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Development of the Table of Initial Isolation and Protective Action Distances for the *2024 Emergency Response Guidebook*

Strategic Security Sciences Division
Argonne National Laboratory

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ABBREVIATIONS USED IN THIS REPORT

ABL	atmospheric boundary layer
ACGIH	American Conference of Governmental Industrial Hygienists
AEGL	acute exposure guideline level
AIHA	American Industrial Hygiene Association
AL	aerosolized liquid release
AS	aerosolized solid release
CAS	Chemical Abstracts Services
CASRAM	Chemical Accident Statistical Risk Assessment Model
CBL	convective boundary layer
CFR	Code of Federal Regulations
CWIC	crosswind-integrated concentration
DOD	U.S. Department of Defense
DOE	U.S. Department of Energy
DOT	U.S. Department of Transportation
EEGL	emergency exposure guidance level
EEL	emergency exposure level
ERG	*Emergency Response Guidebook*
ERPG	emergency response planning guideline
GDP	gross domestic produce
GLB	Great Lakes Buoy
HMIS	Hazardous Materials Information System
IDLH	immediately dangerous to life and health
IID	initial isolation distances
IIZ	initial isolation zone
LC_{50}	concentration lethal for 50% of exposed population
LC_{LO}	lowest reported lethal concentration
LOAEL	lowest observed adverse effect level
LOC	levels of concern

NIOSH	National Institute for Occupational Safety and Health
NOAA	National Oceanic and Atmospheric Administration
NOAEL	no observed adverse effect level
n.o.s.	not otherwise specified
OSHA	Occupational Safety and Health Administration
PAD	protective action distances
PAZ	protective action zone
PEL	permissible exposure limit
SBL	stratified boundary layer
SEB	surface energy budget
SEBMET	Surface Energy Budget Meteorological model
SH	release by shipment sabotage
SP	spray or explosive release
STEL	short-term exposure limit
TEEL	temporary emergency exposure limits
TIH	toxic inhalation hazard
TIHWR	toxic inhalation hazard by water reactivity
TLV	threshold limit value
TLV-C	ceiling TLV
TLV-TWA	time-weighted average TLV
UN	United Nations
USGS	U.S. Geological Survey
WQN	Water Quality Network

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1. INTRODUCTION

The transportation of hazardous materials creates numerous opportunities for the release of toxic substances into the environment, whether caused by traffic accidents, train derailments, equipment failures, or human error. Such releases can pose 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 the Secretariat of Transport and Communications of Mexico; with contributions from Centro de Informaciòn Quìmica para Emergencias of Argentina. The most recent version is the 2024 edition of the ERG (ERG 2024), titled *2024 Emergency Response Guidebook* (ERG2024). The ERG provides essential information about firefighting, 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 of the source of the release within 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 ERG2024 **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*: the probability that the listed PAD will allow sufficient protection of the public. The level of protection adopted for the ERG, going back to the 1993 edition, 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, first 15 minutes, 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 three tables: **Table 1** is the Table of Initial Isolation and Protective Action Distances, **Table 2** lists the materials that emit TIH gases when exposed to water, and **Table 3** provides specific information for six commonly transported TIH materials. Figure 1.1 shows the basic information presented in Tables 1 and 3 and their application. To properly use these Tables, a responder must first determine the following:

- The United Nations (UN) identification number and/or proper shipping name of the material being transported.
- The direction of the prevailing wind.
- Whether the spill is small or large. A small spill is one that involves a single, small package, such as a drum containing up to approximately 208 L (55 U.S. gal), a small cylinder, or a small leak from a large package.
- Whether it is day or night.
- For the six materials in Table 3, the wind speed conditions.
- Any special conditions that could preclude the use of the values given in the Table, such as 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. 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 centered on the accident location, as shown in Figure 1.1. 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 initial isolation distance (IID) specifies a circular zone surrounding the accident site called the initial isolation zone (IIZ). 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/or 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.

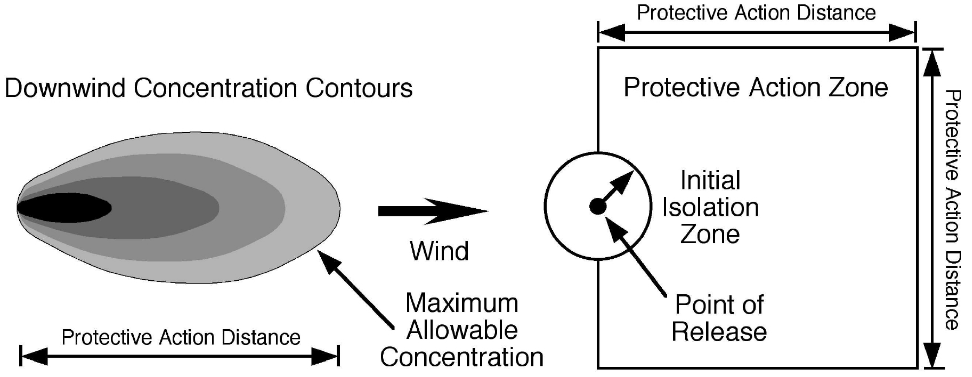

Figure 1.1 How ERG2024 defines the initial isolation zone and protective action zone for use by a first responder.

The range of cases for which the ERG could be used is considerable, covering everything from a minor compressed gas cylinder leak 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 of entries in the ERG reasonable, four PAD values are provided for each material to 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 specific wind speed and release scenarios for the entirety of the TIH list, beginning with the 2012 ERG, more specific information has been included for six chemicals that represent the vast majority of all TIH transportation incidents for which the ERG is consulted. These entries constitute Table 3 of ERG2024 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, including 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. Appendices Appendix A: and Appendix B: present Tables 1 and 3 in the ERG2024 Green Pages (ERG 2024). Appendices Appendix C: and Appendix D: contain chemical data and details of the past 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 ERG2024 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 ERG2020 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 by the DOT Pipeline and Hazardous Material Safety Administration (PHMSA) Hazardous Materials Information Center (HMIS).[1]

Each scenario is then analyzed using detailed emission rate and atmospheric dispersion models to calculate an airborne chemical concentration footprint. For four of the most commonly shipped TIH materials, we also include chemical reactivity data for natural surfaces based on a set of laboratory experiments conducted at Argonne National Laboratory in 2014 and 2015. These experiments are detailed in a companion report (Freeman et al., 2016) and summarized in Section 3. 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 depend on exposure time threshold concentrations, are based on 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 (55 gal or less = small, more than 55 gal = large). The PADs appearing in this table are then selected as the 90th percentile values for these individual categories. The 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 in the same format as when they were first provided in ERG2012 and are available for chlorine, ammonia, hydrogen chloride, hydrogen fluoride, sulfur dioxide, and ethylene oxide. The distances appearing in these tables are also 90th

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[1] Formerly the Hazardous Materials Information System (HMIS). See http://phmsa.dot.gov/hazmat/library/data-stats/incidents.

percentile values but are taken from a smaller subset of the scenario library corresponding to the container type and wind speed range.

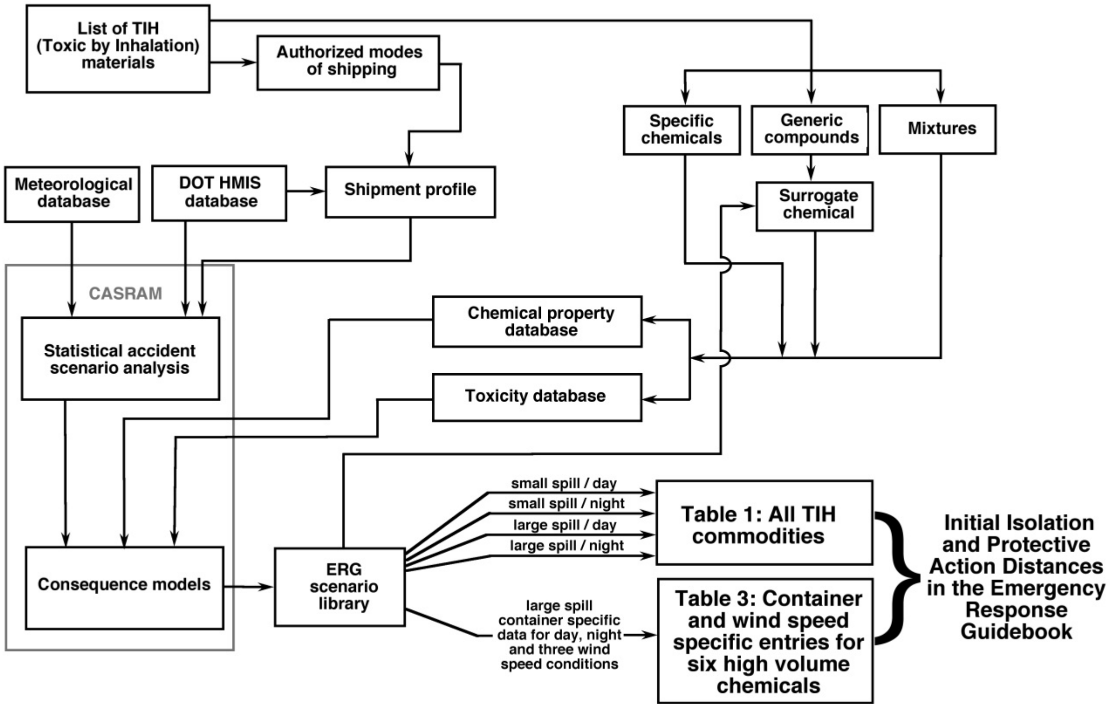

Figure 2.1 Schematic of the methodology used to prepare the ERG2024 Table of Initial Isolation and Protective Action Distances.

2.1 THE TIH LIST

For the purposes of our analysis, we classify materials on the TIH list into four different categories: (1) pure chemicals, (2) mixtures, (3) solutions, and (4) generic compounds, such as UN 1953: compressed gas, poisonous, flammable, not otherwise specified (n.o.s.). 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.[2]

2.1.1 Background

TIH materials fall into four hazard zones for gases (A, B, C, and D) and two for liquids (A and B). ERG2024 lists PADs for 160 single compounds, 19 mixtures, and 38 generics. The TIH list also includes 82 water-reactive materials, defined here as materials that emit a TIH gas on contact with water. Of those 82 water-reactive materials, several are TIH compounds that produce a secondary, sometimes more toxic, TIH gas on exposure to water.

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[2] See https://www.ecfr.gov/current/title-49/subtitle-B/chapter-I/subchapter-C/part-173 for all 29 CFR 173 regulations.

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 similar chemical names or multiple names for the same chemical. It is important to note that the UN number is not a unique identifier: 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 (diphosgene is much less volatile).

Mixtures are classified by considering the combined toxic effects of individual components in the mixture. Generics are modeled by using a surrogate compound, with the surrogate being the median 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 to determine the source emission rate. Water reactivity is discussed in Section 2.4 and Appendix D:.

2.1.2 Changes in the TIH List for ERG2024

There were few substantive changes made in the TIH list for the 2024 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 August 2019. Note that the TIH list contains all entries that have appeared in the previous 10 years of UN lists, as those materials may still be transported and so could be involved in a transportation incident. Those that rolled off the 10-year window in the period since the preparation of the 2020 ERG were removed from the 2024 ERG.

2.2 SHIPMENT AND RELEASE SCENARIOS

To specify a level of protection, 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 at which each container is involved in an incident. The goal of this analysis was to assign each chemical a set of representative shipments that reflects 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: (1) those occurring during a traffic accident or a train derailment, and (2) those occurring 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 in the shipment profiles is the treatment of chemical warfare agents. These materials were first considered in ERG2000. In 2000, entries were given for two release scenarios: (1) a transportation-related release scenario and (2) a weapons-related release scenario in which the material is released in a criminal or terrorist act. The transportation-related release scenario was removed in 2004 (but retained for those chemical agents that have a proper shipping name and are TIH). The treatment of chemical warfare agents is outlined in Section 2.3 and has evolved significantly since 2020.

2.2.1 Shipment Profiles

The starting point for the development of shipment profiles is 49 CFR 172.101 and associated subsections in the Code of Federal Regulations, which 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 discharge fractions (the amount of material released in an incident relative to the container capacity) resulting from releases. For example, most Division 2.3 gases listed 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.

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 2024ERG analysis, the ratio for 111A tank cars is used for TIH liquids transported in Types 112JW and 105A tank cars.

The shipment profiles for most chemicals fall into one of the following ten 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
9. Organophosphates authorized under 49 CFR 173.334
10. Adsorbed gases shipped under 49 CFR 173.302

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 make the results unrealistically conservative, since the probability of these materials being shipped in true bulk form appears to be very low.

Generally, shipments were designated as either rail-dominated 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.

Beginning in 2008, we developed shipment profiles specifically tailored 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 to compile this supply chain information. These chemical-specific shipment profiles were also used in the ERG2024 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. A significant addition initiated for the ERG2016 analysis and continued in ERG2024 is consideration of adsorbed Hazard Zone A gases. As the amount of these gases in cylinders is generally very low, and they are conveyed adsorbed in a substrate that dramatically limits the rate of release, distances for these materials are substantially less than those for the same gases specified for non-adsorbed conveyance.

Examples of mixed rail and highway shipment profiles are provided in Table 2.2 and Table 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 influence of shipment class and release type on the releases modeled in the ERG2024 analysis, the percentage of total releases represented by each type is listed for all releases, releases of 5–55 gal, and releases of more than 55 gal. When all releases are considered, en route/nonaccident incidents make up the majority of releases modeled for the shipment profiles given in Table 2.2 and Table 2.3. However, in considering releases of more than 55 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.

Table 2.2 Mixed rail and highway shipment profile data for liquids.[a]

					Percent of Total Releases by Type, Listed by Release Amount		
Shipment	**Transport Mode**	**Container**	**Shipment Amount**	**Release Type**	**All Releases**	**5–55 gal**[b]	**>55 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 55 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	5–55 gal[b]	>55 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.

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 of malicious use of chemical and biological agents. For this reason, from 2004-2020, the ERG includes IIDs and PADs for various chemical agents that could be used as weapons. As described below, these values have been presented differently in 2024. In addition, a separate section, “Criminal/Terrorist Use of Chemical/Biological/Radiological Agents,” 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.) In past ERGs, entries in the Table for these materials include the statement “when used as a weapon.” Several of these materials are also industrial chemicals that appear separately in ERG2024 as transportation-related releases. In the past, entries for weapons-related use of chemical agents were listed under the common or military names for the compounds, not the chemical names. For example, for weapons-related entries, the compound listed as AC is referred to for transportation-related entries 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.

In the ERG2024, the chemical warfare agents are removed from the Table and placed in a new section entitled Criminal or Terrorist Use of Chemical, Biological and Radiological Agents. Updated in the ERG2024 is the container quantities for some of the agents. Table 2.4 provides the container quantities and type of release specification used in the ERG2020 and Table 2.5 provides the updated values for the ERG2024.

Table 2.4 Chemical warfare agents listed in the ERG2020 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).

Table 2.5 2024 Updated chemical warfare agents listed in the ERG2020 Table of Initial Isolation and Protective Action Distances .

UN No.	Chemical Warfare Agent Name	Class[a]	Chemical Compound Name	Small (kg)	Large (kg)	Type[b]
1051	AC	O	Hydrogen cyanide	100	3600[c]	SH
1076	DP	C	Diphosgene	2	25	AL
1076	CG	C	Phosgene	100	3600	SH
1076	CG	C	Phosgene	2	25	SP
1556	MD	B	Methyldichloroarsine	2	25	AL
1556	PD	B	Phenyldichloroarsine	2	25	AL
1589	CK	O	Cyanogen chloride	2	25	AL[d]
1694	CA	T	Bromobenzyl cyanides	2	25	AL[e]
1697	CN	T	Chloroacetophenone	2	25	AS
1698	DM, Adamsite	V	Diphenylaminechloroarsine (10-Chloro-5,10-dihydrophenarsazine)	2	25	AS
1699	DA	V	Diphenylchloroarsine	2	25	AS
1892	ED	B	Ethyldichloroarsine	2	25	AL
2188	SA	O	Arsine	100	1000 [c]	SH
N/A	H, HD, Mustard	B	Bis-(2-chloroethyl) sulfide	2	25	SP
N/A	HN-1	B	Bis-(2-chloroethyl) ethylamine	2	25	SP
N/A	HN-2	B	Bis-(2-chloroethyl) methylamine	2	25	SP
N/A	HN-3	B	Tris-(2-chloroethyl) amine	2	25	SP
N/A	L, Lewisite, HL, Mustard lewisite[f]	B	Dichloro-(2-chlorovinyl) arsine	2	25	SP
N/A	BZ, Buzz	I	3-Quinuclidinyl benzilate	2	25	AS
N/A	CS	T	O-chlorobenzylidene malononitrile	2	25	AS
N/A	DC	V	Diphenylcyanoarsine	2	25	AS
N/A	GA, Tabun	N	Ethyl N,N-dimethylphosphoramidocyanidate	2	25	SP
N/A	GB, Sarin	N	Isopropyl methylphosphonofluoridate	2	25	SP
N/A	GD, Soman	N	Pinacolyl methylphosphonofluoridate	2	25	SP
N/A	GF	N	Cyclohexyl methylphosphonofluoridate	2	25	SP
N/A	VX	N	O-ethyl S-(2-diisopropylaminoethyl) methylphosphonothiolate	2	25	SP
N/A	CX	B	Phosgene oxime	2	25	AS

[a] Agent class: B = blister, N = nerve, T = tear, O = blood, V = vomiting, C = choking, I = Incapacitating

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

[c] AC was 30000 in previous analysis, and SA was 2000

[d] CK is transported in significant quantities but due to slow evaporation rate is more effectively dispersed as a aerosolized liquid

[e] Previously mis-categorized as solid

[f] Because of uncertainties in defining the composition, HL and mustard lewisite are treated as 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 Tables 2.4 and 2.5 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 particle size of 2 μm to 10 μm. 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 have been no changes in the list of chemical warfare agents since it was first introduced in 2012. The small and large release amounts are set in accordance with assessments (non-classified) of terrorist capabilities. In particular, maximum release amounts for chemical warfare agents are 25 kg or about 5 gal, and release amounts for materials that have no commercial use or availability (such as BZ and CX) are 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.

In the ERG2024, the chemical warfare agents are further aggregated by class of agent (i.e., blister agent, nerve agent, tear gas agent, blood agent, vomiting agent, choking agent, and incapacitating agent) and the IID and PAD values are reported for these classes of agents. The median values of the IID and PAD values for the aggregated classes are then reported in ERG2024 in the Initial Isolation and Protective Action Distances table located within the section on Chemical Warfare Agent, except for nerve agents which are represented by the values from Sarin which is the most recognizable member of this class.

2.3 GENERICS, MIXTURES, AND SOLUTIONS

The Table lists a variety of compounds that are generic in nature. Two examples are UN 3160 (liquefied gas, toxic, flammable, n.o.s.; Inhalation Hazard Zone B) and UN 2927 (toxic liquids, corrosive, organic, n.o.s.). 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 ERG2024 or the Table. As in ERG2020, the IIDs and PADs for generic compounds in ERG2024 are based on the median case (50th percentile) compound from the pool of chemicals in the overall analysis that matches that generic description.

Before the 2008 edition of the ERG, 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 2008 ERG, 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 DOT incident records), use of the worst-case method could lead to an excessive response in a major incident. There are two reasons for this. First, 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 UN 3389, described as Toxic by inhalation liquid, corrosive, n.o.s. (Inhalation Hazard Zone A) is considered below. The chemicals analyzed for ERG2024 that match this category are listed in Table 2.6. Note that this list is ordered by the PAD for a large, nighttime spill. As shown, allyl chloroformate (UN 1722) lies at the median of these nine chemicals when the large spill distances are considered, meaning that half (four) of the chemicals have longer large-spill distances and half have shorter large-spill distances. For small spills, the median chemical is methyl vinyl ketone (UN 1251). Two entries for this generic category that reflect the variations in wording in the Table are also provided. These entries are rounded up to the nearest 0.1 mi (100 ft for Initial Isolation Zones) to reflect their appearance in the Table.

Table 2.6 Chemicals used to determine initial isolation and protective action distances for the generic material UN 3389 described as poisonous liquid, corrosive, n.o.s. (Inhalation Hazard Zone A)[a].

UN No.	Name of Material	Small Spills			Large Spills		
		First Isolate in All Directions (ft)	Then Protect Persons Downwind During		First Isolate in All Directions (ft)	Then Protect Persons Downwind During	
			Day (mi)	Night (mi)		Day (mi)	Night (mi)
Potential Surrogate Compounds							
1670	Perchloromethyl mercaptan	71	0.12	0.19	235	0.45	0.73
1185	Ethyleneimine	76	0.08	0.25	514	0.54	1.06
1238	Methyl chloroformate	62	0.13	0.34	353	0.65	1.28
1244	Methyl hydrazine	61	0.16	0.34	298	0.83	1.29
1722	Allyl chloroformate	242	0.19	0.46	984	0.83	1.56
1251	Methyl vinyl ketone	317	0.14	0.40	2153	0.96	1.71
2474	Thiophosgene	130	0.32	1.02	515	1.29	2.46
1744	Bromine	188	0.48	1.44	919	2.32	4.67
1745	Bromine pentafluoride	203	0.45	1.59	1242	3.39	6.59
Synonymous Entries for Generic Compound Categories							
3389	Poisonous by inhalation liquid, corrosive, n.o.s. (Inhalation Hazard Zone A)	200	0.2	0.4	1000	0.9	1.6
3389	Toxic by inhalation liquid, corrosive, n.o.s. (Inhalation Hazard Zone A)	200	0.2	0.4	1000	0.9	1.6

[a] This table provides distance estimates for all applicable entries in the ERG2024 Table of Initial Isolation and Protective Action Distances (ERG 2024) 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 2.7 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 example, the pool for the generic category described as compressed gas, poisonous, oxidizing, corrosive, n.o.s. (Inhalation Hazard Zones C and D) includes 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 2.8 lists the mixtures and solutions treated in the ERG2024 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.

- When the mixture composition was not specified, we chose a surrogate: 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 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.

