnel, and expert supervision for a safe outcome.

Various types of transportation containers have internal emergency shutoff valves that can reduce or stop outflow from external valves that have been damaged in an accident. Knowledge of the standard placement and use of these valves can be invaluable, most particularly for highway tank vehicles.

Many incidents are brought to a rapid end simply by having the proper common tools available to close a valve or tighten some bolts.

ITEM #SC2

Topic: ***Suppression of Hazardous Gas or Vapor Releases***

When/Where Applicable: Any locale where large quantities of toxic or flammable vapors may be released to the atmosphere.

Planning Goal: To ensure readiness to take rapid measures to reduce the rate or amount of hazardous vapors or gases that enter the atmosphere in an accident.

Action Items:

- Use hazard analysis results to identify all major potential sources of hazardous gas or vapor releases into the atmosphere.
- Identify the specific hazardous materials that may be discharged (to the extent possible).
- Select appropriate vapor or gas hazard mitigation measures for each significant threat.
- Plan for rapid availability of qualified manpower, special equipment, materials, or supplies necessary to mitigate gas or vapor hazards.

Discussion:

Gases or vapors may enter the atmosphere directly from broken, ruptured, or punctured containers, or alternatively, from evaporating or boiling pools of liquid that have been discharged to the environment. There are several response measures beyond plugging or stopping the leak source (discussed elsewhere) that may be used to reduce the rate or amount of airborne contamination. These include:

- Physical restriction of liquid pool surface areas,
- Use of firefighting or specialized hazardous material foams on liquid pools,
- Dilution or coverage of liquid pools with water (or other compatible and safe liquids),
- Use of water sprays or fogs,
- Neutralization of spilled liquids,
- Cooling of spilled liquids or venting tanks, and
- Intentional ignition.

Chapter 3 of this guide reported and explained the observation that the total rate of vapor or gas evolution from a pool of liquid is directly related to the surface area of the pool. Thus, there are benefits to physical restriction of exposed pool surface areas. This can be accomplished by rapid containment of discharging liquids by building dikes or other barriers to flow or digging of trenches or sumps. The goal should be to keep the top surface area of the pool as small as possible.

Once the pool has been contained, other methods may be used to reduce the area exposed to the atmosphere. The most common response is to cover the surface of the liquid with a *compatible* foam, since a thick foam blanket may in many cases greatly reduce gas or vapor evolution, even from pools of quiescent liquefied gases. Note, however, that the application of a warm foam to the surface of a cold pool of liquid may result in even greater gas or vapor evolution for an initial period of time.

When the spilled liquid has a normal boiling point above ambient environmental temperature, is completely or partially soluble in water, and is not dangerously reactive with water, its vapor pressure and therefore its evaporation rate can be reduced by diluting the liquid with large amounts of water. Reductions in the evaporation rate will then result in a smaller downwind hazard zone.

The same technique can also be used for soluble liquids with normal boiling points below the ambient temperature and liquids that generate heat upon contact with water. However, since the introduction of water to such a pool may actually increase gas or vapor generation while water is being introduced, this action should only be undertaken with great caution. It is best for use when the public has been cleared from vulnerable downwind areas and there is a desire to reduce the time duration over which the pool would otherwise pose a downwind hazard.

There are some liquid hazardous materials that are insoluble, heavier than, and non-reactive with water. Once contained, vapor evolution from these liquids can be reduced or eliminated by carefully covering the liquid pool surface with a layer of water that will float on the contained liquid. Occasionally, the same principle can be applied using a compatible and safe liquid other than water.

Many spill response guides suggest the use of water sprays or fogs (from fire hoses and nozzles) to knockdown, absorb, or disperse hazardous vapors in air. If the spilled liquid is dangerously reactive with water, plan to apply the fog or spray at a point sufficiently downwind of the spill point so that water will not contact the pool. If there are hazardous liquid fumes or aerosols in air, or the gas or vapor is soluble in water, give some consideration to the need to contain the possibly contaminated water runoff for later collection and disposal. Finally, realize that the application of water fog or spray to flammable vapors or gases will not necessarily eliminate their fire hazard.

Several hazardous materials, as discussed in Chapter 7 of this guide, can be *neutralized* via a chemical reaction to one or more substances that pose lesser threats to public health or the environment. Where this response may be appropriate for a particular hazardous

material, the response plan should identify sources of necessary neutralization agents and the means to apply them to spilled substances. Solid neutralization agents may possibly be "applied" with snow blowers or seed spreading equipment. Liquids may be applied with spraying equipment. In all cases, pay attention to the fact that the neutralization agent may itself be hazardous in some fashion and that the reaction may potentially produce heat or be violent if improperly controlled. Seek expert advice and assistance where necessary.

Since the evaporation or boiling rate of a liquid is a function of its vapor pressure, and since the vapor pressure is a function of temperature, there may be situations in which the gas or vapor hazard can be reduced by cooling spilled liquids or the containers from which gases are venting. This might be accomplished using large quantities of ice or dry ice. Where available and where the means exist for safe use, liquid nitrogen may also be considered, as may supplies of carbon dioxide. Consult qualified experts for advice to determine if this is a viable and safe option to consider for response purposes.

The last measure to be discussed is not one that is often suggested in spill response guides because its application can often cause additional complications and hazards in densely populated or industrialized areas. Nevertheless, where a highly toxic gas or vapor is being released to the atmosphere, the resulting gas or vapor cloud or plume can cause (or is causing) widespread deaths and/or serious injuries, and the gas or vapor is flammable or capable of being ignited, give careful consideration to the possibility of intentional ignition of escaping hazardous materials, possibly from a distance using a flare gun or other means of ignition. This action can greatly reduce the *toxic hazard* of the escaping gas or vapor in many cases. However, depending on the circumstances and surroundings of the discharge, intentional ignition can also result in flame jets, tank BLEVEs, fireballs, vapor or gas cloud fires or explosions, or pool fires that may themselves cause severe problems. Thus, this must be considered a "last ditch" response not to be undertaken without due consideration of its implications and ramifications.

ITEM #SC3

Topic: ***Containment of Spills of Liquids or Solids on Land***

When/Where Applicable: Any locale where large quantities of liquid or solid hazardous materials may spill on land in an area without secondary containment systems.

Planning Goal: To ensure that equipment, materials, and supplies are available to contain spills of hazardous liquids or solids on land.

Action Items:

- Where necessary, arrange for rapid availability of bulldozers or other earthmoving equipment capable of building dikes or digging trenches.
- Where necessary, arrange for rapid availability of properly equipped work crews with shovels or other equipment to build dikes or dig trenches.
- Where necessary, arrange for rapid availability of plastic sheeting or other compatible materials that can be used to cover spilled solids (to prevent agitation by the wind or wetting) or to line dikes, basins, or trenches used to collect liquids.
- Where necessary, plan for rapid sealing of drains and sewer openings to prevent entry of hazardous materials.
- Where necessary, plan for the rapid plugging of sections of storm drains to limit the spreading of hazardous materials that have entered a drainage system. (Note: Plan for rapid access to a map showing the layout of local systems. See the last paragraph of the discussion section.)

Discussion:

One of the first steps in spill response when a liquid or solid has been discharged onto a land surface is to attempt to contain the spilled material and to prevent the further spread of contamination. Although specialized equipment has been developed to construct dikes of foamed concrete or plastic materials, the most widely available and generally adequate substances to use are earth, sand, clay, and plastic or rubber sheeting.

Dikes or barriers of earth, sand, or clay materials can be quickly constructed with bulldozers, similar equipment, or properly equipped individuals with shovels. Note, however, that motorized equipment should not be used indiscriminately in the vicinity of flammable or explosive vapors or gases. Note also that response personnel may require special protective clothing and breathing apparatus to approach a spill.

Plastic or rubber sheeting can be used to cover spilled solids. This can prevent the wind from causing toxic dusts to become airborne and also protect the bulk of the solid from becoming wet from rain or hose streams used in the area, thus reducing the extent or possibility of soil, groundwater, or surface water contamination by the spilled substance. Such sheeting can also be useful for lining dikes, basins, and trenches for similar purposes where liquids are to be contained. Finally, sheeting materials, together with stones or bricks and soil, sand or clay, can be used to cover storm drain openings in a pinch.

When hazardous materials have already entered a storm drain system, there are benefits to attempting to limit or contain the flow of the material by damming at strategic locations. Since storm drainage systems typically flow into bodies of surface water, containment might prevent significant water pollution and facilitate later cleanup. However, note that at least one authority suggests that volatile chemicals should never be trapped in a closed conduit such as a storm drain, probably due to the possibility that explosive vapors may accumulate and encounter a source of ignition. Thus, judgments on damming must be made on a case-by-case basis, with special attention being given to cases in which contaminants may enter a water treatment plant.

ITEM #SC4

Topic: ***Cleanup of Spills of Liquids or Solids on Land***

When/Where Applicable: Any locale where large quantities of liquid or solid hazardous materials may spill on land.

Planning Goal: To ensure that equipment, materials, and supplies are available to recover spills of hazardous liquids or solids on land.

Action Items:

- Where necessary, arrange for rapid availability of pumps, hoses, and temporary storage containers (or alternatively, vacuum trucks) to recover pools or other accumulations of hazardous liquids.
- Where necessary, arrange for rapid availability of properly equipped work crews with appropriate equipment.
- Where necessary, arrange for rapid availability of drums or other containers to hold contaminated solids, soil, or leaking packages.
- Where necessary, arrange for rapid availability of absorbent materials.
- Where necessary, arrange for rapid availability of front-end loaders and other earthmoving equipment, including dump trucks.

Discussion:

Once a spilled substance has been contained, the next step is to remove it from the environment. The effort is often undertaken by the parties responsible for the spill or discharge or a spill cleanup contractor it may hire, but local, county, and state governments should have a capability to respond when the responsible party is unknown or is unprepared or unwilling to take action and circumstances do not permit waiting for federal intervention under CERCLA, SARA, or the Clean Water Act. The planning effort should involve: 1) a review of federal contingency plans prepared by regional EPA and or U.S. Coast Guard Offices as well as the state agency primarily concerned with environmental protection to learn how these agencies plan to respond when needed; 2) a decision as to whether spills will be cleaned up by local government personnel or by specialized cleanup contractors hired by public authorities; and 3) arrangements for rapid availability of necessary services, equipment, and supplies.

The methods usually applied for "gross" cleanup of contaminated ground surfaces are rather straightforward. They involve:

1) Use of compatible pumps, hoses, and tanks, drums, or vacuum trucks to collect pools of accumulated liquids;

2) Use of soil, sand, clay, straw, sawdust, fly ash, cement powder, perlite, vermiculite, or commercially available mineral or plastic sorbent materials to absorb and mop up liquid residues; and

3) Removal of contaminated surface layers (where cleaning in place is not practical) by shovels or mechanical means.

In all cases, of course, supplies and equipment used must be compatible with the hazardous material spilled, workers must be protected from toxic exposures, and special care must be taken in the presence of potentially flammable or explosive atmospheres.

Other current cleanup techniques include steam-cleaning or detergent washing of solid surfaces where hydrocarbons or similar materials have spilled, burning of flammable or combustible materials in place where it is safe to do so and permitted by regulatory authorities, and application of special mutant bacterial cultures to contaminated soils and liquids to "digest" contaminants over a period of time.

ITEM #SC5

Topic: ***Containment of Spills into Water Bodies***

When/Where Applicable: Any locale where significant quantities of hazardous materials may spill into a body of surface water.

Planning Goal: To ensure that equipment, materials, and supplies are available to contain spills of hazardous liquids or solids into bodies of water.

Action Items:

- Use hazard analysis results to determine the specific materials that may be spilled into a body of water (to the extent possible).
- Where necessary, arrange for rapid availability of waterborne spill containment equipment and supplies.
- Where necessary, arrange for rapid availability of earth moving equipment, boats, spill containment booms, sorbent materials, sand bags, and other potentially necessary items.

Discussion:

The selection of a water-spill containment method for any given substance mostly depends upon how the substance will behave when spilled into water. The potential behavior of such spills was discussed in Chapter 3 of this guide.

Spills of lighter-than-water and mostly insoluble materials are best handled with spill containment equipment and methods. These include use of commercial or home-made oil spill booms, chemical spill herders, or use of hose streams or small-boat propeller washes to control the spread of the substance on water. In addition, where small rivers or streams are affected, underflow dams may be constructed, these being dams with open pipes well below the surface of the water such that water passes through the dam but floating materials are trapped. Oil spill response guides will address these and other potential containment methods in more detail. Due to the specialized nature of the equipment and materials necessary, most jurisdictions are probably best advised to find a local oil spill containment and cleanup contractor willing to respond on an emergency basis for these types of spills.

Spills of heavier-than-water and mostly insoluble substances will sink to the bottom of a water body. Although it is not always effective or possible, consider taking advantage of natural deep-water pockets, using sand bags, or building low underwater dams or dikes to trap the liquid on the bottom and prevent further downstream contamination.

Substances that are partially or completely soluble in water are the most difficult to contain. At best, if the body of water is of a manageable size, an attempt can be made to dike the upper and lower bounds of the body of water and to divert incoming flows of clean water around the contaminated area using earthmoving equipment. This is easier said than done in many cases but has been successfully attempted at times.

ITEM #SC6

Topic: ***Cleanup of Spills into Water Bodies***

When/Where Applicable: Any locale where significant quantities of hazardous materials may spill into a body of surface water.

Planning Goal: To ensure that equipment, materials, and supplies are available to remove or mitigate contaminants in bodies of water.

Action Items:

- Where necessary, arrange for rapid availability of oil spill cleanup equipment and services.
- As and if necessary, arrange for rapid availability of chemical spill treatment and cleanup services.

Discussion:

A variety of methods and equipment have evolved over the years for treating or removing spills of oil-like substances in water. These include use of oil skimming equipment, sorbents, burning agents, sinking agents, and dispersants. The planning effort for such materials should involve a review of federal contingency plans prepared by regional EPA and/or U.S. Coast Guard offices, as well as the state agency primarily concerned with environmental protection, to learn how these agencies plan to respond to major oil spills. Given the special equipment, materials, and training needed for the effort, it is probably best recommended that arrangements then be made with a local oil spill cleanup contractor for emergency response. (Note: There are also advantages to be realized by coordinating and integrating this effort with state and federal plans. Indeed, many jurisdictions may find that state and/or federal plans fully cover them for this type of spill and that no specialized planning is necessary. Others may discover local oil spill cooperatives or other industry groups willing to lend assistance even if a member company is not responsible for the incident.)

The situation gets a bit more complicated where spills of water-soluble materials or heavier-than-water insoluble materials are possible, since the equipment and methods necessary to remove or treat contaminants in the water are even more specialized and sophisticated. Again, it is best to start the process with a review of state and federal contingency plans and to integrate and coordinate planning efforts for these types of materials. Note, however, that any potential contractors identified should have experience with carbon adsorption, chemical neutralization, and other water treatment technologies. These highly specialized contractors are not as easy to find as oil spill cleanup companies that occasionally handle chemical spills, and indeed, may not be found at all within the borders of some states.

ITEM #SC7

Topic: ***Support Services for Field Response Forces***

When/Where Applicable: Any locale that may experience a hazardous material spill or discharge requiring a prolonged response action in the field.

Planning Goal: To provide food, rest areas, and other equipment and supplies necessary to sustain field response forces.

Action Items:

- Where necessary, arrange for canteen services, accommodations, electrical power, lighting, heating, portable toilets, washing facilities, and other supplies and services needed to sustain workers at a spill site.

Discussion:

Several situations can be envisioned in which response personnel in the field may be required or needed at the site of an accident for more than a day. These personnel will require rest areas and food to be able to continue to function, particularly if they are in a remote area or a region that has otherwise been evacuated. Sources of assistance for planning in this area include the American Red Cross, the Salvation Army, and the National Guard or Army Reserve. The latter organizations in particular might be able to provide tents, cots, fans or heaters, lights, and expertise in layout and management of staging or rest areas.

Although the above individuals and their command personnel must be given priority, it may also be prudent to consider how to assist media personnel and government officials from outside the jurisdiction in finding appropriate lodging. At one protracted incident in Florida some years ago, 223 representatives of different federal, state and local agencies were present -- all of them watching a crew of 21 people cleaning up the scene. Add to these media, industry, and other personnel involved in the overall emergency response, and it is easy to see that the total number of "strangers" that may be on scene can be substantial.

The OSHA regulations involving a site safety and health plan (see Item #CC4) contain numerous requirements pertaining to support of field personnel and should be referred to for further guidance. Be especially aware of the need to ensure that established hygiene practices preclude the possibility of ingestion of contaminated food and refreshments.

ITEM #SC8

Topic: ***Maintenance of Apparatus and Equipment***

When/Where Applicable: Any locale that may experience a hazardous material spill or discharge requiring a prolonged response action in the field.

Planning Goal: To provide fuel, engine fluids, and maintenance services to support the on-scene operation of apparatus and equipment operating in hazardous environments.

Action Items:

- Use of the results of the hazard analysis to identify situations where apparatus and equipment operating in contaminated areas may require refueling and minor maintenance to keep them operating.
- Establish arrangements for obtaining fuel, engine fluids, and other maintenance items (e.g., belts, filters, etc.) to support continuous operation of vital apparatus and equipment.
- Establish procedures for providing refueling and maintenance services to on-scene apparatus and equipment operating in potentially contaminated areas.

Discussion:

During long-duration incidents, apparatus (e.g., fire department units, backhoes, etc.) and equipment (e.g., generators, pumps, etc.) may require on-scene refueling and minor maintenance to enable uninterrupted operation. On-scene services of this nature are beneficial in that they eliminate the need to remove deployed apparatus and equipment from the incident scene. By refueling in-place, operations can continue uninterrupted and the need to replace chemically exposed equipment with uncontaminated items is eliminated, thus, reducing the number of units potentially requiring decontamination. Note that operations must be conducted safely and in such a manner that will prevent the spread of contaminants from response vehicles and equipment to maintenance vehicles and refueling tanks. Furthermore, it may be necessary for maintenance personnel to wear appropriate body and respiratory protective gear when operating in hazardous environments. Also note that provision of refueling and maintenance services may not be prudent in particularly hazardous locations. For example, fire department apparatus positioned near a fire should not be refueled where ignition of fuel vapors is possible. One step that may possibly eliminate the need to refuel apparatus and equipment is to fill fuel tanks to capacity prior to deployment.

ITEM #SD1

Topic: ***Documentation of Response Activities and Costs***

When/Where Applicable: Any locale that may find it necessary to undertake a major response action due to a spill or discharge of hazardous material.

Planning Goal: To ensure that a careful record is maintained of what happened and what was done in response.

Action Items:

- Assign responsibility for realtime and post-incident documentation of the accident and resulting response actions.
- Create or adopt appropriate reporting forms and procedures.
- Arrange to collect the records from various sources in a central and safe location.

Discussion:

Detailed records of what happened and what actions were taken in response can help in:

- Attempting to recover response costs and damages from the party responsible for the incident.
- Setting the record straight where there are charges of negligence or mismanagement resulting from the incident.
- Reviewing the efficiency and effectiveness of response actions.
- Preparing for future incident responses.
- Verifying facts, actions, injuries, equipment used, etc. for the purpose of legal proceedings, insurance claims, budget requests, and public inquiries.

In addition to written documentation of an incident, it is good practice to draw diagrams or sketches of containers, vehicles, structures, streets, containment techniques employed, locations of deployment, etc. Photographs and videotapes should also be kept on file for reference purposes.

ITEM #SM1

Topic: ***Monitoring of Atmospheric Conditions***

When/Where Applicable: Any locale with a reasonable potential to experience a major release of hazardous vapors or gases into the environment.

Planning Goal: To ensure that command personnel have continuous access to current data, predictions, and expert advice regarding weather and atmospheric conditions.

Action Items:

- Identify sources of weather data and predictions in the immediate area.
- Arrange for continuous updates of weather information during incidents involving major discharges of hazardous vapors or gases into the environment.

Discussion:

As discussions in Chapter 3 and 12 of this guide have shown, atmospheric stability conditions, wind velocities, and wind directions have a direct impact on the boundaries of downwind areas threatened by a plume or cloud of hazardous vapor or gas. Changes in these conditions over time, particularly in the case of prolonged discharges, can require changes in the boundaries of hazard zones. Consequently, tracking of cloud or plume movements can be greatly facilitated by direct access to a weather station manned by trained meteorologists. Likely locations include major radio and television stations, major airports, and offices of the National Weather Service, a part of the U.S. Department of Commerce.

Other atmospheric conditions of possible interest involve temperature, precipitation, and humidity forecasts. Temperatures can affect the physical state, vapor pressure, and other properties of hazardous materials, as explained in Chapter 2, and also impacts on the length of time a person can safely function inside a fully encapsulating protective suit. Precipitation can impact dispersion of airborne contaminants, lead to runoff of contaminants in water, cause dilution of spilled chemicals, and/or assist fire control efforts. Moisture in the atmosphere may cause either adverse or beneficial chemical reactions involving spilled or discharged materials.

ITEM #SM2

Topic: ***Monitoring of Contaminant Concentrations***

When/Where Applicable: Any locale where the air, water, or land may be contaminated by toxic materials.

Planning Goal: To ensure rapid availability of the personnel and equipment needed to sample, analyze, or otherwise monitor pollutant concentrations in air, water, or soil.

Action Items:

- Contact the nearest EPA regional office and the state agency with primary responsibility for environmental protection to assess their capabilities for determining and monitoring pollutants in the environment during a significant spill or discharge incident.

- If these agencies cannot respond promptly in all cases or do not have a full range of capabilities, particularly for air sampling and analysis under emergency conditions, identify and arrange for the services of university laboratories or commercial firms that have the necessary resources and personnel and who are willing and prepared to respond.

Discussion:

Determination of the concentrations of airborne contaminants at various points downwind of a spill site can greatly help in determining the actual boundaries of hazard zones and in deciding when reentry of these zones is feasible and safe. Similarly, measurements of water or soil contamination can help determine the exact level of contamination of these resources.

In order to assess the potential for adverse health impacts (which may not become immediately apparent), it is often wise to plan for monitoring of contaminant exposures experienced by response personnel and the general public as best possible under emergency conditions.

Where potential exists for contamination of food and/or water supplies, responsibility must be assigned for detection of such contamination via use of the resources identified during this planning activity and for prevention of the consumption of known or potentially contaminated food or water by people or animals.

ITEM #SR1

Topic: ***Provision of Alternate Water Supplies***

When/Where Applicable: Any locale with a water supply vulnerable to contamination by hazardous materials.

Planning Goal: To ensure rapid availability of potable water for affected populations.

Action Items:

- Identify local sources of potable water supplies.
- Determine if there is potential for contamination of these supplies in the event of a hazardous material accident.
- If there is potential, identify alternate sources of clean water and plan for its distribution to residents

Discussion:

There are a number of circumstances under which a potable water supply may become unfit for human consumption for a time and require replacement. This is most commonly accomplished by bringing in supplies of bottled water and/or tank trailers capable of carrying water. The latter may be available from local National Guard units. Tank trucks that carry milk are another possibility for consideration once thoroughly cleaned.

ITEM #SR2

Topic: ***Cleanup of Dead or Contaminated Livestock or Wildlife***

When/Where Applicable: Any locale where the discharge of a toxic gas or vapor into air or the discharge of a toxic substance into water may result in mass casualties among animal populations.

Planning Goal: To make provisions for the collection and disposition of the bodies of dead aquatic and terrestrial animals and decontamination and care of contaminated animals.

Action Items:

- Identify a source of work crews and equipment for the collection and disposal of dead animals.
- Identify a disposal site where the bodies can be buried and or incinerated.
- Identify a source of work crews and equipment for the decontamination and care of contaminated animals.

Discussion:

A large number of animal carcasses, be they hundreds of cows or chickens or many thousands of fish, can pose a variety of health hazards. Emergency response plans do not typically address this topic, possibly because it is somewhat distasteful, but the topic is worthy of consideration during the planning process where applicable. Where oil spills may contaminate waterfowl, consideration might be given to the formation of work crews to collect, clean, and care for the animals under the direction of experienced personnel. State and federal agencies can provide assistance in planning for this latter activity. Local veterinarians and animal conservation groups may also be helpful, but in all cases, ensure that personnel will not be placed at risk of adverse safety or health impacts by their actions.

ITEM #SR3

Topic: ***Post-Incident Testing for Contamination***

When/Where Applicable: Any locale where toxic and potentially persistent contaminants in air or in floodwaters may contaminate exposed surfaces.

Planning Goal: To prepare for the potential need to check crops, ground surfaces, homes, stored foods, and animals that may become part of the human food chain for possible chemical contamination.

Action Items:

- Contact the nearest EPA regional office, the state agency with primary responsibility for environmental protection, the regional Animal & Plant Health Inspection Service office and/or the Food and Safety & Quality Service Office of the U.S. Department of Agriculture, and other appropriate agencies to assess their combined capabilities for contamination testing in the aftermath of a significant spill or discharge incident.

- Where additional services may become necessary, identify and arrange for the services of university laboratories or commercial firms that have the necessary resources and personnel and who are willing and prepared to respond.

Discussion:

To some extent, this item overlaps with Item #SM2, Monitoring of Contaminant Concentrations. However, that item covers sampling and analysis activities during the initial phases of a response action while this one is concerned with the potential for persistent aftereffects.

ITEM #SR4

Topic: ***Structural Inspections after Fires or Explosions***

When/Where Applicable: Any locale where a fire or explosion involving hazardous materials may damage a large number of buildings, a bridge, a tunnel, or other structures.

Planning Goal: To make provisions for inspecting the structural integrity of damaged buildings, bridges, tunnels, or other structures in the aftermath of a fire or explosion.

Action Items:

- Identify the local, county, and/or state personnel with responsibility for various types of structural inspections.
- Establish procedures, where a potential need is envisioned, for inspecting damaged structures that may be contaminated with chemical residues.

Discussion:

A major explosion could damage or destroy numerous buildings and any nearby bridges or tunnels. Similarly, large fires can have major effects over a wide area. In either case, residents of partially damaged buildings will want to know if the structures are safe to occupy while they await repairs. Questions pertaining to the safety of highway or railway bridges or tunnels must be resolved quickly to avoid traffic complications.

Note that inspection personnel may require special precautions (i.e., chemical protective gear) in addition to normal safety equipment in those cases in which the structure may still be contaminated by hazardous residues.

ITEM #SR5

Topic: ***Provision of Post-Incident Recovery Services***

When/Where Applicable: Any locale with the potential to experience a large number of deaths or injuries and/or a large loss of residential properties.

Planning Goal: To provide a central location where people can visit to seek advice or help from social service organizations, government agency representatives, legal aid sources, representatives of the party responsible for the incident, and so forth.

Action Items:

- Identify the key agencies and groups expected to have a role in post-disaster recovery.
- Identify a convenient location where various organizations can set up shop temporarily in the aftermath of a disaster.
- Plan to set up an information clearinghouse for answering questions from the public.

Discussion:

There are numerous organizations that have a role in post-disaster recovery operations. Simultaneously, even if general guidelines are reported by the press, individual members of the public will have specific questions on how to handle recovery of losses, repair of homes and businesses, rerouting of mail, contact with "missing" relatives or friends, etc. These action items set the stage for orderly provision of necessary services.

ITEM #TR1

Topic: ***Training of Response Personnel***

When/Where Applicable: Any locale with the potential to experience significant hazardous material accidents.

Planning Goal: To ensure that key personnel have the necessary training to properly conduct their missions.

Action Items:

- Based upon the types of incidents most likely to occur and the related response and planning activities suggested by this chapter, determine the types of training required for emergency response personnel with responsibilities in any or all phases of the response.
- Determine what training the personnel have already had.
- Identify and provide any new or additional training that might be required.
- Conduct periodic drills to test the overall efficiency and effectiveness of the emergency response plan and emergency response capabilities.

Discussion:

There are a great number of duties and responsibilities associated with spill response that differ significantly from the routine activities of public officials, police and fire department personnel, and everybody from bulldozer operators to bus and ambulance drivers who may have to function in difficult and possibly hazardous environments. Appropriate training can range from formal courses at private spill control schools, universities, or community colleges to training sessions provided by the local or state government in which personnel are briefed on their specific duties in an emergency and shown how to wear and properly use personal protective clothing and devices. The nature and extent of training obviously depend on the nature of hazards to be faced, the specific responsibilities of individuals, local and state training requirements, and federal training requirements specified by OSHA (see 29 CFR 1910.120). Information on federal training opportunities is provided in FEMA 134, the ***Digest of Federal Training in Hazardous Materials***. See Chapter 1 for the address to write for obtaining FEMA publications.

ITEM #WD1

Topic: ***Disposal of Hazardous Wastes***

When/Where Applicable: Any locale where recovered chemicals and/or contaminated materials may require proper disposal.

Planning Goal: To identify appropriate disposal sites for waste chemicals and contaminated materials.

Action Items:

- Identify state and federal regulations pertaining to transportation and disposal of hazardous wastes.
- Identify authorized waste disposal sites.

Discussion:

Where the parties responsible for a spill do not take appropriate action, it may become necessary for public authorities to undertake disposal of hazardous wastes. This requires knowledge of waste disposal regulations, the location of approved and authorized disposal sites, and the proper procedures for transporting and transferring wastes to these sites. Local governments should seek assistance from the state environmental protection agency, the EPA, and the Coast Guard for assistance with these efforts. These agencies will have considered these problems in their own statewide or regional emergency response plans.

APPENDIX A

A TUTORIAL ON FUNDAMENTAL MATHEMATICAL SKILLS

Purpose of Appendix A

Various sections of this guide, literature sources that may be accessed to obtain the information and data necessary for the conduct of a hazard analysis, and certain input parameters required by the computer program provided with this document may require the user to perform various computations, convert the units of certain numerical values, and read various graphs. The purpose of this appendix is to provide a brief tutorial on:

- Basic algebra
- Conversion of units
- Scientific notation
- Reading of log-log and semi-log graphs
- Surface area and container volume estimation methods, and
- Methods to estimate container content weight.

Each of these topics is discussed below for those who may not be familiar with them or may have become a bit rusty on their use since their school days.

A Review of Basic Algebra

Algebraic equations can then be thought of as sentences of instructions, where simple rules replace the words. The main symbols you may come in contact with, and their meanings are:

A/B or $\frac{A}{B}$ means "A divided by B"

A x B or (A)(B) means "A times B"

A + B and A - B respectively mean "A added to B" and "B subtracted from A"

( ) means treat everything inside these parentheses as one variable, or equivalently, perform all computations inside parentheses before performing other computations.

A = B means "A equals B"

A < B means "A is less than B"
A > B means "A is greater than B"

$A \geq B$ and $A \leq B$ respectively mean " A is greater than or equal to B" and "A is less than or equal to B".

