ANL/DIS-13/22

Development of the Table of Initial Isolation and Protective Action Distances for the 2012 Emergency Response Guidebook

Decision and Information Sciences Division

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Development of the Table of Initial Isolation and Protective Action Distances for the 2012 Emergency Response Guidebook

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December 2013

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NOTATION

The following is a list of the acronyms, initialisms, and abbreviations (including units of measure) used in this document.

ACRONYMS AND ABBREVIATIONS

ABL	atmospheric boundary layer
ACGIH	American Conference of Governmental Industrial Hygienists
AEGL	Acute Exposure Guidance Level (National Research Council)
AIHA	American Industrial Hygiene Association
BCl_3	boron trichloride
CAS	Chemical Abstracts Services
CASRAM	Chemical Accident Statistical Risk Assessment Model
CBL	convective boundary layer
CFR	*Code of Federal Regulations*
c_p	specific heat at constant pressure
c_v	specific heat at constant volume
CWIC	crosswind-integrated concentration
DOD	U.S. Department of Defense
DOE	U.S. Department of Energy
DOT	U.S. Department of Transportation
DTRA	Defense Threat Reduction Agency
EEGL	Emergency Exposure Guidance Level (National Research Council)
EEL	Emergency Exposure Level (*AIHA Journal*)
EHS	extremely hazardous substance
EPA	U.S. Environmental Protection Agency
ERG	Emergency Response Guidebook
ERPG	Emergency Response Planning Guideline (AIHA)
ERPG-1	ERPG Level 1
ERPG-2	ERPG Level 2
ERPG-3	ERPG Level 3
GDP	gross domestic product
GLB	Great Lakes Buoy
HCl	hydrogen chloride
HF	hydrogen fluoride
HMIS	Hazardous Materials Information System

IDLH	immediately dangerous to life and health (NIOSH level)
IID	Initial Isolation Distance
IIZ	Initial Isolation Zone
LC	lethal concentration
LC_{50}	median lethal concentration (lethal to 50% of exposed population)
LC_{LO}	lowest reported lethal concentration
LD	lethal dose
LD_{50}	median lethal dose (lethal to 50% of exposed population)
LD_{LO}	lowest reported lethal dose
LOAEL	lowest observed adverse effect level
LOC	level of concern (EPA)
NAC	National Advisory Committee
NIOSH	National Institute for Occupational Safety and Health
N_2O_4	nitrogen tetroxide
NOAA	National Oceanic and Atmospheric Administration
NOAEL	no observed adverse effect level
n.o.s.	not otherwise specified
NRC	National Research Council
NREL	National Renewable Energy Laboratory
OSHA	Occupational Safety and Health Administration
PAD	Protective Action Distance
PAZ	Protective Action Zone
PEL	permissible exposure limit (OSHA)
PHMSA	U.S. Department of Transportation Pipeline and Hazardous Materials Safety Administration
RTECS	Registry of Toxic Effects of Chemical Substances
SBL	stratified boundary layer
SCAPA	Subcommittee on Consequence Assessment and Protective Actions (DOE)
SEB	surface energy budget
SEBMET	Surface Energy Budget Meteorological (model)
SO_3	sulfur trioxide
STEL	short-term exposure limit (ACGIH)
TEEL	temporary emergency exposure guideline (DOE)
TIH	toxic by inhalation
TIHWR	toxic by inhalation by water reaction
TLV	threshold limit value (ACGIH)
TWA	time-weighted average
UN	United Nations

USGS	U.S. Geological Survey
WQN	Water Quality Network

UNITS OF MEASURE

°C	degree(s) Celsius
ft	foot (feet)
g	gram(s)
gal	gallon(s)
h	hour(s)
K	degree(s) Kelvin
kg	kilogram(s)
km	kilometer(s)
kPa	kilopascal(s)
L	liter(s)
m	meter(s)
m^2	square meter(s)
m^3	cubic meter(s)
mg	milligram(s)
mi	mile(s)
min	minute(s)
mL	milliliter(s)
mm	millimeter(s)
mmol	millimole(s)
mph	mile(s) per hour
Pa	Pascal(s)
ppm	part(s) per million
s	second(s)
s^2	second(s) per second
µL	microliter(s)
µm	micrometer(s)

ABSTRACT

The transportation of hazardous materials creates numerous opportunities for the release of toxic substances into the environment as a result of traffic accidents, train derailments, equipment failures, and human error. Many of these toxic substances pose acute hazards to the general public and the emergency response personnel who are the first to arrive at the scene of a release. To help first responders determine whether a shipment is potentially hazardous and decide what actions should be taken if a toxic spill does occur, the Emergency Response Guidebook (ERG) is published by the U.S. Department of Transportation (DOT), Transport Canada, and Secretariat of Transport and Communications of Mexico.

The ERG provides information on fire-fighting and mitigation strategies as well as on potential health effects associated with various chemicals, which it lists under their proper shipping names and four-digit United Nations (UN) identification numbers. The ERG also provides Initial Isolation Distances (IIDs) and Protective Action Distances (PADs) for a subset of the chemicals that are toxic by inhalation (TIH) or that react with water to produce TIH gases (TIHWR). The IID identifies the radius of a zone around the release that should be accessed solely by people directly involved in emergency response activities. The PAD is the downwind distance from the release defining a zone in which persons should be either evacuated or sheltered in place, depending on the nature of the population at risk (e.g., their density, age, health) and the severity of the incident.

This report provides the technical documentation for the values in the ERG2012 "Table of Initial Isolation and Protective Action Distances" and other information appearing in the ERG Green Pages. The goal of choosing the PADs specified in the Guidebook is to balance the need to adequately protect the public from exposure to potentially harmful substances against the need to minimize the risks and expenses that could result from overreacting to a hazardous materials incident. To quantify this balance, a "level of protection" is defined to represent the probability that the listed PAD would allow sufficient protection of the public. A 90% level of protection has been used in PAD estimation since the 1990s.

Quantitative analysis of the level of protection requires a statistical approach to specify the PAD. To achieve this objective, the best available information was used to analyze accident scenarios. The result was a set of up to 1,000,000 hypothetical incidents for each material. Each set accounts for differences in container types, incident types, accident severities (i.e., amounts released), accident locations, times of day, times of year, and meteorological conditions involved. Each scenario was analyzed by using detailed emission rate and atmospheric dispersion models to calculate the downwind chemical concentrations for which a "safe distance" was determined. "Safe distance" is defined as the distance downwind from the source at which the chemical concentration falls below a health protection criterion for that material. The criteria used are the National Research Council's Acute Exposure Guideline Level 2 (AEGL-2), the American Industrial Hygiene Association's Emergency Response Planning Guideline Level 2 (ERPG-2), or equivalent guidelines. The AEGL-2 and ERPG-2 criteria denote the highest chemical concentration at which persons will suffer no irreversible or other serious health effects that could impair their ability to take protective action. The statistical sample of

safe distance values for all incidents for each material was separated into four categories: small spill/daytime release, small spill/nighttime release, large spill/daytime release, and large spill/nighttime release. The 90th-percentile safe distance values for each of these groups are the PADs that appear in Table 1 of the Green Pages of the ERG. For the six most commonly shipped TIH materials, PADs are further refined for various containers (e.g., tank truck, railcar, ton cylinders, etc.) and three wind speed conditions in Table 3 in the Green Pages. Details of this table and its development are highlighted below.

As described in the report, much of the overall methodology used to produce the Initial Isolation and Protective Action Distances is unchanged from the ERG2008 and its companion report. Specific improvements and changes in the methodology from the ERG2008 are noted below.

1. A variety of new ERPG and AEGL data through January 2012 have been added to the analysis routine. In particular, we added more than 40 interim AEGLs. This dramatically reduced the reliance on LC_{50}-based health criteria. As a result for the ERG2012, AEGL values or AEGLs for structurally similar chemicals formed the basis of the health criteria for 90 of 164 chemicals on our TIH list (55%), and ERPG values or ERPGs for structurally similar chemicals formed the health criteria basis for 34 chemicals (21%). For 35 chemicals (21%), LC_{50} values or LC_{50} values for structurally similar chemicals were used to develop the health criteria, and for 5 chemicals (3%), LC_{LO} values formed the basis of the health criteria.

2. For the six most commonly shipped TIH materials, we developed a new table to complement the "Table of Initial Isolation and Protective Action Distances" (Table 1 in the Green Pages). This is referred to as Table 3 in this report and provides more detailed PAD estimates applicable for large spills. Specifically, this table provides PAD estimates for several transportation containers (e.g., tank truck, railcar, ton cylinders, etc.) and for three wind speed conditions. These *container-specific* tables are available for chlorine, ammonia, hydrogen chloride, hydrogen fluoride, sulfur dioxide, and ethylene oxide. The distances appearing in these tables are also 90th-percentile values, but are taken from a smaller subset of the scenario library corresponding to the applicable container type and wind speed range.

3. We updated the meteorological database used in the statistical scenario analysis to include 204 United States weather stations for the years 1996–2005.

4. We initiated a study to address the reactivity and depletion of chlorine and a several other widely transported chemicals. The reactivity of these materials in the environment and the resulting chemical depletion has been identified as a significant gap in current understanding of hazardous material releases. Analyses in the literature have demonstrated that distances to AEGL-3 concentrations are substantially reduced for reactive materials, if simple

surface deposition (reactivity with surface matter) is factored into the modeling. However, there are insufficient empirical data available to estimate these reactivity effects to a satisfactory level of confidence, so these considerations were not included in preparation of the ERG2012. To address this gap, we have initiated an experimental program to address and quantify these effects. These data together with observations in the literature will be used to include these effects in preparation of the ERG2016.

1 INTRODUCTION

The transportation of hazardous materials creates numerous opportunities for the release of toxic substances into the environment due to traffic accidents, train derailments, equipment failures, and human error. Such releases can pose serious acute hazards to the general public and to emergency response personnel who are the first to arrive at the scene. To help first responders determine whether a shipment is potentially hazardous and decide what actions should be taken if a toxic spill does occur, the Emergency Response Guidebook (ERG) is published by the U.S. Department of Transportation (DOT), Transport Canada, and Secretariat of Transport and Communications of Mexico. The most recent version is the 2012 edition of the ERG (DOT et al. 2012), titled *2012 Emergency Response Guidebook* (hereafter referred to as ERG2012). The ERG provides essential information on fire-fighting, spill response, and potential public health effects. For chemicals that are toxic by inhalation (TIH) and chemicals that produce TIH gases upon reaction with water (TIH by water reactivity or TIHWR), the ERG provides Initial Isolation Distances (IIDs) and Protective Action Distances (PADs). The IID defines the radius of the zone around the spill that should be accessed solely by people who are directly involved in emergency response. The PAD is the distance downwind from the source of the release to which persons should be either evacuated or sheltered in place, depending on the severity of the incident and the nature of the population (e.g., density, age, health).

This report was prepared to document the methodology used to prepare the ERG2012 "Table of Initial Isolation and Protective Action Distances" (hereafter referred to as "the Table"). The PADs in the Table were calculated to balance the need to adequately protect the public from exposure to potentially harmful substances against the risks and expenses that could result from overreacting to a spill. In determining the PADs, this balance was quantified in terms of a level of protection; namely, the probability that the listed PAD will allow sufficient protection of the public. The level of protection adopted for the ERG was 90%. Clearly, a quantitative analysis of the level of protection requires a statistical approach, the underlying technical basis of which is described in this report, together with the pertinent chemical and incident data required for the analysis.

1.1 OVERVIEW OF THE EMERGENCY RESPONSE GUIDEBOOK

The ERG is designed for use by first responders to determine the appropriate level of action during the initial stages of an incident involving the transportation of hazardous materials. Although first responders are knowledgeable in the field of law enforcement and public protection, they are usually not experts on hazardous materials. The ERG thus provides a compact source of essential information on which to base reasonable decisions under often difficult conditions.

As noted, for TIH materials, the ERG provides the "Table of Initial Isolation and Protective Action Distances." Figure 1.1 illustrates the basic information presented in the Table and its application. To properly use the Table, a responder must first determine the following:

- United Nations (UN) identification number and/or proper shipping name of the material being transported;

- Direction of the prevailing wind;

- Whether the spill is small or large—a small spill is one that involves a single, small package (e.g., a drum containing up to approximately 208 L [55 US gal]), a small cylinder, or a small leak from a large package;

- Whether it is day or night; and

- Any special conditions that could preclude the use of the values given in the Table (e.g., releases of multiple tank cars, topographical anomalies, etc.).

As depicted in Figure 1.1, releases of TIH materials result in downwind concentrations of vapor that decrease with distance from the release point (assuming that the release is not buoyant). At some downwind distance, the concentration decreases to a level below which no protective action is necessary. This distance is the PAD. The Protective Action Zone (PAZ) is defined as a square region that has a side that is equal in length to the PAD and lies downwind and symmetrical to the accident location. Note that since the PAZ lies downwind of the spill location, the first responder must first ascertain the wind direction to correctly use the information in the ERG. Since wind direction knowledge is inherent in the PAZ definition, the PAZ does not need to be circular.

The IID specifies a circular zone surrounding the accident site. Persons not involved with the response should be kept clear of this zone. Persons in the Initial Isolation Zone may be exposed to potentially life-threatening health effects downwind of the accident site and to dangerous concentrations upwind because of variabilities in the direction of the wind. The IIDs are specified in a method analogous to that used for specifying the PADs.

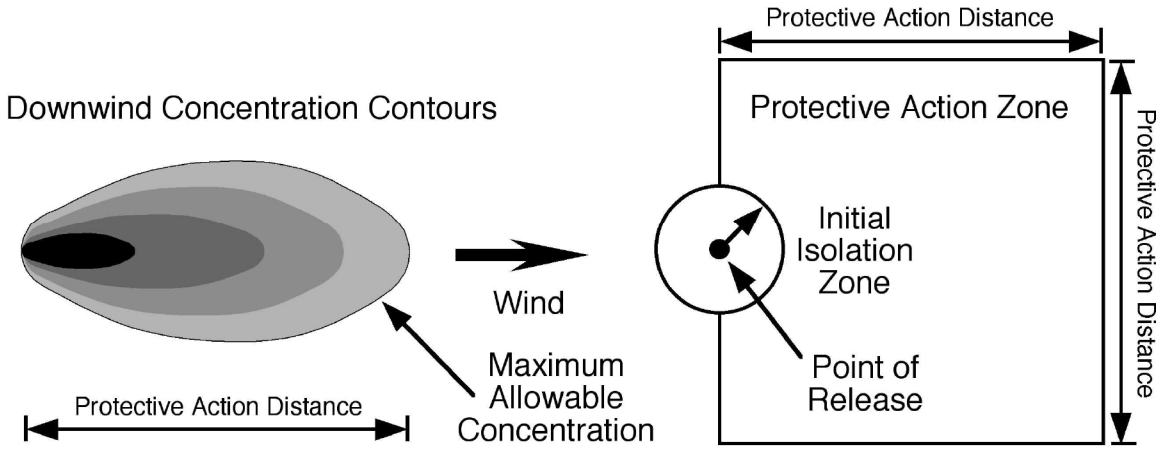

FIGURE 1.1 Illustration Showing How the ERG2012 Defines the Initial Isolation Zone and Protective Action Zone for Use by a First Responder

The range of cases for which the ERG could be used is considerable, covering everything from a minor leak from a compressed gas cylinder to one or more catastrophically ruptured tank cars. However, the space requirements necessary to address the entire range of cases for all the TIH materials in the ERG would be prohibitive. To narrow the range of cases for which a particular PAD is employed and keep the number entries listed in the ERG reasonable, four PAD values are provided for each material that address (1) whether the incident involves a small spill or a large spill and (2) whether it occurs during the day or night. Here, a small spill is defined as the spillage of a single drum or cylinder, or a small leak from a bulk container corresponding to the limits defined previously. Whether the spill occurs during the day or night is very important in considering downwind dispersion of the released chemical, as discussed in Section 3. Of course, a multitude of other weather and spill variables such as wind speed, cloud cover, and time (apart from just day or night) can greatly affect the necessary PAD for a specific incident. For this reason, we have adopted a statistical approach to determine the percentage of time a PAD will be sufficient in actual accidents.

While space considerations preclude PAD estimates for more specific wind speed and release scenarios for the entirety of the TIH list, the 2012 ERG does include more specific information for six chemicals that represent the vast majority of all TIH transportation incidents for which the ERG2012 might be consulted. These entries comprise Table 3 of the ERG2012 and include container- and wind speed-specific PAD estimates for the following chemicals:

- Ammonia (UN 1005)
- Chlorine (UN 1017)
- Ethylene oxide (UN 1040)
- Hydrogen chloride (UN 1050, UN 2186)
- Hydrogen fluoride (UN 1052)
- Sulfur dioxide (UN 1079).

1.2 ORGANIZATION OF THIS REPORT

Section 2 presents a detailed overview of the methodology used to calculate the IIDs and PADs. Included in this discussion is an examination of issues related to the TIH list; treatment of generic compounds, mixtures, and solutions; treatment of chemical warfare agents; and treatment of water-reactive materials. Section 3 provides details on the statistical scenario analysis applied to materials in the Table, as well as technical details on the consequence models used. Section 4 documents the health criteria, or threshold chemical concentrations, used to specify the IIDs and PADs. Section 5 discusses the safe distance distributions developed as a result of the analysis and describes how the PADs were determined from these distributions. Appendixes A and B present Tables 1 and 3 in the ERG2012 Green Pages (DOT et al. 2012). Appendixes C–D

contain chemical data and details of the experiments conducted to identify and quantify TIH gas emission rates from water-reactive materials.

2 GENERAL METHODOLOGY

The methodology used in preparing the Table for the ERG2012 is illustrated schematically in Figure 2.1. The starting point for the analysis is the list of TIH materials developed by DOT and Transport Canada (see discussion in Section 2.1). This list contains few additions to and deletions from the ERG2008 list. For each material in the list, the authorized mode of shipping, as outlined in the *Code of Federal Regulations* (CFR), is combined with commodity flow information and historical incident data to develop a shipment profile. Shipment profiles, which are discussed in Section 2.2.1, are used in the analysis to determine the types of transportation incidents that could occur for particular materials or classes of materials.

The shipment profiles are then used to conduct a statistical analysis of accident scenarios. The result of this analysis is a set of up to 1,000,000 hypothetical incidents based on the best available statistical data. The set accounts for variability in container type, incident type, accident severity (i.e., release amount), location, time of day, time of year, and meteorology. Several of the important release parameters are selected from statistical distributions of transportation-related hazardous material releases cataloged in the Hazardous Materials Information System (HMIS) database maintained by the DOT Research and Special Programs Administration.

Each scenario is then analyzed by using detailed emission rate and atmospheric dispersion models to calculate an airborne chemical concentration footprint. The safe distance for a specific scenario is then chosen as the greatest downwind distance at which the concentration exceeds the health criteria for the chemical involved in the incident. The health criteria, which are exposure-time–dependent threshold concentrations, are based on the Acute Exposure Guideline Level 2 (AEGL-2) or an equivalent guideline, as detailed in Section 4. The safe distance estimates for the entire set of hypothetical incidents considered in the analysis provide a distribution of safe distances that correspond to the many transportation-related releases that could occur. In Table 1 in the Guidebook, incidents are then categorized by time (day, night) and spill size (60 gal or less = small, more than 60 gal = large). The PADs appearing in this table are then selected as the 90th-percentile values for these individual categories. The Initial Isolation Zones (IIZs) are calculated in a similar manner on the basis of health criteria for life-threatening effects.

For the six most commonly shipped TIH materials, PADs are further refined for various containers (e.g., tank truck, railcar, ton cylinders, etc.) and three wind speed conditions in Table 3 in the ERG. These *container specific* tables are a new addition to the ERG for the 2012 edition and are available for chlorine, ammonia, hydrogen chloride, hydrogen fluoride, sulfur dioxide, and ethylene oxide. The distances appearing in these tables are also 90th-percentile values, but are taken from a smaller subset of the scenario library corresponding to the container type and wind speed range.

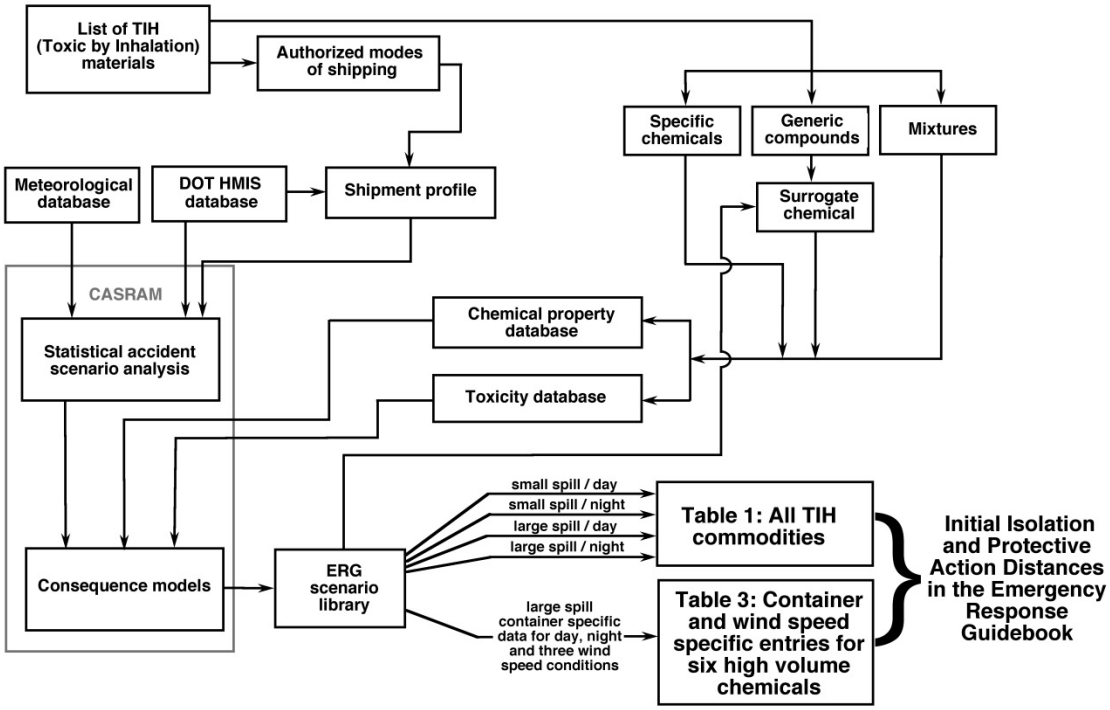

FIGURE 2.1 Schematic of the Methodology Used to Prepare the ERG2012 Table of Initial Isolation and Protective Action Distances

2.1 TIH LIST

2.1.1 Background

For the purposes of our analysis, we classify materials on this TIH list into several different categories as follows: (1) pure chemicals, (2) mixtures, (3) solutions, and (4) generics (e.g., UN 1953: compressed gas, flammable, poisonous, n.o.s.). (The abbreviation n.o.s. stands for not otherwise specified.) As is explained later, generic compounds are further divided into subcategories on the basis of Hazard Zone designation, as defined in Title 49, Part 173, Section 133 of the CFR (49 CFR 173.133). TIH materials fall into four Hazard Zones for gases (A, B, C, and D) and two for liquids (A and B). The ERG2012 lists PADs for 156 single compounds, 15 mixtures, and 26 generics. In addition, 82 water-reactive materials, defined here as materials that emit a TIH gas upon contact with water, are also included in the TIH list. Of the 82 water-reactive materials in the Table, several are also TIH compounds that produce a secondary, sometimes more toxic TIH gas upon reaction with water.

Each category is handled individually. Single chemicals are specified according to a Chemical Abstracts Services (CAS) number, which is a unique numerical identifier for each chemical compound. A unique identifier is necessary to avoid problems with chemical name synonyms. It is important to note that the UN number is not a unique identifier, in that two or more chemicals may be associated with a particular UN number. One example is UN 1076,

which is used for both phosgene (CAS 75-44-5) and diphosgene (CAS 503-38-8), materials with structural similarities but markedly different physical properties. Mixtures are treated by considering the individual components in the mixture. Generics are modeled by using a surrogate compound, with the surrogate being the worst case of the materials considered for the particular generic description and Hazard Zone. Mixtures and generics are discussed in Section 2.3. Water-reactive materials are treated in a manner similar to that used for treating regular TIH materials, with modifications to the physical models for determining the source emission rate. The treatment of water reactivity is discussed in Section 2.4 and Appendix D.

2.1.2 Changes in the TIH List for the ERG2012

There were relatively few substantive changes made in the TIH list for the 2012 Table. Wording revisions and synonym entry additions and deletions resulted in the addition and removal of a few entries in order to bring the names in the Table into agreement with UN naming conventions as of January 2011.

For future editions of the ERG, Argonne recommends deletion of coal gas (UN 1023) and oil gas (UN 1071). These are officially TIH materials; however, our analysis of the mixture constituents for these materials indicates that the median lethal concentration (lethal to 50% of the exposed population; LC_{50}) is well above 10,000 parts per million (ppm). Argonne recommends the addition of acrylonitrile (UN 1093) and methylamine (UN 1061). Acrylonitrile is a liquid with a vapor pressure of 11.9 kPa at 20°C, so in order to fit the criteria as a Hazard Zone B liquid, the LC_{50} would need to be below 1,000 ppm per 49 CFR 173.333. Several references cited in developing National Institute for Occupational Safety and Health (NIOSH) "immediately dangerous to life and health" (IDLH) values indicate that the 1-h LC_{50} may be below 1,000 ppm (see www.cdc.gov/niosh/idlh). Methylamine is a gas. The reference used to set the IDLH value indicates that 1-h LC_{50} is below 5,000 ppm, the necessary criterion to become a Hazard Zone D gas. For reference, if acrylonitrile and methylamine were included in the Table, the large night spill PADs for them would be 0.52 and 1.62 mi, respectively.

2.2 SHIPMENT AND RELEASE SCENARIOS

To specify a level of protection as defined previously, we constructed a set of representative accident scenarios for each material on the TIH list. The first step in this process was to segregate the total transportation of the particular TIH material into a set of discrete shipments by using shipment profiles. Shipment profiles specify the bulk and package freight containers typically used in transporting the material as well as the relative frequency that each container is involved in an incident. The goal of this analysis was to assign each chemical a set of representative shipments that reflect its transportation in the United States. Specification of shipment profiles is discussed in Section 2.2.1. These shipment profiles were used with the Chemical Accident Statistical Risk Assessment Model (CASRAM) to simulate tens of thousands of accidents for each chemical in a fashion similar to that used by Brown et al. (2001).

For each shipment, analyses are conducted for two types of releases: those occurring (1) during a traffic accident or a train derailment and (2) while en route from the origin to the destination but not during an accident or derailment. These release types are referred to as (1) accident-related releases and (2) en route/nonaccident releases. The latter category includes releases occurring as a result of cargo shifts, valve failures, corrosion-induced container failures, etc. Such releases are much more common than accident-related releases, as shown by the HMIS incident data for many container types (several of which are not used to transport TIH materials) summarized in Table 2.1. However, most en route/nonaccident releases are minor.

A special case within the shipment profile concept is the treatment of chemical warfare agents. These materials were first considered in the ERG2000. In 2000, entries were given for two release scenarios: (1) transportation-related release scenario and (2) weapons-related release scenario in which the material is released in a criminal or terrorist act. However, the transportation-related release scenario was removed in 2004 (but retained for those agents that have a proper shipping name and are TIH). The treatment of chemical warfare agents is outlined in Section 2.2.2.

2.2.1 Shipment Profiles

The starting point for the development of shipment profiles is 49 CFR 172.101 and associated subsections that specify the authorized shipping modes and packaging for hazardous materials. These specifications substantially influence the amount of material that could be released in a transport-related accident and other important factors that govern the release hazard, such as the relative frequencies of each container type being involved in a release and the

TABLE 2.1 Ratio of en Route/Nonaccident Releases to Accident-Related Releases for Various Container Types as Derived from the HMIS Database for 1990–2005

Container Type	Ratio of en Route/Nonaccident Releases to Accident-Related Releases
111AW tank car	13
112JW and 105A tank car	24[a]
DOT 306 cargo tank	0.2
DOT 307 cargo tank	2.2
DOT 312 cargo tank	3.3
MC 330/331 cargo tank	0.5
Small and medium drums	20
Large drums and portable tanks	7
Package freight cylinders	5

[a] For the 2012ERG analysis, the ratio for 111A tank cars is used for TIH liquids transported in Types 112JW and 105A tank cars.

discharge fractions resulting from releases (the amount of material released in an incident relative to the container capacity). For example, most Division 2.3 gases under Hazard Zone A cannot be transported in bulk form. Consequently, such materials are shipped only in package freight containers (drums, cylinders). The resultant total shipping volumes are thus much less than those associated with a typical bulk shipment, even though there can be many package freight containers in a single shipment.

The shipment profiles for most chemicals fall into one of the following nine general classes:

1. Gases dominated by rail transportation,
2. Gases with mixed rail and highway transportation,
3. Gases dominated by highway transportation,
4. Liquids dominated by rail transportation,
5. Liquids with mixed rail and highway transportation,
6. Liquids dominated by highway transportation,
7. Bulk-forbidden gases and liquids authorized under 49 CFR 173.192,
8. Bulk-forbidden gases and liquids authorized under 49 CFR 173.302, and
9. Organophosphates authorized under 49 CFR 173.334.

Chemicals with a 49 CFR 173.245 authorization for bulk transportation are included in the bulk-forbidden classes. For these chemicals (and the ones for which bulk is forbidden), the PADs for large spills were estimated from shipments containing up to 25 cylinders or drums. A release from this number of package freight containers is equivalent to a release from a small bulk cargo tank (e.g., 1,500 kg). Larger containers were not included in this analysis because it was believed that they would add an unrealistic degree of conservatism to the results, since the probability of these materials being shipped in true bulk form appears to be very low.

Generally, a shipment was designated as being either rail- or highway-dominated on the basis of available commodity flow data (these data are for several widely shipped chemicals) and a survey of incidents from the HMIS database. If no information other than data on packing authorizations within 49 CFR was known, and if the material was authorized for bulk transport, the mixed rail and highway shipment profile was used.

For 2008, we developed several new shipment profiles tailored specifically to several high-volume chemicals identified on the basis of a detailed study of the supply chains for these materials. These materials include chlorine, ammonia, fuming sulfuric acid, hydrogen chloride, hydrogen fluoride, sodium cyanide, and sulfur dioxide. HMIS data, rail waybill data from the

American Association of Railroads, and other commodity flow information, together with 49 CFR information, were used in compilation of this supply chain information. These chemical-specific shipment profiles were also used in the ERG2012 analysis. In addition, we employed separate profiles for materials called out for specific treatment in 49 CFR, such as arsine, diborane, fluorine, hydrogen cyanide, methyl mercaptan, nickel carbonyl, nitric oxide, and tetranitromethane.

Examples of mixed rail and highway shipment profiles are provided in Tables 2.2 and 2.3 for liquids and gases, respectively. Three classes of shipments are listed for each profile: bulk rail transportation, bulk highway transportation, and package freight transportation. To provide some perspective on the relative influence of the shipment classes and release types on releases modeled in the ERG2012 analysis, the percentage of total releases represented by each type is listed for all releases, releases of 5–60 gal, and releases of more than 60 gal. When all releases are considered, en route/nonaccident incidents make up the majority of releases modeled for the shipment profiles given in Tables 2.2 and 2.3. However, in considering releases of more than 60 gal (i.e., "large spills" in the Table), accident-related incidents make up the majority of cases. For such releases, package freight incidents were the most common, and bulk highway incidents were the least. Because PADs are set by the 90th-percentile value, incidents involving bulk containers had a far greater influence on PAD values than did incidents involving package freight containers, since bulk containers usually involved larger release amounts.

2.2.2 Treatment of Chemical Agents

The 1995 Tokyo subway sarin attack and the events on and after September 11, 2001, have made the first-response community more aware of the threat from the malicious use of chemical and biological agents. For this reason, the ERG includes IIDs and PADs for various chemical agents that could be used as weapons. In addition, a separate section entitled "Criminal/Terrorist Use of Chemical/Biological/Radiological Agents" (page 368 of the ERG2012) provides information on identification, response, and decontamination strategies for personnel who must respond to a suspected release of such materials.

Table 2.4 lists 26 chemical compounds for which IIDs and PADs were calculated for cases in which the chemicals would be used as a weapon. (The table shows 36 chemical warfare agent names for the 26 compounds.) Accordingly, entries in the ERG2012 Table for these materials include the statement "when used as a weapon." Several of these materials are also industrial chemicals that appear separately in ERG2012 as transportation-related releases. Entries for weapons-related use of chemical agents, however, are listed under the common or military names for the compounds, not the chemical names. For example, for weapons-related entries, the first compound in Table 2.4 is listed as AC, whereas for transportation-related entries, this same compound is listed as hydrogen cyanide (UN 1051). These two terms refer to the same compound, but the weapons-related and transportation-related release scenarios are very different.

TABLE 2.2 Mixed Rail and Highway Shipment Profile Data for Liquids[a]

Shipment	Transport Mode	Container	Shipment Amount	Release Type	Percent of Total Releases by Type, Listed by Release Amount: All Releases	5–60 gal[b]	>60 gal[b]
1	Rail	DOT Class 112 tank car	80,000 kg	A	3.2	1.1	24.9
				E	41.6	23.0	21.7
2	Highway	DOT 312 cargo tank	20,000 kg	A	1.6	0.7	13.6
				E	5.0	6.4	6.2
3	Highway	Ten 55-gal 5C drums	550 gal	A	2.3	3.0	14.0
				E	46.2	65.8	19.6

[a] This profile covers three shipment classes and two release types, accident-related (A) and en route/nonaccident (E). Percentages are provided for the total number of incidents that occurred in the various shipment classes and release types. Percentages are given for all releases, releases of 5–60 gal, and releases of more than 60 gal.

[b] Data provided are for methyl hydrazine (UN 1244). Other materials with this profile would have similar results.

TABLE 2.3 Mixed Rail and Highway Shipment Profile Data for Gases[a]

Shipment	Transport Mode	Container	Shipment Amount	Release Type	Percent of Total Releases by Type, Listed by Release Amount: All Releases	5–60 gal[b]	>60 gal[b]
1	Rail	DOT Class 105, 112 tank car	80,000 kg	A	2.5	0.8	27.9
				E	56.5	13.6	18.2
2	Highway	MC331 cargo tank	20,000 kg	A	1.2	1.2	9.9
				E	0.6	0.5	3.7
3	Highway	Fifteen 19-gal 3A or 4A cylinders	285 gal	A	4.9	9.0	27.4
				E	34.4	74.9	13.0

[a] This profile covers three shipment classes and two release types, accident-related (A) and en route/nonaccident (E). Percentages are provided for the total number of incidents that occurred in the various shipment classes and release types. Percentages are given for all releases, releases of 5–60 gal, and releases of more than 60 gal.

[b] Data provided are for chlorine trifluoride (UN 1749). Other materials with this profile would have similar results.

TABLE 2.4 Chemical Warfare Agents Listed in the ERG2012 Table of Initial Isolation and Protective Action Distances

UN No.	Chemical Warfare Agent Name	Chemical Compound Name	Small (kg)	Large (kg)	Type[a]
1051	AC	Hydrogen cyanide	200	30,000	SH
1076	DP	Diphosgene	30	500	AL
1076	CG	Phosgene	20	3600	SH
1556	MD	Methyldichloroarsine	30	500	AL
1556	PD	Phenyldichloroarsine	30	500	AL
1589	CK	Cyanogen chloride	30	500	AL
1694	CA	Bromobenzyl cyanides	10	500	AS
1697	CN	Chloroacetophenone	10	500	AS
1698	DM	Diphenylaminechloroarsine (10-Chloro-5,10-dihydrophenarsazine)	5	100	AS
1698	Adamsite				
1699	DA	Diphenylchloroarsine	10	500	AS
1892	ED	Ethyldichloroarsine	10	500	AL
2188	SA	Arsine	200	2000	SH
2810	H	Bis-(2-chloroethyl) sulfide	2	25	SP
2810	HD				
2810	Mustard				
2810	HN-1	Bis-(2-chloroethyl) ethylamine	2	25	SP
2810	HN-2	Bis-(2-chloroethyl) methylamine	2	25	SP
2810	HN-3	Tris-(2-chloroethyl) amine	2	25	SP
2810	L	Dichloro-(2-chlorovinyl) arsine	2	25	SP
2810	Lewisite				
2810	HL[b]				
2810	Mustard lewisite[b]				
2810	BZ	3-Quinuclidinyl benzilate	2	25	AS
2810	Buzz				
2810	CS	O-chlorobenzylidene malononitrile	10	100	AS
2810	DC	Diphenylcyanoarsine	10	100	AS
2810	GA	Ethyl N,N-dimethylphosphoramidocyanidate	2	25	SP
2810	Tabun				
2810	GB	Isopropyl methylphosphonofluoridate	2	25	SP
2810	Sarin				
2810	GD	Pinacolyl methylphosphonofluoridate	2	25	SP
2810	Soman				
2810	GF	Cyclohexyl methylphosphonofluoridate	2	25	SP
2810	VX	O-ethyl S-(2-diisopropylaminoethyl) methylphosphonothiolate	2	25	SP
2811	CX	Phosgene oxime	2	25	AS

[a] SH = releases by shipment sabotage, AL = aerosolized liquid, AS = aerosolized solid, SP = spray or explosive release.

[b] Because of uncertainties in defining the composition, HL and mustard lewisite were treated as standard lewisite (L).

Release scenarios for weapons-related incidents differ from those for transportation-related incidents because they involve deliberate releases. Two maximum release sizes were used for each material considered in the analysis. In the statistical analysis, release amounts were uniformly distributed between 50% and 100% of these maximum release amounts. Various release types were modeled, depending on the material being released. The release types are denoted in Table 2.4 by two-letter codes. The codes AL and AS refer to aerosolized liquid and aerosolized solid release mechanisms, respectively. It is assumed that AL and AS would be dispersed in aerosolized form with a 2- to 10-μm particle size. This release mechanism is used for solid materials or for materials that have very slow evaporation rates; thus, aerosolization is the only way to disseminate them effectively. The code SP refers to a spray or explosive release. This release mechanism is considered the most likely one to be used to disperse nerve and blister agents, since they are typically thick liquids not readily amenable to direct aerosolization. In the scenario used in this analysis, the spray quickly settles on the ground to a depth up to 0.25 mm and then evaporates. The evaporation rate for these materials is limited by their low vapor pressures. The code SH refers to releases by shipment sabotage. This release mechanism is used for volatile TIH materials. For example, the large release scenario for hydrogen cyanide involves the sabotage of a large bulk container such as a small railcar. Small release amounts for these materials correspond to the release of a standard gas cylinder.

There were no changes in the list of chemical warfare agents from 2008 to 2012. The small and large release amounts are set in accordance with current views on terrorist capabilities. In particular, maximum release amounts for chemical warfare agents are 25 kg, which is about 5 gal. In addition, release amounts for materials that have no commercial use or availability (such as BZ and CX) are set the same as those for nerve and blister agents. We also note that 75% of modeled releases are set in urban areas (versus less than 10% for transportation release scenarios). This is done because there is clearly a greater threat to urban areas from weapons-related releases. This is a mitigating factor that reduces the resulting PAD values by 30–50%, since dispersion in urban areas is much more effective at diluting near-ground concentrations of materials released into the atmosphere, especially at night.

2.3 GENERICS, MIXTURES, AND SOLUTIONS

The Table lists a variety of compounds that are generic in nature. Two examples are liquefied gas, flammable, poisonous, n.o.s. (Inhalation Hazard Zone B) (UN 3160) and toxic liquid, corrosive, organic, n.o.s. (UN 2927). Each generic compound can represent many independent chemicals that fit that description but do not have an independent UN number and therefore are not individually listed in the ERG2012 or the Table. As in ERG2008, the IIDs and PADs for generic compounds in the ERG2012 are based on the median-case (50th-percentile) compound from the pool of chemicals in the overall analysis that matches that generic description.

Prior to the 2008ERG, the generic IIZ and PAD estimates were based on the worst-case compound from the pool of chemicals matching the description. The switch to the median compound was made for the 2008ERG, and we continue that convention here. The worst-case method clearly skewed the distances for the generic compounds and imparted considerable

conservatism beyond the 90th-percentile bases used in the PAD specification for individual materials. Although the various generic classes of compounds are not often used in commerce (as evidenced by HMIS records), use of the worst-case method could lead to an excessive response in a major incident. Because the distances for individual materials are already 90th-percentile values, the use of a worst case among these makes the resulting generic compound distances much more conservative than 90th-percentile distances. Use of a median distance preserves the 90th-percentile definition. The second more subtle reason is that using the worst-case chemical to fit an entire generic class resulted in many entries being more than 7 mi, which we felt diluted the importance of the larger distances for those materials that are truly most dangerous.

As an example of this process, the generic compound described as poisonous liquid, corrosive, inorganic, n.o.s. (Inhalation Hazard Zone B) (UN 3289) is considered below. The 13 chemicals analyzed for the ERG2008 that match this category are listed in Table 2.5. Note that this list is ordered by the PAD for a large, nighttime spill. As shown, trichloroacetyl chloride (UN 2442) lies at the median of these 13 chemicals when the large spill distances are considered, meaning that half of the chemicals (6) have longer large-spill distances and half have shorter large-spill distances. For small spills, the median chemical is boron tribromide (UN 2692) (shown in bold in Table 2.5). Also provided are two entries for this generic category that reflect the variations in wording in the Table. These entries are rounded up to the nearest 0.1 mi (100 ft for Initial Isolation Zones) to reflect their appearance in the Table. Note that if the previous worst-case criteria were used, the distances for bromine would be used as a surrogate for this generic category, as was done for ERG2004.

Table 2.6 lists all the generic compounds included in the Table and provides the subset of chemicals from which their distances were calculated. Synonyms are not listed in Table 2.6, so each entry may have several corresponding entries in the Table. For categories that had fewer than three chemicals from which to pick the worst-case example, the selection pool was enlarged to include materials from the next less restrictive designation. For instance, the pool for the generic category described as compressed gas, poisonous, oxidizing, corrosive, n.o.s. (Inhalation Hazard Zones C and D) included all corrosive gases in Hazard Zones C and D because no corrosive, *oxidizing* gases with those hazard zone designations were identified in the analysis pool.

Table 2.7 lists the mixtures and solutions treated in the ERG2012 analysis and indicates how they were modeled. In general, the distances for mixtures were determined by (1) selecting a surrogate compound, (2) considering the toxic effects of a single hazardous constituent, or (3) considering the toxic effects of multiple hazardous constituents. Surrogates were chosen when the mixture composition was not specified. For these cases, the surrogate was chosen as the worst-case chemical or potential composition in that mixture. As an example, consider chlorosulfonic acid and sulfur trioxide mixtures (UN 1754). In these mixtures, sulfur trioxide is the more hazardous component, primarily because of its higher vapor pressure. The addition of chlorosulfonic acid will act to lower the vapor pressure, so a 100% sulfur trioxide mixture is the worst case and was chosen for analysis. A single hazardous constituent was modeled for several cases involving mixtures in compressed gases and solutions (e.g., diborane, tetraethyl

TABLE 2.5 Chemicals Used to Determine Initial Isolation and Protective Action Distances for the Generic Material Described as Poisonous Liquid, Corrosive, Inorganic, n.o.s. (Inhalation Hazard Zone B) (UN 3289)[a]

		Small Spills			Large Spills		
			Then Protect Persons Downwind during			Then Protect Persons Downwind during	
UN No.	Name of Material	First Isolate in All Directions (ft)	Day (mi)	Night (mi)	First Isolate in All Directions (ft)	Day (mi)	Night (mi)
Potential Surrogate Compounds							
1754	Chlorosulfonic acid	16	0.04	0.04	55	0.14	0.20
1828	Sulfur monochloride	16	0.02	0.04	135	0.17	0.25
1076	Diphosgene	27	0.07	0.09	67	0.16	0.28
1746	Bromine trifluoride	24	0.06	0.09	72	0.18	0.31
1082	Titanium tetrachloride	21	0.05	0.08	95	0.22	0.39
2692	Boron tribromide	24	0.05	0.13	83	0.17	0.39
2032	Nitric acid, fuming	75	**0.06**	**0.14**	347	**0.29**	**0.64**
2442	Trichloroacetyl chloride	**35**	0.09	0.18	246	0.37	0.72
1836	Thionyl chloride	47	0.12	0.42	**202**	0.51	1.17
1834	Sulfuryl chloride	41	0.09	0.31	217	0.55	1.24
1809	Phosphorus trichloride	38	0.09	0.28	232	0.56	1.33
1810	Phosphorus oxychloride	61	0.15	0.38	273	0.69	1.35
1832	Sulfur trioxide	161	0.14	0.50	968	0.84	1.97
Synonymous Entries for Generic Compound Categories							
3289	Poisonous liquid, corrosive, inorganic, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.2	300	0.3	0.7
3289	Toxic liquid, corrosive, inorganic, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.2	300	0.3	0.7

[a] This table provides distance estimates for all applicable entries in the ERG2012 Table of Initial Isolation and Protective Action Distances (DOT et al. 2012) ordered in terms of large spill PAD. The median-case (50th percentile) distances for small spills and large spills for each column are shown in bold.

TABLE 2.6 Summary of Generic Compounds on DOT TIH List and Corresponding Surrogates Employed for the ERG2012 (Note that a different surrogate material may be used for each release category.)

UN Number	Proper Shipping Name	Surrogate
1953	Liquefied gas, poisonous, flammable, n.o.s.	Median cases among all TIH, flammable Hazard Zone A gases
1953	Liquefied gas, poisonous, flammable, n.o.s. (Inhalation Hazard Zone A)	Median cases among all TIH, flammable Hazard Zone A gases
1953	Liquefied gas, poisonous, flammable, n.o.s. (Inhalation Hazard Zone B)	Median cases among all TIH, flammable Hazard Zone B gases
1953	Liquefied gas, poisonous, flammable, n.o.s. (Inhalation Hazard Zone C)	Median cases among all TIH, flammable Hazard Zone C gases
1953	Liquefied gas, poisonous, flammable, n.o.s. (Inhalation Hazard Zone D)	Median cases among all TIH, Hazard Zone D gases
1955	Liquefied gas, poisonous, n.o.s.	Median cases among all TIH, Hazard Zone A gases
1955	Liquefied gas, poisonous, n.o.s. (Inhalation Hazard Zone A)	Median cases among all TIH, Hazard Zone A gases
1955	Liquefied gas, poisonous, n.o.s. (Inhalation Hazard Zone B)	Median cases among all TIH, Hazard Zone B gases
1955	Liquefied gas, poisonous, n.o.s. (Inhalation Hazard Zone C)	Median cases among all TIH, Hazard Zone C gases
1955	Liquefied gas, poisonous, n.o.s. (Inhalation Hazard Zone D)	Median cases among all TIH, Hazard Zone D gases
1955	Organic phosphate mixed with compressed gas	Parathion and compressed gas mixture
1967	Insecticide gas, poisonous, n.o.s.	Parathion and compressed gas mixture
2810	Poisonous liquid, n.o.s.	Median cases among all TIH Hazard Zone A liquids
2810	Poisonous liquid, n.o.s. (Inhalation Hazard Zone A)	Median cases among all TIH Hazard Zone A liquids
2810	Poisonous liquid, n.o.s. (Inhalation Hazard Zone B)	Median cases among all TIH Hazard Zone B liquids
2810	Poisonous liquid, organic, n.o.s.	Median cases among all TIH, organic, Hazard Zone A liquids
2810	Poisonous liquid, organic, n.o.s. (Inhalation Hazard Zone A)	Median cases among all TIH, organic, Hazard Zone A liquids
2810	Poisonous liquid, organic, n.o.s. (Inhalation Hazard Zone B)	Median cases among all TIH, organic, Hazard Zone B liquids
2927	Poisonous liquid, corrosive, n.o.s.	Median cases among all TIH, corrosive, Hazard Zone A liquids
2927	Poisonous liquid, corrosive, n.o.s. (Inhalation Hazard Zone A)	Median cases among all TIH, corrosive, Hazard Zone A liquids
2927	Poisonous liquid, corrosive, n.o.s. (Inhalation Hazard Zone B)	Median cases among all TIH, corrosive, Hazard Zone B liquids
2927	Toxic liquid, corrosive, organic, n.o.s.	Median cases among all TIH, corrosive, organic Hazard Zone A liquids
2927	Toxic liquid, corrosive, organic, n.o.s. (Inhalation Hazard Zone A)	Median cases among all TIH, corrosive, organic Hazard Zone A liquids
2927	Toxic liquid, corrosive, organic, n.o.s. (Inhalation Hazard Zone B)	Median cases among all TIH, corrosive, organic, Hazard Zone B liquids
2929	Poisonous liquid, flammable, n.o.s.	Median cases among all TIH, flammable, Hazard Zone A liquids
2929	Poisonous liquid, flammable, n.o.s. (Inhalation Hazard Zone A)	Median cases among all TIH, flammable, Hazard Zone A liquids
2929	Poisonous liquid, flammable, n.o.s. (Inhalation Hazard Zone B)	Median cases among all TIH, flammable, Hazard Zone B liquids
2929	Poisonous liquid, flammable, organic, n.o.s.	Median cases among all TIH, flammable, organic, Hazard Zone A liquids
2929	Poisonous liquid, flammable, organic, n.o.s. (Inhalation Hazard Zone A)	Median cases among all TIH, flammable, organic, Hazard Zone A liquids
2929	Poisonous liquid, flammable, organic, n.o.s. (Inhalation Hazard Zone B)	Median cases among all TIH, flammable, organic, Hazard Zone B liquids
3122	Poisonous liquid, oxidizing, n.o.s.	Median cases among all TIH, flammable, Hazard Zone A liquids

TABLE 2.6 (Cont.)