Table 2.7 Summary of generic compounds on DOT TIH List and corresponding surrogates employed for ERG2024. (Note that a different surrogate material may be used for each release category, and identical entries with the same UN number are not listed for brevity.)

UN Number	Proper Shipping Name	Surrogate
1953	Compressed gas, toxic, flammable, n.o.s.	Median cases among all TIH, flammable Hazard Zone A gases
1953	Compressed gas, toxic, flammable, n.o.s. (Inhalation Hazard Zone A)	Median cases among all TIH, flammable Hazard Zone A gases
1953	Compressed gas, toxic, flammable, n.o.s. (Inhalation Hazard Zone B)	Median cases among all TIH, flammable Hazard Zone B gases
1953	Compressed gas, toxic, flammable, n.o.s. (Inhalation Hazard Zone C)	Median cases among all TIH, flammable Hazard Zone C gases
1953	Compressed gas, toxic, flammable, n.o.s. (Inhalation Hazard Zone D)	Median cases among all TIH, flammable Hazard Zone D gases
1955	Compressed gas, poisonous, n.o.s.	Median cases among all TIH, Hazard Zone A gases
1955	Compressed gas, poisonous, n.o.s. (Inhalation Hazard Zone A)	Median cases among all TIH, Hazard Zone A gases
1955	Compressed gas, poisonous, n.o.s. (Inhalation Hazard Zone B)	Median cases among all TIH, Hazard Zone B gases
1955	Compressed gas, poisonous, n.o.s. (Inhalation Hazard Zone C)	Median cases among all TIH, Hazard Zone C gases
1955	Compressed 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
2478	Isocyanate solution, flammable, poisonous, n.o.s.	Median cases among all isocyanates
2742	Chloroformates, poisonous, corrosive, flammable, n.o.s.	Median cases among all chloroformates
2985	Chlorosilanes, flammable, corrosive, n.o.s. **(when spilled in water)**	Median cases among all chlorosilanes
2986	Chlorosilanes, corrosive, flammable, n.o.s. **(when spilled in water)**	Median cases among all chlorosilanes
2987	Chlorosilanes, corrosive, n.o.s.**(when spilled in water)**	Median cases among all chlorosilanes
2988	Chlorosilanes, water-reactive, flammable, corrosive, n.o.s. **(when spilled in water)**	Median cases among all chlorosilanes
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

UN Number	Proper Shipping Name	Surrogate
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
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

UN Number	Proper Shipping Name	Surrogate
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
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

UN Number	Proper Shipping Name	Surrogate
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
3361	Chlorosilanes, poisonous, corrosive, n.o.s. **(when spilled in water)**	Median cases among all chlorosilanes
3362	Chlorosilanes, poisonous, corrosive, flammable, n.o.s. **(when spilled in water)**	Median cases among all chlorosilanes
3381	Poisonous by inhalation liquid, n.o.s. (Inhalation Hazard Zone A)	Median cases among all TIH, Hazard Zone A liquids
3382	Poisonous by inhalation liquid, n.o.s. (Inhalation Hazard Zone B)	Median cases among all TIH, Hazard Zone B liquids
3383	Poisonous by inhalation liquid, flammable, n.o.s. (Inhalation Hazard Zone A)	Median cases among all TIH, flammable, Hazard Zone A liquids
3384	Poisonous by inhalation liquid, flammable, n.o.s. (Inhalation Hazard Zone B)	Median cases among all TIH, flammable, Hazard Zone B liquids
3385	Poisonous by inhalation liquid, water-reactive, n.o.s. (Inhalation Hazard Zone A)	Median cases among all TIH, Hazard Zone A liquids
3386	Poisonous by inhalation liquid, water-reactive, n.o.s. (Inhalation Hazard Zone B)	Median cases among all TIH, Hazard Zone B liquids
3387	Poisonous by inhalation liquid, oxidizing, n.o.s. (Inhalation Hazard Zone A)	Median cases among all TIH, Hazard Zone A liquids
3388	Poisonous by inhalation liquid, oxidizing, n.o.s. (Inhalation Hazard Zone B)	Median cases among all TIH, Hazard Zone B liquids
3389	Poisonous by inhalation liquid, corrosive, n.o.s. (Inhalation Hazard Zone A)	Median cases among all TIH, corrosive, Hazard Zone A liquids
3390	Poisonous by inhalation liquid, corrosive, n.o.s. (Inhalation Hazard Zone B)	Median cases among all TIH, corrosive, Hazard Zone B liquids
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, corrosive, flammable, Hazard Zone A liquids

UN Number	Proper Shipping Name	Surrogate
3493	Poisonous by inhalation liquid, corrosive, flammable, n.o.s. (Inhalation Hazard Zone B)	Median cases among all TIH, corrosive, flammable, Hazard Zone A liquids
3512	Adsorbed gas, poisonous, n.o.s.	Median cases among all TIH, Hazard Zone A adsorbed gases
3512	Adsorbed gas, poisonous, n.o.s. (Inhalation Hazard Zone A)	Median cases among all TIH, Hazard Zone A adsorbed gases
3512	Adsorbed gas, poisonous, n.o.s. (Inhalation Hazard Zone B)	Median cases among all TIH, Hazard Zone B adsorbed gases
3512	Adsorbed gas, poisonous, n.o.s. (Inhalation Hazard Zone C)	Median cases among all TIH, Hazard Zone B adsorbed gases
3512	Adsorbed gas, poisonous, n.o.s. (Inhalation Hazard Zone D)	Median cases among all TIH, Hazard Zone B adsorbed gases
3514	Adsorbed gas, poisonous, flammable, n.o.s.	Median cases among all TIH, Hazard Zone A adsorbed gases
3514	Adsorbed gas, poisonous, flammable, n.o.s. (Inhalation Hazard Zone A)	Median cases among all TIH, Hazard Zone A adsorbed gases
3514	Adsorbed gas, poisonous, flammable, n.o.s. (Inhalation Hazard Zone B)	Median cases among all TIH, Hazard Zone B adsorbed gases
3514	Adsorbed gas, poisonous, flammable, n.o.s. (Inhalation Hazard Zone C)	Median cases among all TIH, Hazard Zone B adsorbed gases
3514	Adsorbed gas, poisonous, flammable, n.o.s. (Inhalation Hazard Zone D)	Median cases among all TIH, Hazard Zone B adsorbed gases
3515	Adsorbed gas, poisonous, oxidizing, n.o.s.	Median cases among all TIH, Hazard Zone A adsorbed gases
3515	Adsorbed gas, poisonous, oxidizing, n.o.s. (Inhalation Hazard Zone A)	Median cases among all TIH, Hazard Zone A adsorbed gases
3515	Adsorbed gas, poisonous, oxidizing, n.o.s. (Inhalation Hazard Zone B)	Median cases among all TIH, Hazard Zone B adsorbed gases
3515	Adsorbed gas, poisonous, oxidizing, n.o.s. (Inhalation Hazard Zone C)	Median cases among all TIH, Hazard Zone B adsorbed gases
3515	Adsorbed gas, poisonous, oxidizing, n.o.s. (Inhalation Hazard Zone D)	Median cases among all TIH, Hazard Zone B adsorbed gases
3516	Adsorbed gas, poisonous, corrosive, n.o.s.	Median cases among all TIH, Hazard Zone A adsorbed gases
3516	Adsorbed gas, poisonous, corrosive, n.o.s. (Inhalation Hazard Zone A)	Median cases among all TIH, Hazard Zone A adsorbed gases
3516	Adsorbed gas, poisonous, corrosive, n.o.s. (Inhalation Hazard Zone B)	Median cases among all TIH, Hazard Zone B adsorbed gases
3516	Adsorbed gas, poisonous, corrosive, n.o.s. (Inhalation Hazard Zone C)	Median cases among all TIH, Hazard Zone B adsorbed gases
3516	Adsorbed gas, poisonous, corrosive, n.o.s. (Inhalation Hazard Zone D)	Median cases among all TIH, Hazard Zone B adsorbed gases
3517	Adsorbed gas, poisonous, flammable, corrosive, n.o.s.	Median cases among all TIH, Hazard Zone A adsorbed gases
3517	Adsorbed gas, poisonous, flammable, corrosive, n.o.s. (Inhalation Hazard Zone A)	Median cases among all TIH, Hazard Zone A adsorbed gases
3517	Adsorbed gas, poisonous, flammable, corrosive, n.o.s. (Inhalation Hazard Zone B)	Median cases among all TIH, Hazard Zone B adsorbed gases
3517	Adsorbed gas, poisonous, flammable, corrosive, n.o.s. (Inhalation Hazard Zone C)	Median cases among all TIH, Hazard Zone B adsorbed gases
3517	Adsorbed gas, poisonous, flammable, corrosive, n.o.s. (Inhalation Hazard Zone D)	Median cases among all TIH, Hazard Zone B adsorbed gases
3518	Adsorbed gas, poisonous, oxidizing, corrosive, n.o.s.	Median cases among all TIH, Hazard Zone A adsorbed gases

UN Number	Proper Shipping Name	Surrogate
3518	Adsorbed gas, poisonous, oxidizing, corrosive, n.o.s. (Inhalation Hazard Zone A)	Median cases among all TIH, Hazard Zone A adsorbed gases
3518	Adsorbed gas, poisonous, oxidizing, corrosive, n.o.s. (Inhalation Hazard Zone B)	Median cases among all TIH, Hazard Zone B adsorbed gases
3518	Adsorbed gas, poisonous, oxidizing, corrosive, n.o.s. (Inhalation Hazard Zone C)	Median cases among all TIH, Hazard Zone B adsorbed gases
3518	Adsorbed gas, poisonous, oxidizing, corrosive, n.o.s. (Inhalation Hazard Zone D)	Median cases among all TIH, Hazard Zone B adsorbed gases

Table 2.8 Summary of mixtures and solutions on DOT TIH list and how they were treated for ERG2024.

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
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
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
3494	Mixture	Petroleum sour crude oil, flammable, toxic	Treated as generic category poisonous liquid, flammable, n.o.s. (Inhalation Hazard Zone B)

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).[3] 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. In another, much more recent, incident (January 2, 2017), which did not, however, involve a transportation accident, four children were killed and several people hospitalized in Amarillo, Texas, after water was introduced under a mobile home in which the rodenticide aluminum phosphide was used.

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 and can react with liquid water or scavenge 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 were modeled, and how they were treated in the statistical analysis as part of the ERG2012 study, are detailed in Section 3.3.3, and additional details of the experiments and the parameters employed in the TIHWR modeling appear in Appendix D. The general methodology and reactivity data used for these materials is essentially unchanged from the ERG2012 analysis, except for the addition of a few materials.

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[3] 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.

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 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).
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 ERG2000, the experimental program outlined in Step 4 was initiated. This program was expanded for ERG2004 to include over half of the TIHWR list and further expanded for ERG2008 to encompass more than 70% of the TIHWR list. In addition, the set of materials under consideration for TIHWR status was expanded at that time, thus adding several new materials to the TIHWR list.

The need for such experimental data is underscored by the fact that, with few exceptions, quantitative observations of TIH gas evolving from hazardous chemicals added to water did not exist in the chemical literature prior to our experimental studies. 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 1 millimole (mmol) of the material in question 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 is different from that used for the ERG2000 and ERG2004 analyses, in which the gas volume produced was measured by noting the displacement of manometric fluid; thus, most materials previously analyzed in the experiments were redone for ERG2008, providing an entirely new set of experimental data from which to estimate gas evolution. 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 before, experiments were conducted by using two different amounts of water (the stoichiometric equivalent amount and a fivefold molar excess) for each material considered. These experiments are meant to approximate conditions in which (1) the material is released into a restricted water environment (or perhaps just gets wet) and (2) the material is spilled into a body of water.

The experimental program has not only given us useful quantitative information on the rates of evolution of TIH gases but has over the past decade 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. Data derived from these experiments that were used in preparation of ERG2012 are discussed in Appendix D.

2.4.4 Additional Selection Criteria

A few additional issues associated with the evaluation process 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°C–20°C) presented problems, because they can 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 evolve more rapidly. 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 supplied 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 agitation 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 considered 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 in 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 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 ERG2000, 14 new materials were added to the TIHWR list for 2004, and another 14 were added in ERG2008. There were no changes to the list for ERG2012. Two materials were added in 2016. The full list of TIHWR materials considered in ERG2024 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 (IIZ) around the accident site from which people are to be kept away. The establishment of an IIZ serves two purposes. First, it provides a buffer area 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 it is used to define the IID.

The IID is calculated in much the same way that PAD is, except that a lethality end point is a principal consideration. As such, distances are first evaluated by using the 1-hour LC_{50}.[4] The same 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.

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[4] LC_{50} is the concentration of a material that causes the death of 50% of a group of test animals.

The IID is set at 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 have occurred in the past 20 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 the values used in previous 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 in the Green Pages in ERG2024 and the corresponding isolation distance guidelines in the Orange Pages. 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) is the core of the ERG2024 PAD determination analysis 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 was developed primarily as 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 such as the one employed in the ERG analysis. 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 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 ERG2024 study. The emission rate modeling and dispersion modeling within CASRAM, which make up the consequence modeling effort to determine PADs, are then outlined. We also describe a series of experiments that determined the reactivity of the released chemicals with natural materials, which provided critical data for use in the chemical deposition modeling we incorporated into this analysis cycle, as we did for the 2016 ERG.

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 among 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 is 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), and 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 and time-of-day distributions for incidents in the HMIS database following Brown et al. (2005), where the year is assigned in a 20-year window that corresponds to observations in the meteorological database (1996–2015).

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 an analysis of incidents in the HMIS database. 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. The dispersion calculation is a two-step process: Step 1 is characterizing the meteorology from the available surface observations, and step 2 is 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 the 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 in which 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, catalogs transportation-related incidents involving the release of hazardous materials. In recent years, about 15,000–20,000 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 incidents (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) while 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: 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 about the HMIS database and our previous analyses can be found in Brown et al. (2001).

3.1.3 Geographic Incident Distributions

In the ERG2024 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 2005 through 2018, 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 2018. 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, 87.9% of the incidents modeled in the ERG2024 analysis occurred in the United States, 7.1% occurred in Canada, and 5.0% 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 (less than 0.5% of total Canadian population). Mexico was divided into three regions: Northern (above 22°N latitude), Central (between 18°N and 22°N latitude), and Southern (below 18°N latitude, including the Yucatan Peninsula). A breakdown of the geographic distribution of incidents in the ERG2024 analysis for highway and rail transportation is provided in Table 3.1.

3.1.4 Temporal Incident Distributions

Temporal release distributions are important to specifying 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 the day and month of the year. The hour is critical to meteorology 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 meteorology affects not only the dispersion of the chemicals in the atmosphere but 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 2018 were also analyzed in the course of the ERG2024 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 ERG2016.

Temporal incident statistics are shown in Figure 3.1 and Figure 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 ERG2024 analysis, by percentage.

State	Rail	Highway	State/Province	Rail	Highway
United States					
Alabama	2.18	1.01	New Mexico	0.77	0.36
Alaska	0.10	0.02	New York	1.52	2.85
Arizona	1.36	1.41	North Carolina	1.66	2.94
Arkansas	0.90	1.01	North Dakota	0.50	0.18
California	10.33	7.12	Ohio	3.74	6.71
Colorado	1.10	2.03	Oklahoma	0.72	1.14
Connecticut	0.06	1.49	Oregon	1.14	1.49
District of Columbia	0.01	0.04	Pennsylvania	2.73	5.36
Delaware	0.13	0.13	Rhode Island	0.03	0.21
Florida	1.61	3.44	South Carolina	1.22	0.93
Georgia	2.08	2.45	South Dakota	0.05	0.11
Hawaii	0.01	0.02	Tennessee	2.71	3.36
Idaho	0.46	0.24	Texas	10.86	6.78
Illinois	6.65	6.64	Utah	1.09	1.37
Indiana	1.48	2.36	Vermont	0.04	0.09
Iowa	0.93	0.80	Virginia	1.47	1.03
Kansas	1.75	1.99	Washington	1.63	1.20
Kentucky	1.93	1.16	West Virginia	0.67	0.34
Louisiana	7.35	1.18	Wisconsin	0.79	1.50
Massachusetts	0.45	1.52	Wyoming	0.61	0.12
Maryland	1.06	1.77	***Canada and Mexico***		
Maine	0.12	0.21	British Columbia	0.91	0.91
Michigan	2.37	1.58	Alberta	0.70	0.70
Minnesota	0.94	1.59	Saskatchewan	0.27	0.27
Mississippi	0.89	0.78	Manitoba	0.29	0.29
Missouri	1.65	1.92	Ontario	2.76	2.76
Montana	1.75	1.88	Quebec	1.88	1.88
Nebraska	1.31	0.37	Atlantic Provinces	0.64	0.64
Nevada	0.60	0.54	Northern Mexico	1.32	1.32
New Hampshire	0.03	0.14	Central Mexico	3.22	3.22
New Jersey	1.50	2.16	Southern Mexico	0.96	0.96

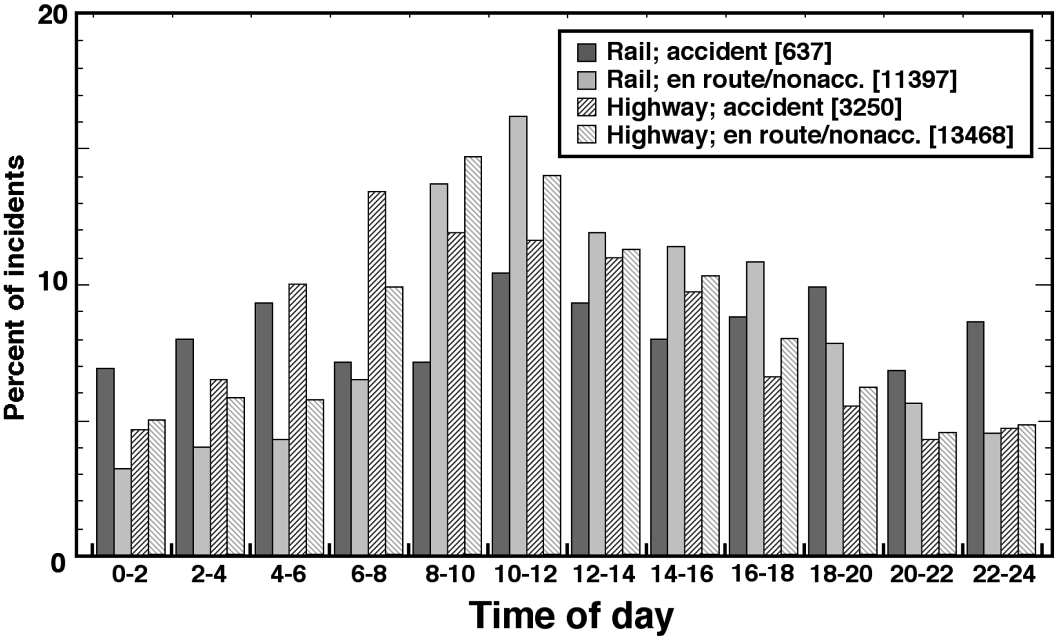

Figure 3.1 Hourly distribution of rail and highway transportation related hazardous material releases occurring during accident related and en route/nonaccident incidents from the HMIS database for 1990–2002.

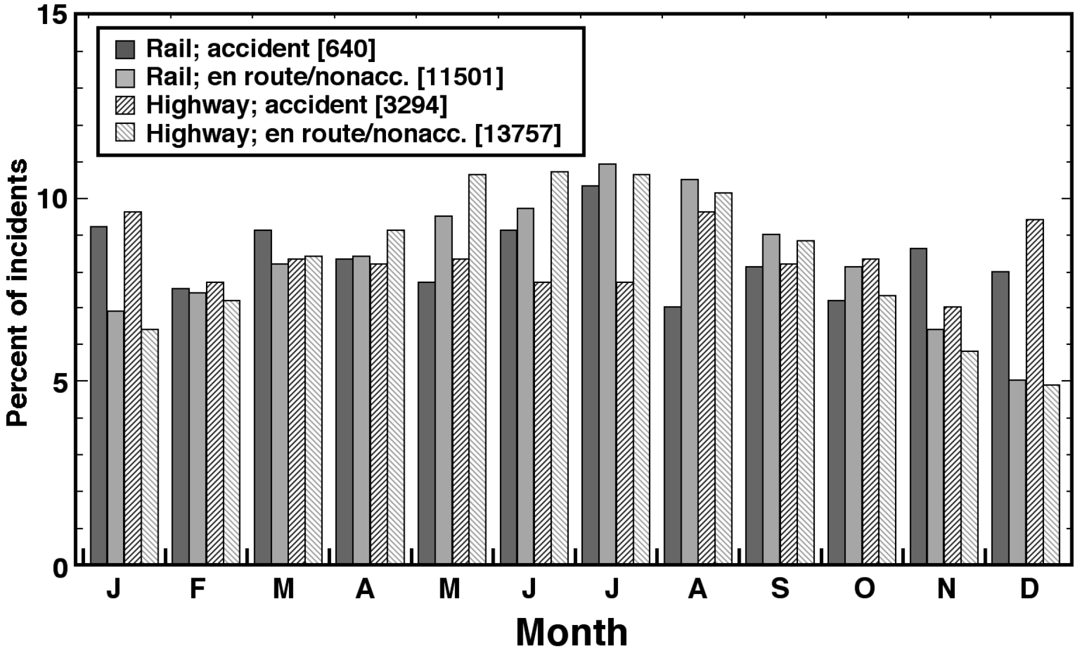

Figure 3.2 Monthly distribution of rail and highway transportation-related hazardous material releases occurring during accident-related and en route/nonaccident incidents from the HMIS database for 1990–2002.

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 referred to 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 discussed below, this incident would be grouped with all other incidents involving releases from pressurized railcars (Type 105 and 112) to construct the discharge fraction distribution 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 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 2018 were also analyzed in the course of the ERG2020 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 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 Figure 3.3 and Figure 3.4. Figure 3.3 shows discharge fraction distribution for containers 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 statistical data for 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 or 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.

To facilitate the use of discharge fractions in computational models, we developed mathematical expressions 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:

$$F(\gamma) = \min(1, e^{\zeta(\gamma)}) \qquad \text{(Eq. 3.1)}$$

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 Table 3.2 and Table 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.