A^B means A raised to the B power

If parentheses don't guide you, mathematical operations are performed in the following order, left to right

1) Raise all powers first
2) Perform all multiplications or divisions second
3) Perform all additions or subtractions third

Some examples of the types of equations that may be encountered in this guide and elsewhere include:

$$A = 2 \times 60 = 120$$

$$B = A \times 10 \times 4 = 120 \times 10 \times 4 = 4800$$

$$C = \frac{10-6}{4-2} = \frac{4}{2} = 2$$

$$F = (1.8 \times C) + 32 = (1.8 \times 2) + 32 = 3.6 + 32 = 35.6$$

A Review of Unit Conversions

It is important that the numbers used in equations or input to a computer program are provided in the proper sets of units. For instance, if the spill amount to be entered into an equation or computer program is desired in pounds, the program will produce wrong answers if the user enters a number expressing this amount in tons. This may seem obvious, but it is a frequently made mistake at all levels of experience. Checking that units are correct (called dimensional analysis) is a straightforward procedure, but still one that requires a little thought.

All mathematical methods and procedures presented in this guide and its associated computer program specify the units in which any values (such as length, weight, or area) must be provided. When the user has these values in the proper set of units, then he or she can use them immediately. However, if one or more of the values are in the wrong units, the values must first be "converted". Although the computer program provided with this document contains a units conversion utility to assist the user in these tasks, it is still a good idea to know how unit conversions are generally accomplished.

Conversions usually involve the multiplication or division of a value in one set of units by a "conversion factor" to change it to another set of units. Some simple and mostly self-explanatory examples of the process include:

$$100 yards \times \frac{3 feet}{yard} = 300 feet$$

$$2 miles \times \frac{5280 feet}{mile} = 10{,}560 feet$$

$$100 gallons \times \frac{1 ft^3}{7.48 gallons} = 13.37 ft^3$$

$$13.37 ft^3 \times \frac{7.48 gallons}{1 ft^3} = 100 gallons$$

$$640 mmHg \times \frac{1 atm}{760 mmHg} \times \frac{14.7 psia}{1 atm} = 12.38 psia$$

$$1.5 tons \times \frac{2000 lbs}{ton} = 3000 lbs$$

Table A.1 lists these and other simple conversion factors that are likely to be most often needed. Note that in each of the above examples the "net" units or both sides of the equal sign are (and should be) the same after units appearing both on the top and bottom of an expression are cancelled out. Special equations for temperature conversions can be found in Section 2.2 of this guide. Conversions between "absolute" and "gauge" pressure are discussed in Section 2.3.

A Review of Scientific Notation

Numerical shorthand called "scientific notation" makes it easier to work with numbers that are very small or very large. Basically, it involves writing a number down (like 3.6) and then showing how many times this number must be multiplied or divided by 10 to obtain the number that is of interest to the reader. For example, assume that the number 360 is to be written in scientific notation. This number would be represented by 3.6×10^2, where the 2 above the 10 means that 3.6 must be multiplied 2 times by 10 ($3.6 \times 10 \times 10 = 360$).

For small numbers less than 1.0 (like 0.036), a minus sign is placed in front of the number above the 10 (this number being the "power" of 10) to show how many times the first number must be divided by 10. Thus, 0.036 would be shown as 3.6×10^{-2} (3.6/10 = 0.36;

TABLE A.1
SELECTED UNIT EQUIVALENCY FACTORS

Length	Pressure
1 mile = 0.62 kilometers	1 atmosphere = 14.7 psia
1 mile = 5280 feet	1 atmosphere = 760 mm Hg
1 nautical mile = 6080 feet	1 atmosphere = 101,325 Pascals
1 kilometer = 1000 meters	14.7 psia = 760 mm Hg
1 yard = 3 feet	
1 meter = 3.281 feet	
1 foot = 12 inches	
1 inch = 2.54 centimeters	

Weight*	Energy
1 ton = 2000 pounds	1 Btu = 252 calories
1 kilogram = 2.2 pounds	1 kilocalorie = 1000 calories
1 kilogram = 1000 grams	1 Btu = 1055 joules
1 pound = 454 grams	
1 gram = 1000 milligrams	

Volume
1 ft^3 = 7.48 gallons
1 m^3 = 35.32 ft^3
1 yd^3 = 27.0 ft^3

*Assuming gravitational acceleration at sea level.

0.36/10 = 0.036). Every time a number is multiplied by 10, its decimal point moves one position to the right. When it is divided by 10, the decimal point moves one position to the left.

The following table should help in gaining a better understanding of the concept:

Number	Scientific Notation
0.000036	3.60×10^{-5}
0.0078	7.80×10^{-3}
0.510	5.10×10^{-1}
9.2	9.2×10^{0} ($10^{0} = 1$)
51.0	5.1×10^{1}
780.0	7.8×10^{2}
36,000.0	3.6×10^{4}

Once this basic concept is mastered, it is necessary to understand how to add, multiply or divide two numbers written in scientific notation. This gets a bit more difficult. In all cases, it is important to keep track of the correct powers of 10.

The easiest way to add two numbers in scientific notation is to convert them back into numbers in standard notation. For example, two numbers like 3.6×10^{2} and 2.2×10^{3} become 360 and 2,200. Adding them together gives 2,560 or 2.56×10^{3}. The numbers 7.8×10^{3} and 5.1×10^{3} become 7,800 and 5,100. Their sum is 12,900 or 1.29×10^{4}. Likewise, 9.2×10^{-4} and 5.1×10^{-2} become 0.00092 and 0.051, and the sum is 0.05192 or 5.192×10^{-2}.

The same technique can be used for multiplication, but there is another way that some might find easier. It involves multiplication of the first numbers in the scientific notation, and then ***addition*** of the powers of 10 involved. For example:

$$(3.6 \times 10^{2}) \times (2.2 \times 10^{3}) = (3.6 \times 2.2) \times 10^{(2+3)}$$
$$= 7.92 \times 10^{5}$$

$$(7.8 \times 10^{3}) \times (5.1 \times 10^{3}) = (7.8 \times 5.1) \times 10^{(3+3)}$$
$$= 39.78 \times 10^{6}$$
$$= 3.978 \times 10^{7}$$

$(9.2 \times 10^{-4}) \times (5.1 \times 10^{-2}) = (9.2 \times 5.1) \times 10^{(-4-2)}$

$= 46.92 \times 10^{-6}$

$= 4.692 \times 10^{-5}$

In division, the front numbers are divided and then the power of 10 for the ***bottom*** number is ***subtracted*** from the power of 10 for the ***top*** number.

$$\frac{3.6 \times 10^{2}}{2.2 \times 10^{3}} = \frac{3.6}{2.2} \times \frac{10^{2}}{10^{3}} = 1.64 \times 10^{(2-3)}$$

$$= 1.64 \times 10^{-1}$$

$$\frac{7.8 \times 10^{3}}{5.1 \times 10^{3}} = \frac{7.8 \times 10^{3}}{5.1 \times 10^{3}} = 1.53 \times 10^{(3-3)}$$

$$= 1.53 \times 10^{0}$$

$$= 1.53$$

$$\frac{9.2 \times 10^{-4}}{5.1 \times 10^{-2}} = \frac{9.2 \times 10^{-4}}{5.1 \times 10^{-2}} = 1.80 \times 10^{(-4--2)}$$

$$= 1.80 \times 10^{(-4+2)}$$

$$= 1.80 \times 10^{-2}$$

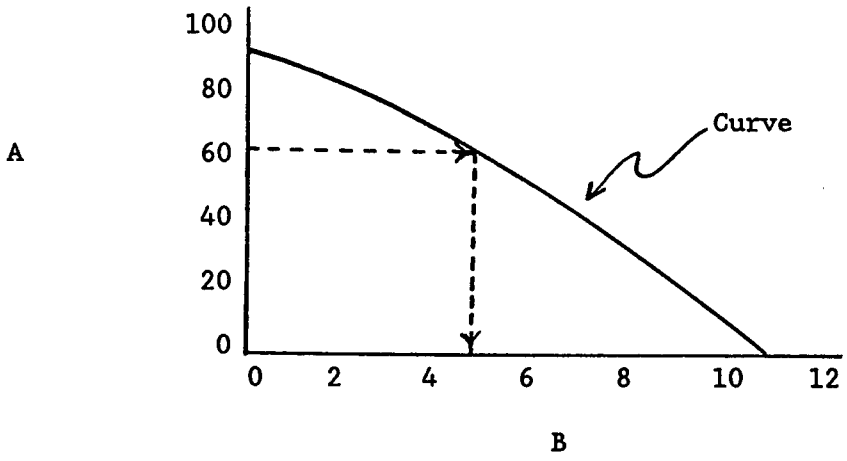
In the last example, it is important to note that two minus signs equal one plus sign. Subtracting -2 from -4 is the same as adding 2 to -4 to get an answer of -2.

Finally, it is necessary to note that computer programs use what is referred to as "E format" to represent numbers in scientific notation. In this format, the letter "E" is used to replace the term "x10" and the powers of 10 simply follow the E without appearing as superscripts. Thus:

- 1.23×10^{6} becomes 1.23E 06
- 8.7654×10^{-5} becomes 8.7654E-05

How to Read Log-Log Graphs

Almost everyone at some time or another has been shown how to use a graph with normal axes (the axes are the lines on the bottom and left side of the graph). This type of graph usually resembles something like:



Given a known value for A on the left vertical scale or axis, the user would move to the right horizontally until he or she meets the curve, and then would go straight down vertically to find the appropriate value for B on the bottom scale of the graph. This procedure is demonstrated by the dotted lines and arrow heads in the above drawing. If the value for B was known instead of A, the value of A could be determined by following the dotted lines in the reverse direction. The reason this type of graph is said to have normal axes is that the gradations on the side and bottom are equidistant. The point for 2 on the B axis is the same distance from 4 as 8 is from 10.

Another type of graph that is used when the ranges on the axes encompass many powers of 10 (from 0.10 to 1,000, for example) is called a log-log graph. In this sort of graph, the axes have logarithmic scales, and do not have gradations which are equidistant. They are a bit more difficult to read than graphs with normal axes, but permit much more information to be placed on a single page.

Figure A.1 is an example of a log-log plot similar to many which may be encountered. To understand how the graph is used, it is necessary to first review:

1. The gradations on the bottom B axis;
2. The gradations on the side A axis; and
3. The curves with different values for C.

The bottom B scale or axis spans 2 powers of ten; from 0.1 to 1.0, and again from 1.0 to 10.0. The arrows show where the intermediate numbers are between 0.1 and 1.0 to demonstrate what a logarithmic scale looks like. Note that the distance for 0.1 to 0.2 is much greater than the distance between 0.8 and 1.0, but that someone can still tell what each gradation means. The second half of the scale (to the right of 1.0) is broken up in the same way.

The left vertical A axis also spans 2 powers of ten, but has markings in scientific notation for numbers which are smaller than 1.0. The biggest number shown is 1×10^{-2}, at the top of the scale, and the smallest is 1×10^{-4} at the bottom. Again, the arrows show the relative locations of intermediate points. It is important to note that two sets of numbers are given on the graph for points at the very top, exactly in the middle, and at the very bottom. That's because 10×10^{-3} equals 1×10^{-2}, 10×10^{-4} equals 1×10^{-3}, and so on. Graphs you may encounter elsewhere may not have such dual markings, so this fact should be remembered.

To add another "dimension" to this particular graph, three curves are shown for different values of C. Many graphs in the literature will have more than one curve or line on them so that more information can be contained in each.

To use the graph, one has to know values for two out of the three parameters that have the relationship shown on the graph. For example, if it is known that A has a value of 2×10^{-3} and that C has a value of 4, the small arrows on Figure A.1 show how one would read across and down to find the previously unknown B value of 0.35.

One problem with using a graph with many curves for different C values is that the known value for C (or whatever else it is called) often lies in between two of the curves, or above or below one of those on the outer boundaries. In such a case, the user must estimate where the correct curve would be if it were shown.

How to Read Semi-Log Graphs

Many graphs may be semi-log graphs. This means that the vertical axis on the left has a logarithmic scale while the horizontal axis on the bottom has a normal axis. Such graphs are just a combination of the two types previously described.

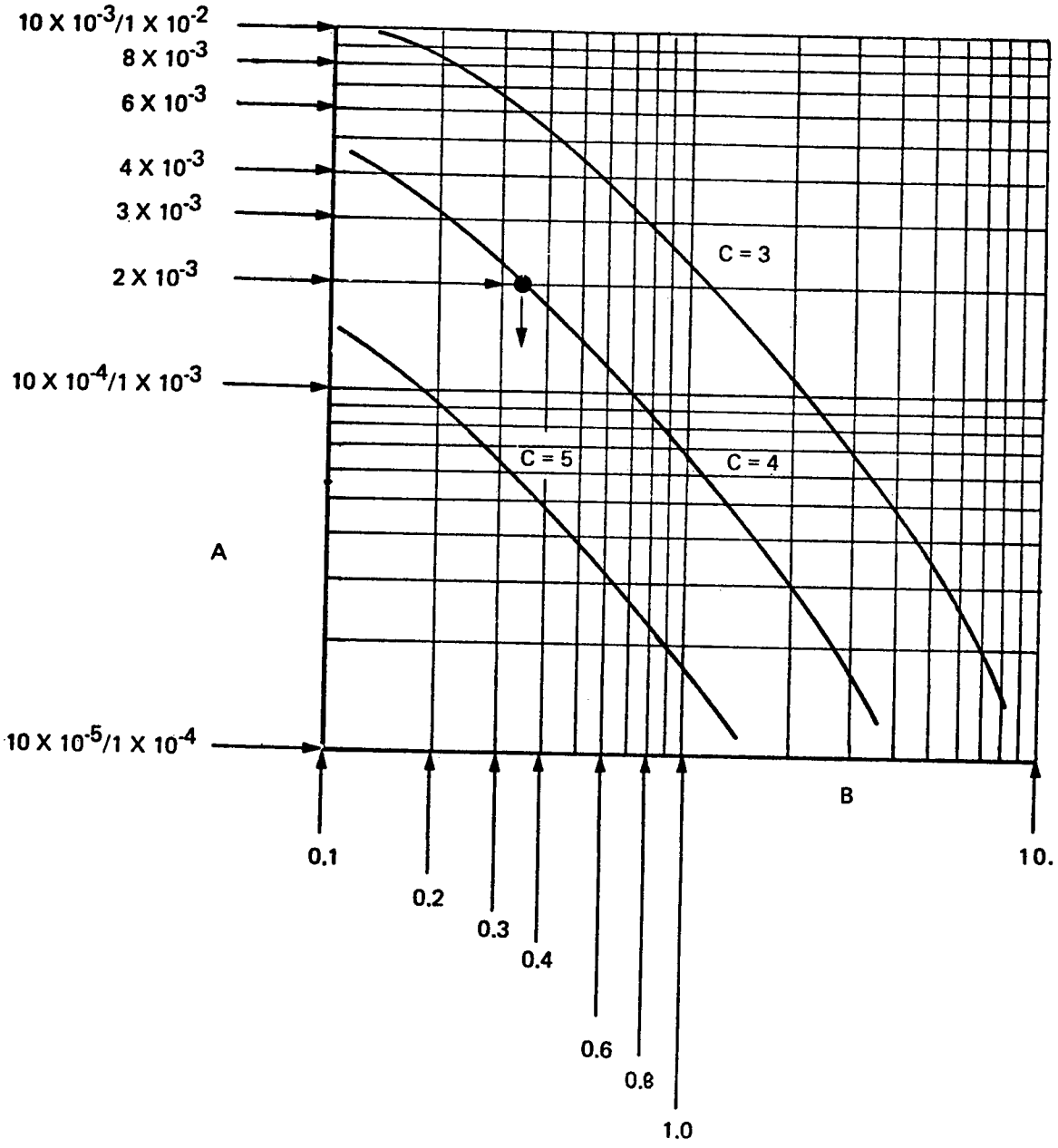


FIGURE A.1
A TYPICAL LOG-LOG GRAPH

Surface Area and Container Volume Estimation Methods

It may be necessary at times for the reader to determine or estimate the surface area of the resulting pool when a liquid is discharged upon the ground. It is well, therefore, to review how the area of a surface can be calculated from its dimensions. Of interest are circles, squares, rectangles, and triangles. The equations used to compute the areas of these shapes are:

For circles:	Area = 3.1416 x radius x radius, or Area = 0.7854 x diameter x diameter
For squares:	Area = length of side x length of side
For rectangles:	Area = length x width
For triangles:	Area = 0.5 x length of base x vertical distance from base to opposite tip of the triangle

There are several instances where the computer program associated with this guide ask the user for the diameter of the hole in a tank or pipeline or of a liquid pool, even though it is clear that pools or holes are not always circular. In such cases, the user of the methods is expected to determine the diameter of a circle that has the same area as the area of the hole or liquid pool. This is accomplished by using the equations:

$$\text{Radius} = \sqrt{\frac{\text{Area}}{3.1416}}$$

Diameter = 2 x Radius

There may be situations in which it is desired to determine the volume of a pipeline, tank, or other container. Equations for volume estimation are:

For spheres:	Volume = 4.19 x radius x radius x radius
For vertical cylinders:	Volume = 3.1416 x height x radius x radius
For pipelines and horizontal cylinders:	Volume = 3.1416 x length x radius x radius

Methods to Estimate Container Content Weight

Once the volume of a container is known, it may be necessary at times to determine its capacity to hold a liquid in units of pounds. It is mostly commonly expected that the user will know the volume in units of gallons or cubic feet and will have access to the liquid specific gravity or liquid density of the contents. Equations to determine weight in pounds from different combinations of these values include:

Weight (lb) = volume (ft^3) x liquid density (lb/ft^3)

Weight (lb) = volume (ft^3) x (62.4 lb/ft^3) x liquid specific gravity

Weight (lb) = volume (gallons) x (1 ft^3/7.48 gallons) x liquid density (lb/ft^3)

Weight (lb) = volume (gallons) x (62.4 lb/ft^3) x (1 ft^3/7.48 gallons) x specific gravity

APPENDIX B [1]
TECHNICAL BASIS FOR CONSEQUENCE ANALYSIS PROCEDURES

B.1 Introduction

This appendix provides a technical overview of the various computational procedures contained in **ARCHIE** and their key assumptions. Many of these models reflect the state-of-the-art in terms of development work undertaken at public and private research facilities, information in the published literature, and data collected or estimated from experiments and actual accidents. Nevertheless, to make models workable for **ARCHIE** within constraints imposed by available data and project resources, it was necessary at times to employ a number of idealizations and assumptions which must not be overlooked in the interpretation of results. Accordingly, it is believed that trends are predicted accurately, but estimated values are less certain. In general, estimates of hazard zones are conservative, in that uncertainties overpredict rather than underpredict the extent of the hazard zones associated with an accidental release. Exceptions are possible and likely, however, so the application of safety factors by users is encouraged.

In selection and development of hazard assessment models for **ARCHIE** , particular emphasis was placed on simplicity of computational procedure, minimization of required input, applicability to a wide range of accident scenarios, and reasonable accuracy of results. Individual subsections below address individual models in the computer program

[1] This appendix was prepared using a special word processing system because of the large number of equations presented. This prevented matching of the fonts and type sizes used throughout the rest of this handbook

B.2 Liquid Discharge Models

For a given liquid height and vapor space pressure, the instantaneous liquid release rate from a tank or other container is commonly given by the equation:

$$m = A_h C_d \sqrt{\rho_l \left[2g\rho_l (H_L - H_h) + 2(P_o - P_a)\right]} \qquad \text{(B.1)}$$

where

m = Discharge rate, kg/s

g = Gravitational constant, 9.8 m/s^2

ρ_l = Liquid density, kg/m^3

P_o = Storage pressure, N/m^2

P_a = Ambient pressure, N/m^2

H_L = Liquid height above bottom of container, m

H_h = Height of discharge opening, m

A_h = Area of discharge opening, m^2

C_d = Discharge coefficient

An average release rate may be obtained for tanks operating at atmospheric pressures by computing the time (T_e) required to empty a tank. Closed form expressions are available for storage tanks of specific geometries [27] and are as follows for the system of units being utilized:

- Rectangular Tank:

$$T_e = \frac{8LW\sqrt{H_T}}{C_d D_o^2 \pi \sqrt{2g}} \qquad \text{(B.2)}$$

- Vertical Cylindrical Tank:

$$T_e = \frac{\sqrt{2H_T} D_T^2}{D_o^2 \sqrt{g} C_d} \qquad \text{(B.3)}$$

- Horizontal Cylindrical Tank:

$$T_e = \frac{16}{3\pi} \frac{H_T D_T^{1.5}}{D_o^2 \sqrt{2g} C_d} \tag{B.4}$$

- Spherical Tank:

$$T_e = \frac{16}{15} \frac{D_T^{2.5}}{D_o^2 \sqrt{2g} C_d} \tag{B.5}$$

where:

D_T = Tank diameter, m
D_o = Opening diameter, m
H_T = Liquid height, m
T_e = Time to empty, sec

In deriving the above equations, it is assumed that the tank is full and a circular opening of diameter D_o is at the bottom of the tank. The average release rate is therefore given by:

$$m_{avg} = \frac{M}{T_e} \tag{B.6}$$

where M is the total liquid mass in the tank in kilograms.

Equation B.1 is also used to calculate pressurized liquid release rates. In this case the difference between the tank pressure and the ambient pressure is much larger than the liquid head. When assuming that liquid head is negligible, Equation B.1 becomes:

$$m = A_h C_d \sqrt{\rho_l 2 (P_o - P_a)} \tag{B.7}$$

This model should be used to calculate liquid discharge from vessels where the discharge outlet is less then 4 inches from the inner wall of the tank. It has been shown by Fletcher [18,19] that a length of pipe of 4 inches is necessary and sufficient to establish two-phase flow independent of the pipe diameter size. The more appropriate discharge rate equation for this latter condition is presented in section B.6.

B.3 Gas Discharge From a Tank

This model calculates the initial discharge rate of a gas from a pressure vessel. The model assumes that the process is adiabatic and that wall friction effects are negligible. Using the mechanical energy balance, an expression for an instantaneous discharge rate under non-choked flow conditions may be calculated from:

$$m = A_h \sqrt{2 p_o \rho_o \left(\frac{\gamma}{\gamma - 1}\right) \left[\left(\frac{p_1}{p_o}\right)^{2/\gamma} - \left(\frac{p_1}{p_o}\right)^{\frac{\gamma+1}{\gamma}}\right]} \tag{B.8}$$

Under choked flow conditions, the mass flow rate is calculated from:

$$m = A_h \sqrt{\gamma p_o \rho_o \left(\frac{2}{\gamma + 1}\right)^{\frac{\gamma+1}{\gamma-1}}} \tag{B.9}$$

where:

m = Discharge rate, kg/s

A_h = Opening area, m^2

γ = Ratio of specific heats

p_o = Tank pressure, *Pascals*

p_1 = Ambient pressure, *Pascals*

ρ_o = Density, kg/m^3

It can be shown that choked flow (maximum flow rate) occurs at a critical pressure ratio of:

$$\left(\frac{p_1}{p_o}\right)_{crit} = \left(\frac{2}{\gamma + 1}\right)^{\frac{\gamma}{\gamma-1}} \tag{B.10}$$

These equations are based on ideal gas behavior. They can be modified using a compressibility factor correlation such as Pitzer's correlation [46] but are not so in **ARCHIE** for model simplification purposes.

B.4 Gas Discharge From a Pipeline

Two primary computational approaches are available for estimation of gas discharge rates from punctured or ruptured pipelines conveying strictly gaseous products. The pipeline can be considered to be a volume of compressed non-flowing gas or it can be considered as a length of pipe with gas velocity increasing towards the discharge location.

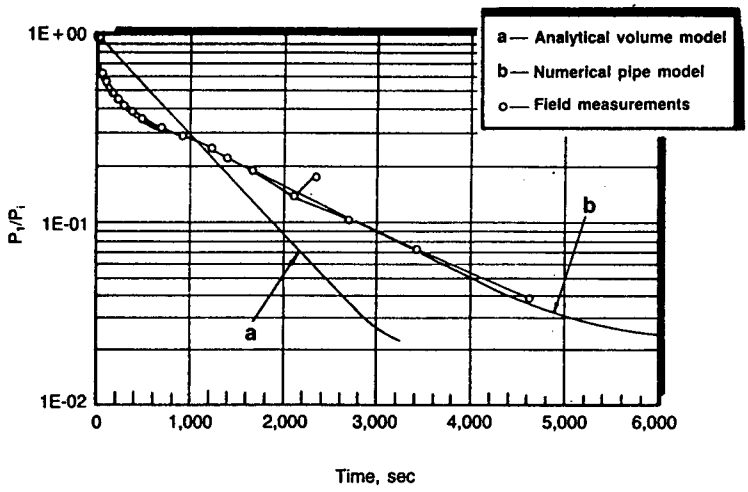
The volume model is simple and relies upon the equations described earlier for gas discharge from a tank. It essentially neglects the effects of friction along the pipe and therefore provides a conservative estimate of the discharge rate. This is the model used in **ARCHIE** .

Consideration of frictional resistance to flow often requires graphical techniques to calculate discharge rates. The charts referred to are those described by Lapple [35] and later corrected by Levenspiel [37]. It is also possible to use a complex numerical algorithm to solve the mass and energy conservation equations needed to describe the problem, with the flow being divided into two parts:

1. A frictionless adiabatic flow at the junction of the reservoir and the pipe.
2. An adiabatic expansion with friction through the pipe.

Weiss et. al [51] present a comparison between field test data, volume model results, and results obtained using a complex numerical model for pipeline blowdown calculation. Although the volume model underpredicts the blowdown time, it leads to generally conservative vapor dispersion calculations since it overpredicts the discharge rate for any given amount of gas in a pipeline (See Figure B.1).

Figure B.1: Models vs. Field Measurements. Taken from Weiss et al.



B.5 Liquid Discharge From a Pipeline

This model is a direct application of the Bernoulli equation [39]. It assumes the density of the liquid is constant and solves for an average discharge velocity without accounting for wall friction. Loss coefficients for valves and fittings may be accounted for by calculating the equivalent pipe length but are set to 0 in **ARCHIE**. The working equation is:

$$\frac{(P_a - P_b)}{\rho} + \frac{g}{g_c}(Z_a - Z_b) = \frac{(V_b^2 - V_a^2)}{2g_c} \tag{B.11}$$

P_a = Pressure at pipe inlet, *Pascals*

P_b = Pressure at pipe outlet, *Pascals*

Z_a = Height above datum plane at pipe inlet, m

Z_b = Height above datum plane at pipe outlet, m

g = Gravitational acceleration, m/s^2

g_c = Newton's law proportionality factor, 1.0

V_a = Inlet velocity, m/s

V_b = Outlet velocity, m/s

B.6 Two-Phase Flow From a Tank

This method is used to estimate the two-phase gas-liquid discharge rate from a tank or other vessel when the discharge outlet is more than four inches from the inner wall of the vessel and the vessel contains a liquefied compressed gas.

The model is based on theoretical and experimental studies conducted by Fauske and Associates [15] under the sponsorship of the Design Institute for Emergency Relief Systems (DIERS). Details of the model are given in Fauske [15] and Lueng [38].

The final equation describing flashing two-phase flow through a line greater than 4 inches in length is:

$$D_r = 0.104 D_o^2 \left(\frac{dP}{dT}\right) \left(\frac{T}{C_p}\right)^{\frac{1}{2}} \tag{B.12}$$

Where:

D_r = discharge rate, lbs/minute

D_o = line or pipe diameter, inches

T = absolute temperature, degrees R

C_p = liquid specific heat, $\frac{Btu}{lb-R}$

$\frac{dP}{dT}$ = slope of vapor pressure curve, $\frac{mmHg}{K}$

Equation B.12 is derived from an equilibrium critical flow model. Fauske (1985) has determined that for a pure flashing component exiting through a line greater than 4 inches in length, the flow rate may be approximated by:

$$G = \frac{dP_s}{dT}\left[\frac{Tg_c}{C_p}\right]^{\frac{1}{2}} \tag{B.13}$$

where:

G = mass flux

$\frac{dP_s}{dT}$ = slope of vapor pressure curve

T = absolute temperature

C_p = liquid specific heat

g_c = gravitational constant

The flow rate given by Equation B.13 is governed by the sonic velocity at equilibrium flash condition and is not significantly affected by frictional effects. In order to estimate this flow rate, it is necessary to determine the heat capacity of the liquid and the slope of the vapor pressure curve.

The slope of the vapor pressure curve may be determined readily if the vapor pressure data are available. However, material safety data sheets usually specify the vapor pressure at only one specific temperature and also typically provide the normal boiling point of the substance. Since the vapor pressure at the normal boiling point is one atmosphere or 760 mm of mercury, these two vapor pressure data points are used in **ARCHIE** to estimate the approximate slope of the vapor pressure curve using the expression:

$$\frac{dP_s}{dT} = \frac{P_s \ln\left(\frac{P_s}{760}\right)}{T_s - T_b} \tag{B.14}$$

Where:

P_s = vapor pressure at temperature T_s, in mm of mercury

T_b = boiling point (the vapor pressure is 760 mm of mercury)

The heat capacity of liquid is not a parameter given in material safety data sheets, but the range of heat capacities for various types of materials is relatively narrow.

- Organic materials made up of predominantly carbon, hydrogen, oxygen, nitrogen and sulfur typically have a heat capacity ranging from 0.3 Btu/lb-F to 0.8 Btu/lb-F.
- Chemicals containing chlorine, fluorine and silicon typically have heat capacities in the range of 0.2 to 0.4 Btu/lb-F.
- Chemicals containing bromine and iodine and metals containing organics typically have heat capacities ranging from 0.1 to 0.2 Btu/lb-F.

In the absence of specific data for a chemical, the program and Chapter 12 suggest use of the following values:

- Chemicals containing carbon, hydrogen, oxygen, nitrogen and sulfur: $C_p = 0.3 Btu/lb - F$.
- Chemicals containing chlorine, fluorine or silicon: $C_p = 0.2 Btu/lb - F$.
- Chemicals containing iodine, bromine or metals: $C_p = 0.1 Btu/lb - F$.

Equation B.12 can be utilized by first applying Equation B.14 to determine the approximate slope of the vapor pressure curve and then identifying or selecting an appropriate liquid heat capacity.

B.7 Pool Size Estimation Methods

Estimation of pool areas resulting from discharges of liquid into the terrestrial environment is one of the most difficult and error prone aspects of

accident scenario evaluations for hazardous materials. Exceptions only involve those cases in which the discharge source is confined by a secondary containment system of known dimensions and the liquid can be expected to cover the exposed surface of the containment area. In the real world, unconfined spills rarely occur in a location where the ground surface if perfectly flat and impermeable. Rather, spilled liquids will typically follow rainwater discharge paths while simultaneously vaporizing, burning, and / or soaking into the ground. Thus, this model is actually comprised of a number of different estimation procedures, all of which are designed to ease the task of the program user in obtaining a result that is reasonable and likely to be within the correct *ballpark*.