UN Number	Proper Shipping Name	Surrogate
3122	Poisonous liquids, oxidizing, n.o.s. (Inhalation Hazard Zone A)	Median cases among all TIH, flammable, Hazard Zone A liquids
3122	Poisonous liquids, oxidizing, n.o.s. (Inhalation Hazard Zone B)	Median cases among all TIH, oxidizing, Hazard Zone B liquids
3123	Poisonous liquid, water-reactive, n.o.s.	Median cases among all TIH Hazard Zone A liquids
3123	Poisonous liquid, water-reactive, n.o.s. (Inhalation Hazard Zone A)	Median cases among all TIH Hazard Zone A liquids
3123	Poisonous liquid, water-reactive, n.o.s. (Inhalation Hazard Zone B)	Median cases among all TIH Hazard Zone B liquids
3123	Poisonous liquid, which in contact with water emits flammable gases, n.o.s.	Median cases among all TIH flammable liquids
3123	Poisonous liquid, which in contact with water emits flammable gases, n.o.s. (Inhalation Hazard Zone A)	Median cases among all TIH, flammable, Hazard Zone A liquids
3123	Poisonous liquid, which in contact with water emits flammable gases, n.o.s. (Inhalation Hazard Zone B)	Median cases among all TIH, flammable, Hazard Zone B liquids
3160	Liquefied gas, poisonous, flammable, n.o.s.	Median cases among all TIH, flammable, Hazard Zone A gases
3160	Liquefied gas, poisonous, flammable, n.o.s. (Inhalation Hazard Zone A)	Median cases among all TIH, flammable, Hazard Zone A gases
3160	Liquefied gas, poisonous, flammable, n.o.s. (Inhalation Hazard Zone B)	Median cases among all TIH, flammable, Hazard Zone B gases
3160	Liquefied gas, poisonous, flammable, n.o.s. (Inhalation Hazard Zone C)	Median cases among all TIH, flammable, Hazard Zone C gases
3160	Liquefied gas, poisonous, flammable, n.o.s. (Inhalation Hazard Zone D)	Median cases among all TIH, flammable, Hazard Zone D gases
3162	Liquefied gas, poisonous, n.o.s.	Median cases among all TIH Hazard Zone A gases
3162	Liquefied gas, poisonous, n.o.s. (Inhalation Hazard Zone A)	Median cases among all TIH Hazard Zone A gases
3162	Liquefied gas, poisonous, n.o.s. (Inhalation Hazard Zone B)	Median cases among all TIH Hazard Zone B gases
3162	Liquefied gas, poisonous, n.o.s. (Inhalation Hazard Zone C)	Median cases among all TIH Hazard Zone C gases
3162	Liquefied gas, poisonous, n.o.s. (Inhalation Hazard Zone D)	Median cases among all TIH Hazard Zone D gases
3275	Nitriles, poisonous, flammable, n.o.s.	Methacrylonitrile
3276	Nitriles, poisonous, n.o.s.	Methacrylonitrile
3278	Organophosphorus compound, poisonous, n.o.s.	Methyl phosphonous dichloride
3279	Organophosphorus compound, poisonous, flammable, n.o.s.	Methyl phosphonous dichloride
3280	Organoarsenic compound, n.o.s.	Tert-butylarsine
3281	Metal carbonyls, n.o.s.	Nickel carbonyl
3287	Poisonous liquid, inorganic, n.o.s.	Median cases among all TIH, inorganic, Hazard Zone A liquids
3287	Poisonous liquid, inorganic, n.o.s. (Inhalation Hazard Zone A)	Median cases among all TIH, inorganic, Hazard Zone A liquids
3287	Poisonous liquid, inorganic, n.o.s. (Inhalation Hazard Zone B)	Median cases among all TIH, inorganic, Hazard Zone B liquids
3289	Poisonous liquid, corrosive, inorganic, n.o.s.	Median cases among all TIH, corrosive, inorganic, Hazard Zone A liquids
3289	Poisonous liquid, corrosive, inorganic, n.o.s. (Inhalation Hazard Zone A)	Median cases among all TIH, corrosive, inorganic, Hazard Zone A liquids
3289	Poisonous liquid, corrosive, inorganic, n.o.s. (Inhalation Hazard Zone B)	Median cases among all TIH, corrosive, inorganic, Hazard Zone B liquids

TABLE 2.6 (Cont.)

UN Number	Proper Shipping Name	Surrogate
3303	Compressed gas, poisonous, oxidizing, n.o.s.	Median cases among all TIH, oxidizing, Hazard Zone A gases
3303	Compressed gas, poisonous, oxidizing, n.o.s. (Inhalation Hazard Zone A)	Median cases among all TIH, oxidizing, Hazard Zone A gases
3303	Compressed gas, poisonous, oxidizing, n.o.s. (Inhalation Hazard Zone B)	Median cases among all TIH, oxidizing, Hazard Zone B gases
3303	Compressed gas, poisonous, oxidizing, n.o.s. (Inhalation Hazard Zone C)	Median cases among all TIH, oxidizing, Hazard Zone C gases
3303	Compressed gas, poisonous, oxidizing, n.o.s. (Inhalation Hazard Zone D)	Median cases among all TIH, oxidizing, Hazard Zone D gases
3304	Compressed gas, poisonous, corrosive, n.o.s.	Median cases among all TIH, corrosive, Hazard Zone A gases
3304	Compressed gas, poisonous, corrosive, n.o.s. (Inhalation Hazard Zone A)	Median cases among all TIH, corrosive, Hazard Zone A gases
3304	Compressed gas, poisonous, corrosive, n.o.s. (Inhalation Hazard Zone B)	Median cases among all TIH, corrosive, Hazard Zone B gases
3304	Compressed gas, poisonous, corrosive, n.o.s. (Inhalation Hazard Zone C)	Median cases among all TIH, corrosive, Hazard Zone C gases
3304	Compressed gas, poisonous, corrosive, n.o.s. (Inhalation Hazard Zone D)	Median cases among all TIH, corrosive, Hazard Zone D gases
3305	Compressed gas, poisonous, flammable, corrosive, n.o.s.	Median cases among all TIH, corrosive, Hazard Zone A gases
3305	Compressed gas, poisonous, flammable, corrosive, n.o.s. (Inh. Hazard Zone A)	Median cases among all TIH, corrosive, Hazard Zone A gases
3305	Compressed gas, poisonous, flammable, corrosive, n.o.s. (Inh. Hazard Zone B)	Median cases among all TIH, corrosive, Hazard Zone B gases
3305	Compressed gas, poisonous, flammable, corrosive, n.o.s. (Inh. Hazard Zone C)	Median cases among all TIH, corrosive, Hazard Zone C gases
3305	Compressed gas, poisonous, flammable, corrosive, n.o.s. (Inh. Hazard Zone D)	Median cases among all TIH, corrosive, Hazard Zone D gases
3306	Compressed gas, poisonous, oxidizing, corrosive, n.o.s.	Median cases among all TIH, oxidizing, corrosive, Hazard Zone A gases
3306	Compressed gas, poisonous, oxidizing, corrosive, n.o.s. (Inh. Hazard Zone A)	Median cases among all TIH, oxidizing, corrosive, Hazard Zone A gases
3306	Compressed gas, poisonous, oxidizing, corrosive, n.o.s. (Inh. Hazard Zone B)	Median cases among all TIH, oxidizing, corrosive, Hazard Zone B gases
3306	Compressed gas, poisonous, oxidizing, corrosive, n.o.s. (Inh. Hazard Zone C)	Median cases among all TIH, corrosive, Hazard Zone C gases
3306	Compressed gas, poisonous, oxidizing, corrosive, n.o.s. (Inh. Hazard Zone D)	Median cases among all TIH, corrosive, Hazard Zone D gases
3307	Liquefied gas, poisonous, oxidizing, n.o.s.	Median cases among all TIH, oxidizing, Hazard Zone A gases
3307	Liquefied gas, poisonous, oxidizing, n.o.s. (Inhalation Hazard Zone A)	Median cases among all TIH, oxidizing, Hazard Zone A gases
3307	Liquefied gas, poisonous, oxidizing, n.o.s. (Inhalation Hazard Zone B)	Median cases among all TIH, oxidizing, Hazard Zone B gases
3307	Liquefied gas, poisonous, oxidizing, n.o.s. (Inhalation Hazard Zone C)	Median cases among all TIH, oxidizing, Hazard Zone C gases
3307	Liquefied gas, poisonous, oxidizing, n.o.s. (Inhalation Hazard Zone D)	Median cases among all TIH, oxidizing, Hazard Zone D gases
3308	Liquefied gas, poisonous, corrosive, n.o.s.	Median cases among all TIH, corrosive, Hazard Zone A gases
3308	Liquefied gas, poisonous, corrosive, n.o.s. (Inhalation Hazard Zone A)	Median cases among all TIH, corrosive, Hazard Zone A gases
3308	Liquefied gas, poisonous, corrosive, n.o.s. (Inhalation Hazard Zone B)	Median cases among all TIH, corrosive, Hazard Zone B gases
3308	Liquefied gas, poisonous, corrosive, n.o.s. (Inhalation Hazard Zone C)	Median cases among all TIH, corrosive, Hazard Zone C gases
3308	Liquefied gas, poisonous, corrosive, n.o.s. (Inhalation Hazard Zone D)	Median cases among all TIH, corrosive, Hazard Zone D gases
3309	Liquefied gas, poisonous, flammable, corrosive, n.o.s.	Median cases among all TIH, corrosive, Hazard Zone A gases
3309	Liquefied gas, poisonous, flammable, corrosive, n.o.s. (Inhalation Hazard Zone A)	Median cases among all TIH, corrosive, Hazard Zone A gases

TABLE 2.6 (Cont.)

UN Number	Proper Shipping Name	Surrogate
3309	Liquefied gas, poisonous, flammable, corrosive, n.o.s. (Inhalation Hazard Zone B)	Median cases among all TIH, corrosive, Hazard Zone B gases
3309	Liquefied gas, poisonous, flammable, corrosive, n.o.s. (Inhalation Hazard Zone C)	Median cases among all TIH, corrosive, Hazard Zone C gases
3309	Liquefied gas, poisonous, flammable, corrosive, n.o.s. (Inhalation Hazard Zone D)	Median cases among all TIH, corrosive, Hazard Zone D gases
3310	Liquefied gas, poisonous, oxidizing, corrosive, n.o.s.	Median cases among all TIH, oxidizing, corrosive, Hazard Zone A gases
3310	Liquefied gas, poisonous, oxidizing, corrosive, n.o.s. (Inhalation Hazard Zone A)	Median cases among all TIH, oxidizing, corrosive, Hazard Zone A gases
3310	Liquefied gas, poisonous, oxidizing, corrosive, n.o.s. (Inhalation Hazard Zone B)	Median cases among all TIH, oxidizing, corrosive, Hazard Zone B gases
3310	Liquefied gas, poisonous, oxidizing, corrosive, n.o.s. (Inhalation Hazard Zone C)	Median cases among all TIH, corrosive, Hazard Zone C gases
3310	Liquefied gas, poisonous, oxidizing, corrosive, n.o.s. (Inhalation Hazard Zone D)	Median cases among all TIH, corrosive, Hazard Zone D gases
3355	Insecticide gas, poisonous, flammable, n.o.s	Median cases among all TIH, flammable, Hazard Zone A gases
3355	Insecticide gas, poisonous, flammable, n.o.s. (Inhalation Hazard Zone A)	Median cases among all TIH, flammable, Hazard Zone A gases
3355	Insecticide gas, poisonous, flammable, n.o.s. (Inhalation Hazard Zone B)	Median cases among all TIH, flammable, Hazard Zone B gases
3355	Insecticide gas, poisonous, flammable, n.o.s. (Inhalation Hazard Zone C)	Median cases among all TIH, flammable, Hazard Zone C gases
3355	Insecticide gas, poisonous, flammable, n.o.s. (Inhalation Hazard Zone D)	Median cases among all TIH, flammable, Hazard Zone D gases
3488	Poisonous by inhalation liquid, flammable, corrosive, n.o.s. (Inhalation Hazard Zone A)	Median cases among all TIH, flammable, corrosive, Hazard Zone A liquids
3489	Poisonous by inhalation liquid, flammable, corrosive, n.o.s. (Inhalation Hazard Zone B)	Median cases among all TIH, flammable. corrosive, Hazard Zone B liquids
3490	Poisonous by inhalation liquid, water-reactive, flammable, n.o.s. (Inhalation Hazard Zone A)	Median cases among all TIH, flammable, Hazard Zone A liquids
3491	Poisonous by inhalation liquid, water-reactive, flammable, n.o.s. (Inhalation Hazard Zone B)	Median cases among all TIH, flammable, Hazard Zone A liquids
3492	Poisonous by inhalation liquid, corrosive, flammable, n.o.s. (Inhalation Hazard Zone A)	Median cases among all TIH, flammable, Hazard Zone A liquids
3493	Poisonous by inhalation liquid, corrosive, flammable, n.o.s. (Inhalation Hazard Zone B)	Median cases among all TIH, flammable, Hazard Zone A liquids

TABLE 2.7 Summary of Mixtures and Solutions on DOT TIH List and How They Were Treated for the ERG2012

UN Number	Category	Proper Shipping Name	Modeled as
Mixtures and Solutions Modeled as Single Toxic Species			
1040	Mixture	Ethylene oxide with nitrogen	100% ethylene oxide
1051	Solution	Hydrocyanic acid, aqueous solutions, with more than 20% hydrogen cyanide	100% hydrogen cyanide
1583	Mixture	Chloropicrin mixture, n.o.s.	100% chloropicrin
1612	Mixture	Hexaethyltetraphosphate and compressed gas mixtures	20% hexaethyltetraphosphate
1613	Solution	Hydrocyanic acid, aqueous solution, with not more than 20% hydrogen cyanide	20% hydrogen cyanide solution in water
1647	Mixture	Ethylene dibromide and methyl bromide mixture, liquid	100% methyl bromide
1744	Solution	Bromine solutions (Inhalation Hazard Zone A)	100% bromine
1744	Solution	Bromine solutions (Inhalation Hazard Zone B)	50% bromine
1754	Mixture	Chlorosulfonic acid and sulfur trioxide mixture	100% sulfur trioxide
1911	Mixture	Diborane	7% diborane
1967	Mixture	Parathion and compressed gas mixtures	20% parathion
1975	Mixture	Nitric oxide and dinitrogen tetroxide mixtures	100% nitric oxide
2600	Mixture	Carbon monoxide and hydrogen mixtures	100% carbon monoxide
3294	Solution	Hydrogen cyanide, solution in alcohol, with not more than 45% hydrogen cyanide	45% hydrogen cyanide solution in alcohol
3300	Mixture	Carbon dioxide and ethylene oxide mixture, with more than 87% ethylene oxide	100% ethylene oxide
3318	Solution	Ammonia solution, with more than 50% ammonia	100% ammonia
Mixtures Modeled with Multiple Toxic Chemical Species			
1581	Mixture	Chloropicrin and methyl bromide mixtures	(i) 5% chloropicrin and (ii) 95% methyl bromide
1582	Mixture	Chloropicrin and methyl chloride mixtures	(i) 2% chloropicrin and (ii) 98% methyl chloride
1023	Mixture	Coal gas	(i) 48% hydrogen, (ii) 27% methane, (iii) 10% carbon monoxide, (iv) 5% carbon dioxide, and (v) 6% nitrogen
1071	Mixture	Oil gas	(i) 55% hydrogen, (ii) 25% methane, (iii) 11% carbon monoxide, (iv) 3% carbon dioxide, (v) 2% ethylene, and (vi) 2% benzene
3494	Mixture	Petroleum sour crude oil, flammable, toxic	Treated as generic category *poisonous liquid, flammable, n.o.s. (Inhalation Hazard Zone B)*

pyrophosphate, hydrocyanic acid solutions). For each case, the worst case as specified in 49 CFR or by the description was modeled. The third class of mixtures involves compounds with more than one hazardous component. For instance, in chloropicrin and methyl bromide mixtures (UN 1581), chloropicrin is dissolved in methyl bromide up to 5% by volume. Therefore, toxic effects of both constituents are taken into account. The result is a mixture that behaves almost identically to pure methyl bromide in terms of release rate and dispersion. However, the mixture is much more toxic than pure methyl bromide as a result of the high toxicity of chloropicrin, so the PAD is longer than that for pure methyl bromide.

2.4 ANALYSIS OF WATER-REACTIVE MATERIALS

2.4.1 Background

Trucks and railcars that transport hazardous chemicals can have accidents in which their solid or liquid cargo spills into a water-filled roadside ditch, stream, river, lake, or estuary. This presents the possibility that a material that otherwise does not pose an inhalation hazard might react with the water to produce toxic gaseous by-products. In the following discussions, materials that generate substantial quantities of toxic gases fairly rapidly after a spill into water are referred to as toxic inhalation hazards by water-reaction (TIHWR).[1] An example of a TIHWR material is silicon tetrachloride, which is not a TIH material but produces airborne hydrogen chloride (HCl) and HCl mist upon exposure to water. Even heavy rainfall at the time of an accident or airborne water vapor can cause the emission of TIH gases from this material. The well-known Chicago spill of silicon tetrachloride from a storage tank in 1976 is an example. At one point in the eight-day episode, heavy rainfall led to a significant increase in emissions and sudden damage to the surroundings because additional HCl was released into the atmosphere. The same problem, though of less magnitude (due to a smaller release amount), would occur if a truck or tank car spilled silicon tetrachloride into water or had an accident resulting in a spill during a rainstorm.

Until recently, little attention was directed to materials that emit gases into the atmosphere when accidentally released into water. Kapias and Griffiths (1999) presented a limited discussion of water-reactive chemicals and the modeling of accidental releases. They used the example of silicon tetrachloride, which is a strong HCl emitter, either reacting with liquid water or scavenging atmospheric water vapor. Over the last decade, however, we have identified numerous such materials and recommended them for inclusion in the ERG as part of a long-term program for identifying TIHWR materials and quantifying their emissions.

This section provides a description of our program for identifying and classifying TIHWR materials, as well as a companion experimental program instituted to provide a quantitative basis for the TIHWR analysis. These experiments were conducted in several phases from 1999 to 2007. The technical aspects of how the TIH emission rates from these materials

[1] Note that materials that evolve into flammable gases but do not otherwise pose a toxic hazard are explicitly excluded from our definition and the discussions that follow.

were modeled and how they were treated in the statistical analysis as part of the ERG2012 study are detailed in Section 3.3.2.3, and additional details on the experiments and the parameters employed in the TIHWR modeling appear in Appendix D.

2.4.2 Identification and Evaluation of Candidates

To compile the list of water-reactive materials for the Guidebook from the large pool of potential TIH emitters, we first screened materials by applying general principles of chemical reactivity, seeking specific reactivity information from the chemical literature and comparing such information among related compounds. Screening started with the 208 chemically distinct materials previously found by Carhart et al. (1996) to be capable of producing TIH gases if spilled into a river, lake, or other body of surface water. The 37 materials that made up the 1996 North American ERG "List of Dangerous Water-Reactive Materials" are a subset of these 208. In the analysis for the ERG2000, 16 more materials were added to the TIHWR candidate list on the basis of a review of other water-reactive lists and recommendations by DOT.

The final initial list of 224 candidate materials was carefully evaluated to determine which ones provided sufficient hazards to warrant their inclusion in the Table. The evaluation process consisted of the following steps:

1. Consideration of general patterns of reactivity,

2. Examination of the primary literature,

3. Examination of standard secondary sources such as Kroschwitz (1991–1996) and Lewis (2000), and

4. Experimental tests on compounds to estimate the yield and rate of production of toxic gases when mixed with water. These experiments both confirmed water reactivity and provided a quantitative basis for TIHWR hazard estimates.

Steps 1 through 3 were used to generate the 1996 TIHWR list. For the ERG2000, the experimental program outlined in Step 4 was initiated. This program was expanded for the ERG2004 to include over half of the TIHWR list and further expanded for the ERG2008 to encompass more than 70% of the TIHWR list. Furthermore, the set of materials under consideration for TIHWR status was expanded, thus adding several new materials to the TIHWR list.

The need for such experimental data is underscored by the fact that quantitative observations of TIH gas evolving from hazardous chemicals added to water do not exist in the chemical literature. The experimental program is outlined below.

2.4.3 Experimental Program

The experimental program consisted of a series of small-scale experiments with candidate materials. The materials were tested for the generation of gases by mixing small amounts of the material in question (about 1 millimole [mmol]) with water in a closed system. The release of gas was measured over time by observing the displacement of a nearly frictionless plunger in a gas syringe. This experimental setup was different than that used for the ERG2000 and ERG2004 analyses, in which the gas volume produced was measured by noting the displacement of manometric fluid. The experimental apparatus was changed to provide higher quality quantitative information and results that are more reproducible, since dissolution of the progeny gases into the manometric fluid was no longer an issue. As was done before, experiments were conducted by using two different amounts of water (the stoichiometric equivalent amount and fivefold molar excess) for each material considered. These experiments are meant to approximate conditions in which (1) a material is released into a restricted water environment (or perhaps just gets wet) and (2) a material is spilled into a body of water. Most materials previously analyzed in the experiments were redone for the ERG2008, thereby providing an entirely new set of experimental data from which to estimate gas evolution.

The experimental program has not only given us useful quantitative information on the rates of evolution of TIH gases, but over the past decade, it has allowed us to delete several chemicals from the initial TIHWR list because no evolution of gas was observed. In a few cases, a reaction actually did occur, but the gas that was produced was rapidly dissolved when water was in excess. This effect might not occur when larger quantities are involved; additional experiments are required to establish whether significant amounts of TIH gases would escape under such conditions.

The experimental procedure and resulting data and analysis are fully described in Brown et al. 2009. Dates derived from these experiments that were used in preparation of the ERG2012 are discussed in Appendix D.

2.4.4 Additional Selection Criteria

There are a few additional issues associated with the evaluation process that deserve special attention:

- Some potential TIHWR materials, especially generic materials, are not sufficiently described chemically to allow a complete assessment of their behavior when spilled into water. Such materials are not included on the TIHWR list unless there is a positive indication that a TIH gas might develop in a spill into water. Examples of materials that are not included on the TIHWR list at this time include pyrophoric organometallic compound, n.o.s. (UN 3203); organometallic compound solution, water-reactive, flammable, n.o.s (UN 3207); water-reactive substances, liquid, corrosive, n.o.s. (UN 3129); water-reactive solid, corrosive, n.o.s. (UN 3131); water-reactive substances, liquid, n.o.s. (UN 3148); water-reactive liquid, toxic, n.o.s.

(UN 3130); and substances which in contact with water emit flammable gases, solid, poisonous, n.o.s. (UN 3134).

- On the other hand, generic alkyl halides and chlorosilanes might generate sufficient gaseous HCl or another hydrogen halide to qualify as TIHWR materials. For this reason, aluminum alkyl halides (UN 3052); metal alkyl halides, n.o.s. (UN 3049); chlorosilanes, n.o.s. (UN 2985); chlorosilanes, flammable, corrosive, n.o.s. (UN 2986); and chlorosilanes, corrosive, n.o.s. (UN 2987) are included.

- Materials that are gaseous at ordinary temperatures (with boiling points below 0°C at atmospheric pressure) were uniformly not recommended for inclusion. An example is trifluoroacetyl chloride, which boils at –18°C. Such compounds would probably boil away too rapidly to allow a significant reaction with surface water under most atmospheric conditions.

- Liquids boiling in the range of ordinary environmental temperature (0–20°C) presented problems, because they occur as a liquid or a gas, depending on water temperature. Cyanogen chloride was rejected because it is a gas at temperatures above most of this range (boiling point 13.1°C) and because it does not require a spill into water to pose a TIH hazard. Chlorine trifluoride (boiling point 11.8°C) was rejected on similar grounds. On the other hand, *boron trichloride* (BCl_3) is included despite being a gas at 20°C, because the reaction of the spilled chemical with water rapidly generates HCl gas, which is more toxic than the parent compound and will be evolved at a more rapid rate. Also, since its boiling point is 12.5°C, the material can remain in the liquid state when spilled into cold water. In addition, BCl_3 is frequently purveyed in solution in an organic solvent.

- Materials that undergo highly exothermic reactions with water sometimes generate acidic mists, depending on the way that they are mixed with water. The mist happens when water at hot spots of reactivity boils violently. The resulting seething and bumping kicks colloidal particles of hydrated or partially hydrated material into the air. For example, oleum (UN 1831) quite often raises a fume containing $SO_3 \bullet H_2O$, H_2SO_4, and related acidic species when it is mixed with water. Such mists present an obvious inhalation hazard. Similar mists can form when sulfur trioxide (UN 1829) and sulfuryl chloride (UN 1834) mix with water. Materials in this category were treated individually. Oleum and sulfur trioxide (SO_3) were not included as TIHWR materials because spills into water would likely not lead to PADs longer than those already listed for land-based spills. Sulfuryl chloride was listed as a TIHWR material on the basis of its co-generation of gaseous HCl. Phosphorus pentoxide (UN 1807) might raise an acidic mist (of oxo-acids of phosphorus) in a spill into water. Although mists present a clear toxic inhalation hazard in certain release scenarios, the generation of mists alone is not currently a sufficient criterion for inclusion in the TIHWR table.

- Certain materials dissolve smoothly in water without generating gases under most circumstances but can decompose to evolve TIH gases, if the mixing with water occurs under conditions that prevent the loss of the heat of dissolution and allow a sufficient rise in temperature. Such conditions were not attained in the water-reactivity experiments (Appendix C).

- Thermal decomposition of calcium hypochlorite (UN 1748) and lithium hypochlorite (UN 1471) generates chlorine and/or HCl (Lewis 2000), which are TIH gases. These two hypochlorites appeared as TIHWR materials in the ERG1996 but were removed as TIHWR materials in subsequent lists because the auto-heating scenario appeared too unlikely.

- A similar decomposition of sodium hydrosulfite (UN 1384), calcium hydrosulfite (UN 1923), and zinc hydrosulfite (UN 1931) can occur with water, generating sulfur dioxide and possibly hydrogen sulfide, which are TIH gases. These three hydrosulfites appear on the TIHWR list on the basis of the behavior of sodium hydrosulfite in a serious plant accident in New Jersey on April 21, 1995 (EPA and OHSA 1997).

2.4.5 Summary

As a result of the steps and considerations detailed above, 37 new materials were proposed for inclusion in the ERG2000, 14 new materials were added to the TIHWR list for 2004, and 14 more were added in the ERG2008. There were no changes to the list for the ERG2012. The full list of TIHWR materials considered in the ERG2012 is presented in Appendix D, along with a brief summary of reasons for the inclusion of each material. Appendix D also provides the parameters necessary to model TIH evolution, such as (1) shipment state, (2) TIH gas(es) evolved, (3) density of the material, (4) stoichiometric yield, (5) overall efficiency factor, and (6) rate constants.

2.5 DETERMINATION OF INITIAL ISOLATION DISTANCES

The IID is the length of the radius of a circular Initial Isolation Zone around the accident site from which people are to be kept away. Establishment of an Initial Isolation Zone serves two purposes. First, it provides a protective barrier upwind to protect against exposures due to wind direction variations. Second, it defines a zone downwind where life-threatening effects might be expected. The latter is generally a more stringent requirement, so that purpose is used to define the IID.

The IID is calculated in a similar manner to the PAD except that a lethality health end point is a principal consideration. As such, distances are first evaluated by using the 1-h LC_{50}. The 1-h value is used in all cases (no time adjustment is made), even though exposure times are generally much shorter, since plume meander is a very transient phenomenon and people would not remain in this zone unless they became incapacitated. Earlier efforts using a 5-min exposure

time together with the Emergency Response Planning Guideline Level 3 (ERPG-3) (or surrogate) yielded longer distances, although the methods were comparable for most materials. We use LC_{50} values because they are experimentally derived and available for nearly all materials on the TIH list.

The IID is set a minimum distance equivalent to 15% of the daytime PAD for gases and 7.5% of the daytime PAD for liquids. This modification was made in 2008 because many of the large-spill IID values appeared too short from a safety standpoint, especially in light of some major accidental releases that occurred in the last several years (e.g., in Minot, North Dakota, in 2002; Festus, Missouri, in 2002; Macdona, Texas, in 2004; and Graniteville, South Carolina, in 2005). The net result of this modification is that for gases, the IID is usually set by this minimum distance criterion rather than the LC_{50}-based value. As such, the IIDs for most gases substantially increased from values used in prior editions of the ERG. As a result of incorporating this minimum distance, this criterion had a much smaller effect for liquid compounds. For presentation in the Guidebook, the IID distances themselves are binned into the values shown below.

- 30 m (100 ft)
- 60 m (200 ft)
- 100 m (300 ft)
- 150 m (500 ft)
- 200 m (600 ft)
- 300 m (1,000 ft)
- 400 m (1,250 ft)
- 500 m (1,500 ft)
- 600 m (2,000 ft)
- 800 m (2,500 ft)
- 1,000 m (3,000 ft)

It is important to note that many TIH materials are also flammable or are oxidizers. The IID is based solely on inhalation toxicity and does not account for the explosive or flammable nature of the material. As a result, there may be substantial differences between the IID that appears on the Green Pages and the corresponding isolation distance guidelines on the Orange Pages in the ERG2012. In some cases, the IID, which is based on inhalation toxicity, can be less than the suggested evacuation distance, which is based on flammability or explosion concerns. The IID and Orange Page distances will be harmonized in future versions of the Guidebook.

3 STATISTICAL ACCIDENT SCENARIO ANALYSIS AND CASRAM

CASRAM (Chemical Accident Statistical Risk Assessment Model) lies at the core of the analysis for PAD determination for the ERG2012 and is the key tool we employ for both constructing accident scenarios and executing consequence models. CASRAM predicts hazard-zone distributions (i.e., areas in which a threshold chemical concentration is exceeded) and/or affected populations resulting from releases associated with hazardous materials transportation or storage. The model uses a variety of statistical data for hazardous materials releases and an extensive meteorological database to statistically generate and analyze release scenarios. For a given health effect (injury, fatality, etc.), hazard-zone distributions are generated stochastically through Monte Carlo sampling of accident scenario parameters (time, location, release amount, meteorology, etc.) and detailed consequence modeling of the hypothetical releases. CASRAM is specifically designed for the *statistical* analysis of hazardous material release problems. It is this feature, in particular, that separates CASRAM from many other hazardous material release models such as ALOHA (Jones et al. 2013; NOAA 2014) and SCIPUFF (Sykes et al. 1998). Rather than specifying a deterministic measure of risk, CASRAM determines the distribution of possible outcomes, thus allowing identification of the probability of a particular consequence within the limits of the statistical data.

CASRAM is primarily a routing-based risk assessment model that requires shipment attributes (e.g., materials, containers) and shipment routes as inputs. It provides distributions of affected persons as outputs (e.g., Brown et al. 2001). However, it is equally applicable to a geographically based incident distribution system. A geographically based system is required for the ERG analysis because the Table must reflect releases that occur anywhere in North America. The statistical accident scenario analysis (see Figure 2.1) combines the shipment profile information discussed in Section 2.2, meteorological observations from a preprocessed meteorological database, and statistical information from the HMIS database to provide a large distribution of incidents. These incidents are then modeled by using the consequence models within CASRAM. The overall goal of this analysis is to identify the distributions of safe distance (i.e., hazard zone length) associated with the transport within North America of all materials that are given in the Table. The PADs and IIDs in the Table are the 90th-percentile values of these safe-distance distributions.

This section first discusses the statistical scenario analysis and then the meteorological database used in the ERG2012 study. The emission rate modeling and dispersion modeling within CASRAM, which make up the consequence modeling effort to determine PADs, are then outlined.

3.1 STATISTICAL SCENARIO ANALYSIS

3.1.1 Overview of Analysis Steps

For each material in the Table, we use CASRAM to model more than 100,000 separate incidents distributed between highway and rail transportation, relevant container types (e.g., DOT Class 105 tank car, MC 330 cargo tank, 1A1 drums), and release types (e.g., accident-related, en route/nonaccident). The distribution of the incidents within the categories above are specified in the shipment profiles discussed in Section 2.2. Incidents are also distributed geographically and temporally on the basis of transportation mode and release type. Geographic and temporal effects have a large influence on meteorology, which in turn directly affects the safe distance calculation. The location of the incident affects the general climate and land use (e.g., dry desert, temperate farmland), whereas the time of day and month affect the weather at that locale.

Each release modeled in the analysis is assigned a random date, time, and location. The locations for U.S.-based accidents are chosen probabilistically on the basis of state distributions of accidents in the HMIS database. Separate distributions are used for accident-related and en route/nonaccident releases for both highway and rail. Locations for Canada and Mexico are based on population density. Date and time are assigned on the basis of month-of-year and time-of-day distributions for incidents in the HMIS database following Brown et al. (2005), where the year is assigned in a 10-year window that corresponds to observations in the meteorological database (1996–2005).

The emission rate model in CASRAM uses the shipment information and meteorology as specified above to determine the rate at which specific materials are released into the atmosphere. The first step is to estimate the discharge fraction on the basis of historical statistical distributions generated from analysis of HMIS database incidents. The emission rates of the material to the atmosphere are then calculated by using physical models for discharge, flashing, and evaporation applicable to that release. Within the emission rate model, the total amount of material spilled (discharge fraction) and median pool depth are treated stochastically.

By using the emission rates for the chemical(s) involved and the ambient meteorology, the dispersion model within CASRAM then determines the affected areas. We view the dispersion calculation as a two-step process. Step 1 involves characterizing the meteorology from the available surface observations, and Step 2 involves estimating the transport and dispersion from the applicable meteorological parameters. Step 1 is accomplished with a meteorological preprocessor, which is a series of algorithms that take raw meteorological data (e.g., wind speed, temperature, humidity, cloud cover) and site information (e.g., land cover type, roughness length) and calculate parameters necessary for estimating dispersion. While this analysis is usually closely associated with dispersion modeling, the atmospheric parameters calculated are also used in estimating source emission rates. Traditionally, these parameters have been represented as stability classes; however, in this analysis, the turbulence of the atmospheric boundary layer is represented by more fundamental turbulence measures, such as friction velocity, surface heat flux, and inversion height. Step 2 is accomplished in CASRAM with a

Lagrangian integral dispersion model for passive releases, coupled with a dense gas dispersion model to address large releases of liquefied gases where heavier-than-air plumes form. The physical relationships that make up the emission rate and dispersion models are outlined in Sections 3.3 and 3.4, respectively.

3.1.2 HMIS Database

The HMIS database, maintained by DOT, catalogues transportation-related incidents involving the release of hazardous materials (PHMSA 2014). In later years, about 15,000–18,000 incidents per year have been catalogued for highway, rail, air, and waterway transportation. In general, 80–85% of the incidents are highway-related, and about 8–10% are rail-related. Air accidents (mainly luggage-related) and a small number of waterway incidents make up the rest. Incidents in the database can occur (a) during an accident (i.e., during a vehicular mishap or a train derailment), (b) en route but not during an accident (e.g., due to a cargo shift or valve failure), or (c) during loading or unloading operations. For highway transportation, about 80% of the incidents in the HMIS database occur during loading and unloading, whereas for rail, about 85% are en route/nonaccident releases.

For each incident catalogued in the HMIS database, information pertaining directly to the hazardous material release is provided, including the (a) name of the chemical shipped, (b) container type and capacity, (c) number of containers shipped, (d) number of containers that failed, and (e) amount of material released. Multiple chemicals released during the same incident are recorded in the database as separate records. The database also contains information concerning the occurrence of fire, explosion, water immersion, and environmental damage, as well as the number of deaths, major and minor injuries, and number of persons evacuated. Death and injury statistics pertain only to the consequence of the hazardous material release and not to physical trauma due to the accident itself. Since this database is composed of data from actual hazardous material incidents, it is an invaluable tool in statistical analyses of hazardous material transportation incidents and the best publicly available source of information on container failures and release amounts. For the ERG analysis and other risk assessments, we use HMIS data to specify geographical incident distributions, temporal incident distributions, and discharge fraction distributions, as described in the subsections below. Further information on the HMIS database and our previous analyses can be found in Brown et al. (2001).

3.1.3 Geographic Incident Distributions

In the ERG2012 analysis, accidents are distributed across all 50 states in the United States, the southern Canadian provinces, and Mexico. Within the United States, the accident distribution is based on incident distributions in the HMIS database for 2000 through 2010, and separate geographic distributions are used for highway and rail. The distribution of accidents among the United States, Canada, and Mexico is based on the relative gross domestic product (GDP) for 2010. GDP was selected as a measure for hazardous material incidents because of the unavailability of detailed data on hazardous material incidents for Mexico. For the United States and Canada, the relative GDP for chemical and chemical products is similar to the

total GDP, but because the industry-specific GDP was not available for Mexico, and because Canadian and U.S. chemical-specific GDPs are calculated slightly differently, the total GDP was considered to be the more robust indicator. On the basis of this breakdown, 86.6% of incidents modeled in the ERG2012 analysis occurred in the United States, 7.6% occurred in Canada, and 5.8% occurred in Mexico. Within Canada and Mexico, incidents were distributed into regions on the basis of population. Canada was divided by province. In this process, New Brunswick, Newfoundland, Nova Scotia, and Prince Edward Island were combined as the "Atlantic Provinces," and the Yukon and Northwest Territories were excluded because of their small populations (more than 0.5% of total Canadian population). Mexico was divided into three regions: Northern (above 22°N latitude), Central (between 18 and 22°N latitude), and Southern (below 18°N latitude, including the Yucatan Peninsula). A breakdown of the geographic distribution of incidents in the ERG2012 analysis for highway and rail transportation is provided in Table 3.1.

3.1.4 Temporal Incident Distributions

Temporal release distributions are important to specify appropriate meteorology. In some risk assessment studies, temporal variables also influence the population at risk since (1) the population density of a particular location can change throughout the day and (2) a greater fraction of people are outside during the daytime. Two temporal variables are defined in our analysis: hour of day and month of year. Concerning meteorology, the hour is critical because of the diurnal cycle of the atmospheric boundary layer, and the month is important because the season affects the temperature, wind speed, and daytime mixing height. Note that the meteorology affects not only the dispersion of the chemicals in the atmosphere but also the evaporation rate of spilled liquids in the atmosphere.

Temporal incident statistics used in CASRAM and the ERG analysis are based on HMIS database records from 1990 through 2004. Data from 2003 through 2010 were also analyzed in the course of the ERG2012 analysis, but it was determined that the additional data did not materially affect the temporal distributions, and they were therefore left unchanged from those developed for the ERG2008.

Temporal incident statistics are shown in Figures 3.1 and 3.2. The figures show the percent of incidents broken into time of day (Figure 3.1) and month (Figure 3.2). Data are shown for accident-related and en route/nonaccident releases for both highway and rail. The numbers of incidents in the statistical samples are provided in the figure legends. The incident sample differs slightly between the figures because some data fields (i.e., hour or month) are missing in a small percentage of HMIS incident records.

TABLE 3.1 Geographic Distribution of Highway and Rail Transportation Incidents Modeled in the ERG2012 Analysis, by Percentage

State	Rail	Highway	State/Province	Rail	Highway
United States					
Alabama	2.17	1.00	New Mexico	0.77	0.36
Alaska	0.10	0.02	New York	1.45	2.80
Arizona	1.35	1.40	North Carolina	1.65	2.93
Arkansas	0.90	1.00	North Dakota	0.44	0.14
California	10.28	7.08	Ohio	3.72	6.68
Colorado	1.09	2.02	Oklahoma	0.72	1.13
Connecticut	0.06	1.48	Oregon	1.13	1.48
District of Columbia	0.01	0.04	Pennsylvania	2.70	5.31
Delaware	0.13	0.13	Rhode Island	0.03	0.21
Florida	1.60	3.42	South Carolina	1.21	0.93
Georgia	2.07	2.44	South Dakota	0.05	0.11
Hawaii	0.00	0.02	Tennessee	2.70	3.34
Idaho	0.46	0.24	Texas	10.98	6.89
Illinois	6.62	6.61	Utah	1.08	1.36
Indiana	1.47	2.35	Vermont	0.04	0.09
Iowa	0.93	0.80	Virginia	1.46	1.02
Kansas	1.74	1.98	Washington	1.62	1.19
Kentucky	1.92	1.15	West Virginia	0.62	0.31
Louisiana	7.25	1.17	Wisconsin	0.79	1.50
Massachusetts	0.43	1.51	Wyoming	0.61	0.12
Maryland	1.05	1.76	*Canada and Mexico*		
Maine	0.12	0.21	British Columbia	0.92	0.92
Michigan	2.34	1.64	Alberta	0.71	0.71
Minnesota	0.94	1.57	Saskatchewan	0.28	0.28
Mississippi	0.89	0.78	Manitoba	0.30	0.30
Missouri	1.74	1.85	Ontario	2.82	2.82
Montana	1.74	1.85	Quebec	1.92	1.92
Nebraska	1.29	0.35	Atlantic Provinces	0.65	0.65
Nevada	0.60	0.54	Northern Mexico	1.33	1.33
New Hampshire	0.03	0.14	Central Mexico	3.48	3.48
New Jersey	1.49	2.15	Southern Mexico	0.98	0.98

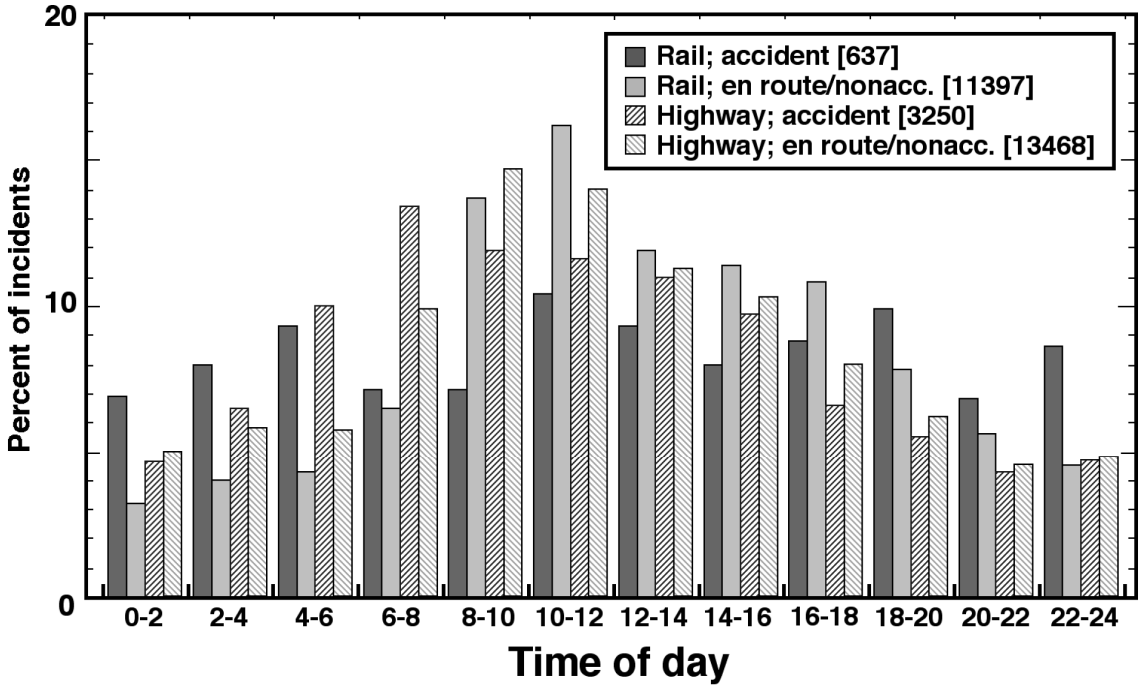

FIGURE 3.1 Hourly Distributions of Rail and Highway Transportation-Related Hazardous Material Releases Occurring during Accident-Related and en Route/Nonaccident Incidents from the HMIS Database for 1990–2002

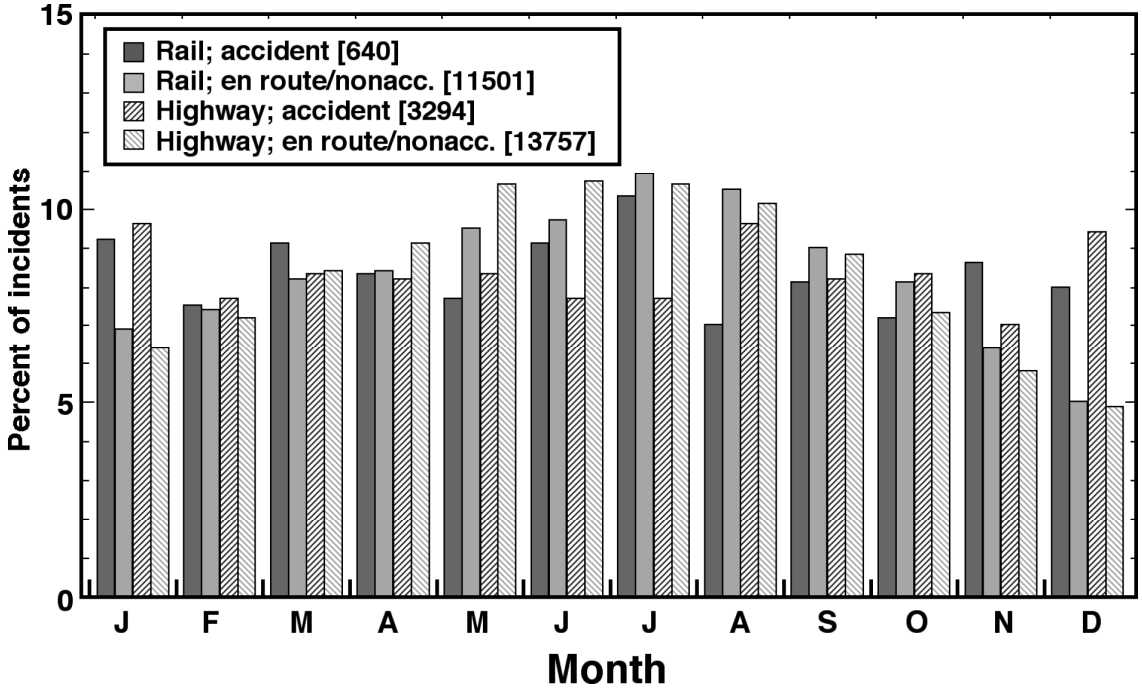

FIGURE 3.2 Monthly Distributions of Rail and Highway Transportation-Related Hazardous Material Releases Occurring during Accident-Related and en Route/Nonaccident Incidents from the HMIS Database for 1990–2002

3.1.5 Discharge Fraction Distributions

In the CASRAM emission model, the discharge fraction is estimated by using statistical distributions developed from an analysis of the HMIS database. HMIS records list the container type, number of containers shipped, number of containers that failed, and amount of material released. This information allowed us to statistically characterize the release amounts for containers of various types and sizes. In this process, we found that the fraction of the container capacity that is released proved to be a robust statistic in terms of both collapsing data from a wide variety of containers and ease of use in subsequent risk assessment studies. This fraction of the total container capacity that is released is defined here as the "discharge fraction." Since the amount of material actually shipped is not currently provided in the HMIS database, the container capacity provides the best estimate of the amount shipped.

As an example, consider a vehicular accident that involves the shipment of chlorine in a 17,000-gal Type 105A300W railcar in which 240 gal are released. The discharge fraction would be 240/17,000, or 0.014. As is discussed later, this incident would be grouped with all other incidents involving releases from pressurized railcars (Type 105 and 112) to construct the discharge fraction distributions for accident-related releases.

In the CASRAM source model, discharge fraction statistics are segregated according to container type. In general, these container types can be classified according to whether they are used for bulk or package freight. As part of the analysis for the ERG2004, we reevaluated our previously published discharge fraction distributions (Brown et al. 2001) by using HMIS data through 2002 (Brown and Dunn 2007). Data from 2000 through 2010 were also analyzed in the course of the ERG2012 analysis, but it was determined that the additional data did not materially affect the discharge fraction distributions, so they were left unchanged from those developed for the ERG2004. The discharge fraction distributions for bulk and package freight are handled in very different ways, as described in the subsections below.

3.1.5.1 Bulk Containers

Discharge fraction statistics for bulk containers are shown in Figures 3.3 and 3.4. Figure 3.3 shows discharge fraction distributions for containers that are used for nonpressurized and low-pressure materials. Figure 3.4 shows the distributions for containers that are used for high-pressure materials. Note that not all container types shown are authorized for transport of TIH materials; these are provided for comparison and for possible use in risk assessments for other types of hazardous materials. Discharge fraction distributions are provided for the two transportation-related phases considered in the ERG analysis: accident-related and en route/nonaccident releases. Discharge fraction statistics for bulk package freight were developed for a specific container type (Type 111A tank cars, MC/DOT 312 tanks, etc.) when sufficient statistical data (i.e., data on at least 25 incidents) were available. In practice, discharge fractions for other container types for which data are insufficient could be estimated by using a surrogate for a similar container type for which data do exist. For example, the surrogate discharge fraction distribution for Type 103 tank cars would be that for Type 111A tank cars, and the surrogate for MC/DOT 338 cargo tanks would be MC/DOT 331 cargo tanks.