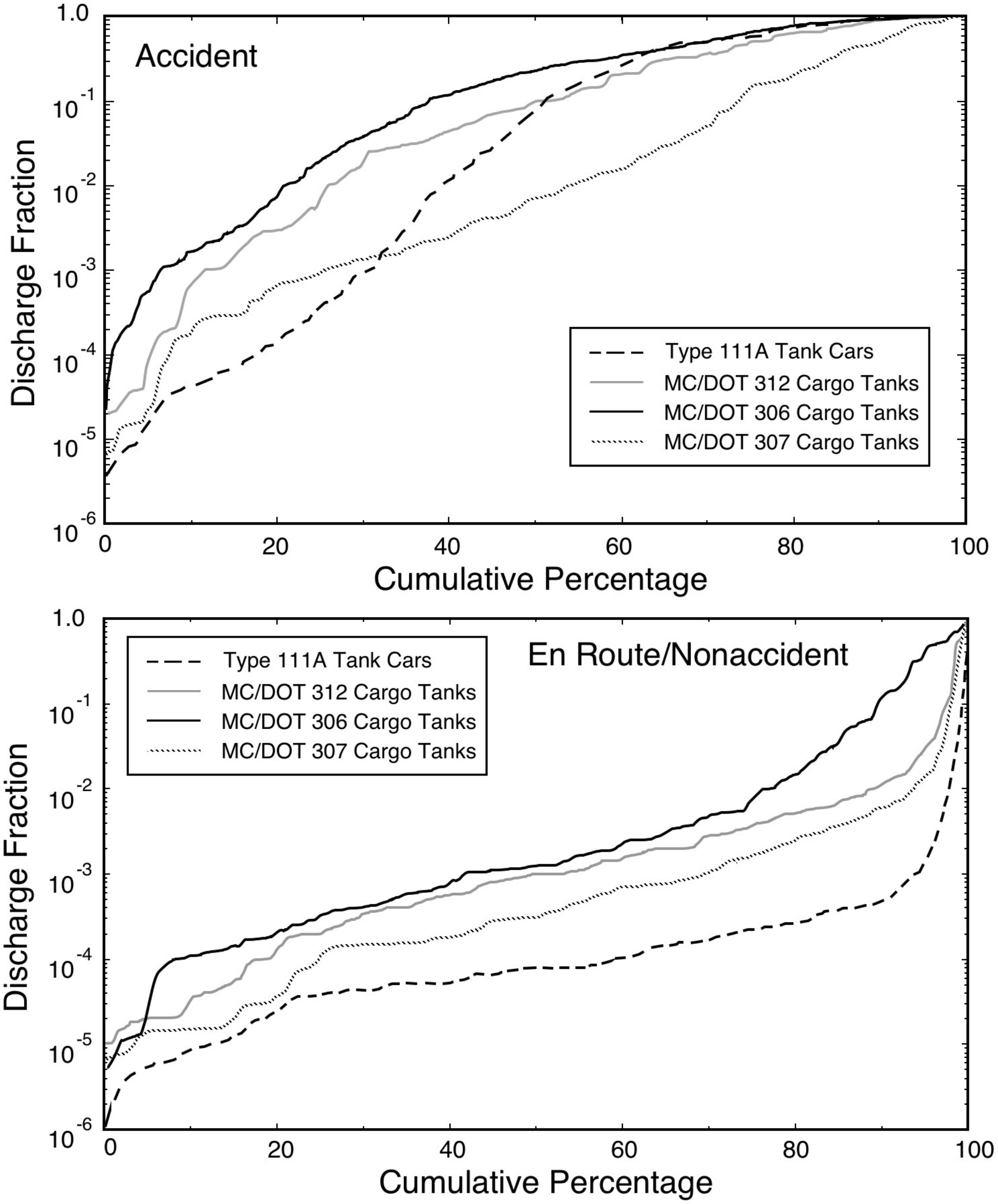

Figure 3.3 Discharge fraction cumulative probability for bulk nonpressurized and low-pressure containers as derived from the analysis of the HMIS database used for the ERG2024 analysis. (Results are shown for accident-related and en route/nonaccident releases).

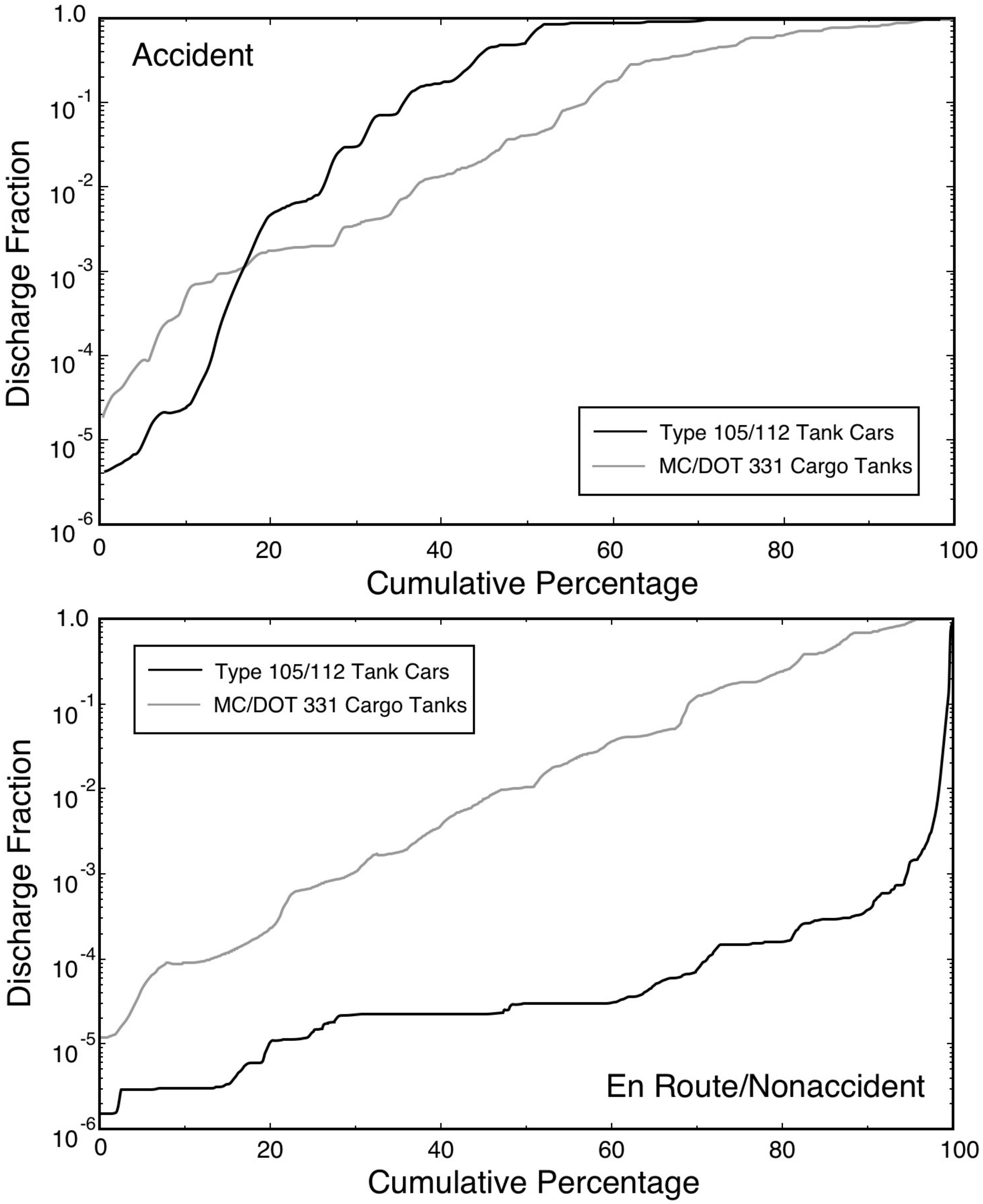

Figure 3.4 Discharge fraction cumulative probability for bulk pressurized containers as derived from the analysis of the HMIS database used for the ERG2024 analysis. (Results are shown for accident-related and en route/nonaccident releases.)

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

3.1.5.2.1 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 could be released. A complicating factor, 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 3.2 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

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 follows:

$$N_f = N_s \gamma^{N_s^a} \qquad \text{(Eq. 3.2)}$$

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 shown below:

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

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.

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

3.1.5.2.2 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 the HMIS statistics in Table 2.1. Usually only one container is involved, even in shipments with large numbers of containers. Table 3.7 and Table 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 Table 3.4 and Table 3.5, the number in which more than 90% of the total shipment amount was released.

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 One Container	Number with >90% Release
1	37	37	16
2–5	45	38	0
>5	43	28	1

To solve the discharge fraction estimation problem for these events, we take an approach similar to the one we took for accident-related events. We first split out those events where only one container is involved, and, 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 3.9 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 ERG2024 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 20 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 like the ERG analyses. A meteorological preprocessor contains a series of algorithms that use routinely measured observations of wind speed, temperature, humidity, cloud cover, and upper-air temperature 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. We 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 2015 (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 includes 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.

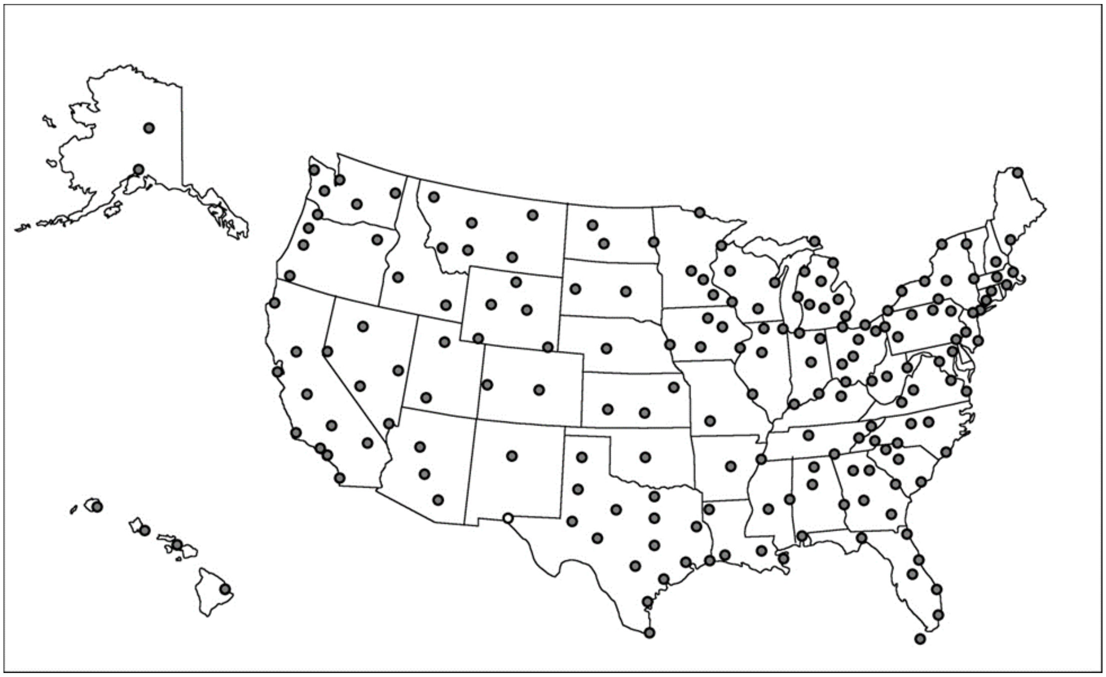

Figure 3.5 Locations of the 204 National Weather Service Stations used for statistical meteorological characterization.

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.

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 ignored, the SEB is most simply represented as follows:

$$Q^* = H + \lambda E_w + G + Q_a \qquad \text{(Eq. 3.4)}$$

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)

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:

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

where

α_s = surface albedo

ε_s = surface emissivity

σ = Boltzmann constant

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 of 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 increases 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 derived from upper-air data, and (5) ozone amount 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 by 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 in 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 conditions 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).[5]

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. These 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 to prepare the ERG since ERG2012 are shown in Figure 3.6.

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[5] 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.

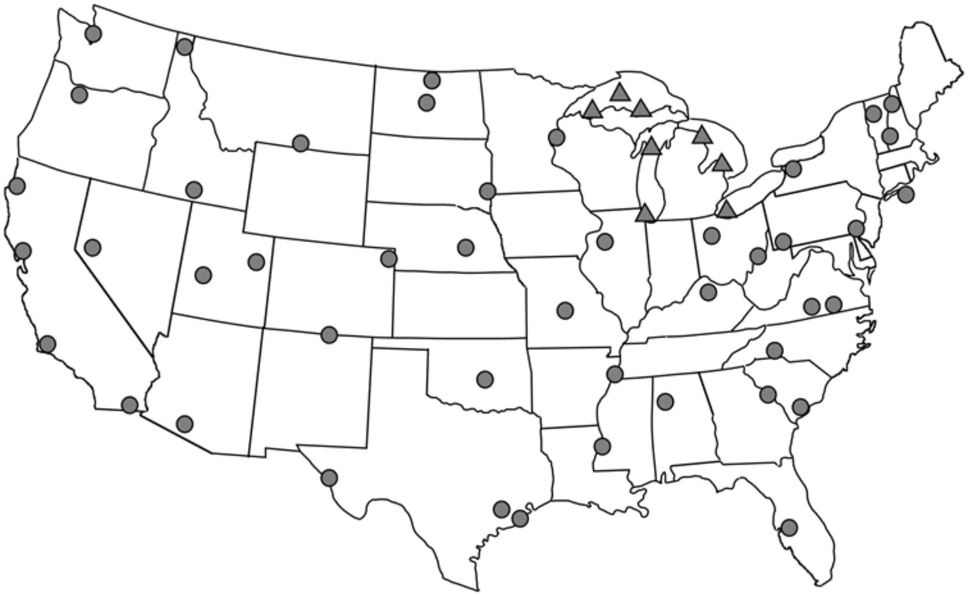

Figure 3.6 Water Quality Network stations used to determine variations of average water temperature by Julian day and location (circles = 45 land-based sampling sites, triangles = 8 GLBs).

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:

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

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 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.

Liquid materials are emitted to the atmosphere through pool evaporation, as illustrated in Figure 3.7a. 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.

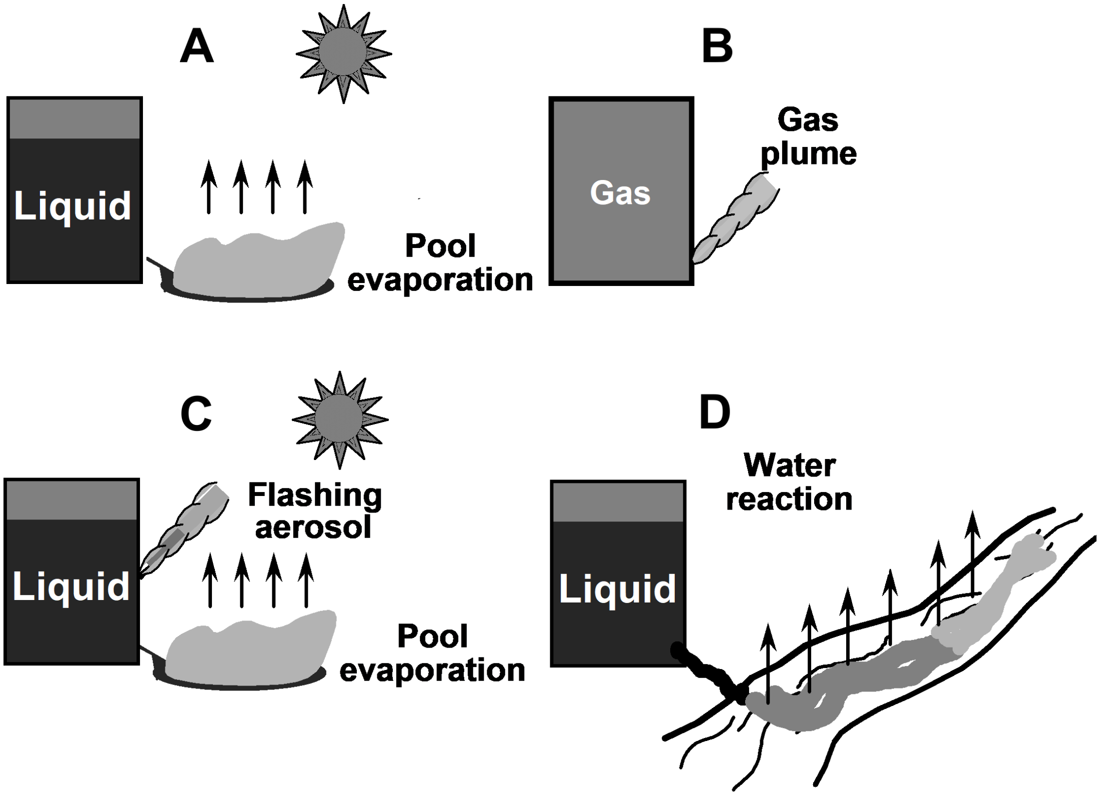

Figure 3.7 Important source types for inhalation risk considered in the ERG2024 analysis (a = ordinary liquids, b = compressed gases, c = liquefied gases, d = water-reactive materials).

Highly volatile liquids evaporate very 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 holding less 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, 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 alternate water exposure mechanism is required for these materials 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 that water acidity may be important. Mixing effects are also important, 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 ERG2024 Analysis

The source component of CASRAM determines hazardous material release rates for each of the spill and/or vaporization scenarios described above. Information on 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 the 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

3.3.2.2.1 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):

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

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)

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). The discharge coefficient c_o, depends on the exit velocity, fluid viscosity, and hole characteristics, as shown by experimental data (Perry et al. 1984). However, at the 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 (in depth) pool 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 the application of techniques (including the ω–method) to address situations when the length is non-negligible is provided by Britter et al. (2011).

3.3.2.2.2 Pool Evaporation

Pool evaporation within CASRAM is determined by using a time-dependent SEB 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 follows:

$$Q_e = A_p E_c \qquad \text{(Eq. 3.8)}$$

where

A_p = pool area (m^2)

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:

$$E_c = h_m \frac{P_v(T_p)}{RT_p} \qquad \text{(Eq. 3.9)}$$

where

h_m is the mass transfer coefficient

P_v is the chemical vapor pressure at the pool temperature T_p

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, used later).

Considering these processes, we write the pool energy budget as follows:

$$Q_p^* = H_p + \lambda E_{wp} + G_p + h_{fg} E_c + m c_p \frac{dT_p}{dt} \qquad \text{(Eq. 3.10)}$$

where Q_p^* is the net radiation given by the following:

$$Q_\mathrm{p}^* = (1 - \alpha_\mathrm{p})\, S^+ + L^+ + \varepsilon_p \sigma\, T_p^4 \qquad \text{(Eq 3.11)}$$

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

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

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. The most important meteorological quantities 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 boiling pools, which 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.

3.3.2.2.3 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:

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

where γ is c_p/c_v, the ratio of the specific heat at constant pressure to 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:

$$P_r = \left(\frac{\gamma + 1}{2} \right)^{\frac{\gamma}{\gamma-1}} \qquad \text{(Eq. 3.14)}$$

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

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

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

3.3.2.2.4 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 fraction that flashes, the flash fraction *f,* is calculated as follows:

$$f = \frac{c_p (T_t - T_b)}{h_{fg}} \qquad \text{(Eq. 3.16)}$$

where T_t is the tank temperature and T_b is the boiling point. The 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 above.

3.3.3 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:

- 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 were initiated during the ERG1996 analysis and supplemented by 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:

$$Q(t) = M_o f_s \beta \lambda e^{-\lambda(t-T_{ind})} \qquad \text{(Eq. 3.17)}$$

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 ($0 \leq \beta \leq 1$

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

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 and 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 ERG2004, and for 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 scaling 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:

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

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 that the reaction is likely autocatalytic. For 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 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 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 dependence of the primary rate constant λ on temperature was included in the analysis via the Arrhenius equation:

$$\lambda = \lambda_o \exp\left[-6610\left(\frac{1}{T_w} - \frac{1}{T_o}\right)\right] \qquad \text{(Eq. 3.19)}$$

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 (a) the release rate in the event of a continuous release or (b) the 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 ERG2020 and ERG2024 is very similar to that employed in preparation of ERG2016, except that we upgraded the vapor deposition model used in 2016 for the four materials, based on laboratory experiments conducted in 2014 and 2015 as well as several Jack Rabbit tests involving large chlorine releases (Fox 2011). 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 (EPA, 2002). 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.

3.4.1 Overview of Atmospheric Dispersion

In this section, we discuss some general concepts of atmospheric dispersion modeling of hazardous material releases and the CASRAM dispersion model as applied to releases of passive and dense gases.

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 the day and the night, leading to boundary layers with dramatically different sizes and characters. These marked differences substantially influence the ability of the ABL to disperse pollutants released near the ground, giving rise to pronounced differences in downwind concentrations and therefore in the 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 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 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 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.