In the case of a liquid not expected to boil upon release to the environment due to the relationship between its normal boiling point and ambient and storage temperatures, **ARCHIE** first estimates the rate at which the liquid will evaporate on a unit area basis using a correlation developed by the U.S. Air Force that is described in section B.8. This evaporation flux is then used as input to a generalized pool spreading model described in section B.10, with substitution of the evaporation regression rate for the burning velocity of the liquid. The result is a maximum credible area for the scenario being evaluated under specified environmental conditions.

Remaining pool size estimation techniques for non-boiling liquids are simple and permit refinement of results. A pool area may be calculated based on user supplied data from observations at the potential accident or incident site, the user may select use of the maximum credible pool area, or the user may choose use of a simple and very crude correlation based on limited experimental data, this being:

$$\log(A) = 0.492 \log(m) + 1.617 \qquad \text{(B.15)}$$

where:

m = Total liquid mass spilled, lbs

A = Pool area, ft^2

Computation of pool areas for boiling liquids is accomplished via use of the boiling rate models described in section B.8 to determine the vaporization flux and the same pool spreading model described in section B.10. In this latter case, the vaporization flux is substituted for the burning velocity of the liquid in appropriate units.

B.8 Emission Rates From Liquid Pools

Pools of evaporating liquids are modeled with one of two methods, depending upon the volatility, normal boiling point, and storage temperature of the liquid and their relationship to the ambient temperature. [11,14,31].

If a discharged liquid is near ambient temperature, a simplified model developed by the U. S. Air Force Engineering and Services Laboratory [32] is used to predict the evaporation rate. This model was correlated to a complex numerical model [31], also developed by the Air Force and validated with experimental data [11]. It requires far less user input, yet yields reasonably accurate answers. The model applies to spills that can vary up and down in temperature as the liquid pool heats and cools, and is limited in emission rate by how fast mass can transfer into the air from the pool surface. It is also reasonably accurate for pools being heated moderately by the sun, but does not fully account for the decreases in evaporation rates that boiling or very volatile liquids may experience as a result of cooling by evaporation. However, the error applies only to one specialized category of spills, and normally results in a conservative answer. Inaccuracies resulting from heating of a relatively low volatility substance spilled onto a hot surface or warmed by the sun over time are counterbalanced by recommendations

made to users of **ARCHIE** in Chapter 12 with respect to specification of ambient and liquid storage temperatures.

The equation used to calculate the evaporation flux of volatile liquid is:

$$E_v = 4.66 \times 10^{-6} U_w^{0.75} T_F \frac{P_s M_w}{P_{sh}} \qquad \text{(B.16)}$$

where

E_v = Evaporation flux, $lbs/min/ft^2$

U_w = Wind speed, mph

P_s = Vapor pressure of chemical, $mm\ Hg$

P_{sh} = Vapor pressure of hydrazine, $mm\ Hg$

M_w = Molecular weight of chemical

T_F = Spill temperature correction factor

The spill temperature correction factor is defined as follows:

$$T_F = 1 \quad T_p < 0\ C \qquad \text{(B.17)}$$

$$T_F = 1 + 4.3 \times 10^{-3} T_p^2 \quad T_p > 0\ C \qquad \text{(B.18)}$$

where T_p is the pool temperature in degrees C. The vapor pressure of hydrazine is given by the following equation:

$$\ln(P) = 65.3319 - \frac{7245.2}{T} - 8.22 \ln(T) + 6.1557 \times 10^{-3}\ T \qquad \text{(B.19)}$$

where T is in kelvins and P is an atmospheres. Note that the total vaporization rate of the pool is obtained by multiplying the evaporation flux by the pool area. The duration of vapor emission is obtained by dividing the total mass of discharged liquid by the total vaporization rate. Equation B.18 is used by **ARCHIE** for all non-boiling liquids and for those liquids which boil at pool temperatures in excess of zero degrees Celcius.

The vaporization rate of cold boiling liquids, including most liquefied gases, is normally driven by the rate of heat transferred from the ground by conduction. Accurate computation of vaporization rates by so-called *ground conduction models* requires knowledge of several ground surface properties as well as the physio-chemical properties of the spilled material. Further complicating the proper use of such models is the fact that rates will vary with time as the surface beneath the pool is cooled. Notwithstanding the above, several existing models without excessive data demands were tested for inclusion in **ARCHIE** , including a novel approach based on observations of the relationship between the boiling and burning rates of liquids which provided the best overall results.

An understanding of the logic applied during development of the latter approach requires knowledge of the following observations:

1. Larger differences in temperature between the ground and the boiling point of the discharged liquid lead to higher vaporization rates in general.
2. The depletion rate of a boiling pool at low temperatures can approach but not exceed the expected rate of depletion if the pool is burning.
3. Burning rates of most common flammable liquids vary within a relatively narrow range regardless of the boiling point of the liquid.
4. The burning rate of a liquid is a function of its boiling point, molecular weight, and density.

Based on the above findings, a simplified method was developed by correlating burning velocities estimated by the equation presented in section B.10 with experimentally derived boiling rates for a variety of hazardous materials, these including butane, sulfur dioxide, propane, methane, and oxygen.

The resulting correlation was:

$$F = 0.5322 - 0.001035T_b \quad \text{(B.20)}$$

$$E_v = Fy\rho \quad \text{(B.21)}$$

where,

E_v = Vaporization flux, $kg/m^2/s$

T_b = Boiling point, F

ρ = Liquid density, kg/m^3

y = Burning velocity, m/s

This approach provides answers of reasonable accuracy within the correct order of magnitude. It is slated for further refinement in a future varsion of **ARCHIE** .

B.9 Vapor Dispersion Model

The size of a dispersion hazard zone depends upon the quantity of the material released, its effective density, volatilization, prevailing atmospheric conditions, source elevation, and the user specified toxicity limit.

The toxicity limit must be selected by the user carefully to reflect both the impact of interest (fatality, serious injury, injury, etc.) and the scenario release conditions (especially duration of release or pool evaporation). Chapter 6 of the guide discusses this topic in detail.

The model in **ARCHIE** is used to determine the downwind distances where the concentrations are at or above a user specified toxic limiting concentration. Among the models required for hazard assessments, vapor dispersion

models are perhaps the most complex. This is primarily due to the varied nature of release scenarios as well as the varied nature of chemicals that may be released into the environment.

In general, dispersion of toxic gases or vapors is influenced by the following parameters:

- Release Rate and Duration
- Prevailing Atmospheric Conditions
- Limiting Concentration
- Duration of Release
- Elevation of the Source
- Surrounding Terrain
- Source Geometry
- Initial Density of the Release

Each one of these parameters are discussed with special emphasis on their influence on estimation of downwind distances.

Release Quantity or Release Rate refers to the total amount of hazardous chemical which has the potential to be released over a given period of time in the event of an accident. This parameter is a major factor in determining the dispersion distance. In general, larger quantities lead to larger dispersion distances. However, the dispersion distance does not increase linearly with quantity or release rate. In fact, a factor of 10 increase in release rate usually increases the dispersion distance by a factor of about 3. A factor of 100 increase in release rate may lead to a factor of 10 increase in the dispersion distance. For gaseous and high vapor pressure liquid releases, the release rate to the atmosphere will be the same as the discharge rate from

a vessel or pipeline. For liquids with low vapor pressures, the vapor release rate will be governed by the liquid-specific evaporation characteristics, the spill area, and the ambient conditions; it can never exceed the liquid spill rate.

Prevailing Atmospheric Conditions include a representative wind speed and an atmospheric stability class. Less stable atmospheric conditions result in shorter dispersion distances than more stable weather conditions. Wind speed affects the dispersion distance inversely. Since weather conditions at the time of an accident can not be determined *a priori*, it is usually prudent to exercise the model for at least typical and worst case weather conditions for hazard analysis purposes.

Limiting Concentration affects the dispersion distance inversely. Lower concentrations lead to larger dispersion distances. As with source release rate, the effect is not linear, with a factor of 100 reduction in the limiting concentration resulting in an increase in the dispersion distance by a factor of about 10.

Duration of Release is a parameter dependent on release conditions. Most dispersion models use one of the two extreme cases, i.e., continuous release or instantaneous release. In the case of instantaneous release (i.e., for very short duration releases), the total quantity of the chemical released during the accident contributes to the dispersion hazard, and the dispersion takes place in longitudinal (along wind), lateral (across wind) and vertical directions. In case of a continuous release (i.e., a release that lasts a long time compared with downwind travel time), the release rate is the important parameter, and dispersion is commonly assumed to take place only in the lateral and vertical directions.

Clearly, most releases do not fall into either one of the above two categories. Models developed to predict strictly continuous or instantaneous releases

cannot be applied with reasonable accuracy because they do not take into account the actual release duration. Consequently, a finite duration correction (see Palazzi [42]) is incorporated into **ARCHIE** . This model approaches the two limiting cases as the release duration is varied from very short to very long times. The finite duration correction was validated by Palazzi et. al. using the experimental data of De Faveri et. al. [13].

The concentration at any location is given in **ARCHIE** by:

$$C_f = \frac{C_c}{2}\left[erf\left(\frac{x}{\sqrt{2}\sigma_x}\right) - erf\left(\frac{x-U_w t}{\sqrt{2}\sigma_x}\right)\right] \quad when \;\; t \le t_R \qquad (B.22)$$

$$C_f = \frac{C_c}{2}\left[erf\left(\frac{x-U_w(t-t_R)}{\sqrt{2}\sigma_x}\right) - erf\left(\frac{x-U_w t}{\sqrt{2}\sigma_x}\right)\right] \quad when \;\; t \ge t_R$$

where:

$$C_c = \frac{Q}{2\pi\sigma_y\sigma_z U_w} e^{-\frac{y^2}{2\sigma_y^2}} \times \left[\exp\left(-\frac{(z-H)^2}{2\sigma_z^2}\right) + \exp\left(-\frac{(z+H)^2}{2\sigma_z^2}\right)\right] \qquad (B.23)$$

Here, t_R is the duration of release in seconds. The maximum concentration is given by the following equation:

$$C_{max} = \frac{C_c}{2}\left[erf\left(\frac{x}{\sqrt{2}\sigma_x}\right) - erf\left(\frac{x-U_w t_R}{\sqrt{2}\sigma_x}\right)\right] \quad x \le \frac{U_w t_R}{2} \qquad (B.24)$$

$$C_{max} = C_c\left[erf\left(\frac{U_w t_R}{2\sqrt{2}\sigma_x}\right)\right] \quad x \ge \frac{U_w t_R}{2} \qquad (B.25)$$

The parameters used in the above equations are defined as follows:

C_{max} = Maximum centerline concentration, kg/m^3

Q = Continuous source release rate, kg/sec

U_w = Wind speed, m/sec

z = Vertical distance, m

y = Crosswind distance, m

x = Downwind distance, m

H = Source height, m

σ_x = Longitudinal standard deviation, m

σ_y = Lateral standard deviation, m

σ_z = Vertical standard deviation, m

The model uses Pasquill-Gifford [43] dispersion coefficients (i.e., standard deviations) which provide a measure of the turbulence intensity in the lateral and vertical directions. These coefficients are a function of downwind distance. It is customary to assume for short duration sources that the longitudinal dispersion coefficient is identical to the lateral dispersion coefficient.

As the duration of the release becomes small, the results approach that of an instantaneous model; conversely, as the duration becomes very large, the results resemble that of a continuous point source model.

Elevation of the Source is attributed to its physical height (such as a tall stack). In general, the effect of source height is to increase dispersion in the vertical direction (since it is not ground restricted), and reduce the concentration at ground level.

Surrounding Terrain affects the dispersion process greatly. For example, rough terrains involving trees, shrubs, buildings and structures usually enhance dispersion, and lead to a shorter dispersion distance than predicted using a flat terrain model. Building and terrain effects are site-specific and cannot be considered in a generalized dispersion model.

Source Geometry refers to the actual size and geometry of the source emission. For example a release from a safety valve may be modeled as a point source. However, an evaporating pool may be very large in area and may require an area source model. The source geometry effects are significant

when considering near-field dispersion (less than ten times the characteristic dimensions of the source). At farther distances, the source geometry effects are smaller and eventually become negligible. Thus, **ARCHIE** uses a point source model in all cases. Since most toxic substances have long dispersion distances, this level of detail was considered adequate for emergency planning purposes.

Initial Density of the release affects the dispersion process. A buoyant release may increase the effective height of the source. By the same token, a *heavier than air* release will slump towards the ground. For heavier-than-air releases at or near ground level, the initial density determines the initial spreading rate. This is particularly true for large releases of liquefied or pressurized chemicals where flashing of vapor and formation of liquid aerosols contribute very significantly to the initial effective vapor density and therefore to the density difference with air.

Results of recent research programs dramatically indicate the importance of heavy gas dispersion in the area of chemical hazard assessment. In fact, heavy gas dispersion phenomena exhibit a predictable pattern.

- The initial rate of spreading (often termed slumping) is significant and is dependent on the differences between the effective mean vapor density and the air density.
- The rapid mixing with ambient air due to slumping leads to lower concentrations at shorter distances than those predicted using neutral density dispersion models.
- There is very little mixing in the vertical direction, and thus, a vapor cloud *hugging* the ground is generated.
- When the mean density difference becomes small, the subsequent dispersion is governed by prevailing atmospheric conditions.

Since *heavy gas dispersion* occurs near the release, it is particularly important when considering large releases of pressurized flammable chemicals. To examine the feasibility of having a simplified version for **ARCHIE** , the results of a detailed heavy gas model [41] were compared with those from a neutral buoyancy vapor dispersion model for both flammable and toxic hazard scenarios. The models were exercised for the following two scenarios with both neutral and stable atmospheric conditions:

- Liquefied propane gas (LPG) released instantaneously with 35 % flashing into vapor and the remaining liquid in the form of aerosols within the vapor cloud. The mass of release was varied from 1 ton to 100 tons. The limiting concentration was chosen to be one-half of lower flammability limit for propane.
- Pressurized releases of chlorine with 20 % flashing and the remaining 80 % in the form of liquid aerosols. The mass of release varied from 0.1 ton to 10 tons. The limiting concentration was chosen to be the IDLH for chlorine (25 ppm).

The results of the model comparison were as follows:

- The heavy gas dispersion model, when exercised for the LPG scenario, gave very similar dispersion distances for both stability categories. The typical distances were between 1000 ft (1 ton release) to 3000 ft (100 ton release).
- The neutral buoyancy dispersion model, when applied to the LPG scenario produced to larger dispersion distances under stable weather conditions. The dispersion distances were typically 50 % to 100 % greater than heavy gas dispersion model predictions for neutral weather conditions. For stable weather conditions, the neutral buoyancy dispersion distances were about 3 to 5 times greater than those given by the

heavy gas dispersion model.

- The heavy gas dispersion model results for chlorine release scenarios were sensitive to the atmospheric stability conditions with stable weather leading to larger dispersion distances than neutral weather conditions. The heavy gas dispersion model resulted in slightly larger dispersion distances than the neutral buoyancy dispersion distances largely due to limited vertical mixing. Over the range of parameters, the differences between the two model results were about 10 %.

Based on this comparison, it was concluded that use of a neutral buoyancy dispersion model would be adequate for toxic release scenarios being evaluated by **ARCHIE** for emergency planning purposes.

The time of arrival of a cloud or plume at a downwind point is often calculated by simply dividing the downwind distance by an average wind speed:

$$t_{arrive} = \frac{X_{dw}}{U_w} \tag{B.26}$$

where:

X_{dw} = Downwind distance, m
U_w = Average wind speed, m/s

In the above expression, the wind speed is assumed to be constant and independent of height. The vapor cloud is assumed to travel at a velocity similar to that of ambient air.

A more realistic estimate may be calculated using a wind speed profile with a power law expression:

$$U_w = U_{ref}\left(\frac{z}{z_{ref}}\right)^{0.14} \tag{B.27}$$

where:

U_{ref} = Reference wind speed, m/s

z_{ref} = Reference height, m (usually 10 m)

To provide conservative estimates of cloud departure and arrival times, **ARCHIE** uses the following logic:

- For discharges with source elevations less than 10 meters, the wind speed reported at a 10 meter height is used to calculate arrival time; 50 % of this speed is used to calculate departure time.
- For discharges with source elevations greater than 10 meters, the power law is used to calculate wind speed for arrival time; 50 % of the 10 meter reference wind speed is used to calculate departure time.

Recommended initial evacuation zone widths are estimated using the methodology described in Chapter 3 of this guide.

B.10 Pool Fire Model

Upon ignition, a spilled liquid hydrocarbon pool will burn in the form of a large turbulent diffusion flame. Calculating the incident flux to an observer involves four steps: geometric characterization of the flame, estimation of flame radiation properties, estimation of attenuation coefficients, and computation of the geometric view factors between the observer and flame. The size of the flame will depend upon the spill surface and thermo-chemical properties of the spilled liquid. In particular, the diameter of the fire (if not confined by a dike), the visible height of the flame, and the tilt and drag of the flame due to wind can be correlated with the burning velocity of the liquid. The radiative output of the flame will depend on the fire size, the extent of mixing with air and the flame temperature. Some fraction of the thermal radiation is absorbed by carbon dioxide and water vapor in the intervening atmosphere. In addition, large hydrocarbon pool fires produce thick smoke which can significantly obscure flame radiation. Finally, the incident flux at an observer location will depend on the radiation view factor which is a function of the distance from the flame surface, the observer's orientation, and the flame geometry.

Experimental data on thermal radiation hazards suggest that an incident flux of about 5 kW/m2 (1600 Btu/hr-ft2) will cause second-degree burn injuries on bare skin if the duration of exposure is about 45 seconds. An incident flux level of 10 kW/m2 (3200 Btu/hr-ft2) quickly causes third-degree burns that are likely to lead to fatality. These two levels are typically used in determining injury and fatality hazard zones (See Buettner [10]).

Estimating the thermal radiation hazards from pool fires involves three main steps: characterization of the flame geometry, approximation of the radiative properties of the fire, and calculation of the safe separation distance to specified levels of thermal radiation. The model is used to calculate the

following parameters:

- Fuel burning velocity;
- Effective emissive power; and
- Fatality and injury hazard zones.

Several simplifying assumptions have been made in the calculation procedure. These are summarized below:

- Pool area is circular
- Observer is at ground level
- Ambient temperature is 20 degrees C.
- Atmospheric absorption of thermal radiation is negligible
- Negligible wind in the vicinity of the flame; thus, uniform thermal radiation field radially and no flame tilt.
- When the user assumes pool ignition occurs shortly after release, the fire achieves a size such that the burning rate equals the spill rate, with some adjustments made for special circumstances. Otherwise, the fire has the base area determined via the use of the evaporating or boiling pool area estimation models.

The burning velocity of a liquid pool is the rate at which the pool level decreases with time. The mass burning rate is a related term, being a product of the burning velocity and the fuel liquid density. Extensive burn rate measurements (See Burgess [9]) have shown a definite relationship between the burning velocity and thermochemical fuel properties, such as the ratio of the net heats of combustion and vaporization. The single most readily available property that best correlates with these heats is the normal boiling point. Therefore, a simple expression for the burning velocity was obtained,

covering a wide range of boiling points. It is important to note that the correlation developed is independent of pool size. In effect, it is assumed there is a large, turbulent diffusion flame behaving as an optically thick gray body. This condition is satisfied for most pool fires exceeding about 10 feet in diameter. The equation to estimate the burning velocity is [2]:

$$y = \frac{92.6e^{-0.0043T_B}M_w}{\rho}\frac{10^{-7}}{6} \tag{B.28}$$

where:

y = Burning velocity, m/s

M_w = Molecular weight, $kg/kgmol$

ρ = Liquid specific gravity

T_B = Normal boiling point, degrees F

The spectrum of hydrocarbon liquid spill scenarios is wide. Spills can be classified based on the rate of release and duration:

- Continuous spills - in which the spill continues at a specified finite rate for a long duration.
- Instantaneous spills - in which all of the spill occurs in a *very short time.*
- Finite duration spills - where a given volume of liquid is spilled over a given duration of time. Both the release rate and the release duration are finite.

The diameter of the pool fire depends upon the release mode, release quantity (or rate) and the burning rate. In addition, if the spill occurs on land,

[2]This equation underpredicts the burning rate for hydrogen. **ARCHIE** therefore includes a special adjustment for hydrogen

the frictional resistance offered by the terrain will limit the spreading velocity of the liquid. In the case of a continuous spill, the liquid spreads and increases the burning area until the total burning rate equals the spill rate. This condition of equilibrium is represented by an equilibrium diameter given by the following equation:

$$D_{eq} = 2\sqrt{\frac{V}{\pi y}} \tag{B.29}$$

Here,

D_{eq} = Steady state diameter of the pool, m
V = Liquid spill rate, m^3/s
y = Liquid burning rate [3], m/s

This equation assumes that the dominant mode of heat transfer to the liquid pool comes from the flame and the burning rate is constant. This is a valid assumption for all liquid hydrocarbons whose boiling temperatures are above ambient. This is also true for liquefied hydrocarbon spills on water where heat transfer from water to the pool is relatively constant. This results in a higher burning rate. The equation, however, ignores the time dependent heat transfer from substrate such as on land where heat transfer decreases with time. It is also assumed in deriving this equation that the mass balance is maintained within the burning pool. Hence, the loss of liquid due to percolation through the soil or dissolution in the water column are not included.

In the absence of frictional resistance during spreading, the equilibrium diameter given by Equation B.29 is reached over a time given by the following equation:

$$t_{eq} = 0.949\frac{D_{eq}}{(\Delta y D_{eq})^{1/3}} \tag{B.30}$$

[3] see section B.5 for equation

where, Δ is the effective gravity.

The effective gravity is equal to the gravitational constant for spills on land. It is important to note that the equilibrium diameter does not represent the maximum diameter of the flame. The excess volume spilled up to the time to reach the equilibrium diameter spreads further. The maximum diameter is given by:

$$D_{max} = \sqrt{2} D_{eq} \tag{B.31}$$

If the spill duration is less than t_{eq}, a steady state diameter is not reached. The maximum diameter and the time to reach this diameter are given by the following expression:

$$D_{max} = \left[\frac{4}{3} + \left(\frac{D_s}{D_{ch}}\right)^4\right]^{1/4} D_{ch} \tag{B.32}$$

$$t_{max} = 0.6966 \left[\frac{V_s}{\Delta y^2}\right]^{1/4} \left(1 + \frac{3}{4}\left[\frac{D_s}{D_{ch}}\right]^4\right)^{1/6} + t_s \tag{B.33}$$

$$D_{ch} = 1.65 \left[\frac{V_s^3 \Delta}{y^2}\right]^{1/8} \tag{B.34}$$

Here,

V_s = Volume remaining in the pool at the end of the spill, m^3

t_s = Spill duration, sec

D_s = Spill diameter at the end of the spill duration, m

A similar expression may be obtained for simultaneous spreading and burning of instantaneous releases in the absence of frictional resistance during spreading. Here the radius of the pool increases until all the material is consumed by the fire. The expressions for the maximum diameter and time to reach maximum diameter are as follows:

$$D_{max} = 1.7766 \left[\frac{V^3 \Delta}{y^2}\right]^{1/8} \tag{B.35}$$

$$t_{max} = 0.6966 \left[\frac{V}{\Delta y^2}\right]^{1/4} \quad \text{(B.36)}$$

Equations B.32, B.33 and B.34 may be used to derive the above equations by substituting the total liquid volume V in place of V_s and setting the initial diameter D_s and spill duration t_s to zero.

For liquid hydrocarbon spills on land, the spreading velocity is largely controlled by frictional resistance offered by the terrain. The maximum pool diameter and the time to reach the maximum for an instantaneous release are given by the following expressions:

$$D_{max} = 1.7982 \left[\frac{V^2}{y}\sqrt{\frac{g}{C_d}}\right]^{2/11} \quad \text{(B.37)}$$

$$t_{max} = 0.5249 \left[\frac{V^3 C_d^2}{g^2 y^7}\right]^{1/11} \quad \text{(B.38)}$$

It should be noted that an instantaneous unconfined pool fire grows in size until a barrier is reached or until all the fuel is consumed. Therefore, the maximum diameters predicted by these equations will exist only for a short duration. Use of maximum pool diameter will therefore lead to very conservative results. A time averaged pool diameter can be obtained by integrating the time dependent expressions for pool diameter or more appropriately by dividing the maximum diameter by the square root of two, this being the approach taken in **ARCHIE** .

A similar expression may be devised for a continuous spill on ground, taking frictional resistance into consideration. The equilibrium diameter is given by equation B.29. The maximum diameter and time to reach the maximum diameter are as follows:

$$D_{max} = 1.254 D_{eq} \quad \text{(B.39)}$$

$$t_{max} = 0.897 \left[\frac{D_{eq}^3 C_d}{y^2 g}\right]^{1/4} \quad \text{(B.40)}$$

Here C_d is the ground friction coefficient. It has been assigned a value of 0.5 in **ARCHIE** for general application purposes.

The criteria by which a given spill situation can be categorized as instantaneous or continuous are difficult to establish. Comparisons can be made only between the rapid release of a given volume of liquid and the release of the same volume of liquid relatively slowly. One criterion for classification is the maximum radius of the burning pool. That is, for a given situation, the maximum radii of spread are calculated using both instantaneous and continuous models, and the spill is classified into the category which gives the smaller of the two spread extents. Raj [45] indicates that a spill can be treated as instantaneous if its dimensionless time, τ, is less that 0.002:

$$\tau = \frac{t_s y}{V^{1/3}} \tag{B.41}$$

where, t_s is the spill duration.

The mean visible flame height, estimated by **ARCHIE** is based on the correlation of experimental data for laboratory-scale wooden crib fires (See Thomas [49]) which agrees well with observations of actual liquid pool fires. Based on these experimental data, Thomas developed a correlation for the mean visible flame height, H_{flame}:

$$H_{flame} = 42 D_p \left[\frac{BV\rho}{\rho_a \sqrt{g D_p}} \right]^{0.61} \tag{B.42}$$

where:

H_{flame} = Flame height, m

ρ = Liquid density, kg/m^3

ρ_a = Air density at ambient temperature, kg/m3

D_p = Pool diameter, m

g = Gravitational acceleration, 9.8 m/s^2

The emissive power of a large turbulent fire is a function of the black body emissive power and the flame emissivity. The black body emissive power, in turn, can be computed using Planck's law of radiation, if the mean radiation flame temperature is known. For incident flux calculations, however, it is more important to estimate the effective emissive power of the flame, which accounts for shielding by surrounding layers of smoke for liquid hydrocarbon fires. Based on observed values of emissive powers reported in the literature and other available data (See Huggland et al [24] and Alger et al. [2]), the effective emissive power was correlated to the normal boiling point for selected fuels by the expression:

$$E_P = -0.313\ T_B + 117 \tag{B.43}$$

where:

E_P = Effective emissive power, kW/m^2
T_B = Normal boiling point in degrees F

Materials with a boiling point above 30 degrees F typically burn with sooty flames. The emissive power from the sooty portion, based on limited data, is on the order of 20 $\frac{kW}{m^2}$. An effective sooty flame average emissive power can therefore be estimated by assigning relative areas of sooty and unshielded flame and calculating an area based average emissive power.

The incident flux at any given location is given by the equation:

$$Q_{incident} = EP \times \tau \times VF \tag{B.44}$$

where:

$Q_{incident}$ = Incident flux, kW/m^2
τ = Transmissivity
VF = Geometric view factor

τ, the transmissivity coefficient, is mainly a function of the path- length (distance from observer to flame surface), relative humidity, and the flame temperature. For the calculation scheme in **ARCHIE** , τ has been set to 1, and the attenuation of thermal flux due to atmospheric absorption is not taken into account. This assumption provides a conservative hazard estimate, since the presence of water and carbon dioxide tends to reduce the incident flux at any given location.

The view factor defines the fraction of flame that is *seen* by a given observer. This geometric term has been calculated as a function of distance from the flame center for an upright flame approximated by a cylinder. It has also been assumed that the optimum orientation between observer and flame that yields a maximum view factor prevails. The resulting equation is as follows:

$$VF = 1.143 \left[\frac{R_p}{X}\right]^{1.757} \tag{B.45}$$

where:

X = Distance from flame center, m
R_p = Pool radius, m

For fatality, the incident flux level is set to 10 kW/m2. For injury, the corresponding level is 5 kW/m2. These levels are based on analysis of numerous sources of experimental burn data (Mudan,1984). Applying these two damage criteria, the above equations were rearranged to solve for hazard distances X_{10} and X_{05} for fatality and injury, respectively:

$$X_{10} = 0.30 \frac{R_p}{0.3048} EP^{0.57} \tag{B.46}$$

$$X_{05} = 0.43 \frac{R_p}{0.3048} EP^{0.57} \tag{B.47}$$

where:

X_{10} = Radius for expected fatalities, feet

X_{05} = Radius for expected injuries, feet

B.11 Fireball Model

A large release of a liquefied hydrocarbon (e.g., propane) may burn in the form of a fireball. When this occurs, the fireball grows larger and also moves upwards continuously because of buoyancy. The thermal radiation depends on the size of the fireball, the distance to the observer (which is continuously changing), and the observer's orientation. Experimental data and observation indicate that the duration of a fireball is typically a few seconds. Therefore, the incident flux at an observer location changes rapidly with time, and as before, is dependent upon flame shape, emissive power, attenuation and view factor (See Fay et al. [17]).

Due to the transient nature of both the size and location of a fireball, the thermal radiation field also varies with time. The equations that follow define the maximum diameter and height the fireball attains in a short duration, as well as the safe separation distances for fatality and injury. Several simplifying assumptions have been made in the calculation procedure. These are summarized below:

- The fuel is propane or has similar characteristics
- Ambient temperature is 20 degrees C. (68 degrees Fahrenheit)
- Atmospheric absorption of thermal radiation is negligible
- Fraction of combustion energy radiated = 0.2
- Observer is at ground level
- Directly under the fireball, the high levels of thermal radiation would be fatal. Therefore, the minimum fatality zone is equal to half the maximum diameter calculated.

A series of experiments involving pure vapor samples of methane, ethane, and propane suggest geometric and dynamic scaling relationships for the geometry of fireballs (Fay & Lewis,1977). The first of these involve the maximum diameter, height, and duration of the fireball according to the following equations:

$$D_{max} = 16W^{1/3} \quad \text{(B.48)}$$

$$Z = 26.3W^{1/3} \quad \text{(B.49)}$$

$$T = 2.23W^{1/6} \quad \text{(B.50)}$$

where:

W = Mass in vessel, *lbs*

D_{max} = Maximum diameter of fireball, ft

Z = Maximum height of fireball, ft

T = Duration of fireball, *seconds*

Based on extensive experimental data on pigskin burns, damage criteria for fatality and injury have been established. A *Critical Energy Model* ,which assumes that the burn severity depends upon the amount of energy that is absorbed by the skin after the surface temperature reaches 55 degrees C, provides a basis for the damage criteria from fireballs. These criteria represent two levels of thermal radiation: a heat flux in excess of 160 kilojoules per square meter (kJ/m2) could be fatal for humans due to irreversible skin tissue damage. A lesser level of 40 kJ/m2 could cause pain or mild second-degree burns (Modeled, Wong and Williams, 1973). Therefore, in this calculation scheme, these two values have been used to define the safe separation downwind distances from a fireball for fatality and injury, respectively (Mudan & Desgroseilliers,1981). Simple equations were developed by numerical analysis of results from the rigorous model of fireball hazards.