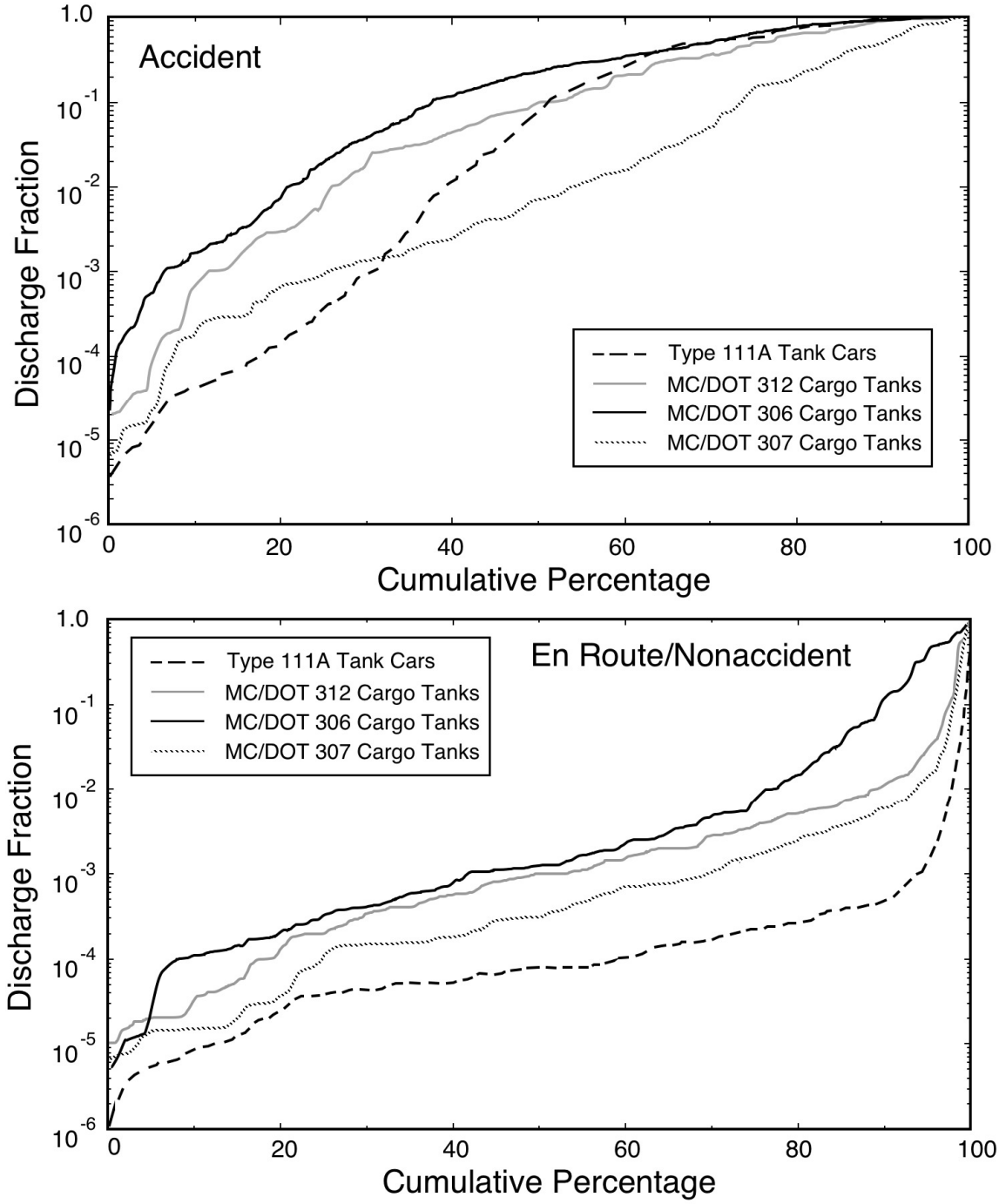

FIGURE 3.3 Discharge Fraction Cumulative Probability for Bulk Nonpressurized and Low-Pressure Containers as Derived from the Analysis of the HMIS Database Used for the ERG2012 Analysis (Results are shown for accident-related and en route/nonaccident releases.)

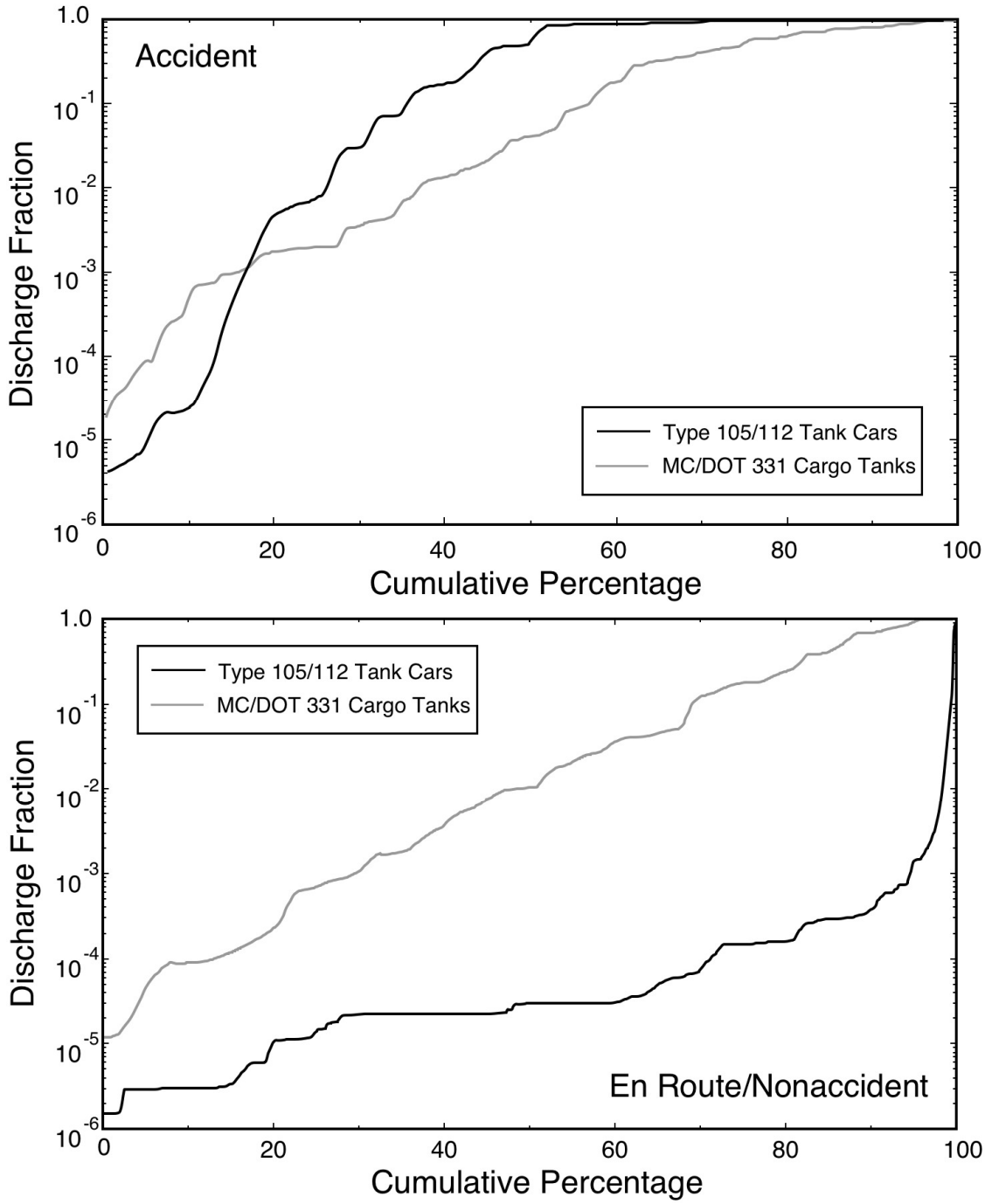

FIGURE 3.4 Discharge Fraction Cumulative Probability for Bulk Pressurized Containers as Derived from the Analysis of the HMIS Database Used for the ERG2012 Analysis (Results are shown for accident-related and en route/nonaccident releases.)

To facilitate their use in computational models, we developed mathematical expressions for the discharge fraction that can be employed in Monte Carlo analyses. We believe use of these functional forms is preferable to using the raw discrete distributions, as was done previously, since they eliminate discretization problems that sometimes occur in the raw distributions. Distributions for bulk containers were fit to the following functional form:

$$F(\gamma) = \min(1, e^{\zeta(\gamma)}), \tag{3.1}$$

where $\zeta(\gamma) = \sum_{n=1}^{N} a_i \gamma^{nb}$.

Here, F is the discharge fraction, γ is a uniform random deviate from 0 to 1, and a_i and b are coefficients that depend on container type and incident type. N, the number of coefficients a_i (i = 1,N) that are necessary, is either 6 or 8, depending on the complexities of the distribution, particularly near the ends. The coefficient b serves to stretch the very low probability end of the distribution and is necessary to accurately capture the frequency of rare en route/nonaccident events where a large fraction of the container capacity is released while correctly representing the remainder of the distribution. For all accident-related events, b = 1, and for en route/nonaccident events, b is <0.5. The coefficients for Equation 3.1 for accident and en route/nonaccident events are listed in Tables 3.2 and 3.3, respectively.

3.1.5.2 Package Freight Containers

For package freight containers, we had previously developed discharge fraction distributions for accident-related releases that specified the total amount released as a fraction of the total container capacity (i.e., capacity of all containers combined). Discharge fraction distributions for en route/nonaccident releases were represented as the fraction of the capacity of an *individual container* in the shipment that is released (see Brown et al. 2001). One drawback of this release fraction normalization was that the distributions did not properly represent shipments that contain only a few containers. For the ERG2004 analysis, we revised this framework for drums and cylinders on the basis of our reanalysis of HMIS data through 2002 to specify both the (1) percentage of containers that leaked or failed and (2) discharge fraction distribution applicable to each failed container. In addition, for accident-related incidents, we specified a probability that the entire shipment was released. Since almost all cases of practical interest in evaluating inhalation hazards from package freight shipments involve drums or cylinders, we limited our discharge fraction framework for these two classes of containers.

We divide our discussion below into accident-related and en route/nonaccident releases since the methods employed to treat these cases are substantially different.

Accident-Related Releases. The first step in the analysis framework is to determine the percentage of cases in which the entire shipment amount is released. Typically, only a few containers of a multiple container shipment are compromised in a traffic accident. However, in more serious accident-related events, the entire shipment can be released. A complicating factor,

TABLE 3.2 Coefficients for Calculating Discharge Fraction Cumulative Probability Distributions for Accident-Related Releases for a Variety of Containers

Container	b	a_1	a_2	a_3	a_4	a_5	a_6	a_7	a_8
Type 111A tank cars	1	–12.2825	25.2135	–97.7815	382.86	–468.648	–106.407	513.26	–235.777
Type 105/112 tank cars	1	–13.5011	29.0148	64.2486	–235.971	223.212	–65.2201	0	0
MC/DOT 306 cargo tanks	1	–8.02475	6.20446	104.348	–325.183	284.727	149.822	–358.121	146.299
MC/DOT 307 cargo tanks	1	–12.5422	50.5658	–169.235	257.71	–84.3257	–130.654	108.216	–19.6658
MC/DOT 312 cargo tanks	1	–11.3375	43.4848	–101.806	149.477	–112.577	32.859	0	0
MC/DOT 331 cargo tanks	1	–10.8601	43.6839	–181.754	440.336	–466.95	175.992	0	0

TABLE 3.3 Coefficients for Calculating Discharge Fraction Cumulative Probability Distributions for en Route/Nonaccident Releases for a Variety of Containers

Container	b	a_1	a_2	a_3	a_4	a_5	a_6	a_7	a_8
Type 111A tank cars	0.5	0.624664	–44.0097	39.2814	150.665	–334.474	50.9987	318.078	–194.708
Type 105/112 tank cars	0.33	20.2316	–171.317	379.325	–285.744	–97.0904	46.2262	278.699	–184.156
MC/DOT 306 cargo tanks	0.33	4.67339	–71.6677	378.743	–859.395	610.244	368.827	–653.445	210.363
MC/DOT 307 cargo tanks	0.36	4.46934	–41.2228	51.6474	–6.432	–32.2012	5.55689	11.7468	–5.51775
MC/DOT 312 cargo tanks	0.4	4.15943	–39.2797	54.9507	–21.9882	–17.3163	5.09395	16.6091	–13.8431
MC/DOT 331 cargo tanks	0.5	0.338613	0.285349	–6.47588	–5.23065	0	0	0	0

though, is that the probability of the entire shipment being released decreases as the number of containers in the shipment increases. Table 3.4 shows the number of accident-related incidents catalogued in the HMIS database for 1990 through 2002 involving metal drums, and it also shows the number of these cases in which more than 90% of the total shipment amount was released. In more than half of the incidents involving a single metal drum, the entire shipment contents were released; in shipments containing multiple drums, the percentage of such releases decreased to 10%. Table 3.5 shows identical information for cylinders, for which a similar trend was found. Note that the total incident counts are rather low, especially for cylinders, so there is significant statistical uncertainty in these data.

TABLE 3.4 Incident Counts Involving Drums in Accident-Related Releases in the HMIS Database (1990–2002), Showing the Number in Which More Than 90% of the Total Shipment Amount Was Released

Number of Drums in Shipment	Total Number of Incidents	Number with >90% Release
1	25	14
2–5	26	3
6–10	36	3
10–20	42	3
20–50	27	1
>50	37	4

TABLE 3.5 Incident Counts Involving Cylinders in Accident-Related Releases in the HMIS Database (1985–2002), Showing the Number in Which More Than 90% of the Total Shipment Amount Was Released

Number of Drums in Shipment	Total Number of Incidents	Number with >90% Release
1	22	12
2–5	14	2
>5	13	3

To account for these maximum release events in a robust manner, we first select a fraction of the incidents for which the entire shipment is released. The percentages of such incidents are 10% and 25% for shipments of drums and cylinders, respectively. In practice, these are the limiting cases, as the number of containers becomes large. The increase in the percentage of total releases in which more than 90% of the shipment is released, which occurs for shipments involving small numbers of containers, is accounted for in the second analysis step detailed below.

For the remainder of the shipments, we then specify the number of failed containers N_f as

$$N_f = N_s \gamma^{N_s^a} , \tag{3.2}$$

where N_s is the number of containers shipped, γ is a uniform random deviate from 0 to 1, and a is a coefficient. In this expression, N_f is an integer that is rounded up from the value on the right-hand side.

The total amount of material released is then written as

$$F = \min\left(1, \sum_{i=1}^{N_f}\left[c_1 + c_2\gamma_i + c_3\gamma_i^{d_3}\right]\right), \tag{3.3}$$

where γ_i is a set of independent (i.e., uncorrelated) uniform random deviates from $i = 1$; and N_f and c_1, c_2, c_3, and d_3 are constants, the values of which, along with a in Equation 3.2 above, are provided in Table 3.6. Note that each failed container is treated independently in Equation 3.3.

En Route/Nonaccident Releases. From a statistical perspective, en route/nonaccident events are fundamentally different from accident-related events. Like bulk transportation, the total release amounts are typically very small compared with accident-related releases. En route/nonaccident events are also much more common, as evidenced from HMIS statistics presented previously in Table 2.1. Usually only one container is involved, even in shipments with large numbers of containers. Tables 3.7 and 3.8 provide incident counts involving drums and cylinders, respectively, from en route/nonaccident releases in the HMIS database (1990–2002), together with the number that involved only one container and, for comparison with Tables 3.4 and 3.5, the number in which more than 90% of the total shipment amount was released.

To treat the discharge fraction estimation problem for these events, we take an approach similar to the one we take for accident-related events. We first split out those events where only one container is involved. For both drums and cylinders, we set this as 75% of incidents. For the other 25% of incidents, we calculate the number of failed containers with Equation 3.2, with different values for the coefficient a. Then for all incidents, we use Equation 3.3 again, with different values for the coefficients. The coefficients for Equations 3.2 and 3.3 for en route/nonaccident releases are provided in Table 3.9.

TABLE 3.6 Coefficients for Calculating Discharge Fraction Cumulative Probability Distributions in Equation 3.3 for Accident-Related Releases Involving Drums and Cylinders

Container	a	c_1	c_2	c_3	d_3
Drums	0.5	0	0	2.0	1.5
Cylinders	0.65	0	0.167	3.1	3.5

TABLE 3.7 Incident Counts Involving Drums in en Route/Nonaccident Releases in the HMIS Database (1990–2002), Showing the Number That Involved Only One Container and the Number in Which More Than 90% of the Total Shipment Amount Was Released (for Comparison with Table 3.4)

Number of Drums in Shipment	Total Number of Incidents	Number Involving One Container	Number with >90% Release
1	730	730	63
2	335	291	3
3–5	552	491	2
5–10	464	403	1
10–20	399	345	0
20–50	437	337	0
>50	705	472	0

TABLE 3.8 Incident Counts Involving Cylinders in en Route/Nonaccident Releases in the HMIS Database (1990–2002), Showing the Number That Involved Only One Container and the Number in Which More Than 90% of the Total Shipment Amount Was Released (for Comparison with Table 3.4)

Number of Cylinders in Shipment	Total Number of Incidents	Number Involving 1 Container	Number with >90% Release
1	37	37	16
2–5	45	38	0
>5	43	28	1

TABLE 3.9 Coefficients for Calculating Discharge Fraction Cumulative Probability Distributions in Equation 3.3 for en Route/Nonaccident Releases Involving Drums and Cylinders

Container	a	c_1	c_2	c_3	d_3
Drums	0.75	0.0025	0	1.23	4.0
Cylinders	0.75	0	0.167	3.5	4.5

3.2 METEOROLOGICAL DATABASE USED TO PREPARE THE GUIDEBOOK

The meteorological database is a critical component of the ERG2012 analysis, since it provides the historical meteorological data necessary to model hazardous material incidents anywhere in the United States, Canada, and Mexico. This database was generated directly from 5 years of observational data from 105 cities in the United States with supplemental data from several stations in Canada and Mexico. The data were first preprocessed by using the Surface Energy Budget Meteorological (SEBMET) model (Brown 1997; Brown and Dunn 1998). This meteorological preprocessor was designed for use with statistical dispersion studies such as the ERG analyses. A meteorological preprocessor contains a series of algorithms that use routinely measured observations of wind speed, temperature, humidity, and cloud cover, along with upper-air temperature soundings, to calculate the key parameters related to the atmospheric boundary layer needed to model source thermodynamics, transport, and dispersion. The following sections first discuss the raw meteorological data used in the analysis and then provide a brief overview of SEBMET's methodology. They then describe a companion database employed to estimate water temperature for analysis of water-reactive spills.

3.2.1 Meteorological and Site Data

For the ERG analysis, CASRAM uses a meteorological database that includes hourly meteorological parameters from 204 U.S. cities in 1996 through 2005 (as illustrated in Figure 3.5) and supplemental data from several stations in Canada and Mexico. The stations were chosen to provide a roughly uniform coverage area. Raw meteorological data included yearly surface files listing hourly values of wind speed, temperature, cloud cover (height and fraction), dew point temperature, pressure, and visibility, among other variables. In addition, upper air data from 80 stations across North America were employed to evaluate the atmospheric temperature profile up to the 7,000-m altitude necessary for determining the daytime mixing height. Site characteristics determined for each station included land cover, vegetative types, the monthly leaf area index (a measure of the canopy density) for each vegetative type, roughness length, albedo, and soil types. These site-specific parameters were determined through a climatological study of the areas surrounding each site.

3.2.2 Meteorological Preprocessor

The meteorological preprocessor contains two primary components: a surface energy budget (SEB) model that determines the surface-layer turbulence parameters and an integral model that determines inversion height in convective conditions. Each component is briefly outlined below. Brown (1997) and Brown and Dunn (1998) contain additional information on the meteorological preprocessor, including details on its development and validation.

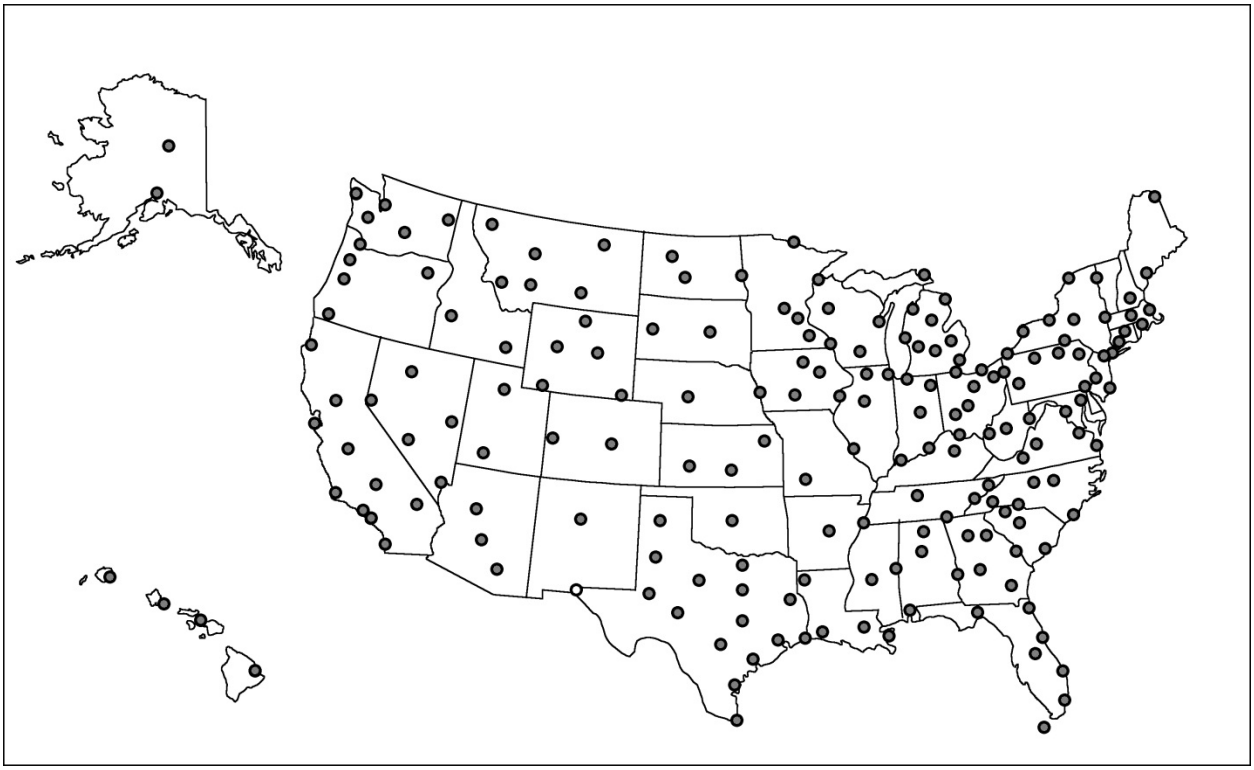

FIGURE 3.5 Locations of the 204 National Weather Service Stations Used for Statistical Meteorological Characterization

3.2.2.1 Surface Turbulence Parameters

The surface-layer parameters are determined by using an SEB model that consists of parameterizations of the various SEB components and well-known flux-profile relationships. The goal of this modeling approach is to isolate the sensible heat flux H from the other energy budget components. The starting point for this analysis is the SEB at the ground. When advection, photosynthesis, and snow melt are neglected, the SEB is most simply represented as follows:

$$Q^* = H + \lambda E_w + G + Q_a , \tag{3.4}$$

where

Q^* = net surface radiative heat flux,

G = conductive soil heat flux,

λ = heat of vaporization for water,

E = evaporation rate (together, λE_w is the latent heat flux), and

Q_a = anthropogenic heat flux.

The net surface radiative heat flux is the residual from the absorbed solar radiation S, incoming long-wave radiation L^+, and outgoing long-wave radiation $\varepsilon\sigma T_S^4$. It is written as follows:

$$Q^* = (1-\alpha_s)\,S + L^+ + \varepsilon_s \sigma T_s^4, \tag{3.5}$$

where

α_s = surface albedo,

ε_s = surface emissivity,

σ = Boltzmann constant, and

T_s = surface temperature.

At the surface, the short-wave balance is always positive, while the outgoing long-wave radiation generally exceeds incoming long-wave radiation. The model is constructed by parameterizing each of the components in the SEB in terms of routinely observed meteorological observations and site characteristics. A brief description of the SEB component parameterizations is presented below.

Incoming solar radiation at the surface is determined by using a variation of the Parameterization C model (Iqbal 1983). In this model, the solar radiation incident on top of the atmosphere is determined from earth-sun relationships and then adjusted via transmittance functions to account for atmospheric absorption and scattering. Separate transmittances are specified for (1) absorption due to (a) ozone, (b) water vapor, and (c) aerosols and for (2) scattering due to (a) Rayleigh particles (molecules) and (b) aerosols. In addition, the model accounts for multiple reflections of solar radiation between the ground and the atmosphere, which significantly increase solar radiation when the surface albedo is high (e.g., deserts or snow cover). Along with data on location and time, the model requires data on (1) local atmospheric pressure; (2) surface albedo; (3) visibility; (4) precipitable water content, which is derived from upper-air data; and (5) ozone amount, which is estimated from latitudinal-seasonal averages. Attenuation due to cloud cover is estimated from the opaque and total cloud cover and cloud height by a semi-empirical model that was developed by Brown (1997) from an analysis of the National Solar Radiation Database (NREL 1992).

Net long-wave radiation at the surface is determined by using data on surface temperature, emissivity, near-surface temperature profiles, and humidity profiles. In particular, incoming long-wave radiation is estimated on the basis of a semi-empirical relationship developed from parameterizing long-wave radiation estimates from a detailed narrow-band radiation model. This relationship relies on data on the near-ground temperature profile, 10-m

water vapor pressure, cloud fraction, and cloud height. Outgoing long-wave radiation is represented directly by using ground and foliage temperatures that are solved for in the model.

At the surface, the solar radiation and incoming long-wave radiation are balanced against the (1) sensible heat transfer, (2) latent heat transfer, (3) ground conduction heat transfer, and (4) outgoing long-wave radiation. To provide a physical, unified treatment valid under both daytime and nighttime conditions, SEBMET employs a two-layer canopy model that evaluates energy transfer components from both the ground and the vegetative layer. The model is formulated by writing separate energy-balance relationships for the ground and the vegetative canopy similar to Equations 3.4 and 3.5 and by parameterizing the energy transfer components in terms of available meteorological measurements and known vegetation and ground characteristics. The vegetative layer is characterized by the leaf area index and the bulk stomatal resistance, which is a measure of the latent heat transfer resistance. The key parameter is the bulk stomatal resistance, which embodies the physiological response of the vegetation to the ambient environment. In the SEBMET canopy model, this parameter is estimated by modeling the stomatal responses to (1) ambient temperature, (2) vapor pressure deficit, (3) solar radiation, and (4) moisture stress. Evaporation from the soil is considered by defining a moisture store in the soil layer that is reduced through evaporation and replenished by precipitation. The outgoing long-wave radiation is estimated directly from the canopy and ground temperatures and the canopy coverage percentage. Heat conduction into the ground is estimated by using a numerical finite-difference algorithm that allows the dependence of soil properties and the insulating effect of overlying vegetation and snow to be explicitly treated. Such a scheme allows the ground temperature profile to be saved for use in pool evaporation calculations in the CASRAM emission rate model.

3.2.2.2 Inversion Height and Boundary Layer Height

The inversion height in convective condition is estimated with a one-dimensional model of the atmospheric boundary layer based on the Driedonks slab model (Driedonks 1982). In the Driedonks model, as in similar models, the surface turbulence fluxes u_* and H are integrated over time so the boundary layer evolves from an initial early morning height. The Driedonks model was chosen because of its comprehensive treatment of dynamics at the inversion, favorable comparison with field data, and ease of inclusion in the preprocessor.

In neutral and stable conditions, the boundary layer height is less well defined. Generally, the boundary layer height (at least in stable conditions) is taken to be the height at which surface-induced turbulence drops to a negligible value. Here, the diagnostic relations for stable conditions defined by Nieuwstadt (1981) and provided by the neutral limit ($h = 0.3u_*/f$, where f is the Coriolis force) are used, following the recommendations of Hanna and Paine (1989). (Hanna and Paine recommend that the neutral relation be used when L is greater than or equal to 100 and that Nieuwstadt's relation be used when L is more than zero but less than 100.)

3.2.3 Water Temperature for TIHWR Reaction Rates

As discussed in Section 3.3.3, temperature is the most sensitive environmental variable affecting reaction rates of spilled chemicals with water. In general, the reaction rate roughly doubles for every 10°C increase in temperature. To account for this effect in our statistical hazardous materials analysis, we developed a database for water temperature as a function of location and Julian day. We investigated the following three sources of water temperature data:

1. *Great Lakes Buoys (GLBs).* Data were available from eight buoys scattered throughout the Great Lakes, whose reported temperatures yielded a multiyear average that was parameterized as a function of Julian day (Lesht and Brandner 1992).

2. *U.S. Geological Survey (USGS) Water Quality Network (WQN).* The USGS gathered data on stream water temperatures for periods of up to 30 years before 1990 at about 680 water stations (the WQN data). The data were for uneven durations and taken at uneven frequencies. In the best cases, monthly temperature values were recorded for a period of 20 years or more. For most stations, the day of the month and the time of day on which measurements were recorded varied, and about one month elapsed between measurements.

3. *National Oceanic and Atmospheric Administration (NOAA) Ocean Harbor Buoys.* Data from a series of harbor buoys along the Atlantic and Pacific coasts were recorded for years. Data from a representative set of locations were examined and found to substantively agree with the USGS data as a function of latitude. Therefore, the harbor buoy data were not specifically used for this study.

Stations were selected to meet several criteria. We wanted the network of stations to cover the United States evenly, or, if concentrated, to represent population centers. We needed data from a period of 20 years to permit meaningful climatological modeling. In actuality, while the target was about 240 temperature values, we chose stations that had recorded between about 150 and 450 values. Locations for WQN stations and Great Lakes buoys used in preparation of ERG2012 are shown in Figure 3.6.

We used a special parameterization of average GLB values by Julian day published by Lesht and Brandner (1992) for this study. For each WQN station or harbor buoy, the full set of values was fitted to the following equation:

$$T(J) = T_{avg} + (\Delta T)\sin\left(2\pi\frac{J - J_o}{365}\right). \tag{3.6}$$

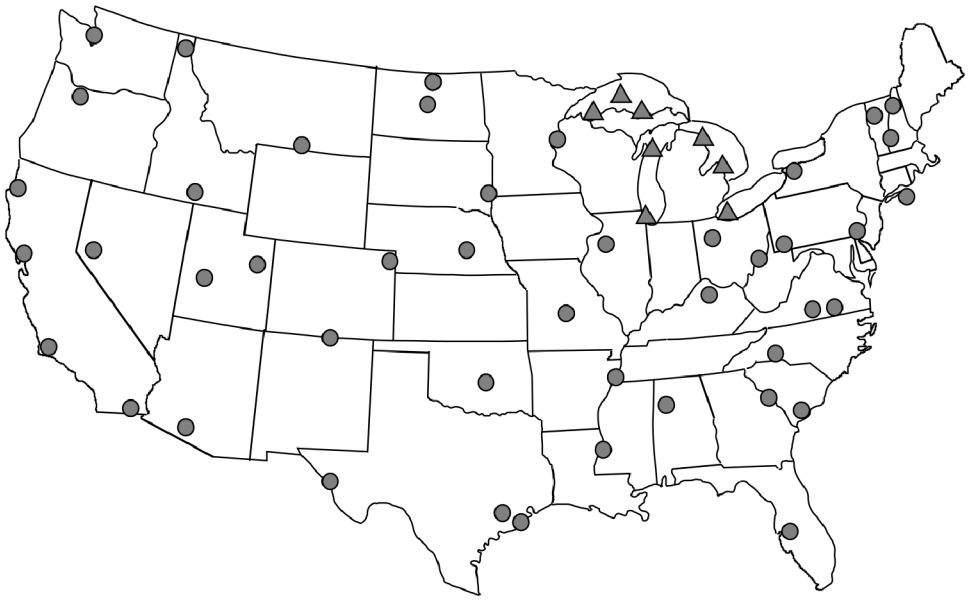

FIGURE 3.6 Water Quality Network Stations Used to Determine Variations of Average Water Temperature by Julian Day and Location (circles = 45 land-based sampling sites; triangles = 8 GLBs)

The values of T_{avg}, ΔT, and J_o were fitted to all of the values. The GLBs were fitted with a six-parameter function given by Lesht and Brandner (1992). Because the formula has six adjustable constants and is somewhat detailed, it is not provided here. Interested readers are referred to the Lesht and Brandner (1992).

3.3 EMISSION RATE CHARACTERIZATION

3.3.1 Overview of Release Types

Materials are shipped as either (a) solids, (b) ordinary liquids, (c) compressed gases, or (d) liquefied gases. The emission rate of a chemical to the atmosphere is largely dependent on the shipment state. Because of their low volatility, solids typically exhibit low emission rates. Therefore, with the exception of certain water-reactive materials, no solid materials appear on the ERG TIH list. Release mechanisms for the other shipment states (b–d above), together with water-reactive materials, are illustrated in Figure 3.7 and discussed next.

Liquid materials are emitted to the atmosphere through pool evaporation, as illustrated in Figure 3.7a. As shall be discussed shortly, the pool evaporation rate depends on many factors, particularly the vapor pressure of the material. For volatile liquids (high vapor pressure), the evaporation rate is often limited by the available energy, whereas for low-volatility liquids, wind speed and atmospheric stability become very important. Highly volatile liquids evaporate very

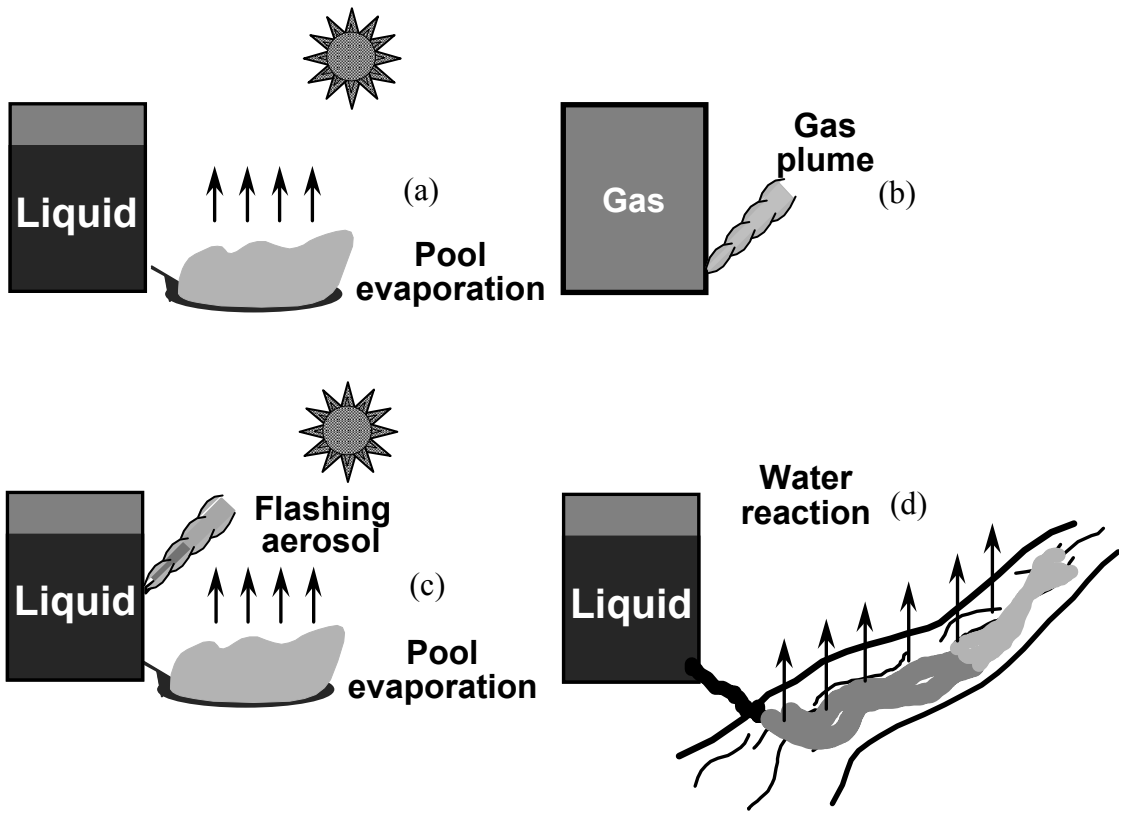

FIGURE 3.7 Important Source Types for Inhalation Risk Considered in the ERG2012 Analysis (a = ordinary liquids, b = compressed gases, c = liquefied gases, d = water-reactive materials)

quickly, sometimes cooling the pool to more than 30°C below the ambient temperature. For certain materials, the evaporating material can cool so much that it freezes.

Compressed gases are released in a so-called "blowdown" process, as illustrated in Figure 3.7b. The blowdown process usually empties the container rapidly and, in the case of severe accidents, may result in a nearly instantaneous release. All else being equal, release rates for compressed gases are many times higher than those for ordinary liquids. Exceptions to this rule include valve leaks and minor cracks, for which release rates may be very small. Valve leaks are the most common release mechanism for en route/nonaccident releases. With the exception of hydrogen, compressed gases are usually shipped in cylinders smaller than 100 gal.

The most catastrophic releases involve liquefied gases, as illustrated in Figure 3.7c. These materials are gases at atmospheric pressure but are liquefied through pressurization and, in some cases, refrigeration. For these materials, the release is broken into two phases. In the initial phase, denoted as the flashing and entrainment phase, a fraction of the material (usually 0–30% of the total) is instantaneously vaporized upon exiting the vessel as a result of the sudden reduction of pressure. Because of the rapid expansion of the material, much of the remaining liquid exiting the vessel is broken into tiny drops, forming an aerosol. The flashed vapor

typically entrains substantial quantities of this aerosol, with the larger droplets quickly settling to the ground or "raining out." This aerosol usually evaporates quickly when exposed to air, cooling the vapor/air mixture to the point where the density of the mixture can become considerably heavier than air. The second phase involves evaporation of the liquid that falls to the ground. Since the vapor pressures for such materials are usually well above atmospheric pressure, the evaporation phase is usually short in comparison to that for materials that are liquids at atmospheric pressure. Liquefied gas releases yield the largest overall emission rates in comparison to liquid and compressed-gas releases and generally represent the greatest danger to the public.

An additional class of materials discussed throughout this report and treated in the ERG analysis is water-reactive materials. These materials release toxic gases to the atmosphere through the reaction of a parent chemical with water. Therefore, a waterway entry or an additional water exposure mechanism is required for them to become an inhalation hazard. The release rate of the toxic byproduct to the atmosphere depends primarily on chemical reactivity, although many other factors can also influence the reaction rate. Key among these is water temperature, since higher water temperatures can greatly accelerate the reaction rate. Evidence also suggests water acidity may be important. Mixing effects are also clear, since greater mixing will generally accelerate the reaction rate. Rivers are generally more turbulent than some other bodies of water and will enhance mixing, and thus the TIH gas evolution rate. Also, whether the parent chemical is heavier or lighter than water (solids and some liquids) can affect the mixing rate. Finally, highly exothermic water reactions will result in faster reactions through heating and mixing and also release (typically acid) mists, which can be very corrosive and toxic.

3.3.2 CASRAM Emission Model and Its Application to the ERG2012 Analysis

The source component of CASRAM determines hazardous material release rates for each of the spill and/or vaporization scenarios described above. Information on the shipment, location, and meteorology are employed in the emission rate model to determine the amount of material spilled and the release rate. First the discharge fraction is estimated by using statistical distributions generated from analysis of HMIS database incidents, as discussed in Section 3.1.2. Then one or more physical models are employed to estimate chemical discharge rates and evaporation rates.

3.3.2.1 Assumptions Used to Develop Accident Scenarios

In developing the accident scenarios, the following assumptions were used:

- For accident-related releases from rail tank cars involving a container breach (60% of total set of such releases), the release rate of material from the container is regulated by the size of the hole, which is specified statistically according to hole-size distributions presented by Raj and Turner (1993). Since no comparable data exist for highway transportation, the hole-size distributions for highway bulk containers are set to those for tank car types having similar specifications (wall thickness, insulation). Total release

amounts are limited to conform to discharge fraction distributions in the HMIS database by varying the location of the hole in the container.

- For en route/nonaccident incidents and for package freight accident-related incidents, release amounts are determined directly from the HMIS database release-fraction distributions. For these incidents, the release is assumed to occur uniformly over a period of 15 min. This method overpredicts the impacts from slow leaks. However, this has no effect on values appearing in the Table, since slow vapor releases typically involve the release of small amounts of material, and therefore those incidents fall well below the 90th-percentile level of protection cutoff.

- Liquids released from the container that are not flashed or entrained with the flashed liquid form a pool of parabolic depth on the ground that expands and contracts in response to gravity-driven fluid flow and evaporation. Maximum pool depth is determined by Monte Carlo sampling for the particular incident being modeled from a clipped exponential distribution, the mean of which is set by the total volume of spilled liquid. For highway-related releases, 50% of spills are assumed to occur on paved surfaces. For rail releases, 25% of spills are assumed to occur on roadbeds. All other spills are assumed to occur on natural surfaces characteristic of the accident locale. Ground temperature profiles to a depth of 1 m are provided in the preprocessed meteorological database to facilitate the ground conduction calculation, which is very important for high-volatility liquids.

- The discharge rate of water-reactive materials from their containers is varied so that 18%, 40%, 60%, and 95% of the total release amount is discharged in the first 5, 15, 30, and 60 min, respectively. The total release amounts are selected to conform with discharge fraction distributions in the HMIS database for the container involved. The time-dependent emission rate of the TIH byproduct from the water is calculated from the container release rate and the reaction rate of the chemical with water.

- Except for the reaction of water-reactive materials to produce TIH byproducts, chemical transformation is not considered.

- The temperature of the material upon release is taken as a weighted average of the air temperature and 285 K, with the exact weight depending on the container type.

3.3.2.2 Physical Considerations

Discharge from Tanks. For liquids and liquefied gases, the first step in this process is determining the time-dependent discharge rate from the tank. Tanks punctured below the liquid line release their contents according to the Bernoulli equation (Perry et al. 1984); namely,

$$Q_l = c_o A_h \rho_l \left[2g\Delta h + 2\left(\frac{P_t - P_a}{\rho_l} \right) \right]^{\frac{1}{2}}, \tag{3.7}$$

where

Q_l = liquid release rate (kg/s),

c_o = discharge coefficient,

A_h = hole area (m^2),

ρ_l = liquid density (kg/m^3),

g = gravitational acceleration (9.81 m/s^2),

Δh = height of liquid above the hole (m),

P_t = tank pressure (Pa), and

P_a = atmospheric pressure (Pa).

Equation 3.7 is used to calculate the discharge rates from all bulk containers in CASRAM, where A_h is provided by the hole-size distributions given by Raj and Turner (1993). Concerning the discharge coefficient c_o, experimental data show that c_o depends on the exit velocity, fluid viscosity, and hole characteristics (Perry et al. 1984). However, at high exit velocities, characteristic of the incidents modeled in CASRAM, c_o is 0.6. Therefore, we set c_o to 0.6 for all releases modeled in CASRAM. If the material is a liquid, it forms a parabolic pool (in depth) on the ground or pavement, which expands and contracts in response to gravity-driven fluid flow and evaporation. Liquefied gases, on the other hand, equilibrate to atmospheric pressure through flashing (explosive evaporation of a fraction of the released material). A fraction of the remaining material is aerosolized and entrained in the flashed vapor, and the remaining material falls to the ground and evaporates.

Note that we assume that the thickness of the container is much less than the effective diameter of the hole. When this criterion is not met, Eq. 3.7 overpredicts the discharge rate, especially for two-phase mixtures. An excellent discussion of application of techniques (including the ω–method) to address situations when the length is non-negligible is provided by Britter et al. (2011).

Pool Evaporation. Pool evaporation within CASRAM is determined by using a time-dependent, energy-budget model that accounts for the important air-pool-ground energy fluxes that govern the evaporation rate. The emission rate of material from an evaporating pool Q_e is represented as

$$Q_e = A_p E_c, \tag{3.8}$$

where

A_p = pool area (m^2) and

E_c = evaporation rate from pool [kg s^{-1} m^{-2}].

Assuming that the ambient concentration of the evaporating chemical is zero, the evaporation rate is a function of the chemical vapor pressure and transfer coefficients, such that

$$E_c = h_m \frac{P_v(T_p)}{RT_p}, \tag{3.9}$$

where

h_m is the mass transfer coefficient,

P_v is the chemical vapor pressure at the pool temperature T_p, and

R is the ideal gas constant for air.

The mass transfer coefficient h_m is a function of pool size, meteorology, and chemical properties. The key variable parameter in Equation 3.9 is the pool temperature, since the vapor pressure on which the evaporation rate depends usually varies exponentially with temperature. The pool temperature (and hence the evaporation rate) is determined by using a time-dependent, energy-budget model that considers heat transfer to and from the pool via radiation, convection, conduction, and evaporation. In particular, the conductive heat flux from the ground is especially important and is often the dominant source for available energy, especially for very volatile liquids. Treating the conduction correctly, especially the initial and boundary conditions, was a principal motivation in the development of the CASRAM evaporation model.

The energy budget of the pool is a balance between solar radiation S^+, incoming longwave radiation L^+, outgoing longwave radiation $\varepsilon_p \sigma T_p^4$, convective heat transfer H_p, latent heat transfer of water vapor from plant material λE_{wp}, conductive heat transfer G_p, evaporative heat loss $h_{fg}E_c$, and pool energy storage $mc_p dT_p/dt$. (p-subscripted variables refer to pool-specific quantities except c_p). Considering these processes, we write the pool energy budget as

$$Q_p^* = H_p + \lambda E_{wp} + G_p + h_{fg} E_c + mc_p \frac{dT_p}{dt}, \tag{3.10}$$

where Q_p^* is the net radiation given by

$$Q_p^* = (1 - \alpha_p) S^+ + L^+ + \varepsilon_p \sigma T_p^4, \tag{3.11}$$

and G_p is the ground heat flux to the pool given by Fourier's law as

$$G_p = -k_g \left(\frac{dT}{dz} \right)_{z=0}. \tag{3.12}$$

In these relationships, m is the pool mass per unit area, t is time, z is depth into the ground, ε_p is the pool emissivity, α_p is the pool albedo, k_g is the ground heat conductivity, and σ is the Boltzmann constant (5.67×10^{-8}). The necessary transfer coefficients for evaporation are provided by a chemical property database and the preprocessed meteorological database. In particular, the meteorological quantities of interest include aerodynamic resistances based on stability and wind speed, air temperature, incoming solar and longwave radiation, and the initial ground temperature profile. The relative importance of the terms in Equation 3.10 depends largely on the volatility of the chemical in the pool. For highly volatile liquids (i.e., ones that quickly evaporate), the evaporative cooling term is large and must be balanced by the available energy provided by the net radiation, convective heat transfer, and ground conduction terms. Therefore, the amount of available energy often limits the evaporation rate for these materials. For low-volatility liquids, the evaporative cooling term is small, and the remaining terms are similar to what they would be in the absence of a pool. In these materials, evaporation is governed by the vapor pressure, wind speed, and surface turbulence characteristics.

One special case for the pool model is for boiling pools as would occur after the breach of a liquefied gas container. In this case, the ground temperature is initially fixed at the boiling point of the liquid until such time that the heat transfer to the pool from conduction drops below that of convection. At this point, the ground temperature is allowed to drop further as the pool evaporatively cools below the boiling point.

Compressed Gas Releases. In CASRAM, compressed gas releases are modeled by using semi-empirical blowdown relationships based on compressible-flow theory. Releases are assumed to be isentropic rather than isenthalpic. The isentropic assumption is that heat transfer to the vessel is negligible, which is a reasonable approximation for most accidental releases. The isenthalpic approximation, on the other hand, requires sufficient heat transfer to maintain isothermal conditions (assuming the specific heat at constant pressure c_p is constant).

For compressed gas releases, the release rate is calculated on the basis of hole size, tank pressure, and gas density, such that

$$Q = c_o A_h \left[P_t \rho_g \gamma \left(\frac{2}{\gamma+1} \right)^{\frac{\gamma+1}{\gamma-1}} \right]^{\frac{1}{2}}, \tag{3.13}$$

where γ is c_p/c_v, the ratio of the specific heat at constant pressure and the specific heat at constant volume. As in the case of liquid releases, c_o is set to 0.6 for all releases.

Equation 3.13 is applicable until the tank pressure drops below a critical value, given as

$$P_r = \left(\frac{\gamma+1}{2} \right)^{\frac{\gamma}{\gamma-1}}, \tag{3.14}$$

where P_r is ratio of the tank pressure to atmospheric pressure. After this criterion is reached, the discharge rate is given by

$$Q = c_o A_h \left[P_t \rho_g \left(\frac{2\gamma}{\gamma-1} \right) \left(P_r^{-\frac{2}{\gamma}} - P_r^{-\frac{\gamma+1}{\gamma}} \right) \right]^{\frac{1}{2}}. \tag{3.15}$$

Calculations are conducted iteratively by adjusting the tank pressure and density at each time step with the isentropic assumption.

Liquefied Gas Releases. Liquefied gas releases are treated by first calculating the liquid release rate from the container given by Equation 3.7. As discussed previously, this type of release results is a two-phase mixture of liquid and vapor leaving the container. Typically, some fraction of the material will flash to vapor in a very energetic process whereby some of the remaining liquid will be aerosolized and entrained with the vapor. The remaining liquid falls (or "rains out") to the ground. The traction that flashes is known as the flash fraction f and is given by

$$f = \frac{c_p (T_t - T_b)}{h_{fg}}, \tag{3.16}$$

where T_t is the tank temperature and T_b is the boiling point. This fraction of remaining material that is aerosolized and entrained into the flashed vapor is calculated by using empirical relationships based on the discharge kinetic energy of the two-phase mixture provided by Johnson and Woodward (1999). Evaporation of the remaining material that rains out of the aerosol/vapor cloud is then estimated by using the pool evaporation algorithms as noted above.

3.3.2.3 Water-Reactive Materials

For water-reactive materials, a different method is needed to estimate TIH emission rates to the atmosphere. The treatment of water-reactive materials is especially challenging for a variety of reasons. These include the following:

- Water reaction can result from spills into waterways and from other wetting mechanisms, such as rain or, in extreme cases, exposure to very high humidity.
- For waterway spills, the large variety of water body types, accident scenarios, and release characteristics adds considerable complexity to the problem.
- There is a very small amount of historical data on water entry releases, and the characterizations of water body turbulence and mixing are inadequate.
- Prior to our DOT-sponsored experimental studies, there was an almost complete lack of quantitative data with which to validate sophisticated water-reactivity models.

Our efforts to develop a robust approach for assessing the level of public protection required for TIHWR spills was initiated during the ERG1996 analysis and supplemented with an experimental program that was conducted over the following 12 years. The basic formula employed to compute the release rate of TIHWR gases for most materials assumes that the reaction rate exponentially decreases with time, such that

$$Q(t) = M_o f_s \beta \lambda e^{-\lambda(t - T_{ind})} \ , \tag{3.17}$$

where

$Q(t)$ = time dependent release rate of TIHWR product (kg/s),

M_o = initial mass of parent chemical released into water (kg),

f_S = maximum stoichiometric yield (kg TIHWR/kg parent chemical),

β = efficiency factor for the reaction ($0 \le \beta \le 1$),

λ = first-order rate coefficient (s^{-1}), and

T_{ind} = induction time (s).

In the CASRAM source model, Equation 3.17 is discretized to yield values for ΔQ for each parcel of a parent chemical ΔM_o released into a water body. The time-dependent total evolution rate of TIH product(s) from the spill is then the sum of the individual releases arising

from each parcel, where the time in Equation 3.17 is that elapsed since each parcel entered the water.