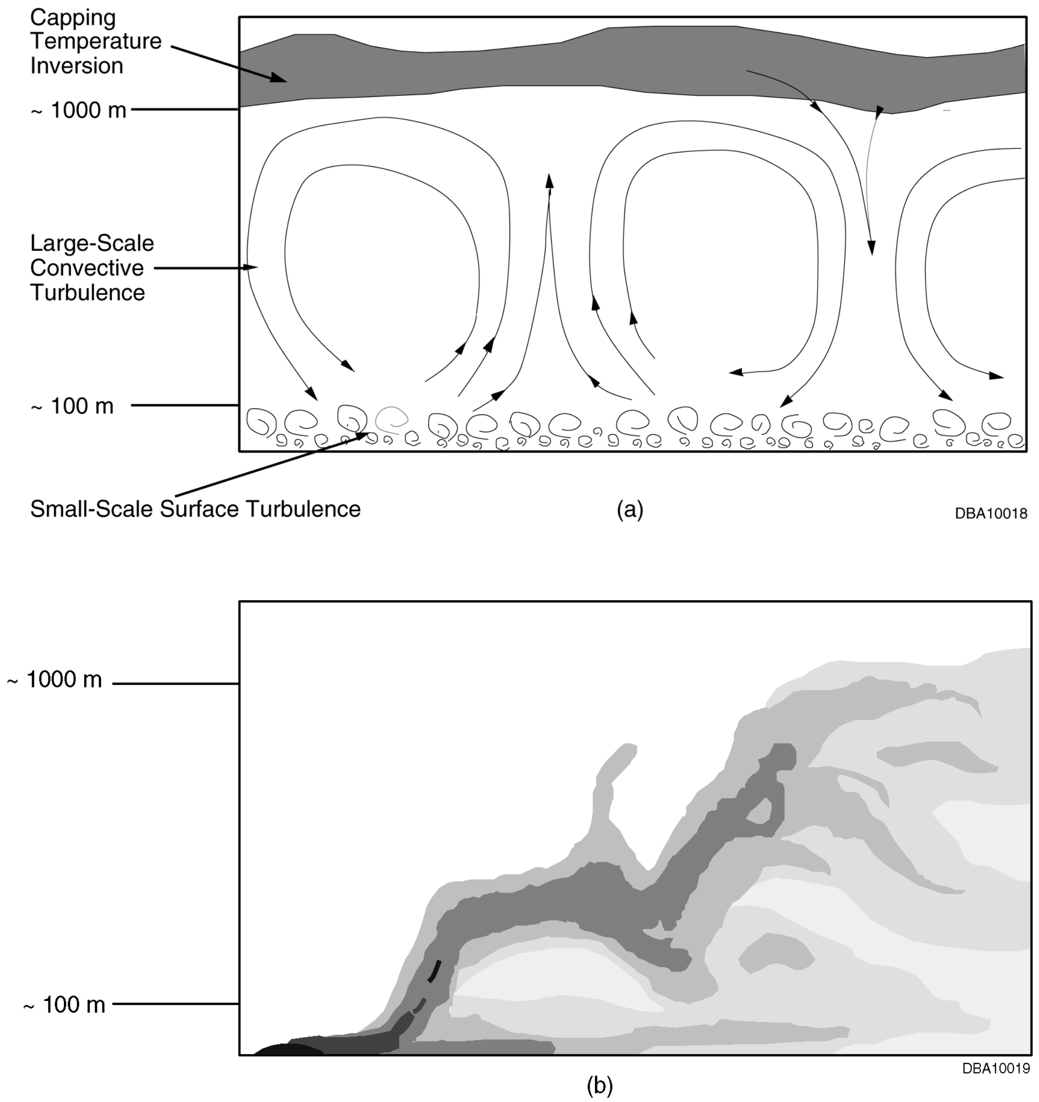

Figure 3.8 Typical daytime convective boundary layer showing (a) an instantaneous wind field and (b) an instantaneous material concentration field from a ground-level release. (Characteristic heights of about 1,000 m for the boundary layer and about 100 m for the surface layer are provided for reference.)

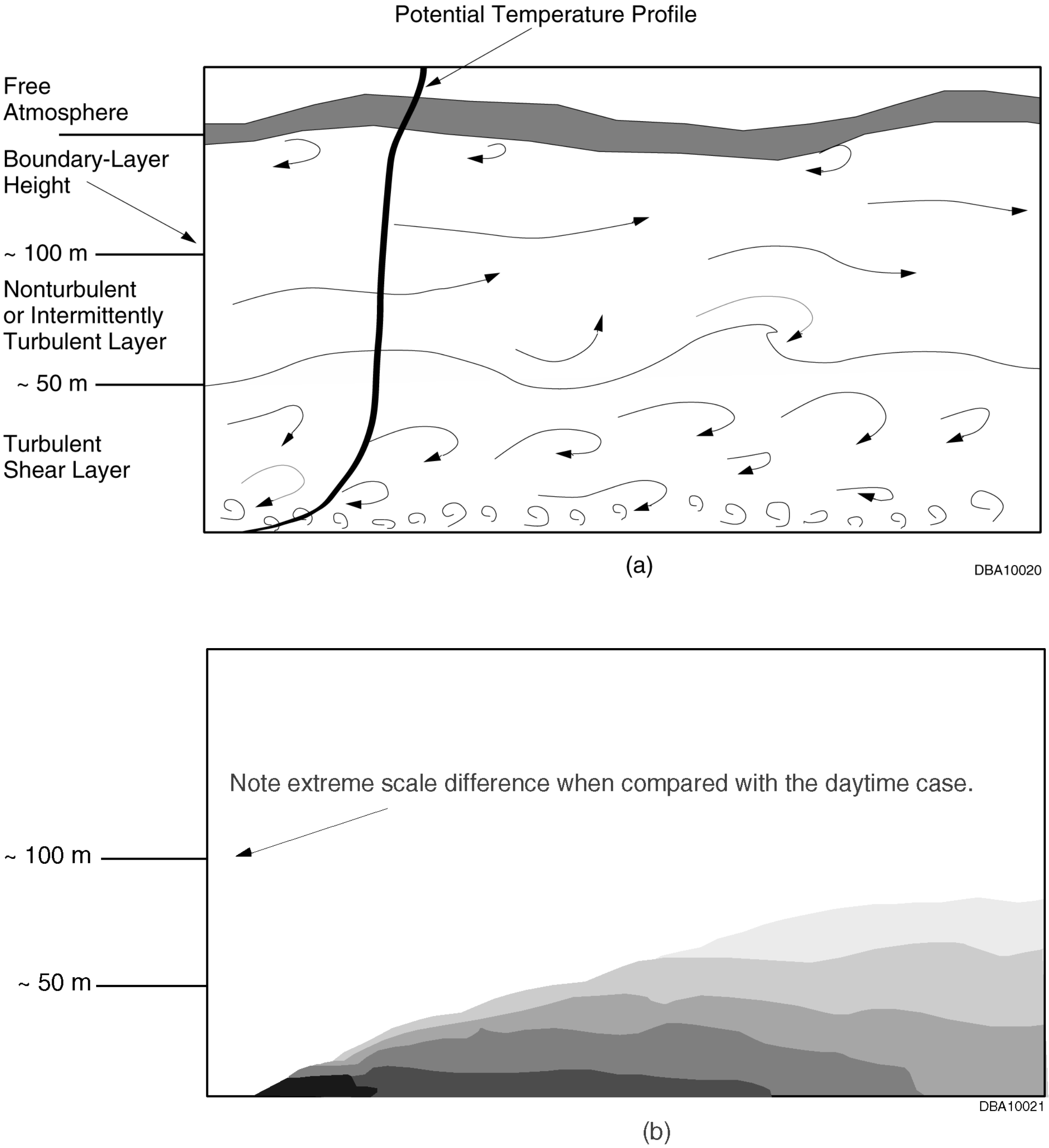

Figure 3.9 Typical nighttime stable boundary layer showing (a) an instantaneous wind field and (b) an instantaneous material concentration field from a ground-level release. (Characteristic heights of about 50 m for the surface shear layer and about 100 m for the boundary layer are provided for reference.)

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 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).
- Pressurized liquids containing chemicals with a low to moderate molecular weight that while 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.
- Chemicals that undergo molecular association, such as hydrogen fluoride (HF), and/or transform to secondary hazardous compounds because of their ambient water-vapor reactivity, such as sulfur trioxide (SO_3)/oleum, and nitrogen tetroxide (N_2O_4). (These are not necessarily the same 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 magnitude of these dense gas effects depends on the size of the release, local meteorological conditions, and the 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:

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

where

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

σ_y = lateral plume spread

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:

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

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

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

where

$M =$ total release amount

$T =$ averaging time

$U =$ 10 m wind speed

We shall first present the methodology for determining vertical dispersion (i.e., for determining C_y as a function of downwind distance). Then we shall discuss the determination of σ_y, thus providing horizontal dispersion.

3.4.2.1.1 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 on an exact solution of the advection–diffusion equation. When written in terms of the CWIC form, and ignoring stream-wise diffusion, it reads as follows:

$$U(z)\frac{\partial C_y}{\partial z} = \frac{\partial}{\partial z}\left[K_z(z)\frac{\partial C_y}{\partial z}\right] \qquad \text{(Eq. 3.23)}$$

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 as follows:

$$U(z) = u_o z^m \qquad \text{(Eq. 3.24)}$$

and

$$K_z(z) = k_o z^n \qquad \text{(Eq. 3.25)}$$

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 is shown below:

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

where

$$A = \frac{s\Gamma(2/s)}{\Gamma(1/s)^2} \quad \text{(Eq. 3.27)}$$

$$B = \frac{\Gamma(2/s)}{\Gamma(1/s)} \quad \text{(Eq. 3.28)}$$

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 follows:

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

where z_u is defined such that

$$U(z_u) = \overline{U_p} \quad \text{(Eq. 3.30)}$$

and

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

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.

3.4.2.1.2 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 produced by the following:

$$\sigma_y = \sigma_v f_y \left(\frac{t}{T_d} \right) \qquad \text{(Eq. 3.32)}$$

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

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):

$$f_y = \frac{1}{1 + 0.9\sqrt{t / T_d}} \qquad \text{(Eq. 3.33)}$$

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 1922).

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):

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

in unstable conditions, and the proportionality relation of Panofsky and Dutton (1984):

$$\sigma_v = 1.92\, u \qquad \text{(Eq. 3.35)}$$

in 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 in the CASRAM framework: DEGADIS (EPA 2002), HEGADAS (Post 1994), SLAB (Ermak 1990), SCIPUFF (DTRA 1999), and TSCREEN (EPA 1992). Based on a number of considerations, the most important being accuracy and ease of incorporation into the CASRAM framework, we opted to rely on the empirical entrainment parameterizations in the DEGADIS formulation for the CASRAM heavy gas dispersion model. We anticipate a major revision of DEGADIS in response to the Jack Rabbit II and upcoming Jack Rabbit III tests. Future applications of CASRAM 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 $\dot{V}_{sv}$:

$$\dot{V}_{sv} = \frac{Q_v}{\rho_v} \qquad \text{(Eq. 3.36)}$$

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 measured as follows:

$$\dot{V}_{ci} = (1+\beta_{ei})\dot{V}_{sv} \qquad \text{(Eq. 3.37)}$$

where β_{ei} is the entrainment parameter at the source, which we set at 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 requires solving the following relationship:

$$h_{ci} = \frac{\dot{V}_{ci}}{2\overline{U_p} r_i} \qquad \text{(Eq. 3.38)}$$

where

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

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:

$$\rho_{ci} = \frac{Q_v + Q_a + \beta_{ei}\dot{V}_v\rho_a}{\dot{V}_{ci}} \qquad \text{(Eq. 3.40)}$$

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):

$$\frac{dr}{dx} = \frac{\beta_e u_*}{U_p} \sqrt{Ri_*} \qquad \text{(Eq. 3.41)}$$

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

$$Ri_* = \frac{g h_c (\rho_c - \rho_a)}{\rho_a u_*^2} \qquad \text{(Eq. 3.42)}$$

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:

$$\frac{dh_c}{dx} = \frac{v_e}{U_p} \qquad \text{(Eq. 3.43)}$$

where the vertical entrainment velocity is as used in the DEGADIS model:

$$v_e = \frac{0.4 u_*}{0.88 + 0.099 Ri_*^{1.04}} \qquad \text{(Eq. 3.44)}$$

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 from the local cloud Richardson number:

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

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 $2r$, so the parameter y_o in Equation 3.21 is set to r.

3.5 CHEMICAL REACTIVITY EFFECTS

Living plants, soils, and open water absorb toxic gases from the air. Such uptake can moderate the hazard when toxic gases are accidentally released, especially for moderately and highly reactive gases (see Dillon, 2009). Green belts have been planted near facilities where toxic gases are produced or used in order to mitigate air pollution (Dimbour et al. 2002; Rakhi et al. 2008; Khan and Abbasi 2000, and Khan and Abbasi 2001). Values of a quantity called the canopy deposition velocity are required to estimate the rates of sorption of gases by environmental substrates. As part of the ERG2016 analysis, we conducted a series of experiments at Argonne to determine the canopy deposition velocities of hydrogen chloride, sulfur dioxide, chlorine, and ammonia to open water, soils, growing plants and fresh-cut plant materials. The results were used in the calculation of protective action distances (PADs) for spills of these four materials, and in certain cases they reduced the large spill PAD estimates by around 30%. In this section, we briefly describe these experiments and the use of the resulting data in our dispersion modeling. A fuller description of the experiments can be found in a companion report, Freeman et al. (2016).

The experiments had two critical parts:

- Measurement of the areas of the exposed surfaces of samples of different kinds of vegetation and soil and of open water. Rates of sorption vary in proportion to the area of the sorbing surface.
- Confinement of the samples in contact with the air-diluted toxic gases and observation of the changes in the concentrations of the gases versus time. Seventy-two separate gas-to-substrate interactions were studied, each with multiple trials.

3.5.1 Deposition Velocities

Deposition is the transfer of a gas to a surface, and there are several different processes that can result in this material loss from the pollutant cloud. Deposition by rainout occurs when drops of rain capture the gas and carry it down; dry deposition occurs when aerosol particles sorb the gas and settle to the surface; gaseous dry deposition occurs when gases make direct contact with vegetation, soil or open water and their molecules are sorbed. Our experimental program focuses on gaseous dry deposition, as that is the most critical process for TIH plumes in most circumstances in terms of their effect on safe distances estimates. In gaseous dry deposition, the flux F of a gas to a surface equals the product of the concentration C of the gas in the air and its deposition velocity V_d:

$$F = C\,V_d \qquad \text{(Eq. 3.46)}$$

Typical units in the preceding are g m^{-3} for C, g m^{-2} s^{-1} for F and cm s^{-1} for V_d. Deposition velocities summarize the kinetics of sorption. They vary with the nature and condition of the receiving surface and with the weather.

The kinetics of gaseous dry deposition are usually parameterized in terms of deposition resistances, the reciprocals of deposition velocities:

$$R_d = \frac{1}{V_d} \qquad \text{(Eq. 3.47)}$$

The resistance to gaseous deposition to surfaces in the open environment is viewed as arising from the serial combination of smaller resistances that account for different transfer mechanisms:

$$R_d = r_a + r_b + r_c \qquad \text{(Eq. 3.48)}$$

This is equivalent to the following:

$$V_d = \frac{1}{r_a + r_b + r_c} \qquad \text{(Eq. 3.49)}$$

where r_a is aerodynamic resistance that arises in the turbulent layer that extends some tens of meters above the surface, r_b is boundary layer resistance caused by the thin quasi-laminar layer of atmosphere just at the surface, and r_c is the so-called canopy resistance, a property of the plant, soil, or liquid that is sorbing the gas. Canopy resistance depends on the physical, chemical, and biological processes by which the sorption occurs.

Local meteorology causes substantial variations in the aerodynamic resistance r_a. These in turn cause large variations in the overall deposition velocities of gases in the environment (Erisman and Baldocchi, 1994). Fortunately, the aerodynamic resistance can be estimated theoretically and is done in the meteorological database used by CASRAM. Theoretical methods also exist to estimate boundary-layer resistances, though the boundary layer resistance is usually small. No such methods exist for estimating canopy resistances, which are properties of the substrates and the reacting gas. Our experiments were designed to directly measure r_c for use with values of r_a and r_b in the calculation of the deposition velocities of toxic gases.

The experimental approach to r_c relies on the fact that r_a and r_b are inversely proportional to the square or cube of wind speed (e.g., Wanninkhof, 1992). The two are therefore eliminated (or very greatly reduced) if the toxic gas (mixed with air) is vigorously stirred during its contact with the substrate. Stirring minimizes the aerodynamic resistance r_a by eliminating stratification of the gas and minimizes the boundary layer resistance r_b by thinning the layer essentially to zero. Reducing r_a and r_b to negligibility allowed direct measurement of r_c, which varies from one type of vegetation or soil to the next and also, in the case of soils, varies with moisture content.

Canopy resistance to gaseous deposition has practical importance but is itself often viewed as a composite quantity. For example, the canopy resistance of a green leaf can be subdivided and assigned to its different structures. These are its stomata (the pores on its undersurface that allow gas exchange), its mesophyll (the site of photosynthesis inside the leaf) and its cuticle (its waxy top and bottom surfaces). The inherent resistance of a leaf to the uptake of a gas is divided among these structures as follows:

$$r_c = \left(\frac{1}{r_{meso} + r_s} + \frac{2}{r_{cut}}\right)^{-1} \qquad \text{(Eq. 3.50)}$$

where the subscripts refer to stomata, mesophyll, and cuticle. The resistances r_s and r_{meso} are added because the two structures are in series: gases gain access to the mesophyll only through the stomata. Meanwhile, deposition occurs in parallel processes at the two cuticles. Thus, resistances of the different structures of the leaf combine both in series, which requires simple addition of the resistances, and in parallel, which requires addition of the reciprocals of the resistances, just as with electrical resistances wired in series and parallel.

The experiments we conducted here were devised to measure the canopy deposition velocities of toxic gases to different kinds of vegetation and different soils in varied degrees of hydration. The reciprocals of these deposition velocity values, r_c, can be combined with r_a and r_b from other sources to estimate the deposition resistance R_d and its reciprocal, the deposition velocities V_d of the gases to the different substrates.

3.5.2 Experiment Details

3.5.2.1 Vegetation Samples

Four common kinds of vegetation—white clover (*Trifolium repens*), shamrock (*Oxalis regnellii*), white spruce (*Picea glauca*), and Kentucky bluegrass, (*Poa pratensis*) were cultivated or collected for use. Leaves of clover and shamrock were detached from the growing plants for immediate use. Sprigs of spruce were similar detached. Circular plugs of rooted bluegrass of known area and stem length were cut from sod. These living plugs were supported in a beaker having the same diameter as the plug.

The leaf areas of the shamrock and clover samples were determined photographically using the image analysis program ImageJ.[6] Leaves were separated from the living plants, placed on white paper, covered with a transparent acrylic sheet to flatten them, and photographed with a digital camera. The photos included a ruler to indicate scale. They were edited using ImageJ to produce black and white shadow images.

The program then scaled these images to the standard to provide one-sided leaf areas. Values were doubled to give total leaf areas. These computed areas were combined to give an average leaf area for all of the samples of the clover and another average of all of the shamrock plants.

Figure 3.10 shows a typical photo and its corresponding shadow photo.

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[6] Freely available from the U.S. National Institute of Health. See http://imagej.nih.gov/ij/docs/index.html. ImageJ was developed to calculate the areas of colonies of bacteria growing on flat surfaces. It has been widely used to calculate leaf and petal areas.

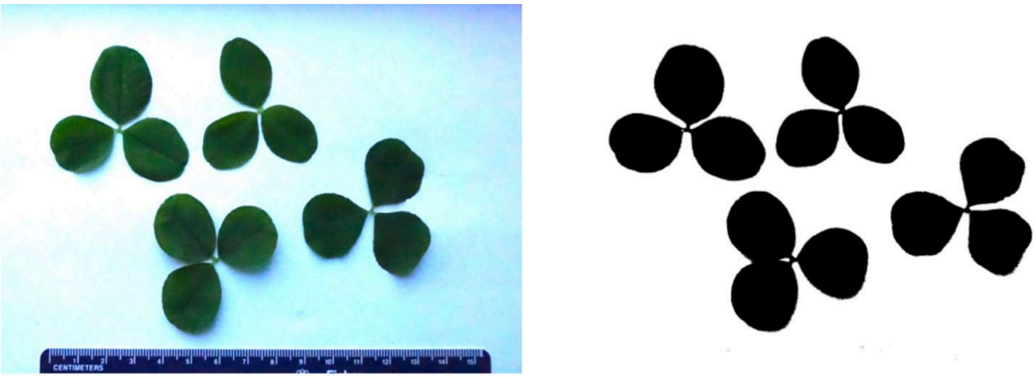

Figure 3.10 At left is the starting photograph for the determination of the area of a group of clover leaves. The ruler used to give the scale appears at the bottom of the image. At right is the corresponding shadow image from ImageJ.

Similarly, the needles on sprigs of conifer were counted and the surface area estimated as the product of this number and the surface area of a typical needle. To this was added an estimate of the area of the woody portion of the sprig. The plugs of Kentucky bluegrass sod were transferred to plastic beakers. Their sorbing area was estimated by multiplying the area of the mouth of the beaker by a leaf-area index of 7. This figure was obtained by counting the blades of grass and multiplying by the average of the measured areas of typical blades. The leaves or sprigs were positioned in clean petri dishes with stems propped on the edge in a way that exposed both sides of the leaf to the atmosphere. Delays between the cutting of leaves or sprigs and the beginning of their exposure to the toxic gases were minimized, never exceeding 30 minutes, so that the leaves were still actively transpiring in the test chamber.

3.5.2.2 Sources and Preparation of the Soil Samples

The soil studies used 25 g portions of three soils gathered at widely separated U.S. locations.[7] They were labeled Soil 6, Soil 7, and Soil 8. The pH of each soil sample was determined by a standard method. All were acidic, with a pH between 5.6 and 5.9.

The moisture contents of the soils were controlled. They were dried at 115°C for a minimum of four hours and cooled with the exclusion of airborne moisture. Samples having moisture contents of 2.0, 4.0 and 8.0% by mass were then prepared by adding appropriate amounts of distilled water to weighed portions of the dry soil. These samples were sealed in heavy-duty plastic bags and kneaded thoroughly to assure uniform distribution of the moisture. Experiments were also performed on the dried soils, which were taken to contain 0.0% water by mass.

Soil samples were arranged in petri dishes so that their surfaces were flat, finely grained and uniform in granularity (as judged by inspection). The sorbing area of the soil samples was taken to equal 60.5 cm^2, the face area of the petri dishes in which they were

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[7] The soil samples were kindly donated to the project by Dr. Laura Skubal of Argonne National Laboratory.

contained. Samples of distilled water were exposed to the gases in petri dishes of the same size.

3.5.2.3 The TIH Gases

The four toxic gases were acquired from Airgas Incorporated. Chlorine was supplied as a 1.976% (by volume) mixture in argon, ammonia as a 99.9% gas, sulfur dioxide as a 1.250% mixture with air, and hydrogen chloride as a 3.01% mixture in nitrogen. The gases were used as supplied. Portions were transferred from their cylinders into plastic bags just before use. Appropriate volumes were then drawn from the bags into syringes and injected into the experimental system at the start of the experimental runs.