The safe separation distance for fatality, XF, in feet, was found to be:

$$XF = 1.48W^{0.56} \quad W \geq 2000 \ lbs \tag{B.51}$$

$$XF = 8.0W^{0.33} \quad W < 2000 \ lbs \tag{B.52}$$

Note: The minimum fatality zone equals half the calculated fireball diameter D_{max} *,i.e. the fireball radius. This assumes that anyone directly* under *the fireball is in a fatality zone.*

For injury, the safe separation distance, XI, in feet, is:

$$XI = 4.53W^{0.52} \tag{B.53}$$

Note: For mass W less than 2000 lbs, the hazard zones are limited to the immediate vicinity of the fireball.

B.12 Flame Jet Model

The flame length expression for momentum dominated jets is based on models in the literature with correlating experimental data (See [25,28]). Flame length is proportional to the molecular weight of the fuel relative to air, and the diameter of the jet; in addition, it is inversely proportional to the lean limit concentration of the fuel.

For turbulent flame jets, the jet momentum governs the shape of the flame. In addition, the momentum-induced mixing with ambient air is very efficient and results in higher effective emissive powers for jet flames. A detailed flame jet model takes these differences into account to estimate incident fluxes at various locations.

The flame length correlation by Brzustowski (1973) for momentum- domi-

nated jets is given by the following equation:

$$\frac{F_{len}}{D_{jet}} = \frac{1050}{C_{cl}}\sqrt{\frac{M_a}{M_f}} \tag{B.54}$$

where:

F_{len} = Flame length, m

D_{jet} = jet diameter,m

C_{cl} = Lean limit concentration, $vol\%$

M_a = Molecular weight of air

M_f = Molecular weight of fuel

Some of the theoretical assumptions in this model are as follows:

- For turbulent, momentum-dominated flame jets, flame length is independent of mass flow rate.
- In order to account for both visible and non-visible portion of flame length, a concentration criterion is applied. Essentially, the end of a turbulent diffusion flame occurs at that point on the longitudinal axis where the fuel concentration equals its lean limit. In view of extensive laboratory data, this assumption appears valid.
- Effect of crosswind on flame length not included.
- The incident flux levels for observer locations at radial distances from the flame are not computed. Since the direction of the jet cannot be predicted, it is assumed that the hazards in the longitudinal (axial) direction represent the maximum distance of impact.
- The flame length is correlated against a jet pseudo-diameter for expanded turbulent jets.
- The model does not distinguish among vertical, horizontal, or inclined jet flames.

- Hazards are evaluated at the plane of the jet. For jet flames at an elevation, the height and orientation of the jet should be considered.

The thermal radiation hazards from flame jets have been estimated by characterizing the flame length as a a function of the fuel, and assuming twice the length dimension to represent the hazard zone.

The primary purpose of the model is to point out possible knock-on effects. The thermal radiation hazards to personnel are generally exceeded by potential damage to equipment which may be in the path of a flaming jet.

B.13 Vapor Cloud Fire Model

This method is applicable for a cloud or plume of flammable vapor which is released to the atmosphere and is ignited as it drifts downwind. A flame burns and propagates through the space occupied by the cloud. The hazard zone is defined by the length and width dimensions of this cloud. **ARCHIE** uses the model for toxic vapor dispersion for neutrally buoyant gases or vapors and a simplified heavy gas model for negatively buoyant gases to determine the length and width of the hazard zone. The heavy gas procedure was developed as follows:

- Using the results of a detailed heavy gas model applied to a number of pressurized releases, logarithmic plots were developed for instantaneous and steady-state releases at neutral (Pasquill D) and stable (Pasquill F) atmospheric conditions. The model was exercised for various flammable materials, such as propane, ethylene, ethane, butane, and LNG, over a wide range of release rates and quantities. The distance to the lower flammability limit (LFL) was calculated and correlated with a dimensional parameter, which is a function of the release

rate (or quantity for instantaneous spill scenarios), and selected properties of the material, such as molecular weight and LFL. The resulting correlating expressions were found to yield good approximations of the more rigorously calculated downwind hazard zones under a given set of atmospheric conditions and were incorporated into **ARCHIE** .

- All releases were assumed to occur at or near groundlevel. Elevated releases of heavy gases are assumed to fall to the ground before dispersing.
- Ambient temperature was assumed to be 20 C.
- In order to estimate the maximum crosswind dimensions of the cloud, the results of the more detailed model were again reviewed and correlated resulting in a series of rules-of-thumb that are applied under various release conditions.
- The effects of finite release duration were included in a semi-quantitative manner. Given a release rate and duration, the model assumes steady state, and computes the downwind hazard distance. The characteristic travel time of the cloud to this distance is then compared to the release duration. If the release duration is significantly larger than the characteristic travel time, then the steady state assumption is considered valid; if it is smaller, then the release is modeled as instantaneous. Where the two terms are comparable in magnitude, finite duration effects may be significant. In general, the model predicts that, for a given quantity of flammable material, a shorter release duration results in a larger hazard zone. Since an release assumption provides the largest zone, relatively short-duration releases were assumed to be instantaneous.

Readers should note that dispersion distances computed using the neutrally buoyant vapor dispersion model are generally 2 to 5 times larger

than those using the heavy gas model. Since the width of the flammable zone typically ranges from 16 to 50 % of the downwind dispersion distance, **ARCHIE** assumes 50 % of the downwind hazard as being the approximate total cloud width for neutrally buoyant gases and vapors.

B.14 Unconfined Vapor Cloud Explosion Model

The explosive effect that may be produced by the ignition of unconfined flammable vapor clouds is one of the less frequent but severe consequences of spills. Although the precise form of the vapor cloud explosion is still not fully understood (detonation vs. high speed vs. low speed deflagration), it is common practice to express the energy released as a TNT-equivalent charge, and utilize extensive overpressure data available for TNT explosions (Zabetakis [53]). This is accomplished by comparing the combustion energy per unit mass of a vapor cloud with that of TNT, and taking into account that only a fraction of the energy in the cloud will contribute to the explosion. Overpressure data compiled from measurements on TNT explosions are then used to relate overpressure to distance from the explosion. Tables B.1 and B.2 show typical damage criteria as a function of overpressure for all types of explosions.

TABLE B.1

Explosion Overpressure Damage Estimates

Overpressure* (psig)	Expected Damage
0.03	Occasional breaking of large windows already under stress.
0.04	Loud noise (143 dB); sonic boom glass failures.
0.10	Breakage of small windows under strain.
0.15	Typical pressure for glass failure.
0.30	Some damage to house ceilings; 10% window glass breakage.
0.40	Limited minor structural damage.
0.50 - 1.0	Windows usually shattered; some window frame damage.
0.7	Minor damage to house structures.
1.0	Partial Demolition of houses; made uninhabitable.
1.0 - 2.0	Corrugated metal panels fail and buckle. Housing wood panels blown in.
1.0 - 8.0	Range for slight to serious injuries due to skin lacerations from flying glass and other missiles.
1.3	Steel frame of clad building slightly distorted.
2.0	Partial collapse of walls and roofs of houses.
2.0 - 3.0	Non-reinforced concrete or cinder block walls shattered.
2.3	Lower limit of serious structural damage.
2.4 - 12.2	Range for 1-90% eardrum rupture among exposed populations.
2.5	50% destruction of home brickwork.
3.0	Steel frame building distorted and pulled away from foundation.
3.0 - 4.0	Frameless steel panel building ruined.
4.0	Cladding of light industrial buildings ruptured.
5.0	Wooded utility poles snapped.
5.0 - 7.0	Nearly complete destruction of houses.
7.0	Loaded train wagons overturned.
7.0 - 8.0	8-12 in. thick non-reinforced brick fail by shearing of flexure.
9.0	Loaded train box cars demolished.
10.0	Probable total building destruction.
15.5 - 29.0	Range for 1-99% fatalities among exposed populations due to direct blast effects.

* These are the peak pressures formed in excess of normal atmospheric pressure by blast and shock waves.

Source: Lees, F.P, Loss Prevention in the Process Industries, Vol. 1, Butterworths, London and Boston, 1980.

Equipment	Overpressure PSI																							
	0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5	5.0	5.5	6.0	6.5	7.0	7.5	8.0	8.5	9.0	9.5	10.0	12.0	14.0	16.0	18.0	20.0
Control house steel roof	A	C	D				N																		
Control house concrete roof	A	E	P	D			N																		
Cooling tower	B			F			O																		
Tank: cone roof		D				K							U												
Instrument cubicle			A			LM						T													
Fire heater				G	I					T															
Reactor: chemical				A				I					P					T							
Filter				H					F										V		T				
Regenerator						I				IP					T										
Tank: floating roof						K							U												D
Reactor: cracking							I							I							T				
Pine supports							P					SO													
Utilities: gas meter									Q																
Utilities: electric transformer									H						L					T					
Electric motor										H								I							V
Blower										Q										T					
Fractionation column											R			T											
Pressure vessel horizontal												PI						T							
Utilities: gas regulator												I								MQ					
Extraction column													I							V	T				
Steam turbine															I						M	S			V
Heat exchanger															I			T							
Tank sphere																I						I	T		
Pressure vessel: vertical																					I	T			
Pump																					I		Y		

A. Windows and guages break
B. Louvers fall at 0.3 - 0.5 psi
C. Switchgear is damaged from roof collapse
D. Roof collapses
E. Instruments are damaged
F. Inner parts are damaged
G. Brick cracks
H. Debris-missile damage occurs
I. Unit moves and pipes break
J. Bracing fails
K. Unit uplifts (half-filled)
L. Power lines are severed
M. Controls are damaged
N. Block walls fail
O. Frame collapses
P. Frame deforms
Q. Case is damaged
R. Frame cracks
S. Piping breaks
T. Unit overturns or is destroyed
U. Unit uplifts (0.9 filled)
V. Unit moves on foundations

Source: Stephens, M. M., Minimizing Damage to Refineries, U.S. Dept. of the Interior, Office of Oil & Gas, February 1970.

TABLE B.2
Explosion Overpressure Damage Estimates

The most serious limitation of the TNT-equivalent model for use in evaluating this type of scenario is that it may overestimate overpressures in the near field. TNT detonates and produces extremely high pressure shock waves at short distances with complete destruction of practically everything within the immediate area. Several actual unconfined vapor cloud incidents seem to indicate, however, that the overpressure within the near field is well below the level predicted by the TNT equivalent model. Based on these data, the Health and Safety Executive in England (HSE second report [26]), suggests that the maximum overpressure resulting from an unconfined vapor cloud explosion model be limited to 1 bar (15 psi) and this recommendation, with a minor exception, is incorporated into **ARCHIE** .

Of the total energy available for explosion, only a fraction (given by the yield factor) actually contributes to the explosive effect. The yield factor is probably the most important, yet least precisely known parameter in explosion hazard analysis. It generally ranges from 2 to 20 percent. For most aliphatic hydrocarbons, 3 percent is a commonly recommended value. For certain alkenes, approximately 6 percent has been observed. Those fuels that contain oxygen tend to have a higher explosive yields, of up to 16-18 percent. Table B.3 presents typical yield factor values for several chemicals.

TABLE B.3

Yield Factors for Explosive Vapors and Gases

Substances With Yield Factors of Y = .03	
Acetaldehyde	3-Methyl-Butene-1
Acetone	Methyl-Butyl-Ketone
Acrylonitrile	Methyl Chloride
Amyl Alcohol	Methyl-Ethyl-Ketone
Benzene	Methyl Formate
1,3-Butadiene	Methyl Mercaptan
Butene-1	Methyl-Propyl-Ketone
Carbon Monoxide	Monochlorobenzene
Cyanogen	N-Amyl Acetate
1,1-Dichloroethane	Naphthalene
1,2-Dichloroethane	N-Butane
Di-Methyl Ether	N-Butyl Acetate
Dimethyl Sulphide	N-Decane
Ethane	N-Heptane
Ethanol	N-Hexane
Ethyl Acetate	N-Pentane
Ethylamine	N-Propanol
Ethyl Benzene	N-Propyl Acetate
Ethyl Chloride	O-Dichlorobenzene
Ethyl Cyclohexane	P-Cymene
Ethyl Formate	Petroleum Ether
Ethyl Proprionate	Phthalic Anhydride
Furfural Alcohol	Propane
Hydrocyanic Acid	Proprionaldehyde
Hydrogen	Propylene
Hydrogen Sulphide	Propylene Dichloride
Iso-Butyl Alcohol	P-Xylene
Isobutylene	Styrene
Iso-Octane	Tetrafluroethylene
Iso-Propyl Alcohol	Toluene
Methalamine	Vinyl Acetate
Methane	Vinyl Chloride
Methanol	Vinylidene Chloride
Methyl Acetate	Water Gas

Substances With Yield Factors of Y = .06	
Acrolein	Ethylene
Carbon Disulphide	Ethyl Nitrite
Cyclohexane	Methyl-Vinyl-Ether
Di-Ethyl Ether	Phthalic Anhydride
Di-Vinyl Ether	Propylene Oxide

Substances With Yield Factors of Y = .19	
Acetylene	Isopropyl Nitrate
Ethylene Oxide	Methyl Acetylene
Ethyl Nitrate	Nitromethane
Hydrazine	Vinyl Acetylene

Although overpressures in the near field may be significantly overestimated, estimates of overpressure experienced in the far field are believed to be more accurate and applicable. Note that the far field region is usually of greater interest because a relatively small pressure rise is sufficient to cause failures of buildings and structures.

It should be noted that the model in **ARCHIE** does not account for unignited cloud drift. For the total explosion hazard zone, a drift factor, calculated using the vapor cloud fire model, must be added to the radial overpressure distance. This explains the note to users in Chapter 12 that the center of the equation can be anywhere within the hazard zone computed by the vapor cloud fire model for the LFL boundary.

Note that the model gives the user a choice of computing radial hazard zone distances for a free spherical air explosion (above ground) or groundlevel explosion (hemi-spherical). The distances calculated by **ARCHIE** for free air events are lesser by a factor of 1.260 than groundlevel hazard zone distances.

Selected simplifying assumptions made in the calculation procedure are:

- Ambient temperature is 20 degrees C. (68 degrees Fahrenheit)
- The mass of explosive is compared against an equivalent charge of TNT
- The effects of terrain, buildings, obstacles have not been considered.

The calculational procedure itself begins by computing the adjusted equivalent mass of TNT using the following equation:

$$m_{TNT} = \left[m_{cloud} \times \frac{\Delta H_c}{1155} \times Y_f \right] \qquad \text{(B.55)}$$

where:

m_{TNT} = TNT equivalent mass, *lbs*

ΔH_c = Lower heat of combustion, $kcal/kg$

m_{cloud} = Mass in cloud, *lbs*

Y_f = Yield factor

The distance to a given overpressure is then calculated from the equation:

$$X = m_{TNT}^{1/3} \exp\left(3.5031 - 0.7241 \ln(O_p) + 0.0398(\ln O_P)^2\right) \qquad \text{(B.56)}$$

where:

X = Distance to given overpressure, ft

O_p = Peak overpressure, *psi*

Data in Lee's [36] which provide the curve of overpressure versus scaled distance were utilized to obtain these working equations using regression analysis.

B.15 Tank Overpressurization Explosion Model

As discussed in Chapter 5, explosion hazard zones can also result from the violent rupture of an overpressurized container without combustion taking place. The energy that produces the overpressure field comes from the volume and internal pressure of the vapor space in the container. Thus, a nearly empty pressurized container of gas can be a more severe explosion hazard than a container nearly full of liquid that ruptures at the same pressure.

ARCHIE utilizes a model that assumes that the tank ruptures in manner in which the blast wave propagates omni-directionally (See Baker [3]). It assumes a ground level, hemi-spherical field and yields ground level hazard zones. If the ruptured container is elevated, calculated hazard zone distances

should be reduced by a factor of 1.26 to yield the radial hazard zone from the center of the explosion.

The computational algorithm proceeds as follows:

1. Calculate the ratio P_i/P_a where P_a is the absolute ambient pressure and P_i is the absolute internal gas pressure at which the tank is expected to rupture.

2. Compute the ratio T_i/T_a where T_a is the absolute ambient air temperature and T_i is the absolute temperature of the gas in the tank.

3. Determine the initial overpressure ratio, P_{so}, by solving the following equation by trial and error:

$$\begin{aligned} f &= 0 \\ &= \ln(P_i/P_a) - \ln(1+P_{so}) \\ &- \frac{2\gamma_i}{1-\gamma_i} \ln\left[1 - \frac{(\gamma_i - 1)P_{so}}{2\sqrt{T_i/T_a}\sqrt{\gamma_a^2 + 0.5\gamma_a(\gamma_a+1)P_{so}}}\right] \end{aligned}$$

   where, γ is the ratio of specific heat at constant pressure to that at constant volume.

4. Compute the nondimensional starting distance R_o from:

$$R_o = \frac{1}{\left[\frac{\frac{4\pi}{3}\left(\frac{P_i}{P_a}-1\right)}{\gamma_i - 1}\right]^{1/3}} \tag{B.57}$$

5. compute the value of R from:

$$R = \frac{r}{\left[\frac{V\left(\frac{P_i}{P_a}-1\right)}{\gamma_i - 1}\right]^{1/3}} \tag{B.58}$$

   where,

V = Volume of the gas in the tank

r = Distance from the center of the tank at which the side-on overpressure is desired [4].

6. Locate the point associated with P_{so} and R_o on Figure B.2. This is the starting point [5].

7. Follow the nearest curve for P_s vs. R to the R value computed in step 5. Read the P_s value associated with this R value. If the gas vessel is on the ground and/or close to a reflecting surface, increase P_s by 100 % for R less than 1 and by 10 % for R greater than 1.

8. The side-on overpressure is determined by multiplying the above resultant value of P_s by the absolute value ambient atmospheric pressure P_a.

If the volume of the gas in the bursting tank is better represented by a cylinder [6] than a sphere, adjust the above result for side-on overpressure as follows:

- For R less than 0.3, the calculated overpressure should be multiplied by a factor of 4 or 5.
- For R near 1.0, multiply the answer by a factor of 1.6.
- for R greater than about 3.5, multiply the answer by a factor of 1.4.

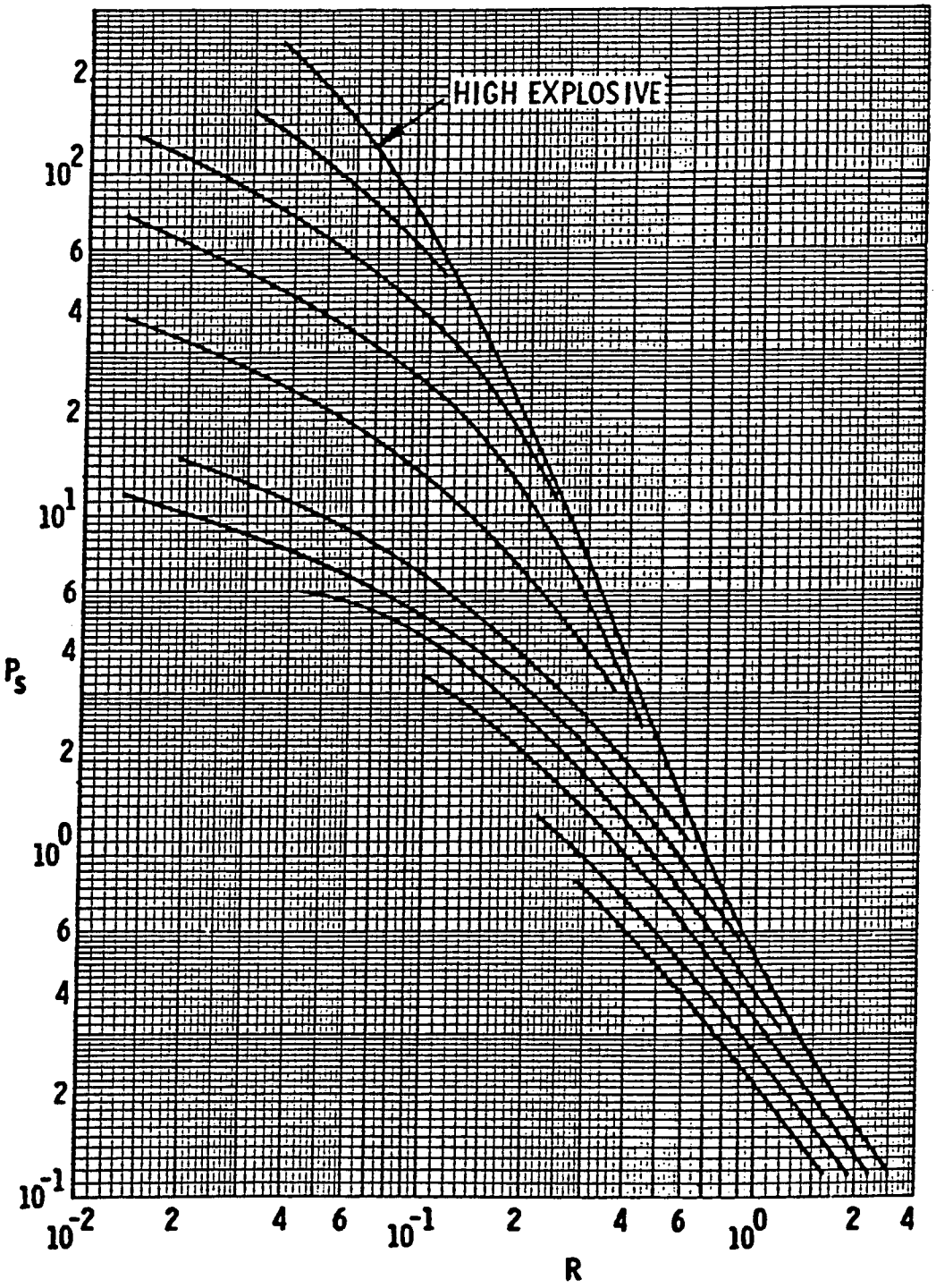
Note that the difference between spherical and cylindrical vessel bursts is only known qualitatively. Therefore, the corrections are very crude.

[4] The above equation is for gas vessel bursts far from reflecting surfaces. If the gas vessel is on ground, multiply V above by a factor of 2, as is done in **ARCHIE**

[5] **ARCHIE** uses a curve fit of this graph.

[6] Although not discussed with respect to this estimation procedure, NASA workbooks typically assume cylinders have a length to diameter ratio of 10 while spheres have a ratio of one.

Figure B.2: Ps vs. R for Overpressure Calculations. Taken from Baker



B.16 Condensed Phase Explosion Model

This model calculates the explosion hazard zones resulting from the detonation of solid or liquid explosives. This method is essentially the same as the TNT model upon which the previously described UVCE model is based. This model takes into account the difference in available combustion energy between the material of concern and TNT. Since the explosive material will also detonate, the yield factor is unity and no limit is placed on the near field overpressures.

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APPENDIX C

OVERVIEW OF "SHELTER-IN-PLACE" CONCEPTS

Introduction

There are essentially two ways to protect the public from the effects of toxic gas or vapor discharges into the atmosphere. One of these methods is evacuation and involves relocation of threatened populations to shelters in safer areas. The other involves giving instructions to people to remain inside their homes or places of business until the danger passes. In other words, it involves telling people to "shelter-in-place."

Evacuation is clearly safer with respect to the specific hazards posed by a toxic gas or vapor release but has certain limitations and may pose new problems. For example, it is fairly well appreciated that a major evacuation takes time and may not be feasible once large amounts of toxic gases or vapors have actually entered the atmosphere. Indeed, asking people in the path of a toxic cloud or plume to leave their homes may actually cause greater harm than good in some cases. Thus, large-scale evacuations in response to toxic gas or vapor hazards are best considered when:

- There is a strong potential for a toxic discharge, the discharge has not yet taken place, and there appears to be time available to relocate people.
- The discharge has taken place but people are sufficiently far downwind to permit time for evacuation.
- People not yet in the direct path of a cloud or plume are threatened by a future shift in the wind direction.
- The safety hazards of evacuation are outweighed by benefits of the action, and/or
- Telling people to shelter-in-place might not fully protect them from serious consequences.

Much has been written and said over the years pertaining to the merits and disadvantages of evacuation, but little information has been made available on sheltering-in-place, and indeed, far too many people and organizations have come to believe that sheltering-in-place will provide adequate protection to the public under a wide variety of circumstances without actually studying the issues involved. It is therefore the purpose of

this appendix to explain why staying indoors provides some degree of protection, to discuss the degree of protection that might be expected, and to discuss how best to instruct the public to shelter-in-place.

Outside Air Entry Into Buildings

If a building or other structure is airtight, i.e., like a sealed box, people inside will be completely immune from exposure to any toxic gases or vapors outside its walls. On the other hand, if walls on the upwind and downwind sides of the building are missing, these people will be exposed to the same level of contamination "indoors" as they would be if they were in the open. It is easy to understand, therefore, that the exposure of people inside a structure to toxic gases or vapors in the external environment is a function of the "airtightness" of the building and the rate at which outdoor air passes in and out.

There are essentially three main ways in which air can enter (and exit) a structure, these being:

- Natural ventilation
- Mechanical ventilation, and
- Infiltration

Natural ventilation refers to entry of outdoor air into a building through open windows or doors without assistance from fans. Obviously, the more openings in a building, the greater the rate at which outdoor air can pass through. Occupants can generally control this rate by opening and closing various windows and doors.

Mechanical ventilation refers to the use of fans and other equipment to bring air into a building, possibly heat, cool, filter, and/or recirculate it several times, and then exhaust it from the structure. This type of system is most often seen in office buildings, other commercial establishments, and factories. As above, occupants usually have considerable control over the rate of ventilation.

Infiltration is air leakage into a building through cracks and small openings around windows and doors and through floors and walls. The rate at which air enters a building by this mechanism depends on the type of building, workmanship and materials applied during construction, and the condition of the building. Infiltration differs from natural and mechanical ventilation in the sense that occupants are *generally* considered to have little effective control over its rate. The total rate at which outdoor air enters a building, for the purposes of this discussion, can be considered as being the sum of the three types of ventilation described above.

Rates of outdoor air ventilation are typically expressed in units of air changes per hour (acph), this being the number of building *volumes* of outdoor air that enter the building or other structure in the course of an hour. For example, if a building has an internal volume of 10,000 cubic feet, and 20,000 cubic feet of outdoor air enters the building each hour, its total "fresh air" ventilation rate is said to be 2.0 acph. If only 5,000 cubic feet of air enter the building in the same span of time, the rate becomes 0.5 acph.

The natural ventilation rate in structures with open windows and doors can vary widely and depends on the area of openings, the wind speed, the orientation of openings with respect to the wind direction, and the building volume. It could be as little as a fraction of 1.0 acph or as high as 80-90 acph, and possibly even more if residents do not mind a strong breeze blowing through the structure on a windy day.

Mechanical ventilation rates in office buildings and the like typically range from 4 to 12 acph with certain exceptions. During pleasant weather, 90 to 100 percent of this air might be from the outdoors. In very cold or very hot weather, building operators often have the option to reduce heating or cooling costs by lowering the fresh air entry rate to 5 to 35 percent of the mechanical ventilation rate by recirculating (reusing) large volumes of air.

There are a great many factors that influence infiltration rates in homes and other buildings. When outdoor wind velocities are very low and indoor-outdoor temperature differences are minimal, infiltration rates may be as low as 0.1 acph. The average rate in American homes, however, is on the order of 0.8-0.9 acph, and "leaky" homes may experience 2.5 acph or so, especially under poor weather conditions with high winds and low temperatures. Available data on other types of building construction are limited but suggest an average infiltration rate of about 1.0 acph for office-type buildings.

Effect of Total Outdoor Air Ventilation Rates on Indoor Exposures

The overall subject of how outdoor air pollutants can affect exposures indoors is rather complex and is best discussed using two examples; one for the case when a distinct cloud of airborne contaminants passes a building, and another for the case when the building is engulfed by a plume of vapor or gas for a prolonged period of time. The cloud is assumed to pass in a total time period of 30 minutes, while the plume is assumed to last 10 hours. Both the cloud and plume are assumed to have an average contaminant concentration of 100 ppm for the duration of their existence at any outdoor location.

Table C.1, developed from a mass balance model of indoor-outdoor pollutant relationships, presents average indoor contaminant concentrations expected for the *cloud* scenario when outdoor air ventilation rates range from 0.1 to 50 acph. Important observations are that:

TABLE C.1
INDOOR CONCENTRATIONS FOR HYPOTHETICAL CLOUD PASSAGE

	Internal Concentrations (ppm) at Various Air Change Rates (acph)								
Time (minutes)	**0.1 acph**	**0.5 acph**	**1.0 acph**	**1.5 acph**	**2.0 acph**	**2.5 acph**	**5.0 acph**	**10.0 acph**	**50.0 acph**
0	0	0	0	0	0	0	0	0	0
5	0.8	4.1	8.0	11.8	15.4	18.8	34.1	56.5	98.4
10	1.7	8.0	15.4	22.2	28.3	34.1	56.5	81.1	100
15	2.5	11.8	22.1	31.3	39.3	46.5	71.3	91.8	100
20	3.3	15.4	28.3	39.3	48.7	56.5	81.1	96.4	100
25	4.1	18.8	34.1	46.5	56.5	64.7	87.5	98.4	100
30	4.9	22.1	39.3	52.8	63.2	71.3	91.8	99.3	100
40	4.8	20.3	33.3	41.1	45.3	47.0	39.9	18.8	0
50	4.7	18.7	28.2	32.0	32.4	31.0	17.3	3.5	0
60	4.6	17.2	23.8	24.9	23.3	20.4	7.5	0.7	0
90	4.4	13.4	14.5	11.8	8.6	5.9	0.6	0	0

Note: The cloud is assumed to have an average concentration of 100 ppm outdoors. Its leading edge reaches the building at time equals zero. Its trailing edge passes the building at time equals 30 minutes, at which point internal contaminant concentrations begin to drop.

- Indoor concentrations increase steadily until the point in time that the discharge ceases and the last of the airborne contamination passes a building.

- Tight buildings or average buildings in highly favorable weather, with air change rates of 0.1 acph, are expected to experience a peak indoor contaminant concentration only 5 percent of the outdoor average after 30 minutes. Due to the lack of ventilation, however, indoor levels will drop slowly after the cloud has passed.