The key empirical parameters necessary to apply Equation 3.17 are β are λ, since the stoichiometric yield is easily calculated. As discussed below, an additional parameter, the induction time T_{ind} in Equation 3.17, accounts for the autocatalytic nature of the reactions for a small class of silanes. When T_{ind} is >0, $Q(t)$ is 0 for all times until T_{ind}. Experimental data for β and λ are not available in the chemical literature. In our past efforts, an extensive search of the chemical literature yielded only qualitative descriptions of water reactivity for most of the TIHWR materials identified over the previous decade of ERG analyses. Such descriptions allow only a crude estimate of β and λ, accurate to a factor of 2, at best. Moreover, troubling inconsistencies in these qualitative descriptions were sometimes found in different literature sources. In several cases, the descriptions disagreed with the direct experience of at least one of the authors. Furthermore, we could not find any examples in which the deliberate release of a bulk chemical into a relatively large amount of water had been followed by the measurement of TIHWR production amounts.

To help provide a quantitative basis for the TIHWR analysis, we conducted a series of direct experiments on more than 70 potentially water-reactive chemicals beginning in 1999 (for the ERG2000 analysis) and continuing through the ERG2008 analysis. Specifically, for the ERG2000 analysis, we investigated 21 materials. We added experiments on 35 additional materials for the ERG2004, and for the ERG2008 analysis, we conducted experiments on 18 new materials and repeated experiments on 34 materials that had been previously investigated using a significantly improved experimental apparatus. The experimental program and resultant data generated are described in Appendix D. These experiments were small in scale, which leads to some uncertainty in trying to scale the results up to the size of transportation spills. Nevertheless, the experiments greatly increased the accuracy of estimates for β and also provided a direct measure of λ, which is even more difficult to estimate from the qualitative descriptions.

In the course of this experimental program, we used a few different formulations to empirically describe the reaction rates for use in our modeling framework. In particular, we found that Equation 3.17 was not adequate for fully describing the reaction for a narrow class of silanes that exhibit apparent autocatalytic reactions. For nine of these materials in our experimental series, there appeared to be an initial induction period characterized by a slow constant release rate, such that

$$Q(t) = M_o \frac{m_i}{T_{ind}}, \ (t \text{ is } \leq T_{ind}), \tag{3.18}$$

where m_i is an initial production coefficient and T_{ind} is the induction time.

For these materials, the gas evolution starts slowly and then greatly accelerates after the initial induction period, indicating the reaction is likely autocatalytic. For the ERG2004, we developed a combined evolution equation from Equations 3.17 and 3.18. However, for simplicity in treating the full range of cases treated in the ERG2008, we opted to ignore the slow initial

constant release described by Equation 3.18 and instead simply use Equation 3.17 with an induction time offset. We used this approach for the ERG2012 as well. For calculations of practical interest, this simplification has no effect on the resulting hazard estimates, since release rates during the induction period are very small when compared with those after the induction period.

A review of the literature on TIHWR chemicals showed that only two water body characteristics seemed likely to influence their reactions in water: acidity and temperature. For a few chemicals, the presence of acidity was reported to increase the speed and degree of the reaction. However, the characterization of these effects is not well-developed. Because of this situation, and the difficulty of obtaining water acidity data for natural water bodies, we do not attempt to account for water acidity variations in the ERG analysis. The effect of temperature is substantially stronger than the effect of acidity, however, and it is also simpler to treat in a quantitative fashion. The reaction rate of many materials roughly doubles with every 10°C increase in temperature. Fortunately, the temperature of natural water bodies is well-characterized by a network of water quality stations and buoys, as discussed in Section 3.2.3. The temperature dependence of the primary rate constant λ was included in the analysis via the Arrhenius equation, written as

$$\lambda = \lambda_o \exp\left[-6610\left(\frac{1}{T_w} - \frac{1}{T_o}\right)\right], \tag{3.19}$$

where T_o is a reference temperature (20°C for our analyses) and T_w is the water temperature determined by the procedures outlined in Section 3.2.3. The chemical-specific constant λ_o was determined experimentally. In applying this relationship, the rate constant λ for a given hypothetical spill was specified by finding T_w on the Julian day of the simulated accident at the nearest WQN or GLB station. Then the Arrhenius formula was applied to the rate constant listed as the constant λ_o in Table C.1 in Appendix C.

3.4 ANALYSIS OF ATMOSPHERIC DISPERSION

In the atmospheric dispersion modeling phase of the problem, the hazardous material release rate and meteorology are used to estimate chemical concentrations downwind of the release. When plume buoyancy is insignificant (i.e., passive dispersion), downwind concentrations are linearly related to the (a) release rate in the event of a continuous release or (b) release amount in the event of an instantaneous release. The dispersion of the material is strongly dependent on the meteorology. In relative terms, dispersion is very good during daytime with no cloud cover (i.e., maximum surface heating) and very poor during nighttime with clear skies and light winds. Given the same emission rate, ground-level material concentrations downwind of a near-surface release can vary by three orders of magnitude between these two extremes. For moderate-to-high wind speeds and/or overcast conditions, atmospheric dispersion falls between these two limiting cases.

The dispersion method used in the ERG2012 is very similar to that employed in preparation of the ERG2004 and ERG2008. For passive dispersion, we use the vertical dispersion model of Brown (1997), which is applicable for calculating ground-level concentrations from near-ground releases. For heavier-than-air or so-called dense gas releases, we use relationships from the DEGADIS model. The dense gas model is employed for liquefied gas releases in which the cooling of the plume and aerosol entrainment increase the plume density to the point where the passive dispersion assumption is no longer valid. For many liquefied gases, especially those that are highly toxic, the use of a dense gas dispersion model in the initial phases of the plume trajectory calculation does not have a significant impact on the final PAD estimates. For a narrow class of less toxic liquefied gases, such as ammonia, incorporation of a dense gas model has a more substantial effect.

We discuss some general concepts about atmospheric dispersion modeling of hazardous material releases in Section 3.4.1, then describe the CASRAM dispersion model as applied to releases of both passive and dense gases.

3.4.1 Overview of Atmospheric Dispersion

3.4.1.1 Diurnal Aspects of Plume Dispersion

The physical processes governing the development and maintenance of the atmospheric boundary layer (ABL) are very different during day and night, leading to boundary layers with extremely different sizes and characters. These marked differences substantially influence the ability of the ABL to disperse pollutants released near the ground, thereby giving rise to the pronounced differences in downwind concentrations and therefore in PAD values appearing in the Table. This section briefly describes the characteristics that distinguish the daytime and nighttime ABLs and elucidates how these variations lead to the differences in PAD values between the two cases.

The unstable or convective boundary layer (CBL), typical of daytime conditions, is shown in Figure 3.8a. The boundary layer structure is a result of the surface heating caused by solar radiation. This heating destabilizes the lower layers of the ABL, producing large convective cells. These convective cells extend vertically to the lowest temperature inversion, and they efficiently transport heat, momentum, and any material contaminants released into the atmosphere. As the day progresses, the temperature inversion marking the top of the boundary layer rises from near the ground to between 0.5 and 4 km above the surface as a result of the entrainment of stably stratified air above the inversion into the cooler air of the boundary layer below.

An example of a dispersing plume in a typical CBL is pictured in Figure 3.8b. Experimental observations, most notably those of Willis and Deardorff (1976), have indicated that vigorous convection, which typifies the CBL, results in a “rising centerline” phenomenon. In this process, energetic thermals lift the plume or cloud off the ground faster than it disperses downward. This consequence of dispersion in a fully convective boundary layer is primarily

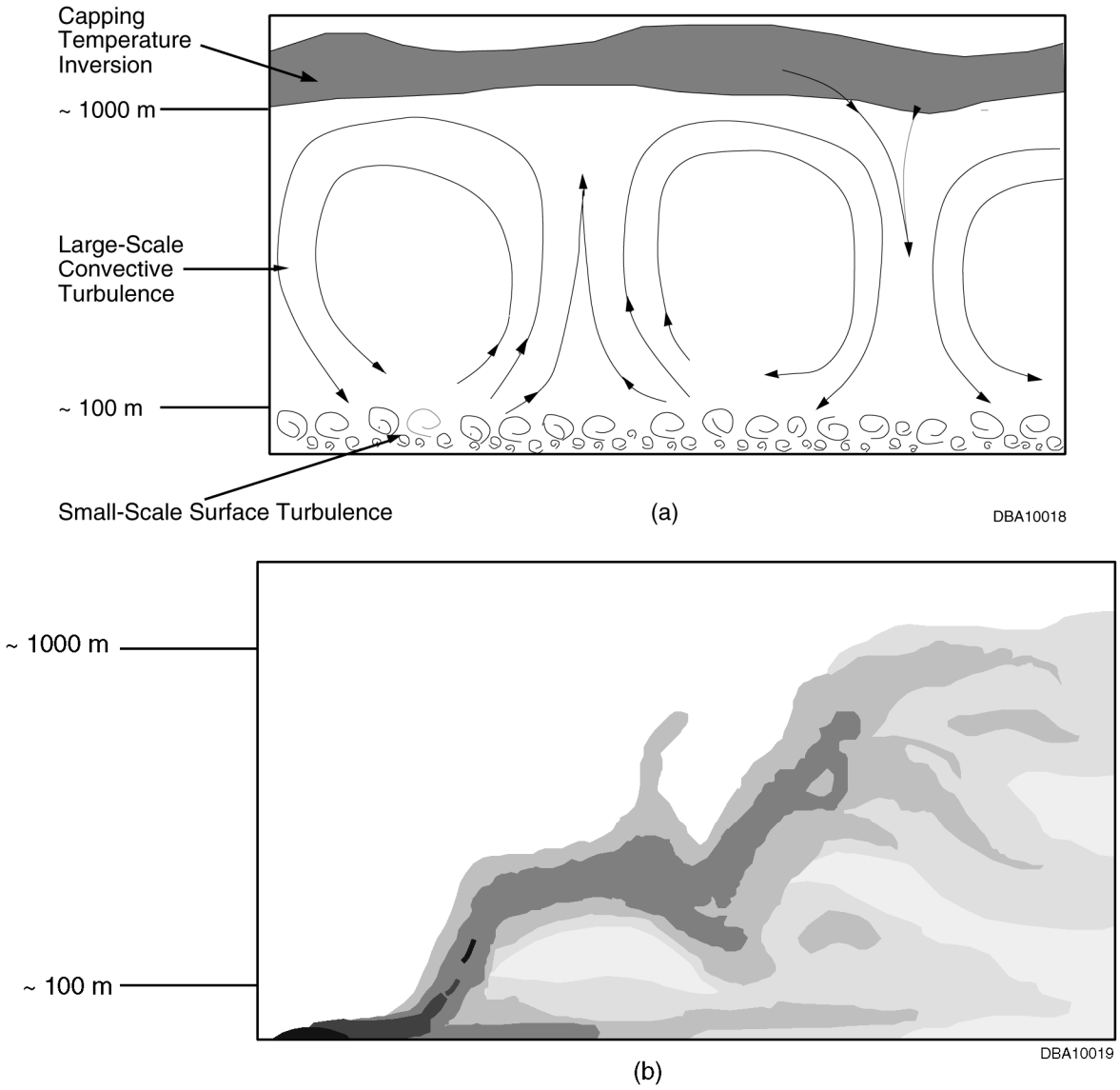

FIGURE 3.8 Typical Daytime Convective Boundary Layer Showing (a) an Instantaneous Wind Field and (b) an Instantaneous Material Concentration Field from a Ground-Level Release (Characteristic heights of about 1,000 m for the boundary layer and about 100 m for the surface layer are provided for reference.)

responsible for the rapid decay of material concentrations downwind from ground-level sources when the release occurs in the middle of the day.

In the absence of solar heating, the nighttime ABL structure is driven by cooling at the surface as heat is radiated to space. This situation leads to the development of a stably stratified boundary layer (SBL), which is typically much shallower and less energetic than its unstable counterpart, as illustrated in Figure 3.9a. The surface cooling strongly stratifies the low-level air, thereby creating a tenuous balance between the turbulence produced by wind shear and turbulent energy dissipation. The rapid dissipation of turbulent energy greatly limits the vertical eddy size and restricts vertical mixing.

Dispersion in a typical SBL is pictured in Figure 3.9b. The vertical stability and shallow depth profoundly affect dispersion processes by confining material contaminants to a thin layer near the ground. In very stable conditions, such as those represented in the 90th-percentile level of safe distance distributions, the SBL is usually less than 100 m deep. When a contaminant is released into the SBL, it diffuses to its maximum vertical extent in a relatively a short distance, forcing most of the dispersion to occur two-dimensionally along the ground. This plume confinement allows comparatively high concentrations to be observed near the surface at considerable distances from the release site, leading to PADs that are farther from the source than are necessary for daytime incidents.

3.4.1.2 Effects of Dense Gas on Plume Dispersion

The discussion of atmospheric dispersion to this point has been confined to passive dispersion (i.e., cases in which the density of the ambient plume does not affect its dispersion). However, for many large TIH chemical releases, the effect of a high-density (relative to air) hazardous chemical discharge becomes important in considering impacts within 1 to 2 km of the release point. So-called dense gas effects result not only from the properties of the material released but also from the methods of storage and the conditions of the release. Most cases of interest have focused on combustibles or toxic compounds that have boiling points below ambient temperature. These compounds are commonly transported or stored as liquids and then maintained in the liquid phase (1) at or near their saturation temperature at atmospheric pressure by refrigeration and insulation (i.e., refrigerated liquid) or (2) at ambient temperature by pressurization (i.e., pressurized liquid or liquefied gas). For transportation incidents, cases that could lead to significant dense gas effects fall into one or more of the following broad categories:

- Chemicals with a high molecular weight when compared with air (e.g., chlorine, arsine) coupled with a large release quantity or high release rate (i.e., much greater than 1 kg/s);

- Refrigerated chemicals with a relatively low molecular weight when their temperature upon release is cold relative to the ambient temperature (e.g., a cold methane release evolving from the boiling of refrigerated liquefied natural gas);

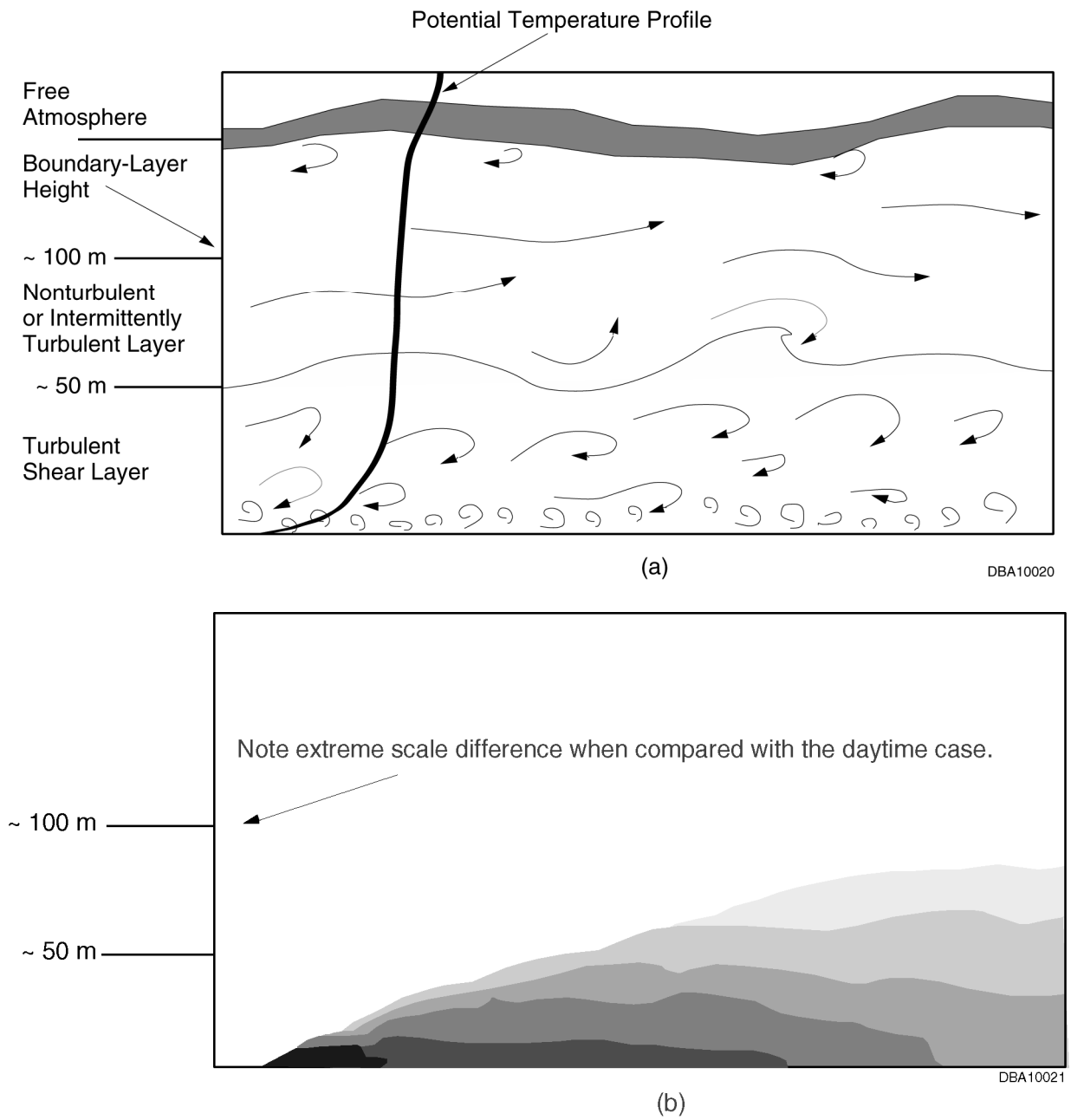

FIGURE 3.9 Typical Nighttime Stable Boundary Layer Showing (a) an Instantaneous Wind Field and (b) an Instantaneous Material Concentration Field from a Ground-Level Release (Characteristic heights of about 50 m for the surface shear layer and about 100 m for the boundary layer are provided for reference.)

- Pressurized liquids containing chemicals with a low to moderate molecular weight that, although they are less dense than air at their boiling point, cool rapidly and entrain aerosol generated in the release process, thereby creating a denser-than-air plume; and

- Chemicals that undergo molecular association (hydrogen fluoride [HF]) and/or transform to secondary hazardous compounds because of their ambient water-vapor reactivity (e.g., sulfur trioxide [SO_3]/oleum, nitrogen tetroxide [N_2O_4]). (These are not necessarily the same group of compounds that are water-reactive as defined in this report.)

Two major effects can be observed during the dispersion of a ground-level dense gas cloud that do not occur during the dispersion of a neutrally buoyant cloud. The first is that there is much less vertical turbulent mixing between the dense gas cloud and the ambient atmosphere because of the strong stable density stratification of the cloud relative to the surrounding ambient air. The second is the presence of gravity-induced flow resulting from horizontal density gradients. These two effects result in a shallower and much wider cloud than the cloud that results from an analogous neutral density release. In addition, the movement of the dense gas cloud on uneven terrain can follow the downhill slope independent of the wind direction, and the cloud can become trapped in valleys or low spots. The magnitudes of these dense gas effects depend on the size of the release, local meteorological conditions, and physical properties of the chemical release.

As the dense plume travels downwind, the plume warms through ambient heating (e.g., from sunlight, ground heating) and entrainment of warmer air. At some downwind distance, the density of the plume will decrease to the point where the density can no longer retard the vertical dispersion of the plume by ambient turbulence, and the plume will subsequently disperse as a passive cloud.

3.4.2 CASRAM Dispersion Model

3.4.2.1 Passive Dispersion

Like many other dispersion models, CASRAM separates the dispersion calculation into two components: horizontal dispersion and vertical dispersion. In CASRAM, vertical turbulent dispersion is treated with a Lagrangian-integral model parameterized in terms of mean plume height, average advection velocity, and a dimensionless travel time. These parameters are expressed as integral equations written in terms of plume travel time and atmospheric boundary layer parameters. Continuous releases are treated as plumes, and instantaneous releases are treated as puffs. Horizontal turbulent dispersion is represented via Gaussian relationships that are parameterized in terms of the Lagrangian time scale and lateral wind direction fluctuations. Plume calculations are straight-line in nature, since terrain effects are not currently considered in CASRAM.

The concentration relationship for continuous plume releases from point sources is represented in terms of the crosswind-integrated concentration (CWIC), chemical mass release rate Q, and the traditional Gaussian expression for the horizontal plume spread. The ground-level concentration distribution is represented as follows:

$$C(x, y, z = 0) = \frac{Q\hat{C}_y(x, z = 0)}{\sqrt{2\pi}\sigma_y} \exp\left[-\left(\frac{y}{\sqrt{2}\sigma_y}\right)^2\right], \tag{3.20}$$

where

$\hat{C}_y$ = CWIC normalized by the release rate,

σ_y = lateral plume spread, and

y = lateral distance from the plume centerline.

For releases with finite width, corresponding to large pool releases or dense gas releases as they become passive, the following expression is used:

$$C(x, y, z = 0) = Q\hat{C}_y(x, z = 0)\left(erf\left[\frac{y_o - y}{\sqrt{2}\sigma_y}\right] + erf\left[\frac{y_o + y}{\sqrt{2}\sigma_y}\right]\right). \tag{3.21}$$

Peak concentration averages resulting from instantaneous releases are calculated according to the relationship

$$C(x, y, z = 0) = \frac{M\hat{C}_y(x, z = 0)}{\sqrt{2\pi}\sigma_y T} erf\left[\frac{UT}{2\sqrt{2}\sigma_y}\right] exp\left[-\left(\frac{y}{\sqrt{2}\sigma_y}\right)^2\right], \tag{3.22}$$

where

M = total release amount,

T = averaging time, and

U = 10-m wind speed.

The subsections below first present the methodology for determining vertical dispersion (i.e., for determining C_y as a function of downwind distance). They then discuss the determination of σ_y, thus providing horizontal dispersion.

Vertical Dispersion. The vertical dispersion model in CASRAM is a natural extension of the surface-layer, similarity-based model of van Ulden (1978). The van Ulden approach centered around an exact solution of the advection-diffusion equation. When written in terms of the CWIC form and neglecting stream-wise diffusion, it reads as follows:

$$U(z)\frac{\partial C_y}{\partial z} = \frac{\partial}{\partial z}\left[K_z(z)\frac{\partial C_y}{\partial z}\right], \tag{3.23}$$

where K_z is the vertical diffusivity for a passive contaminant.

The solution van Ulden advances is written in terms of the mean plume height $\bar{z}$, the average plume advection velocity $\overline{U_p}$, the power-law wind speed coefficient *m*, and the diffusivity coefficient *n.* The coefficients *m* and *n* are defined such that

$$U(z) = u_o z^m \tag{3.24}$$

and

$$K_z(z) = k_o z^n, \tag{3.25}$$

where u_o and k_o are constants representing the wind speed and diffusivity at 1 m.

The advection-diffusion equation subject to the above power-law relationships yields an exact solution (see Roberts 1923; Calder 1949). The work of van Ulden (1978) extends this analysis by using the power-law coefficients to determine the concentration profile shape *a priori* (from the Roberts analysis) and then formulates integral relationships for the mean plume height and average advection velocity in terms of the more physically correct similarity functions for wind speed and diffusivity. The van Ulden (1978) solution reads

$$\hat{C}_y(x,z) = \frac{A}{\bar{z}\overline{U_p}}\exp\left[-\left(\frac{Bz}{\bar{z}}\right)^s\right], \tag{3.26}$$

where

$$A = \frac{s\Gamma(2/s)}{\Gamma(1/s)^2}, \tag{3.27}$$

$$B = \frac{\Gamma(2/s)}{\Gamma(1/s)}, \tag{3.28}$$

and *s* is a shape parameter given by $1 - m - n$. In Equations 3.27 and 3.28, Γ represents the gamma function.

In applying this model, van Ulden (1978) parameterized the mean plume height and average advection velocity by using surface-layer similarity functions for wind speed and diffusivity. In a subsequent study, Gryning et al. (1983) extended this analysis by adding a sophisticated relationship to determine the shape parameter s as a function of stability and downwind distance. The relationships for s were determined through analysis of numerical solutions for the advection-diffusion equation for a wide range of conditions. In a detailed model-data comparison that used CWIC data from the Prairie Grass experiments (Barad 1958), Gyning and colleagues demonstrated the utility of the Lagrangian empirical model in representing the concentration profile as well as in estimating ground-level concentrations. This model provided an excellent description of dispersion in the surface layer. However, its application is limited to dispersion problems where the plume is confined to the surface layer. When the plume rises above the surface layer, the concentration profile given by Equation 3.26 as well as the similarity relationships for $\bar{z}$ and $\overline{U_p}$ lose validity. For problems of practical interest, this rather severe constraint strongly limits the applicability of Equation 3.26.

Brown (1997) modified the original van Ulden work to correct this limitation. In this revised formulation, the normalized ground-level concentration is expressed as

$$\hat{C}_y(x, z=0) = \frac{A'(\tilde{s})F(x; u_*, z_i, H_s)}{z_u \overline{U_p}} \ , \tag{3.29}$$

where z_u is defined such that

$$U(z_u) = \overline{U_p} \ , \tag{3.30}$$

and

$$A'(\tilde{s}) = \frac{1.6\,\tilde{s}\,\Gamma(2/\tilde{s})}{\Gamma(1/\tilde{s})^2} \tag{3.31}$$

Here, A' takes the same functional form as A in van Ulden's model, except that it is multiplied by 1.6 to account for the ratio of $\bar{z}$ to z_u and depends on a modified shape parameter denoted as $\tilde{s}$.

The main departure of this approach from the models of van Ulden and Gryning et al. is in the boundary-layer function F. This empirical function is added to treat dispersion within the greater ABL outside the surface layer. As previously noted, the van Ulden model was developed by using the quasi-exponential concentration profile. For surface-layer dispersion, this assumed form for the concentration profile adequately represents the concentration profiles observed in field studies, most notably the Prairie Grass experiments. However, once the plume is influenced by boundary-layer effects outside of the surface layer, the concentration profiles depart significantly from the exponential form. In unstable conditions, this departure is particularly pronounced, since the plume centerline can actually lift off the ground, creating a maximum concentration aloft. In stable conditions, the opposite effect is observed, in which the concentration profile is flattened as a result of the rapid decrease in turbulent energy with height.

The transition function F allows us to adapt this methodology, which was originally developed to model surface-layer dispersion, in order to treat dispersion throughout the entire ABL.

Brown (1997) developed relationships for z_u, $\tilde{s}$, and F by using a parametric analysis of a Langevin-equation Monte Carlo dispersion model validated with data from field and laboratory experiments. In applying the CASRAM vertical dispersion model, $\tilde{s}$ is a function of meteorology, and therefore does not vary with distance, and F is represented as a function of travel time and meteorology. The heart of the calculation lies in z_u, which is calculated by using integral relationships represented as a function of travel time. Numerical integration of this relationship provides z_u as a function of downwind distance, which, together with $\tilde{s}$ and F, allows the evaluation of Equation 3.24 and ultimately Equation 3.20, 3.21, or 3.22.

Horizontal Dispersion. Under horizontal homogeneous conditions, the Gaussian model correctly represents lateral concentration distributions. In CASRAM, the lateral spread from nonbuoyant releases can be related to the standard deviation of the horizontal wind fluctuations and is determined by using relationships originally proposed by Draxler (1976). Here, σ_y is given by

$$\sigma_y = \sigma_v f_y\left(\frac{t}{T_d}\right), \tag{3.32}$$

where

σ_v = standard deviation of transverse velocity,

t = transit time (estimated by using wind speed at 3 m and distance),

T_d = dispersion time scale related to the Lagrangian time scale, and

f_y = a nondimensional function of travel time.

The empirical form of f_y is estimated through evaluating field data. Several forms of f_y have been proposed (Irwin 1983; Gryning and Lyck 1984), but the empirical expression that provides the best overall fit with available field data is the form proposed by Draxler (1976). His function is given by

$$f_y = \frac{1}{1 + 0.9\sqrt{t / T_d}}. \tag{3.33}$$

For surface releases, a T_d of 300 s is used for unstable conditions and a maximum of 300 s or 0.001 t^2 s is used for stable conditions. The appeal of Draxler's relation is that it is developed from diffusion data from many experiments and that it is consistent with Taylor's limit for both small ($\sigma_y \sim t$) and large ($\sigma_y \sim t^{1/2}$) travel times (Taylor 1921).

Equation 3.32 requires the standard deviation of transverse velocity σ_v. In the absence of observational data, σ_v is determined by using the interpolation equation of Panofsky et al. (1977)

$$\sigma_v = u_* \left(12 - 0.5 \frac{z_i}{L} \right)^{1/3} \tag{3.34}$$

during unstable conditions and the proportionality relation of Panofsky and Dutton (1984)

$$\sigma_v = 1.92\, u \tag{3.35}$$

during stable conditions.

In very stable conditions, Equation 3.35 fails to adequately represent σ_v, since wind speed and friction velocity become very small. For instance, if the friction velocity is about 0.015 m/s, indicative of a wind speed of about 0.5 m/s with z_o = 0.1 m on a clear night, Equation 3.35 predicts σ_v = 0.03 m/s. At a distance of 1 km from the source, this value of σ_v yields σ_y = 36 m from Equation 3.32. Considering the 2,000-s travel time, such a narrow plume width at ground level is not realistic when the meandering nature of stable boundary layer flows is considered. To overcome this problem, we assign a minimum value of 0.15 m/s for σ_v on the basis of observations presented by Hanna and Chang (1992).

3.4.2.2 Dense Gas Dispersion

A dense gas algorithm was added to the CASRAM methodology as part of the ERG2000 study after a detailed review of available dense gas models. The review identified five dense gas models that were well documented and would be applicable within the CASRAM framework: DEGADIS (Havens 1988), HEGADAS (Post 1994), SLAB (Ermak 1990), SCIPUFF (DTRA 1999), and TSCREEN (EPA 1992). On the basis of many considerations, the most important being accuracy and ease of incorporation into the CASRAM framework, we opted to rely on the empirical entrainment parameterizations within the DEGADIS formulation for the CASRAM heavy gas dispersion model. As of this writing, DEGADIS is undergoing a major revision, so future applications of CASRAM (in particular, the ERG2016 analysis) will likely incorporate an updated version of this formulation.

Like the passive gas dispersion model used in CASRAM, the dense gas algorithm is integral in nature. The initial conditions are specified by the vapor release rate Q_v and aerosol release rate Q_a from the container, which are calculated from the CASRAM emission rate model. The first step is evaluating the volumetric flow rate of vapor exiting the container $\dot{V}_{sv}$, which is given by

$$\dot{V}_{sv} = \frac{Q_v}{\rho_v} \,, \tag{3.36}$$

where ρ_v is the density of the chemical vapor at the boiling point. The initial volumetric flow rate of the cloud $\dot{V}_{ci}$ is taken as

$$\dot{V}_{ci} = (1+\beta_{ei})\dot{V}_{sv}, \tag{3.37}$$

where β_{ei} is the entrainment parameter at the source taken as two.

This is a rough estimate that depends on many factors. However, the model results at distances more than 10 to 20 m from the source are not sensitive to β_{ei}.

The initial cloud is assumed to have a cylindrical shape with a width of $2r_i$ and height h_i, where $r_i = h_i$. To estimate the cloud dimensions from the volumetric flow rate, one must solve the relationship

$$h_{ci} = \frac{\dot{V}_{ci}}{2\overline{U_p} r_i} \ , \tag{3.38}$$

where

$$\overline{U_p} = u(z = 0.6h_{ci}). \tag{3.39}$$

The solutions of Equations 3.38 and 3.39 are necessarily iterative and subject to the constraint that h_{ci} is more than 1.5 m.

The initial cloud density is then defined in terms of the sum of the mass flow rates of the "flashed" vapor and aerosol plus the entrained air as

$$\rho_{ci} = \frac{Q_v + Q_a + \beta_{ei}\dot{V}_v\rho_a}{\dot{V}_{ci}}, \tag{3.40}$$

where the last term on the right side of the numerator accounts for the mass of air initially entrained into the plume.

After release, the cloud spreads horizontally under the influence of its negative buoyancy while it grows vertically through entrainment of air from above. Note that dense gas plumes are marked by a horizontal growth rate that is much higher than the vertical growth rate. The horizontal gravity spread is assumed to depend on the cloud advection speed and Richardson number for continuous releases and is computed in a form equivalent to the model of Raj (1985) such that

$$\frac{dr}{dx} = \frac{\beta_e u_*}{\overline{U_p}} \sqrt{Ri_*} \ . \tag{3.41}$$

Here, β_e is an entrainment parameter taken as 1.15 and Ri_* is the local cloud Richardson number given by

$$Ri_* = \frac{gh_c(\rho_c - \rho_a)}{\rho_a u_*^2}. \tag{3.42}$$

Vertical cloud growth is governed by vertical entrainment of air into the cloud, which can be conveniently defined in terms of cloud advection speed and entrainment velocity v_e in the integral equation

$$\frac{dh_c}{dx} = \frac{v_e}{\overline{U}_p} \quad , \tag{3.43}$$

where the vertical entrainment velocity is as used in the DEGADIS model; namely,

$$v_e = \frac{0.4u_*}{0.88 + 0.099Ri_*^{1.04}} \ . \tag{3.44}$$

Equations 3.41 and 3.43 make up a coupled set of differential equations that are solved at successive points downwind of the source. The solution proceeds until the critical Richardson number *Ri* is less than 50. This critical Richardson number is defined differently than the local cloud Richardson number and is given by

$$Ri_c = \frac{U(h_c)(\rho_c - \rho_a)g\,h_c}{\rho_a u_*^3} \ . \tag{3.45}$$

After this Richardson number criterion is met, we initialize the passive gas dispersion model by matching the cloud height and assuming a uniform concentration across the width of the cloud of $2r$. Therefore, the parameter y_o in Equation 3.21 is set to r.

4 HEALTH CRITERIA

Over the past 25 years, various health criteria have been used to develop Initial Isolation Zones and PADs. Early efforts employed occupational exposure guidelines such as threshold limit values (TLVs) established by the American Conference of Governmental Industrial Hygienists (ACGIH). Beginning in 1990, the Emergency Response Planning Guidelines (ERPGs) developed by the American Industrial Hygiene Association (AIHA) were used as criteria for evaluating the health significance of accidental releases, and hence formed the basis for defining PADs. Use of the ERPGs was based on a number of factors, including the high quality of documentation, the consensus approach upon which the values are derived, and the consideration of exposure to the general population. In the late 1990s, Acute Exposure Guideline Level (AEGL) values for chemicals, developed by a committee of federal, state, and private sector scientists in a manner similar to that used for ERPG development, began to be available. For the 2012ERG, final AEGL values are considered to be the preferred health criteria; however, ERPG values are also used for chemicals that do not have final AEGL values. Fortunately, 51 new AEGL values (interim and final) were published for TIH materials between early 2008 and early 2012, so now AEGLs compose a majority of protective action health criteria in the 2012ERG analysis. For substances without AEGL or ERPG values, data on acute inhalation lethality in animals are used to develop the PADs. The acute inhalation data consist of concentrations determined to be lethal to 50% of animals exposed (LC_{50} values), or the lowest reported lethal concentrations (LC_{LO} values). In 2008, over half of the list required LC_{50}-based values. However, for the 2012ERG just over a quarter of the list required the use of these lethality data for PAD estimation.

The development of and definitions for the various health criteria used as the basis for chemical-specific PADs are described in Section 4.1. Other considerations, such as data sources and exposure duration adjustments, are discussed in Section 4.2. The final health criteria used in the 2012ERG for each of the substances considered (mainly TIH chemicals, but also including some components of mixtures and some pesticides) are listed in Appendix B.

As part of the ongoing process of identifying the best applicable health criteria for the TIH chemicals, the published studies on health criteria used to evaluate accidental releases have been reviewed. For the current 2012 revision of the ERG, the health criteria used to develop the PADs have been reviewed to incorporate the most recently available values, and health criteria were identified for newly listed TIH substances. Also, for LC_{50}- and LC_{LO}-based health criteria, acute toxicity databases were reviewed to ascertain that the correct study was being used for each chemical, based on the methods discussed in Section 4.2.

4.1 REVIEW OF HEALTH CRITERIA DEVELOPMENT FOR THE ERG ANALYSIS

4.1.1 Acute Exposure Guideline Levels

AEGLs are developed under the auspices of the National Research Council's National Advisory Council (NRC NAC), and are intended to describe the risk to humans resulting from once-in-a-lifetime, or rare, exposure to airborne chemicals. The NAC for AEGLs is developing these guidelines to help both federal agencies (e.g., DOT, NIOSH, U.S. Environmental Protection Agency [EPA], U.S. Department of Defense [DoD], U.S. Department of Energy [DOE], and Occupational Safety and Health Administration [OSHA]) and local authorities, as well as private companies, deal with emergencies involving spills, or other catastrophic exposures. The NAC is composed of scientists representing federal, state, and local agencies and organizations from the private sector with an interest in emergency planning, prevention, and response programs for acutely toxic chemicals.

After AEGL values are drafted and approved by vote by the NAC, they are considered "proposed" and are published in the *Federal Register* for review and public comment (EPA 2007). Once public comments have been addressed and the NAC committee again votes on the specific values, they are considered "interim" and are submitted to the NRC AEGL subcommittee for review and comment. When concurrence with the NRC subcommittee is reached, the AEGL values are considered "final" and are published by the NRC.

In November 2011, a new AEGL process was unveiled whereby the finalization of AEGL values of chemicals that are in "interim" would be prioritized. In this new process, the NAC was disbanded for future work of the AEGL program. At this juncture, the NAC had addressed 324 of the 329 chemicals originally listed in the AEGL Chemical Priority Lists (see http://www.epa.gov/oppt/aegl/pubs/process.htm#new_aegl). As such, it is unclear at the time of this writing whether additional AEGL values will be available in future ERG editions.

The AEGL values are developed for exposure times of 10 min, 30 min, 60 min, 4 h, and 8 h, and for three effect categories. The values are intended to be applicable to the general population including infants and children and other individuals who may be sensitive and susceptible. Definitions generally parallel those of the ERPGs and are as follows:

- AEGL-1 is the airborne concentration of a substance above which it is predicted that the general population, including susceptible individuals, could experience notable discomfort, irritation, or certain asymptomatic nonsensory effects. However, the effects are not disabling and are transient and reversible upon cessation of exposure.

- AEGL-2 is the airborne concentration of a substance above which it is predicted that the general population, including susceptible individuals, could experience irreversible or other serious, long-lasting adverse health effects or an impaired ability to escape.

- AEGL-3 is the airborne concentration of a substance above which it is predicted that the general population, including susceptible individuals, could experience life-threatening health effects or death.

The AEGL levels are based on no observed adverse effect levels (NOAELs) in human populations, where possible (NRC 2001); however, it is often necessary to use data from animal studies. If no studies are available with multiple exposure levels and an identified NOAEL, a lowest observed adverse effect level (LOAEL) is used as the starting point for the guideline level. Uncertainty factors of 1, 3, or 10 are generally used to ensure that the guidelines are protective. Uncertainty factors are used to account for interspecies variability, intraspecies variability, use of LOAEL data when no NOAEL level is available, and for other database deficiencies. The uncertainty factors used for each priority chemical are described in chemical-specific AEGL documentation.

As of January 2012, the deadline for inclusion in the ERG2012 analysis, the NRC had published final AEGLs for 73 chemicals, interim AEGLs for 184 chemicals, and proposed AEGLs for 15 chemicals. For the development of PADs, only final and interim AEGL-2 values for 1 hour, 30 minute and 15 minute exposure periods were used. We note that since January 2012, many of the Interim AEGL values have been finalized.

4.1.2 Emergency Response Planning Guidelines

ERPGs are developed by the American Industrial Hygiene Association through a rigorous peer-review process that emphasizes human experience to the extent that such information is available. However, as for the AEGLs, data from animal studies are often used as the basis for the ERPG concentrations. Similar to the AEGLs, ERPGs are defined for three effect levels, as follows:

- ERPG-1: The maximum airborne concentration below which it is believed nearly all individuals could be exposed for up to 1 h without experiencing other than mild, transient adverse health effects or perceiving a clearly defined objectionable odor.

- ERPG-2: The maximum airborne concentration below which it is believed nearly all individuals could be exposed for up to 1 h without experiencing or developing irreversible or other serious health effects, or symptoms that could impair an individual's ability to take protective action.

- ERPG-3: The maximum airborne concentration below which it is believed that nearly all individuals could be exposed for up to 1 h without experiencing or developing life-threatening health effects.

As of 2012, the AIHA has published ERPG concentrations for 145 different chemicals (AIHA 2012). Typically the AIHA adds about 2–3 chemicals per year to its list, and modifies previously published values for another 3–5 materials.

4.1.3 Comparisons of AEGLs, ERPGs, and other Health Criteria

As industry and federal agencies have increased emergency preparedness efforts over the last few decades, several chemical-specific health criteria levels have been developed by various groups using differing methodologies, leading to some uncertainty over which values and methods to use for emergency planning. Some of the criteria developed include the AEGLs and ERPGs discussed above; NIOSH's immediately dangerous to life and health (IDLH) levels; levels of concern (LOCs) developed by the EPA to evaluate releases of extremely hazardous substances (EPA 1991) and to aid consequence analyses required to comply with requirements of Section 112 R of the Clean Air Act (EPA 1996); temporary emergency exposure limits (TEELs) developed by the DOE's Subcommittee on Consequence Assessment and Protective Actions (SCAPA); and occupational health guidelines. The IDLH, LOC, and TEEL values are discussed briefly in this section; occupational health guidelines are not relevant to the derivation of PADs and are not further discussed, except as related to LOC levels.

4.1.3.1 IDLH Values

The IDLH concentration is defined as "an atmospheric concentration of any toxic, corrosive, or asphyxiant substance that poses an immediate threat to life or would cause irreversible or delayed adverse health effects or would interfere with an individual's ability to escape from a dangerous atmosphere" (NIOSH 1994). IDLH values were originally developed in the 1970s for about 400 substances; these values have since been updated. In the procedure described by NIOSH to develop IDLHs, human data are preferred. However, many of the IDLHs are based on adjusting the results of acute inhalation lethality data in animals to a 30-min exposure duration. Since IDLH values are developed for exposure durations of 30 min and for healthy adult workers, they would be expected to be higher than ERPG-2 or 1-h AEGL-2 levels, which are for an exposure duration twice as long and are protective for most of the general population.

4.1.3.2 LOC Values

The LOC, as originally defined by EPA (1987) is "the concentration of an extremely hazardous substance (EHS) in the air above which there may be serious irreversible health effects or death as a result of a single exposure for a relatively short period of time." In the EPA procedure to derive LOC values, the IDLH divided by 10 was the preferred value (EPA 1987). Since IDLHs were developed for the purpose of selecting respirators in the event of an emergency in the work place, the tenfold uncertainty factor is intended to account for the greater sensitivity of the general population versus the worker population. When IDLHs were unavailable, estimated IDLHs based on $LC_{50}/100$, or lowest reported lethal dose (LD_{LO})/100 are used. As a third choice, ACGIH TLVs (8-h TLV time-weighted average [TLV-TWA], short-term exposure limit [STEL], and TLV-Ceiling values) and National Research Council EEGLs were also used to derive a number of LOCs (see Section 4.4 Glossary for definitions). AIHA ERPGs were cited as alternative criteria to use to develop LOCs. However, because only 15 draft

ERPGs were available at the time the LOC guidance was originally developed, ERPGs did not form the basis for any LOC.

Similarities exist between the procedure used by the EPA to develop LOCs and the procedure used by DOT to develop health criteria for deriving Initial Isolation Zones and PADs, most notably that many LOC levels and DOT 1-h protective levels are based on adjusted LC_{50} or LC_{LO} values divided by 100. There are also several important differences in these two procedures. In the DOT approach, AEGLs and ERPGs are the preferred choice for deriving health criteria. We believe this to be a sounder approach, since these values are considered by many authorities to be the best available criteria for evaluating accidental releases. Also, in the DOT procedure, when it was necessary to use acute lethality data in animals, a critical review of the available data was performed, which included a scheme for selecting the best study when multiple studies were available. In the DOT approach, when LC_{LO} data were employed, use of a hundredfold instead of a tenfold uncertainty factor was maintained. This recommendation was based on the concept that a significant number of LC_{LO} values represent concentrations that produce a significant percentage of mortality, including 100% mortality.

In the approach described in the EPA's guidance document for off-site consequence analysis (EPA 2009), ERPGs were recommended as the preferred values, followed by LOC values. Since AEGLs and ERPGs are also used as first priority in the DOT scheme, followed by the time-adjusted $LC_{50}/100$, and many LOCs are based on $LC_{50}/100$, the two approaches are quite similar. However, as described above, there are differences in the methods used to select the acute lethality data.

4.1.3.3 TEEL Values

TEEL values are available for over 3,000 chemicals. They have been developed for chemicals that do not have AEGL or ERPG values available, and are considered temporary values subject to change as new or better information becomes available. The methodology for the derivation of TEEL values (Craig et al. 2000) is of interest because it has some similarities to the methods described here for the derivation of health criteria levels for generating PADs for DOT's ERG. However, for substances without AEGL or ERPG values, TEEL-2 levels (TEEL definition is the same as the ERPG-2 definition, but for a 15-min exposure duration) are based on a fairly complex hierarchy of emergency planning and occupational guideline levels, whereas the PAD health criteria levels are based on a simpler use of acute inhalation toxicity data (i.e., LC_{50}s and LC_{LO}s; see Section 4.2.2).

The TEEL developers also have conducted studies examining the statistical relationships between ERPG levels and some other planning levels, including the IDLH values and EPA's LOC values (Craig et al. 1995). For example, the mean, coefficient of variation, and coefficient of determination of ratios of ERPG-2 to other health criteria were calculated. The analysis included ERPG data for 35 chemicals. It was found that NIOSH IDLH values overestimated ERPG-2 values (mean ratio = 2.48). A good correlation was observed between ERPG-2 values and EPA LOCs (mean ratios of 0.99 and 0.82, respectively).

The study by Craig et al. (1995) confirms the validity of using LC_{50} values divided by a factor of 100 as surrogates for ERPG values, as was done for deriving health criteria for the TIH chemicals (see Section 4.2.2.4). This conclusion is based on the good correlation between the EPA LOC and ERPG-2. Since many EPA LOC values were derived by dividing the IDLH by 10, and many IDLHs were derived by dividing an LC_{50} value by 10, a relationship between the ERPG-2 (and by extension the AEGL-2) and $LC_{50}/100$ is inferred.

4.2 PROCEDURE USED TO SELECT HEALTH CRITERIA FOR THE ERG

The hierarchy for selection of protective action health criteria is illustrated in Figure 4.1. Final AEGL-2 values are the preferred health criteria. In the absence of final AEGL-2 values, ERPG-2 values, interim AEGL-2 values, and acute inhalation lethality data were used to identify the health criteria used to determine PADs. The health criteria for ERG2012 analysis changes substantially from the 2008 ERG due to the increasing availability of final and interim AEGL values. Health criteria for roughly half of our TIH list changed between 2008 and 2012. Many of the changes were fairly minor; however, three notable changes were for sulfur dioxide, carbon monoxide, and phosphine. For both sulfur dioxide and carbon monoxide, final AEGL values were published which were much more conservative than the previously used ERPG-2 values. For sulfur dioxide and carbon monoxide, the 1-h AEGL-2 values were 0.75 ppm and 82 ppm versus the previously used ERPG values of 3 ppm and 350 ppm, respectively. Health criteria for phosphine went the other direction, increasing from the 1-h ERPG-2 value of 0.05 ppm to the final AEGL-2 value of 2 ppm. Phosphine is important in the ERG analysis as it is a Hazard Zone A gas that is in commerce as well as a gas evolved when certain solid phosphides are exposed to water (e.g., UN 2004, magnesium phosphide)

The ranking of AEGL and ERPG values and the use of acute inhalation data to derive health criteria are described in greater detail below.

4.2.1 Use of AEGL and ERPG Data

When final AEGL values were available for the chemical of interest, the 60-min, 30-min, and 10-min final AEGL-2 were employed. If no final AEGL value was available, the ERPG-2 value was used as the health criterion, using a twofold factor to estimate a 15-min health criterion (use of the twofold factor is explained in Section 4.2.2.4 below). If final AEGL or ERPG values were unavailable, then interim AEGL-2 values were used, if available. In several instances in which AEGLs or ERPGs were available for a closely related structural analog to the chemical of interest, the AEGL or ERPG value for the structural analog was used for the chemical of interest.