3.5.2.4 Fumigation Chamber and Sampling Loop

The fumigation chambers were glass vacuum desiccators modified to allow for inlet and outlet of gases at well-separated locations. The inlet port was the original serrated tube at the rotatable head of the desiccator. The outlet port was a new tube extending through the top of the head nearly to the bottom of the desiccator. The volumes of the chambers were all between 9.1 and 9.2 L, as determined by weighing the water required to fill them, and were taken to equal 9.15 L. The use of any one chamber was restricted to a single gas.

Lengths of Tygon tubing connected the outlet and inlet of the fumigation chamber to the inlet and outlet of a Dräger Polytron 7000 unitized pump/sensor. The Dräger unit pumped the gaseous contents of the chamber through the sampling loop as it measured the concentration of the toxic gas at 10 s intervals. A second in-line sensor in the same loop concurrently measured the temperature and humidity. (See Figure 3.11.) The flow rate of the gas through the sampling loop was 775–900 mL per second (as measured by water displacement). Ports in the sampling loop allowed injection of the toxic gases and access to an electrical line to power an interior fan. The volume of the sampling loop was negligible compared to the volume of the fumigation chamber. Experiments employing this "non-steady-state flow-through" or "closed-dynamic-chamber" method have been conducted previously (Griffiths and Smith, 1990); it is the (Cowan et al. 2014).

The starting air was outside winter air heated to a room temperature of 21°C–23°C and had a relative humidity of approximately 20%. The humidity in the system was not controlled but was monitored. It was found to rise slightly during some runs as the environmental materials lost moisture.

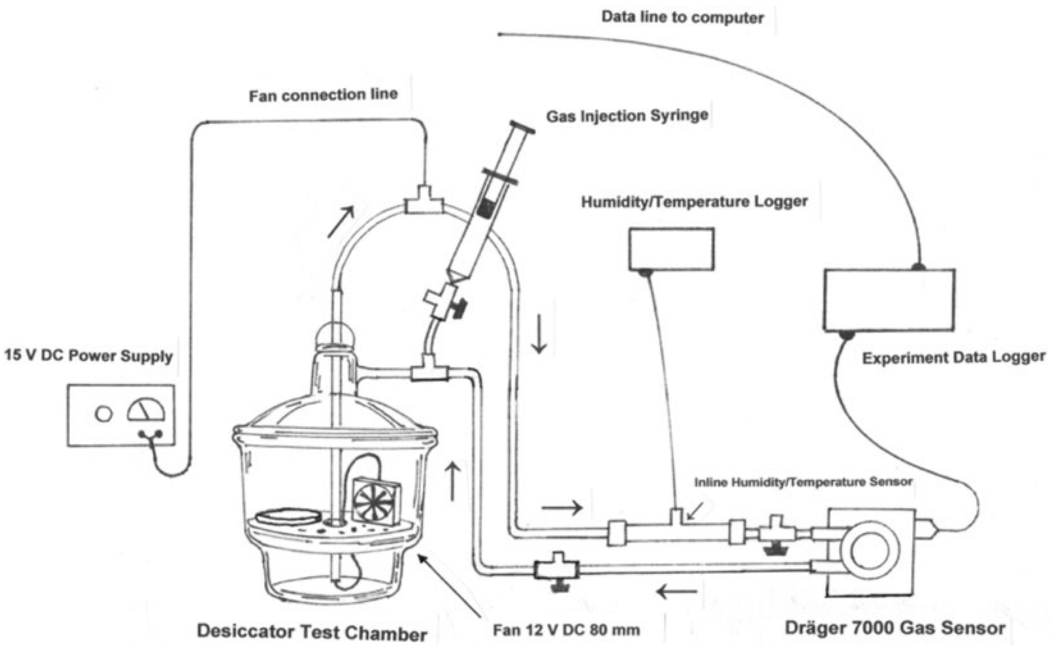

Figure 3.11 The experimental set-up consisted of a large-volume fumigation chamber connected to a small-volume sampling loop. The chamber contained the soil or vegetation along with a powerful fan. The sampling loop included a combination pump/sensor that circulated gas through the loop quickly enough to turn over the gas in the fumigation chamber every 10 to 12 seconds. The action of fan eliminated aerodynamic and boundary layer resistance to sorption.

3.5.2.5 Experimental Procedure

Runs started with the positioning of a freshly prepared sample (held in or on a 10-cm diameter petri dish) on an elevated porcelain plate within the chamber, as shown in Figure 3.11. The lid was then sealed in place (using silicon grease), and the fan, the detector pump, and the data loggers were started. Immediately, a pre-calculated quantity of toxic gas was injected into the sampling loop through a port located downstream from the detector and upstream of the fumigation chamber. The sampling pump quickly drew the toxic gas into the fumigation chamber where the fan mixed it with the air. The concentration of the toxic gas in the closed system was then tracked as a function of time as the sampling pump continued to circulate the gaseous contents of the chamber past the detector. Concentration data were recorded at 10 s intervals. The maximum duration of the runs was 1800 s. Concentrations of the toxic gases often fell rapidly, dropping to less than 10 percent of their starting values well before 1800 s had elapsed. Runs in which most of the toxic gas was removed in the early seconds were usually discontinued before their scheduled conclusion.

Two chambers were used in alternation in a series of runs to allow time for thorough venting of residual adsorbed gas before a subsequent run. The samples of vegetation were examined for signs of damage after their exposure to the toxic gases. Such damage was never evident.

The Dräger sensor could not accurately measure the concentrations of the gas above certain maxima. These maxima were used as initial concentrations during the experimental runs: 50 ppm for Cl_2, 400 ppm for NH_3, 100 ppm for SO_2, and 100 ppm for HCl. Because the starting concentrations of the toxic gases were on the order of hundreds of parts per million, only small volumes of the toxic gases were injected, even though the gases were already diluted. For example, Cl_2 was supplied at a concentration of 2.0% percent by volume (20,000 ppmv) in argon, and the upper limit of the detector was 50 ppm. Obtaining a starting concentration of 50 ppmv in the fumigation systems, which had volumes of approximately 10 L, required the addition of only about 25 mL of 2.0% Cl_2. Such an injection of gas increased the initial pressure in the system by only 0.25 percent, which is less than changes in atmospheric pressure caused by the weather.

3.5.2.6 Determination of the Deposition Velocities

As mentioned, the goal of the experiments was to determine the deposition velocities of toxic gases to typical substrates under environmental conditions. The deposition velocities decreased as uptake lowered the concentration of the toxic gases in the closed experimental systems. The *initial* deposition velocities of the toxic gases to the different substrates were to be used in the estimation of PADs. Reliable initial deposition velocities were adduced by analyzing the kinetics of the decrease.

The average rate of uptake of any of the toxic gases over an interval of time was the change in its concentration divided by its average concentration over the interval:

$$\bar{u} = \frac{2(C_1 - C_2)}{(C_1 + C_2)\,(t_2 - t_1)} \qquad \text{(Eq. 3.51)}$$

where $\bar{u}$ is the interval averaged uptake rate, $(t_2 - t_1)$ represents the duration of the interval (10 s in the experiments), and C_1 and C_2 are the concentrations of the toxic gas at times t_1 and t_2 respectively. It can be shown that the (interval-averaged) deposition velocity is the following:

$$V_d = \frac{V}{A}\bar{u} \qquad \text{(Eq. 3.52)}$$

where the factor V/A is the volume of the closed experimental system divided by the sorbing area of the substrate. The dimension of the rate of uptake $\bar{u}$ is the reciprocal of time. Multiplying the dimension of V/A by length results in velocity.

The difference C_1 - C_2 and the sum $C_1 + C_2$ both tend toward zero as the substrate takes up the toxic gas in the closed system. But C_1 - C_2 is always smaller than $C_1 + C_2$; therefore, the interval-average rate $\bar{u}$ and the interval-averaged velocity V_d both tend toward zero. The fumigation runs gave the concentration of the toxic gases in parts per million by volume (ppmv) at 10 s intervals. Use of the preceding equations generated $\bar{u}$ and V_d for each of the 10 s intervals that composed the duration of the runs.[8]

The resulting data is summarized in Table 3.10 and Table 3.11 below. Additional details of the experimental results and data analysis are discussed in Freeman et al. (2016). These tables provide values for the initial values of V_d for the four toxic gases, obtained by multiplying the initial rates of uptake by the size factor.

Table 3.10 Initial canopy transfer velocities (cm/sec) in for uptake of gases by vegetation.

Substrate	Size Factor (cm)	HCl	SO_2	CL_2	NH_3
Clover	9150/ 81	0.155	0.0148	0.286	0.0302
Conifer	9150/ 192	0.0667	0.102	0.102	0.152
Grass	9150/ 111	0.645	0.0751	0.418	0.111
Shamrock	9150/ 101	0.0503	0.00915	0.0790	0
Water	9150/ 69.5	0.982	0.151	0.122	0.337

Table 3.11 Initial canopy deposition velocities (cm/sec) for the uptake of gases by soils.

Substrate	Size Factor	HCl	SO_2	Cl_2	NH_3
Soil 6 0% H_2O	9150/69.5	0.682	0.200	0.469	0.966
Soil 6 2% H_2O	9150/69.5	0.948	0.279	0.456	0.883
Soil 6 4% H_2O	9150/69.5	1.24	0.395	0.550	0.965
Soil 6 8% H_2O	9150/69.5	1.51	0.462	0.666	0.469
Soil 7 0% H_2O	9150/69.5	0.702	0.204	0.495	0.764
Soil 7 2% H_2O	9150/69.5	0.910	0.344	0.633	0.860
Soil 7 4% H_2O	9150/69.5	1.30	0.402	0.754	0.588
Soil 7 8% H_2O	9150/69.5	1.63	0.373	0.781	0.698
Soil 8 0% H_2O	9150/69.5	0.610	0.275	0.399	0.529
Soil 8 2% H_2O	9150/69.5	0.795	0.409	0.523	0.783
Soil 8 4% H_2O	9150/69.5	1.26	0.494	0.673	0.603
Soil 8 8% H_2O	9150/69.5	2.00	0.711	0.786	0.312

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[8] If the interval of time is infinitesimal, then $t_2 - t_1 = dt$, $C_1 - C_2 = dC$ and $C_1 + C_2 = 2C$, from which $V_d = \frac{V}{A}\left(\frac{1}{C}\right)\left(\frac{dC}{dt}\right)$ = instantaneous deposition velocity.

These results are reasonable in the light of previous research. Kerstiens et al. (1992) report a survey of 14 papers in which the overall transfer velocities of SO_2 to vegetation were given or were implicit in other data. These transfer velocities range between 0.0028 and 0.39 cm s^{-1}, which is comparable to the range of canopy transfer velocities for SO_2 in the preceding table. Dillon (2009) draws on the work of Wesely (1989) to estimate canopy resistance r_c for acidic moderately reactive gases to be on the order of 700 s m^{-1}. This is equivalent to a canopy transfer velocity of 0.14 cm s^{-1}, which is comparable to many of the values obtained here. Highly reactive gases have much higher transfer velocities, as reflected in some of the data for HCl and Cl_2.

3.5.3 Derived Canopy Resistances

The final step in translating the observed experimental deposition velocities into canopy resistances that can be applied in CASRAM is to map the experimental values into land use categories employed in the CASRAM meteorological model. These are provided for 15 land use types in Brown and Dunn (1998). The derived values for the four TIH gases under consideration are provided in Table 3.12. Note that these are simply the inverse of V_d as described in Eq. 3.49 (r_a and r_b are both set to zero as the chamber was agitated and well mixed).

Table 3.12 Derived canopy resistances (s/m) for land use categories.

Land Use Category/Soil Moisture	HCl	SO_2	Cl_2	NH_3
Broadleaf evergreen forest	1592	9208	1023	8801
Broadleaf deciduous forest	1592	9208	1023	8801
Broadleaf and needleleafed mixed	1378	9164	869	4992
Needleleaf deciduous forest	1592	9208	1023	8801
Needleleaf evergreen forest	1392	8887	930	1985
Tundra	147	490	220	166
Broadleaf shrubs	1989	10929	1266	11038
Grassland/prairie	401	4045	295	2089
Field crops	929	6333	618	5067
Suburban areas	930	6339	618	5072
Urban areas	930	6339	618	5072
Bare areas	106	354	174	135
Water	102	660	821	297
Soil low moisture	66	217	128	104
Soil high moisture	147	490	220	166

3.5.4 Application in the CASRAM Dispersion Model

Employing the data in Table 3.12 coupled with (1) aerodynamic resistance r_a (Brown, 1997; and Brown and Dunn, 1998) provided by SEBMET, (2) simple empirical estimates for r_b (which is usually small), and (3) the leaf area index provided by our land use database as a function of vegetation class and month (see Section 3.2.2.1), we estimate the deposition velocity V_d as a function of meteorology, location, month of year, and soil moisture conditions (wet or dry). In this process, the leaf area index provides the amount of vegetation material available for reaction. Through analysis of the vegetation and soil layers, we estimate an overall deposition velocity combining the soil and vegetation layers. Deposition velocity values range from near zero (< 0.01 cm/s) to up to 10 cm/s for cases with a large amount of vegetation (leaf area indices above 5).

Given the deposition velocity V_d, the deposition rate D of the cloud (in kg/s) is given by the following:

$$D(t) = \int_{-\infty}^{\infty}\int_{0}^{\infty} V_d C(x,y,z=0)dxdy \qquad \text{(Eq. 3.53)}$$

which, for a continuous point source (see Equation 3.20 for example), can be simplified to the following:

$$D'(x) = \frac{Q}{U}\int_{-\infty}^{\infty} V_d C(x,y,z=0)dy \qquad \text{(Eq. 3.54)}$$

where D' is the deposition rate per meter downwind at distance x.

Several approaches are used to apply deposition velocities in atmospheric dispersion models (e.g., Jonsson et al. 2005). The simplest is the so-called source depletion approach (van der Hoven, 1968) in which the source strength is adjusted downward to account for the depletion of the deposited mass from the plume. Here, the relative source strength versus time (or rather distance) is provided by the following integral equation, which is easily solved numerically:

$$\frac{dQ(t)}{dt} = \int_{-\infty}^{\infty}\int_{0}^{x} V_d C\big(x,y,z=0\big)dxdy \qquad \text{(Eq. 3.55)}$$

This formulation is easy to implement but has the disadvantage that the surface depletion at any point is instantly well mixed throughout the atmospheric boundary layer. This is generally a poor assumption and can lead to significant errors, especially in stable atmospheric conditions.

A significantly more sound approach is to consider the problem using a surface depletion approach (Horst, 1977), whereby the deposited amounts are treated as material sinks that can be continually superimposed,[9] providing separate “negative” plumes

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[9] Superposition of the solutions is possible as the differential equations governing our dispersion relationships are linear in nature.

originating at each downwind increment when solved numerically. Formally, this can be represented for a continuous source:

$$C(x,y,z=0) = \frac{QC_{ref}(x,y,z=0)}{U} - \frac{1}{U}\int_{-\infty}^{\infty}\int_{0}^{x} V_d C(\eta,\varphi,z=0)C_{ref}(x-\eta,y-\varphi,z=0)d\eta d\varphi$$

(Eq. 3.56)

where C_{ref} is the reference concentration, defined as the concentration field that would be present without deposition.

When implemented within the context of our overall dispersion model, the equations employed for C_{ref} follow directly from the methods described in Section 3.4.2.1. A very similar approach is used to adapt this to the dense gas dispersion model described in Section 3.4.2.2. As discussed in Section 5, the deposition amounts that affect the PAD estimates range from almost negligible for cases with low deposition velocities, high wind speeds, or deep atmospheric boundary layers, to over 75% deposition for certain low wind speed nighttime cases. Deposition amounts also closely follow the health end point, as that governs how low the concentration must drop to define the protective action distance. As such, the effect is much greater for chlorine or sulfur dioxide than for ammonia, as the distances and therefore areas that account for the overall deposition losses are much greater. The overall effect of inclusion of chemical reactivity induced dry deposition is further discussed in Section 5.

4. HEALTH CRITERIA

Over the past 35 years, various health criteria have been used to develop IIZs and PADs in the ERG. 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 airborne releases of toxic materials and hence formed the basis for defining PADs. Use of the ERPGs was based on a number of factors, including the high quality of the documentation, the consensus approach with 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. In ERG2024, as in the previous four ERGs, 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, and many additional values were published between 2012 and 2020, so now AEGLs are a large majority of the protective action health criteria in the ERG2020 and ERG2024 analyses.

For substances without AEGL or ERPG values, data on acute inhalation lethality in animals are used to develop the PADs. The acute inhalation data are the 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 used LC_{50}-based values. However, for ERG2020 and ERG2024, just 20% of the list used these lethality data for PAD estimation. 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

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

4.1.1 Acute Exposure Guideline Levels

AEGLs are intended to determine short-term exposure limits for acutely toxic chemicals for use in chemical emergency planning, prevention and response programs. The National Academies (formerly National Academy of Science [NAS]) is the final peer reviewer of AEGL values and methods.

Until 2011, AEGLs were developed through the National Advisory Committee for Acute Exposure Guideline Levels for Hazardous Substances (NAC/AEGL Committee), a federal advisory committee. The process consisted of four basic stages, based on the review level and concurrent status of the AEGL values: (1) draft AEGLs, (2) proposed AEGLs, (3) interim AEGLs, and (4) final AEGLs. After AEGL values were drafted and approved by vote by the NAC, they were considered "proposed" and published in the *Federal Register* for review and public comment (EPA 2021). Once public comments were addressed, and the NAC committee again voted on the specific values, they were considered "interim" and submitted to the NRC AEGL subcommittee for review and comment. After the NRC subcommittee review, the AEGL values were considered "final" and were published by the NRC. A fourth designation, "holding," was assigned to chemicals that have been reviewed but for which there was deemed to be insufficient data to develop AEGL values.

When the NAC/AEGL Committee's federal advisory committee charter expired in October 2011, the current process was developed to finalize interim AEGLs. At that point, the AEGL program had successfully addressed all but five of the 329 chemicals listed in the AEGL chemical priority lists. Budget constraints resulted in redirecting funding towards the finalization of AEGL values through the NAS Subcommittee, and the NAC/AEGL Committee was eliminated. The new process focuses on finalizing interim AEGL chemicals through the NAS with the limited resources available.[10]

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:

- 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

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[10] Details of the current AEGL process can be found at https://www.epa.gov/aegl/process-developing-acute-exposure-guideline-levels-aegls#:~:text=The%20process%20consists%20of%20four,and%20(4)%20final%20AEGLs.

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 July 2019, the deadline for inclusion in the ERG2020 analysis, the NRC had published final AEGLs for 65 chemicals, interim AEGLs for 98 chemicals, and proposed AEGLs for 12 chemicals. For the development of PADs, only final and interim AEGL-2 values for 1 h, 30 min and 15 min exposure periods were used. These values were used in the ERG2024.

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 AEGLs, data from animal studies are often used as the basis for the ERPG concentrations. Like AEGLs, ERPGs are defined for three effect levels:

- 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 2018, AIHA has published ERPG concentrations for 150 different chemicals (AIHA 2018). Typically, AIHA adds about two or three 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 last revised in 2016, and occupational health guidelines. 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 IDLH values 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 LH 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

An 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." The preferred EPA procedure to derive LOC values is to divide the IDLH by 10 (EPA 1987). Since IDLHs were developed for the purpose of selecting respirators in the event of an emergency in the workplace, the tenfold uncertainty factor is intended to account for the greater sensitivity of the general population versus the worker population. When IDLHs are unavailable, estimated IDLHs based on LC_{50}/100 or lLD_{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-C [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 IIZs 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. However, there are also several important differences between 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 primarily 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 the ERG. However, for substances without AEGL or ERPG values, TEEL-2 levels (TEEL-2 is the same as the ERPG-2, 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} and LC_{LO}; 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 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 the selection of protective action health criteria is illustrated in Figure 4.1. It is identical to that used in the ERG2016 and ERG2020 analysis. Final AEGL-2 values are the preferred health criteria.

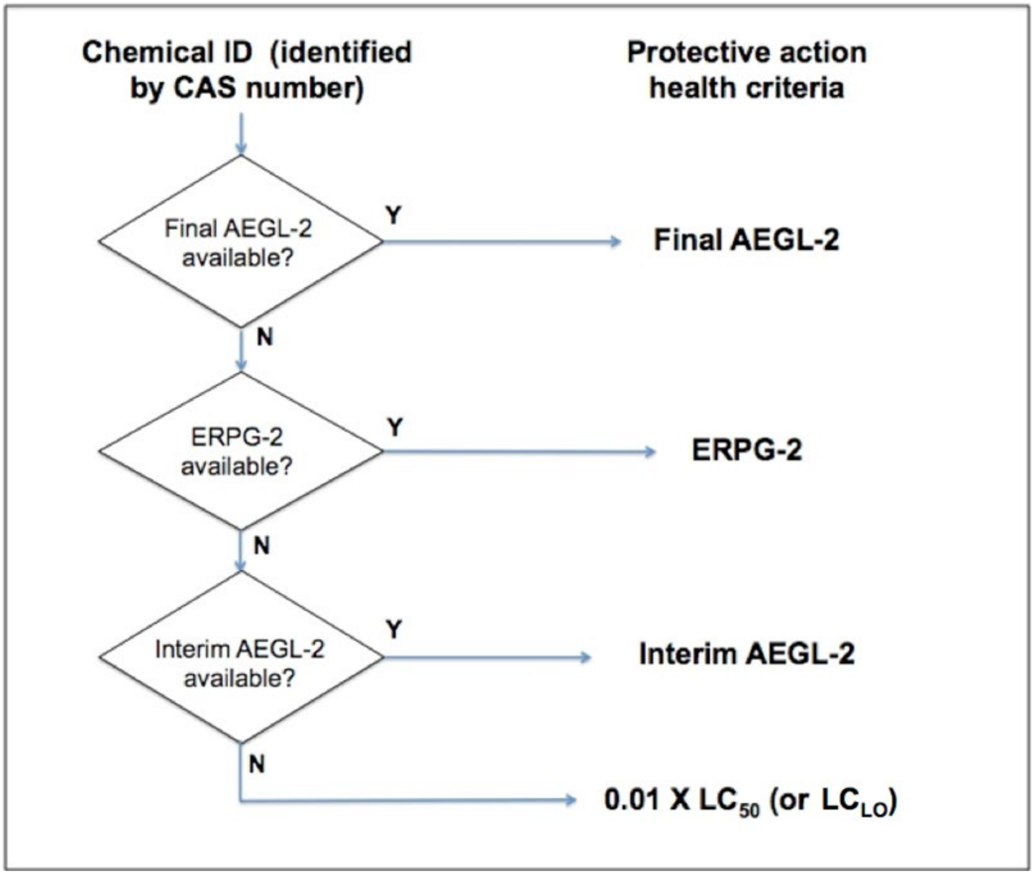

Figure 4.1 Hierarchy for selection of protective action health criteria.