- "Average" homes and buildings under average conditions, with air change rates of 0.5 to 1.0 acph, may experience indoor concentrations on the order of 20-40 percent of outdoor levels after 30 minutes.

- "Leaky" buildings or average buildings exposed to severe weather conditions, with air change rates of 1.5 to 2.5 acph, may experience 45 to 65 percent of outdoor concentrations in 30 minutes.

- Buildings that have open windows or doors or mechanical ventilation systems bringing in outdoor air at high rates will experience contaminant concentrations close to those experienced outdoors.

- Peak indoor levels will be lower if the cloud passes in less than 30 minutes and higher if the cloud requires more than 30 minutes to pass.

- There are benefits to be realized by telling people to open their windows and turn on ventilation systems as soon as possible after the danger has passed. This will help "flush out" any contaminants trapped in buildings.

Table C.2 demonstrates average indoor contaminant concentrations expected while a building is exposed to a plume of vapor or gas for 10 hours. Outdoor air ventilation rates on the table again range from 0.1 to 50 acph. Important observations are that:

- Indoor concentrations increase steadily until the point in time that the discharge ceases and the last of the airborne contamination passes a building.

- Average buildings under average weather conditions, with outdoor air ventilation rates of 0.5 to 1.0 acph, will have indoor contaminant concentrations of 40 to 65 percent of those outdoors in an hour, 60 to 85 percent or so in two hours, and 75 to 95 percent in three hours. Buildings with higher rates of outdoor air entry will require less time to reach these levels.

TABLE C.2
INDOOR CONCENTRATIONS FOR HYPOTHETICAL PLUME EXPOSURE

	Internal Concentrations (ppm) at Various Air Change Rates (acph)								
Time (hours)	**0.1 acph**	**0.5 acph**	**1.0 acph**	**1.5 acph**	**2.0 acph**	**2.5 acph**	**5.0 acph**	**10.0 acph**	**50.0 acph**
0	0	0	0	0	0	0	0	0	0
1	9.5	39.3	63.2	77.7	86.5	91.8	99.3	100	100
2	18.1	63.2	86.4	97.0	98.2	99.3	100	100	100
3	25.9	77.7	95.0	98.9	99.8	99.9	100	100	100
4	33.0	86.4	98.2	99.8	100	100	100	100	100
5	39.3	91.8	99.3	99.9	100	100	100	100	100
6	45.1	95.0	99.8	100	100	100	100	100	100
7	50.3	97.0	99.9	100	100	100	100	100	100
8	55.1	98.2	100	100	100	100	100	100	100
9	59.3	98.9	100	100	100	100	100	100	100
10	63.2	99.3	100	100	100	100	100	100	100
11	57.2	60.2	36.8	22.3	13.5	8.2	0.7	0	0
12	51.7	36.5	13.5	5.0	1.8	0.7	0	0	0

Note: The plume is assumed to have an average concentration of 100 ppm outdoors. Its leading edge reaches the building at time equals zero. Its trailing edge passes the building at time equals 10 hours, at which time internal contaminant concentrations begin to drop.

- Sheltering-in-place may not make sense when discharges are expected to be prolonged and outdoor concentrations are expected to be harmful.

Recommended Shelter-In-Place Instructions

The previous sections have demonstrated the circumstances under which sheltering-in-place can provide some degree of protection from toxic gases and vapors in the atmosphere and those circumstances under which the practice may not be effective. They have also demonstrated limitations of the practice and shown how minimization of outdoor air infiltration and/or ventilation rates into buildings is critical. This section draws upon the information presented above and substantial other data to present a list of suggested instructions to be given populations asked to shelter-in-place, these being:

1. Close all doors to the outside and close and lock all windows (windows sometimes seal better when locked).

2. Building superintendents should set all ventilation systems to 100 percent recirculation so that no outside air is drawn into the structure. Where this is not possible, ventilation systems should be turned off.

3. Turn off all heating systems.

4. Turn off all air-conditioners and switch inlets to the "closed" position. Seal any gaps around window type air-conditioners with tape and plastic sheeting, wax paper, or aluminum wrap.

5. Turn off all exhaust fans in kitchens, bathrooms, and other spaces.

6. Close all fireplace dampers.

7. Close as many internal doors as possible in your home or other building.

8. Use tape and plastic food wrapping, wax paper, or aluminum wrap to cover and seal bathroom exhaust fan grilles, range vents, dryer vents, and other openings to the outside to the extent possible (including any obvious gaps around external windows and doors).

9. If the gas or vapor is soluble or even partially soluble in water -- hold a wet cloth or handkerchief over your nose and mouth if the gases start to bother you. For a higher degree of protection, go into the bathroom, close the door, and turn on the shower in a strong spray to "wash" the air. Seal any

openings to the outside of the bathroom as best as you can. Don't worry about running out of air to breathe. That is highly unlikely in normal homes and buildings.

10. If an explosion is possible outdoors -- close drapes, curtains, and shades over windows. Stay away from external windows to prevent potential injury from flying glass.

11. Minimize the use of elevators in buildings. These tend to "pump" outdoor air in and out of a building as they travel up and down.

12. Tune into the Emergency Broadcast System on your radio or television for further information and guidance.

As a final note, be advised that this appendix mostly deals with the problem of toxic gases and vapors in the atmosphere. Since these substances can pass through tiny spaces where dusts and other aerosols in air may not, sheltering-in-place may provide a much greater degree of protection when airborne contaminants are in the form of liquid or solid particles.

Technical Basis for Internal Concentration Estimates

Given the potential importance of this topic and the possible desire of emergency planning personnel and others to undertake more formal analyses of indoor/outdoor pollutant relationships in occupied structures, this subsection of the appendix presents the technical basis for the estimates shown in Tables C.1 and C.2.

Figure C.1 illustrates a structure with a forced air ventilation system. With an initial assumption that all external windows and doors to the structure have been closed, outdoor air with a contaminant concentration of C_{mu} enters the internal space via infiltration and a mechanical make-up air system (i.e., a system using one or more fans to force air into the structure to replace air supplies being exhausted to the outdoors via exhaust fans). Besides being mechanically forced out, air also exits the structure via exfiltration in a process similar but opposite to infiltration.

As is the case in most structures with forced air systems, heating and/or cooling costs are minimized by recirculating some fraction of the total internal ventilation rate through an air filter of some type before reintroduction to occupied spaces. For completeness, the illustration also shows a source of airborne contaminants within the structure itself, though the actual presence of such a source is unlikely in the case of the vast majority of hazardous materials that may be released to the external environment.

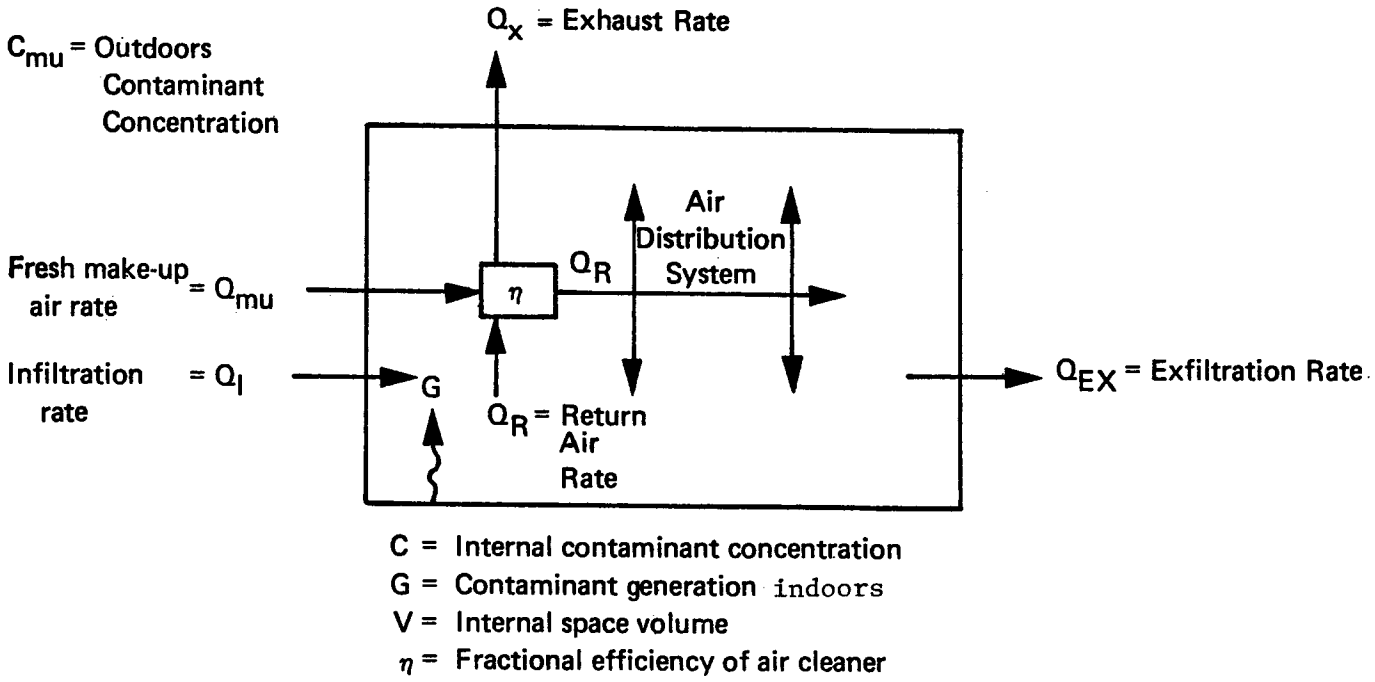

FIGURE C.1
ILLUSTRATION OF VENTILATED STRUCTURE

Table C.3 presents a formal derivation of the equation necessary to evaluate the buildup of internal contaminant concentration (C) in the structure as a function of elapsed time (t) when the structure is first exposed to contamination at time "t_o". The resulting equation is then simplified for use with structures in which forced-air ventilation systems are turned off (or never existed in the first place) in response to emergency shelter-in-place instructions from public authorities. This equation is only valid up to the instant in time that the trailing edge of the external contaminant cloud or plume passes the structure and therefore only applies while contaminant concentrations are increasing indoors. If it is desired to express the natural air infiltration rate in units of air changes per hour (acph), and this rate is simply shown as Q, the buildup phase equation becomes:

$$C = C_{\infty} [1 - \exp (-Qt)]$$

Thus, if external concentration C_{∞} equals 100 ppm, the total ventilation rate is one air change per hour, and the structure has been engulfed in a plume for one-half hour, the internal contaminant concentration can be estimated as being 39.3 ppm.

Once the trailing edge of a cloud or plume passes a structure, the external environment will be generally free of contamination, but it will take additional time for contaminants to be purged from the structure if new sources of fresh air are not introduced. Derivation of the equation for the purging phase of contamination is similar to that shown in Table C.3 until the final steps. Instead of being equated to zero, the parameter C_o is used to represent the concentration in the structure at the instant the trailing edge of the cloud or plume passes. Similarly, parameter t_o is equated to the elapsed time of this occurrence, and finally C_{∞} is set to zero. The resulting equation for the purging phase becomes:

$$C = C_o \exp [- Q (t-t_o)]$$

Thus, if the trailing edge of a plume passes a structure in an elapsed time (t_o) of one-half hour, the internal contaminant concentration (C_o) is 39.3 ppm at this time, the total ventilation rate is one air change per hour, and it desired to determine the internal concentration (C) at a total elapsed time of one hour from initial exposure of the structure, the above equation can be used to predict a concentration of 23.8 ppm.

The model is based upon several assumptions requiring explanation. These involve:

- Perfect mixing
- Use of a single compartment
- Negligible deposition or decay of contaminant
- Perfect air balance
- Constant external contaminant concentration

TABLE C.3
DERIVATION OF MODEL FOR CONTAMINANT BUILDUP PHASE IN STRUCTURES

$$Rate\ of\ Accumulation\ =\ Rate\ of\ Generation\ -\ Rate\ of\ Removal$$

$$VdC = Gdt + C_{MU}Q_I dt + C_{MU}Q_{MU}dt + (1-\eta)CQ_R dt - CQ_X dt - CQ_{EX}dt - CQ_R dt$$

$$\frac{1}{V}\int_{t_o}^{t} dt = \int_{C_o}^{C} \frac{dC}{G + C_{MU}Q_I + C_{MU}Q_{MU} + (1-\eta)CQ_R - CQ_X - CQ_{EX} - CQ_R}$$

$$\ln\left[\frac{G + C_{MU}(Q_I + Q_{MU}) + C_2(\eta Q_R + Q_X + Q_{EX})}{G + C_{MU}(Q_I + Q_{MU}) - C_o(\eta Q_R + Q_X + Q_{EX})}\right] = -\frac{\eta Q_R + Q_X + Q_{EX}}{V}(t - t_o)$$

$$Let\ \ A = G + C_{MU}(Q_I + Q_{MU})$$

$$B = \eta Q_R + Q_X + Q_{EX}$$

$$\ln\left[\frac{A - BC}{A - BC_o}\right] = -\frac{B}{V}(t - t_o)$$

$$C = \frac{A}{B}\left[1 - e^{-\frac{B}{V}(t-t_o)}\right] + C_o e^{-\frac{B}{V}(t-t_o)}$$

$$C = \frac{G + C_{MU}(Q_I + Q_{MU})}{\eta Q_R + Q_X + Q_{EX}}\left[1 - e^{-\frac{B}{V}(t-t_o)}\right]\ \ when\ \ C_o = 0$$

Note:

1. $Q_X + Q_{EX} = Q_{MU} + Q_I$ in all cases.
2. $Q_{EX} = Q_I$ when fans are turned off or are not present.
3. $G = 0$ where there are no internal contaminant sources.
4. $Q_{MU} = 0$ and $Q_R = 0$ when fans are turned off or are not present.
5. $t_o = 0$ when time (t) is measured from the instant a cloud or plume reaches the structure.
6. C_o, the internal contaminant concentration at time = 0, can be assumed to be zero when there are no internal contaminant sources. With these simplifications:

$$C = C_{MU}\left[1 - e^{\frac{-Q_I t}{V}}\right]$$

The first assumption involves the contention that all air volumes entering a specific internal area of a structure will instantly and perfectly mix with all other air volumes that occupy that area. Its use permits one to ignore details of complex interactions between air streams of differing flowrate and orientation, and force attention upon the overall average contamination level expected.

Earlier literature dealing with the dilution of airborne contaminants within an industrial setting typically suggested that actual contaminant levels at specific sites may be greater than the overall average by a factor in the range of 3 to 10. More recent work, however, has shown that the "mixing factor" is more often on the order of 2, and sometimes considerably less than 1 in typical rooms. This latter finding is completely logical and recognizes the law of mass conservation and its application to the scenarios of interest. In consequence, the assumption of perfect mixing has the following ramifications:

- It ignores the potential adverse effects of "hotspots" within a given space; and

- It ignores the potential benefits to the analysis of locations that are less contaminated than average conditions.

The assumption that the entire internal volume of a structure can be treated as a single compartment is essentially an extrapolation of the perfect mixing assumption from the boundaries of any specific room to the outer boundary of all building areas served by the same ventilation system. The advantages and disadvantages of this action are analogous to those itemized for perfect mixing.

As formulated, the model does not address the possibility that the contaminant may become deposited on exposed surface areas or somehow decay. In this respect, it may provide conservative results for reactive or particulate contaminants but underestimate exposures resulting from radioactive particles that have settled on internal surfaces (and which may pose threats unrelated only to inhalation of toxic substances). The assumption of a perfect air balance simply contends that the total volumetric rate of air entering the structure of interest is exactly equal to the rate of air leaving.

The assumption that the external contaminant concentration is a constant is most significant for short duration cloud passage, but can be mitigated by use of an average rather than peak value for C_{mu}. The assumption has little impact in the case of relatively long duration plumes of contaminants evolved at a fairly constant emission rate. Consideration of time dependent source terms and resulting transient contamination levels within a structure requires a substantially more sophisticated computational procedure, albeit one that would be based on the same fundamental principles of the model presented herein.

APPENDIX D

CHEMICAL COMPATIBILITY CHART

Introduction

Most information sources on the reactivity hazards of hazardous materials list and describe the specific consequences of combining specific chemicals. The best and most complete of these are cross-referenced compilations of reports of past mishaps which occurred during experimentation or use of specific chemicals or substances, *as reported in the general literature*. Two particularly well researched and readily available compilations were referenced in Chapter 7.

Since there are literally tens of thousands of known chemicals in commerce, and since the consequences of only a small fraction of the possible combinations of these materials have been reported upon in the general literature, none of these information sources can claim (and none do) that combinations of unlisted materials will not produce a hazardous reaction. Thus, although these information sources provide valuable guideposts for evaluating potential chemical compatibility hazards, they are inherently limited in scope, and cannot always be relied upon to provide the user with desired and/or necessary information.

To help fill gaps in available information and data with a reasonable amount of effort, a relatively little known project was undertaken by the California Department of Health Services some years ago to develop a single chemical compatibility chart which would provide its user with a *general* indication of the *typical* effects of mixing a substance from one chemical *family* with a substance from another *family*. By concentrating on the most common families of chemicals (i.e., substances with generally similar molecular structure), and by studying the effects of combining the most reactive chemicals in each family, researchers were able to produce a chart that provides an excellent tool to screen lists of chemicals (as might be found at a facility or in a transportation vehicle) for those which may pose an unusual and/or dangerous threat when inadvertently combined (as might occur during some sort of process upset, transportation accident, or mismanaged material transfer operation). Although a later brief and apparently unpublished paper provides additional information, the primary reference for the work being cited is:

- Hatayama, H.K., Chen, J.J., de Vera, E.R., Stephens, R., and Storm, D.L., ***A Method of Determining the Compatibility of Hazardous Wastes***, EPA Report No. EPA-600/2-80-076, Municipal Environmental Research Laboratory, U.S. Environmental Protection Agency, Cincinnati, Ohio, April 1980. Available as publication PB80-221005 form the National Technical Information Service, Springfield, Virginia 22161.

This appendix describes and presents the chart discussed above for use by emergency planning personnel in screening chemical substances in close proximity for potential incompatibilities. Note that the chart was developed by investigation of reactions between relatively pure chemical substances and therefore is *not* at all restricted to use for substances only considered to be hazardous wastes. Indeed, the chart is likely to be more reliable for combinations of relatively pure chemicals than for multicomponent waste streams.

A Word of Caution

Before introducing the chart and describing how it is used, it is well to first present somewhat modified and expanded versions of the warnings that its authors wished to provide all potential users, these being:

> *The chart is intended to provide an indication of **some** of the hazards that can be expected upon mixing of chemical substances. Because of the differing activities of the thousands of compounds that may be encountered, it is **not possible** to make any chart definitive and all inclusive. It cannot be assumed that members of chemical families not listed on the chart will be compatible with each other or with listed families. Although blanks on the chart generally indicate that there is no hazardous incompatibility expected between the families being considered, it cannot be guaranteed that this will always be the case. **Detailed instructions as to the hazards involved in handling and/or disposing of any given substance should be obtained from the originator of the material or other expert source of information.***
>
> *The potential reaction consequences predicted by the chart are based on pure chemical reactions only at ambient temperature and pressure. Concentration, synergistic, and antagonistic effects have been assumed not to influence the reactions. The reactions have not yet been validated on actual waste materials containing individual chemicals.*

To the above caution must be added the observation that the chart is *solely* applicable to the combination of *two* materials from different families. The addition of one or more other materials to a mixture may (or may not) produce substantially different hazards. The chart should not be used in any attempt to identify materials that may be self-reactive (i.e., capable of runaway exothermic polymerization, runaway exothermic decomposition, explosion, or other hazardous activity upon simple heating or exposure to air).

Introduction to Table D.1

Although the chemical compatibility chart is presented as Figure D.1 and directly follows this introductory text for convenience in future use, it is first necessary to discuss the concept of *Reactivity Group Numbers* (RGNs) and to introduce Table D.1.

The compatibility chart addresses 41 classes or families of chemical substances, each of which has been assigned a specific Reactivity Group Number that appears on the left and bottom margins of the chart. Each of the first 34 classes or families are listed alphabetically and are consecutively numbered one through 34. Members of each of these classes or families generally share structural similarities with other members of their class or family at the molecular level. The last seven reactivity groups are numbered 101 to 107 and are generic classes based on similarities in general behavior vis-a-vis chemical reactivity rather than similarities in chemical structure or properties.

Since the first 34 classes or families are differentiated on the basis of the presence of a particular type of molecular subgroup within the overall chemical molecule, and since the other seven classes are relatively generic in nature, it is important to realize that any given specific chemical can belong to more than one class or family. Indeed, some specific materials may belong to several, exhibiting one or more of the reactive properties of each.

To assist readers in determining the appropriate Reactivity Group Numbers (RGNs) to be assigned to any given material, Table D.1 lists a large number of common chemical substances together with their respective RGNs. The list of chemicals (including tradename materials denoted with asterisks) in the table was compiled from several sources, with lists of Hazardous Wastes and Hazardous Materials, Extremely Hazardous Wastes, and Extremely Hazardous Materials denoted in California's Industrial Waste Law of 1972 (Ref. 44) serving as a starting point. Other sources of information used to compile the list included references 1, 7, 10, 12, 13, 14, 32, 52, and 77 cited at the end of this appendix. The remaining references were used to develop the chart and are presented as a resource for those who wish to further investigate the reactivity of various substances.

Introduction and Use of the Chemical Compatibility Chart

As noted above, the actual chemical compatibility chart is presented in Figure D.1 that directly follows this introductory text. The first column of the chart lists the RGNs and is followed by a second column providing the respective names of the reactivity groups (i.e., the various classes and families of chemical substances). The RGNs are repeated on both the top and bottom of each page of the chart (which could not be placed on one page while maintaining readability) to facilitate finding of the specific square containing either a blank or the *Reactivity Codes* (RCs) for specific combinations of classes or families.

Reactivity Codes (RCs) are abbreviations for the various hazardous phenomena expected to occur when two materials are combined and are defined on the second page of the chart. They include letters or combinations of letters such as:

- H to indicate heat may be evolved.
- F to indicate potential for fire.
- E to indicate potential for an explosion.
- P to indicate potential for violent polymerization.
- GT to indicate potential evolution of toxic gases.
- GF to indicate potential evolution of flammable gases.
- G to indicate potential evolution of innocuous gases.
- S to indicate solubilization of toxic substances.
- U to indicate an unknown but potentially hazardous reaction.

Where more than one code appears in a square, the one on the left (and generally the highest) indicates the primary consequence of the combination, the next to the right indicates the potential secondary effect, and so forth. The appearance of both GT and GF do not necessarily mean that two different gases will evolve, since any of a number of gases may be *both* flammable and toxic. (Note: As a precaution, it is well to treat the presence of a G in a square with a grain of salt. Until the gas is identified, treat it at least as being toxic. The chart is good, but not necessarily perfect.)

Follow the instructions presented below to find the Reactivity Codes (RCs) for the desired combination of two chemicals. Assume for the moment that each chemical has only one RGN, but realize that the procedure may have to be repeated several times for substances with multiple RGNs, once for each valid combination of RGNs.

Step 1: Using a knowledge of chemistry or the list of chemicals in Table D.1, determine the Reactivity Group Number (RGN) appropriate for each of the two chemical substances of concern. If a specific chemical is not found in the table, look for one with similar characteristics and molecular groups (usually indicated -- but not always -- by similar name fragments).

Step 2: For the first chemical, find its RGN on the first column of the chart.

Step 3: Find the RGN of the second chemical on the bottom row of the chart.

Step 4: Find the intersecting square for the two RGNs. For example, the intersection of RGN 101 with RGN 2 has reaction codes of H plus F plus GT in the correct square. The intersection of RGN 21 and RGN 20 has reaction codes of GF and H in the correct square.

Step 5: Note the Reaction Codes (RCs) in the square and refer to the chart legend for their definition.

Step 6: If no RCs are in the square (i.e., the square is blank), the combination is generally considered to be safe, keeping in mind the cautions presented earlier.

FIGURE D.1
COMPATIBILITY CHART

Reactivity Group No.	REACTIVITY GROUP NAME										
1	Acids Mineral Non-oxidizing	1									
2	Acids Mineral Oxidizing		2								
3	Acids Organic		G H	3							
4	Alcohols and Glycols	H	H F	H P	4						
5	Aldehydes	H P	H F	H P		5					
6	Amides	H	H GI				6				
7	Amines, Aliphatic and Aromatic	H	H GT	H		H		7			
8	Azo Compounds, Diazo Compounds, and Hydrazines	H G	H GT	H G	H G	H			8		
9	Carbamates	H G	H GT						G H	9	
10	Caustics	H	H	H		H				H G	10
11	Cyanides	GT GF	GT GF	GT GF					G		
12	Dithiocaramates	H GF F	H GH F	H GF GT		GF GT		U	H G		
13	Esters	H	H F						H G		H
14	Ethers	H	H F								
15	Fluorides, Inorganic	GT	GT	GT							
16	Hydrocarbons, Aromatic		H F								
17	Halogenated Organics	H GT	H F GT					H GT	H G		H GF
18	Isocyanates	H G	H F GT	H G	H P			H P	H G		H P G
19	Ketones	H	H F						H G		H
20	Mercaptans and Other Organic Sulfides	GT GF	H F GT						H G		
21	Metals, Alkali and Alkaline Earth, Elemental	GF H F	GF H F	GF H F	GF H F	GF H F	GF H	GF H	GF H	GF H	GF H
22	Metals, Other Elemental & Alloys as Powders, Vapors, or Sponges	GF H F	GF H F	GF					H E GT	U	GF H
23	Metals, Other Elemental & Alloys as Sheets, Rod, Drops, Moldings etc.	GF H F	GF H F						H F G		
24	Metals and Metal Compounds, Toxic	S	S	S			S	S			S
25	Nitrides	GF H F	H F F	H GF	GF H F	GF H F			U	H G	U
26	Nitriles	H GT GF	H F GF	H							U
27	Nitro Compounds, Organic		H F GT			H					H E
28	Hydrocarbons, Aliphatic, Unsaturated	H	H F			H					
29	Hydrocarbons, Aliphatic, Saturated		H F								
30	Peroxides and Hydroperoxides, Organic	H G	H E		H F	H G		H GT	H F E	H F GT	
31	Phenols and Cresols	H	H F						H G		
32	Organophosphates, Phosphothioates, Phosphodithioates	H GT	H GT						U	H E	
33	Sulfides, Inorganic	GT GF	HF GT	GT		H			E		
34	Epoxides	H P	H P	H P	H P	U		H P	H P		H P
101	Combustible and Flammable Materials, Miscellaneous	H G	H F GT								
102	Explosives	H E	H E	H E					H E		H E
103	Polymeriable Compounds	P H	P H	P H					P H		P H
104	Oxidizing Agents, Strong	H GT		H GT	H F	H F	H F GT	H F GT	H E	H F GT	
105	Reducing Agents, Strong	H GF	H F GT	H GF	H GF F	H F	GF H	H GF	H G		
106	Water and Mixtures Containing Water	H	H						G		
107	Water Reactive Substances	EXTREMELY REACTIVE									
		1	2	3	4	5	6	7	8	9	10

Reactivity Group No.															
11	11														
12		12													
13			13												
14				14											
15					15										
16						16									
17	H						17								
18	H G	U						18							
19	H								19						
20							H	H	H	20					
21	GR H	GF GT H	GR H				H E	GR H	GF H	GF H	21				
22							H E	GR H		H GF F		22			
23							H F						23		
24														24	
25	GR H	GR H	GF H				GR H	U	GF H	GF H	E				25
26											H P			S	GR H
27											H GF E				H GF F
28												H E			
29															
30	H E GT	H E GT					H E	H	E	H E GT	H E	H H		H G	H GF F
31								H P			GF H				GF H
32											H				
33								H							
34	H P	U								H P	H P	H P		H P	H P
101											H G F				H GF F
102			H E								H E	H E	H E	E	E
103	P H	U									P H	P H	P H	P H	P H
104	H F GT	H F GT	H F	H F		H F	H GT	H F GT	H F	H F GT	H F E	H F E	H F		H F E
105		H GT	H F				H E	GF H	GF H	GF H					
106								H G			GF H	GF H		S	GF H
107	DO NOT MIX WITH ANY CHEMICAL OR WASTE MATERIAL														
	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25

Reactivity Code	Consequences
H	Heat generation by chemical reaction
F	Fire from extremely exothermic reaction, ignition of reaction products or mixtures
G	Innocuous and non-flammable gas generation such as N_2, CO_2, etc. causes pressurization and rupture of closed containers
GT	Toxic gas generation
GF	Flammable gas generation
E	Explosion due to extremely vigorous reaction or reactions produce enough heat to detonate unstable reactants or reactions products
P	Violet polymerization with extreme heat and sometimes toxic and flammable gases
S	Solubilization of toxic substances including metals
U	May be hazardous but unknown

Example:

H

F Heat generation, fire, and toxic gas generation

GT

Reactivity Group No.	26	27	28	29	30	31	32	33	34	101	102	103	104	105	106	107
26	26															
27		27														
28			28													
29				29												
30	$H\ P_{GT}$		$H\ P$		30											
31					H	31										
32					U		32									
33					H_{GT}			33								
34					$H\ P$	$H\ P$	U	$H\ P$	34							
101					$H\ F_{GT}$					101						
102					$H\ E$	$H\ E$		$H\ E$	$H\ E$	$H\ E$	102					
103					$P\ H$	$P\ H$		$P\ H$			$H\ E$	103				
104	$H\ F_{GT}$	$H\ E$	$H\ E$	$H\ E$	$H\ G$	$H\ E$	$H\ F_{GT}$	$H\ F_{GT}$	$H\ F_G$	$H\ F_G$	$H\ E$	$H\ F_{GT}$	104			
105	H_{GF}	$H\ E$			$H\ E$	GF_H	GT_{GF_H}		H	GF_H	$H\ E$	$H\ P_{GP}$	$H\ P_E$	105		
106								GT_{GF}						GF_{GT}	106	
107	EXTREMELY REACTIVE															107
	26	27	28	29	30	31	32	33	34	101	102	103	104	105	106	107

RGN'S FOR SELECTED MATERIALS

Names	RGN
Abate*	32
Acenaphthene	16
Acetamide	6
Acetaldehyde	5
Acetic acid	3
Acetic anhydride	107
Acetone	19
Acetone cyanohydrin	4, 26
Acetonitrile	26
Acetophenone	19
Acetoxybutane	13
Acetoxypentane	13
Acetyl acetone	19
Acetyl azide	102
Acetyl benzoyl peroxide	30
Acetyl bromide	17, 107
Acetyl chloride	17, 107
Acetylene	28
Acetyl nitrate	27, 102
Acetyl peroxide	30
Acrolein	5, 103
Acrylic acid	3, 103
Acrylonitrile	26, 103
Adipic acid	3
Adiponitrile	26
Agallol	24
Agaloaretan	24
Aldicarb	9, 20
Aldrin	17
Alkyl aluminum chloride	107
Alkyl resins	101
Allene	28
Allyl alcohol	4
Allyl bromide	17
Allyl chloride	17
Allyl chlorocarbonate	13, 17
Allyl chloroformate	13, 17
Allyl trichlorosilane	107
Aluminum	22, 23
Aluminum aminoborohydride	107
Aluminum borohydride	105, 107
Aluminum bromide	107
Aluminum carbide	105

Names	RGN
Aluminum chloride	107
Aluminum diethyl monochloride	105, 107
Aluminum fluoride	15, 107
Aluminum hydride	105
Aluminum hypophosphide	107
Aluminum phosphide	107
Aluminum tetraazidoborate	8
Aminobenzene	7
Aminobutane	7
Aminochlorotoluene	7, 17
Aminodiphenyl	7
Aminoethane	7
Aminoethanol	4, 7
Aminoethanolamine	7
Aminohexane	7
Aminomethane	7
Aminopentane	7
Aminophenol	7, 31
Aminopropane	7
Amino propionitrile	7, 26
Aminothiazole	7, 8
Aminotoluene	7
Ammonia	10
Ammonium arsenate	24
Ammonium azide	102
Ammonium bifluoride	15
Ammonium chlorate	102, 104
Ammonium dichromate	24, 102
Ammonium fluoride	15
Ammonium hexanitrocobaltate	24, 102
Ammonium hydroxide	10
Ammonium hypophosphide	105
Ammonium molybdate	24
Ammonium nitrate	102
Ammonium nitridoosmate	24, 104
Ammonium nitrite	102
Ammonium perchlorate	104
Ammonium periodate	102, 104
Ammonium permanganate	24, 102, 104
Ammonium persulfate	104
Ammonium picrate	102
Ammonium sulfide	33, 105
Ammonium tetrachromate	24, 104

FIGURE B.2 (Cont.)