4.2.2 Use of Acute Inhalation Lethality Data in Animals

When neither final or interim AEGLs nor ERPGs were available, health criteria were derived by using median lethal concentration (LC_{50}) data from acute inhalation studies on

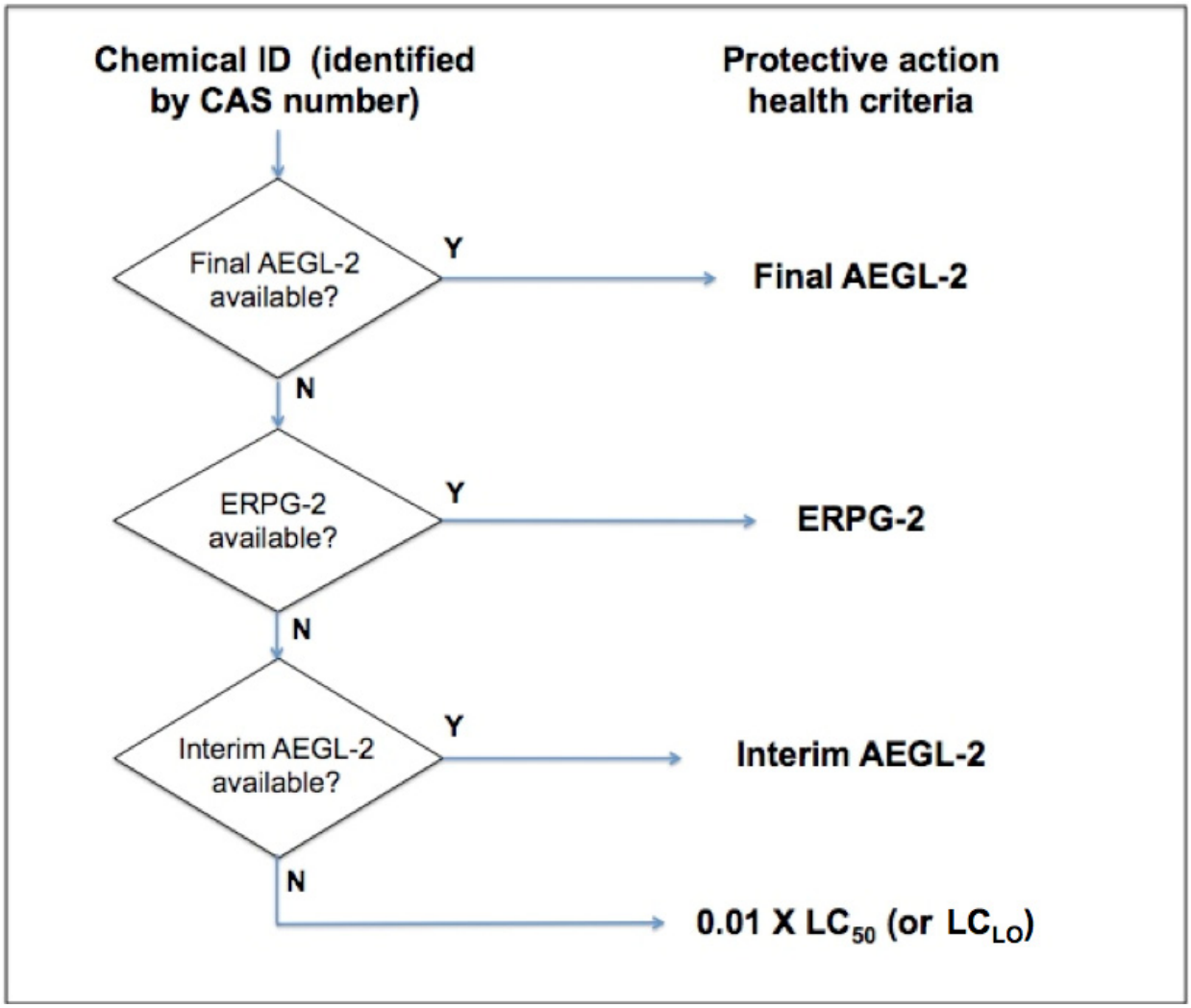

FIGURE 4.1 Hierarchy for Selection of Protective Action Health Criteria

animals, adjusted to approximate 1-h AEGL or ERPG values. When LC_{50} data were not available, lowest reported lethal concentration (LC_{LO}) data were used. Several factors were considered in selecting and using the LC_{50} and LC_{LO} data. These factors included species, experimental exposure duration, data source, and structural analog considerations, as discussed below.

4.2.2.1 Species Considerations

Data from studies using rats and mice are preferred for several reasons. Studies conducted with these species tend to use standardized protocols. Also, there is a wealth of comparative lethality data on rats and mice and much less comparative data on other species. Data on primates are rare, so using these data would limit the ability to compare responses across chemicals. However, acute lethal responses in this species might more closely simulate human

responses. Therefore, if such data were available, they would be included after the data for rats and mice but before data for other species. The amount of comparative data on rabbits is limited. Results for this species are not as representative as data for primates, so they appear lower in the ranking scheme.

4.2.2.2 Experimental Exposure Duration Considerations

The most commonly reported acute lethality studies are for 1-h and 4-h exposure durations. Therefore, use of data from studies in the range of these durations provides a measure of consistency in estimating health criteria. There is also a tendency for 1-h and 4-h LC_{50} values to have been calculated by using standard protocols. For developing ERG health criteria, data from 1-h exposures were preferred since data from this duration require no adjustments. However, data from studies using exposure durations from 10 min to 6 h were used, because many chemicals did not have data for 1-h exposures.

For exposures less than 30 min long, concerns over chamber equilibration time (T_{99}) are increased. For exposures more than 4 h long, concerns are increased that effects other than acute lethal effects might influence the study results. Also, LC_{LO} data are considered inferior to LC_{50} data, because no information is available concerning the slope of the dose response curve from these studies.

Data from exposures other than 1 h were adjusted to predict results for 1-h exposures. To develop an approach for making the adjustments, various reports published by investigators who have examined the relationship between exposure duration and acute mortality response were reviewed (Doe and Milburn 1983; Haber 1924; Klimisch et al. 1987; Ten Berge et al. 1986).

In the simplest case, where the inhaled substance accumulates in the body and is not rapidly destroyed or excreted, the dose accumulated is directly proportional to the concentration, *c*, and the exposure time, *t*, and uptake is linear. This concept, known as Haber's rule or law, would result in the following relationship:

$$W = c\,t, \tag{4.1}$$

where *W* is a constant dose specific for any given effect. This relationship is applicable for many reactive gases or highly lipid-soluble vapors over a limited range of concentrations and time.

However, many other relationships are possible. For example, for chemicals that are excreted as fast as they are inhaled and for which accumulation does not occur until a certain threshold concentration is reached, the following generalized dose-response equation applies:

$$W = (c - a)\,t^{b}, \tag{4.2}$$

where *a* is the threshold concentration and *b* is derived from experimental data.

For a significant percentage of chemicals, the following relationship has been observed:

$$LC_{50}\ (for\ T_1) = LC_{50}\ (for\ T_0)\ [T_0/T_1]^{1/n} \tag{4.3}$$

where

T_1 = modeled exposure time (e.g., 1 h),

T_0 = experimental exposure time, and

n = constant.

Klimisch et al. (1987), citing Doe and Milburn (1983), found that for many chemicals, n centers around a value of 0.5. Ten Berge et al. (1986) determined that for 18 of 20 chemicals studied, n values were greater than 0.3.

For deriving the health criteria, acute lethality data for exposure durations T_0 longer than 1 h were normalized by using the following quadratic dose-response function:

$$LC_{50}(1h) = LC_{50}(T_o)\left(\frac{T_o}{1h}\right)^{0.5}. \tag{4.4}$$

This approach is conservative, in that it predicts lower LC_{50}/LC_{LO} values than does Haber's rule. Acute lethality data for exposure durations T_0 of less than 1 h were conservatively predicted by using a linear dose-response function (i.e., Haber's rule):

$$LC_{50}(1hr) = LC_{50}(T_o)\left(\frac{T_o}{1hr}\right). \tag{4.5}$$

4.2.2.3 Data Source Considerations

The source of the data is another important consideration. Information from mainstream, peer-reviewed toxicology and industrial hygiene journals is preferable to information from auxiliary, non-peer-reviewed sources. The publication date may also be important. Many studies conducted before 1950 did not include analytical verification of concentrations. Information from foreign journals tends to contain more transposition errors, especially as cited in the Registry of Toxic Effects of Chemical Substances (RTECS). RTECS is a widely used toxicity database built and maintained by NIOSH from 1971 through 2001, but now maintained and updated by a private company under contract to NIOSH. Further information can be found at http://www.cdc.gov/niosh/rTecs/.

Based on these considerations, recent peer-reviewed US data sources were preferred for the selection of health criteria for PAD development. However, for several chemicals, the only

available lethal concentration data were either dated, from foreign sources, or were industry data that had not been through the peer-review process. Nonetheless, these data had often been in use for a number of years without reports of discrepancies between the reported lethality concentrations and toxicity experienced in industrial use. For example, such data are reported fairly often in the RTECS database, and also in another standard source of lethality data for chemicals, Sax's Dangerous Properties of Industrial Compounds (Lewis 2000). Therefore, the use of these less than superior data for some chemicals was retained for the 2008 ERG; it was considered preferable to having no PAD values for those chemicals.

The data sources for the chemical-specific health criteria given in Appendix B include AEGL values, ERPG values (AIHA 2006), and LC_{50} and LC_{LO} data from several sources, including Sax data (Lewis 2000), RTECS data, and data from miscellaneous sources. Chemical-specific source data can be obtained from the authors upon request.

4.2.2.4 Adjustment Factors

As described in Section 4.1, the 1-h $LC_{50}/100$ or the time-adjusted $LC_{50}/100$ are reasonable estimators for AEGL-2 or ERPG-2. Therefore, 1-h or adjusted 1-h LC_{50} or LC_{LO} values were divided by 100 to estimate 1-h protective health criteria.

Members of the AIHA ERPG Committee indicate that when 1-h ERPGs are extrapolated to values of shorter duration, there is concern that the potential effects of peak, high-level exposures should be minimized. A default value of 2 was suggested for these purposes. Therefore, to estimate 15-min protective health criteria from 1-h values, a factor of 2 was employed in estimating the 15-min criteria from the 1-h criteria (rather than the factor of 4 that would be used if a direct linear extrapolation were used).

4.2.3 Use of Data for Structurally Similar Substances

Where health criteria were not available for a chemical of interest, corresponding data for a structural analog were used. For example, for certain isocyanates for which there were no acute lethality data, data for n-butyl-isocyanate were used. Similarly, lethality data for boron trifluoride were used for boron tribromide. Protective action health criteria were based on structural analog data for about 5% of the TIH chemicals in the ERG2012, which is a marked decrease from the 10% used in preparation of the 2008 Guidebook due to the availability of many more AEGL values.

4.3 SUMMARY

A summary of the basis for health criteria for the 164 chemicals included in the 2012ERG analysis appears in Table 4.1. Documentation of the health criteria for individual chemicals is presented in Appendix B. For 90 chemicals (55%), AEGL values or AEGLs for

TABLE 4.1 Summary of the Basis for Health Criteria Used to Prepare the ERG2012

Basis of Health Criteria	No. of Materials	Percentage
Final AEGL for chemical of concern	38	
Interim AEGL for chemical of concern	50	
Final AEGL for structurally similar chemical	1	
Interim AEGL for structurally similar chemical	1	
Subtotal for AEGLs	90	55
ERPG for chemical of concern	28	
ERPG for structurally similar chemical	6	
Subtotal for ERPGs	*34*	*21*
LC_{50} for chemical of concern	31	
LC_{50} for structurally similar chemical	3	
Estimated LC_{50}[a]	1	
Subtotal for LC_{50} values	35	21
LC_{LO} for chemical of concern	5	3
Total	164	100

[a] For one chemical (hexaethyltetraphosphate), inhalation toxicity data were not available, and the health criterion was estimated as the median of four median lethal dose (lethal to 50% of exposed population) (LD_{50}) values by using standard assumptions to convert to air concentrations.

structurally similar chemicals formed the basis of the health criteria. For 34 chemicals (21%), ERPGs or ERPGs for a structurally similar chemical formed the health criteria basis. For 35 chemicals (21%), LC_{50} values or LC_{50} values for a structurally similar chemical were used to develop the health criteria. For 5 chemicals (3%), LC_{LO} values formed the basis of the health criteria. For 1 chemical, oral toxicity data were used to estimate an inhalation LC_{50} and to derive the health criteria.

Through continued efforts of the AEGL committee and the AIHA ERPG committee, new AEGLs and ERPGs are developed annually. The AEGL committee also finalizes interim AEGLs and completes the public review process necessary for proposed AEGLs to be considered interim AEGLs. ERPGs for additional chemicals are being provided at a rate of 2–4 per year, and already published values are occasionally revised. Not all of the chemicals on the AEGL and ERPG lists appear in the Table of Initial Isolation Zones and PADs, since many of the chemicals do not meet the specific toxicity and physical criteria for listing in the Table (as specified in 49 CFR 173.133). When new AEGL or ERPGs become available for chemicals on the DOT Table, the values will be incorporated into the development of Isolation Zones and PADs in future editions of the ERG.

4.4 GLOSSARY FOR CHAPTER 4

ACGIH 8-h TLV TWA: American Conference of Governmental Industrial Hygienists 8-h threshold limit time-weighted average value (or simply 8-h TLV) (ACGIH 2013). This is the time-weighted average concentration to which nearly all workers may be repeatedly exposed, day after day, without adverse effect.

ACGIH TLV Ceiling: American Conference of Governmental Industrial Hygienists threshold limit value ceiling (ACGIH 2013). This is the concentration that should not be exceeded during any part of the working exposure.

AEGLs: National Research Council Acute Exposure Guidance Levels. These levels are described in the text.

AIHA EEL: American Industrial Hygiene Association Emergency Exposure Level published in the *American Industrial Hygiene Association Journal* (Frawley et al. 1964). This is the concentration of a contaminant that can be tolerated without adversely affecting health but not necessarily without acute discomfort or other evidence of irritation or intoxication. The level is intended to provide guidance in managing single, brief exposures to airborne contaminants in the working environment.

ERPGs: American Industrial Hygiene Association Emergency Response Planning Guidelines (AIHA 2012). These are described in the text.

EPA LOC: U.S. Environmental Protection Agency level of concern (EPA et al. 1987). This is the concentration of an extremely hazardous substance in the air above which there may be serious irreversible health effects or death as a result of a single exposure for a relatively short period of time.

LC_{50}: This is the median (50%) lethal concentration; it is a lethal concentration to 50% of the exposed population.

LC_{LO}: This is the lowest reported lethal concentration.

NIOSH IDLH: National Institute for Occupational Safety and Health immediately dangerous to life and health level (NIOSH 1994). This is the minimum concentration of a toxic, corrosive, or asphyxiant substance that poses an immediate threat to life or would cause irreversible or delayed adverse health effects or would interfere with an individual's ability to escape from a dangerous atmosphere.

NRC EEGL: National Research Council Emergency Exposure Guidance Level (NRC 1984–1987). This is the concentration of a substance in air (as gas, vapor, or aerosol) that will permit continued performance of specific tasks during rare emergency conditions lasting for periods of 1 to 24 h.

OSHA PEL Ceiling: Occupational Safety and Health Administration permissible exposure limit ceiling (OSHA 1989). This is the concentration that should not be exceeded during any part of the workday.

5 SUMMARY

Sections 2–4 of this report detail the statistical methodology for developing our incident scenario library and safe distance distributions, the consequence models used in the analysis, and the health criteria that define the safe distance. This section summarizes the results and discusses the presentation of the distances in Tables 1 and 3 in the ERG2012. These are contained in Appendix A and Appendix B, respectively. Section 5 then concludes with some potential extensions of this analysis for situations when more information (in addition to the gross spill size and whether it is day or night) is immediately available.

5.1 SAFE DISTANCE DISTRIBUTIONS AND PROTECTIVE ACTION DISTANCES

The statistical accident scenario and consequence analysis set forth in previous sections resulted in a set of up to 1,000,000 hypothetical incidents for each material appearing in Table 1. This set of incidents accounts for variability in container type, incident type, accident severity (i.e., release amount), location, time of day, time of year, and meteorology. Each of these scenarios was evaluated using detailed emission rate and atmospheric dispersion models to calculate downwind chemical concentration footprints, with the safe distance for each incident defined as the distance downwind from the source at which the chemical concentration falls below the health protection criteria. The safe distance estimates for the entire set of hypothetical incidents considered in the analysis provide a safe distance distribution that corresponds to a wide spectrum of potential transportation-related releases. In the final step of the analysis, these incidents are categorized according to whether they occur during the day or during the night and whether they involve small (≤60 gal) or large (>60 gal) spills for presentation in Table 1. In Table 3, they are further organized by container type and wind speed range for six widely transported TIH materials. We discuss each of these below.

5.1.1 Generation of Table 1 Protective Action Distances

To illustrate application of the statistical results in development of Table 1 of the ERG2012, safe distance distributions for chlorine (a Hazard Zone B gas), ammonia (a Hazard Zone D gas), and calcium phosphide (a water-reactive material) are given in Figures 5.1–5.8. Chlorine and ammonia (large spill accidents only) are provided because they are the most common TIH materials involved in transportation chemical accidents, and calcium phosphide is a potent phosphine emitter and therefore one of the more hazardous water-reactive materials. Distributions are separated according to spill size (large or small) and time of day (day or night). In all eight figures, the 50th, 70th, 80th, 90th, and 95th percentiles are identified. The PADs in the guidebook correspond with the 90th-percentile values for the individual categories (shown in bold in Tables 5.1–5.4). Tables 5.1 and 5.2 provide safe distance estimates at several percentiles for chlorine and ammonia, respectively. Tables 5.3 and 5.4 provide corresponding data for phosphorous trichloride, a commonly transported Hazard Zone B liquid, and for calcium phosphide spills into water. Results for phosphorous trichloride in Table 5.3 are for land-based

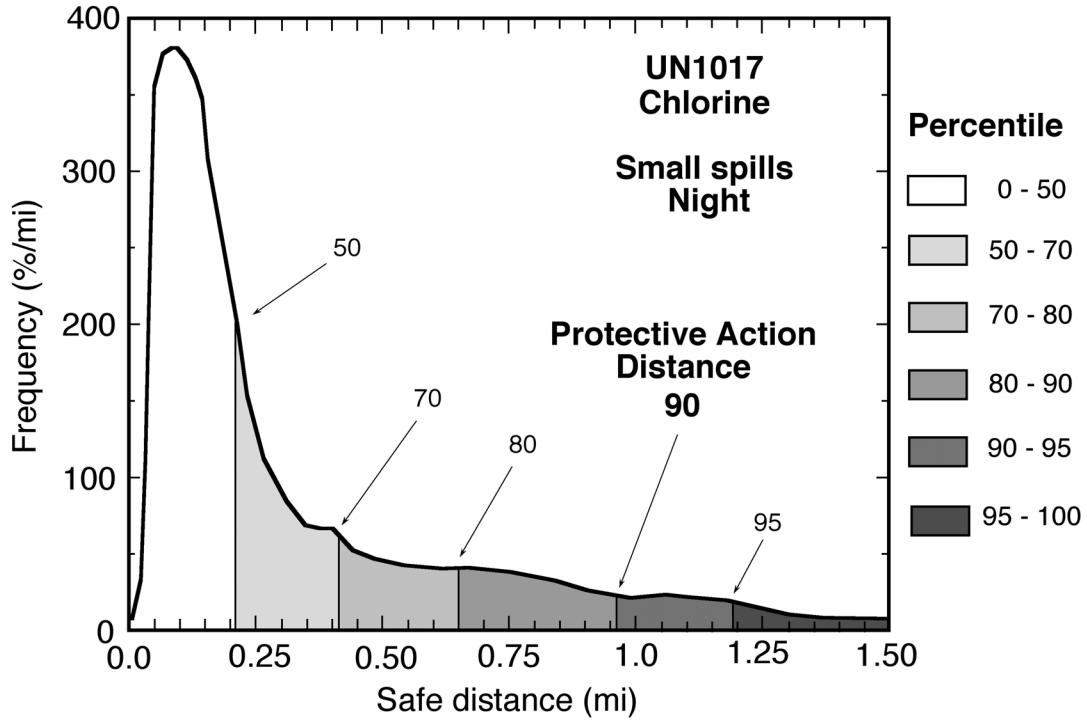

FIGURE 5.1 Frequency of Safe Distances for Small Nighttime Chlorine Spills as Determined in the ERG2012 Analysis

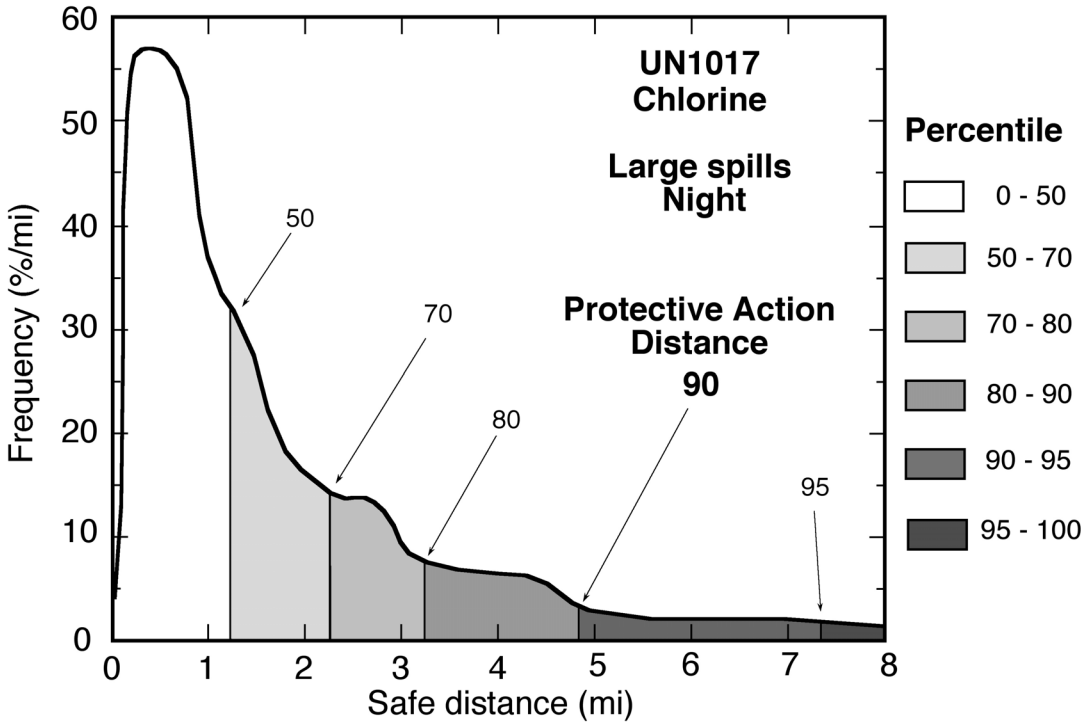

FIGURE 5.2 Frequency of Safe Distances for Large Nighttime Chlorine Spills as Determined in the ERG2012 Analysis

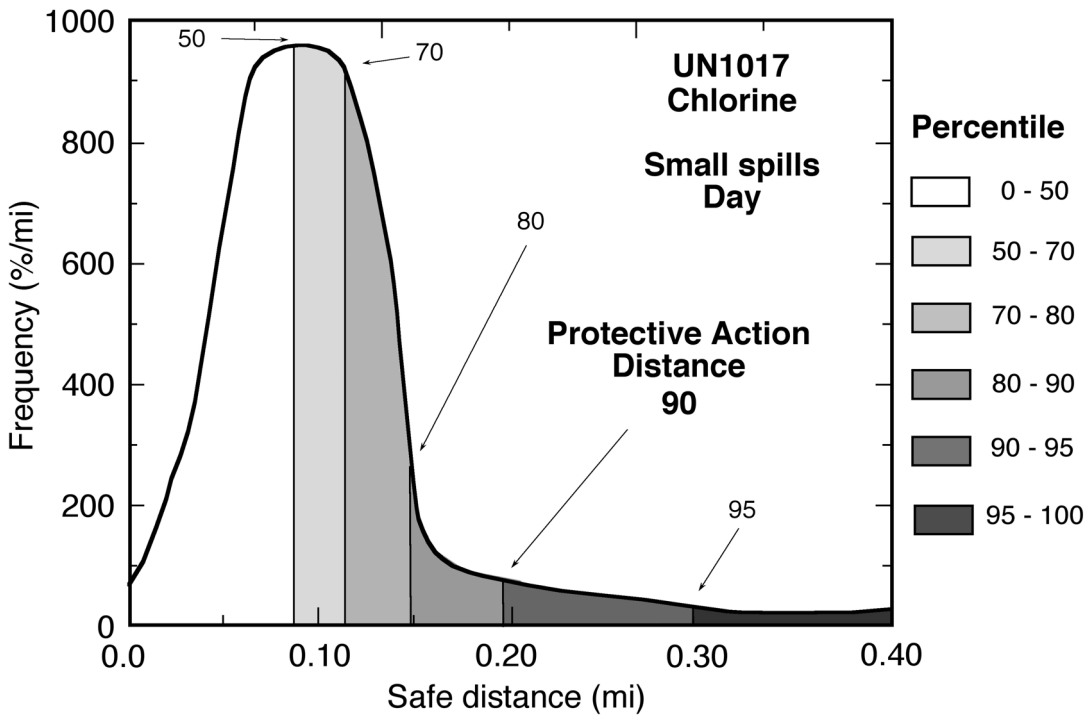

FIGURE 5.3 Frequency of Safe Distances for Small Daytime Chlorine Spills as Determined in the ERG2012 Analysis

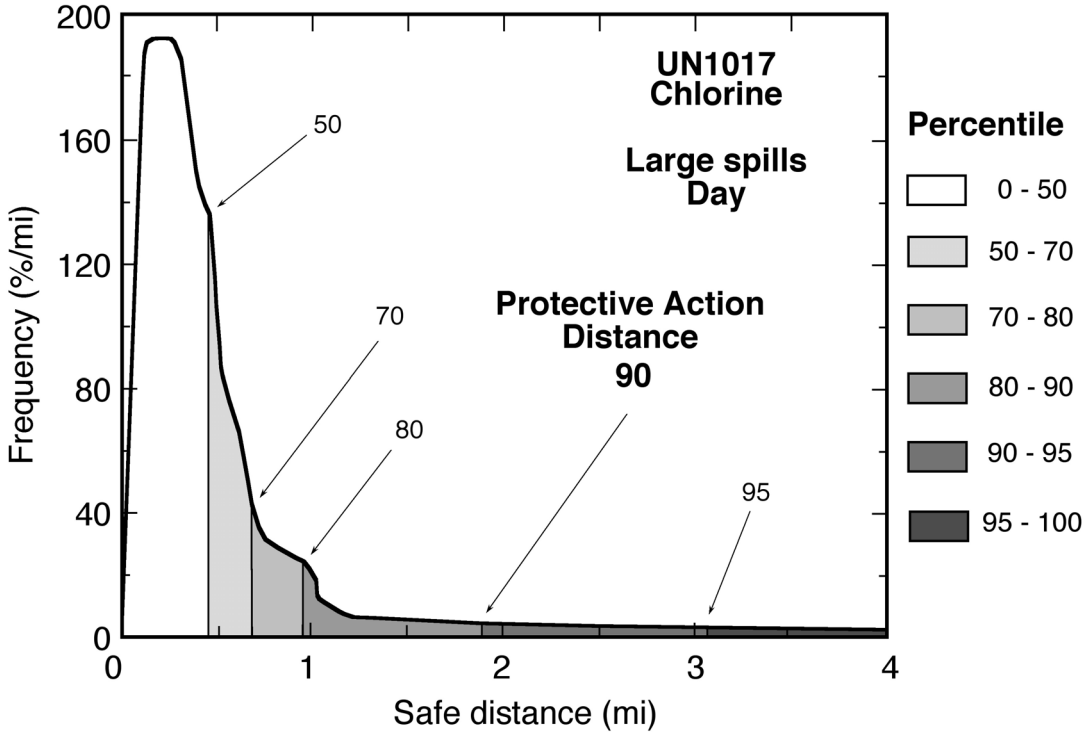

FIGURE 5.4 Frequency of Safe Distances for Large Daytime Chlorine Spills as Determined in the ERG2012 Analysis

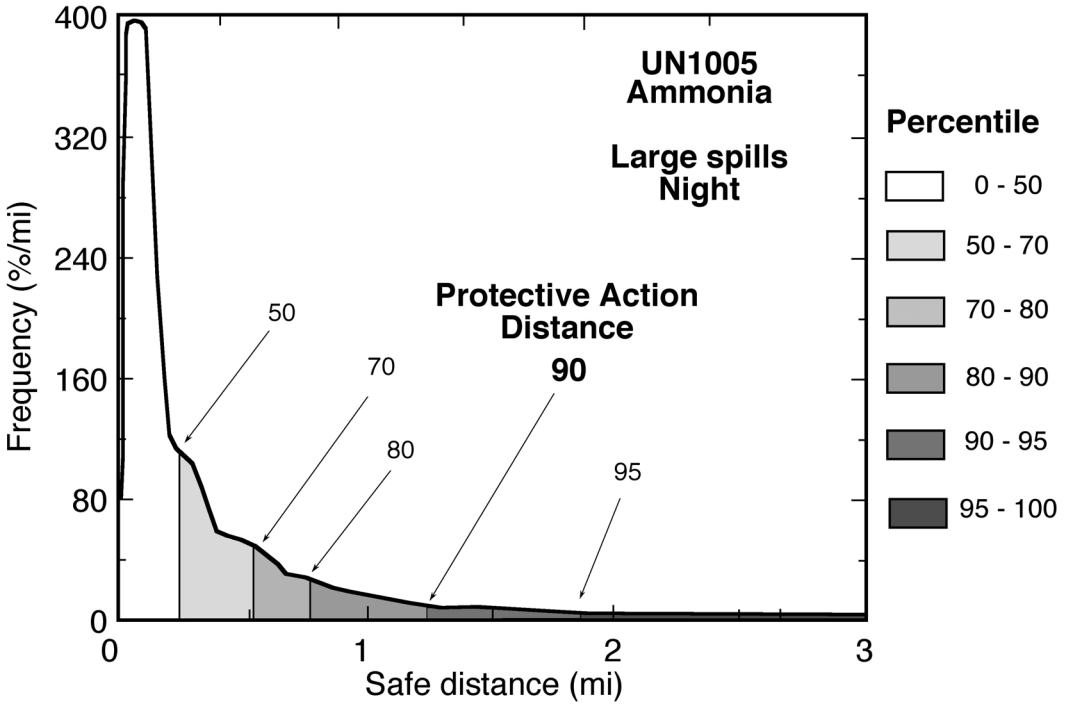

FIGURE 5.5 Frequency of Safe Distances for Large Nighttime Ammonia Spills as Determined in the ERG2012 Analysis

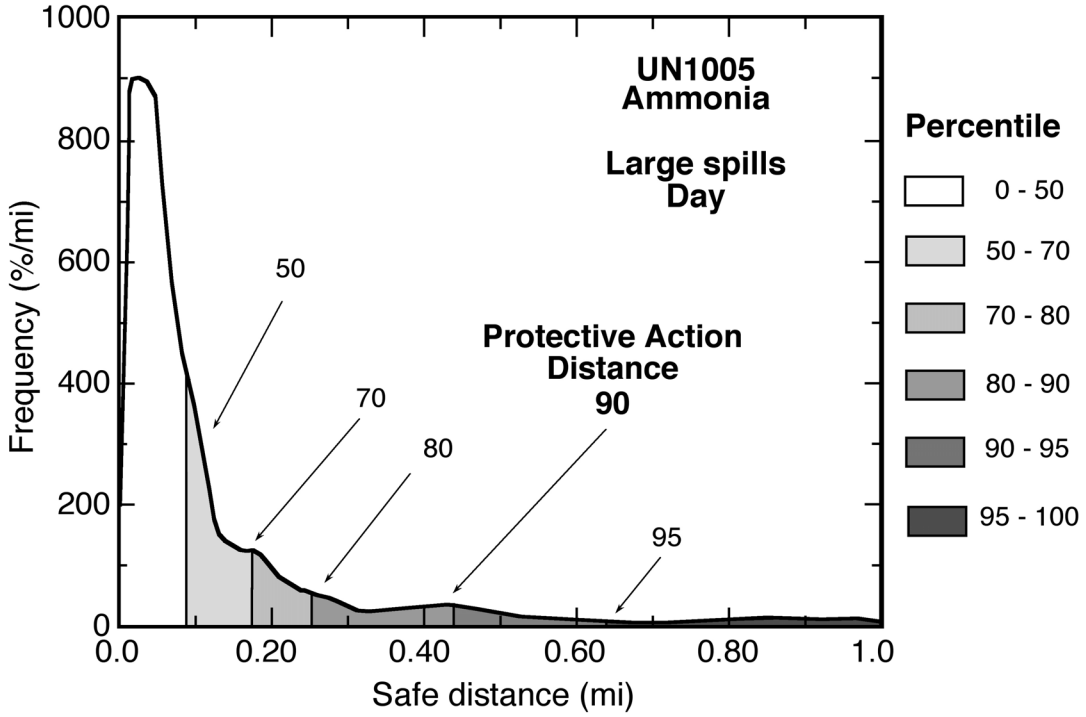

FIGURE 5.6 Frequency of Safe Distances for Large Daytime Ammonia Spills as Determined in the ERG2012 Analysis

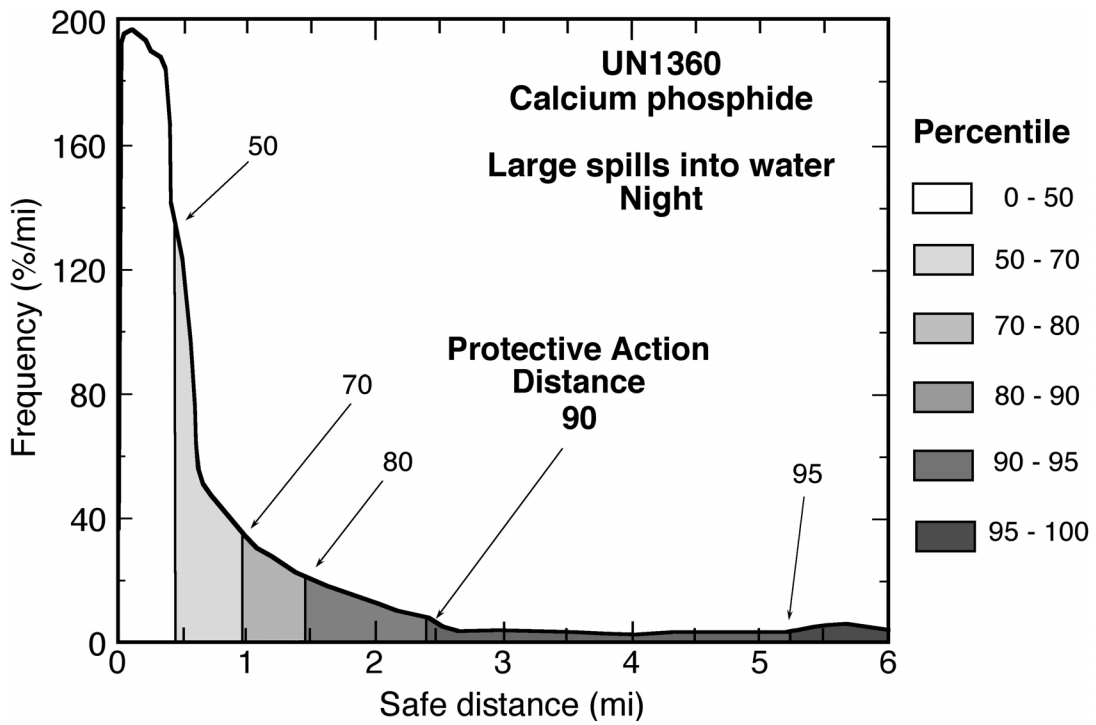

FIGURE 5.7 Frequency of Safe Distances for Large Nighttime Calcium Phosphide Spills into Water as Determined in the ERG2012 Analysis

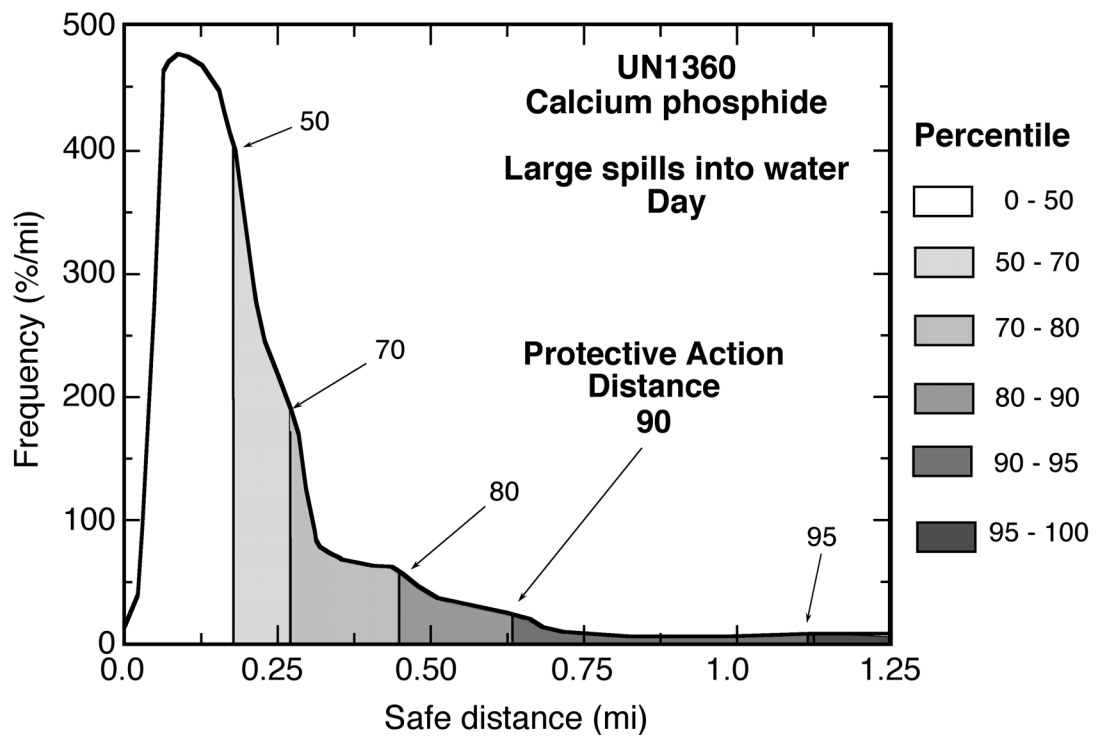

FIGURE 5.8 Frequency of Safe Distances for Large Daytime Calcium Phosphide Spills into Water as Determined in the ERG2012 Analysis

TABLE 5.1 Safe Distances at Several Percentiles for Chlorine (UN 1017) Releases as Determined in the ERG2012 Analysis

		Safe Distance (mi) at Percentile					
Release Size	Time	50	70	80	90	95	99
Small	Day	0.09	0.11	0.14	0.19[a]	0.29	0.86
	Night	0.20	0.42	0.65	0.95	1.19	1.68
Large	Day	0.40	0.62	0.95	1.84	3.12	8.63
	Night	1.19	2.18	3.19	4.89	7.40	14.6

[a] Bold values indicate the PADs in the ERG2012, which correspond with the 90th-percentile values for the individual categories.

TABLE 5.2 Safe Distances at Several Percentiles for Ammonia (UN 1005) Releases as Determined in the ERG2012 Analysis

		Safe Distance (mi) at Percentile					
Release Size	Time	50	70	80	90	95	99
Small	Day	0.01	0.01	0.02	**0.02**[a]	0.03	0.08
	Night	0.02	0.04	0.06	**0.10**	0.14	0.26
Large	Day	0.09	0.16	0.25	**0.44**	0.64	1.43
	Night	0.23	0.52	0.77	**1.23**	1.78	3.95

[a] Bold values indicate the PADs in the ERG2012 that correspond with the 90th-percentile values for the individual categories.

releases only. A separate set of safe distance distributions was developed for spills of phosphorous chloride into water.

As demonstrated in these examples, the safe distance distributions exhibit substantial tails, denoting the presence of low-probability/high-consequence events. A comparison of the 50th- and 90th-percentile values reveals that the 90th-percentile values are often a factor of 4 above the 50th-percentile values. Clearly, use of the 90th-percentile value for the PAD affords a substantial level of protection for most incidents. The 95th and 99th percentiles do show that the PADs will not be sufficient for all incidents, however. The 99th-percentile events, corresponding to large releases in very unfavorable meteorology, can result in safe distances that exceed the PAD by roughly a factor of 4 for daytime releases and a factor of 2 for nighttime

TABLE 5.3 Safe Distances at Several Percentiles for Land-Based Phosphorous Trichloride (UN 1809) Releases as Determined in the ERG2012 Analysis

		Safe Distance (mi) at Percentile					
Release Size	Time	50	70	80	90	95	99
Small	Day	0.04	0.05	0.07	**0.09**[a]	0.11	0.30
	Night	0.07	0.12	0.17	**0.28**	0.41	0.70
Large	Day	0.17	0.27	0.38	**0.56**	0.73	1.43
	Night	0.33	0.62	0.86	**1.33**	1.91	3.66

[a] Bold values indicate the PADs in the ERG2012 that correspond with the 90th-percentile values for the individual categories.

TABLE 5.4 Safe Distances at Several Percentiles for Calcium Phosphide (UN 1360) Releases into Water as Determined in the ERG2012 Analysis

		Safe Distance (mi) at Percentile					
Release Size	Time	50	70	80	90	95	99
Small	Day	0.03	0.04	0.05	**0.07**[a]	0.12	0.42
	Night	0.06	0.13	0.22	**0.38**	0.51	0.77
Large	Day	0.15	0.27	0.41	**0.65**	1.12	4.21
	Night	0.49	0.95	1.39	**2.36**	5.11	10.4

[a] Bold values indicate the PADs in the ERG2012 that correspond with the 90th-percentile values for the individual categories.

releases. However, using the 99th-percentile criterion to define the PAD would result in extreme overreaction to the vast majority of incidents first responders face. The 90th-percentile criterion was selected to strike a reasonable balance between adequately protecting the public from exposure to potentially harmful substances and avoiding the needless risks and expense associated with overreaction.

5.1.2 Generation of Table 3 Protective Action Distances

Table 3 of the ERG2012 further breaks down the PADs in Table 1 of the ERG 2012 into individual container types and wind speed categories for large spills for six widely transported

chemicals. It is envisioned that a first responder would easily be able to discern the wind conditions and obviously the container involved; therefore, this additional information is potentially very useful and provides a more refined PAD estimate than that available in Table 1. To illustrate application of the statistical results in development of Table 3 of the ERG2012, safe distance distributions for large rail daytime chlorine releases and large rail daytime ammonia releases are provided in Figures 5.9 and 5.10, respectively. In these statistical distributions, various percentiles are shown, including the 90th percentile, which corresponds to the PAD listed in Table 3. In these figures, the distributions are shown with the ordinate on a log scale to emphasize differences at higher percentiles. Note that there is a considerable variation with wind speed range in these figures; the 90th-percentile values for the high wind speed cases are 30–40% of the distances for the low wind speed values. Additional examples showing variations of safe distance estimates with container type and other environmental variables are provided in Section 5.3.

5.2 PRESENTATION OF THE TABLES IN THE GUIDEBOOK

Appendix A provides the Table of Initial Isolation and Protective Action Distances as it appears in the ERG2012 (DOT et al. 2012), with one important modification discussed below. The PADs in the table are the 90th percentiles of the safe distance distributions presented in the previous section. As discussed in Section 2, three distinct types of materials are listed in the table. The first includes TIH materials released in transportation-related incidents. The second includes water-reactive materials that emit TIH gases when spilled into water. These entries are denoted by the phrase "when spilled in water." For TIH materials that emit a secondary TIH product when spilled in water, two entries are listed; they correspond to spills in water and on land. The third includes chemical warfare agents released in a malicious manner. These entries are denoted by the phrase "when used as a weapon." Some chemical warfare agents, such as arsine and hydrogen cyanide, are TIH industrial chemicals as well and contain additional entries for transportation-related releases; however, weapons-related entries are listed under their military name (AC for hydrogen cyanide, SA for arsine, etc.).

In all cases, the PADs have been rounded *up* to the next 0.1 mi. Appendix A differs from the presentation in the ERG2012 in that distances are not limited to 7 mi (or 11 km). These "unclipped" values are provided to more accurately show the relative risk of the high-hazard materials for which PADs can exceed 7 mi. IIDs are rounded up and binned as described in Section 2.5.

Appendix B provides the container-specific tables for six commonly transported TIH materials that appear in Table 3 of the ERG2012. These six materials are chlorine, ammonia, sulfur dioxide, hydrogen chloride, hydrogen fluoride, and ethylene oxide. For each material, either three or four entries are provided for commonly employed transportation containers ranging from railcars to multiple single cylinders. In these tables, distances are provided for three wind-speed ranges corresponding to low, medium, and high winds. As discussed in Section 2 and Section 5.1.2, these distances are calculated using the same scenario library as those listed in Appendix A, except that results are further broken down by container type and wind speed as illustrated in Figures 5.9 and 5.10. One artifact of representing the data in this

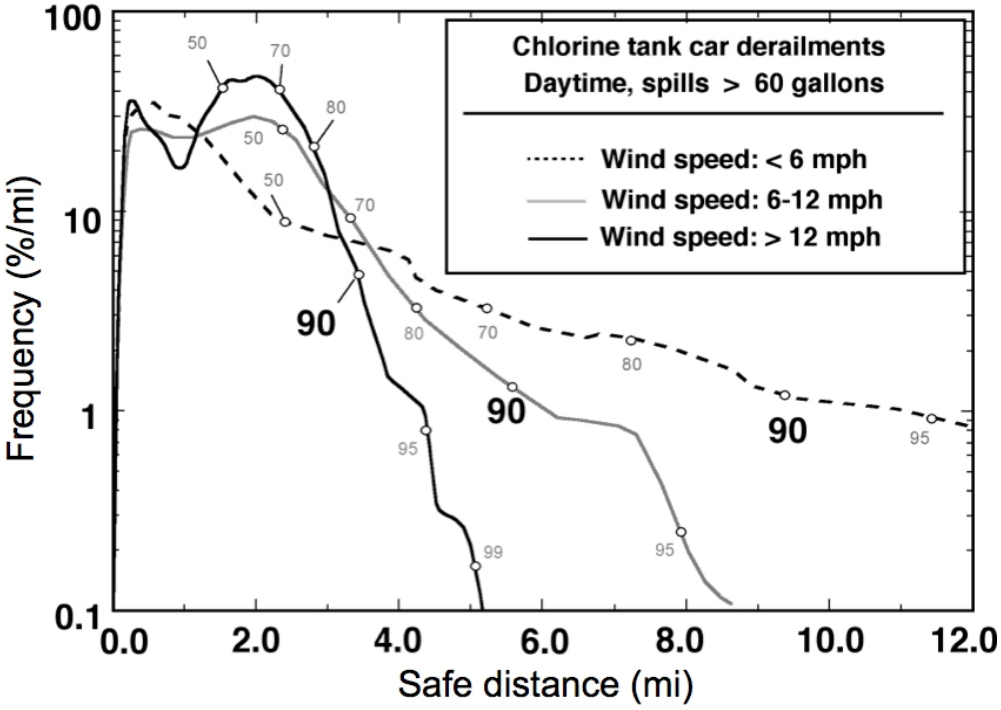

FIGURE 5.9 Frequency of Safe Distances for Large Daytime Chlorine Spills from Railcars for Different Wind Speed Ranges as Determined in the ERG2012 Analysis

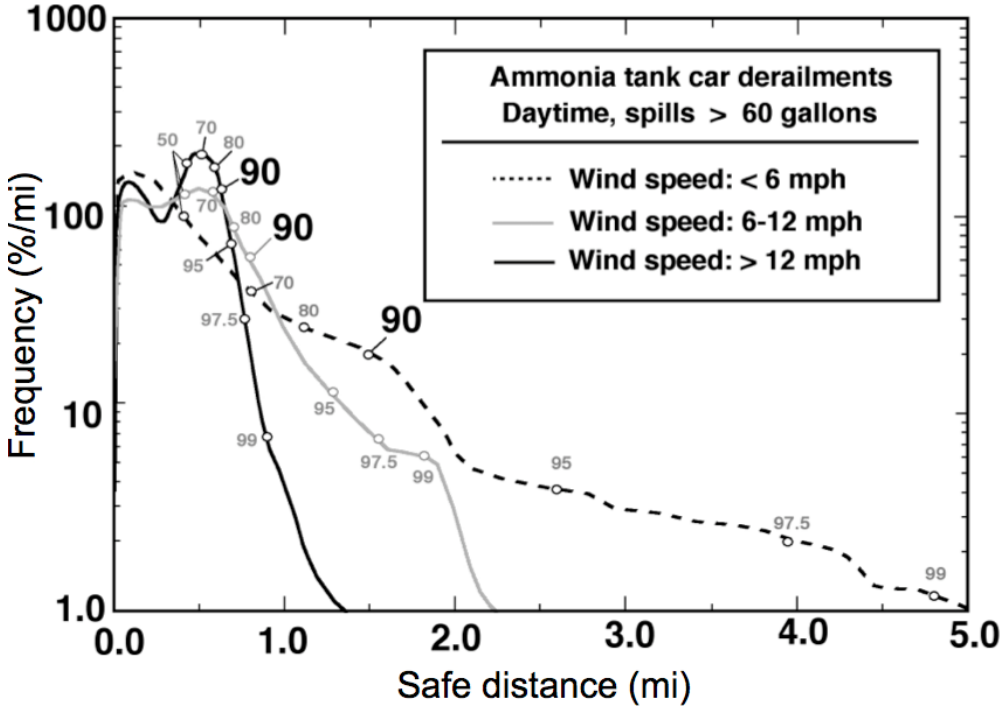

FIGURE 5.10 Frequency of Safe Distances for Large Daytime Ammonia Spills from Railcars for Different Wind Speed Ranges as Determined in the ERG2012 Analysis

form is that, except for high wind speed cases, the rail distances are substantially higher than the corresponding regular large spill distances in Appendix A and Table 1 of the ERG2012. These tables also demonstrate that large-spill distances from other bulk and multiple package freight containers are generally less than those provided on Appendix A and Table 1 of the 2012 ERG, with the exception of highway cargo tanks in low wind speed conditions.

5.3 EXTENSIONS OF THE ERG ANALYSIS

Prior to 2012, the key limitation of PAD estimates in the ERG was that the PAD estimates were only available for only two spill sizes (large or small), and incidents were assumed to happen in one of two timeframes (day or night). Clearly, the distributions in Figures 5.1–5.8 show wide variability in PAD estimates, and the data used to construct them contain a great amount of additional information that could be very useful in emergency response situations as well as a wide variety of other analyses. Factors that could be easily ascertained by emergency response personnel are whether the incident is a highway or rail incident, whether a vehicular accident or derailment is involved (as opposed to an en-route/nonaccident event), and what the general wind conditions (e.g., high or low wind speed), temperature, and cloud cover (clear or overcast) are. Each of these factors can affect the safe-distance estimate by a factor of 3 or more. Indeed, this fact was a key motivating factor in developing Table 3 of the ERG2012 Green Pages (the container-specific tables).

Examples of additional information that can considerably narrow the safe-distance distributions are shown in Figures 5.11–5.13. This analysis was described in the Argonne documentation for the ERG2004 and in Brown and Dunn (2007), and that description is repeated here. Note that the underlying analysis for chlorine was modified for the ERG2008 and ERG2012 by including more detailed shipment profiles and incorporating AEGL health criteria and minor changes to the source and dispersion models used within CASRAM. The relative benefit of using more detailed information, however — as illustrated in this example — remains the same. In these figures, the distributions are shown with the ordinate on a log scale to emphasize differences at higher percentiles (as was also shown in Figures 5.9 and 5.10). The percentiles of the distributions are shown as circles superimposed on the curves. Figure 5.11 compares safe-distance distributions for large, daytime chlorine spills from rail-transported tank cars and highway-transported cargo tanks. Since railcars contain approximately four times more chlorine than do highway vehicles, safe-distance estimates are higher at all percentiles for tank cars than for highway cargo tanks. At the 50th, 70th, 80th, and 90th percentiles, safe distances for rail releases falling under the definition of a large spill as found in the ERG (>60 gal) are about double those for corresponding highway cargo tank releases.