In the absence of final AEGL-2 values, ERPG-2 values, interim AEGL-2 values, and acute inhalation lethality data, in that order, were used to identify the health criteria used to determine PADs. We note that health criteria for roughly half of our TIH list changed between 2008 and 2012. Fewer changes occurred between 2012 and 2020, though many interim AEGL values became final and subsequently replaced the previously used ERPG values. Many of the changes were fairly minor: Final AEGLs replaced previously employed ERPG-2 values (for 12 materials), and most of these differences were less than a factor of 2. However, notable changes were for acrylonitrile and many isocyanates, where final AEGL values were published that were much more conservative than the previously used ERPG-2 values. 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, 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 animals, adjusted to approximate 1 h AEGL or ERPG values. LC_{50} data are also used in part for determining the IID, as described in Section 2.5. When LC_{50} data were not available, the 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 of less than 30 min, concerns over chamber equilibration time (T_{99}) are increased. For exposures of more than 4 h, there are increased concerns 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, would result in the following relationship:

$$W = c\, t \qquad \text{(Eq. 4.1)}$$

where W is a constant dose specific to 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:

$$W = (c - a)t^b \qquad \text{(Eq. 4.2)}$$

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:

$$LC_{50}\ (for\ T_1) = LC_{50}\ (for\ T_0)\ [T_0/T_1]^{1/n} \qquad \text{(Eq. 4.3)}$$

where

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

T_0 = experimental exposure time

n = constant

Klimisch et al. (1987), citing Doe and Milburn (1983), found that for many chemicals, n centers on 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 using the following quadratic dose–response function:

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

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

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

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. More information can be found at http://www.cdc.gov/niosh/rTecs/.

Based on these considerations, newer peer-reviewed U.S. data sources are 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 2012). Therefore, the use of these less than superior data for some chemicals was retained for our PAD analysis as this was considered preferable to having no PAD values for those chemicals.

The data sources for the chemical-specific health criteria given in Appendix C include AEGL values, ERPG values (AIHA 2018), and LC_{50} and LC_{LO} data from several sources, including Sax data (Lewis 2012), 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 and the time-adjusted LC_{50}/100 are reasonable estimates of 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 have indicated that when 1 h ERPGs are extrapolated to values of shorter duration, the potential effects of peak, high-level exposures could be minimized. A default value of 2 was suggested for these purposes. Therefore, to estimate 15 min protective health criteria based on 1 h values, a factor of 2 was used to estimate 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 less than 5% of the TIH chemicals in ERG2024.

4.3 SUMMARY

A summary of the basis for health criteria for the 163 chemicals included in the ERG2024 analysis appears in Table 4.1. Documentation of the health criteria for individual chemicals is presented in Appendix B:. For 109 chemicals (67%), AEGL values or AEGLs for structurally similar chemicals formed the basis of the health criteria. For 19 chemicals (14%), ERPGs or ERPGs for a structurally similar chemical formed the health criteria basis. For 28 chemicals (17%), LC_{50} values or LC_{50} values for a structurally similar chemical were used to develop the health criteria. For four chemicals (~2%), LC_{LO} values formed the basis of the health criteria. For one chemical, oral toxicity data were used to estimate an inhalation LC_{50} and derive the health criteria.

Table 4.1 Summary of the basis for health criteria used to prepare ERG2024.

Basis of Health Criteria	No. of Materials	Percentage
Final AEGL for chemical of concern	80	
Interim AEGL for chemical of concern	23	
Final AEGL for structurally similar chemical	6	
Interim AEGL for structurally similar chemical	0	
Subtotal for AEGLs	109	67
ERPG for chemical of concern	19	
ERPG for structurally similar chemical	4	
Subtotal for ERPGs	23	14
LC_{50} for chemical of concern	25	
LC_{50} for structurally similar chemical	2	
Estimated LC_{50}[a]	1	
Subtotal for LC_{50} values	28	17
LC_{LO} for chemical of concern	4	2
Total	163	100

as 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.

Through the continued efforts of the AIHA ERPG committee, new ERPGs are developed annually. 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 Protective Action Distances, 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 ERPGs become available for chemicals in the Table, the values will be incorporated into the development of isolation zones and PADs in future editions of 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 2015). 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 2015). This is the concentration that should not be exceeded during any part of 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 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 2018). 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 lethal 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 hours.

OSHA PEL ceiling: Occupational Safety and Health Administration permissible exposure limit ceiling (OSHA n.d.). 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, including the experimental data employed, and the health criteria that define the safe distance based on dilution of the plume as it progresses downwind from the release site. This section summarizes these results and discusses the presentation of the distances in Tables 1 and 3 in the Green Pages of ERG2024. These tables appear in Appendix A[11] and Appendix B, respectively, and are in the same general form as Tables 1 and 3 in ERG2020, although the distances themselves are updated and, in few cases, substantially different.

We also discuss comparisons with other measures and experimental studies conducted before and during the 2020 update cycle. Section 5 concludes with a few potential extensions of this analysis for situations in which more information (in addition to the spill size and whether it is day or night) is immediately available, as summarized from previous work. Readily discernable details, such as those illustrated, could be the basis for possible extensions of the ERG adapted for real-time use, including simple cell phone or personal digital assistant (PDA) applications.

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 Tables 1 and 3 referenced above. This set of incidents accounts for variability in container type, incident type, release amount (typically based on container type, accident severity, and chemical properties), location, time of day, time of year, and meteorology. Each of these scenarios was evaluated using detailed emission rates 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 the night and whether they involve small (≤55 gal) or large (>55 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.

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[11] Appendix A provides the composite large spill distance for all materials. As presented in the ERG, large spill entries for the six materials appearing in Table 3 have the entry "Refer to Table 3."

5.1.1 Generation of Table 1 Protective Action Distances

To illustrate the application of the statistical results in the development of ERG2024 Table 1, safe distance distributions for small chlorine releases (a Hazard Zone B gas), large phosphorus trichloride releases (a Hazard Zone B liquid), and large calcium phosphide releases (a water-reactive material) are shown in Figure 5.1-5.6 (ERG2020 data are used in these examples and subsequent tables as the method of statistical analyses has not changed between guide publications). Chlorine (small spill accidents only) is shown because it is the second most common TIH material involved in transportation chemical accidents (Table 5.1). As noted in Table 5.2, the corresponding small spill distances for ammonia are very small and therefore are omitted from this illustration. Phosphorous trichloride is shown as it is a commonly transported liquid, and calcium phosphide because it is a potent phosphine emitter and therefore one of the more hazardous water-reactive materials. Large chlorine and ammonia releases for rail tank cars are discussed in the next section, and distributions are broken out for different wind speeds, as in ERG2024 Table 3.

Distributions are separated according to spill size (large or small) and time of day (day or night), paralleling their entries in the Table. In all six 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 Figure 5.1–5.4). Figure 5.1 and Figure 5.2 provide examples of safe distance estimates at several percentiles for small chlorine spills. Figures 5.3 and 5.4 and Table 5.3 provide examples of corresponding data for phosphorous trichloride, a commonly transported Hazard Zone B liquid, and for calcium phosphide spills into water (for both large and small spills) in Figures 5.5-5.6 and Table 5.4.

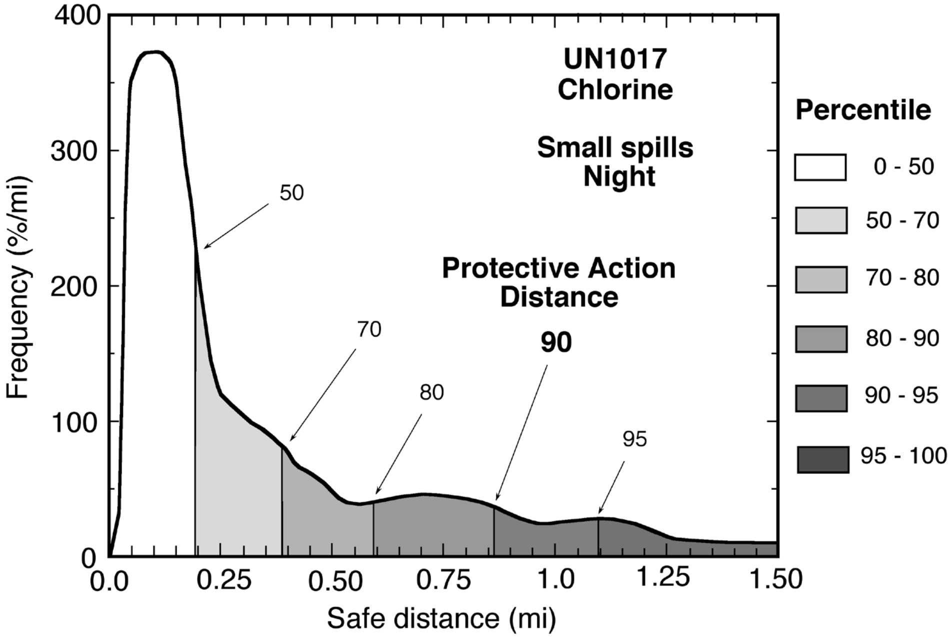


Figure 5.1 Frequency of safe distances for small nighttime chlorine spills as determined in the ERG2020 analysis.

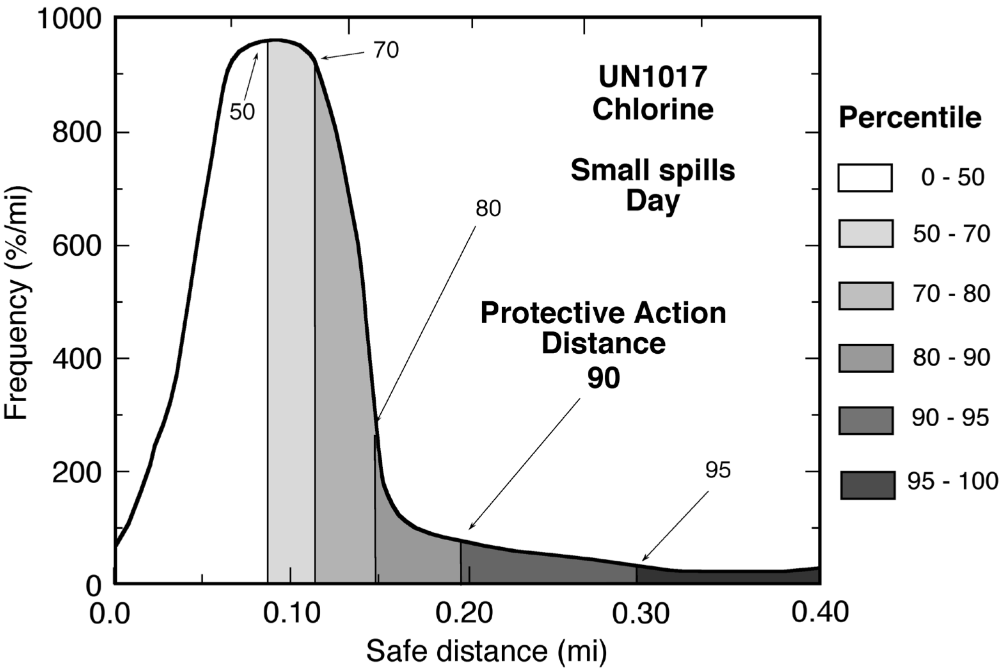


Figure 5.2 Frequency of safe distances for small daytime chlorine spills as determined in the ERG2020 analysis.

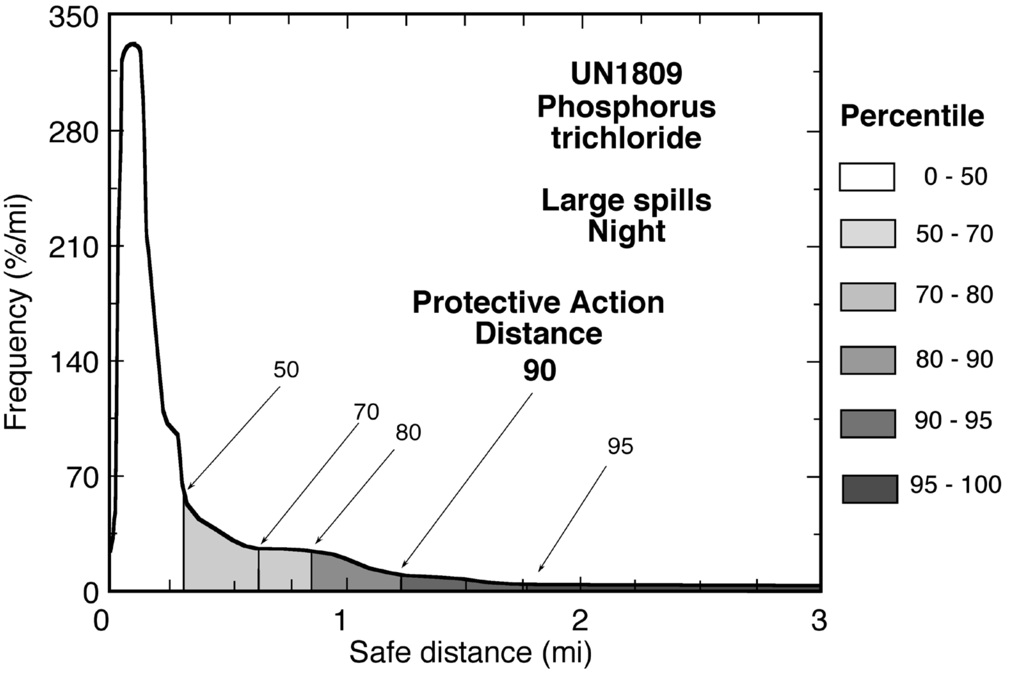


Figure 5.3 Frequency of safe distances for large nighttime phosphorus trichloride spills as determined in the ERG2020 analysis.

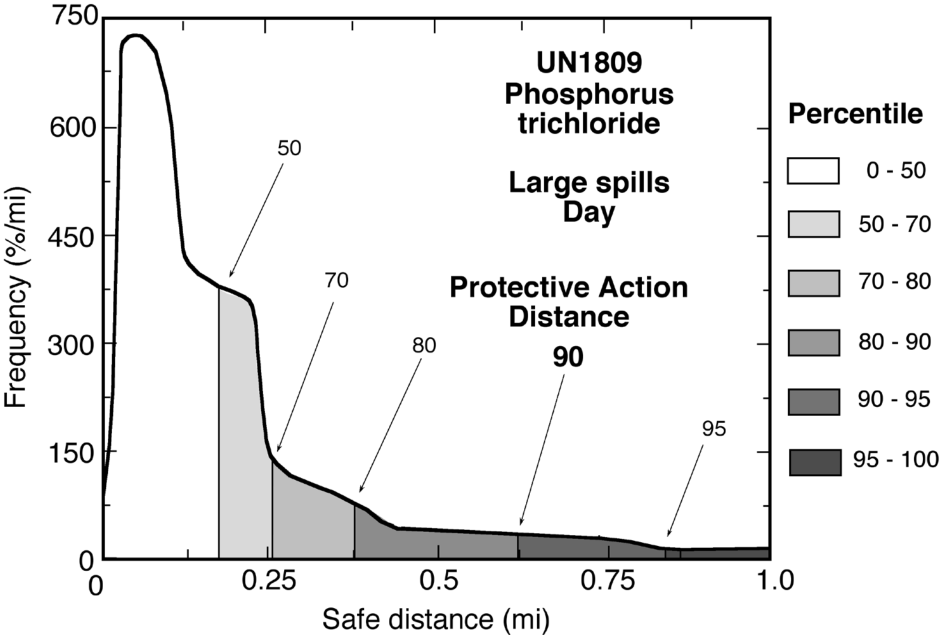


Figure 5.4 Frequency of safe distances for large daytime phosphorus trichloride spills as determined in the ERG2020 analysis.

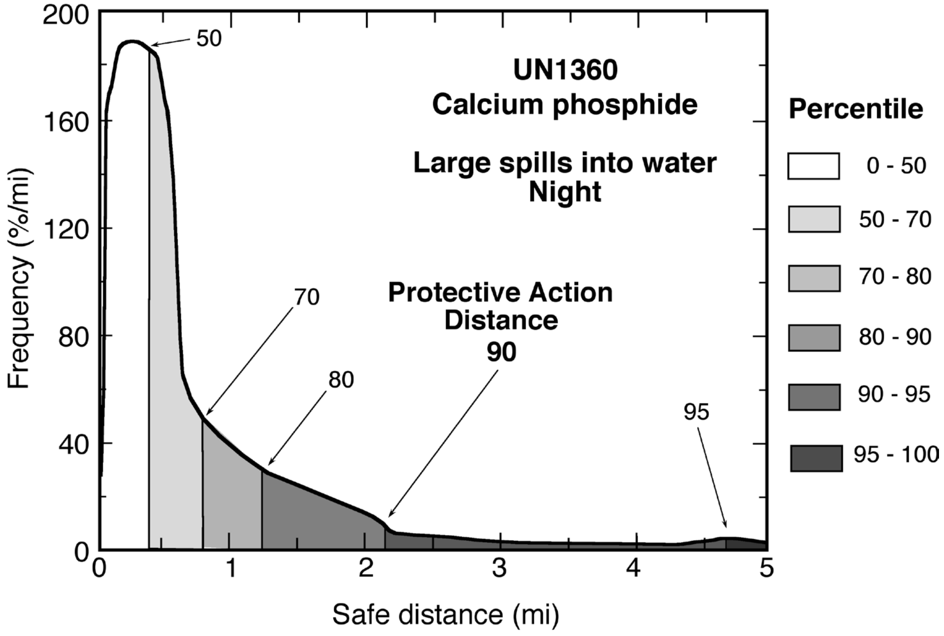


Figure 5.5 Frequency of safe distances for large nighttime calcium phosphide spills into water as determined in the ERG2020 analysis.

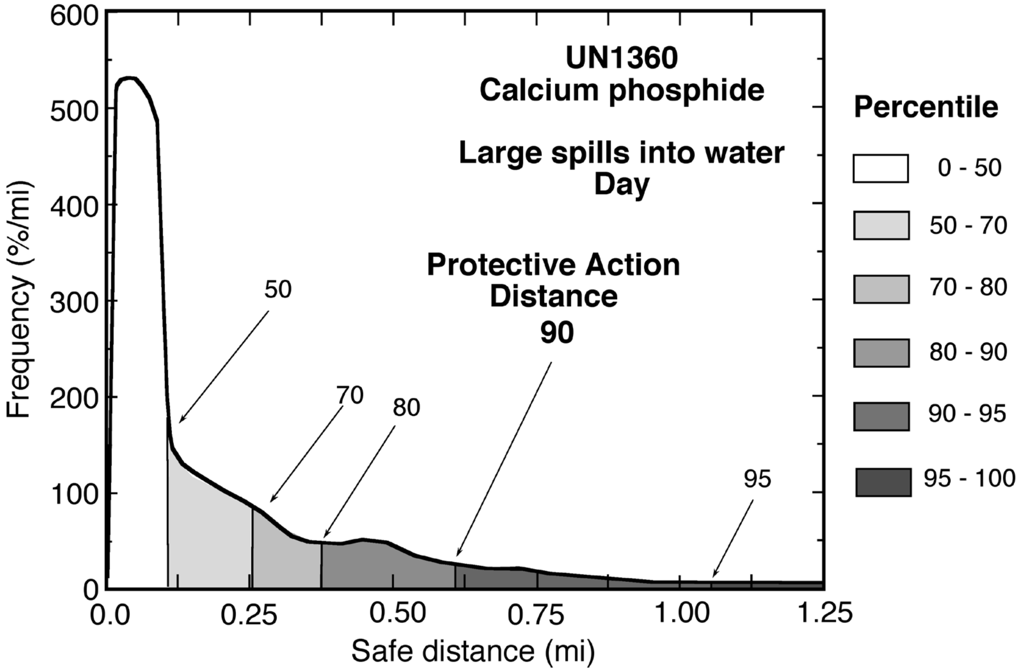


Figure 5.6 Frequency of safe distances for large daytime calcium phosphide spills into water as determined in the ERG2020 analysis.

Table 5.1 Safe distances at several percentiles for small chlorine (UN 1017) releases as determined in the ERG2020 analysis.

		Safe Distance (mi) at Percentile					
Release Size	**Time**	**50**	**70**	**80**	**90**	**95**	**99**
Small	Day	0.09	0.11	0.13	**0.18**[a]	0.29	0.88
	Night	0.19	0.38	0.59	**0.86**	1.08	1.46

[a] Bold values indicate the PADs in the ERG2020, which correspond with the 90th percentile values for the individual categories.

Table 5.2 Safe distances at several percentiles for small ammonia (UN 1005) releases as determined in the ERG2020 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	0.09
	Night	0.02	0.04	0.06	**0.09**	0.13	0.24

[a] Bold values indicate the PADs in the ERG2020 that correspond with the 90th percentile values for the individual categories (rounded up to nearest 0.1 mi).

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 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.

Example results for phosphorous trichloride in Table 5.3 are for land-based releases only. A separate set of safe distance distributions was developed for spills of calcium phosphide into water (Table 5.4).

Table 5.3 Safe distances at several percentiles for land-based phosphorous trichloride (UN 1809) releases as determined in the ERG2020 analysis.