RGN'S FOR SELECTED MATERIALS

Names	RGN
Ammonium tetraperoxychromate	24, 102, 104
Ammonium trichromate	24, 104
Amyl acetate	13
Amyl alcohol	4
Amyl chloride	17
Amyl cyanide	26
Amylamine	7
Amylene	28
Amyl mercaptan	20
Aniline	7
Animert* V-101	20
Anisole	14
Anisole chloride	107
Anthracene	16
Antimony	23, 24
Antimony chloride	24, 107
Antimony fluoride	24, 107
Antimony nitride	24, 25
Antimony oxychloride	24
Antimony oxide	24
Antimony pentachloride	24
Antimony pentafluoride	24
Antimony pentasulfide	24, 33, 105
Antimony perchlorate	24, 104
Antimony potassium tartrate	24
Antimony sulfate	24
Antimony sulfide	24, 33, 105
Antimony tribromide	24, 107
Antimony trichloride	24, 107
Antimony trifluoride	24, 107
Antimony triiodide	24, 107
Antimony trioxide	24
Antimony trisulfate	24
Antimony trisulfide	24, 33
Antimony trivinyl	24, 107
Aqualin	5, 103
Aqueous solutions & mixtures	106
Aretan*	24
Aroclor*	17
Arsenic	24
Arsenic bromide	24, 107
Arsenic chloride	24, 107
Arsenic dislufide	24, 33, 105

Names	RGN
Arsenic iodide	24, 107
Arsenic oxide	24
Arsenic pentaselenide	24
Arsenic pentasulfide	24, 33
Arsenic pentoxide	24
Arsenic sulfide	24, 33, 105
Arsenic tribromide	24, 107
Arsenic trichloride	24, 107
Arsenic trifluoride	24
Arsenic triiodide	24, 107
Arsenic trisulfide	24, 33, 105
Arsine	24, 105
Askarel	17
Asphalt	101
Azidocarbonyl guanidine	8, 102
Azido-s-triazole	8
Azinphos ethyl	32
Aziridine	7, 103
a,a-Azodiisobutyronitrile	8, 26
Azodrin*	32
Bakelite*	101
Banol	9
Barium	21, 24, 107
Barium azide	24, 102
Barium bromate	24, 104
Barium carbide	24, 105, 107
Barium chlorate	24, 104
Barium chloride	24
Barium chromate	24, 104
Barium fluoride	15, 24
Barium fluosilicate	24
Barium hydride	24, 105
Barium hydroxide	10, 24
Barium hypophosphide	24, 105
Barium iodate	24, 104
Barium iodide	24
Barium monoxide	10, 24, 107
Barium nitrate	24, 104
Barium oxide	10, 24, 107
Barium perchlorate	24, 104
Barium permanganate	24, 104
Barium peroxide	24, 104
Barium phosphate	24

RGN'S FOR SELECTED MATERIALS

Names	RGN
Barium stearate	24
Barium sulfide	24, 33, 105, 107
Barium sulfite	24
Bassa*	9
Bayer 25141	32
Baygon*	9
Benzadox	6
Benzal bromide	17
Benzal chloride	17
Benzaldehyde	5
Benz-a-pyrene	16
Benzene	16
Benzene diazonium chloride	8, 102
Benzene phosphorus dichloride	107
Benzidine	7
Benzoic acid	3
Benzonitrile	26
Benzophenone	19
Benzoquinone	19
Benzotriazole	8, 102
Benzotribromide	17
Benzotrichloride	17
Benzotrifluoride	17
Benzoyl chloride	107
Benzoyl peroxide	30, 102
Benzyl alcohol	4
Benzylamine	7
Benzyl benzene	16
Benzyl bromide	17
Benzyl chloride	17
Benzyl chlorocarbonate	17
Benzyl chloroformate	17
Benzyl silane	105, 107
Benzyl sodium	105
Beryllium	24
Beryllium copper alloy	24
Beryllium fluoride	15, 24
Beryllium hydride	24, 105, 107
Beryllium hydroxide	10, 24
Beryllium oxide	24
Beryllium sulfide	33, 105
Beryllium tetrahydroborate	24, 105, 107
Bidrin*	32

Names	RGN
Bismuth	22, 23, 24
Bismuth chromate	24
Bismuthic acid	24
Bismuth nitride	24, 25, 102
Bismuth pentafluoride	24, 107
Bismuth pentaoxide	24
Bismuth sulfide	24, 33, 105
Bismuth tribromide	24
Bismuth trichloride	24
Bismuth triiodide	24
Bismuth trioxide	24
Bismuth trisulfide	24, 33, 105
Blada-fum*	32
Blue vitriol	24
Bomyl	32
Borane	24, 107
Bordeaux arsenites	24
Boric acid	1
Boron arsenotribromide	24, 105
Boron bromodiiodide	24, 107
Boron dibromoiodide	24, 107
Boron nitride	24, 25
Boron phosphide	24, 107
Boron triazide	24, 10[illegible]
Boron tribromide	24, 107
Boron trichloride	24, 107
Boron trifluoride	24, 107
Boron triiodide	24, 107
Boron trisulfide	24, 33, 105
BPMC	9
Brass	23
Bromic acid	2
Bromine	104
Bromine azide	102
Bromine cyanide	11
Bromine monofluoride	104, 107
Bromine pentafluoride	104, 107
Bromine trifluoride	104, 107
Bromoacetylene	17
Bromobenzoyl acetanilide	6, 19
Bromobenzyl trifluoride	17
Bromodiborane	105
Bromodiethylaluminum	107

FIGURE D.2 (Cont.)
RGN'S FOR SELECTED MATERIALS

Names	RGN
Bromodimethoxyaniline	14
Bromoform	17
Bromomethane	17
Bromophenol	17, 31
Bromopropene	17
Bromopropyne	17
Bromosilane	105
Bromotoluene	17
Bromotrichloromethane	17
Bromotrifluomethane	17
Bromoxynil	17, 26, 31
Bronze	23
Buna-N*	101
Bunker fuel oil	101
Butacarb	9
Butadiene	28, 103
Butadiyne	28
Butanal	5
Butane	29
Butanediol	4
Butanethiol	20
Butanetriol trinitrate	102
Butanol	4
Butanone	19
Butenal	5
Butene	28
Butene-2-one	19
Butyl acetate	13
n-Butyl acrylate	13, 103
Butylamine	7
Butyl alcohol	4
t-Butyl azidoformate	8
Butyl benzene	16
Butyl benzyl phthalate	13
Butyl cellusolve*	4
Butyl dichloroborane	105
Butyl ether	14
Butyl formate	13
Butyl fluoride	17
Butyl glycidyl ether	34
Butyl hydroperoxide	30
t-Butyl hypochlorite	102, 104
n-Butyl lithium	105, 107

Names	RGN
Butyl mercaptan	20
Butyl peroxide	30
Butyl peroxyacetate	30
Butyl peroxybenzoate	30
Butyl peroxypivalate	30
t-Butyl perbenzoate	30
t-Butyl-3-phenyl oxazirane	34
Butyl trichlorosilane	107
Butyramide	6
Butyraldehyde	5
Butyric acid	3
Butyronitrile	26
Bux*	9
Cacodylic acid	24
Cadmium	23, 24
Cadmium acetylide	24, 105, 107
Cadmium amide	24, 10, 107
Cadmium azide	24, 102
Cadmium bromide	24
Cadmium chlorate	24, 104
Cadmium chloride	24
Cadmium cyanide	11, 24
Cadmium fluoride	15, 24
Cadmium hexamine chlorate	24, 102
Cadmium hexamine perchlorate	24, 102
Cadmium iodide	24
Cadmium nitrate	24, 102, 104
Cadmium nitride	24, 25, 102
Cadmium oxide	24
Cadmium phosphate	24
Cadmium sulfide	24, 33, 105
Cadmium trihydrazine chlorate	24, 102
Cadmium trihydrazine perchlorate	24, 104
Calcium	24, 102
Calcium arsenate	24
Calcium arsenite	24
Calcium bromate	104
Calcium carbide	105, 107
Calcium chlorate	104
Calcium chlorite	104
Calcium fluoride	15
Calcium hexammoniate	105
Calcium hydride	105, 107

FIGURE D.2 (Cont.)
RGN'S FOR SELECTED MATERIALS

Names	RGN
Calcium hydroxide	10
Calcium hypochlorite	104
Calcium hypophosphide	105
Calcium iodate	104
Calcium-manganese-silicon alloy	23
Calcium nitrate	104
Calcium oxide	10, 107
Calcium oxychloride	104
Calcium perchromate	104
Calcium permanganate	104
Calcium peroxide	104
Calcium phosphide	107
Calcium sulfide	33, 105
Camphor oil	101
Capric acid	3
Caproic acid	3
Caprylic acid	3
Caprylyl peroxide	30
Carbacrol	31
Carbaryl	9
Carbetamide	6
Carbanolate	9
Carbofuran	9
Carbolic acid	31
Carbolic oil	31
Carbon, activated, spent	101
Carbon bisulfide	20
Carbon disulfide	20
Carbon tetrachloride	17
Carbon tetrafluoride	17
Carbon tetraiodide	17
Castrix	7
Catechol	31
Caustic potash	10
Caustic soda	10
CDEC	12
Cellulose	101
Cellulose nitrate	27, 102
Cerium	22
Cerium hydride	105
Cerium trisulfide	33, 105
Cerous phosphide	105
Cesium	21

Names	RGN
Cesium amide	107
Cesium azide	102
Cesium carbide	105
Cesium fluoride	15
Cesium hexahydroaluminate	105
Cesium hydride	105, 107
Cesium phosphide	107
Cesium sulfide	33, 105
Chloral hydrate	5
Chlordane	17
Chlorestol	17
Chlorfenvinphos	32
Chloric acid	2, 104
Chlorine	104
Chlorine azide	102
Chlorine dioxide	102, 104, 107
Chlorine fluoroxide	102, 104
Chlorine monofluoride	104, 107
Chlorine monoxide	104
Chlorine pentafluoride	104, 107
Chlorine trifluoride	104, 107
Chlorine trioxide	102, 104
Chloroacetaldehyde	5, 17
Chloroacetic acid	3, 17
Chloroacetone	17, 19
Chloroacetophenone	17, 19
Chloroacetyl chloride	107
Chloroacetylene	102
Chloroacrylonitrile	17, 26
Chloroazodin	8, 17
Chlorobenzene	17
Chlorobenzotriazole	8, 17
Chlorobenzoyl peroxide	17, 30
Chlorobenzylidene malononitrile	17, 26
Chlorobutyronitrile	17, 26
Chloro chromic anhydride	24, 104, 107
Chlorocreosol	17, 31
Chlorodiborane	105
Chlorodiisobutyl aluminum	105, 107
Chlorodimethylamine diborane	105
Chlorodinitrobenzene	17, 27
Chloro dinitrotoluene	17, 27
Chlorodipropyl borane	105

FIGURE D.2 (Cont.)
RGN'S FOR SELECTED MATERIALS

Names	RGN
Chloroethane	17
Chloroethanol	4, 7
Chloroethylenimine	17
Chloroform	17
Chlorohydrin	17
Chloromethane	17
Chloromethyl methyl ether	17
Chloromethyl phenoxyacetic acid	3, 17
Chloronitroaniline	17, 27
Chloronitrobenzene	17, 27
Chloropentane	17
Chlorophenol	31
Chlorophenyl isocyanate	17, 18, 107
Chloropicrin	17, 27, 102
Chloropropane	17
Chloropropene	17
Chloropropylene oxide	17, 34
Chlorosilane	105
Chlorosulfonic acid	1
Chlorothion*	17, 32
Chlorotoluene	17
Chlorotoluidine	7, 17
Chlorotrinitrobenzene	17, 27, 102
B-Chlorovinyldichloroarsine	24
Chlorpicrin	17, 27, 102
Chromic acid	2, 24, 104
Chromic anyhdride	2, 24, 104
Chromic chloride	24
Chromic fluoride	15, 24
Chromic oxide	24
Chromic sulfate	24
Chromium	23, 24
Chromium sulfate	24
Chromic sulfide	24, 33, 105
Chromium trichloride	24
Chromium trifluoride	15, 24
Chromium trioxide	2, 24, 104
Chromyl chloride	24, 104, 107
Chrysene	16
CMME	14, 17
Coal oil	101
Coal tar	31
Cobalt	22, 23, 24

Names	RGN
Cobalt bromide	24
Cobalt chloride	24
Cobalt nitrate	24, 104
Cobaltous bromide	24
Cobaltous chloride	24
Cobaltous nitrite	24, 104
Coibaltous resinate	24
Cobaltous sulfate	24
Cobalt resinate	24
Cobalt sulfate	24
Collodion	27
Copper	23, 24
Copper acetoarsenite	24
Copper acetylide	24, 102, 105, 107
Copper arsenate	24
Copper arsenite	24
Copper chloride	24
Copper chlorotetrazole	24
Copper cyanide	11, 24
Copper nitrate	24, 104
Copper nitride	24, 25
Copper sulfate	24
Copper sulfide	24, 33, 105
Compound 1836	17, 32
Coroxon*	32
Coumafuryl	19
Coumatetralyl	19
Cresol	31
Cresol glydicyl ether	34
Cresote	31
Crimidine	7
Crotonaldehyde	5
Crotyl alcohol	4
Crotyl bromide	17
Crotyl chloride	17
Cumene	16
Cumene hydroperoxide	30
Cupric arsenate	24
Cupric arsenite	24
Cupric chloride	24
Cupric cyanide	11, 24
Cupric nitrate	24, 104
Cupric sulfate	24

FIGURE D.2 (Cont.)
RGN'S FOR SELECTED MATERIALS

Names	RGN
Cupriethylenediamine	7, 24
Cyanoacetic acid	3, 26
Cyanochloropentane	17, 26
Cyanogen	26
Cyanogen bromide	11
Cyanophenphos	26, 32
Cyanuric triazide	102
Cycloheptane	29
Cyclohexane	29
Cyclohexanol	4
Cyclohexanone	19
Cyclohexanone peroxide	30
Cyclohexylamine	7
Cyclohexenyl trichlorosilane	107
Cyclohexyl phenol	31
Cyclohexyl trichlorosilane	107
Cyclopentane	29
Cyclopentanol	4
Cyclopentene	28
Cyclopropane	29
Cyclotrimethylene trinitraamine	27, 102
Cymene	16
Cyolan*	20, 32
2,4-D	3, 17
Dasanit*	32
DBCP	17
DCB	17
DDD	17
DDNP	8, 27, 102
DDT	17
DDVP	17, 32
DEAC	105, 107
Decaborane	107
Decahydronaphthalene	29
Decalin	29
Decane	29
Decanol	4
Decene	28
Decyl benzene	16
Delnav*	32
Demeton-s-methyl sulfoxid	32
Diacetone alcohol	4, 19
Diacetyl	19

Names	RGN
Diacetylene	28
Diamine	8, 105
Diaminobenzene	7
Diaminohexane	7
Diazidoethane	8, 102
Diazinon*	32
Diazodinitrophenol	27, 102
Dibenzoyl peroxide	30, 102
Diborane	105, 107
Diboron hexahydride	105, 107
Dibutyl ether	14
Dibutyl phthalate	13
3,5-Dibromo-4-hydroxybenzonitrile	17, 26, 31
Dibromochloropropane	17
Dibromoethane	17
Dichloroacetone	17, 19
Dichloroamine	104
Dichlororobenzene	17
Dichlorobenzidine	7, 17
Dichlorodimethylsilane	107
Dichloroethane	17
Dichloroethene	17
Dichloroether	14, 17
Dichloroethylarsine	24, 107
Ethyl dichlorosilane	107
Ethyl ether	14, 17
Dichloroisocyanuric acid	104
Dichloromethane	17
Dichlorophene	17
Dichlorophenol	17, 31
Dichlorophenoxyacetic acid	3, 17
Dichloropropane	17
Dichloropropanol	4, 17
Dichloropropene	17
Dichloropropylene	17
Dichloro-s-triazine-2,4,5-trione	104
Dichlorovos	17, 32
Dicumyl peroxide	30
Dicyclopentadiene	28
Dieldrin	17
Diethanolamine	4, 7
Diethyl aluminum chloride	105, 107
Diethylamine	7

FIGURE D.2 (Cont.)
RGN'S FOR SELECTED MATERIALS

Names	RGN
Diethyl benzene	16
Diethyl chlorovinyl phosphate	17, 32
Diethyl dichlorosilane	107
Diethylene dioxide	14
Diethylene glycol dinitrate	27, 102
Diethylene glycol monobutyl ether acetate	13
Diethylene triamine	7
Diethyl ether	14
Diethyl ketone	19
Diethyltoluamide	6
Diethyl zinc	24, 105, 107
Diesel oil	101
Difluorophosphoric acid	1
Diglycidyl ether	34
Diisobutylene	28
Diisobutyl ketone	19
Diisopropanolamine	4, 17
Diisopropylbenzene hydroperoxide	30
Diisopropyl beryllium	24, 104, 107
Diisopropyl ether	14
Diisopropyl peroxydicarbonate	30
Dimecron*	32
Dimefox	6, 32
Dimethyl acetylene	28
Dimethyl amine	7
Dimethylamino azobenzene	7, 8
Dimethyl arsenic acid	24
Dimethyibenzyl hydroperoxide	30
Dimethyl butane	29
Dimethyl butyne	28
Dimethyl dichlorosilane	107
Dimethyldithiophosphoric acid	32
Dimethyl ether	14
Dimethyl formal	19
Dimethyl formamide	6
Dimethylhexane dihydroperoxide	30
Dimethyl hydrazine	8
Dimethyl ketone	19
Dimethyl magnesium	105, 107
Dimethylnitrobenzene	27
Dimethylnitrosoamine	7, 27
Dimethyl sulfide	20
Dimeton	32

Names	RGN
Dinitrobenzene	27
Dinitrochlorobenzene	17, 27
2,4-Dinitro-6-sec-butyl phenol	27, 31
Dinitrocresol	27, 31
Dinitrophenol	27, 31
Dinitrophenyl hydrazine	8, 27
Dinitrotoluene	27
Dinoseb	27, 31
Dioxacarb	9
Dioxane	14
Dioxathion	32
Dipentaerythritol hexanitrate	27, 102
Dipentene	28
Diphenamide	6
Diphenyl	16
Diphenyl acetylene	16
Diphenylamine	7
Diphenylamine chloroarsine	7, 24
Diphenyl ethane	16
Diphenyl ethylene	16
Diphenyl methane	16
Diphenylmethane diisocyanate	18, 107
Diphenyl oxide	14
Dipicryl amine	7, 27, 102
Dipropyl amine	7
Disulfoton	32
Disulfuric acid	1
Disulfur dinitride	25, 102
Disulfuryl chloride	107
Disyston*	32
Dithane* M-45	12
Dithione*	32
DNOC	27, 31
Dodecene	28
Dodecyl benzene	16
Dodecyl trichlorosilane	107
Dowco-139*	9
Dowicide I	31
Dowtherm	16
Durene	16
Dyfonate*	32
Dynes Thinner	101
Elgetol 30	27, 31

FIGURE D.2 (Cont.)

RGN'S FOR SELECTED MATERIALS

Names	RGN
Endolsulfan	17, 20
Endothall	3
Endothion	32
Endrin	17
EPN	32
Epichlorohydrin	17, 34
Epoxybutane	34
Epoxybutene	34
Epoxyethane	34, 103
Epoxyethylbenzene	34
Bis(2-3-Epoxypropyl) ether	34
Ethane	29
Ethanethiol	20
Ethanol	4
Ethion*	32
Ethoxyethanol	4, 14
Ethyl acetate	13
Ethyl acetylene	28
Ethylacrylate	13, 103
Ethyl alcohol	4
Ethylamine	7
Ethyl benzene	16
Ethyl butanoate	13
Ethyl butyrate	13
Ethyl chloride	17
Ethyl chloroformate	13, 17
Ethyl dichloroarsine	24, 107
Ethyl dichlorosilane	107
Ethyl ether	14
Ethylene	28
Ethylene chromic oxide	24, 104
ethylene chlorohydrin	4, 17
Ethylene cyanohydrin	4, 26
Ethylene diamine	7
Ethylene dibromide	17
Ethylene dichloride	17
Ethylene glycol	4
Ethylene glycol dinitrate	27, 102
Ethylene glycolmonomethyl ether	4, 14, 17
Ethyleneimine	7, 103
Ethylene oxide	34, 103
Ethyl formate	13
2-Ethylhexyl acrylate	13, 103

Names	RGN
Ethyl mercaptan	20
Ethyl nitrate	27, 102
Ethyl nitrite	27, 102
Ethyl pripionate	13
Ethyl trichlorosilane	107
Exothion	32
Eugenol	31
Fensulfothion	32
Ferbam	12
Ferric arsenate	24
Ferric sulfide	33
Ferrous arsenate	24
Ferrous sulfide	33, 105
Fluoranthrene	16
Fluorene	16
Fluorine	104, 107
Fluorine azide	102
Fluorine monoxide	104, 107
Fluoroacetanilide	6, 17
Fluoroacetic acid	3
Fluoroboric acid	1, 15
Fluorosulfonic acid	1, 107
Fluosulfonic acid	1, 107
Fluosilicic acid	1, 15
Fonofos*	32
Formaldehyde	5
Formamide	6
Formetanate hydrochloride	6
Formic acid	3
Fostion*	32
Freon*	17
Fumaric acid	3
Fumarin	19
Fumazone*	17
Furadan*	9
Furan	14
Furfural	5
Furfuran	14
Gas oil, cracked	101
Gasoline	101
Germanium sulfide	33, 105
Glutaraldehyde	5
Glycerin	4

FIGURE D.2 (Cont.)
RGN'S FOR SELECTED MATERIALS

Names	RGN
Glycidol	34
Glycol diacetate	13
Glycol dinitrate	27, 102
Glycol ether	14
Glycolic acid	3
Glycol monolactate trinitrate	27, 102
Glycolonitrile	26
Gold acetylide	105, 107
Gold cyanate	102
Gold fulminate	102
Gold sulfide	33, 105
Grease	101
Guaiacol	31
Guanyl nitrosaminoguanylidene hydrazine	8, 102
Guanidine nitrate	27, 104
Gun cotton	27, 102
Guthion*	32
Hafnium	22
Hanane*	6, 32
Hemimellitene	16
Heptachlor	17
Heptane	29
Heptanal	5
Heptanol	4
Heptanone	19
Heptene	28
Hexaborane	105
Hexachlorobenzene	17
Hexadecyl trichorosilane	107
Hexaethyl tetraphosphate	32
Hexafluorophosphoric acid	1, 15
Hexahydride diborane	105, 107
Hexamethyl benzene	16
Hexamethylenediamine	7
Hexamethylenetetraamine	7
Hexanal	5
Hexanitrodiphenylamine	7, 27, 102
Hexanol	4
Hexanoic acid	3
Hexene	28
Hexylamine	7
Hexyl trichlorosilane	107
Hexyne	28

Names	RGN
HMX	102
Hopcide*	9
Hydrated lime	10
Hydrazine	8, 105
Hydrazine azide	8, 102
Hydrazoic acid	102
Hydriodic acid	1
Hydrobromic acid	1, 107
Hydrochloric acid	1
Hydrocyanic acid	1, 11
Hydrofluoric acid	1, 15
Hydrogen azide	102
Hydrogen bromide	1, 107
Hydrogen cyanide	1, 11
Hydrogen fluoride	1, 15
Hydrogen iodide	1
Hydrogen peroxide	104
Hydrogen phosphide	105
Hydrogen selenide	24, 105
Hydrogen sulfide	33, 105
Hydroquinone	31
Hydroxyacetophenone	19, 31
Hydroxydibromobenzoic acid	3, 17
Hydroxydiphenol	31
Hydroxyhydroquinone	31
Hydroxyacetophenone	19, 31
Hydroxyisobutyronitrile	4, 26
Hydroxyl amine	105
Hydroxypropionitirle	4, 26
Hypochlorous acid	2
Indene	16
Indium	22, 23, 24
Inerteen	17
Iodine monochloride	107
Iodine pentoxide	104
Iron	23
Iron arsenate	24
Isobutane	29
Isobutanol	4
Isobutyl acetate	13
Isobutyl acrylate	13, 103
Isobutylene	28
Isodecyl acrylate	13

FIGURE D.2 (Cont.)
RGN'S FOR SELECTED MATERIALS

Names	RGN
Isodurene	16
Isoeugenol	31
Isohexane	29
Isooctane	29
Isooctene	28
Isopentane	29
Isophorone	19
Isoprene	28, 103
Isopropanol	4
Isopropyl acetate	13
Isopropyl acetylene	28
Isopropylamine	7
Isopropyl benzene	16
Isopropyl chloride	17
Isopropyl ether	14
Isopropyl mercaptan	20
N-Isopropylmethylcarbamate	9
α-Isopropyl methylphosphoryl fluoride	17, 32
Isopropyl percarbonate	30
Isotactic propylene	101
J-100	101
Jet oil	101
Kerosene	101
Lacquer thinner	101
Landrin*	9
Lannate*	9, 20
Lauroyl peroxide	30
Lead	23, 24
Lead acetate	24
Lead arsenate	24
Lead arsenite	24
Lead azide	24, 102
Lead carbonate	24
Lead chlorite	24, 104
Lead cyanide	11, 24
Lead dinitroresorcinate	24, 27, 102
Lead mononitroresorcinate	24, 27, 102
Lead nitrate	24, 104
Lead orthoarsenate	24
Lead oxide	24
Lead styphnate	24, 27, 102
Lead sulfide	24, 33, 104
Lead trinitroresorcinate	24, 27, 102

Names	RGN
Lewisite	24
Lime nitrate	104
Lindane	17
Lithium	21, 107
Lithium aluminum hydride	105, 107
Lithium amide	10, 107
Lithium ferrosilicon	107
Lithium hydride	105, 107
Lithium hydroxide	10
Lithium hypochlorite	104
Lithium nitride	25
Lithium peroxide	104, 107
Lithium silicon	107
Lithium sulfide	33, 105
London purple	24
Lye	10
Magnesium	21, 22
Magnesium arsenate	24
Magnesium arsenite	24
Magnesium chlorate	104
Magnesium fluoride	15
Magnesium nitrate	104
Magnesium perchlorate	104
Magnesium peroxide	104
Magnesium sulfide	33, 105
Malathion	32
Maleic acid	3
Malonic nitrile	3, 26
Maneb	12
Manganese	22, 23, 24
Manganese acetate	24
Manganese arsenate	24
Manganese bromide	24
Manganese chloride	24
Manganese methylcyclopentadienyltricarbonyl	24
Manganese nitrate	24, 104
Manganese sulfide	24, 33, 105
Manganous arsenate	24
Manganous bromide	24
Manganous chloride	24
Manganous nitrate	104
Mannitol hexanitrate	27, 102
Matacil*	9

FIGURE D.2
RGN'S FOR SELECTED MATERIALS

Names	RGN
Mayer's reagent	24
Medinoterb acetate	13, 27
Meobal	9
Mercaptobenzothiazole	8, 20
Mercatoethanol	4, 20
Mercarbam	32
Mercuric acetate	24
Mercuric ammonium chloride	24
Mercuric benzoate	24
Mercuric bromide	24
Mercuric chloride	24
Mercuric cyanide	11, 24
Mercuric dioxysulfate	24
Mercuric iodide	24
Mercuric nitrate	24, 104
Mercuric oleate	24
Mercuric oxide	24
Mercuric oxycyanide	11, 24, 102
Mercuric potassium iodide	24
Mercuric salicylate	24
Mercuric subsulfate	24
Mercuric sulfate	24
Mercuric sulfide	24, 33, 105
Mercuric thiocyanate	24
Mercuric thiocyanide	24
Mercurol	24
Mercurous bromide	24
Mercurous gluconate	24
Mercurous iodide	24
Mercurous nitrate	24, 104
Mercurous oxide	24
Mercurous sulfate	24
Mercury	24
Mercury (vapor)	22, 24
Mercury acetate	24
Mercury ammonium chloride	24
Mercury benzoate	24
Mercury bisulfate	24
Mercury chloride	24
Mercury cyanide	11, 24
Mercury fulminate	24, 102
Mercury iodide	24
Mercury nitrate	24, 104

Names	RGN
Mercury nucleate	24
Mercury oleate	24
Mercury sulfate	24
Mesitylene	16
Mesityl oxide	19
Mesurol*	9
Metasystox-R	32
Metham	12
Methanal	5
Methane	29
Methanethiol	20
Methanoic acid	3
Methanol	4
Methomyl	9, 20
Methoxyethylmercuric chloride	24
Methyl acetate	13
Methyl acetone	101
Methyl acetylene	28
Methyl acrylate	13, 103
Methyl alcohol	4
Methyl aluminum sesquibromide	105, 107
Methyl aluminum sesquichloride	105, 107
Methylamine	7
Methyl amyl acetate	13
N-Methyl aniline	7
Methyl aziridine	7
Methyl benzene	16
Methyl bromide	17
Methyl butadiene	28, 103
Methyl butane	29
Methyl butene	28
Methyl butyl ether	14
Methyl t-butyl ketone	19
Methyl butyne	28
Methyl butyrate	13
Methyl chloride	17
Methyl chlorocarbonate	13, 17
Methyl chloroform	17
Methyl chloroformate	13, 17
Methyl chloromethyl ether	14, 17
Methyl cyanide	26
Methyl cyclohexane	29
Methyl dichloroarsine	24