Figure 5.12 compares safe-distance distributions for two different times of year. It shows results for a volatile liquid, fuming nitric acid. Higher temperatures characteristic of summer increase the pool evaporation rate and therefore increase safe distances. Again, we see about factor-of-2 differences between percentiles for summer and winter cases. These distributions could be refined much further if the ERG analysis considered a particular location rather than the full range of locations.

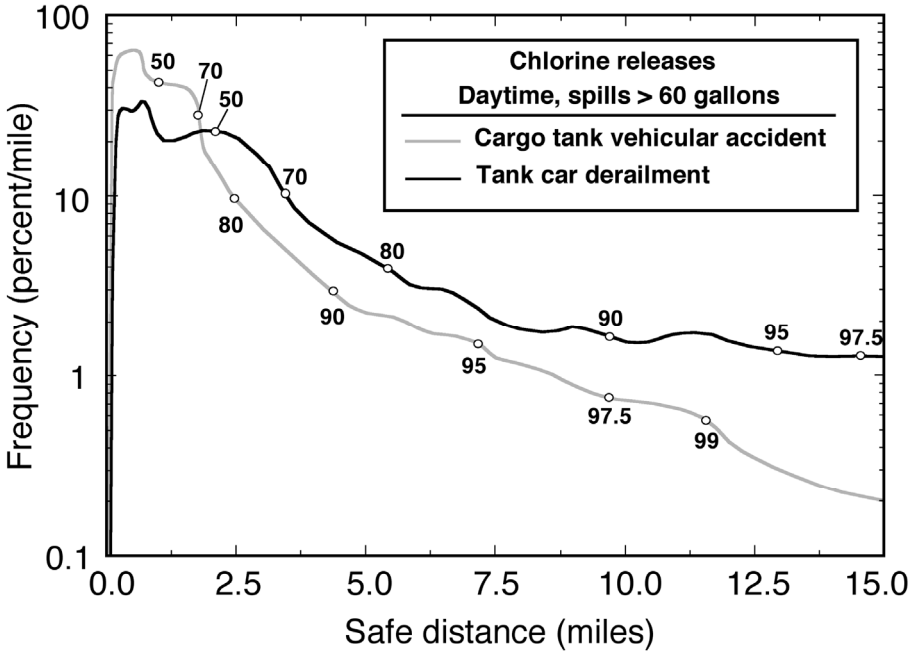

FIGURE 5.11 Frequency of Safe Distances for Large Daytime Chlorine Spills Resulting from Vehicular Accidents and Tank Car Derailments (Percentiles are denoted by open circles superimposed on the curves. These are a subset of cases shown in Figure 5.3.)

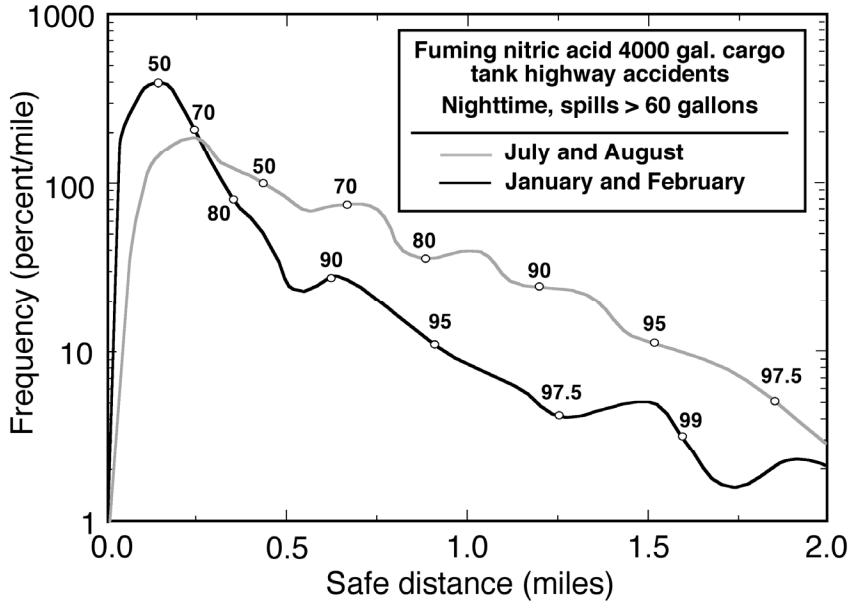

FIGURE 5.12 Frequency of Safe Distances for Highway Accidents Involving 4,000-gal Cargo Tanks of Fuming Nitric Acid in Summer and Winter Conditions (This shows the effects of seasonal climatology. Percentiles are denoted by open circles superimposed on the curves.)

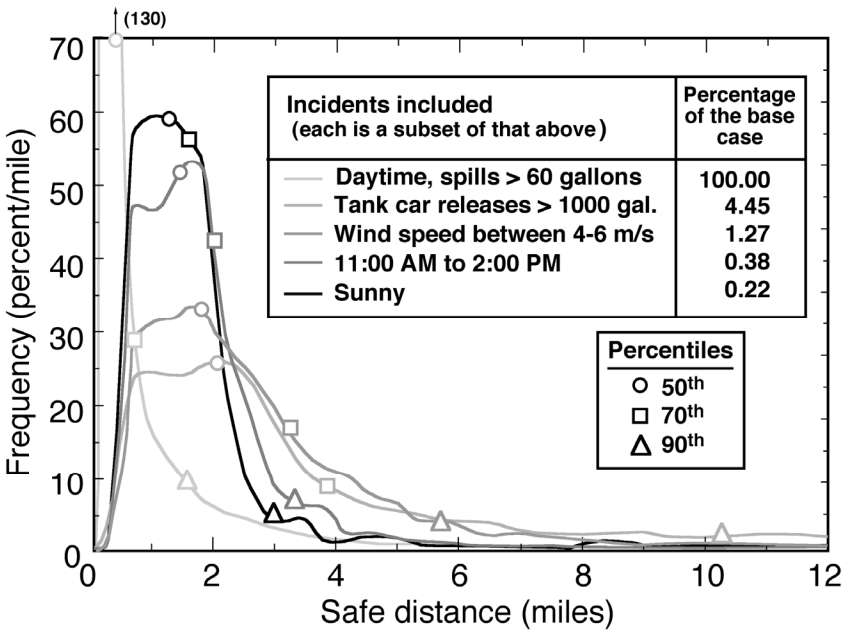

FIGURE 5.13 Frequency of Safe Distances for a Chlorine Tank Car Release of More Than 1,000 gal, Occurring between 11 a.m. and 2 p.m. on a Sunny Day with the Wind between 4 and 6 m/s (This shows the effect on the safe-distance distribution as each constraint is imposed. Percentiles are denoted as shown in the legend. The percentage of the base case, as given in Figure 5.3, is also provided.)

The last example is Figure 5.13, which shows the effect of increased information on safe-distance estimates for a rail chlorine spill involving more than 1,000 gal. Each factor listed in the figure could be easily determined by personnel arriving at the accident scene. The first curve shown is the large spill daytime distribution illustrated in Figure 5.3. This distribution encompasses more than 422,451 safe-distance estimates from our statistical analysis. Next, the estimate is narrowed down to tank car spills involving more than 1,000 gal. These incidents constitute 4.45% of the original distribution.

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APPENDIX A:

TABLE OF INITIAL ISOLATION AND PROTECTIVE ACTION DISTANCES IN THE *2012 EMERGENCY RESPONSE GUIDEBOOK*

TABLE A.1 Initial Isolation and Protective Action Distances for TIH Materials as Determined in the ERG2012 Analysis

UN ID No.	Name of Material	Small Spills			Large Spills		
		First Isolate in All Directions (ft)	Then Protect Downwind during		First Isolate in All Directions (ft)	Then Protect Downwind during	
			Day (mi)	Night (mi)		Day (mi)	Night (mi)
1005	Ammonia, anhydrous	100	0.1	0.1	500	0.5	1.3
1005	Anhydrous ammonia	100	0.1	0.1	500	0.5	1.3
1008	Boron trifluoride	100	0.1	0.4	1,000	1.1	3.0
1008	Boron trifluoride, compressed	100	0.1	0.4	1,000	1.1	3.0
1016	Carbon monoxide	100	0.1	0.1	600	0.8	3.0
1016	Carbon monoxide, compressed	100	0.1	0.1	600	0.8	3.0
1017	Chlorine	200	0.2	1.0	1,500	1.9	4.9
1023	Coal gas	200	0.1	0.1	300	0.2	0.3
1023	Coal gas, compressed	200	0.1	0.1	300	0.2	0.3
1026	Cyanogen	100	0.1	0.3	200	0.2	1.0
1026	Cyanogen gas	100	0.1	0.3	200	0.2	1.0
1040	Ethylene oxide	100	0.1	0.1	500	0.5	1.3
1040	Ethylene oxide with Nitrogen	100	0.1	0.1	500	0.5	1.3
1045	Fluorine	100	0.1	0.1	300	0.3	1.4
1045	Fluorine, compressed	100	0.1	0.1	300	0.3	1.4
1048	Hydrogen bromide, anhydrous	100	0.1	0.2	600	0.8	2.4
1050	Hydrogen chloride, anhydrous	100	0.1	0.2	200	0.2	0.8
1051	AC **(when used as a weapon)**	200	0.2	0.6	3,000	2.3	5.3
1051	Hydrocyanic acid, aqueous solutions, with more than 20% Hydrogen cyanide	200	0.1	0.4	1,250	0.9	2.4
1051	Hydrogen cyanide, anhydrous, stabilized	200	0.1	0.4	1,250	0.9	2.4
1051	Hydrogen cyanide, stabilized	200	0.1	0.4	1,250	0.9	2.4
1052	Hydrogen fluoride, anhydrous	100	0.1	0.3	1,000	0.9	2.0
1053	Hydrogen sulfide	100	0.1	0.3	1,000	1.0	3.5
1053	Hydrogen sulphide	100	0.1	0.3	1,000	1.0	3.5
1062	Methyl bromide	100	0.1	0.2	300	0.4	1.2
1064	Methyl mercaptan	100	0.1	0.2	500	0.7	2.0
1067	Dinitrogen tetroxide	100	0.1	0.2	1,000	0.7	1.7
1067	Nitrogen dioxide	100	0.1	0.2	1,000	0.7	1.7
1069	Nitrosyl chloride	100	0.2	0.7	2,000	2.3	5.9
1071	Oil gas	200	0.1	0.1	300	0.2	0.3
1071	Oil gas, compressed	200	0.1	0.1	300	0.2	0.3
1076	CG **(when used as a weapon)**	500	0.5	2.0	3,000	4.7	7.0+
1076	Diphosgene	100	0.1	0.1	100	0.2	0.3
1076	DP **(when used as a weapon)**	100	0.1	0.4	600	0.7	1.5
1076	Phosgene	300	0.4	1.7	1,500	1.9	6.7
1079	Sulfur dioxide	300	0.4	1.7	3,000	3.5	7.0+
1079	Sulphur dioxide	300	0.4	1.7	3,000	3.5	7.0+
1082	Trifluorochloroethylene, stabilized	100	0.1	0.1	200	0.3	0.6
1092	Acrolein, stabilized	500	0.9	2.5	2,500	5.8	7.0+
1098	Allyl alcohol	100	0.1	0.1	200	0.2	0.3
1135	Ethylene chlorohydrin	100	0.1	0.1	200	0.2	0.3
1143	Crotonaldehyde	100	0.1	0.1	200	0.3	0.6
1143	Crotonaldehyde, stabilized	100	0.1	0.1	200	0.3	0.6
1162	Dimethyldichlorosilane **(when spilled in water)**	100	0.1	0.2	200	0.4	1.2

TABLE A.1 (Cont.)

UN ID No.	Name of Material	Small Spills			Large Spills		
		First Isolate in All Directions (ft)	Then Protect Downwind during Day (mi)	Then Protect Downwind during Night (mi)	First Isolate in All Directions (ft)	Then Protect Downwind during Day (mi)	Then Protect Downwind during Night (mi)
1163	1,1-Dimethylhydrazine	100	0.1	0.4	300	0.7	1.4
1163	Dimethylhydrazine, unsymmetrical	100	0.1	0.4	300	0.7	1.4
1182	Ethyl chloroformate	100	0.1	0.1	200	0.2	0.4
1183	Ethyldichlorosilane **(when spilled in water)**	100	0.1	0.2	200	0.5	1.4
1185	Ethyleneimine, stabilized	100	0.1	0.3	300	0.6	1.3
1196	Ethyltrichlorosilane **(when spilled in water)**	100	0.1	0.5	600	1.3	3.9
1238	Methyl chloroformate	100	0.2	0.4	500	0.7	1.4
1239	Methyl chloromethyl ether	100	0.2	0.7	600	1.4	2.9
1242	Methyldichlorosilane **(when spilled in water)**	100	0.1	0.2	200	0.5	1.6
1244	Methylhydrazine	100	0.2	0.4	300	0.9	1.4
1250	Methyltrichlorosilane **(when spilled in water)**	100	0.1	0.2	300	0.6	1.7
1251	Methyl vinyl ketone, stabilized	300	0.2	0.5	2,500	1.0	1.9
1259	Nickel carbonyl	300	0.9	3.4	3,000	7.0+	7.0+
1295	Trichlorosilane **(when spilled in water)**	100	0.1	0.2	200	0.4	1.4
1298	Trimethylchlorosilane **(when spilled in water)**	100	0.1	0.1	200	0.4	1.0
1305	Vinyltrichlorosilane, stabilized **(when spilled in water)**	100	0.1	0.2	200	0.4	1.3
1340	Phosphorus pentasulfide, free from yellow and white Phosphorus **(when spilled in water)**	100	0.1	0.1	200	0.2	0.9
1340	Phosphorus pentasulphide, free from yellow and white Phosphorus **(when spilled in water)**	100	0.1	0.1	200	0.2	0.9
1360	Calcium phosphide **(when spilled in water)**	100	0.1	0.4	1,000	0.7	2.4
1380	Pentaborane	200	0.4	1.2	600	1.7	5.1
1384	Sodium dithionite **(when spilled in water)**	100	0.1	0.4	200	0.5	1.7
1384	Sodium hydrosulfite **(when spilled in water)**	100	0.1	0.4	200	0.5	1.7
1384	Sodium hydrosulphite **(when spilled in water)**	100	0.1	0.4	200	0.5	1.7
1397	Aluminum phosphide **(when spilled in water)**	200	0.2	0.6	1,500	1.3	4.7
1419	Magnesium aluminum phosphide **(when spilled in water)**	200	0.1	0.5	1,500	1.2	4.1
1432	Sodium phosphide **(when spilled in water)**	100	0.1	0.4	1,250	0.9	2.6
1510	Tetranitromethane	100	0.2	0.2	200	0.4	0.6
1541	Acetone cyanohydrin, stabilized **(when spilled in water)**	100	0.1	0.1	300	0.2	0.7
1556	MD **(when used as a weapon)**	1000	1.0	2.7	3,000	7.0+	7.0+
1556	Methyldichloroarsine	300	0.9	1.4	1,000	2.4	4.3
1556	PD **(when used as a weapon)**	200	0.3	0.3	1,000	1.0	1.0
1560	Arsenic chloride	100	0.1	0.2	300	0.6	1.0
1560	Arsenic trichloride	100	0.1	0.2	300	0.6	1.0
1569	Bromoacetone	100	0.3	0.8	500	1.2	2.3
1580	Chloropicrin	100	0.3	0.6	500	1.0	1.9
1581	Chloropicrin and Methyl bromide mixture	100	0.1	0.4	1,000	1.3	3.7
1581	Methyl bromide and Chloropicrin mixture	100	0.1	0.4	1,000	1.3	3.7
1582	Chloropicrin and Methyl chloride mixture	100	0.1	0.3	200	0.2	1.1
1582	Methyl chloride and Chloropicrin mixture	100	0.1	0.3	200	0.2	1.1
1583	Chloropicrin mixture, n.o.s.	100	0.3	0.6	500	1.0	1.9
1589	CK **(when used as a weapon)**	500	0.6	2.4	2,500	3.6	7.0+
1589	Cyanogen chloride, stabilized	300	0.3	1.4	1,250	1.7	5.4
1595	Dimethyl sulfate	100	0.1	0.1	200	0.3	0.5

TABLE A.1 (Cont.)

UN ID No.	Name of Material	Small Spills			Large Spills		
		First Isolate in All Directions (ft)	Then Protect Downwind during Day (mi)	Then Protect Downwind during Night (mi)	First Isolate in All Directions (ft)	Then Protect Downwind during Day (mi)	Then Protect Downwind during Night (mi)
1595	Dimethyl sulphate	100	0.1	0.1	200	0.3	0.5
1605	Ethylene dibromide	100	0.1	0.1	100	0.1	0.1
1612	Hexaethyl tetraphosphate and compressed gas mixture	300	0.5	1.7	1,250	2.2	5.1
1613	Hydrocyanic acid, aqueous solution, with not more than 20% Hydrogen cyanide	200	0.1	0.1	500	0.3	0.8
1613	Hydrogen cyanide, aqueous solution, with not more than 20% Hydrogen cyanide	200	0.1	0.1	500	0.3	0.8
1614	Hydrogen cyanide, stabilized (absorbed)	200	0.1	0.4	500	0.4	1.1
1647	Ethylene dibromide and Methyl bromide mixture, liquid	100	0.1	0.2	300	0.4	1.2
1647	Methyl bromide and Ethylene dibromide mixture, liquid	100	0.1	0.2	300	0.4	1.2
1660	Nitric oxide	100	0.1	0.4	300	0.4	1.5
1660	Nitric oxide, compressed	100	0.1	0.4	300	0.4	1.5
1670	Perchloromethyl mercaptan	100	0.2	0.2	300	0.5	0.8
1680	Potassium cyanide **(when spilled in water)**	100	0.1	0.1	300	0.2	0.8
1680	Potassium cyanide, solid **(when spilled in water)**	100	0.1	0.1	300	0.2	0.8
1689	Sodium cyanide **(when spilled in water)**	100	0.1	0.1	300	0.2	0.9
1689	Sodium cyanide, solid **(when spilled in water)**	100	0.1	0.1	300	0.2	0.9
1694	CA **(when used as a weapon)**	100	0.1	0.3	300	0.4	1.6
1695	Chloroacetone, stabilized	100	0.1	0.1	200	0.3	0.5
1697	CN **(when used as a weapon)**	100	0.1	0.1	200	0.2	0.8
1698	Adamsite **(when used as a weapon)**	100	0.1	0.2	200	0.2	0.9
1698	DM **(when used as a weapon)**	100	0.1	0.2	200	0.2	0.9
1699	DA **(when used as a weapon)**	100	0.1	0.5	1,000	1.2	4.7
1716	Acetyl bromide **(when spilled in water)**	100	0.1	0.1	200	0.3	0.8
1717	Acetyl chloride **(when spilled in water)**	100	0.1	0.2	300	0.6	1.7
1722	Allyl chlorocarbonate	300	0.2	0.6	1,250	1.0	1.9
1722	Allyl chloroformate	300	0.2	0.6	1,250	1.0	1.9
1724	Allyltrichlorosilane, stabilized **(when spilled in water)**	100	0.1	0.2	200	0.4	1.2
1725	Aluminum bromide, anhydrous **(when spilled in water)**	100	0.1	0.1	100	0.1	0.4
1726	Aluminum chloride, anhydrous **(when spilled in water)**	100	0.1	0.2	200	0.4	1.4
1728	Amyltrichlorosilane **(when spilled in water)**	100	0.1	0.2	200	0.4	1.2
1732	Antimony pentafluoride **(when spilled in water)**	100	0.1	0.3	500	0.7	2.6
1741	Boron trichloride **(when spilled on land)**	100	0.1	0.2	300	0.4	0.9
1741	Boron trichloride **(when spilled in water)**	100	0.1	0.3	300	0.8	2.4
1744	Bromine	200	0.4	1.2	1,000	1.8	4.0
1744	Bromine, solution	200	0.4	1.2	1,000	1.8	4.0
1744	Bromine, solution (Inhalation Hazard Zone A)	200	0.4	1.2	1,000	1.8	4.0
1744	Bromine, solution (Inhalation Hazard Zone B)	200	0.3	0.8	500	1.1	2.6
1745	Bromine pentafluoride **(when spilled on land)**	100	0.2	0.9	600	1.4	3.2
1745	Bromine pentafluoride **(when spilled in water)**	100	0.1	0.4	500	0.8	2.7
1746	Bromine trifluoride **(when spilled on land)**	100	0.1	0.1	100	0.2	0.4
1746	Bromine trifluoride **(when spilled in water)**	100	0.1	0.3	300	0.7	2.5
1747	Butyltrichlorosilane **(when spilled in water)**	100	0.1	0.2	200	0.4	1.1

TABLE A.1 (Cont.)

UN ID No.	Name of Material	Small Spills			Large Spills		
		First Isolate in All Directions (ft)	Then Protect Downwind during Day (mi)	Then Protect Downwind during Night (mi)	First Isolate in All Directions (ft)	Then Protect Downwind during Day (mi)	Then Protect Downwind during Night (mi)
1749	Chlorine trifluoride	200	0.2	0.8	1,000	0.9	2.9
1752	Chloroacetyl chloride **(when spilled on land)**	100	0.2	0.4	300	0.8	1.4
1752	Chloroacetyl chloride **(when spilled in water)**	100	0.1	0.1	100	0.2	0.6
1753	Chlorophenyltrichlorosilane **(when spilled in water)**	100	0.1	0.1	100	0.2	0.7
1754	Chlorosulfonic acid **(when spilled on land)**	100	0.1	0.1	100	0.2	0.2
1754	Chlorosulfonic acid **(when spilled in water)**	100	0.1	0.2	200	0.5	1.5
1754	Chlorosulfonic acid and Sulfur trioxide mixture **(when spilled on land)**	300	0.2	0.5	1,250	1.8	3.5
1754	Chlorosulfonic acid and Sulfur trioxide mixture **(when spilled in water)**	100	0.1	0.2	200	0.5	1.5
1754	Chlorosulphonic acid **(when spilled on land)**	100	0.1	0.1	100	0.2	0.2
1754	Chlorosulphonic acid **(when spilled in water)**	100	0.1	0.2	200	0.5	1.5
1754	Chlorosulphonic acid and Sulphur trioxide mixture **(when spilled on land)**	300	0.2	0.5	1,250	1.8	3.5
1754	Chlorosulphonic acid and Sulphur trioxide mixture **(when spilled in water)**	100	0.1	0.2	200	0.5	1.5
1754	Sulfur trioxide and Chlorosulfonic acid mixture **(when spilled on land)**	300	0.2	0.5	1,250	1.8	3.5
1754	Sulfur trioxide and Chlorosulfonic acid mixture **(when spilled in water)**	100	0.1	0.2	200	0.5	1.5
1754	Sulphur trioxide and Chlorosulphonic acid mixture **(when spilled on land)**	300	0.2	0.5	1,250	1.8	3.5
1754	Sulphur trioxide and Chlorosulphonic acid mixture **(when spilled in water)**	100	0.1	0.2	200	0.5	1.5
1758	Chromium oxychloride **(when spilled in water)**	100	0.1	0.1	100	0.2	0.5
1762	Cyclohexenyltrichlorosilane **(when spilled in water)**	100	0.1	0.1	100	0.3	0.9
1763	Cyclohexyltrichlorosilane **(when spilled in water)**	100	0.1	0.1	100	0.3	0.9
1765	Dichloroacetyl chloride **(when spilled in water)**	100	0.1	0.1	100	0.2	0.6
1766	Dichlorophenyltrichlorosilane **(when spilled in water)**	100	0.1	0.2	200	0.4	1.3
1767	Diethyldichlorosilane **(when spilled in water)**	100	0.1	0.1	100	0.3	0.7
1769	Diphenyldichlorosilane **(when spilled in water)**	100	0.1	0.1	100	0.3	0.8
1771	Dodecyltrichlorosilane **(when spilled in water)**	100	0.1	0.1	200	0.3	0.9
1777	Fluorosulfonic acid **(when spilled in water)**	100	0.1	0.1	100	0.2	0.5
1777	Fluorosulphonic acid **(when spilled in water)**	100	0.1	0.1	100	0.2	0.5
1781	Hexadecyltrichlorosilane **(when spilled in water)**	100	0.1	0.1	100	0.2	0.4
1784	Hexyltrichlorosilane **(when spilled in water)**	100	0.1	0.1	200	0.3	0.9
1799	Nonyltrichlorosilane **(when spilled in water)**	100	0.1	0.1	200	0.3	1.0
1800	Octadecyltrichlorosilane **(when spilled in water)**	100	0.1	0.1	200	0.3	1.0
1801	Octyltrichlorosilane **(when spilled in water)**	100	0.1	0.1	200	0.3	1.0
1804	Phenyltrichlorosilane **(when spilled in water)**	100	0.1	0.1	200	0.3	1.0
1806	Phosphorus pentachloride **(when spilled in water)**	100	0.1	0.2	100	0.3	0.9
1808	Phosphorus tribromide **(when spilled in water)**	100	0.1	0.2	200	0.4	1.2
1809	Phosphorus trichloride **(when spilled on land)**	100	0.1	0.3	300	0.6	1.4
1809	Phosphorus trichloride **(when spilled in water)**	100	0.1	0.2	200	0.5	1.6
1810	Phosphorus oxychloride **(when spilled on land)**	100	0.2	0.4	300	0.7	1.4
1810	Phosphorus oxychloride **(when spilled in water)**	100	0.1	0.2	200	0.4	1.4
1815	Propionyl chloride **(when spilled in water)**	100	0.1	0.1	100	0.2	0.5

TABLE A.1 (Cont.)

UN ID No.	Name of Material	Small Spills			Large Spills		
		First Isolate in All Directions (ft)	Then Protect Downwind during Day (mi)	Then Protect Downwind during Night (mi)	First Isolate in All Directions (ft)	Then Protect Downwind during Day (mi)	Then Protect Downwind during Night (mi)
1816	Propyltrichlorosilane **(when spilled in water)**	100	0.1	0.2	200	0.4	1.3
1818	Silicon tetrachloride **(when spilled in water)**	100	0.1	0.2	300	0.6	1.7
1828	Sulfur chlorides **(when spilled on land)**	100	0.1	0.1	200	0.2	0.3
1828	Sulfur chlorides **(when spilled in water)**	100	0.1	0.1	100	0.2	0.8
1828	Sulphur chlorides **(when spilled on land)**	100	0.1	0.1	200	0.2	0.3
1828	Sulphur chlorides **(when spilled in water)**	100	0.1	0.1	100	0.2	0.8
1829	Sulfur trioxide, stabilized	300	0.2	0.5	1,250	1.8	3.5
1829	Sulphur trioxide, stabilized	300	0.2	0.5	1,250	1.8	3.5
1831	Sulfuric acid, fuming	300	0.2	0.5	1,250	1.8	3.5
1831	Sulfuric acid, fuming, with not less than 30% free Sulfur trioxide	300	0.2	0.5	1,250	1.8	3.5
1831	Sulphuric acid, fuming	300	0.2	0.5	1,250	1.8	3.5
1831	Sulphuric acid, fuming, with not less than 30% free Sulphur trioxide	300	0.2	0.5	1,250	1.8	3.5
1834	Sulfuryl chloride **(when spilled on land)**	100	0.1	0.4	300	0.6	1.3
1834	Sulfuryl chloride **(when spilled in water)**	100	0.1	0.1	200	0.3	1.1
1834	Sulphuryl chloride **(when spilled on land)**	100	0.1	0.4	300	0.6	1.3
1834	Sulphuryl chloride **(when spilled in water)**	100	0.1	0.1	200	0.3	1.1
1836	Thionyl chloride **(when spilled on land)**	100	0.2	0.5	300	0.6	1.2
1836	Thionyl chloride **(when spilled in water)**	300	0.7	1.9	2,500	6.2	7.0+
1838	Titanium tetrachloride **(when spilled on land)**	100	0.1	0.1	100	0.3	0.4
1838	Titanium tetrachloride **(when spilled in water)**	100	0.1	0.1	200	0.3	1.1
1859	Silicon tetrafluoride	100	0.1	0.5	300	0.4	1.6
1859	Silicon tetrafluoride, compressed	100	0.1	0.5	300	0.4	1.6
1892	ED **(when used as a weapon)**	500	0.6	1.3	3,000	3.7	5.2
1892	Ethyldichloroarsine	500	1.0	1.2	1,000	2.4	2.3
1898	Acetyl iodide **(when spilled in water)**	100	0.1	0.2	200	0.3	0.7
1911	Diborane	200	0.2	0.7	600	0.8	2.5
1911	Diborane, compressed	200	0.2	0.7	600	0.8	2.5
1923	Calcium dithionite **(when spilled in water)**	100	0.1	0.4	200	0.5	1.7
1923	Calcium hydrosulfite **(when spilled in water)**	100	0.1	0.4	200	0.5	1.7
1923	Calcium hydrosulphite **(when spilled in water)**	100	0.1	0.4	200	0.5	1.7
1929	Potassium dithionite **(when spilled in water)**	100	0.1	0.4	200	0.4	1.5
1929	Potassium hydrosulfite **(when spilled in water)**	100	0.1	0.4	200	0.4	1.5
1929	Potassium hydrosulphite **(when spilled in water)**	100	0.1	0.4	200	0.4	1.5
1931	Zinc dithionite **(when spilled in water)**	100	0.1	0.4	200	0.5	1.6
1931	Zinc hydrosulfite **(when spilled in water)**	100	0.1	0.4	200	0.5	1.6
1931	Zinc hydrosulphite **(when spilled in water)**	100	0.1	0.4	200	0.5	1.6
1953	Compressed gas, flammable, poisonous, n.o.s. (Inhalation Hazard Zone A)	300	0.3	1.4	2,000	1.7	5.4
1953	Compressed gas, flammable, poisonous, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.2	1,000	0.8	2.2
1953	Compressed gas, flammable, poisonous, n.o.s. (Inhalation Hazard Zone C)	100	0.1	0.2	600	0.7	2.0
1953	Compressed gas, flammable, poisonous, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.1	600	0.5	1.3
1953	Compressed gas, flammable, toxic, n.o.s. (Inhalation Hazard Zone A)	300	0.3	1.4	2,000	1.7	5.4

TABLE A.1 (Cont.)

UN ID No.	Name of Material	Small Spills			Large Spills		
		First Isolate in All Directions (ft)	Then Protect Downwind during Day (mi)	Then Protect Downwind during Night (mi)	First Isolate in All Directions (ft)	Then Protect Downwind during Day (mi)	Then Protect Downwind during Night (mi)
1953	Compressed gas, flammable, toxic, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.2	1,000	0.8	2.2
1953	Compressed gas, flammable, toxic, n.o.s. (Inhalation Hazard Zone C)	100	0.1	0.2	600	0.7	2.0
1953	Compressed gas, flammable, toxic, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.1	600	0.5	1.3
1953	Compressed gas, poisonous, flammable, n.o.s.	300	0.3	1.4	2,000	1.7	5.4
1953	Compressed gas, poisonous, flammable, n.o.s. (Inhalation Hazard Zone A)	300	0.3	1.4	2,000	1.7	5.4
1953	Compressed gas, poisonous, flammable, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.2	1,000	0.8	2.2
1953	Compressed gas, poisonous, flammable, n.o.s. (Inhalation Hazard Zone C)	100	0.1	0.2	600	0.7	2.0
1953	Compressed gas, poisonous, flammable, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.1	600	0.5	1.3
1953	Compressed gas, toxic, flammable, n.o.s.	300	0.3	1.4	2,000	1.7	5.4
1953	Compressed gas, toxic, flammable, n.o.s. (Inhalation Hazard Zone A)	300	0.3	1.4	2,000	1.7	5.4
1953	Compressed gas, toxic, flammable, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.2	1,000	0.8	2.2
1953	Compressed gas, toxic, flammable, n.o.s. (Inhalation Hazard Zone C)	100	0.1	0.2	600	0.7	2.0
1953	Compressed gas, toxic, flammable, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.1	600	0.5	1.3
1955	Compressed gas, poisonous, n.o.s.	300	0.3	1.4	2,000	2.2	5.9
1955	Compressed gas, poisonous, n.o.s. (Inhalation Hazard Zone A)	300	0.3	1.4	2,000	2.2	5.9
1955	Compressed gas, poisonous, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.5	1,000	0.9	2.9
1955	Compressed gas, poisonous, n.o.s. (Inhalation Hazard Zone C)	100	0.1	0.2	500	0.6	1.7
1955	Compressed gas, poisonous, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.1	500	0.5	1.3
1955	Compressed gas, toxic, n.o.s.	300	0.3	1.4	2,000	2.2	5.9
1955	Compressed gas, toxic, n.o.s. (Inhalation Hazard Zone A)	300	0.3	1.4	2,000	2.2	5.9
1955	Compressed gas, toxic, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.5	1,000	0.9	2.9
1955	Compressed gas, toxic, n.o.s. (Inhalation Hazard Zone C)	100	0.1	0.2	500	0.6	1.7
1955	Compressed gas, toxic, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.1	500	0.5	1.3
1955	Organic phosphate compound mixed with compressed gas	300	0.6	1.6	1,500	2.4	5.9
1955	Organic phosphate mixed with compressed gas	300	0.6	1.6	1,500	2.4	5.9
1955	Organic phosphorus compound mixed with compressed gas	300	0.6	1.6	1,500	2.4	5.9
1967	Insecticide gas, poisonous, n.o.s.	300	0.6	1.6	1,500	2.4	5.9

TABLE A.1 (Cont.)

UN ID No.	Name of Material	Small Spills			Large Spills		
		First Isolate in All Directions (ft)	Then Protect Downwind during Day (mi)	Then Protect Downwind during Night (mi)	First Isolate in All Directions (ft)	Then Protect Downwind during Day (mi)	Then Protect Downwind during Night (mi)
1967	Insecticide gas, toxic, n.o.s.	300	0.6	1.6	1,500	2.4	5.9
1967	Parathion and compressed gas mixture	300	0.6	1.6	1,500	2.4	5.9
1975	Dinitrogen tetroxide and Nitric oxide mixture	100	0.1	0.4	300	0.4	1.5
1975	Nitric oxide and Dinitrogen tetroxide mixture	100	0.1	0.4	300	0.4	1.5
1975	Nitric oxide and Nitrogen dioxide mixture	100	0.1	0.4	300	0.4	1.5
1975	Nitric oxide and Nitrogen tetroxide mixture	100	0.1	0.4	300	0.4	1.5
1975	Nitrogen dioxide and Nitric oxide mixture	100	0.1	0.4	300	0.4	1.5
1975	Nitrogen tetroxide and Nitric oxide mixture	100	0.1	0.4	300	0.4	1.5
1994	Iron pentacarbonyl	300	0.6	1.3	1,250	3.0	5.2
2004	Magnesium diamide **(when spilled in water)**	100	0.1	0.3	300	0.5	1.5
2011	Magnesium phosphide **(when spilled in water)**	200	0.1	0.5	1,500	1.1	3.8
2012	Potassium phosphide **(when spilled in water)**	100	0.1	0.4	1,000	0.8	2.5
2013	Strontium phosphide **(when spilled in water)**	100	0.1	0.4	1,000	0.7	2.4
2032	Nitric acid, fuming	100	0.1	0.2	500	0.3	0.7
2032	Nitric acid, red fuming	100	0.1	0.2	500	0.3	0.7
2186	Hydrogen chloride, refrigerated liquid	100	0.1	0.2	1,000	1.3	4.7
2188	Arsine	500	0.6	2.5	3,000	3.6	7.0+
2188	SA **(when used as a weapon)**	1000	1.2	3.6	3,000	5.6	7.0+
2189	Dichlorosilane	100	0.1	0.2	600	0.8	1.8
2190	Oxygen difluoride	600	0.3	1.3	3,000	1.4	5.4
2190	Oxygen difluoride, compressed	600	0.3	1.3	3,000	1.4	5.4
2191	Sulfuryl fluoride	100	0.1	0.3	1,000	1.2	3.2
2191	Sulphuryl fluoride	100	0.1	0.3	1,000	1.2	3.2
2192	Germane	500	0.5	2.0	2,500	2.7	6.6
2194	Selenium hexafluoride	600	0.7	2.3	2,500	3.1	7.0+
2195	Tellurium hexafluoride	600	0.7	2.8	3,000	4.2	7.0+
2196	Tungsten hexafluoride	100	0.1	0.5	500	0.6	2.0
2197	Hydrogen iodide, anhydrous	100	0.1	0.2	500	0.6	1.7
2198	Phosphorus pentafluoride	100	0.1	0.5	500	0.5	2.0
2198	Phosphorus pentafluoride, compressed	100	0.1	0.5	500	0.5	2.0
2199	Phosphine	200	0.2	0.7	1,250	0.8	2.5
2202	Hydrogen selenide, anhydrous	600	0.7	3.1	3,000	5.3	7.0+
2204	Carbonyl sulfide	100	0.1	0.2	1,000	0.8	2.2
2204	Carbonyl sulphide	100	0.1	0.2	1,000	0.8	2.2
2232	2-Chloroethanal	100	0.1	0.2	200	0.5	0.8
2232	Chloroacetaldehyde	100	0.1	0.2	200	0.5	0.8
2308	Nitrosylsulfuric acid **(when spilled in water)**	100	0.1	0.3	1,000	0.6	1.6
2308	Nitrosylsulfuric acid, liquid **(when spilled in water)**	100	0.1	0.3	1,000	0.6	1.6
2308	Nitrosylsulfuric acid, solid **(when spilled in water)**	100	0.1	0.3	1,000	0.6	1.6
2308	Nitrosylsulphuric acid **(when spilled in water)**	100	0.1	0.3	1,000	0.6	1.6
2308	Nitrosylsulphuric acid, liquid **(when spilled in water)**	100	0.1	0.3	1,000	0.6	1.6
2308	Nitrosylsulphuric acid, solid **(when spilled in water)**	100	0.1	0.3	1,000	0.6	1.6
2334	Allylamine	100	0.1	0.4	500	0.9	1.7
2337	Phenyl mercaptan	100	0.1	0.1	100	0.2	0.3
2353	Butyryl chloride **(when spilled in water)**	100	0.1	0.1	100	0.2	0.6
2382	1,2-Dimethylhydrazine	100	0.1	0.2	200	0.5	1.0
2382	Dimethylhydrazine, symmetrical	100	0.1	0.2	200	0.5	1.0

TABLE A.1 (Cont.)

UN ID No.	Name of Material	Small Spills			Large Spills		
		First Isolate in All Directions (ft)	Then Protect Downwind during		First Isolate in All Directions (ft)	Then Protect Downwind during	
			Day (mi)	Night (mi)		Day (mi)	Night (mi)
2395	Isobutyryl chloride **(when spilled in water)**	100	0.1	0.1	100	0.2	0.4
2407	Isopropyl chloroformate	100	0.1	0.2	200	0.3	0.6
2417	Carbonyl fluoride	300	0.4	1.4	2,000	2.3	5.0
2417	Carbonyl fluoride, compressed	300	0.4	1.4	2,000	2.3	5.0
2418	Sulfur tetrafluoride	300	0.4	1.6	2,000	2.2	5.9
2418	Sulphur tetrafluoride	300	0.4	1.6	2,000	2.2	5.9
2420	Hexafluoroacetone	200	0.2	0.9	3,000	4.7	7.0+
2421	Nitrogen trioxide	200	0.3	1.1	1,000	1.2	4.2
2434	Dibenzyldichlorosilane **(when spilled in water)**	100	0.1	0.1	100	0.1	0.4
2435	Ethylphenyldichlorosilane **(when spilled in water)**	100	0.1	0.1	100	0.2	0.7
2437	Methylphenyldichlorosilane **(when spilled in water)**	100	0.1	0.1	100	0.3	0.9
2438	Trimethylacetyl chloride	100	0.2	0.4	300	0.8	1.3
2442	Trichloroacetyl chloride	100	0.1	0.2	200	0.4	0.8
2474	Thiophosgene	200	0.4	1.2	1,000	1.7	3.4
2477	Methyl isothiocyanate	100	0.1	0.1	100	0.2	0.2
2480	Methyl isocyanate	500	1.1	3.6	3,000	7.0+	7.0+
2481	Ethyl isocyanate	500	1.2	3.7	3,000	7.0+	7.0+
2482	n-Propyl isocyanate	300	0.7	1.7	2,000	4.9	7.0+
2483	Isopropyl isocyanate	300	0.8	1.9	2,500	6.3	7.0+
2484	tert-Butyl isocyanate	300	0.7	1.7	2,000	4.5	7.0+
2485	n-Butyl isocyanate	200	0.5	1.1	1,000	2.5	4.2
2486	Isobutyl isocyanate	200	0.5	1.1	1,000	2.5	4.1
2487	Phenyl isocyanate	100	0.2	0.2	200	0.5	0.8
2488	Cyclohexyl isocyanate	100	0.1	0.1	200	0.3	0.5
2495	Iodine pentafluoride **(when spilled in water)**	100	0.1	0.4	500	0.8	2.9
2521	Diketene, stabilized	100	0.1	0.1	100	0.2	0.3
2534	Methylchlorosilane	100	0.1	0.2	300	0.4	1.1
2548	Chlorine pentafluoride	100	0.2	0.7	1,000	1.1	4.6
2600	Carbon monoxide and Hydrogen mixture, compressed	100	0.1	0.1	600	0.8	3.0
2600	Hydrogen and Carbon monoxide mixture, compressed	100	0.1	0.1	600	0.8	3.0
2605	Methoxymethyl isocyanate	100	0.2	0.4	300	0.8	1.2
2606	Methyl orthosilicate	100	0.1	0.1	100	0.1	0.2
2644	Methyl iodide	100	0.1	0.1	300	0.2	0.5
2646	Hexachlorocyclopentadiene	100	0.1	0.1	100	0.2	0.3
2668	Chloroacetonitrile	100	0.1	0.1	100	0.1	0.1
2676	Stibine	200	0.2	1.1	1,000	1.2	4.0
2691	Phosphorus pentabromide **(when spilled in water)**	100	0.1	0.1	100	0.2	0.6
2692	Boron tribromide **(when spilled on land)**	100	0.1	0.2	100	0.2	0.4
2692	Boron tribromide **(when spilled in water)**	100	0.1	0.3	200	0.5	1.6
2740	n-Propyl chloroformate	100	0.1	0.2	200	0.4	0.7
2742	sec-Butyl chloroformate	100	0.1	0.1	100	0.3	0.4
2742	Isobutyl chloroformate	100	0.1	0.1	100	0.2	0.3
2743	n-Butyl chloroformate	100	0.1	0.1	100	0.2	0.4
2806	Lithium nitride **(when spilled in water)**	100	0.1	0.3	200	0.4	1.3
2810	Buzz **(when used as a weapon)**	200	0.2	1.1	1,250	1.4	5.0
2810	BZ **(when used as a weapon)**	200	0.2	1.1	1,250	1.4	5.0
2810	CS **(when used as a weapon)**	100	0.1	0.4	300	0.3	1.2

TABLE A.1 (Cont.)

UN ID No.	Name of Material	Small Spills			Large Spills		
		First Isolate in All Directions (ft)	Then Protect Downwind during		First Isolate in All Directions (ft)	Then Protect Downwind during	
			Day (mi)	Night (mi)		Day (mi)	Night (mi)
2810	DC **(when used as a weapon)**	100	0.1	0.4	200	0.3	1.1
2810	GA **(when used as a weapon)**	100	0.1	0.1	300	0.4	0.4
2810	GB **(when used as a weapon)**	200	0.3	0.7	1,250	1.3	3.0
2810	GD **(when used as a weapon)**	200	0.3	0.5	1,000	1.1	1.7
2810	GF **(when used as a weapon)**	100	0.2	0.2	500	0.5	0.6
2810	H **(when used as a weapon)**	100	0.1	0.1	200	0.2	0.3
2810	HD **(when used as a weapon)**	100	0.1	0.1	200	0.2	0.3
2810	HL **(when used as a weapon)**	100	0.1	0.2	300	0.3	0.6
2810	HN-1 **(when used as a weapon)**	200	0.2	0.3	600	0.7	1.1
2810	HN-2 **(when used as a weapon)**	200	0.2	0.4	1,000	0.8	1.3
2810	HN-3 **(when used as a weapon)**	100	0.1	0.1	200	0.2	0.2
2810	L (Lewisite) **(when used as a weapon)**	100	0.1	0.2	300	0.3	0.6
2810	Lewisite **(when used as a weapon)**	100	0.1	0.2	300	0.3	0.6
2810	Mustard **(when used as a weapon)**	100	0.1	0.1	200	0.2	0.3
2810	Mustard Lewisite **(when used as a weapon)**	100	0.1	0.2	300	0.3	0.6
2810	Poisonous liquid, n.o.s.	200	0.3	0.8	600	1.4	3.2
2810	Poisonous liquid, n.o.s. (Inhalation Hazard Zone A)	200	0.3	0.8	600	1.4	3.2
2810	Poisonous liquid, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.1	200	0.3	0.5
2810	Poisonous liquid, organic, n.o.s.	100	0.2	0.7	1,000	1.1	2.8
2810	Poisonous liquid, organic, n.o.s. (Inhalation Hazard Zone A)	100	0.2	0.7	1,000	1.1	2.8
2810	Poisonous liquid, organic, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.1	200	0.3	0.5
2810	Sarin **(when used as a weapon)**	200	0.3	0.7	1,250	1.3	3.0
2810	Soman **(when used as a weapon)**	200	0.3	0.5	1,000	1.1	1.7
2810	Tabun **(when used as a weapon)**	100	0.1	0.1	300	0.4	0.4
2810	Thickened GD **(when used as a weapon)**	200	0.3	0.5	1,000	1.1	1.7
2810	Toxic liquid, n.o.s.	200	0.3	0.8	600	1.4	3.2
2810	Toxic liquid, n.o.s. (Inhalation Hazard Zone A)	200	0.3	0.8	600	1.4	3.2
2810	Toxic liquid, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.1	200	0.3	0.5
2810	Toxic liquid, organic, n.o.s.	100	0.2	0.7	1,000	1.1	2.8
2810	Toxic liquid, organic, n.o.s. (Inhalation Hazard Zone A)	100	0.2	0.7	1,000	1.1	2.8
2810	Toxic liquid, organic, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.1	200	0.3	0.5
2810	VX **(when used as a weapon)**	100	0.1	0.1	200	0.2	0.2
2811	CX **(when used as a weapon)**	200	0.2	0.7	600	0.7	3.2
2826	Ethyl chlorothioformate	100	0.1	0.1	100	0.3	0.4
2845	Ethyl phosphonous dichloride, anhydrous	100	0.2	0.5	500	0.9	1.7
2845	Methyl phosphonous dichloride	100	0.3	0.8	600	1.4	2.7
2901	Bromine chloride	200	0.2	0.7	1,250	1.5	4.2
2927	Ethyl phosphonothioic dichloride, anhydrous	100	0.1	0.1	100	0.1	0.1
2927	Ethyl phosphorodichloridate	100	0.1	0.1	100	0.1	0.1
2927	Poisonous liquid, corrosive, n.o.s.	200	0.2	0.6	600	1.0	1.9
2927	Poisonous liquid, corrosive, n.o.s. (Inhalation Hazard Zone A)	200	0.2	0.6	600	1.0	1.9
2927	Poisonous liquid, corrosive, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.1	100	0.3	0.4

TABLE A.1 (Cont.)

UN ID No.	Name of Material	Small Spills			Large Spills		
		First Isolate in All Directions (ft)	Then Protect Downwind during		First Isolate in All Directions (ft)	Then Protect Downwind during	
			Day (mi)	Night (mi)		Day (mi)	Night (mi)
2927	Poisonous liquid, corrosive, organic, n.o.s.	200	0.2	0.5	1,000	1.0	1.9
2927	Poisonous liquid, corrosive, organic, n.o.s. (Inhalation Hazard Zone A)	200	0.2	0.5	1,000	1.0	1.9
2927	Poisonous liquid, corrosive, organic, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.1	100	0.3	0.4
2927	Toxic liquid, corrosive, n.o.s.	200	0.2	0.6	600	1.0	1.9
2927	Toxic liquid, corrosive, n.o.s. (Inhalation Hazard Zone A)	200	0.2	0.6	600	1.0	1.9
2927	Toxic liquid, corrosive, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.1	100	0.3	0.4
2927	Toxic liquid, corrosive, organic, n.o.s.	200	0.2	0.5	1,000	1.0	1.9
2927	Toxic liquid, corrosive, organic, n.o.s. (Inhalation Hazard Zone A)	200	0.2	0.5	1,000	1.0	1.9
2927	Toxic liquid, corrosive, organic, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.1	100	0.3	0.4
2929	Poisonous liquid, flammable, n.o.s.	200	0.5	1.1	1,000	2.5	4.1
2929	Poisonous liquid, flammable, n.o.s. (Inhalation Hazard Zone A)	200	0.5	1.1	1,000	2.5	4.1
2929	Poisonous liquid, flammable, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.1	200	0.3	0.5
2929	Poisonous liquid, flammable, organic, n.o.s.	100	0.3	0.8	600	1.4	2.9
2929	Poisonous liquid, flammable, organic, n.o.s. (Inhalation Hazard Zone A)	100	0.3	0.8	600	1.4	2.9
2929	Poisonous liquid, flammable, organic, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.1	200	0.3	0.5
2929	Toxic liquid, flammable, n.o.s.	200	0.5	1.1	1,000	2.5	4.1
2929	Toxic liquid, flammable, n.o.s. (Inhalation Hazard Zone A)	200	0.5	1.1	1,000	2.5	4.1
2929	Toxic liquid, flammable, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.1	200	0.3	0.5
2929	Toxic liquid, flammable, organic, n.o.s.	100	0.3	0.8	600	1.4	2.9
2929	Toxic liquid, flammable, organic, n.o.s. (Inhalation Hazard Zone A)	100	0.3	0.8	600	1.4	2.9
2929	Toxic liquid, flammable, organic, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.1	200	0.3	0.5
2977	Radioactive material, Uranium hexafluoride, fissile **(when spilled in water)**	100	0.1	0.3	200	0.3	1.5
2977	Uranium hexafluoride, fissile containing more than 1% Uranium-235 **(when spilled in water)**	100	0.1	0.3	200	0.3	1.5
2978	Radioactive material, Uranium hexafluoride **(when spilled in water)**	100	0.1	0.3	200	0.3	1.5
2978	Uranium hexafluoride **(when spilled in water)**	100	0.1	0.3	200	0.3	1.5
2978	Uranium hexafluoride, non fissile or fissile-excepted **(when spilled in water)**	100	0.1	0.3	200	0.3	1.5
2985	Chlorosilanes, flammable, corrosive, n.o.s. **(when spilled in water)**	100	0.1	0.1	200	0.3	1.0
2985	Chlorosilanes, n.o.s. **(when spilled in water)**	100	0.1	0.1	200	0.3	1.0

TABLE A.1 (Cont.)