		Safe Distance (mi) at Percentile					
Release Size	**Time**	**50**	**70**	**80**	**90**	**95**	**99**
Small	Day	0.05	0.07	0.08	**0.11**[a]	0.13	0.36
	Night	0.08	0.14	0.20	**0.33**	0.45	0.72
Large	Day	0.16	0.26	0.37	**0.62**	0.85	1.59
	Night	0.31	0.59	0.82	**1.25**	1.76	3.63

[a] Bold values indicate the PADs in the ERG2020 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 ERG2020 analysis.

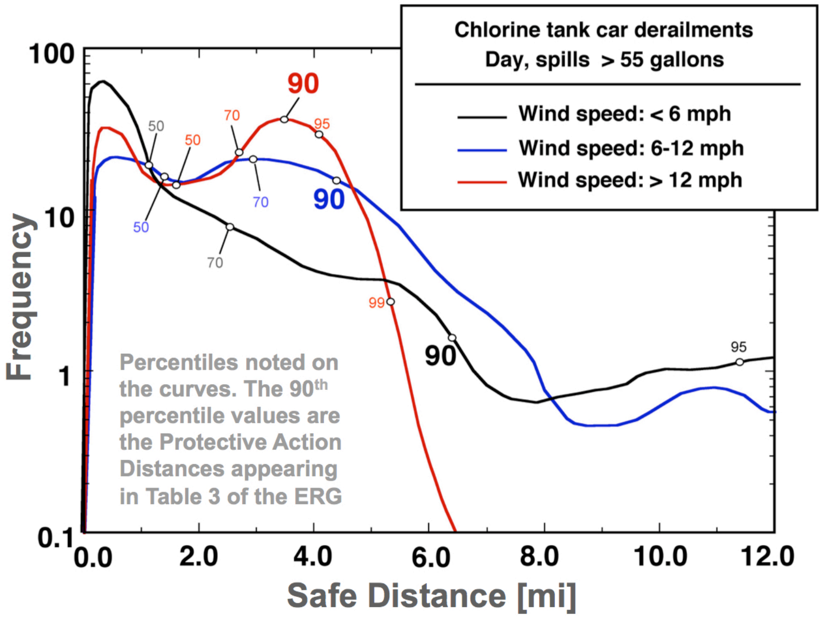
		Safe Distance (mi) at Percentile					
Release Size	**Time**	**50**	**70**	**80**	**90**	**95**	**99**
Small	Day	0.01	0.01	0.02	**0.03**[a]	0.06	0.27
	Night	0.01	0.04	0.10	**0.23**	0.38	0.67
Large	Day	0.10	0.26	0.37	**0.59**	1.05	4.02
	Night	0.38	0.85	1.25	**2.12**	4.63	9.87

[a] Bold values indicate the PADs in the ERG2020 that correspond with the 90th percentile values for the individual categories.

5.1.2 Generation of Table 3 Protective Action Distances

ERG2024 Table 3 further breaks down the PADs in Table 1 into individual container types and wind speed categories for large spills for six widely transported chemicals. Table 3 was a new addition in ERG2012, and the same six chemicals appear in ERG2024. Addition of this supplemental information was deemed very valuable, as a first responder would easily be able to discern the general wind conditions and the container involved. This additional information provides a significantly more refined PAD estimate than that available in Table 1.

To illustrate applying the statistical results to the development of Table 3, safe distance distributions for large rail daytime and nighttime chlorine and ammonia releases are provided in Figure 5.7–Figure 5.10 (ERG2020 data are used in these examples as the method of statistical analyses has not changed between guide publications). In these statistical distributions, various percentiles are shown, from the 50th to the 99th, including the 90th percentile, which corresponds to the PAD values listed in Table 3. 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, as developed from previous work, are provided in Section 5.3.



Percentiles noted on the curves. The 90th percentile values are the Protective Action Distances appearing in Table 3 of the ERG

Figure 5.7 Frequency of safe distances for large daytime chlorine spills from railcars for different wind speed ranges as determined in the ERG2020 analysis. (Percentiles are denoted by open circles superimposed on the curves.)

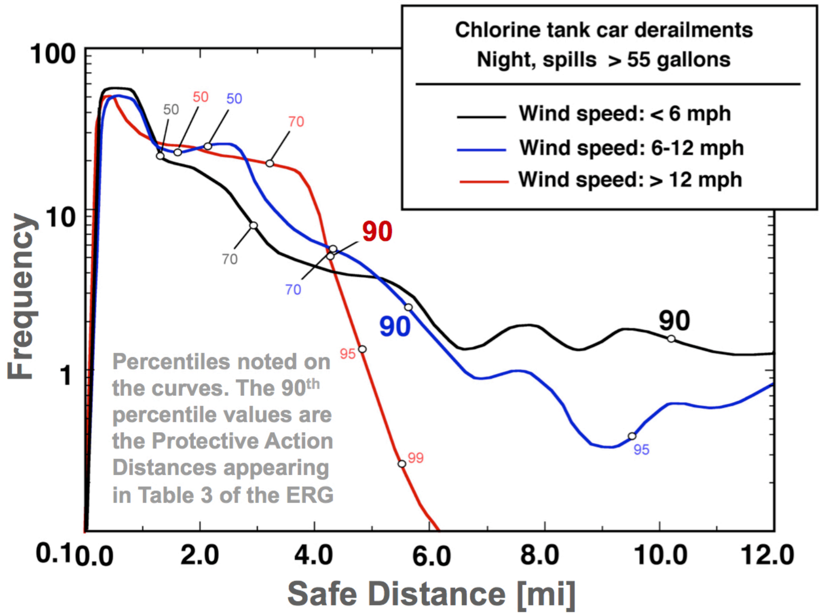


Figure 5.8 Frequency of safe distances for large nighttime chlorine spills from railcars for different wind speed ranges as determined in the ERG2020 analysis. (Percentiles are denoted by open circles superimposed on the curves.)

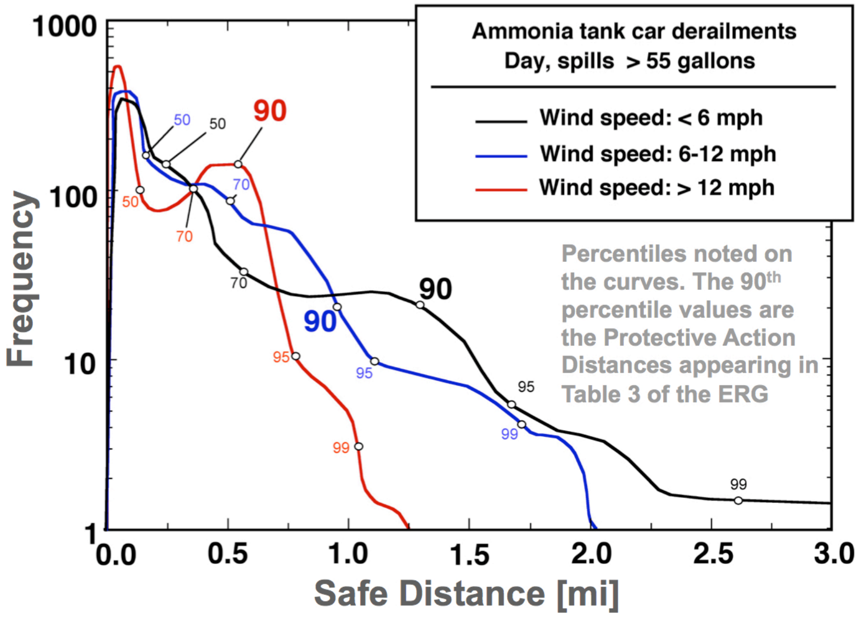


Figure 5.9 Frequency of safe distances for large daytime ammonia spills from railcars for different wind speed ranges as determined in the ERG2020 analysis. (Percentiles are denoted by open circles superimposed on the curves.)

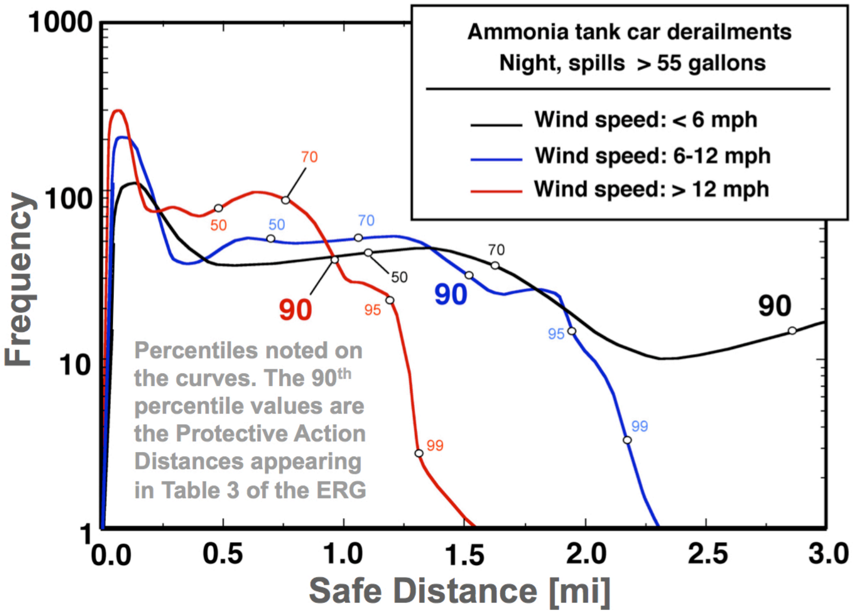


Figure 5.10 Frequency of safe distances for large nighttime ammonia spills from railcars for different wind speed ranges as determined in the ERG2020 analysis. (Percentiles are denoted by open circles superimposed on the curves.)

5.2 PRESENTATION OF THE TABLES IN THE GUIDEBOOK

Appendix A provides the information in Table 1 "Initial Isolation and Protective Action Distances" as it appears in ERG2024 (ERG 2024) for all chemicals and a separate table "Initial Isolation and Protective Action Distances" for chemical warfare agents. The PADs in the tables 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 tables:

- 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 that correspond to whether spills occur in water or on land.
- The third includes chemical warfare agents released in a malicious manner. In ERG2020 and prior publications of the ERG, these entries were denoted by the phrase "when used as a weapon" in the Table 1 "Isolation and Protective Action Distances." For 2020, weapons-related entries appeared at the beginning of Table 1 under the military name for the chemical and a blank UN number, as the military name does not have an associated UN number. These were listed in alphabetical order under the military name. For example, arsine entries for

> transportation-related incidents appeared under UN 2188, and weapons-related releases of arsine appeared at the beginning of Table 1 under the military name SA. For ERG2024, the chemical warfare agents are separated into a section titled Chemical Warfare Agents that is located in the section on “Criminal or Terrorist Use of Chemical, Biological, and Radiological Agents” (starting on page 360 of the ERG2024). Some chemical warfare agents, such as arsine and hydrogen cyanide, are TIH industrial chemicals as well and contain additional entries for transportation-related releases in Table 1. In the 2024 ERG, the chemical warfare agents were further aggregated according to agent class and the median IID and PAD values are shown for each individual class rather than for all chemical warfare agents.

Appendix B provides the container-specific tables for six commonly transported TIH materials that appear in ERG2024 Table 3. 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 Figure 5.7–Figure 5.10. One result of representing the data in this form is that, except for high wind speed cases, the rail distances are substantially higher than the corresponding regular large spill distances that have appeared in previous versions of the ERG (notably those in Table 1 of the 2012 ERG). These tables also demonstrate that large-spill distances from other bulk and multiple package freight containers are generally less than those provided in Table 1 of the 2012 ERG, with the exception of highway cargo tank releases in low wind speed conditions.

5.3 ADDITIONAL EXTENSIONS OF THE ERG ANALYSIS

Before 2012, the key limitation of PAD estimates in the ERG was that the PAD estimates were only available for two spill sizes (large or small), and incidents were assumed to happen in one of two timeframes (day or night). Clearly, the distributions in Figure 5.1–Figure 5.10 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 (the container-specific tables) of ERG2012 and subsequent editions.

Examples of additional information that can considerably narrow the safe-distance distributions are shown in Figure 5.11–Figure 5.13. This analysis was described in Brown and Dunn (2007), and that description is repeated here. Note that the underlying analysis for chlorine was modified for ERG2008, ERG2012, and in a substantial way for ERG2016 through ERG 2024 through the addition of more detailed shipment profiles, incorporating AEGL health criteria and changes to the source and dispersion models used in CASRAM, including the inclusion chemical reactivity. However, as illustrated in this example, the relative benefit of using more detailed information remains the same.

In these figures, the distributions are shown with the ordinate on a log scale to emphasize differences at higher percentiles (as in Figure 5.7–Figure 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 the chlorine that highway vehicles do, 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 meeting the definition of a large spill, as found in the ERG (> 55 gal), are about double those for corresponding highway cargo tank releases. For chlorine, this information is in fact included in Table 3 of the Green Pages, though as noted the methodology has evolved considerably since this original work.

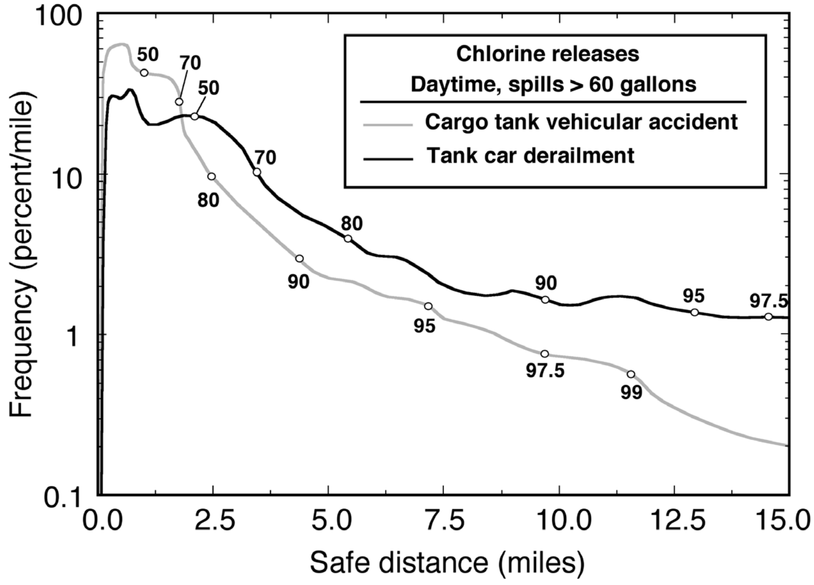


Figure 5.11 Frequency of safe distances for large daytime chlorine spills resulting from vehicular accidents and tank car derailments. (Percentiles are denoted by open circles superimposed on the curves. These are a subset of cases shown in Error! Reference source not found.**)**

Figure 5.12 compares safe-distance distributions for two different times of year. It shows results for fuming nitric acid, a volatile liquid. The higher temperatures characteristic of summer increase the pool evaporation rate and therefore increase safe distances. Again, we see differences—about factor of 2—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.

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 shown 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.

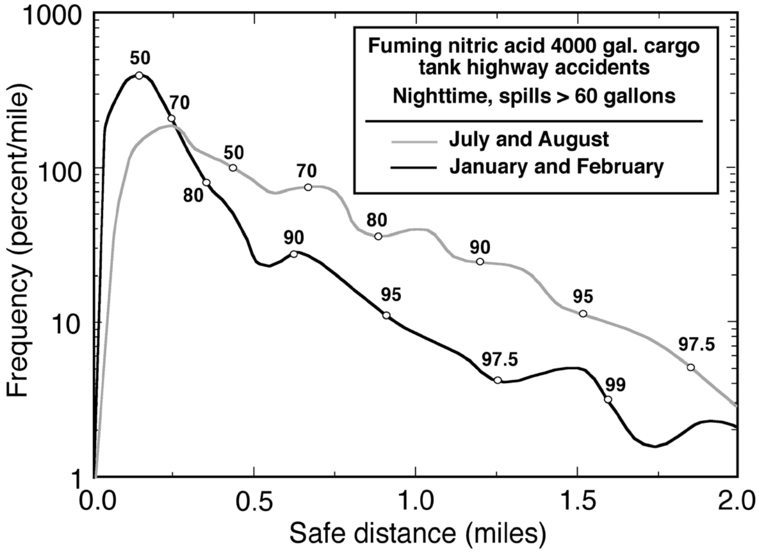


Figure 5.12 Frequency of safe distances for highway accidents involving 4,000 gal cargo tanks of fuming nitric acid in summer and winter conditions. (This shows the effects of seasonal climatology. Percentiles are denoted by open circles superimposed on the curves.)

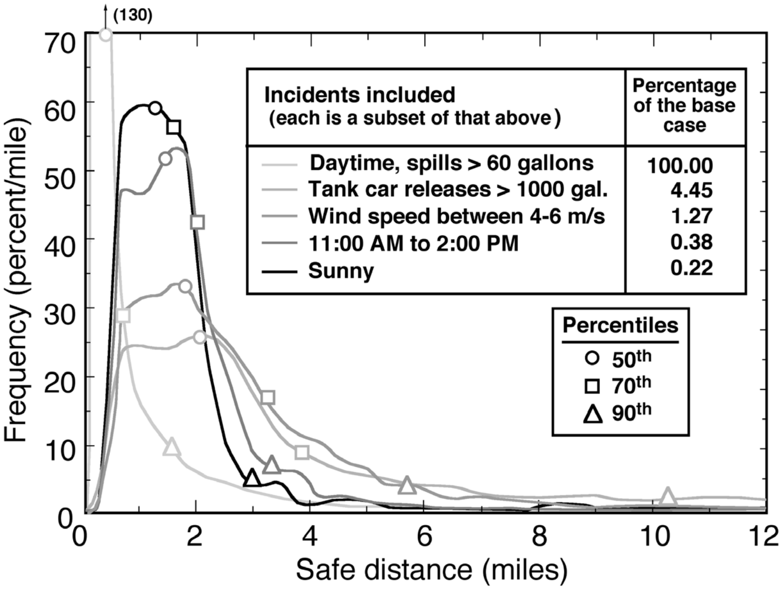


Figure 5.13 Frequency of safe distances for a chlorine tank car release of more than 1,000 gal, occurring between 11 a.m. and 2 p.m. on a sunny day with the wind between 4 and 6 m/s. (This shows the effect on the safe-distance distribution as each constraint is imposed. Percentiles are denoted as shown in the legend. The percentage of the base case, as given in Figure 5.11, is also provided.)

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APPENDIX A:
TABLES OF INITIAL ISOLATION AND PROTECTIVE ACTION DISTANCES IN THE *2024 EMERGENCY RESPONSE GUIDEBOOK* (TIH CHEMICALS FOLLOWED BY CHEMICAL WARFARE AGENTS)

Table A. 1 Initial Isolation and Protective Action Distances in the *2024 Emergency Response Guidebook*.

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	Table 3	Table 3	Table 3
1005	Anhydrous ammonia	100	0.1	0.1	Table 3	Table 3	Table 3
1008	Boron trifluoride	100	0.1	0.5	1250	1.5	2.9
1008	Boron trifluoride, compressed	100	0.1	0.5	1250	1.5	2.9
1016	Carbon monoxide, compressed	100	0.1	0.1	600	0.7	2.4
1017	Chlorine	200	0.2	0.9	Table 3	Table 3	Table 3
1026	Cyanogen	100	0.1	0.3	200	0.2	0.7
1040	Ethylene oxide	100	0.1	0.2	Table 3	Table 3	Table 3
1040	Ethylene oxide with nitrogen	100	0.1	0.2	Table 3	Table 3	Table 3
1045	Fluorine, compressed	100	0.1	0.1	300	0.3	1.4
1048	Hydrogen bromide, anhydrous	100	0.1	0.2	500	0.7	2
1050	Hydrogen chloride, anhydrous	100	0.1	0.2	Table 3	Table 3	Table 3
1051	Hydrogen cyanide, stabilized	200	0.1	0.4	600	0.5	1.1
1052	Hydrogen fluoride, anhydrous	100	0.1	0.3	Table 3	Table 3	Table 3
1053	Hydrogen sulfide	100	0.1	0.3	1250	1.5	4
1053	Hydrogen sulphide	100	0.1	0.3	1250	1.5	4
1061	Methylamine, anhydrous	100	0.1	0.1	600	0.4	1.3
1062	Methyl bromide	100	0.1	0.1	500	0.2	0.5
1064	Methyl mercaptan	100	0.1	0.2	600	0.8	2.4
1067	Dinitrogen tetroxide	100	0.1	0.3	1250	0.9	2.1
1067	Nitrogen dioxide	100	0.1	0.3	1250	0.9	2.1
1069	Nitrosyl chloride	100	0.2	0.7	2500	2.7	6
1076	Phosgene	300	0.4	1.6	1500	1.9	5.9
1079	Sulfur dioxide	300	0.4	1.6	Table 3	Table 3	Table 3
1079	Sulphur dioxide	300	0.4	1.6	Table 3	Table 3	Table 3
1082	Refrigerant gas R-1113	100	0.1	0.1	200	0.3	0.5
1082	Trifluorochloroethylene, stabilized	100	0.1	0.1	200	0.3	0.5
1092	Acrolein, stabilized	300	0.8	2.2	2000	4.2	6.9
1093	Acrylonitrile, stabilized	100	0.2	0.4	300	0.8	1.5
1098	Allyl alcohol	100	0.1	0.2	200	0.5	0.8