FIGURE D.2 (Cont.)
RGN'S FOR SELECTED MATERIALS

Names	RGN
Methyl dichlorosilane	107
Methylene chloride	17
Methylene diisocyanate	18, 107
4,4-Methylene bis(2-chloroaniline)	7, 17
Methyl ethyl chloride	17
Methyl ethyl ether	14
Methyl ethyl ketone	19
Methyl ethyl ketone peroxide	30
Methyl ethyl pyridine	7
Methyl formate	13
Methyl hydrazine	8
Methyl iodide	17
Methyl isobutyl ketone	19
Methyl isocyanate	18, 107
Methyl isopropenyl ketone	19
Methyl magnesium bromide	105, 107
Methyl magnesium chloride	105, 107
Methyl magnesium iodide	105, 107
Methyl mercaptan	20
Methyl methacrylate	13, 103
Methyl napthalene	16
Methyl parathion	32
Methyl pentanoate	13
Methyl propionate	13
Methyl n-propyl ketone	19
Methyl styrene	28, 103
Methyl sulfide	20
Methyl trichlorosilane	107
Methyl valerate	13
Methyl vinyl ketone	19
Methyl yellow	7, 8
Mevinphos	32
Mexacarbate	9
Mineral spirits	101
Mintacol*	32
Mipcin*	9
Mobam*	9
Mocap*	32
Molybdenum	22, 23, 24
Molybdenum anhydride	24
Molybdenum sulfide	24, 33, 105
Molybdenum trioxide	24
Molybdic acid	24

Names	RGN
Monochloroacetone	17, 19
Monochloroacetic acid	3, 17
Monocroptophos	32
Monoethanol amine	4, 7
Monofluorophosphoric acid	1
Monoisopropanolamine	4, 7
Monomethyl hydrazine	8
Morpholine	7
Municipal solid waste	101
Muriatic acid	1
Nabam	12
Nack	21, 107
Nak	21, 107
Naptha	101
Naphthalene	16
Napthol	31
Napthylamine	7
Naphthyl mercaptan	20
Naphtite	27, 102
Nemagon*	17
Neohexane	29
4-NBP	27
Niacide*	12
Nialate	32
Nickel	22, 24
Nickel acetate	24
Nickel antimonide	24, 107
Nickel arsenate	24
Nickel arsenite	24
Nickel carbonyl	24
Nickel chloride	24
Nickel cyanide	11, 24
Nickel nitrate	24, 104
Nickelous arsenate	24
Nickelous arsenite	24
Nickelous chloride	24
Nickelous nitrate	24, 104
Nickel selenide	24
Nickel subsulfide	24, 33, 105
Nickel sulfate	24
Nickel tetracarbonyl	24
Nitraniline	7, 27
Nitric acid	2

FIGURE D.2 (Cont.)
RGN'S FOR SELECTED MATERIALS

Names	RGN
Nitroaniline	7, 27
Nitrobenzene	27
Nitrobenzol	27
Nitrobiphenyl	27
Nitrocalcity	104
Nitrocellulose	27, 102
Nitrochlorobenzene	17, 27
Nitrogen dioxide	104
Nitromannite	27, 102
Nitrogen mustard	7, 17
Nitrogen tetroxide	104
Nitroglycerin	27, 102
Nitrohydrochloric acid	2
Nitrophenol	27, 31
Nitropropane	27
Nitrosodimethylamine	7, 27
Nitrosoguandine	27, 102
Nitrostarch	27, 102
Nitroxylene	27
Nitroxylos	27
N-Nitrosodimethylamine	7, 27
Nonyl phenol	31
Nonyl trichlorosilane	107
Nonane	29
Nonene	28
Nonanone	19
Nonanal	5
Nonanol	4
Octadecyl trichlorosilane	107
Octadecyne	28
Octamethylpyrophosphoramide	6, 32
Octanal	5
Octane	29
Octanone	19
Octanol	4
Octene	28
Octyl peroxide	30
Octyl trichlorosilane	107
Oil of bergamot	101
Oil of vitriol	1
Oleum	2, 24
Orris root	101
Orthozenol	31

Names	RGN
Osmium	23, 24
Osmium amine nitrate	24, 104
Osmium amine perchlorate	24, 104
Oxamyl	9
Oxalic acid	3
Oxygen difluoride	104, 107
PCB	17
Paper	101
Paraoxon	32
Parathion	32
Paris green	24
PETD	12
PETN	27, 102
Pentaborane	105
Pentachlorophenol	17, 31
Pentaerythritol tetranitrate	27, 102
Pentamethyl benzene	16
Pentane	29
Pentanethiol	20
Pentanal	5
Pentanone	19
Pentene	28
Pentylamine	7
Pentyne	28
Peracetic acid	3, 30
Perbromic acid	2
Perchloric acid	2
Perchloroethylene	17
Perchloromethyl mercaptan	17, 20
Perchlorous acid	2
Perchloryl fluoride	104
Periodic acid	2
Permonosulfuric acid	1
Peroxyacetic acid	3, 30
PETD	12
Petroleum naptha	101
Petroleum oil	101
Phenanthrene	16
Phenarsazine chloride	7, 24
Phenol	31
Phenyl acetic acid	3
Phenyl acetonitrile	26
Phenyl acetylene	16

FIGURE D.2 (Cont.)
RGN'S FOR SELECTED MATERIALS

Names	RGN
Phenylaniline	7
Phenylbenzene	16
Phenylbutane	16
Phenylchloromethyl ketone	17, 19
Phenyl dichloroarsine	24
Phenylene diamine	7
Phenylethane	16
Phenyl hydrazine hydrochloride	8
o-Phenyl phenol	31
Phenyl trichlorosilane	107
Phenyl valerylnitrile	26
Phenylpropane	16
Phloroglucinol	31
Phorate	32
Phosdrin*	32
Phosphamidon	32
Phosphine	105
Phospholan	20, 32
Phosphonium iodide	105, 107
Phosphoric acid	1
Phosphoric anhydride	107
Phosphoric sulfide	33, 105, 107
Phosphorus (Amorphous red)	105, 107
Phosphorus (White-Yellow)	105
Phosphorus heptasulfide	33, 105
Phosphorus oxybromide	104, 107
Phosphorus oxychloride	104, 107
Phosphorus pentachloride	107
Phosphorus pentasulfide	33, 105, 107
Phosphorus pentoxide	107
Phosphorus sesquisulfide	33, 105, 107
Phosphorus tribromide	107
Phosphorus trichloride	107
Phosphorus trisulfide	33, 105, 107
Phosphoryl bromide	104, 107
Phosphoryl chloride	104, 107
Phthalic acid	3
Picramide	7, 27, 102
Picric acid	27, 31, 102
Picridine	7
Picryl chloride	17, 27, 102
Piperidine	7
Pirimicarb	9

Names	RGN
Polyglycol ether	14
Polyamide resin	101
Polybrominated biphenyl	17
Polybutene	28
Polychlorinated biphenyls	17
Polychlorinated triphenyls	17
Polethylene	101
Polyester resin	101
Polymeric oil	101
Polyphenyl polymethylisocyanate	18, 107
Polypropylene	28, 101
Polyram combi*	12
Polysulfide polymer	20, 101
Polystyrene	101
Polyurethane	101
Polyvinyl acetate	101
Polyvinyl chloride	101
Polyvinyl nitrate	27, 102
Potasan	32
Potassium	21, 107
Potassium acid fluoride	15
Potassium aluminate	10
Potassium arsenate	24
Potassium arsenite	24
Potassium bifluoride	15
Potassium bichromate	24, 104
Potassium bromate	104
Potassium butoxide	10
Potassium cyanide	11
Potassium dichloroisocyanurate	104
Potassium dichromate	24, 104
Potassium dinitrobenzfuroxan	27, 102
Potassium fluoride	15
Potassium hydride	105, 107
Potassium hydroxide	10
Potassium nitrate	102, 104
Potassium nitride	25
Potassium nitrite	104
Potassium oxide	107
Potassium perchlorate	104
Potassium permanganate	24, 104
Potassium peroxide	104, 107
Potassium sulfide	33, 105

FIGURE D.2 (Cont.)
RGN'S FOR SELECTED MATERIALS

Names	RGN
Promecarb	9
Propanal	5
Propane	29
Propanethiol	20
Propanoic acid	3
Propanol	4
Propargyl bromide	17
Propargyl chloride	17
2-Propen-1-ol	4
Proppiolactone	13
Propionaldehyde	5
Propionamide	6
Propionic acid	3
Propionitrile	26
Propyl acetate	13
Propyl alcohol	4
Propylamine	7
Propyl benzene	16
Propylene dichloride	17
Propylene glycol	4
Propylene glycol monomethyl ether	4, 14
Propylene oxide	34, 103
Propyleneimine	7
Propyl ether	14
Propyl formate	13
Propyl mercaptan	20
Propyl Trichlorosilane	107
Prothoate	32
Pseudocumene	16
Pyridine	7
Pyrogallol	31
Pyrosulfuryl chloride	107
Pyroxylin	27
Quinone	19
Raney nickel	22
RDX	27, 102
Refuse	101
Resins	101
Resorcinol	31
Rubidium	21
Salicylated mercury	24
Saligenin	31
Saltpeter	102, 104

Names	RGN
Schradan	6, 32
Selenious acid	1, 24
Selenium	22, 23, 24
Selenium diethyldithiocarbamate	12, 24
Selenium fluoride	15, 24
Selenous acid	1, 24
Silicochloroform	107
Silicon tetrachoride	107
Silicon tetrafluoride	15, 107
Silver acetylide	24, 102, 105, 107
Silver azide	24, 102
Silver cyanide	11, 24
Silver nitrate	24, 104
Silver nitride	24, 25, 102
Silver styphnate	24, 27, 102
Silver sulfide	24, 33, 105
Silver tetrazene	24, 102
Silver trinitroresorcinate	24, 27, 102
Slaked lime	10, 107
Smokeless powder	102
Sodamide	10, 107
Soda niter	104
Sodium	21, 105, 107
Sodium acid fluoride	15
Sodium aluminate	10, 105
Sodium aluminum hydride	105, 107
Sodium amide	10, 107
Sodium arsenate	24
Sodium arsenite	24
Sodium azide	102
Sodium bichromate	24, 104
Sodium bifluoride	15
Sodium bromate	104
Sodium cacodylate	24
Sodium carbonate	10
Sodium carbonate peroxide	104
Sodium chlorate	104
Sodium chlorite	104
Sodium chromate	24
Sodium cyanide	11
Sodium dichloroisocyanurate	104
Sodium dichromate	24, 104
Sodium dimethylarsenate	24

FIGURE D.2 (Cont.)
RGN'S FOR SELECTED MATERIALS

Names	RGN
Sodium fluoride	15
Sodium hydride	105, 107
Sodium hydroxide	10
Sodium hypochlorite	10, 104
Sodium hyposulfite	105
Sodium methylate	10, 107
Sodium methoxide	10, 107
Sodium molybdate	24
Sodium monoxide	10, 107
Sodium nitrate	104
Sodium nitride	25
Sodium nitrite	104
Sodium oxide	10, 107
Sodium pentachlorophenate	31
Sodium perchlorate	104
Sodium permanganate	24, 104
Sodium peroxide	104, 107
Sodium phenolsulfonate	31
Sodium picramate	27, 102
Sodium polysulfide	101
Sodium potassium alloy	21, 107
Sodium selenate	24
Sodium sulfide	24, 33, 105
Sodium thiosulfate	105
Stannic chloride	24, 107
Stannic sulfide	33, 105
Starch nitrate	27, 102
Stilbene	16
Stoddard solvent	101
Strontium	24
Strontium arsenate	24
Strontium dioxide	24, 104
Strontium monosulfide	24, 33, 105
Strontium nitrate	24, 104
Strontium peroxide	104
Strontium tetrasulfide	24, 33, 105
Styphnic acid	27, 31, 102
Styrene	16, 28, 103
Succinic acid	3
Succinic acid peroxide	30
Sulfonyl chloride	107
Sulfonyl flouride	107
Sulfotepp	32

Names	RGN
Sulfur chloride	107
Sulfur (elemental)	101
Sulfuric acid	2, 107
Sulfuric anhydride	104, 107
Sulfur monochloride	107
Sulfur mustard	20
Sulfur oxychloride	107
Sulfur pentafluoride	15, 107
Sulfur trioxide	104, 107
Sulfuryl chloride	107
Sulfuryl fluoride	107
Supracide*	32
Surecide*	32
Synthetic rubber	101
TCDD	14, 17
TEDP	32
TEL	24
TEPA	6, 32
TEPP	32
THF	14
TMA	7
TML	24
TNB	27, 102
TNT	27, 102
Tall oil	101
Tallow	101
Tar	101
Tellurium hexafluoride	15, 24
Temik*	9, 20
Tetraborane	105
Tetrachlorodibenzo-p-dioxin	14, 17
Tetrachloroethane	17
Tetrachloroethylene	17
Tetrachloromethane	17
Tetrachlorophenol	17, 31
Tetrachloropropyl ether	14, 17
Tetradecene	28
Tetraethyl dithionopyrophosphate	32
Tetraethyl lead	24
Tetraethyl pyrophosphate	32
Tetrahydrofuran	14
Tetramethylenediamine	7
Tetramethyl lead	24

FIGURE D.2 (Cont.)
RGN'S FOR SELECTED MATERIALS

Names	RGN
Tetramethyl succinonitrile	26
Tetranitromethane	27, 102
Tetraphenyl ethylene	16
Tetraphosphorus trisulfide	33, 105, 107
Tetraselenium tetranitride	24, 25, 102
Tetrasul	20
Tetrasulfur tetranitride	25, 102
Tetrazene	8, 102
Thallium	24
Thallium nitride	24, 25, 102
Thallium sulfide	24, 33, 105
Thallous sulfate	24
Thimet*	32
Thionyl chloride	107
Thiocarbonyl chloride	107
Thiodan*	17, 20
Thionazin	32
Thionyl chloride	107
Thiophosgene	107
Thiophosphoryl chloride	107
Thiram	12
Thorium	22, 23, 24
Tin tetrachloride	24, 107
Titanic chloride	24, 107
Titanium	22, 23, 24
Titanium sesquisulfide	24, 33, 105
Titanium sulfate	24
Titanium sulfide	24, 33, 105
Titanium tetrachloride	24, 107
TMA	7
TNB	27, 102
TNT	27, 102
Tolualdehyde	5
Toluene	16
Toluene diisocyanate	18, 107
Toluic acid	3
Toluidine	7
Toluol	16
Topcide*	6
Tranid*	9, 26
Triamphos	6, 32
Tribromomethane	17
Tri-n-butylaluminum	107

Names	RGN
Tricadmium dinitride	24, 25
Tricalcium dinitride	25
Tricesium nitride	24, 25
Trichloroacetaldehyde	5, 17
Trichloroborane	107
Trichloroethane	17
Trichloroethene	17
Trichloroisocyanuric acid	104
Trichloromethane	17
Trichloromethyl sulfenyl chloride	17, 20
Trichloronitromethane	17, 27, 102
Trichlorophenoxyacetic acid	3, 17
Trichloropropane	17
Trichlorosilane	107
Tridecene	28
Triethanolamine	4, 7
Triethyl aluminum	105, 107
Triethyl antimony	24, 105, 107
Triethyl arsine	24, 107
Triethyl bismuthine	24
Triethylamine	7
Triethylene phosphoramide	6, 32
Triethylene tetraamine	7
Triethyl stibine	24, 105, 107
Trifluoroethane	17
Trifluoromethylbenzene	17
Triisobutyl aluminum	105, 107
Trilead dinitride	24, 25, 102
Trimercury dinitride	24, 25, 102
Trimethyl aluminum	105, 107
Trimethylamine	7
Trimethyl antimony	24, 105
Trimethyl arsine	24, 107
1,2,4-Trimethylbenzene	16
1,3,5-Trimethylbenzene	16
Trimethyl bismuthine	24
Trimethyl pentane	29
Trimethylstibine	24, 105, 107
Tri-n-butylborane	105, 107
Trinitroaniline	7, 27, 102
Trinitroanisole	14, 27
Trinitrobenzene	27, 102
Trinitrobenzoid acid	3, 27, 102

FIGURE D.2 (Cont.)
RGN'S FOR SELECTED MATERIALS

Names	RGN
Trinitroglycerin	27, 102
Trinitronaphthalene	27, 102
Trinitrophenol	27, 31, 102
Trinitrophenyl methyl ether	14, 27
Trinitroresorcinol	27, 31, 102
Trinitrotoluene	27, 102
Trioctyl aluminum	105, 107
Triphenyl ethylene	16
Triphenyl methane	16
Tripropylamine	7
Tripropyl stibine	24, 107
Trisilyl arsine	24, 107
Tris-(1-aziridinyl) phosphine oxide	6, 32
Trithion	32
Trithorium tetranitride	24, 25
Trivinyl stibine	24, 107
Tsumacide*	9
Tungstic acid	24
Turpentine	101
UDMH	8
Ultracide*	32
Undecene	28
Unisolve	101
Uranium nitrate	24, 104
Uranium sulfide	24, 33, 105
Uranyl nitrate	24, 104
Urea formaldehyde	5
Urea nitrate	27, 102, 104
VC	17, 103
Valeraldehyde	5
Valeramide	6
Valeric acid	3
Vanadic acid anhydride	24
Vanadium oxytrichloride	24
Vandadium pentoxide	24
Vanadium sulfate	24
Vanadium tetroxide	24
Vanadium trichloride	24, 107
Vanadium trioxide	24
Vanadyl sulfate	24
Vapona*	32
Vinyl acetate	13, 103
Vinyl azide	102

Names	RGN
Vinylbenzene	16, 28, 103
Vinyl chloride	17, 103
Vinyl cyanide	26, 103
Vinyl etheyl ether	14
Vinyl isopropyl ether	17
Vinylidene chloride	17, 103
Vinyl toluene	28, 103
Vinyl trichlorosilane	107
VX	20, 32
Water	106
Waxes	101
Wepsyn* 155	6, 32
Wood	101
Zectran*	9
Zinc	22, 23, 24
Zinc acetylide	24, 105, 107
Zinc ammonium nitrate	24, 104
Zinc arsenate	24
Zine arsenite	24
Zinc chloride	24
Zinc dioxide	24, 102, 104, 107
Zinc ethyl	24, 105, 107
Zinc cyanide	11, 24
Zinc fluoborate	24, 15
Zinc nitrate	24, 104
Zinc permanganate	24, 104
Zinc peroxide	24, 102, 104, 107
Zinc phosphide	24, 107
Zinc salts of dimethyl dithiocarbamic acid	12, 24
Zinc sulfate	24
Zinc sulfide	24, 33, 105
Zineb*	12, 24
Zinophos*	20
Ziram*	12, 24
Zirconium	22, 23, 24
Zirconium chloride	24
Zirconium picramate	24, 104
Zirconium tetrachloride	24

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APPENDIX E

GUIDE TO INSTALLATION OF THE ARCHIE COMPUTER PROGRAM

Introduction

The purpose of this appendix is to provide assistance with installation of the Automated Resource for Chemical Hazard Incident Evaluation (ARCHIE) computer program. Due to the very unusual nature of the installation procedure, it is highly recommended that ***all*** users read and follow subsequent instructions as closely as possible. It is also suggested that introductory portions of Chapter 12 be read prior to program installation up to and including the section on system initialization.

System Requirements

ARCHIE may be installed on IBM™ personal computers (PCs) and those other such computers that are fully compatible with IBM products and which operate under PC-DOS or MS-DOS disk operating systems of Version 2.0 or higher (with certain exceptions noted below). Hardware requirements include:

- A monochrome or color 80-column monitor linked to a monochrome display adaptor (MDA), color graphics adaptor (CGA), enhanced graphics adaptor (EGA), or video graphics array (VGA) video display card.
- Two disk drives, at least one of which can read 5.25 inch double-sided, double density, floppy diskettes of 360k capacity.
- 512k of free random access memory (RAM)
- A compatible printer if written summaries are desired.

Special Self-Extracting Program Feature

ARCHIE and its associated program files do *not* normally fit within the space available on a single 360k diskette, yet this is currently the most common type of disk in use and therefore the best choice for widespread distribution of the program. In order to fit the program on *one* disk, and thereby save substantial duplication and distribution costs for a second, the developers of ARCHIE licensed use of an unusual and possibly unique program utility from a private vendor. This utility is *unusual* in that it permitted the author of ARCHIE to *compress* many program files to a fraction of their normal size and then *pack* them together into just the two files that appear on the distribution disk. The utility is rather

unique in that a single command will cause each resulting file to *unpack* and *decompress* itself while *automatically* directing decompressed files to the drive and/or path specified by the end user. The original packed files are not altered or modified in any way by this process. Thus, the user may start over at any time if a mistake is made during program installation.

The two *packed* files provided on the diskette received with this document are respectively named VOLUME1.EXE and VOLUME2.EXE. How one goes about unpacking and decompressing them for final use depends on the types of disk drives installed in the user's computer system and is discussed in the next section.

Note that the following instructions assume that the user has at least minimal knowledge of file management techniques on personal computers. Where instructions are not understood, please refer to the manuals that accompanied your DOS diskettes. Key words to look for in these manuals are shown in italics.

Program Installation Instructions

The following instructions should be adequate to install ARCHIE on the majority of IBM and compatible personal computer systems. Users who encounter difficulty should consult a more experienced computer user for assistance.

For those of you with fairly new computers having *only* 3.5 inch floppy drives, it will be necessary to copy the ARCHIE program files to a 3.5 inch disk prior to installation. Since most of you will have encountered this type of disk conversion problem before, it is expected that relatively few users will experience insurmountable problems in undertaking this task.

For Systems with a Hard Drive or Card:

Assuming that the computer will *boot* automatically (i.e., show a *system prompt*) when turned on, the best approach is to install the entire contents of the program diskette on the hard drive or card in its own separate *directory*. Once all files have been unpacked, decompressed, and copied to this directory, and this directory is the *current* directory, it is only necessary to type "ARCHIE" followed by a press of the ENTER key to start the program.

A directory is created on a hard disk, when the user in the *root directory*, by typing "MD\DIRNAME" (leaving out the quote marks shown here and in other commands that follow), where DIRNAME can be any one to eight-letter name of the users choosing. The user can enter or proceed to the new directory (and thereby make it the current directory) at any time by typing "CD\DIRNAME" when the hard drive is the *default* drive (i.e., when "C:>" appears on screen as the *system prompt*).

With the ARCHIE distribution disk in drive A, the user should next type "A:" and press ENTER so that drive A becomes the default drive with "A:>" appearing as the system prompt on the screen. It then becomes time to actually unpack and decompress the ARCHIE program files, this being accomplished by typing:

- "VOLUME1 C:\DIRNAME" followed by a press of the ENTER key.
- "VOLUME2 C:\DIRNAME" followed by a press of the ENTER key.

As the program files unpack and decompress, numerous messages will be shown on screen. It is prudent to wait until VOLUME1 has decompressed and the system prompt has reappeared before giving the second command listed above.

While VOLUME2 is decompressing, the user will be asked whether or not existing files should be overwritten. The answer that should be given in response does not make a difference, but a *no* answer will save a few seconds of file transfer time. When the system prompt reappears:

- Type "C:" followed by a press of the ENTER key.
- Type "CD DIRNAME" followed by a press of the ENTER key.
- Type "ARCHIE" followed by a press of the ENTER key to start the program.
- See Chapter 12 to learn more about what happens next.

A viable alternative for those who do not wish to copy the program onto their hard drive or card is to follow the directions given below for systems with two floppy drives with two possible modifications. The first is that the diskette(s) to which the decompressed files are to be directed *may* not need to be formatted with the "/S" suffix. The second is that the user has a choice of either drive B (if present) or drive C as storage locations for the Accident Scenario Files (ASF) described in Chapter 12.

For Systems With Two 360k Floppy Drives and No Hard Drive

If your computer has two 5.25 inch floppy drives of 360K capacity, follow these instructions.

- Format ***two*** blank diskettes as you normally would, but add the suffix "/S" to the format command. For example, with your DOS diskette in drive A, and an unformatted diskette in drive B, type "FORMAT B:/S".

- If the system prompt is not "A:>"at this time, type "A:" followed by a press of the ENTER key.

- Place one of the newly formatted diskettes in drive B and place the ARCHIE distribution diskette in drive A.

- Type "VOLUME1 B:" followed by a press of the ENTER key and wait for the system prompt to reappear after various messages.

- Remove the disk from drive B and label it as "ARCHIE Volume I". This disk will contain the first of two sets of ARCHIE program files and can be used to boot the system.

- Place the second newly formatted diskette in drive B.

- Type "VOLUME2 B:" followed by a press of the ENTER key and wait for the system prompt to reappear after various messages.

- Remove the disk from drive B and label it as "ARCHIE Volume II". This disk will contain the second of two sets of program files.

- Remove the DOS diskette from drive A and place the ARCHIE Volume I disk in this drive.

- Type "ARCHIE" followed by a press of the ENTER key to start the program. See Chapter 12 for what happens next.

For Systems With Two Floppy Drives of Different Capacity and No Hard Drive

If your computer has two floppy drives, one of which is of 360K capacity, and the other of which is of higher capacity (*and therefore uses high density diskettes*), it is assumed that the higher capacity drive is drive A, since this is the most common system configuration. Follow these instructions to place both sets of ARCHIE program files on one high density diskette together with the operating system files.

- Format ***one*** blank high density diskette as you normally would, but add the suffix "/S" to the format command. For example, with your 360k DOS diskette in drive B, and an unformatted high density diskette in drive A, type "B:FORMAT A:/S".

- If the system prompt is not "B:>"at this time, type "B:" followed by a press of the ENTER key.

- Place the newly formatted high density diskette in drive A and place the ARCHIE distribution diskette in drive B.

- Type "VOLUME1 A:" followed by a press of the ENTER key and wait for the system prompt to reappear after various messages.

- Type "VOLUME2 A:" followed by a press of the ENTER key. While VOLUME2 is unpacking and decompressing, expect to be asked whether or not existing files should be overwritten. The answer that should be given in response does not make a difference, but a *no* response will save a few seconds of file transfer time.

- When the system prompt reappears, remove the high density disk from drive A, label it as "ARCHIE", and replace it in drive A. Remove your DOS diskette from drive B. The single high density diskette will contain all program files of ARCHIE plus sufficient room for quite a few Accident Scenario Files (ASF). The disk can be used to boot the system.

- Type "A:" followed by a press of the ENTER key to make drive A the default drive. Type "ARCHIE" followed by a press of the ENTER key to start the program, and see Chapter 12 for what happens next.

Additional Instructions For any System With a Color Monitor

In order for ARCHIE to display certain screens in full color, it is necessary for the ANSI.SYS driver to be installed in the CONFIG.SYS file of the computer. For those readers that do not understand the above statement, follow these instructions:

- Locate the file named ANSI.SYS on your DOS diskettes.

- Copy this file to the floppy diskette or root directory of the hard drive from which the system is booted up when power is turned on.

- Look at the above diskette or location using the DIR command to determine whether a file with the name CONFIG.SYS exists.

- If CONFIG.SYS does exist, add the line "DEVICE = ANSI.SYS" without quotes to the list of commands in the file. Modify the file using the *copy con* command described in your DOS manuals, the *edlin* editor provided on your DOS diskettes, or any other ASCII file editor.

- If CONFIG.SYS does not exist, see your DOS manuals for the purpose of this file and its contents. Create the file using the *copy con* command described in your manuals, the *edlin* editor provided on your DOS diskettes, or any other ASCII file editor.

Potential Problems that May be Experienced

In order to properly unpack and decompress ARCHIE, the self-extracting program utility requires access to specific portions of the computer's memory. This access may at times be impeded or interrupted by TSR (terminate and stay resident) programs that may have been installed earlier in memory. Thus, if problems are experienced during file decompression or initial use of ARCHIE, it may be necessary to reboot the computer (or otherwise ensure that TSR programs have not be installed) and repeat the installation procedure. (Note: A TSR program is usually one that can be activated at any time by the user, even while he or she is in the middle of another program, by pressing a specific combination of keys. Alternatively, it may be a performance enhancement utility of some type loaded into memory for one reason or another.) Users in office environments who experience problems and are not sure whether or not their system automatically installs one or more TSRs should seek assistance from a more experienced computer user -- who is advised to check the contents of the AUTOEXEC.BAT file on the boot disk or drive for indications that a TSR program is being installed.

Some versions of DOS 2.X have been identified as having difficulties executing an important and frequently used instruction in ARCHIE referred to as a "SHELL" command, even though their documentation has always claimed that use of this instruction is fully acceptable. If problems are experienced during program use, it may be necessary to obtain and install DOS version 3.0 or above in order for ARCHIE to function properly. (Note: Typical manifestations of this problem produce "Illegal Function Call" and "Wrong Version of Command.Com" error messages during program use. Although special steps have been taken to avoid the problem and it should arise infrequently, some users may nevertheless experience difficulties).

Users who have a color monitor, and who neglect to install the ANSI.SYS driver as instructed above, may not be able to proceed past the second screen of the program initialization procedure discussed in Chapter 12. The presence of this driver is mandatory if the user specifies that a color monitor is present.

APPENDIX F

BASIS OF PROBABILITY ANALYSIS PROCEDURES

Introduction

This appendix provides and discusses the basis for the probability analysis procedures presented in Chapter 11 of the guide.

Transportation of Hazardous Materials by Highway

Available Accident Data for Bulk Transportation by Highway

Although numerous data bases and compilations of spill records are available for highway transportation, the purpose of many of them is such that they are not conducive to obtaining accident frequency estimates, primarily because they keep track of the number of events but not the total exposure. Such data bases can still be useful, however, in determining breakdowns of accidents by size or cause. Available data bases and their completeness, as noted above, are described by both the July 1986 OTA report and a series of reports prepared by Midwest Research Institute for the Federal Highway Administration (1987a and b). This section presents some of the failure rates and other statistics given in the literature. Values actually recommended for use in emergency planning follow in a later section.

The rate of accidents can be a function of road type (urban, rural, etc.), number of lanes, traffic density, average speeds, type of vehicle, number of intersections, road conditions, weather conditions, geometry of the road, grade, etc. However, differences attributed to these various causes tend to give results that are within roughly one order of magnitude, with the range usually being 1 to 10 x 10^{-6}/mile or between one and ten accidents per million miles driven. (Urbanek and Barber: 1980, API: 1983, Smith and Wilmot: 1982, National Safety Council: 1988).