UN ID No.	Name of Material	Small Spills			Large Spills		
		First Isolate in All Directions (ft)	Then Protect Downwind during		First Isolate in All Directions (ft)	Then Protect Downwind during	
			Day (mi)	Night (mi)		Day (mi)	Night (mi)
2986	Chlorosilanes, corrosive, flammable, n.o.s. **(when spilled in water)**	100	0.1	0.1	200	0.3	1.0
2986	Chlorosilanes, n.o.s. **(when spilled in water)**	100	0.1	0.1	200	0.3	1.0
2987	Chlorosilanes, corrosive, n.o.s. **(when spilled in water)**	100	0.1	0.1	200	0.3	1.0
2987	Chlorosilanes, n.o.s. **(when spilled in water)**	100	0.1	0.1	200	0.3	1.0
2988	Chlorosilanes, n.o.s. **(when spilled in water)**	100	0.1	0.1	200	0.3	1.0
2988	Chlorosilanes, water-reactive, flammable, corrosive, n.o.s. **(when spilled in water)**	100	0.1	0.1	200	0.3	1.0
3023	2-Methyl-2-heptanethiol	100	0.1	0.2	200	0.3	0.5
3023	tert-Octyl mercaptan	100	0.1	0.2	200	0.3	0.5
3048	Aluminum phosphide pesticide **(when spilled in water)**	200	0.2	0.6	1,500	1.3	4.6
3049	Metal alkyl halides, water-reactive, n.o.s. **(when spilled in water)**	100	0.1	0.1	200	0.3	0.8
3049	Metal aryl halides, water-reactive, n.o.s. **(when spilled in water)**	100	0.1	0.1	200	0.3	0.8
3052	Aluminum alkyl halides **(when spilled in water)**	100	0.1	0.1	200	0.3	0.8
3052	Aluminum alkyl halides, liquid **(when spilled in water)**	100	0.1	0.1	200	0.3	0.8
3052	Aluminum alkyl halides, solid **(when spilled in water)**	100	0.1	0.1	200	0.3	0.8
3057	Trifluoroacetyl chloride	100	0.1	0.6	2,500	2.7	7.0+
3079	Methacrylonitrile, stabilized	100	0.1	0.1	200	0.3	0.5
3083	Perchloryl fluoride	100	0.1	0.4	1,250	1.6	4.8
3122	Poisonous liquid, oxidizing, n.o.s.	100	0.2	0.9	600	1.4	3.2
3122	Poisonous liquid, oxidizing, n.o.s. (Inhalation Hazard Zone A)	100	0.2	0.9	600	1.4	3.2
3122	Poisonous liquid, oxidizing, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.2	200	0.4	0.6
3122	Toxic liquid, oxidizing, n.o.s.	100	0.2	0.9	600	1.4	3.2
3122	Toxic liquid, oxidizing, n.o.s. (Inhalation Hazard Zone A)	100	0.2	0.9	600	1.4	3.2
3122	Toxic liquid, oxidizing, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.2	200	0.4	0.6
3123	Poisonous liquid, water-reactive, n.o.s.	200	0.3	0.8	600	1.4	3.2
3123	Poisonous liquid, water-reactive, n.o.s. (Inhalation Hazard Zone A)	200	0.3	0.8	600	1.4	3.2
3123	Poisonous liquid, water-reactive, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.1	200	0.3	0.5
3123	Poisonous liquid, which in contact with water emits flammable gases, n.o.s.	200	0.3	0.8	600	1.4	3.2
3123	Poisonous liquid, which in contact with water emits flammable gases, n.o.s. (Inhalation Hazard Zone A)	200	0.3	0.8	600	1.4	3.2
3123	Poisonous liquid, which in contact with water emits flammable gases, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.1	200	0.3	0.5
3123	Toxic liquid, water-reactive, n.o.s.	200	0.3	0.8	600	1.4	3.2

TABLE A.1 (Cont.)

UN ID No.	Name of Material	Small Spills			Large Spills		
		First Isolate in All Directions (ft)	Then Protect Downwind during		First Isolate in All Directions (ft)	Then Protect Downwind during	
			Day (mi)	Night (mi)		Day (mi)	Night (mi)
3123	Toxic liquid, water-reactive, n.o.s. (Inhalation Hazard Zone A)	200	0.3	0.8	600	1.4	3.2
3123	Toxic liquid, water-reactive, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.1	200	0.3	0.5
3123	Toxic liquid, which in contact with water emits flammable gases, n.o.s.	200	0.3	0.8	600	1.4	3.2
3123	Toxic liquid, which in contact with water emits flammable gases, n.o.s. (Inhalation Hazard Zone A)	200	0.3	0.8	600	1.4	3.2
3123	Toxic liquid, which in contact with water emits flammable gases, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.1	200	0.3	0.5
3160	Liquefied gas, poisonous, flammable, n.o.s.	300	0.3	1.4	2,000	1.7	5.4
3160	Liquefied gas, poisonous, flammable, n.o.s. (Inhalation Hazard Zone A)	300	0.3	1.4	2,000	1.7	5.4
3160	Liquefied gas, poisonous, flammable, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.2	1,000	0.8	2.2
3160	Liquefied gas, poisonous, flammable, n.o.s. (Inhalation Hazard Zone C)	100	0.1	0.2	600	0.7	2.0
3160	Liquefied gas, poisonous, flammable, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.1	600	0.5	1.3
3160	Liquefied gas, toxic, flammable, n.o.s.	300	0.3	1.4	2,000	1.7	5.4
3160	Liquefied gas, toxic, flammable, n.o.s. (Inhalation Hazard Zone A)	300	0.3	1.4	2,000	1.7	5.4
3160	Liquefied gas, toxic, flammable, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.2	1,000	0.8	2.2
3160	Liquefied gas, toxic, flammable, n.o.s. (Inhalation Hazard Zone C)	100	0.1	0.2	600	0.7	2.0
3160	Liquefied gas, toxic, flammable, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.1	600	0.5	1.3
3162	Liquefied gas, poisonous, n.o.s.	300	0.3	1.4	2,000	2.2	5.9
3162	Liquefied gas, poisonous, n.o.s. (Inhalation Hazard Zone A)	300	0.3	1.4	2,000	2.2	5.9
3162	Liquefied gas, poisonous, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.5	1,000	0.9	2.9
3162	Liquefied gas, poisonous, n.o.s. (Inhalation Hazard Zone C)	100	0.1	0.2	500	0.6	1.7
3162	Liquefied gas, poisonous, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.1	500	0.5	1.3
3162	Liquefied gas, toxic, n.o.s.	300	0.3	1.4	2,000	2.2	5.9
3162	Liquefied gas, toxic, n.o.s. (Inhalation Hazard Zone A)	300	0.3	1.4	2,000	2.2	5.9
3162	Liquefied gas, toxic, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.5	1,000	0.9	2.9
3162	Liquefied gas, toxic, n.o.s. (Inhalation Hazard Zone C)	100	0.1	0.2	500	0.6	1.7
3162	Liquefied gas, toxic, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.1	500	0.5	1.3
3246	Methanesulfonyl chloride	100	0.1	0.1	100	0.1	0.2
3246	Methanesulphonyl chloride	100	0.1	0.1	100	0.1	0.2

TABLE A.1 (Cont.)

UN ID No.	Name of Material	Small Spills			Large Spills		
		First Isolate in All Directions (ft)	Then Protect Downwind during Day (mi)	Then Protect Downwind during Night (mi)	First Isolate in All Directions (ft)	Then Protect Downwind during Day (mi)	Then Protect Downwind during Night (mi)
3275	Nitriles, poisonous, flammable, n.o.s.	100	0.1	0.1	200	0.3	0.5
3275	Nitriles, toxic, flammable, n.o.s.	100	0.1	0.1	200	0.3	0.5
3276	Nitriles, liquid, poisonous, n.o.s.	100	0.1	0.1	200	0.3	0.5
3276	Nitriles, liquid, toxic, n.o.s.	100	0.1	0.1	200	0.3	0.5
3276	Nitriles, poisonous, liquid, n.o.s.	100	0.1	0.1	200	0.3	0.5
3276	Nitriles, poisonous, n.o.s.	100	0.1	0.1	200	0.3	0.5
3276	Nitriles, toxic, liquid, n.o.s.	100	0.1	0.1	200	0.3	0.5
3276	Nitriles, toxic, n.o.s.	100	0.1	0.1	200	0.3	0.5
3278	Organophosphorus compound, liquid, poisonous, n.o.s.	100	0.3	0.8	600	1.4	2.7
3278	Organophosphorus compound, liquid, toxic, n.o.s.	100	0.3	0.8	600	1.4	2.7
3278	Organophosphorus compound, poisonous, liquid, n.o.s.	100	0.3	0.8	600	1.4	2.7
3278	Organophosphorus compound, poisonous, n.o.s.	100	0.3	0.8	600	1.4	2.7
3278	Organophosphorus compound, toxic, liquid, n.o.s.	100	0.3	0.8	600	1.4	2.7
3278	Organophosphorus compound, toxic, n.o.s.	100	0.3	0.8	600	1.4	2.7
3279	Organophosphorus compound, poisonous, flammable, n.o.s.	100	0.3	0.8	600	1.4	2.7
3279	Organophosphorus compound, toxic, flammable, n.o.s.	100	0.3	0.8	600	1.4	2.7
3280	Organoarsenic compound, liquid, n.o.s.	100	0.1	0.5	500	1.1	2.8
3280	Organoarsenic compound, n.o.s.	100	0.1	0.5	500	1.1	2.8
3281	Metal carbonyls, liquid, n.o.s.	300	0.9	3.4	3,000	7.0+	7.0+
3281	Metal carbonyls, n.o.s.	300	0.9	3.4	3,000	7.0+	7.0+
3287	Poisonous liquid, inorganic, n.o.s.	200	0.4	1.2	1,000	1.8	4.0
3287	Poisonous liquid, inorganic, n.o.s. (Inhalation Hazard Zone A)	200	0.4	1.2	1,000	1.8	4.0
3287	Poisonous liquid, inorganic, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.2	300	0.6	1.0
3287	Toxic liquid, inorganic, n.o.s.	200	0.4	1.2	1,000	1.8	4.0
3287	Toxic liquid, inorganic, n.o.s. (Inhalation Hazard Zone A)	200	0.4	1.2	1,000	1.8	4.0
3287	Toxic liquid, inorganic, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.2	300	0.6	1.0
3289	Poisonous liquid, corrosive, inorganic, n.o.s.	100	0.2	0.9	600	1.4	3.2
3289	Poisonous liquid, corrosive, inorganic, n.o.s. (Inhalation Hazard Zone A)	100	0.2	0.9	600	1.4	3.2
3289	Poisonous liquid, corrosive, inorganic, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.2	300	0.3	0.7
3289	Toxic liquid, corrosive, inorganic, n.o.s.	100	0.2	0.9	600	1.4	3.2
3289	Toxic liquid, corrosive, inorganic, n.o.s. (Inhalation Hazard Zone A)	100	0.2	0.9	600	1.4	3.2
3289	Toxic liquid, corrosive, inorganic, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.2	300	0.3	0.7
3294	Hydrogen cyanide, solution in alcohol, with not more than 45% Hydrogen cyanide	200	0.1	0.2	600	0.4	1.2
3300	Carbon dioxide and Ethylene oxide mixture, with more than 87% Ethylene oxide	100	0.1	0.1	500	0.5	1.3

TABLE A.1 (Cont.)

UN ID No.	Name of Material	Small Spills			Large Spills		
		First Isolate in All Directions (ft)	Then Protect Downwind during Day (mi)	Then Protect Downwind during Night (mi)	First Isolate in All Directions (ft)	Then Protect Downwind during Day (mi)	Then Protect Downwind during Night (mi)
3300	Ethylene oxide and Carbon dioxide mixture, with more than 87% Ethylene oxide	100	0.1	0.1	500	0.5	1.3
3303	Compressed gas, poisonous, oxidizing, n.o.s.	200	0.3	1.3	2,000	1.7	5.4
3303	Compressed gas, poisonous, oxidizing, n.o.s. (Inhalation Hazard Zone A)	200	0.3	1.3	2,000	1.7	5.4
3303	Compressed gas, poisonous, oxidizing, n.o.s. (Inhalation Hazard Zone B)	200	0.2	0.7	1,250	1.5	4.2
3303	Compressed gas, poisonous, oxidizing, n.o.s. (Inhalation Hazard Zone C)	100	0.1	0.2	600	0.6	1.7
3303	Compressed gas, poisonous, oxidizing, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.1	600	0.4	1.3
3303	Compressed gas, toxic, oxidizing, n.o.s.	200	0.3	1.3	2,000	1.7	5.4
3303	Compressed gas, toxic, oxidizing, n.o.s. (Inhalation Hazard Zone A)	200	0.3	1.3	2,000	1.7	5.4
3303	Compressed gas, toxic, oxidizing, n.o.s. (Inhalation Hazard Zone B)	200	0.2	0.7	1,250	1.5	4.2
3303	Compressed gas, toxic, oxidizing, n.o.s. (Inhalation Hazard Zone C)	100	0.1	0.2	600	0.6	1.7
3303	Compressed gas, toxic, oxidizing, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.1	600	0.4	1.3
3304	Compressed gas, poisonous, corrosive, n.o.s.	300	0.4	1.6	2,000	2.2	5.9
3304	Compressed gas, poisonous, corrosive, n.o.s. (Inhalation Hazard Zone A)	300	0.4	1.6	2,000	2.2	5.9
3304	Compressed gas, poisonous, corrosive, n.o.s. (Inhalation Hazard Zone B)	200	0.2	0.8	1,000	0.9	2.9
3304	Compressed gas, poisonous, corrosive, n.o.s. (Inhalation Hazard Zone C)	100	0.1	0.2	500	0.6	1.7
3304	Compressed gas, poisonous, corrosive, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.1	500	0.5	1.3
3304	Compressed gas, toxic, corrosive, n.o.s.	300	0.4	1.6	2,000	2.2	5.9
3304	Compressed gas, toxic, corrosive, n.o.s. (Inhalation Hazard Zone A)	300	0.4	1.6	2,000	2.2	5.9
3304	Compressed gas, toxic, corrosive, n.o.s. (Inhalation Hazard Zone B)	200	0.2	0.8	1,000	0.9	2.9
3304	Compressed gas, toxic, corrosive, n.o.s. (Inhalation Hazard Zone C)	100	0.1	0.2	500	0.6	1.7
3304	Compressed gas, toxic, corrosive, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.1	500	0.5	1.3
3305	Compressed gas, poisonous, flammable, corrosive, n.o.s.	300	0.4	1.6	2,000	2.2	5.9
3305	Compressed gas, poisonous, flammable, corrosive, n.o.s. (Inhalation Hazard Zone A)	300	0.4	1.6	2,000	2.2	5.9
3305	Compressed gas, poisonous, flammable, corrosive, n.o.s. (Inhalation Hazard Zone B)	200	0.2	0.8	1,000	0.9	2.9
3305	Compressed gas, poisonous, flammable, corrosive, n.o.s. (Inhalation Hazard Zone C)	100	0.1	0.2	600	0.6	1.7
3305	Compressed gas, poisonous, flammable, corrosive, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.1	600	0.5	1.3

TABLE A.1 (Cont.)

UN ID No.	Name of Material	Small Spills			Large Spills		
		First Isolate in All Directions (ft)	Then Protect Downwind during		First Isolate in All Directions (ft)	Then Protect Downwind during	
			Day (mi)	Night (mi)		Day (mi)	Night (mi)
3305	Compressed gas, toxic, flammable, corrosive, n.o.s.	300	0.4	1.6	2,000	2.2	5.9
3305	Compressed gas, toxic, flammable, corrosive, n.o.s. (Inhalation Hazard Zone A)	300	0.4	1.6	2,000	2.2	5.9
3305	Compressed gas, toxic, flammable, corrosive, n.o.s. (Inhalation Hazard Zone B)	200	0.2	0.8	1,000	0.9	2.9
3305	Compressed gas, toxic, flammable, corrosive, n.o.s. (Inhalation Hazard Zone C)	100	0.1	0.2	600	0.6	1.7
3305	Compressed gas, toxic, flammable, corrosive, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.1	600	0.5	1.3
3306	Compressed gas, poisonous, oxidizing, corrosive, n.o.s.	300	0.4	1.6	2,000	2.2	5.9
3306	Compressed gas, poisonous, oxidizing, corrosive, n.o.s. (Inhalation Hazard Zone A)	300	0.4	1.6	2,000	2.2	5.9
3306	Compressed gas, poisonous, oxidizing, corrosive, n.o.s. (Inhalation Hazard Zone B)	200	0.2	0.7	1,250	1.5	4.2
3306	Compressed gas, poisonous, oxidizing, corrosive, n.o.s. (Inhalation Hazard Zone C)	100	0.1	0.2	600	0.6	1.7
3306	Compressed gas, poisonous, oxidizing, corrosive, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.1	600	0.5	1.3
3306	Compressed gas, toxic, oxidizing, corrosive, n.o.s.	300	0.4	1.6	2,000	2.2	5.9
3306	Compressed gas, toxic, oxidizing, corrosive, n.o.s. (Inhalation Hazard Zone A)	300	0.4	1.6	2,000	2.2	5.9
3306	Compressed gas, toxic, oxidizing, corrosive, n.o.s. (Inhalation Hazard Zone B)	200	0.2	0.7	1,250	1.5	4.2
3306	Compressed gas, toxic, oxidizing, corrosive, n.o.s. (Inhalation Hazard Zone C)	100	0.1	0.2	600	0.6	1.7
3306	Compressed gas, toxic, oxidizing, corrosive, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.1	600	0.5	1.3
3307	Liquefied gas, poisonous, oxidizing, n.o.s.	200	0.3	1.3	2,000	1.7	5.4
3307	Liquefied gas, poisonous, oxidizing, n.o.s. (Inhalation Hazard Zone A)	200	0.3	1.3	2,000	1.7	5.4
3307	Liquefied gas, poisonous, oxidizing, n.o.s. (Inhalation Hazard Zone B)	200	0.2	0.7	1,250	1.5	4.2
3307	Liquefied gas, poisonous, oxidizing, n.o.s. (Inhalation Hazard Zone C)	100	0.1	0.2	600	0.6	1.7
3307	Liquefied gas, poisonous, oxidizing, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.1	600	0.4	1.3
3307	Liquefied gas, toxic, oxidizing, n.o.s.	200	0.3	1.3	2,000	1.7	5.4
3307	Liquefied gas, toxic, oxidizing, n.o.s. (Inhalation Hazard Zone A)	200	0.3	1.3	2,000	1.7	5.4
3307	Liquefied gas, toxic, oxidizing, n.o.s. (Inhalation Hazard Zone B)	200	0.2	0.7	1,250	1.5	4.2
3307	Liquefied gas, toxic, oxidizing, n.o.s. (Inhalation Hazard Zone C)	100	0.1	0.2	600	0.6	1.7
3307	Liquefied gas, toxic, oxidizing, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.1	600	0.4	1.3
3308	Liquefied gas, poisonous, corrosive, n.o.s.	300	0.4	1.6	2,000	2.2	5.9

TABLE A.1 (Cont.)

UN ID No.	Name of Material	Small Spills			Large Spills		
		First Isolate in All Directions (ft)	Then Protect Downwind during Day (mi)	Then Protect Downwind during Night (mi)	First Isolate in All Directions (ft)	Then Protect Downwind during Day (mi)	Then Protect Downwind during Night (mi)
3308	Liquefied gas, poisonous, corrosive, n.o.s. (Inhalation Hazard Zone A)	300	0.4	1.6	2,000	2.2	5.9
3308	Liquefied gas, poisonous, corrosive, n.o.s. (Inhalation Hazard Zone B)	200	0.2	0.8	1,000	0.9	2.9
3308	Liquefied gas, poisonous, corrosive, n.o.s. (Inhalation Hazard Zone C)	100	0.1	0.2	500	0.6	1.7
3308	Liquefied gas, poisonous, corrosive, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.1	500	0.5	1.3
3308	Liquefied gas, toxic, corrosive, n.o.s.	300	0.4	1.6	2,000	2.2	5.9
3308	Liquefied gas, toxic, corrosive, n.o.s. (Inhalation Hazard Zone A)	300	0.4	1.6	2,000	2.2	5.9
3308	Liquefied gas, toxic, corrosive, n.o.s. (Inhalation Hazard Zone B)	200	0.2	0.8	1,000	0.9	2.9
3308	Liquefied gas, toxic, corrosive, n.o.s. (Inhalation Hazard Zone C)	100	0.1	0.2	500	0.6	1.7
3308	Liquefied gas, toxic, corrosive, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.1	500	0.5	1.3
3309	Liquefied gas, poisonous, flammable, corrosive, n.o.s.	300	0.4	1.6	2,000	2.2	5.9
3309	Liquefied gas, poisonous, flammable, corrosive, n.o.s. (Inhalation Hazard Zone A)	300	0.4	1.6	2,000	2.2	5.9
3309	Liquefied gas, poisonous, flammable, corrosive, n.o.s. (Inhalation Hazard Zone B)	200	0.2	0.8	1,000	0.9	2.9
3309	Liquefied gas, poisonous, flammable, corrosive, n.o.s. (Inhalation Hazard Zone C)	100	0.1	0.2	600	0.6	1.7
3309	Liquefied gas, poisonous, flammable, corrosive, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.1	600	0.5	1.3
3309	Liquefied gas, toxic, flammable, corrosive, n.o.s.	300	0.4	1.6	2,000	2.2	5.9
3309	Liquefied gas, toxic, flammable, corrosive, n.o.s. (Inhalation Hazard Zone A)	300	0.4	1.6	2,000	2.2	5.9
3309	Liquefied gas, toxic, flammable, corrosive, n.o.s. (Inhalation Hazard Zone B)	200	0.2	0.8	1,000	0.9	2.9
3309	Liquefied gas, toxic, flammable, corrosive, n.o.s. (Inhalation Hazard Zone C)	100	0.1	0.2	600	0.6	1.7
3309	Liquefied gas, toxic, flammable, corrosive, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.1	600	0.5	1.3
3310	Liquefied gas, poisonous, oxidizing, corrosive, n.o.s.	300	0.4	1.6	2,000	2.2	5.9
3310	Liquefied gas, poisonous, oxidizing, corrosive, n.o.s. (Inhalation Hazard Zone A)	300	0.4	1.6	2,000	2.2	5.9
3310	Liquefied gas, poisonous, oxidizing, corrosive, n.o.s. (Inhalation Hazard Zone B)	200	0.2	0.7	1,250	1.5	4.2
3310	Liquefied gas, poisonous, oxidizing, corrosive, n.o.s. (Inhalation Hazard Zone C)	100	0.1	0.2	600	0.6	1.7
3310	Liquefied gas, poisonous, oxidizing, corrosive, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.1	600	0.5	1.3
3310	Liquefied gas, toxic, oxidizing, corrosive, n.o.s.	300	0.4	1.6	2,000	2.2	5.9
3310	Liquefied gas, toxic, oxidizing, corrosive, n.o.s. (Inhalation Hazard Zone A)	300	0.4	1.6	2,000	2.2	5.9

TABLE A.1 (Cont.)

UN ID No.	Name of Material	Small Spills			Large Spills		
		First Isolate in All Directions (ft)	Then Protect Downwind during		First Isolate in All Directions (ft)	Then Protect Downwind during	
			Day (mi)	Night (mi)		Day (mi)	Night (mi)
3310	Liquefied gas, toxic, oxidizing, corrosive, n.o.s. (Inhalation Hazard Zone B)	200	0.2	0.7	1,250	1.5	4.2
3310	Liquefied gas, toxic, oxidizing, corrosive, n.o.s. (Inhalation Hazard Zone C)	100	0.1	0.2	600	0.6	1.7
3310	Liquefied gas, toxic, oxidizing, corrosive, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.1	600	0.5	1.3
3318	Ammonia solution, with more than 50% Ammonia	100	0.1	0.1	500	0.5	1.3
3355	Insecticide gas, poisonous, flammable, n.o.s.	300	0.3	1.4	2,000	1.7	5.4
3355	Insecticide gas, poisonous, flammable, n.o.s. (Inhalation Hazard Zone A)	300	0.3	1.4	2,000	1.7	5.4
3355	Insecticide gas, poisonous, flammable, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.2	1,000	0.8	2.2
3355	Insecticide gas, poisonous, flammable, n.o.s. (Inhalation Hazard Zone C)	100	0.1	0.2	600	0.7	2.0
3355	Insecticide gas, poisonous, flammable, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.1	600	0.5	1.3
3355	Insecticide gas, toxic, flammable, n.o.s.	300	0.3	1.4	2,000	1.7	5.4
3355	Insecticide gas, toxic, flammable, n.o.s. (Inhalation Hazard Zone A)	300	0.3	1.4	2,000	1.7	5.4
3355	Insecticide gas, toxic, flammable, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.2	1,000	0.8	2.2
3355	Insecticide gas, toxic, flammable, n.o.s. (Inhalation Hazard Zone C)	100	0.1	0.2	600	0.7	2.0
3355	Insecticide gas, toxic, flammable, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.1	600	0.5	1.3
3361	Chlorosilanes, poisonous, corrosive, n.o.s. **(when spilled in water)**	100	0.1	0.1	200	0.3	1.0
3361	Chlorosilanes, toxic, corrosive, n.o.s. **(when spilled in water)**	100	0.1	0.1	200	0.3	1.0
3362	Chlorosilanes, poisonous, corrosive, flammable, n.o.s. **(when spilled in water)**	100	0.1	0.1	200	0.3	1.0
3362	Chlorosilanes, toxic, corrosive, flammable, n.o.s. **(when spilled in water)**	100	0.1	0.1	200	0.3	1.0
3381	Poisonous by inhalation liquid, n.o.s. (Inhalation Hazard Zone A)	200	0.3	0.8	600	1.4	3.2
3381	Toxic by inhalation liquid, n.o.s. (Inhalation Hazard Zone A)	200	0.3	0.8	600	1.4	3.2
3382	Poisonous by inhalation liquid, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.1	200	0.3	0.5
3382	Toxic by inhalation liquid, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.1	200	0.3	0.5
3383	Poisonous by inhalation liquid, flammable, n.o.s. (Inhalation Hazard Zone A)	200	0.5	1.1	1,000	2.5	4.1
3383	Toxic by inhalation liquid, flammable, n.o.s. (Inhalation Hazard Zone A)	200	0.5	1.1	1,000	2.5	4.1
3384	Poisonous by inhalation liquid, flammable, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.1	200	0.3	0.5

TABLE A.1 (Cont.)

UN ID No.	Name of Material	Small Spills			Large Spills		
		First Isolate in All Directions (ft)	Then Protect Downwind during Day (mi)	Then Protect Downwind during Night (mi)	First Isolate in All Directions (ft)	Then Protect Downwind during Day (mi)	Then Protect Downwind during Night (mi)
3384	Toxic by inhalation liquid, flammable, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.1	200	0.3	0.5
3385	Poisonous by inhalation liquid, water-reactive, n.o.s. (Inhalation Hazard Zone A)	200	0.3	0.8	600	1.4	3.2
3385	Toxic by inhalation liquid, water-reactive, n.o.s. (Inhalation Hazard Zone A)	200	0.3	0.8	600	1.4	3.2
3386	Poisonous by inhalation liquid, water-reactive, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.1	200	0.3	0.5
3386	Toxic by inhalation liquid, water-reactive, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.1	200	0.3	0.5
3387	Poisonous by inhalation liquid, oxidizing, n.o.s. (Inhalation Hazard Zone A)	100	0.2	0.9	600	1.4	3.2
3387	Toxic by inhalation liquid, oxidizing, n.o.s. (Inhalation Hazard Zone A)	100	0.2	0.9	600	1.4	3.2
3388	Poisonous by inhalation liquid, oxidizing, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.2	200	0.4	0.6
3388	Toxic by inhalation liquid, oxidizing, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.2	200	0.4	0.6
3389	Poisonous by inhalation liquid, corrosive, n.o.s. (Inhalation Hazard Zone A)	200	0.2	0.6	600	1.0	1.9
3389	Toxic by inhalation liquid, corrosive, n.o.s. (Inhalation Hazard Zone A)	200	0.2	0.6	600	1.0	1.9
3390	Poisonous by inhalation liquid, corrosive, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.1	100	0.3	0.4
3390	Toxic by inhalation liquid, corrosive, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.1	100	0.3	0.4
3456	Nitrosylsulfuric acid, solid **(when spilled in water)**	100	0.1	0.3	600	0.5	1.6
3456	Nitrosylsulphuric acid, solid **(when spilled in water)**	100	0.1	0.3	600	0.5	1.6
3461	Aluminum alkyl halides, solid **(when spilled in water)**	100	0.1	0.1	200	0.3	0.8
3488	Poisonous by inhalation liquid, flammable, corrosive, n.o.s. (Inhalation Hazard Zone A)	200	0.5	1.1	1,000	2.5	4.1
3488	Toxic by inhalation liquid, flammable, corrosive, n.o.s. (Inhalation Hazard Zone A)	200	0.5	1.1	1,000	2.5	4.1
3489	Poisonous by inhalation liquid, flammable, corrosive, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.1	200	0.3	0.5
3489	Toxic by inhalation liquid, flammable, corrosive, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.1	200	0.3	0.5
3490	Poisonous by inhalation liquid, water-reactive, flammable, n.o.s. (Inhalation Hazard Zone A)	200	0.5	1.1	1,000	2.5	4.1
3490	Toxic by inhalation liquid, water-reactive, flammable, n.o.s. (Inhalation Hazard Zone A)	200	0.5	1.1	1,000	2.5	4.1
3491	Poisonous by inhalation liquid, water-reactive, flammable, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.1	200	0.3	0.5
3491	Toxic by inhalation liquid, water-reactive, flammable, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.1	200	0.3	0.5
3492	Poisonous by inhalation liquid, corrosive, flammable, n.o.s. (Inhalation Hazard Zone A)	200	0.5	1.1	1,000	2.5	4.1

TABLE A.1 (Cont.)

UN ID No.	Name of Material	Small Spills			Large Spills		
		First Isolate in All Directions (ft)	Then Protect Downwind during		First Isolate in All Directions (ft)	Then Protect Downwind during	
			Day (mi)	Night (mi)		Day (mi)	Night (mi)
3492	Toxic by inhalation liquid, corrosive, flammable, n.o.s. (Inhalation Hazard Zone A)	200	0.5	1.1	1,000	2.5	4.1
3493	Poisonous by inhalation liquid, corrosive, flammable, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.1	200	0.3	0.5
3493	Toxic by inhalation liquid, corrosive, flammable, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.1	200	0.3	0.5
3494	Petroleum sour crude oil, flammable, toxic	100	0.1	0.1	200	0.3	0.5
9191	Chlorine dioxide, hydrate, frozen **(when spilled in water)**	100	0.1	0.1	100	0.2	0.4
9202	Carbon monoxide, refrigerated liquid (cryogenic liquid)	100	0.1	0.1	600	0.8	3.0
9206	Methyl phosphonic dichloride	100	0.1	0.1	100	0.3	0.4
9263	Chloropivaloyl chloride	100	0.1	0.1	100	0.2	0.2
9264	3,5-Dichloro-2,4,6-trifluoropyridine	100	0.1	0.1	100	0.2	0.2
9269	Trimethoxysilane	100	0.1	0.3	300	0.6	1.2

APPENDIX B:

INITIAL ISOLATION AND PROTECTIVE ACTION DISTANCES FOR SIX COMMON TIH GASES PROVIDED IN TABLE 3 OF ERG2012

APPENDIX B:

INITIAL ISOLATION AND PROTECTIVE ACTION DISTANCES FOR SIX COMMON TIH GASES PROVIDED IN TABLE 3 OF ERG2012

Tables B.1–B6 provide the container-specific tables for six commonly transported TIH materials that appear in Table 3 of ERG2012. These six materials are chlorine, ammonia, sulfur dioxide, hydrogen chloride, hydrogen fluoride, and ethylene oxide. For each material, either three or four entries are provided for commonly employed transportation containers. Also, distances are provided for three wind speed ranges:

- Less than 6 mph
- Between 6 and 12 mph
- Greater than 12 mph.

These tables are strictly for "large spills" from a bulk container or multiple small cylinders (i.e., releases over 60 gal), and are 90th-percentile values as appear in Table 1 of the ERG (as listed in Appendix A).

TABLE B.1 Container-Specific Table for Chlorine (UN 1017)

Transport container	First ISOLATE in all Directions [ft]	Then PROTECT persons Downwind during					
		Day [mi]			Night [mi]		
		Low wind [< 6 mph]	Moderate wind [6-12 mph]	High wind [> 12 mph]	Low wind [< 6 mph]	Moderate wind [6-12 mph]	High wind [> 12 mph]
Rail tank car	3000	7+	5.6	3.4	7+	7+	4.4
Highway tank truck or trailer	3000	6.6	2.2	1.8	7+	3.4	2.6
Multiple ton cylinders	1250	2.5	0.9	0.7	4.9	1.7	0.9
Multiple small cylinders or single ton cylinder	800	1.6	0.6	0.5	3.5	1.1	0.5

TABLE B.2 Container-Specific Table for Ammonia (UN 1015)

Transport container	First ISOLATE in all Directions [ft]	Then PROTECT persons Downwind during					
		Day [mi]			Night [mi]		
		Low wind [< 6 mph]	Moderate wind [6-12 mph]	High wind [> 12 mph]	Low wind [< 6 mph]	Moderate wind [6-12 mph]	High wind [> 12 mph]
Rail tank car	1000	1.4	0.8	0.6	3.9	1.6	0.8
Highway tank truck or trailer	400	0.6	0.3	0.2	1.6	0.5	0.3
Agricultural nurse tank	200	0.4	0.2	0.2	0.9	0.3	0.2
Multiple small cylinders	100	0.2	0.1	0.1	0.5	0.2	0.1

TABLE B.3 Container-Specific Table for Sulfur Dioxide (UN 1079)

Transport container	First ISOLATE in all Directions [ft]	Then PROTECT persons Downwind during					
		Day [mi]			Night [mi]		
		Low wind [< 6 mph]	Moderate wind [6-12 mph]	High wind [> 12 mph]	Low wind [< 6 mph]	Moderate wind [6-12 mph]	High wind [> 12 mph]
Rail tank car	3000	7+	7+	4.7	7+	7+	6.7
Highway tank truck or trailer	3000	7+	4.7	3.2	7+	6.2	3.8
Multiple ton cylinders	2000	4.4	1.7	1.2	6.5	2.9	1.8
Multiple small cylinders or single ton cylinder	1000	3.3	1.0	0.7	4.9	1.7	0.9

TABLE B.4 Container-Specific Table for Hydrogen Chloride (UN 1050 and UN 2186)

Transport container	First ISOLATE in all Directions [ft]	Then PROTECT persons Downwind during					
		Day [mi]			Night [mi]		
		Low wind [< 6 mph]	Moderate wind [6-12 mph]	High wind [> 12 mph]	Low wind [< 6 mph]	Moderate wind [6-12 mph]	High wind [> 12 mph]
Rail tank car	2000	3.8	1.4	1.1	7+	2.5	1.6
Highway tank truck or trailer	1000	1.9	0.7	0.5	4.6	1.3	0.6
Multiple ton cylinders	200	0.4	0.2	0.1	1.1	0.2	0.1
Multiple small cylinders or single ton cylinder	150	0.3	0.1	0.1	0.9	0.2	0.1

TABLE B.5 Container-Specific Table for Hydrogen Fluoride (UN 1052)

Transport container	First ISOLATE in all Directions [ft]	Then PROTECT persons Downwind during					
		Day [mi]			Night [mi]		
		Low wind [< 6 mph]	Moderate wind [6-12 mph]	High wind [> 12 mph]	Low wind [< 6 mph]	Moderate wind [6-12 mph]	High wind [> 12 mph]
Rail tank car	1250	2.0	1.2	1.0	4.9	1.9	1.2
Highway tank truck or trailer	700	1.2	0.6	0.5	2.4	1.0	0.6
Multiple small cylinders or single ton cylinder	300	0.5	0.2	0.2	1.0	0.3	0.2

TABLE B.6 Container-Specific Table for Ethylene Oxide (UN 1040)

Transport container	First ISOLATE in all Directions [ft]	Then PROTECT persons Downwind during					
		Day [mi]			Night [mi]		
		Low wind [< 6 mph]	Moderate wind [6-12 mph]	High wind [> 12 mph]	Low wind [< 6 mph]	Moderate wind [6-12 mph]	High wind [> 12 mph]
Rail tank car	600	0.9	0.5	0.4	2.5	0.9	0.5
Highway tank truck or trailer	300	0.5	0.3	0.2	1.3	0.4	0.3
Multiple small cylinders or single ton cylinder	100	0.2	0.1	0.1	0.5	0.2	0.1

APPENDIX C:

CHEMICALS ANALYZED IN THE ERG2012 ANALYSIS

APPENDIX C:

CHEMICALS ANALYZED IN THE ERG2012 ANALYSIS

Table C.1 lists the 164 chemicals analyzed in the *2012 Emergency Response Guidebook* (ERG2012) analysis in alphabetical order by U.S. Department of Transportation (DOT) name. Most of these materials are toxic by inhalation (TIH) materials; however, several are surrogates for generic table entries (e.g., 2-amino-2-methylpropanenitrile) or mildly toxic components of mixtures (benzene, methyl chloride, etc.). For reference, the Chemical Abstract Services (CAS) number, boiling point, vapor pressure at 20°C, and toxicological data are provided. Additional chemical data used in the analysis include critical temperature, critical volume, melting point, and the following temperature-dependent properties: heat of vaporization, vapor pressure, liquid density, specific heat of the liquid, viscosity, and surface tension.

TABLE C.1 Chemicals Analyzed in Preparation of ERG2012 (abbreviations are defined at end of table)

DOT Name	CAS #	Mol. Weight	Boiling Point (°C)	Vapor Pressure at 20°C (kPa)	LC_{50} or LC_{LO} (ppm)	1-h Protective (ppm)	10-min or 15-min Protective (ppm)	Basis
Acrolein	107-02-8	56.1	52.7	29.69	62	0.10	0.44	AEGL-F[a]
Acrylonitrile	107-13-1	53	77.4	11.4	392	35	70	ERPG
Aldicarb	116-06-3	N/A	N/A	N/A	1	0.01	0.01	LC_{50}
Allyl alcohol	107-18-6	58.1	97.1	2.491	330	13	87	AEGL-I
Allyl chloroformate	2937-50-0	120.5	112.9	6.194	7	0.7	1.30	AEGL-I[a]
Allyl isothiocyanate	57-06-7	99.2	150.7	0.516	635	6.4	12.7	LC_{50}[a]
Allylamine	107-11-9	57.1	53.4	25.69	572	3.3	3.3	AEGL-F[a]
2-Amino-2-methylpropanenitrile	19355-69-2	84.1	159.5	0.099	111	1.1	2.2	LC_{50}
Ammonia	7664-41-7	17	–33.5	854.5	7,338	160	220	AEGL-F[a]
Arsenic trichloride	7784-34-1	181.2	130.1	1.113	56	0.56	1.12	LC_{LO}
Arsine	7784-42-1	77.9	–62.5	1475	30	0.17	0.30	AEGL-F
Benzene	71-43-2	78.1	80.1	9.983	26,458	150	300	ERPG
Bis-(2-chloroethyl) ethylamine	538-07-8	170.1	193.9	0.023	3.59	0.0032	0.0187	AEGL-I[a]
Bis-(2-chloroethyl) methylamine	51-75-2	156.1	174.9	0.039	7.83	0.0034	0.0204	AEGL-I[a]
Bis-(2-chloroethyl) sulfide	505-60-2	159.1	216.9	0.010	6.5	0.020	0.090	AEGL-F
Boron tribromide	10294-33-4	251.5	89.0	7.336	387-S	7.3	33.0	AEGL-I[a]
Boron trichloride	10294-34-5	117.2	12.5	132.2	2541	25	51	LC_{50}
Boron trifluoride	7637-07-2	67.8	–99.8	4,264	387	11	14	AEGL-F[a]
Bromine	7726-95-6	159.8	58.8	22.87	310	0.24	0.55	AEGL-F[a]
Bromine chloride	13863-41-7	115.4	4.9	220.0	290	2.5	3.2	AEGL-I[a]
Bromine pentafluoride	7789-30-2	174.9	40.9	42.88	299-S	1.0	3.0	AEGL-I[a]
Bromine trifluoride	7787-71-5	136.9	125.9	0.774	299-S	2.0	8.1	AEGL-I[a]
Bromoacetone	598-31-2	137	135.9	11.431	95	0.33	1.40	AEGL-I[a]
n-Butyl chloroformate	592-34-7	136.6	137.9	0.765	323-S	2.2	4.0	AEGL-I[a]
sec-Butyl chloroformate	17462-58-7	136.6	127.9-E	1.051-E	323	2.2	4.0	AEGL-I[a]
n-Butylisocyanate	111-36-4	99.1	115.0-S	1.755-S	105	0.050	0.100	ERPG
tert-Butyl-isocyanate	1609-86-5	99.1	86.0	4.888-E	22	0.050	0.100	ERPG-S
tert-Butylarsine	117791-53-4	134	44.4-E	40.35-E	147	1.5	2.9	LC_{50}
Carbon monoxide	630-08-0	28	–191.5	2,792	4,590	83	420	AEGL-F[a]
Carbonyl fluoride	353-50-4	66	–84.6	5,211	360	0.38	0.35	AEGL-I[a]
Carbonyl sulfide	463-58-1	60.1	–50.2	1,124	924	55	69	AEGL-I[a]
Chlorine	7782-50-5	70.9	–34.1	679.7	293	2.0	2.8	AEGL-F

TABLE C.1 (Cont.)

DOT Name	CAS #	Mol. Weight	Boiling Point (°C)	Vapor Pressure at 20°C (kPa)	LC_{50} or LC_{LO} (ppm)	1-h Protective (ppm)	10-min or 15-min Protective (ppm)	Basis
Chlorine pentafluoride	13637-63-3	130.4	–13.9	332.1	122	1.0	3.0	AEGL-I[a]
Chlorine trifluoride	7790-91-2	92.4	11.8	148.0	299	2.0	8.1	AEGL-F[a]
Chloroacetaldehyde	107-20-0	78.5	84.9	3.522	200	2.2	9.8	AEGL-I[a]
Chloroacetone	78-95-5	92.5	120.1	1.567	262	4.4	8.0	AEGL-I[a]
Chloroacetonitrile	107-14-2	75.5	126.0	1.087	500	32	49	AEGL-I[a]
Chloroacetyl chloride	79-04-9	112.9	106.0	2.522	660	0.50	1	ERPG
Chloromethyl methyl ether	107-30-2	80.5	59.5	21.14	441	1.0	2.0	ERPG
p-Chlorophenyl isocyanate	104-12-1	153.6	199.0	0.069	18	0.36	0.72	LC_{50}
Chloropicrin	76-06-2	164.4	111.9	3.190	28	0.30	0.6	ERPG
Chloropivaloyl chloride	4300-97-4	155	147.9	0.189-E	126	1.3	2.5	LC_{50}
Chlorosulfonic acid	7790-94-5	116.5	153.9	0.309	195	2.1	4.2	ERPG
Crotonaldehyde	4170-30-3	70.1	104.9	3.121	380	4.4	27.0	AEGL-F[a]
Cyanogen	460-19-5	52	–21.2	489.7	350	8.3	50.0	AEGL-I[a]
Cyanogen chloride	506-77-4	61.5	12.9	135.0	80	0.40	0.8	ERPG
Cyclohexyl isocyanate	3173-53-3	125.2	169.0	0.094	15	0.050	0.100	ERPG-S
Cyclohexyl methylphosphonofluoridate	329-99-7	180.2	238.9	0.006	1.25	0.0024	0.0062	AEGL-F
Diamylamine	2050-92-2	157.3	203.0	0.013	126	1	2	LC_{LO}
Diborane	19287-45-7	27.7	–92.6	3438	80	1.0	2.0	AEGL-F
Dichloro-(2-chlorovinyl) arsine	541-25-3	207.3	463	0.055	2.4	0.0142	0.0767	AEGL-I[a]
Dichlorosilane	4109-96-0	101	8.4	154.2	215	11	50	AEGL-I[a]
3,5-Dichloro-2,4,6-trifluoropyridine	1737-93-5	202	177.5-S	0.104-S	62	0.62	1.24	LC_{50}
Diketene	674-82-8	84.1	126.1	1.064	750	5.0	10.0	ERPG
1,1-Dimethyl hydrazine	57-14-7	60.1	63.4	16.38	504	3.0	18.0	AEGL-F
1,2-Dimethyl hydrazine	540-73-8	60.1	87.1	7.230	680	3.0	18.0	AEGL-F
Dimethyl sulfate	77-78-1	126.1	188.9	0.069	17	0.12	0.17	AEGL-I[a]
Diphosgene	503-38-8	197.8	127.9	0.553	74	0.74	1.48	LC_{50}
Ethyl chloroformate	541-41-3	108.5	92.9	2.121	145	5.0	10.0	ERPG
Ethylchlorothioformate	2812-73-9	124.6	131.9	0.685-E	138-S	0.26	0.33	AEGL-I-S[a]
Ethylchlorothiolformate	2941-64-2	124.6-S	131.9-S	0.685-S	138-S	0.26	0.33	AEGL-I[a]
Ethyl dichloroarsine	598-14-1	174.9	155.9	0.281	36	0.0041	0.0238	AEGL-I[a]
Ethyl N,N-dimethylphosphoramido-cyanidate	77-81-6	162.3	239.9-E	0.005-E	2.5	0.0053	0.0130	AEGL-F
Ethyl isocyanate	109-90-0	71.1	61.6	24.50	15	0.053	0.070	AEGL-I[a]
Ethyl phosphonothionic dichloride	993-43-1	162.9	176.9	0.026-E	52	0.52	1.04	LC_{50}

TABLE C.1 (Cont.)

DOT Name	CAS #	Mol. Weight	Boiling Point (°C)	Vapor Pressure at 20°C (kPa)	LC_{50} or LC_{LO} (ppm)	1-h Protective (ppm)	10-min or 15-min Protective (ppm)	Basis
Ethyl phosphonous dichloride	1498-40-4	130.9	113.0-E	4.762-E	62	0.62	1.24	LC_{LO}
Ethyl phosphorodichloridate	1498-51-7	162.9	166.9	0.040-E	43	0.60	1.10	AEGL-I[a]
Ethylacrolein	922-63-4	84.1	92.9	5.392-E	578	5.8	11.6	LC_{50}
Ethylene chlorohydrin	107-07-3	80.5	128.7	0.699	66	4.0	7.0	AEGL-I[a]
Ethylene dibromide	106-93-4	187.9	131.4	1.357	691	24	73	AEGL-I[a]
Ethylene oxide	75-21-8	44.1	10.5	146.3	5,840	45	80	AEGL-F[a]
Ethylenimine	151-56-4	43.1	55.9	22.18	80	4.6	33.0	AEGL-F[a]
Fluorine	7782-41-4	38	–188.3	4,160	185	5.0	20.0	AEGL-F[a]
Germanium tetrachloride	10038-98-9	214.4	83.9	9.51	7,100	71	142	LC_{50}
Germanium tetrahydride	7782-65-2	76.6	–88.2	3,870	440	0.17	0.30	AEGL-I[a]
Hexachlorocyclopentadiene	77-47-4	272.8	239.1	0.0052	3	0.030	0.060	LC_{50}
Hexaethyltetraphosphate	757-58-4	506.2	GS	GS	85-E	0.9	1.9	LC_{50}-E
Hexafluoroacetone	684-16-2	166	–27.3	584.19	476	1.0	2.0	ERPG
Hydrogen bromide	10035-10-6	80.9	–66.8	2,182	2,860	25	150	AEGL-I[a]
Hydrogen chloride	7647-01-0	36.5	–85.1	4,206	3,124	22	100	AEGL-F
Hydrogen cyanide	74-90-8	27	25.8	81.63	71	7.1	17.0	AEGL-F
Hydrogen fluoride	7664-39-3	20	19.6	102.7	1,300	24	95	AEGL-F
Hydrogen iodide	10034-85-2	127.9	–35.6	691.0	2,860	25	150	AEGL-I[a]
Hydrogen selenide	7783-07-5	81	–42.1	911.1	5	0.20	0.4	ERPG
Hydrogen sulfide	7783-06-4	34.1	–60.4	1781	712	27	41	AEGL-F[a]
Iron pentacarbonyl	13463-40-6	195.9	102.8	3.142	57	0.060	0.077	AEGL-F[a]
Isobutyl chloroformate	543-27-1	136.6	128.1	0.751	299	2.2	4.0	AEGL-I[a]
Isobutyl isocyanate	1873-29-6	99.1	115.0	1.755	28-S	0.050	0.100	ERPG-S
Isopropyl chloroformate	108-23-6	122.6	104.9-S	4.698-S	299	5.0	10.0	ERPG[a]
Isopropyl isocyanate	1795-48-8	85.1	82.9	7.372	28-S	0.050	0.100	ERPG-S
Isopropyl methylphosphonofluoridate	107-44-8	140.1	157.9	0.283	1.22	0.0060	0.0150	AEGL-F
Methacrylonitrile	126-98-7	67.1	90.4	7.541	656	13	16	AEGL-I
Methanesulfonyl monochloride	124-63-0	114.6	162.4	0.190	325	2.1	4.0	AEGL-I[a]
Methanesulfonyl dichloride	3518-65-8	149	178	0.121	325-S	3.3	6.6	LC_{50}-S
Methoxymethyl isocyanate	6427-21-0	87.1	165.7-E	0.250-E	28-S	0.067	0.400	AEGL-F-S[a]
Methyl bromide	74-83-9	94.9	3.6	184.3	1007	50	100	ERPG
Methyl chloride	74-87-3	50.5	–24.3	495.4	5,133	400	800	ERPG
Methyl chloroformate	79-22-1	94.5	70.9	11.20	88	2.0	4.0	ERPG

TABLE C.1 (Cont.)