Frequently cited average accident rates in prior studies are:

- 5.0 x 10^{-6}/mile for trucks in the petroleum industry (API, 1983)
- 2.5 x 10^{-6}/mile for trucks (Dennis et al: 1978, Rhoads et al: 1978 and others)
- 1.4 x 10^{-6}/mile for trucks with trailers in California (Smith and Wilmot, 1982)
- 1.2 x 10^{-5}/mile for all trucks, and
- 3.1 x 10^{-6}/mile for intercity trucks (National Safety Council, 1988)

- 1.5×10^{-6}/mile for bulk hazardous materials trucks (Ichniowski, 1984)
- 8.3×10^{-7}/mile for trucks (Kloeber et al, 1979)
- $0.9 - 2.1 \times 10^{-6}$/mile for single trailer trucks (IIHS, 1985)

Yet other rates have been reported for specific locations or road types. Much of the variation in these average rates can be explained by level of compliance with reporting requirements and different reporting thresholds in terms of damages sustained for the various data bases, as well as the road and weather conditions in the subject area. (Note: See Appendix A if you are not familiar with scientific notation of numbers such as 5×10^{-6}.)

With respect to the fraction of all reported accidents that result in a spill or discharge, the range of estimates in the literature include 0.20 (ICF, 1984), 0.115 (OTA, July 1986), 0.30 (Elder et al, 1978), 0.46 (ADL, 1979), and other values which range from less than 0.01 to about 0.50. One source states that 0.3-1.2% (0.003-0.012) of most types of truck accidents result in a fire (Dennis et al, 1978). Some data sources combine the accident rate with prespecified levels of accident severity; for example (Clarke et al, 1976):

Minor	2.4×10^{-6}/mile
Moderate	4.5×10^{-8}/mile
Severe	7.2×10^{-9}/mile
Extra severe	3.5×10^{-9}/mile
Extreme	1.2×10^{-9}/mile

A review of hazardous material accidents on highways over the five-year period 1981 through 1985 was carried out by MRI (1987). This study concluded that, based on truck accidents reported to the Bureau of Motor Carrier Safety (BMCS) of the Federal Highway Administration, 15.2 percent of accidents involving hazardous material-carrying vehicles resulted in a release. Accidents involving tank trucks resulted in releases 16.6 percent of the time based on 1984-1985 BMCS-reported accident data. It is not clear whether accidents involving empty trucks which normally carry hazardous materials were included in the data base; the implication in this study, however, is that only loaded trucks are included.

The distribution of spill amounts in accidents involving spills is somewhat less variable. One study of data in the Pollution Incident Reporting System (PIRS) of the U.S. Coast Guard found an average spill volume of 1880 gallons for highway transport spills of hazardous materials. An analysis of LPG truck accidents (Croce et al, 1982) gave breakdowns as follows for small (<7000 gal) and large (>7000 gal) trucks:

Spill Size	Small Trucks	Large Trucks
<100 gal	49%	44%
100 - 1,000 gal	18%	19%
1,000 - 5,000 gal	27%	12%
5,000 -10,000 gal	6%	25%

Another study found an average truck release volume of 2900 gallons (excluding spills of less than 100 gal), with 23% being less than 100 gal, 22% from 100 - 500 gal, 8% from 500 - 1000 gal, 16% from 1000 - 5000 gal, and 31% from 5000 to roughly 10,000 gal (ADL, 1978). Rhoads et al (1978) found that about 7% of all spills from gasoline trucks exceed 3000 gallons.

The Hazardous Material Information System of the U.S. Department of Transportation has maintained a data base on the size of reported releases of LPG. For the eleven-year period of 1976-1986, 76 releases of LPG were reported in highway accidents. These were distributed as follows:

Small releases (1 - 1000 gallons)	= 53 percent
Large releases (> 1000 gallons)	= 47 percent

Use of Local Data

State and local highway departments may maintain accident counts or rates, but it is less likely that they will have information on commodity flows. For most types of accidents, it is probably desirable to stay at the level of state or regionwide data in order to avoid excluding very low frequency events. Nationwide data on accident rates is probably a reasonable approximation, and the focus should be on improving the commodity flow data base rather than on the accident data base if only one can be addressed. However, whenever local or state data is available, it can be substituted for the values used in the worksheet given in Chapter 11.

The City of Portland, Oregon, is an example of a community that has conducted a detailed analysis of the materials spilled in past accidents and the types of accidents causing these releases. It found that 24.5% of truck accidents resulted in spills. From 1976-1980, gasoline accounted for 47.3% of spills, diesel 23%, asphalt 8.2%, fuel oil 4.1% and other materials 17.4%. Commodity flow data were also obtained, but it was acknowledged that this information was somewhat incomplete (Robison, 1981). Table F.1 summarizes statistics on truck accidents gathered for the state of Pennsylvania in recent years.

TABLE F.1
PENNSYLVANIA HIGHWAY ACCIDENTS

	1980	1981	1982	1982	1984
Accidents reported	174	165	274	186	207
Fatalities	24	9	11	16	14
Injured	73	200	257	164	184
Caused by drivers with cargoes of hazardous materials	89	81	86	55	48
Caused by other drivers	82	62	88	75	76
Other causes	5	10	88	56	83
Number of hours highways were restricted	137	77	96	112	110
Number of hours highways were closed	140	164	146	246	110
Accidents resulting in loss of product	33	31	47	27	30
Accidents resulting in fire	4	1	4	4	0
Accidents involving:					
Explosives and blasting agents	2	6	6	1	2
Flammable liquids and solids	87	67	100	73	91
Oxidizing materials, poisons, and corrosive materials	20	22	43	20	25
Radioactive materials	3	1	3	0	0
Compressed gases - cryogenics	16	20	17	32	29
Combustible liquids	46	49	106	73	76
Percentage of accidents involving cargoes of:					
Flammable liquids and solids, %	50	41	36	37	41
Compressed gases - cryogenics, %	9	12	6	16	13
Explosives and blasting agents, %	1	4	2	1	1
Radioactive materials, %	2	1	1	0	0
Oxidizing materials, poisons, and corrosive materials, %	12	13	16	10	11
Combustible liquids, %	26	29	39	37	34

Suggested Approach for Assessment of Accident Potential

Since we are concerned with accidents with the potential to cause major problems for a community or other jurisdiction and not those which are handled on a routine basis, it is best to focus on vehicular accidents rather than relatively minor leaks from valves, fittings, or open relief valves. Based on the information presented above, an average accident rate of 2×10^{-6} accidents/mile is considered representative of the general experience of trucks carrying bulk quantities of hazardous materials. If adequate local/state data are available for determination of individual accident rates for divided and undivided roadways, their use is recommended because the resulting rates will more accurately reflect accident probabilities under local conditions.

With respect to the fraction of truck accidents that result in a spill or discharge, the available data suggest a consensus opinion on the order of 0.50 (50%) if all spills including very minor valve and fitting leaks are considered. Omitting these, a spill appears to result from an accident in about 0.15 - 0.20 (15 - 20%) of accidents. A value of 0.20 (20%) is therefore suggested for the sake of conservatism.

Based upon the available spill amount distributions, and considering the likely causes of accidents, the following distribution is suggested for general use:

- 10% cargo loss (thru 1" hole) ***or*** 1000 gal --- 60% of the time
- 30% cargo loss (thru 2" hole) ***or*** 3000 gal --- 20% of the time
- 100% cargo loss (instantly) ***or*** 10,000 gal --- 20% of the time

These values cover the range of significant releases. If desired, a two-point distribution assuming 3000 gallon spills 80% of the time and 10,000 gallon spills 20% of the time may be used to simplify accident consequence estimation procedures.

Transportation of Hazardous Materials by Rail

Available Accident Data for Bulk Transportation by Rail

The overall accident rate for railroads has been reported as being 4.6×10^{-6} accidents per train-mile traveled in 1987. This rate was comprised of 4.9×10^{-7} collisions per train-mile, 3.2×10^{-6} derailments per train-mile, and 8.6×10^{-7} other types of accidents per train-mile. The general trend has been a reduction in the overall accident rate, the collision rate, and the derailment rate, with only the rate for "other" accidents holding at about one per million train-miles (FRA, 1988), as might be expected due to the many new regulations adopted in recent years to improve railroad safety. For example, the overall accident rates reported for the period 1979-1984 were:

Year	Accidents per million train-miles
1984	6.6
1983	7.0
1982	8.0
1981	8.6
1980	11.8
1979	12.8

(Note: Some adjustments were made in the rates to account for changes in reporting thresholds.) This compares to the rate of 4.6 per million train-miles in 1987.

There were 54 railroad accidents in 1984 in which hazardous materials were released. The number of cars that released hazardous materials in these 54 accidents was 100, with 89 of these being involved in derailments. Collisions accounted for about 11% of the 54 accidents, with derailments accounting for another 75% (FRA, 1985). Over 90% of releases have been attributed to derailments in the past (von Herberg, 1979), so design improvements may be having a beneficial effect.

The overall rate of 4.6×10^{-6} accidents per train-mile can be split into a rate of about 2.9×10^{-6} per train-mile for mainline track and 1.3×10^{-5} per train-mile for rail yards (FRA, 1988). For a recent five-year period, the average number of cars per freight train has been about 70 (AAR, 1985), and the number of cars involved in each accident has been estimated as between ten and twenty percent of these on average. Trains with hazardous materials cars that experienced accidents in 1984 contained a total of 2826 cars with these materials. Of these, 581 were damaged and 100 actually released some part or all of their cargo (FRA, 1985). Statistics for 1982 and 1983 give comparable results (FRA, 1983 and 1984), with the overall fraction of cars being damaged being in the range of 0.21-0.29 (21-29%) and the fraction of these actually releasing cargo being in the range of 0.11-0.20 (11-20%). Data for 1987 give a value of 0.18. Harvey et al (1987) report that the trend has remained constant at about 0.17, for the last several years.

Rates reported in other studies typically reflect accident experience for a year prior to that in which the study was completed (or some average of the preceding years), with many presenting or using an average annual accident rate of 10^{-5} accidents per train-mile. One particular study found that the chance of an accident resulting in a hazardous cargo release was 2×10^{-7} per car-mile for cars conveying Liquefied Petroleum Gases -- LPG for short (Kot et al, 1983). Another reported a rate of 4×10^{-7} spills per loaded car-mile using 1976 data (Chemical

Week, March 15, 1978), while a third reported the chance of a fire occurring as 2.8×10^{-8} per car-mile (Geffen et al, 1980). Note, however, that many of the rates per car-mile that appear in the literature were obtained by dividing the overall accident rate for trains on a mileage basis by roughly 70 cars per train, without accounting for the fact that multiple cars are generally involved in each accident. Thus, such rates must be used with care.

Spill amount distributions for rail accidents are provided by only a limited number of sources. One analyzed 130 accidents to develop the following distribution (Nayak et al, 1983):

Gallons	Fraction of Spills
Less than 1,000	0.37 (37%)
1,000 - 5,000	0.12 (12%)
5,000 - 10,000	0.12 (12%)
10,000 - 25,000	0.22 (22%)
25,000 - 50,000	0.09 (9%)
50,000 -100,000	0.08 (8%)

Although no single tank car can contain so much, spills of 50,000 gallons or more are reported above because more than one car may spill its contents in an accident. The average spill size has also been reported as being 11,100 gallons, with 27% of spills being found to be less than 1,000 gallons, 13% being between 1,000 and 5,000 gallons, 25% between 5,000 and 10,000 gallons and the rest being over 10,000 gallons (ADL, 1978).

Use of Local Data

General accident rates for rail transportation can usually be obtained for individual states and even for individual railroad companies. It is also possible to obtain commodity flow data on this basis, or even at a more local level by contacting the company operating the track of concern. For example, the City of Portland, Oregon found the following commodity breakdown based on number of railcars in a fairly recent effort (Robison, 1981):

Flammable liquids	31.1%
Flammable compressed gases	15.9%
Oxidizers	14.6%
Corrosives	11.7%
Mixed loads	11.5%
Non-flammable compressed gases	9.4%
Class B poisons	3.1%

Other	0.8%
Flammable solids	0.7%
Combustible liquids	0.7%
Explosives A,B,C	0.3%
Radioactive material	0.02%

The Portland researchers point out that this list may over-estimate flammable liquids and underestimate both toxic and flammable liquefied compressed gases.

Harvey et al (1987) give accident rates by material for several materials, ranging from 0.3×10^{-6}/car-mile for chlorine to 9.6×10^{-6}/car-mile for hydrochloric acid. The latter material is thought to have such a high rate in part due to ruptured frangible discs and failure of the rubber lining in the car.

Total mileage of track (excluding yards and sidings) is readily available by state (AAR, 1985) and should also be fairly easy to obtain on a subregional or community basis. In such determinations, the mileage within rail yards will be important not so much in terms of total track available, but rather in terms of total miles travelled by any one train or car on average within the yard. Where local data exist as accident rates or spill frequencies, they can be directly substituted for the values given in the next section.

Suggested Approach for Assessment of Accident Potential

Based on the data presented above, it is suggested that an accident rate of 3×10^{-6} per train-mile be used for mainline track. To convert this to a per car-mile basis, it is assumed that 0.20 (20%) of the cars will be damaged in an accident (based upon data presented in Nayak, 1979). The overall rate therefore becomes $0.2 \times 3 \times 10^{-6}$/ train-miles or about 6×10^{-7} per car-mile.

The accident rate for rail yards is obtained by taking 1.3×10^{-5} accidents per train-mile and a 20% damage estimate to obtain about 3×10^{-6}/car-mile for the track in yards. Sidings also pose a risk, but these risks are considered herein to be overshadowed by those associated with mainline and yard track.

It is suggested that 0.15 (15%) of accidents be assumed as resulting in a spill for both mainline and yard accidents, as no data are available to permit distinctions between these events.

With respect to the distributions of spill amounts in accidents, the available data suggest use of:

- 3,000 gallons ***or*** 10% of cargo (thru 2" hole) - 50% of the time
- 10,000 gallons ***or*** 30% of cargo (thru 2" hole) - 20% of the time
- 30,000 gallons ***or*** total loss of cargo - 30% of the time

The higher weighting of the last category partially accounts for the potential for more than one car to release part of its contents in an accident.

Marine Transportation of Hazardous Materials

Available Accident Data for Marine Transportation

The accidents of concern for marine transportation include collisions (moving and while moored or docked), groundings, and rammings. Accident rates may be expressed as per port call, per transit, per mile, per shipment, or per ton-mile.

An analysis of accident rate estimates for collisions, groundings, and all types of moving vessel casualties in harbors along with moored casualties has demonstrated that accident rates derived from different data bases for various harbors were quite similar, with each type of casualty having accident rate estimates ranging within a single order of magnitude (ADL, 1983). Studies of tank barge casualties by the U.S. Coast Guard (1979) and by the Maritime Transportation Research Board (1981) have tallied 229 collisions, 173 rammings, and 71 groundings from 1972-1976. Although marine traffic data are not available for the same time period, Corps of Engineers data for 1982 permit computation of the following overall accident rates on a per transit basis:

Collision	3×10^{-3}/transit
Ramming	7×10^{-4}/transit
Grounding	3×10^{-4}/transit

Assuming an average trip length of 200 miles, a conservative collision rate in the Gulf Intercoastal Waterway, which is representative of the Intercoastal Waterway and other relatively narrow waterways and rivers, can be estimated as being on the order of 5×10^{-6} collisions/mile. For more highly traveled inland waterways and major rivers, increased traffic levels, higher speeds, and larger tows would be expected to increase the rate of collisions.

The Houston-Galveston Vessel Traffic Service (operated by the U.S. Coast Guard) has compiled statistics showing an annual collision rate within the Service area ranging from 1.5×10^{-4} to 4.7×10^{-4} per transit in the period 1977 to 1984, with a mean value of 2.8×10^{-4} collisions/ transit. Studies of marine casualty rates for conventional self-powered ships and tankers found a grounding casualty rate in the range of 5×10^{-4} to 4×10^{-5} per transit. Moving collisions ranged from 6×10^{-4} to 5×10^{-5} per transit and collisions while moored ranged from

1-7 x 10^{-5} per port call (ADL, 1983). A study by Todd Shipyards (1976) for the Houston-Galveston port system over the five-year period of 1970-1974 calculated a moored casualty rate of 1.8 x 10^{-4} collisions/port call.

The fraction of accidents that result in a discharge were found by the above studies to range from a low value of about 0.01 (1%) for groundings in deep water and collisions involving double hulled vessels to a high of about 0.40 (40%) for collisions involving vessels with single hulls. As reported by Abkowitz and Galarraga (1986), one study found that the percentage of accidents that results in spills does not vary considerably for different causes of accidents. This study suggests that about 0.15 (15%) of the accidents of concern result in spills or discharges.

With respect to the expected volumes of spills, the Coast Guard's Pollution Incident Reporting System (PIRS) provides data indicating the following average spill amounts during 1983:

Commodity	Tank ships	Tank barges
Oil	543 gal	3309 gal
Hazardous substances	108 gal	4301 gal
Other polluting substances	152 gal	84 gal
Total	492 gal	3275 gal

These spill volumes are lower, however, than the averages found in other studies. Abkowitz and Galaraga (1986) have reported average spill size by location and given:

Piers	25,000 gal
Harbors	47,000 gal
Entrances	115,000 gal
Coastal	416,000 gal

Other analyses have found that while more than 70% of all spills are less than 100 gal and 95% or so are less than 10,000 gal (ADL, 1978 and Stewart and Kennedy, 1978), the average spill volume from a marine vessel is on the order of 44,500 gallons (ADL, 1978). One reason for discrepancies among studies is that spills of several million gallons can and do occur on occasion and have the effect of distorting average values for the time periods in which they occur.

Use of Local Data

Local data are available from a variety of sources and can be useful for increasing the accuracy and specificity of accident rate estimates. Marine traffic data for waterways and harbor systems in the United States are compiled annually by the Corps of Engineers and published in a document entitled Waterborne Commerce of the United States. The U.S. Coast Guard keeps records of all major accidents/incidents whether or not they result in a loss of cargo both in regional offices and in a central system in Washington.

Collision and grounding rates have been determined for the seven locations listed in Table F.2 and may be of use to these locales and others with similar characteristics. Each rate is derived from actual location-specific data. The rates for any particular body of water or river, however, may vary from these or national average accident rates as a result of differences in:

- Traffic density
- Vessel design
- Vessel size
- Vessel speeds
- Local weather conditions
- Traffic controls and restrictions, and
- Use of harbor pilots

Where local data exist, they may be used in place of the suggested values given in the next section.

Suggested Approach for Assessment of Accident Potential

Based upon the information and data presented above, and given the understanding that harbors and inland waterbodies are of greater concern than shipping activities on the open ocean and/or otherwise distant from coastlines (in terms of the distances typically associated with spill effects that may pose a threat to human life and health), accident rates and other spill characterization factors are presented below for:

- Collisions in lakes, rivers, and intercoastal waterways
- Groundings in lakes, rivers, and intercoastal waterways
- Collisions and groundings in harbors and bays
- Collisions/casualties while vessels are moored/docked

An accident rate of 10^{-5}/mile of travel is suggested for use for collisions in the first category to cover both the lower expected accident rates on certain slow speed waterways and the higher ones for congested, highly utilized routes. Based on Gulf Intercoastal Waterway (ICWW) statistics, a grounding casualty rate of 5×10^{-6}/ mile is suggested for the serious type

TABLE F.2
LOCATION SPECIFIC CASUALTY RATES

Location	Casualty/Mile	Collisions and Groundings/ Harbor Transit
Mobile	1.22×10^{-4}	2.89×10^{-3}
Houston Ship Channel	7.78×10^{-5}	2.08×10^{-3}
Corpus Christi	1.80×10^{-4}	1.81×10^{-4}
Combined Gulf Ports	9.27×10^{-5}	2.11×10^{-3}
Delaware Bay	3.61×10^{-5}	1.22×10^{-3}
Providence	1.03×10^{-4}	7.06×10^{-4}
Combined Atlantic Ports	3.74×10^{-5}	1.78×10^{-3}

Reference: Abkowitz and Galarraga, 1986

of grounding which could lead to a release. Note that this is also a "per mile" rate. The harbor/bay area grounding and collision rate given below is "per transit", while the moored collision rate is "per port call." (There are two transits per port call.) The suggested rate for groundings and collisions in a harbor area is 10^{-3}/transit, while the suggested casualty rate for moored or docked vessels is 2×10^{-4} per port call.

If no distinction is being made with regard to vessel type and construction, it should be assumed that 0.15 (15%) of accidents result in actual loss of cargo to the environment. Alternatively, it can be assumed that accidents involving single-hulled vessels result in cargo loss 0.25 (25%) of the time and that accidents involving double-hulled and bottomed watercraft result in cargo loss 0.05 (5%) of the time.

The recommended distribution of spill amounts is:

- 10% loss of cargo in one tank/compartment -- 35% of the time
- 30% loss of cargo in one tank/compartment -- 35% of the time
- Full loss of cargo in one tank/compartment -- 30% of the time

This distribution is somewhat more "severe" than those provided by the spill distributions presented earlier because those distributions are heavily influenced by minor fitting leaks and the like.

Transportation of Hazardous Materials by Pipeline

Available Accident Data for Pipelines

Failure rates for pipelines are generally given in terms of failures per unit length per year. Specific data sources may indicate failure rates by product carried, by diameter, and even by year of installation. This section presents some of the failure rates and other statistics given in the literature. Values recommended for use in emergency response planning are given in a later subsection.

Two studies have focused on the differences between oil and gas pipelines and onshore and offshore pipelines (de la Mare and Andersen, 1980 and Andersen and Misund, 1983). Each concluded that the differences in failure rates showed more of a diameter-dependent effect (the rate decreases as the diameter increases) than anything else. The later study came up with two basic results -- an overall pipeline failure rate of about 1.5×10^{-3} per mile per year for all diameters, and one of about 5×10^{-4} per mile-year for pipelines with a diameter of 20 inches or greater. These rates were derived from several studies which all had extremely consistent results. Fourteen years of data for gas transmission and gathering lines in the U.S. are also very consistent with these rates (Jones et al, 1986).

Unlike transportation by marine, truck, or rail which can have accidents/incidents without a release of hazardous materials, a pipeline failure or accident by definition involves a release (or partial release) of contents. In the event that there is a failure in a pipeline, most often the outcome will be a small leak. The leak may persist for a long period of time, however, before being detected. This can lead to a larger total volume being released than one would otherwise have expected.

Historical data on spill size distribution includes an average spill size of 8,060 gal, with the following spill size breakdown (ADL, 1978):

Gallons	
Less than 100	23%
500 - 1,000	15%
1,000 - 5,000	8%
10,000 - 25,000	23%
5,000 - 10,000	8%
More than 100,000	23%

The average spill size for polluting incidents was found to be (U.S. Coast Guard, 1983): 5,140 gal for oil spills, 350 gal for hazardous substances, and 4,980 gal for all polluting materials.

The chance of pipelines rupturing has been estimated in a number of studies to be on the order of 10% - 20%. One study of a propane pipeline cited a figure of 14% (Grollier Baron et al, 1976). Jones et al (1986) classifies almost 36% of all releases as ruptures, but uses many definitions of rupture. Very few studies have detailed data on hole size.

It has been estimated that about one-third of natural gas pipeline ruptures ignite, with this estimate increasing to 45% for very large ruptures. Of the leaks which ignite, a further 30% are estimated to explode (Kot et al, 1983). Other data sources (including Jones et al, 1986) are consistent with this or slightly lower.

Use of Local Data

While using national or worldwide pipeline accident rates can accurately estimate the likelihood of releases from oil or gas pipelines, these rates may overestimate failures for lines with no internal corrosion possibilities or with many protective design features. Likewise,

failures may be underestimated if there is an extremely corrosive material involved or if other factors pose a greater than average risk. Using local or state data on lines could reflect some of these differences, if sufficient information was available.

Suggested Approach for Assessment of Accident Potential

Based on the information presented above, an accident rate of 1.5 x 10^{-3}/mi-yr is suggested for lines of unknown size or lines less than 20" in diameter. For pipelines with diameters greater than or equal to 20", a rate of 5 x 10^{-4}/mi-yr is proposed.

With due consideration to data limitations and the capabilities of pipeline discharge consequence analysis procedures presented in this guide, the following spill size distribution is suggested for analyzing pipeline releases of hazardous materials:

- Discharge computed using consequence analysis procedures of Chapter 12 assuming a complete line break along the route of the pipeline - - - - - 20% of the time
- 1 hour release through 1" hole - - - - - 80% of the time

Handling of Hazardous Materials at Fixed Facilities

Available Accident Data for Fixed Facilities

Most accident data for fixed facilities focuses on incidents in which fatalities occurred, although polluting incidents are also reported to some level of compliance. More important, however, is the fact that what information is recorded does not include the necessary exposure information to determine accident rates. Data are presented below to demonstrate the type of information available. The approach and values recommended for use by emergency planners are presented in a later subsection.

One very large plant was reported as having a total of 110 spills in 1973 -- 23 in the marine terminal area (with an average spill volume of 2000 gal) and 87 spills in the plant area (with an average spill volume of 1000 gal). Many of these were contained onsite and corrected (Carlson et al, 1974).

In the area of loading/unloading spills, very little data is available specifically for rail cars. Just as for trucks there is a potential for overfills of the receiving storage tank or the rail car, depending on which is being filled. Trucks, however, are often emptied/filled by the driver as opposed to plant personnel. The spill distributions given a little farther below incorporate the results of the reported spills in these areas. While one study found that storage vessels were about twice as likely to be the cause of injuries and fatalities as other in-plant events, loading and unloading operations were also cited for causing injuries and fatalities (Industrial Economics, 1985).

Upset conditions were cited as being responsible for less than 5% of the release events, except for process vessels where the percentage rose to 13% (Industrial Economics, 1985). These figures give credence to the concept of basing accident rates on equipment failure rates rather than historical release data. COVO (1982) and Considine et al are two sources of some of the needed failure rate data, many others are also available.

The relative hazards of process versus storage activities have been an ongoing topic of debate, with the common theory being that process activities are much less safe. However, it has been shown that for large numbers of fatalities (as is the concern of this report) this is not the case, because of the large volumes generally involved in storage areas (Lees, 1983). This same study also reported on the frequencies of fires in various types of facilities in 1977:

Refineries	> 1/year
Natural gas plants	3.7×10^{-2}/year
Tank farms	1.1×10^{-2}/year
Bulk terminals-shore	2.1×10^{-2}/year
Bulk terminals-inland	1.0×10^{-2}/year

Fires are of particular concern in warehouses and other storage situations where they may be the most likely cause of a hazardous materials release, at least for significant releases. (Forklift handling of various storage containers is very likely to damage packages, but the damage will generally be quite limited and any releases readily controlled.)

An analysis performed by the NFPA Fire Analysis Division showed the following average annual number of fires, based on 1980 to 1983 data:

Florist shops, greenhouses	569
Gasoline service stations	1789
Chemical, medical laboratories	172
Agricultural laboratory	22
General research laboratory	733

The exact exposure in each of these categories is not known, but as a rough upper bound it can be assumed that the average rate of fires per property is 10^{-3}/year (perhaps higher for gasoline service stations).

Spill size information is widely variable, again reflecting the diversity of facilities falling into this category. One study (ADL, 1978) found the following distributions:

	Avg.Spill	<100 gal	100-500	500-1000	1000-5000	>5000
Fixed facility Loading/unloading	18,110 gal	48%	20%	7%	14%	11%
- truck	300	50%	50%			
- rail	7,390	11%	33%	12%	22%	22%
- marine	7,840	68%	20%	2%	4%	6%

The average for marine is very high relative to the distribution because of a few very large releases.

Another study found that the average spill sizes for polluting incidents were (U.S. Coast Guard, Calendar Year 1982 and 1983):

Non-Transportation Spills	Oil	Hazardous Substances	Total
Refinery	400 gal	12,500	1,530
Bulk storage	1,290	210	1,240
Onshore production	4,660	--	5,660
Offshore production	95	114	95
Marine Facilities			
Fuel transfer	310	--	320
Bulk transfer	510	1,290	500
Non-bulk transfer	55	--	190
Land Facilities	400	100	460

Use of Local Data

Local data is obviously critical in terms of determining the exposure, but is not as important for determining accident rates, because of the approach outlined below. If a particular facility has completed a risk assessment for some reason, and makes the results of this study available to the local emergency response planner, then the study's release estimates may be replaced for the analysis called out below. The relative rarity of some of the failures makes it very unlikely that local historical data will include the full range of potential release events.

Local or regional data may also be used to determine spill size estimates if insufficient information is provided by the facilities of concern. EPA regions tend to provide semi-annual summaries of the releases reported to them.

Suggested Approach for Assessment of Accident Potential

Based upon the information presented above, the approach suggested for getting a handle on fixed facility risks is to consider three basic types of release events for plants; one or two release scenarios for facilities such as water treatment plants, laboratories and industrial facilities; and one release scenario for warehouses and other facilities storing hazardous materials. It has been shown that very little specific historical information exists upon which to base accident rates. Hence, the best approach is to look at equipment failure rates. The increasing use of physical barriers to limit spills, drainage systems to channel spills and venting and scrubbing systems to control releases all help to render this simplified accident estimation procedure more meaningful.

For example, a large facility may be coarsely modelled as having storage operations, loading/unloading operations, and processing operations. These can respectively be represented by storage tank failures and leaks, hose failures, and piping and process vessel failures. The rates suggested for each of these are:

Storage tank - double walled	10^{-6}/tank-year
Storage tank - single walled	10^{-4}/tank-year
Pressure vessels	10^{-4}/vessel-year
Piping	1.5×10^{-6}/ft-year
Loading hoses	10^{-4}/operation or 10^{-2}/hose-year

While these certainly do not cover all potential release scenarios, they do capture some of the more likely ways to lose large volumes of material. The only piping of prime concern is that of relatively large diameter and long segments. In other words, a 100-foot expanse of 8" pipe should be counted if it contains hazardous materials, but not 10 or 20 foot sections between vessels. The spill size is generally taken to be a function of the specific release scenario since historical averages are difficult to apply.

For the middle category of industrial users, water treatment plants, laboratories, etc., the main focus should be on storage tank or container failures. Piping failures or loading hose failures may be considered if there is a significant amount of piping (say over 100 feet) or if there are a lot of loadings/unloadings (say 10 or more per year). The rates to be used are the same as those listed above.

Storage of hazardous materials, such as in warehouses or greenhouses, may also result in failures of storage containers, but the greater threat here is probably from a fire which spreads to the storage area and results in release, ignition, explosion, and/or combustion of stored materials (with attendant evolution of potentially toxic smoke). The occurrence rate of such fires is suggested to be 10^{-3}/yr, with a release of 10% to 100% of the stored volume. This is one area in which more specific local data and information would be particularly helpful for better definition of scenarios and estimation of their likelihood.

The approach of this section is not to cover all potential sources of hazardous materials releases, but to cover some of the larger and more likely events.

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