DOT Name	CAS #	Mol. Weight	Boiling Point (°C)	Vapor Pressure at 20°C (kPa)	LC_{50} or LC_{LO} (ppm)	1-h Protective (ppm)	10-min or 15-min Protective (ppm)	Basis
Methyl hydrazine	60-34-4	46.1	87.6	4.997	68	0.90	5.30	AEGL-F
Methyl iodide	74-88-4	141.9	42.5	44.33	448	50	100	ERPG
Methyl isocyanate	624-83-9	57.1	38.9	50.18	15	0.067	0.400	AEGL-F
Methyl isothiocyanate	556-61-6	73.1	118.9	3.205	635	23	43	AEGL-I[a]
Methyl mercaptan	74-93-1	48.1	6.0	169.8	1340	25	50	ERPG
Methyl phosphonic dichloride	676-97-1	132.9	162.9-E	0.040-E	52	0.52	1.04	LC_{50}
Methyl phosphonous dichloride	676-83-5	116.9	81.9-E	11.89-E	62	0.62	1.24	LC_{50}
Methyl phosphonic difluoride	676-99-3	100.0	98	3.685	780	7.8	15.6	LC_{LO}
Methyl silicate	681-84-5	152.2	120.9	1.613	500	10.0	20.0	ERPG[a]
Methyl vinyl ketone	78-94-4	70.1	81.5	9.274	5	1.2	1.5	AEGL-I[a]
Methylamine	74-89-5	31.1	–6.3	295.7	708	100	200	ERPG
Methylchlorosilane	993-00-0	80.6	8.8	149.6	600	22	100	AEGL-I[a]
Methyldichloroarsine	593-89-5	160.9	135.9	1.034	68	0.0081	0.0958	AEGL-I[a]
Nickel carbonyl	13463-39-3	170.8	42.5	43.50	18	0.036	0.100	AEGL-F[a]
Nitric acid	7697-37-2	63	83.0	6.401	67	6.0	12.0	ERPG
Nitric oxide	10102-43-9	30	–151.8	5,093	1,708	17	34	LC_{50}
Nitrogen dioxide	10102-44-0	46	21.0	96.04	115	15	30	ERPG
Nitrogen fluoride oxide	13847-65-9	87.1	–129.1-E	3,979-E	48	0.48	0.96	LC_{50}
Nitrogen trioxide	10544-73-7	76	2.0	218.3	57-S	15	30	ERPG-S
Nitrosyl chloride	2696-92-6	65.5	–5.3	270.4	29-S	2.9	5.9	LC_{50}-S
tert-octyl mercaptan	141-59-3	146.3	155.9	0.488	102	0.60	0.77	AEGL-I[a]
O-Ethyl S-(2-diisopropylaminoethyl) methylphosphonothiolate	50782-69-9	267.4	297.9	0.00005	0. 06	0.00027	0.00065	AEGL-F
Oxygen difluoride	7783-41-7	54	–145.0	2,789	2.6	0.83	4.30	AEGL-I[a]
Parathion	56-38-2	291.3	GS	GS	14	0.14	0.28	LC_{50}
Pentaborane	19624-22-7	63.2	58.4	22.70-E	12	0.14	0.56	AEGL-I[a]
Perchloromethyl mercaptan	594-42-3	185.9	148.0	0.642	11	0.30	0.53	AEGL-F
Perchloryl fluoride	7616-94-6	102.4	–46.7	1,060	770	7.7	15.4	LC_{50}
Phenyl isocyanate	103-71-9	119.1	165.7	0.250	16	0.15	0.18	AEGL-I[a]
Phenyl mercaptan	108-98-5	110.2	169.2	0.142	66	0.53	1.00	AEGL-I[a]
Phosgene	75-44-5	98.9	7.6	159.3	10	0.30	0.60	AEGL-F
Phosphine	7803-51-2	34	–87.8	3,517	22	2.0	4.0	AEGL-F[a]
Phosphorous oxychloride[b]	10025-87-3	153.3	105.5	3.273	66	0.66	1.32	LC_{50}
Phosphorous pentafluoride	7647-19-0	126	–84.6	56,888	260	2.6	5.2	LC_{50}

TABLE C.1 (Cont.)

DOT Name	CAS #	Mol. Weight	Boiling Point (°C)	Vapor Pressure at 20°C (kPa)	LC_{50} or LC_{LO} (ppm)	1-h Protective (ppm)	10-min or 15-min Protective (ppm)	Basis
Phosphorous trichloride	7719-12-2	137.3	76.1	12.82	208	2.0	2.5	AEGL-F[a]
Phosphorous trifluoride	7783-55-3	88	–101.3	6,902	420	4.2	8.4	LC_{50}
Pinacolyl methylphosphonofluoridate	96-64-0	182.2	197.9	0.037	1.25	0.00220	0.00570	AEGL-F
n-Propyl chloroformate	109-61-5	122.6	104.9	4.698	319	3.7	6.7	AEGL-I[a]
n-Propyl isocyanate	110-78-1	85.1	82.9	5.274	44	0.050	0.100	ERPG-S
Selenium hexafluoride	7783-79-1	193	–34.7	2,854	50	0.087	0.110	AEGL-I[a]
Silicon tetrafluoride	7783-61-1	104.1	–95.2	3,205	922	3.3	6.3	AEGL-I[a]
Stibine	7803-52-3	124.8	–18.5	286.1-E	20	0.50	1	ERPG
Sulfur chloride pentafluoride	13780-57-9	162.5	–21.2	442.0-S	100	1.0	2.0	LC_{50}
Sulfur dioxide	7446-09-5	64.1	–10.1	336.5	2,520	0.75	0.75	AEGL-F[a]
Sulfur monochloride	10025-67-9	135	137.9	0.944	150a	6.4	8.1	AEGL-I[a]
Sulfur tetrafluoride	7783-60-0	108.1	–40.4	1,785	40	0.4	0.8	LC_{LO}
Sulfur trioxide	7446-11-9	80.1	44.8	26.5	26.5	2.1	4.1	ERPG
Sulfuryl chloride	7791-25-5	135	69.4	14.811	318	3.7	4.7	AEGL-F[a]
Sulfuryl fluoride	2699-79-8	102.1	–55.4	1,964	1,982	21	27	AEGL-I[a]
Tellurium hexafluoride	7783-80-4	241.6	–38.2	709.6	10	0.018	0.032	AEGL-I[a]
Tetraethyl dithiopyrophosphate	3689-24-5	322.3	GS	GS	6	0.06	0.12	LC_{50}
Tetraethyl pyrophosphate	107-49-3	290.1	GS	GS	6-S	0.06	0.12	LC_{50}-S
Tetrafluorohydrazine	10036-47-2	104	–74.3	2,515	900	9.0	18.0	LC_{50}
Tetramethyl tin	594-27-4	178.8	77.9	17.92-E	58	0.58	1.16	LC_{50}
Tetranitromethane	509-14-8	196	125.8	1.121	36	0.52	0.66	AEGL-F[a]
Thionyl chloride	7719-09-7	119	75.7	12.77	500	2.0	4.0	ERPG
Thiophosgene	463-71-8	115	72.9	15.04	25	0.25	0.5	AEGL-F-S
Titanium tetrachloride	7550-45-0	189.7	135.9	1.253	168	2.6	5.2	ERPG
Trichloroacetyl chloride	76-02-8	181.8	118.0	2.189	128	1.3	2.6	LC_{50}
Trifluoroacetyl chloride	354-32-5	132.5	–17.9	356.2-S	208	2.1	4.2	LC_{50}
Trifluorochloroethylene	79-38-9	116.5	–27.9	531.4	2,000	100	200	ERPG
3-Trifluoromethyl phenyl isocyanate	329-01-1	187.1	179.6	0.33	43	0.43	0.86	LC_{50}
Trimethoxy silane	2487-90-3	122.3	80.9	20.40-E	84	2.0	4.0	ERPG
Trimethylacetyl chloride	3282-30-2	120.6	106.9	2.866	250	0.53	0.67	AEGL-I[a]
Tris-(2-chloroethyl) amine	817-09-4	204.5	255.9	0.00094	2.99	0.0026	0.0156	AEGL-I[a]
Tungsten hexafluoride	7783-82-6	297.8	17.4	111.8	217	2.2	4.3	LC_{50}

Footnotes and definitions of abbreviations appear on next page.

TABLE C.1 (Cont.)

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[a] Denotes a change in basis from ERG2008.

[b] Only interim AEGL-3 values for phosphorous oxychloride are available, because AEGL documentation did not recommend development of AEGL-2 values. Therefore, the PAD value was based on an LC_{50} level.

Abbreviations

AEGL = Acute Emergency Guideline Level established by the National Research Council
AEGL-F = final AEGL
AEGL-I = interim AEGL
E = estimated value
ERPG = Emergency Response Planning Guideline established by the American Industrial Hygiene Association
GS = solid or liquid in solution with gas
LC_{50} = median lethal concentration in animals exposed via inhalation
LC_{50}-E = LC_{50} estimated from oral toxicity data
LC_{50}-S = LC_{50} from structurally similar chemical used
LC_{LO} = lowest lethal concentration reported in an animal study
N/A = not applicable
S = data are for a structurally similar chemical

APPENDIX D:

ADDITIONAL DETAILS ON WATER-REACTIVE MATERIALS

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ADDITIONAL DETAILS ON WATER-REACTIVE MATERIALS

This appendix provides detailed information on the water-reactive materials listed in the Table of Initial Isolation and Protective Action Distances. Data for most of the materials we considered were developed from laboratory work undertaken in 1999–2007 to extend the experimental basis for estimates of the *amounts* of TIH (toxic-inhalation hazard) gases that might evolve when water-reactive materials are spilled into water and the *rates* at which such gases might evolve. Experiments in 1999–2000 developed preliminary information on 21 materials in support of the 2000 edition of the Emergency Response Guidebook (ERG2000). Experiments in 2003–2004 in support of the 2004 edition of the Emergency Response Guidebook (ERG2004) added 35 new materials and repeated or extended observations on 10 materials from the first group. The experiments in support of the 2008 edition of the Emergency Response Guidebook (ERG2008) covered 52 materials. The experimental procedures and raw data from this experimental program are detailed in the support documentation for ERG2008 (Brown et al. 2009).

We begin in Section D.1 with a description of the experiments. Next, we detail how these experimental data are used to determine the key parameters necessary to model toxic inhalation hazards by water-reaction (TIHWR) releases in Section D.2. The parameters themselves for all TIHWR materials considered in the 2012 edition of the Emergency Response Guidebook (ERG2012) are then provided in Section D.3. Finally, Sections D.4 and D.5 explain why various materials were selected for the TIHWR list and reviews changes from previous recommendations.

D.1 DESCRIPTION OF THE TIHWR EXPERIMENTS CONDUCTED THROUGH 2007

Small (millimole, or mmol) amounts of water-reactive substances were stirred in contact with water in a closed, nonrigid system at near-constant temperature and pressure. The evolution of gas caused the system to expand, and the change in volume was recorded. For a pure gas (or for a mixed gas of known composition), the change in volume as time went on was proportional to the mass of new gas that was generated. If no concurrent reactions (such as dissolution) occurred to remove gas, then the rate of change of the volume was the rate of the gas-generating reaction. Materials were reacted with water in two ways:

- **Method A.** After the nitrogen purge, 1.00 mmol (typically) of the material was injected into the reaction flask through an inlet covered with a rubber septum and stirred. A chemically equivalent amount of water was then rapidly injected. Equivalency was determined from a chemical equation written to represent the anticipated reaction.[4]

[4] This reaction, of course, is not necessarily the only chemical reaction that occurred, nor is it even a reaction that occurred at all.

For example, 1.00 mmol (115 μL, 170 mg) of tetrachlorosilane ($SiCl_4$) was injected into the reaction flask followed by 2.00 mmol (36.0 μL, 36.0 mg) of H_2O. This 1:2 molar ratio ensured that both reactants would be consumed entirely if the reaction

$$SiCl_4 + 2\ H_2O \longrightarrow 4\ HCl + SiO_2$$

went to completion. Method A was designed to verify the evolution of gases, measure their yield, and estimate the rate of their production.

- **Method B.** The material was added to the water (rather than the reverse), and a fivefold molar excess of water was used. For example, 10.0 mmol of H_2O was put in the reaction flask and stirred, and then 1.00 mmol of $SiCl_4$ was rapidly injected. This method was intended to model an actual spill more realistically.

  Multiple runs (usually three, but as many as seven) were carried out on each material using each method.

Additional details on the experimental procedures and equipment as well as detailed discussions of each compound studied can be found in Brown et al. (2009)

D.2 ANALYSIS OF EXPERIMENTAL DATA: EXTRACTION OF KEY PARAMETERS

As discussed in Section 3.3, we model the evolution of a TIHWR gas by using the first-order rate equation with an induction time offset

$$M(t) = M_{st}\beta(1 - e^{-\lambda(t - T_{ind})}), \tag{D.1}$$

where M_{st} is the stoichiometric mass that could evolve and $M(t)$ is the total mass of TIH gas actually emitted from the spill by time t. The parameter λ is the first-order rate constant for the process, and β is an empirically determined efficiency factor defined from Equation D.1 as

$$\beta = \frac{M_\infty}{M_{st}}, \tag{D.2}$$

where M_∞ is the maximum mass of TIH gas that evolves from the water at long times and T_{ind} is an induction time as described below. Note that more product may be formed than the amount that actually evolves from the water as a result of the dissolution of the gas in the water, as discussed in Section D.2.3. We generally determine these parameters by least-squares fitting from the amount of TIH gas emitted as a function of time, as observed in our experiments.

Throughout the course of our experimental program for the 2000, 2004, and 2008 editions of the Emergency Response Guidebook (ERG), we observed four general types of behavior. They are described in the following subsections to provide context for understanding the data used in our TIHWR analysis.

D.2.1 No Emissions

Some experiments did not produce any TIH gases with either the stoichiometric amount of water (Method A) or with a fivefold molar excess (Method B), even though we had descriptive evidence that the TIH gases were quite reactive with water. A related class of materials exhibited slow emissions when Method A was used but no emissions when Method B was used because of sequestration of the evolved gas by the excess water. Examples of these materials include hexadecyltrichlorosilane (UN 1781) and phosphorus oxybromide (UN 1939). Note that not all of the materials that failed to exhibit significant evolution of TIH gases in the experiments were removed from the TIHWR list, as discussed in Section D.4.3.

D.2.2 Simple First-Order Process

Many experiments showed the simple first-order process described above in Equation C.1 with no induction time ($T_{ind} = 0$). Typical examples where we observed a first-order process were methyltrichlorosilane (UN 1250) and chlorosulfonic acid (UN 1754). For these materials, we used the actual observed maximum mass of gas evolved, M_∞, divided by the stoichiometric maximum, M_{st}, to determine β. Using a least-squares fit for M_∞ gave almost identical results in all cases. The λ value was determined by using a least-squares fit as well. An example of experimental data used in generation of parameters for methyltrichlorosilane (UN 1250) is shown in Figure D.1.

D.2.3 First-Order Process with Dissolution

Several experiments showed an apparent first-order process in which the evolved TIH gas dissolved back into the water, thus serving as a removal mechanism. This process was especially apparent when Method B was used, involving a fivefold molar excess of water. Classic examples of these for Method B include boron trichloride (UN 1741) and nitrosylsulfuric acid (UN 2308). Because the TIH gas was kept in contact with water in the experimental apparatus in a closed environment, dissolution was promoted. In a natural environment, the TIH gas that would be produced would likely bubble out of the water quickly and dilute in the atmosphere, thus avoiding significant dissolution. For this reason, M_∞ was determined by using a least-squares fit of the data up to the peak measured evolution amount to obtain the completion fraction β, rather than by simply using the observed maximum that occurred as dissolution overcame the rate of evolution. Admittedly, this procedure could overestimate the source term for atmospheric dispersion of the TIH gas, but it was chosen because it offered the most reasonable solution for determining the model parameters from the experimental data. An example of experimental data used in generation of parameters for boron trichloride (UN 1741) is shown in Figure D.2.

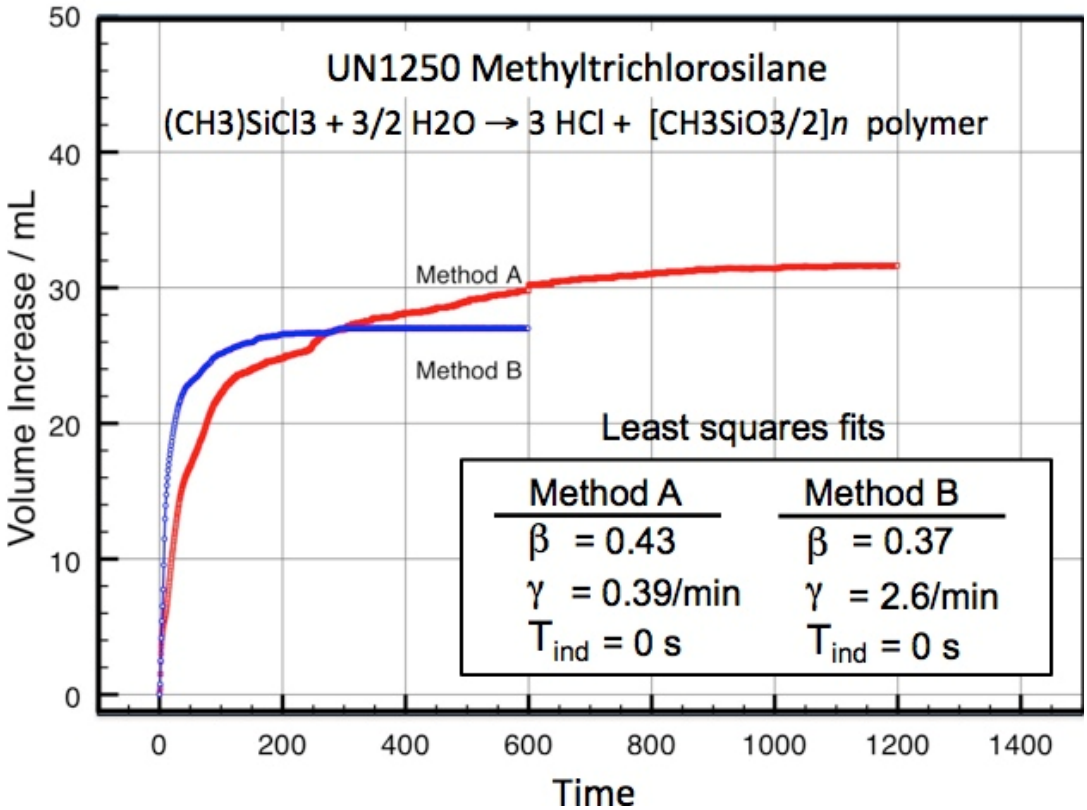

FIGURE D.1 Example of a First-Order Process from the Experimental Series where Dissolution of the TIH Product Competes with the Evolution (Data are shown together with the derived parameters for Equation D.1. Results are shown for methyltrichlorosilane [UN 1250]. The stoichiometric yield is 72.2 mL of HCl, equating to 0.732 g HCl per g of methyltrichlorosilane.)

D.2.4 Autocatalytic Reactions

In a few of the experiments, we observed a more complex reaction pattern, in which a polymeric byproduct formed during the first stages. This slowed the reaction of the remaining material with water. All of these cases involved silanes. Classic examples are cyclohexyltrichlorosilane (UN 1763) and octadecyltrichlorosilane (UN 1800). In these reactions, slow emissions of gas at a constant rate ensued for a period of 2–10 min. At that point, the reactions appeared to autocatalyze, and they subsequently followed what appeared to be a normal first-order reaction process. In these cases, we used a three-parameter fit. The values of M_∞ and λ were given their normal meaning, but the time was measured from T_{ind}, a new parameter that indicated when the autocatalysis began strongly. An example of experimental data used in generation of parameters for octadecyltrichlorosilane (UN 1800) is shown in Figure D.3.

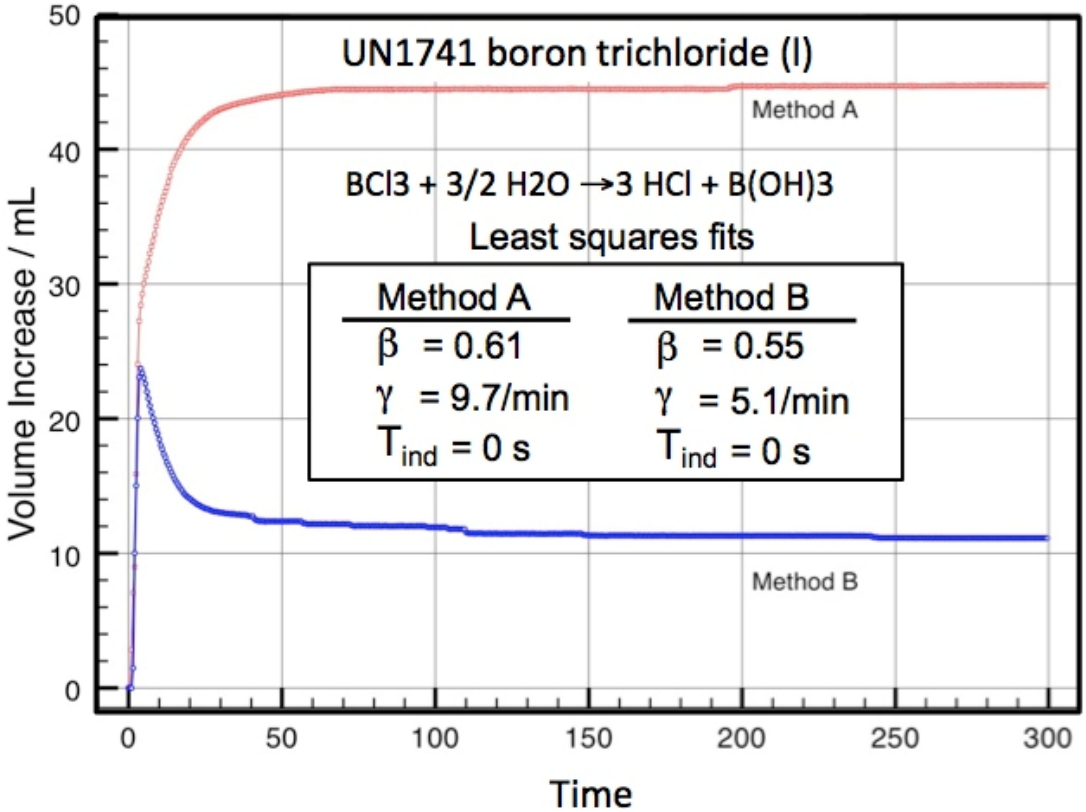

FIGURE D.2 Example of a First-Order Process from the Experimental Series where Dissolution of the TIH Product Competes with the Evolution (Data are shown together with the derived parameters for Equation D.1. Results are for boron trichloride [UN 1741]. The stoichiometric yield is 72.2 mL of HCl, equating to 0.934 g HCl per g of boron trichloride.)

In previous analyses (Brown et al. 2005) we also separately considered the mass of gas that had evolved during the interval from $t = 0$ to $t = T_{ind}$ defining an induction mass m_i. The formal relationships are as follows:

$$M(t) = m_i \frac{t}{T_{ind}} \qquad (t \le T_{ind}) \tag{D.3}$$

$$M(t) = m_i + M_{st}\beta'(1 - e^{-\lambda(t - T_{ind})}), \qquad (t > T_{ind}) \tag{D.4}$$

where

$$\beta' = \beta - \frac{M_i}{M_{st}} .$$

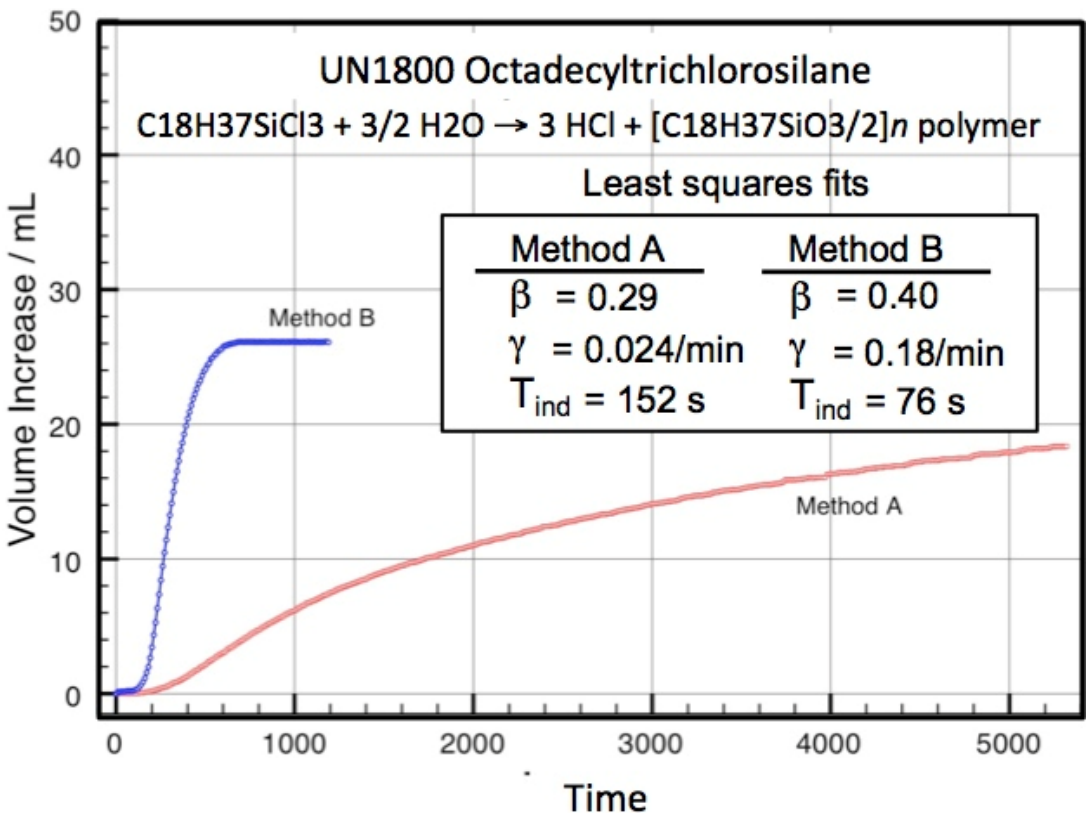

FIGURE D.3 Example of an Autocatalytic Reaction with an Initial Byproduct Greatly Reducing Availability of Water for Subsequent Reaction (Data are shown together with the derived parameters for Equation D.1. Results are shown for octadecyltrichlorosilane [UN 1800]. The stoichiometric yield is 72.2 mL of HCl, equating to 0.282 g HCl per g of octadecyltrichlorosilane.)

In compiling the experimental data for the ERG2008, however, we found that we could simplify this analysis and the reduction of experimental data by ignoring the slow initial constant release described by Equation D.3 and instead simply use Equation D.1 with an induction time offset. For calculations of practical interest, this practice has no discernable effect on the hazard predictions.

D.2.5 Summary

We applied least-squares fits to the data measured in the experimental program previously described to provide β, λ, and T_{ind} as represented in Equation D.1 for experimental trials of both Method A and Method B. These parameters were subsequently used in the Chemical Accident Statistical Risk Assessment Model (CASRAM) to model time-dependent emissions of TIH gas for cases in which a water-reactive substance spills into water or becomes wet during a spill (e.g., because of rain). Note that we used data from both Method A (stoichiometric water added) and Method B to model TIHWR incidents in order to account for cases in which water was limited and cases in which excess water was available. Model

parameters for materials for which experimental data are not available are estimated on the basis of qualitative descriptions in the literature and/or chemical similarities to materials for which data do exist, as described in Section D.4. In the future, larger-scale experiments should verify that these millimole results do indeed give a good approximation of an actual large-scale spill.

D.3 KEY PARAMETERS EMPLOYED IN THE TIHWR ANALYSIS

Supplementary information on all water-reactive materials in the ERG2012 TIHWR list is provided in Table D.1. As denoted in the table, values for 12 of these chemicals are updated from those used in preparation of the ERG2008 because the experiments were conducted after February 2007, which was the cutoff for inclusion in the ERG2008. Experiments for these 12 materials were repeats of experiments conducted for ERG2000 or ERG2004, but had a more advanced experimental setup and procedure.

D.4 SUPPLEMENTARY DETAILS IN SUPPORT OF MATERIALS APPEARING IN TABLE D.1

Most materials appear in the ERG2012 TIHWR list (and consequently in Table D.1) either because TIH gases evolved from them at reasonable rates in the experiments described previously or because the chemical literature says that TIH gases evolve from them. Sections D.4.1–D.4.3 give reasons these materials are included on the TIHWR list. Section D.4.4 briefly describes why other materials were never included on the list or were deleted from the list.

D.4.1 Materials That Evolved TIH Gases during Experiments

The ERG2012 TIHWR list contains 62 materials from which TIH gases evolved during the experimental program described previously. These materials and the experimental studies used available for analysis are listed in Table D.1.

D.4.2 Materials Described as TIHWR in the Literature

The ERG2012 TIHWR list includes 23 materials on the basis of the descriptions of their water reactivity in the chemical literature. These are listed in Table D.2.

TABLE D.1 Supplementary Information on Water-Reactive Materials in the ERG2012[a]

UN No.	Name	St.	Den.	Prod.	Experiments Conducted 00	04	08	S.Y.	Method A β	λ (min^{-1})	T_{ind} (s)	Method B β	λ (min^{-1})	T_{ind} (s)
1162	Dimethyldichlorosilane	L	1.06	HCl	X	X	X	0.565	0.54	0.15	0	0.25	0.93	0
1183	Ethyldichlorosilane	L	1.09	HCl			X	0.565	0.74	0.68	0	0.33	2.03	0
1196	Ethyltrichlorosilane	L	1.24	HCl		X	X	0.669	0.63	0.24	31	0.39	1.55	5
1242	Methyldichlorosilane[b]	L	1.11	HCl		X	X	0.634	0.60	5.1	0	0.39	3.5	0
1250	Methyltrichlorosilane[b]	L	1.27	HCl	X	X	X	0.732	0.43	0.39	0	0.37	2.6	0
1295	Trichlorosilane	L	1.34	HCl			X	0.808	0.31	1.83	0	0.21	24	0
1298	Trimethylchlorosilane[b]	L	0.85	HCl	X	X	X	0.336	0.35	0.29	0	0.47	0.40	0
1305	Vinyltrichlorosilane	L	1.26	HCl			X	0.677	0.47	0.17	0	0.23	3.76	0
1339	Phosphorus heptasulfide	S	2.19	H_2S				0.685	0.15	0.23	31	0.15	0.12	71
1340	Phosphorus pentasulfide	S	2.09	H_2S			X	0.767	0.15	0.23	31	0.15	0.12	71
1360	Calcium phosphide[b]	S	2.51	PH_3	X	X	X	0.374	0.12	0.30	0	0.11	0.21	0
1384	Sodium hydrosulfite[c]	S	2.20	SO_2	X			0.735	0.05	0.10	0	0.03	0.10	0
1397	Aluminum phosphide	S	2.40	PH_3				0.588	0.35	0.045	0	0.35	0.045	0
1412	Lithium amide	S	1.18	NH_3		X		0.742	0.19	1.0	0	0.16	3.0	0
1419	Magnesium aluminum phosphide	S	2.20	PH_3				0.530	0.35	0.045	0	0.35	0.045	0
1432	Sodium phosphide	S	1.74	PH_3				0.342	0.35	0.045	0	0.35	0.045	0
1541	Acetone cyanohydrin	L	0.93	HCN		X		0.318	0.20	0.060	0	0.05	0.060	0
1680	Potassium cyanide	S	1.52	HCN			X	0.415	0.20	0.060	0	0.05	0.060	0
1689	Sodium cyanide	S	1.60	HCN			X	0.551	0.20	0.060	0	0.05	0.060	0
1716	Acetyl bromide	L	1.66	HBr		X	X	0.658	0.43	8.20	0	0.43	8.20	0
1717	Acetyl chloride	L	1.11	HCl		X	X	0.464	0.70	6.38	0	0.70	6.38	0
1724	Allyltrichlorosilane	L	1.21	HCl		X	X	0.623	0.50	0.94	0	0.21	2.38	0
1725	Aluminum bromide[b]	S	2.64	HBr	X		X	0.910	0.05	0.70	0	0.05	0.70	0
1726	Aluminum chloride	S	2.44	HCl	X			0.820	0.20	30	0	0.20	30	0
1728	Amyltrichlorosilane	L	1.13	HCl		X	X	0.532	0.63	0.067	91	0.30	0.22	27
1732	Antimony pentafluoride	L	2.99	HF		X		0.462	0.40	0.60	0	0.40	0.60	0
1741	Boron trichloride[d]	L	1.35	HCl			X	0.934	0.61	9.73	0	0.55	5.14	0
1745	Bromine pentafluoride[c,d]	L	2.47	HF				0.572	0.40	0.60	0	0.40	0.60	0
1746	Bromine trifluoride[c,d]	L	2.80	HF				0.438	0.40	0.60	0	0.40	0.60	0
1747	Butyltrichlorosilane[b]	L	1.16	HCl		X	X	0.571	0.67	0.030	76	0.28	0.19	53
1752	Chloroacetyl chloride[b]	L	1.50	HCl	X	X	X	0.323	0.57	0.04	127	0.09	0.31	41
1753	Chlorophenyltrichlorosilane	L	1.25	HCl			X	0.445	0.36	0.11	24	0.10	0.37	0
1754	Chlorosulfonic acid[b]	L	1.76	HCl		X	X	0.313	0.72	15	1	0.59	15	0

TABLE D.1 (Cont.)

UN No.	Name	St.	Den.	Prod.	Experiments Conducted 00	04	08	S.Y.	Method A β	λ (min^{-1})	T_{ind} (s)	Method B β	λ (min^{-1})	T_{ind} (s)
1758	Chromium oxychloride	L	1.91	HCl		X		0.471	0.06	0.067	0	0.06	0.067	0
1762	Cyclohexenyltrichlorosilane	L	1.23	HCl				0.507	0.50	0.025	265	0.24	0.060	144
1763	Cyclohexyltrichlorosilane	L	1.30	HCl		X	X	0.503	0.50	0.025	265	0.24	0.060	144
1765	Dichloroacetyl chloride	L	1.53	HCl			X	0.247	0.60	0.15	48	0.11	0.74	4
1766	Dichlorophenyltrichlorosilane[e]	L	1.56	HCl		X		0.421	0.25	0.059	180	0.40	0.50	0
1767	Diethyldichlorosilane	L	1.05	HCl		X	X	0.464	0.45	0.019	0	0.26	0.048	0
1769	Diphenyldichlorosilane[b]	L	1.22	HCl		X	X	0.288	0.23	0.038	191	0.36	0.084	114
1771	Dodecyltrichlorosilane	L	1.03	HCl		X	X	0.360	0.47	0.054	0	0.32	0.64	23
1777	Fluorosulfonic acid	L	1.73	HF			X	0.200	0.09	0.028	0	0.05	6.0	0
1781	Hexadecyltrichlorosilane	L	1.25	HCl			X	0.304	0.44	0.026	125	0.10	0.060	0
1784	Hexyltrichlorosilane	L	1.30	HCl		X	X	0.498	0.71	0.021	32	0.19	0.28	0
1799	Nonyltrichlorosilane	L	1.30	HCl		X		0.418	0.20	0.060	0	0.50	0.037	0
1800	Octadecyltrichlorosilane[b]	L	1.30	HCl		X	X	0.282	0.29	0.024	152	0.40	0.18	76
1801	Octyltrichlorosilane	L	1.30	HCl		X	X	0.442	0.38	0.027	0	0.27	0.24	0
1804	Phenyltrichlorosilane	L	1.33	HCl		X	X	0.517	0.50	0.50	0	0.17	0.27	0
1806	Phosphorus pentachloride	S	1.60	HCl		X	X	0.875	0.34	0.53	0	0.11	1.28	0
1808	Phosphorus tribromide	L	2.86	HBr	X		X	0.897	0.65	0.061	0	0.65	0.061	0
1809	Phosphorus trichloride[d]	L	1.57	HCl	X		X	0.796	0.56	1.25	0	0.25	4.8	0
1810	Phosphorus oxychloride	L	1.67	HCl	X	X	X	0.713	0.23	0.10	0	0.23	6.0	0
1815	Propionyl chloride	L	1.06	HCl			X	0.394	0.70	1.11	12	0.06	7.74	0
1816	Propyltrichlorosilane	L	1.30	HCl	X	X	X	0.616	0.73	0.20	31	0.27	0.33	5
1818	Silicon tetrachloride[d]	L	1.48	HCl		X	X	0.858	0.49	2.88	0	0.30	1.81	0
1828	Sulfur chlorides[c,d]	L	1.62	HCl			X	0.540	0.45	0.027	78	0.09	0.39	0
1834	Sulfuryl chloride[c,d]	L	1.63	HCl	X		X	0.540	0.35	0.051	0	0.28	0.080	0
1836	Thionyl chloride[c,d]	L	1.63	SO_2	X			0.538	1.00	2.75	0	1.00	2.75	0
1838	Titantium tetrachloride[d]	L	1.73	HCl	X	X		0.769	0.20	1.35	0	0.13	1.35	0
1898	Acetyl iodide	L	2.07	HI			X	0.753	0.52	7.42	0	0.48	37.2	0
1923	Calcium hydrosulfite[c]	S	2.20	SO_2				0.761	0.05	0.10	0	0.03	0.10	0
1929	Potassium hydrosulfite[c]	S	2.20	SO_2				0.621	0.05	0.10	0	0.03	0.10	0
1931	Zinc hydrosulfite[c]	S	2.20	SO_2				0.662	0.05	0.10	0	0.03	0.10	0
2004	Magnesium diamide	S	1.39	NH_3				0.604	1.00	60	0	1.00	60	0
2011	Magnesium phosphide	S	2.06	PH_3				0.505	0.35	0.045	0	0.35	0.045	0
2012	Potassium phosphide	S	2.50	PH_3				0.230	0.35	0.045	0	0.35	0.045	0

TABLE D.1 (Cont.)

UN No.	Name	St.	Den.	Prod.	Experiments Conducted 00	04	08	S.Y.	Method A β	λ (min^{-1})	T_{ind} (s)	Method B β	λ (min^{-1})	T_{ind} (s)
2013	Strontium phosphide	S	2.68	PH_3				0.210	0.35	0.045	0	0.35	0.045	0
2308	Nitrosylsulfuric acid (liquid)	L	1.89	NO_2	X		X	0.362	0.43	4.94	0	0.43	4.98	0
2353	Butyryl chloride	L	1.03	HCl			X	0.342	0.62	0.48	8	0.14	1.48	0
2395	Isobutyryl chloride	L	1.03	HCl			X	0.342	0.71	0.17	21	0.05	2.4	0
2434	Dibenzyldichlorosilane	L	1.30	HCl			X	0.263	0.23	0.071	180	0.08	0.13	60
2435	Ethylphenyldichlorosilane	L	1.30	HCl			X	0.355	0.43	0.011	528	0.41	0.021	86
2437	Methylphenyldichlorosilane[b]	L	1.30	HCl		X	X	0.382	0.69	0.0065	0	0.27	0.14	43
2495	Iodine pentafluoride	L	3.75	HF				0.451	0.40	0.60	0	0.40	0.60	0
2691	Phosphorus pentabromide[b]	S	3.60	HBr		X	X	0.940	0.12	2.2	0	0.11	0.14	40
2692	Boron tribromide[d]	L	2.65	HBr		X	X	0.969	0.64	3.94	0	0.64	3.94	0
2806	Lithium nitride	S	1.27	NH_3		X		0.489	1.00	18	0	1.00	18	0
2977	Uranium hexafluoride, fissile	S	4.68	HF				0.341	0.20	0.60	0	0.20	0.60	0
2978	Uranium hexafluoride, non-fissile	S	4.68	HF				0.341	0.20	0.60	0	0.20	0.60	0
3048	Aluminum phosphide pesticide	S	2.40	PH_3				0.588	0.35	0.045	0	0.35	0.045	0
3456	Nitrosylsulfuric acid (solid)	S	1.89	NO_2				0.362	0.33	6.0	0	0.75	6.0	0
3052	Aluminum alkyl halides	S	1.60	HCl				0.500	0.05	5.0	0	0.05	5.0	0
9191	Chlorine dioxide, hydrate, frozen	S	1.40	Cl_2				0.084	0.05	5.0	0	0.05	5.0	0

[a] St = normal state during shipment (solid, liquid); Den. = density (g/cm^3); Prod. = primary TIH product produced (see footnote c); Experiments Conducted = ERG edition (2000, 2004, or 2008) for which experiments on the compound were performed; S.Y. = stoichiometric yield of TIH gas (kg TIH gas/kg spilled parent); β = efficiency factor (average fraction of S.Y. produced), λ_o = primary rate constant at 20°C (min^{-1}); and T_{ind} = initial induction period(s).

[b] Parameters for this chemical updated from those used in the EGR2008 analysis as experiments were conducted in mid-2007 (as reported in Brown et al. 2009).

[c] Multiple TIH gases produced, most hazardous shown (in terms of production rate and toxicity).

[d] Parent chemical is TIH gas.

[e] Experiments performed on the closely related compound 4-(chloromethyl)phenyltrichlorosilane were taken to apply to this compound.

TABLE D.2 Chemicals Reported to Be Water-Reactive in the Scientific Literature

UN No.	Name	Comment	Reference
1397	Aluminum phosphide	Slowly evolves PH_3 in contact with water.	Lewis (2000)
1419	Magnesium aluminum phosphide	Evolves PH_3 in contact with water.	Lewis (2000)
1432	Sodium phosphide	Is known to evolve PH_3 in contact with water.	Lewis (2000)
1680	Potassium cyanide	Is included on the basis of its chemical similarity to sodium cyanide.	
1745	Bromine pentafluoride	Explodes on contact with water. Products of this rapid reaction include HF and possibly Br_2.	Lewis (2000)
1746	Bromine trifluoride	Smokes in air and decomposes violently in water. Products of reaction include HF and possibly Br_2.	Budavari (1996); Lewis (2000)
1923	Calcium hydrosulfite	Is included by analogy to sodium hydrosulfite.	
1931	Zinc hydrosulfite	Is included by analogy to sodium hydrosulfite.	
2004	Magnesium diamide	Reacts violently with water, evolving NH_3.	Budavari (1996)
2011	Magnesium phosphide	Phosphides tend to decompose to PH_3 upon contact with moisture or acids.	Lewis (2000)
2012	Potassium phosphide	Phosphides tend to decompose to PH_3 upon contact with moisture or acids.	Lewis (2000)
2013	Strontium phosphide	Phosphides tend to decompose to PH_3 upon contact with moisture or acids.	Lewis (2000)
2495	Iodine pentafluoride	Violently reacts with water. Products include HF.	Lewis (2000)
2977	Uranium hexafluoride, fissile	Is rapidly hydrolyzed by water and reacts vigorously with water. Products include HF.	Cotton and Wilkinson (1966); Lewis (2000)
2978	Uranium hexafluoride, non-fissile	Is rapidly hydrolyzed by water and reacts vigorously with water. Products include HF.	Cotton and Wilkinson (1966); Lewis (2000)
2985	Chlorosilanes, n.o.s.[a]	Most chlorosilanes generate HCl at some rate upon contact with water.	
2986	Chlorosilanes, flammable, corrosive, n.o.s.	Most chlorosilanes generate HCl at some rate upon contact with water.	
2987	Chlorosilanes, corrosive, n.o.s.	Most chlorosilanes generate HCl at some rate upon contact with water.	
2988	Chlorosilanes, water reactive, flammable, corrosive, n.o.s.	Most chlorosilanes generate HCl at some rate if spilled into water.	
3048	Aluminum phosphide pesticide	Aluminum phosphide slowly evolves PH_3 in contact with water. Is included despite the fact that the coating applied to the particles in the pesticide application is likely to slow the hydrolysis.	Lewis (2000)
3049	Metal alkyl halides, n.o.s.	Metal alkyl halides generally react to form hydrogen halides (HCl, HBr, HI) when mixed with water.	
3052	Aluminum alkyl halides	Aluminum alkyl halides generally react to form hydrogen halides (HCl, HBr, HI) when mixed with water.	
9191	Chlorine dioxide hydrate, frozen	Decomposes in water. Products likely to include gaseous Cl_2.	Lewis (2000)

[a] n.o.s. = not otherwise specified.

D.4.3 Materials Included Due to Special Concerns

In the course of our experimental program, TIH gases did not evolve from four materials that appear in Table D.1. They were still included on the TIHWR list because TIH gases might evolve from them under the right circumstances if they spilled.

1. **UN 1384 — sodium hydrosulfite.** Experiments conducted in 1999 found no evolution of gas when the chemical was mixed with room-temperature water, although both SO_2 and H_2S were detected because of their odor. This material was retained on the TIHWR list, however, because of the possibility that a substantial amount of TIH gas could evolve as a result of decomposition caused by the confined heat of dissolution in restricted amounts of water in spills having the proper geometry (such as a heap on a puddle). Of particular note is the following statement from the EPA/OSHA Joint Chemical Accident Investigation Report of an accident on April 21, 1995, at Napp Technologies, Inc., in Lodi, New Jersey: "Sodium hydrosulfite is unstable in the presence of water, heat or humid air, giving off sulfur dioxide gas and other sulfur products in an exothermic reaction. Once initiated, the decomposition process of sodium hydrosulfite supports continued decomposition due to the generation of heat in the exothermic reaction."

2. **UN 1541 — acetone cyanohydrin.** Experiments conducted in 2003 found no evolution of gas when the chemical was mixed with room-temperature water. This material was retained on the TIHWR list, however, because of its chemical similarity to sodium cyanide. A May 20, 1998, spill of sodium cyanide into a river in Kyrgyzstan led to evolution of gaseous HCN, as discussed below.

3. **UN 1689 — sodium cyanide.** Experiments conducted for the ERG2008 found no evolution of gas when the chemical was mixed with room-temperature water. Despite the negative result, this compound was retained on the TIHWR list because of the conclusions found in Cleven and van Bruggen (2000). This report on a large spill of sodium cyanide into a river in Kyrgyzstan in May 1998 stated that "...a large part of the dissolved cyanide must have been rapidly transformed into HCN, which will have been released into the air." The report continues that people "…must have been at considerable risk for life-threatening disease through inhalatory uptake of HCN (gas)." Several deaths were attributed to either dermal or inhalatory contact with HCN in this incident.

4. **UN 1726 — aluminum chloride (anhydrous).** Experiments in 1999 found no evolution of gas when the chemical was mixed with room-temperature water. This chemical was retained on the TIHWR list, however, because the small scale of the experiment might have masked its TIHWR character. Aluminum chloride is cited in Carson and Mumford (1994) as generating HCl in contact

with water: "Reacts with air moisture to form corrosive HCl gas. Violent reaction when a stream of water hits a large amount."

D.5 MATERIALS NO LONGER RECOMMENDED AS TIHWR MATERIALS

Ten materials previously recommended as TIWHR materials by Argonne National Laboratory and the University of Illinois at Chicago have been subsequently removed from the TIHWR list prior to 2008. Note that not all of these materials actually appeared in previous editions of the ERG. Reasons for their exclusion are detailed below.

1. **UN 1433 — stannic phosphide.** No evolution of TIH gas was observed in the experiments (see Appendix C).

2. **UN 1714 — zinc phosphide.** No evolution of TIH gas was observed in the experiments (see Appendix C).

3. **UN 1736 — benzoyl chloride.** No evolution of TIH gas was observed in the experiments (see Appendix C). However, literature sources do mention TIH gas evolution; for example, see Carson and Mumford (1994): "Reacts strongly with water or water vapor, producing heat and toxic, corrosive fumes."

4. **UN 1749 — chlorine trifluoride.** This material reacts explosively with water to generate HF and possibly Cl_2. The compound is gaseous above 11.8°C and was therefore treated as a TIH gas in its own right.

5. **UN 1807 — phosphorus pentoxide.** This material reacts explosively with water to generate water-soluble phosphoric acid. It had been previously included on the TIHWR list by analogy to SO_3 — because of the possibility that this very rapid, exothermic reaction might raise a toxic acidic mist in a spill. However, since phosphoric acid is not a TIH material, the U.S. Department of Transportation (DOT) excluded phosphorus pentoxide on the TIHWR list.

6. **UN 1831 — fuming sulfuric acid (oleum).** Oleum is a solution of sulfur trioxide in sulfuric acid. It fumes strongly in moist air (Lewis 2000) and reacts with water and water vapor to form sulfuric acid mists (National Institute for Occupational Safety and Health [NIOSH] Substance Profile; see http://ntp.niehs.nih.gov/ntp/roc/eleventh/profiles/s164sulf.pdf). The reaction is quite exothermic. However, oleum is already a TIH material, and spills into water would likely not lead to Protective Action Distances (PADs) in excess of those already listed for land-based spills.

7. **UN 1829 — sulfur trioxide.** Like oleum, this compound reacts with water and water vapor to form sulfuric acid mists (NIOSH Substance Profile).

However, it was excluded from the TIHWR list for the same reasons that oleum was excluded.

8. **UN 1939 — phosphorus oxybromide (solid).** This compound reacted with water, in a manner similar to that of phosphorus tribromide in 2003 experiments. However, it was excluded from the TIHWR list because the HBr apparently dissolved into the excess water as rapidly as it was formed.

9. **UN 2442 — trichloroacetyl chloride.** This compound reacted with water in the experiments, but it was not included on the TIHWR list because no evolution of gaseous HCl was observed (see Appendix C).

10 **Sodium methylcarbamodithioate (metam sodium) (no UN number).** This material has a known history of water reactivity, but it was excluded from the TIHWR list because it does not have a UN number.

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