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)
1135	Ethylene chlorohydrin	100	0.1	0.1	100	0.1	0.1
1143	Crotonaldehyde	100	0.1	0.1	200	0.3	0.5
1143	Crotonaldehyde, stabilized	100	0.1	0.1	200	0.3	0.5
1162	Dimethyldichlorosilane (when spilled in water)	100	0.1	0.1	100	0.2	0.8
1163	Dimethylhydrazine, unsymmetrical	100	0.1	0.3	300	0.7	1.1
1182	Ethyl chloroformate	100	0.1	0.2	200	0.4	0.6
1183	Ethyldichlorosilane (when spilled in water)	100	0.1	0.1	200	0.3	0.9
1185	Ethyleneimine, stabilized	100	0.1	0.3	600	0.6	1.1
1196	Ethyltrichlorosilane (when spilled in water)	100	0.1	0.3	500	1.2	2.3
1238	Methyl chloroformate	100	0.2	0.4	500	0.7	1.4
1239	Methyl chloromethyl ether	200	0.3	1	1000	2.1	3.6
1242	Methyldichlorosilane (when spilled in water)	100	0.1	0.1	200	0.4	1.1
1244	Methylhydrazine	100	0.2	0.4	500	0.9	1.4
1250	Methyltrichlorosilane (when spilled in water)	100	0.1	0.1	200	0.4	1.2
1251	Methyl vinyl ketone, stabilized	300	0.2	0.5	2500	1.1	1.8
1259	Nickel carbonyl	300	0.9	3.3	3000	7.0+	7.0+
1295	Trichlorosilane (when spilled in water)	100	0.1	0.1	200	0.3	0.9
1298	Trimethylchlorosilane (when spilled in water)	100	0.1	0.1	100	0.2	0.6
1305	Vinyltrichlorosilane (when spilled in water)	100	0.1	0.1	100	0.3	0.8
1340	Phosphorus pentasulfide, free from yellow and white phosphorus (when spilled in water)	100	0.1	0.1	100	0.2	0.6
1340	Phosphorus pentasulphide, free from yellow and white phosphorus (when spilled in water)	100	0.1	0.1	100	0.2	0.6
1360	Calcium phosphide (when spilled in water)	100	0.1	0.3	600	0.5	1.7
1380	Pentaborane	200	0.4	1.3	1000	1.9	4.1
1384	Sodium dithionite (when spilled in water)	100	0.1	0.3	200	0.3	1.3
1384	Sodium hydrosulfite (when spilled in water)	100	0.1	0.3	200	0.3	1.3
1384	Sodium hydrosulphite (when spilled in water)	100	0.1	0.3	200	0.3	1.3
1390	Alkali metal amides (when spilled in water)	100	0.1	0.2	200	0.3	1.1
1397	Aluminum phosphide (when spilled in water)	100	0.1	0.4	1250	1	2.9
1419	Magnesium aluminum phosphide (when spilled in water)	100	0.1	0.4	1250	0.9	2.6
1432	Sodium phosphide (when spilled in water)	100	0.1	0.2	1000	0.6	1.9
1510	Tetranitromethane	100	0.1	0.2	100	0.3	0.4
1541	Acetone cyanohydrin, stabilized (when spilled in water)	100	0.1	0.1	200	0.1	0.3
1556	Methyldichloroarsine	500	0.9	1.4	1000	2.5	3.6
1560	Arsenic chloride	100	0.1	0.2	300	0.7	1
1560	Arsenic trichloride	100	0.1	0.2	300	0.7	1
1569	Bromoacetone	100	0.3	0.8	500	1.1	2.1
1580	Chloropicrin	200	0.4	0.8	600	1.5	2.3

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)
1581	Chloropicrin and methyl bromide mixture	100	0.1	0.4	1000	1.3	3.7
1582	Chloropicrin and methyl chloride mixture	100	0.1	0.3	200	0.3	1.3
1583	Chloropicrin mixture, n.o.s.	100	0.1	0.4	1000	1.3	3.7
1589	Cyanogen chloride, stabilized	1000	1.2	4.1	3000	7.0+	7.0+
1595	Dimethyl sulfate	100	0.1	0.1	200	0.1	0.4
1595	Dimethyl sulphate	100	0.1	0.1	200	0.1	0.4
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	1250	2.2	5.1
1613	Hydrocyanic acid, aqueous solution, with not more than 20% hydrogen cyanide	100	0.1	0.1	300	0.3	0.7
1613	Hydrogen cyanide, aqueous solution, with not more than 20% hydrogen cyanide	100	0.1	0.1	300	0.3	0.7
1614	Hydrogen cyanide, stabilized (absorbed)	200	0.1	0.4	500	0.3	1
1647	Methyl bromide and ethylene dibromide mixture, liquid	100	0.1	0.1	500	0.2	0.5
1660	Nitric oxide, compressed	100	0.1	0.4	300	0.4	1.4
1670	Perchloromethyl mercaptan	100	0.2	0.2	300	0.5	0.8
1672	Phenylcarbylamine chloride	100	0.1	0.1	200	0.3	0.4
1680	Potassium cyanide, solid (when spilled in water)	100	0.1	0.1	200	0.1	0.4
1689	Sodium cyanide, solid (when spilled in water)	100	0.1	0.1	200	0.2	0.6
1695	Chloroacetone, stabilized	100	0.1	0.1	200	0.3	0.4
1716	Acetyl bromide (when spilled in water)	100	0.1	0.1	100	0.2	0.4
1717	Acetyl chloride (when spilled in water)	100	0.1	0.1	200	0.4	1.2
1722	Allyl chlorocarbonate	300	0.2	0.5	1250	0.9	1.5
1722	Allyl chloroformate	300	0.2	0.5	1250	0.9	1.5
1724	Allyltrichlorosilane, stabilized (when spilled in water)	100	0.1	0.1	100	0.2	0.8
1725	Aluminum bromide, anhydrous (when spilled in water)	100	0.1	0.1	100	0.1	0.1
1726	Aluminum chloride, anhydrous (when spilled in water)	100	0.1	0.1	100	0.2	1
1728	Amyltrichlorosilane (when spilled in water)	100	0.1	0.1	100	0.2	0.7
1732	Antimony pentafluoride (when spilled in water)	100	0.1	0.2	300	0.5	1.9
1741	Boron trichloride (when spilled on land)	100	0.1	0.2	300	0.4	0.8
1741	Boron trichloride (when spilled in water)	100	0.1	0.2	300	0.6	1.7
1744	Bromine	200	0.5	1.5	1250	2.6	4.7
1744	Bromine, solution	200	0.5	1.5	1250	2.6	4.7
1744	Bromine, solution (Inhalation Hazard Zone A)	200	0.5	1.5	1250	2.6	4.7

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)
1744	Bromine, solution (Inhalation Hazard Zone B)	100	0.1	0.1	100	0.3	0.3
1745	Bromine pentafluoride (when spilled on land)	300	0.5	1.7	1500	3.6	6.7
1745	Bromine pentafluoride (when spilled in water)	100	0.1	0.2	300	0.6	1.9
1746	Bromine trifluoride (when spilled on land)	100	0.1	0.1	100	0.2	0.3
1746	Bromine trifluoride (when spilled in water)	100	0.1	0.2	300	0.5	1.8
1747	Butyltrichlorosilane (when spilled in water)	100	0.1	0.1	100	0.2	0.7
1749	Chlorine trifluoride	100	0.2	0.7	1000	0.9	2.3
1752	Chloroacetyl chloride (when spilled on land)	100	0.2	0.4	300	0.8	1.2
1752	Chloroacetyl chloride (when spilled in water)	100	0.1	0.1	100	0.1	0.3
1753	Chlorophenyltrichlorosilane (when spilled in water)	100	0.1	0.1	100	0.1	0.4
1754	Chlorosulfonic acid (with or without sulfur trioxide) (when spilled on land)	100	0.1	0.1	100	0.2	0.2
1754	Chlorosulfonic acid (with or without sulfur trioxide) (when spilled in water)	100	0.1	0.1	200	0.3	1.1
1754	Chlorosulphonic acid (with or without sulphur trioxide) (when spilled on land)	100	0.1	0.1	100	0.2	0.2
1754	Chlorosulphonic acid (with or without sulphur trioxide) (when spilled in water)	100	0.1	0.1	200	0.3	1.1
1758	Chromium oxychloride (when spilled in water)	100	0.1	0.1	100	0.1	0.2
1762	Cyclohexenyltrichlorosilane (when spilled in water)	100	0.1	0.1	100	0.2	0.5
1763	Cyclohexyltrichlorosilane (when spilled in water)	100	0.1	0.1	100	0.2	0.5
1765	Dichloroacetyl chloride (when spilled in water)	100	0.1	0.1	100	0.1	0.3
1766	Dichlorophenyltrichlorosilane (when spilled in water)	100	0.1	0.1	100	0.3	0.9
1767	Diethyldichlorosilane (when spilled in water)	100	0.1	0.1	100	0.2	0.4
1769	Diphenyldichlorosilane (when spilled in water)	100	0.1	0.1	100	0.2	0.5
1771	Dodecyltrichlorosilane (when spilled in water)	100	0.1	0.1	100	0.2	0.5
1777	Fluorosulfonic acid (when spilled in water)	100	0.1	0.1	100	0.1	0.2
1777	Fluorosulphonic acid (when spilled in water)	100	0.1	0.1	100	0.1	0.2
1781	Hexadecyltrichlorosilane (when spilled in water)	100	0.1	0.1	100	0.1	0.2
1784	Hexyltrichlorosilane (when spilled in water)	100	0.1	0.1	100	0.2	0.6
1799	Nonyltrichlorosilane (when spilled in water)	100	0.1	0.1	100	0.2	0.6
1800	Octadecyltrichlorosilane (when spilled in water)	100	0.1	0.1	100	0.2	0.6

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			Day (mi)	Night (mi)		Day (mi)	Night (mi)
1801	Octyltrichlorosilane (when spilled in water)	100	0.1	0.1	100	0.2	0.6
1804	Phenyltrichlorosilane (when spilled in water)	100	0.1	0.1	100	0.2	0.6
1806	Phosphorus pentachloride (when spilled in water)	100	0.1	0.1	100	0.2	0.6
1808	Phosphorus tribromide (when spilled in water)	100	0.1	0.1	100	0.2	0.7
1809	Phosphorus trichloride (when spilled on land)	100	0.2	0.4	300	0.7	1.3
1809	Phosphorus trichloride (when spilled in water)	100	0.1	0.1	200	0.3	1.1
1810	Phosphorus oxychloride (when spilled on land)	100	0.2	0.4	300	0.7	1.2
1810	Phosphorus oxychloride (when spilled in water)	100	0.1	0.1	200	0.3	1
1815	Propionyl chloride (when spilled in water)	100	0.1	0.1	100	0.1	0.2
1816	Propyltrichlorosilane (when spilled in water)	100	0.1	0.1	100	0.3	0.8
1818	Silicon tetrachloride (when spilled in water)	100	0.1	0.1	200	0.4	1.3
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	0.1	0.4
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	0.1	0.4
1829	Sulfur trioxide, stabilized	200	0.2	0.6	1000	1.8	4
1829	Sulphur trioxide, stabilized	200	0.2	0.6	1000	1.8	4
1831	Sulfuric acid, fuming	200	0.2	0.6	1000	1.8	4
1831	Sulphuric acid, fuming	200	0.2	0.6	1000	1.8	4
1834	Sulfuryl chloride (when spilled on land)	100	0.1	0.3	200	0.5	0.9
1834	Sulfuryl chloride (when spilled in water)	100	0.1	0.1	100	0.2	0.7
1834	Sulphuryl chloride (when spilled on land)	100	0.1	0.3	200	0.5	0.9
1834	Sulphuryl chloride (when spilled in water)	100	0.1	0.1	100	0.2	0.7
1836	Thionyl chloride (when spilled on land)	100	0.1	0.2	100	0.2	0.4
1836	Thionyl chloride (when spilled in water)	300	0.6	1.8	2000	4.7	7.0+
1838	Titanium tetrachloride (when spilled on land)	100	0.1	0.1	100	0.3	0.3
1838	Titanium tetrachloride (when spilled in water)	100	0.1	0.1	100	0.2	0.7
1859	Silicon tetrafluoride	100	0.1	0.5	300	0.3	1.2
1859	Silicon tetrafluoride, compressed	100	0.1	0.5	300	0.3	1.2
1892	Ethyldichloroarsine	500	1	1.4	1250	3.2	4
1898	Acetyl iodide (when spilled in water)	100	0.1	0.1	100	0.2	0.6
1911	Diborane	200	0.2	0.7	1000	1	2.9
1911	Diborane mixtures	200	0.2	0.7	1000	1	2.9
1923	Calcium dithionite (when spilled in water)	100	0.1	0.3	200	0.4	1.3
1923	Calcium hydrosulfite (when spilled in water)	100	0.1	0.3	200	0.4	1.3

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1923	Calcium hydrosulphite (when spilled in water)	100	0.1	0.3	200	0.4	1.3
1929	Potassium dithionite (when spilled in water)	100	0.1	0.2	200	0.3	1.2
1929	Potassium hydrosulfite (when spilled in water)	100	0.1	0.2	200	0.3	1.2
1929	Potassium hydrosulphite (when spilled in water)	100	0.1	0.2	200	0.3	1.2
1931	Zinc dithionite (when spilled in water)	100	0.1	0.2	200	0.3	1.2
1931	Zinc hydrosulfite (when spilled in water)	100	0.1	0.2	200	0.3	1.2
1931	Zinc hydrosulphite (when spilled in water)	100	0.1	0.2	200	0.3	1.2
1953	Compressed gas, poisonous, flammable, n.o.s.	500	0.6	2.4	3000	3.9	6.5
1953	Compressed gas, poisonous, flammable, n.o.s. (Inhalation Hazard Zone A)	500	0.6	2.4	3000	3.9	6.5
1953	Compressed gas, poisonous, flammable, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.2	1000	0.9	1.9
1953	Compressed gas, poisonous, flammable, n.o.s. (Inhalation Hazard Zone C)	100	0.1	0.2	500	0.6	1.7
1953	Compressed gas, poisonous, flammable, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.2	500	0.6	1.7
1953	Compressed gas, toxic, flammable, n.o.s.	500	0.6	2.4	3000	3.9	6.5
1953	Compressed gas, toxic, flammable, n.o.s. (Inhalation Hazard Zone A)	500	0.6	2.4	3000	3.9	6.5
1953	Compressed gas, toxic, flammable, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.2	1000	0.9	1.9
1953	Compressed gas, toxic, flammable, n.o.s. (Inhalation Hazard Zone C)	100	0.1	0.2	500	0.6	1.7
1953	Compressed gas, toxic, flammable, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.2	500	0.6	1.7
1955	Compressed gas, poisonous, n.o.s.	500	0.6	2.4	3000	3.9	6.5
1955	Compressed gas, poisonous, n.o.s. (Inhalation Hazard Zone A)	500	0.6	2.4	3000	3.9	6.5
1955	Compressed gas, poisonous, n.o.s. (Inhalation Hazard Zone B)	100	0.2	0.7	1000	0.9	2.3
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	0.2	500	0.6	1.7
1955	Compressed gas, toxic, n.o.s.	500	0.6	2.4	3000	3.9	6.5
1955	Compressed gas, toxic, n.o.s. (Inhalation Hazard Zone A)	500	0.6	2.4	3000	3.9	6.5
1955	Compressed gas, toxic, n.o.s. (Inhalation Hazard Zone B)	100	0.2	0.7	1000	0.9	2.3
1955	Compressed gas, toxic, n.o.s. (Inhalation Hazard Zone C)	100	0.1	0.2	500	0.6	1.7

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1955	Compressed gas, toxic, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.2	500	0.6	1.7
1955	Organic phosphate compound mixed with compressed gas	300	0.7	2.1	1500	2.7	6
1955	Organic phosphate mixed with compressed gas	300	0.7	2.1	1500	2.7	6
1955	Organic phosphorus compound mixed with compressed gas	300	0.7	2.1	1500	2.7	6
1967	Insecticide gas, poisonous, n.o.s.	300	0.7	2.1	1500	2.7	6
1967	Insecticide gas, toxic, n.o.s.	300	0.7	2.1	1500	2.7	6
1967	Parathion and compressed gas mixture	300	0.7	2.1	1500	2.7	6
1975	Nitric oxide and dinitrogen tetroxide mixture	100	0.1	0.4	300	0.4	1.4
1975	Nitric oxide and nitrogen dioxide mixture	100	0.1	0.4	300	0.4	1.4
1994	Iron pentacarbonyl	300	0.6	1.3	1250	3.2	4.8
2004	Magnesium diamide (when spilled in water)	100	0.1	0.2	200	0.3	1.1
2011	Magnesium phosphide (when spilled in water)	100	0.1	0.4	1250	0.9	2.4
2012	Potassium phosphide (when spilled in water)	100	0.1	0.2	600	0.6	1.8
2013	Strontium phosphide (when spilled in water)	100	0.1	0.2	600	0.5	1.7
2032	Nitric acid, red fuming	100	0.1	0.1	500	0.2	0.3
2186	Hydrogen chloride, refrigerated liquid	100	0.1	0.2	Table 3	Table 3	Table 3
2188	Arsine	500	0.6	2.4	3000	3.9	6.5
2189	Dichlorosilane	100	0.1	0.2	1000	0.9	1.9
2190	Oxygen difluoride, compressed	1000	1.1	4.5	3000	7.0+	7.0+
2191	Sulfuryl fluoride	100	0.1	0.3	1250	1.4	3.1
2191	Sulphuryl fluoride	100	0.1	0.3	1250	1.4	3.1
2192	Germane	500	0.5	2.1	2000	2.3	4.6
2194	Selenium hexafluoride	600	0.7	2.1	2000	2.4	4.8
2195	Tellurium hexafluoride	3000	3.7	6.9	3000	7.0+	7.0+
2196	Tungsten hexafluoride	100	0.1	0.5	500	0.5	1.7
2197	Hydrogen iodide, anhydrous	100	0.1	0.2	500	0.6	1.7
2198	Phosphorus pentafluoride	100	0.2	0.7	600	0.7	2.2
2198	Phosphorus pentafluoride, compressed	100	0.2	0.7	600	0.7	2.2
2199	Phosphine	200	0.2	0.7	1250	0.8	2.3
2202	Hydrogen selenide, anhydrous	1000	1.1	3.7	3000	7.0+	7.0+
2204	Carbonyl sulfide	100	0.1	0.2	1000	1	2.3
2204	Carbonyl sulphide	100	0.1	0.2	1000	1	2.3
2232	Chloroacetaldehyde	100	0.1	0.2	200	0.4	0.7
2232	2-Chloroethanal	100	0.1	0.2	200	0.4	0.7
2285	Isocyanatobenzotrifluorides	100	0.1	0.1	200	0.3	0.4
2308	Nitrosylsulfuric acid, liquid (when spilled in water)	100	0.1	0.2	1000	0.5	1.4

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2308	Nitrosylsulphuric acid, liquid (when spilled in water)	100	0.1	0.2	1000	0.5	1.4
2334	Allylamine	100	0.1	0.4	500	1	1.6
2337	Phenyl mercaptan	100	0.1	0.1	100	0.2	0.2
2353	Butyryl chloride (when spilled in water)	100	0.1	0.1	100	0.1	0.3
2382	Dimethylhydrazine, symmetrical	100	0.1	0.2	200	0.5	0.8
2395	Isobutyryl chloride (when spilled in water)	100	0.1	0.1	100	0.1	0.2
2407	Isopropyl chloroformate	100	0.1	0.2	200	0.4	0.6
2417	Carbonyl fluoride	300	0.5	1.6	2000	2.4	5.1
2418	Sulfur tetrafluoride	300	0.3	1.5	1250	1.5	3.7
2418	Sulphur tetrafluoride	300	0.3	1.5	1250	1.5	3.7
2420	Hexafluoroacetone	300	0.4	1.7	3000	7.0+	7.0+
2421	Nitrogen trioxide	200	0.2	0.8	600	0.9	2.7
2434	Dibenzyldichlorosilane (when spilled in water)	100	0.1	0.1	100	0.1	0.2
2435	Ethylphenyldichlorosilane (when spilled in water)	100	0.1	0.1	100	0.1	0.4
2437	Methylphenyldichlorosilane (when spilled in water)	100	0.1	0.1	100	0.2	0.5
2438	Trimethylacetyl chloride	200	0.3	0.7	600	1.5	2.1
2442	Trichloroacetyl chloride	100	0.1	0.2	200	0.5	0.7
2474	Thiophosgene	200	0.4	1.1	600	1.4	2.6
2477	Methyl isothiocyanate	100	0.1	0.1	100	0.2	0.3
2478	Isocyanate solution, flammable, poisonous, n.o.s.	200	0.5	1.2	1250	3	4.4
2478	Isocyanate solution, flammable, toxic, n.o.s.	200	0.5	1.2	1250	3	4.4
2478	Isocyanates, flammable, poisonous, n.o.s.	200	0.5	1.2	1250	3	4.4
2478	Isocyanates, flammable, toxic, n.o.s.	200	0.5	1.2	1250	3	4.4
2480	Methyl isocyanate	500	1.1	3.3	3000	7.0+	7.0+
2481	Ethyl isocyanate	500	1.3	3.3	3000	7.0+	7.0+
2482	n-Propyl isocyanate	300	0.8	1.8	2000	4.8	6.6
2483	Isopropyl isocyanate	500	1	2.1	3000	7.0+	7.0+
2484	tert-Butyl isocyanate	200	0.5	1.2	1250	3	4.4
2485	n-Butyl isocyanate	200	0.4	0.8	1000	1.8	2.6
2486	Isobutyl isocyanate	200	0.4	0.8	1000	2.1	3
2487	Phenyl isocyanate	300	0.6	0.9	1250	2.6	3.4
2488	Cyclohexyl isocyanate	100	0.2	0.3	300	0.7	0.9
2495	Iodine pentafluoride (when spilled in water)	100	0.1	0.2	300	0.6	2
2521	Diketene, stabilized	100	0.1	0.2	200	0.4	0.6
2534	Methylchlorosilane	100	0.1	0.2	500	0.5	1.1
2548	Chlorine pentafluoride	300	0.3	1.6	2500	3.2	7.0+
2605	Methoxymethyl isocyanate	100	0.1	0.2	200	0.4	0.6

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2606	Methyl orthosilicate	100	0.1	0.2	200	0.5	0.7
2644	Methyl iodide	100	0.1	0.1	300	0.2	0.4
2646	Hexachlorocyclopentadiene	100	0.1	0.1	100	0.2	0.2
2668	Chloroacetonitrile	100	0.1	0.1	100	0.2	0.2
2676	Stibine	200	0.2	1	600	0.8	2.6
2691	Phosphorus pentabromide (when spilled in water)	100	0.1	0.1	100	0.1	0.3
2692	Boron tribromide (when spilled on land)	100	0.1	0.1	100	0.1	0.3
2692	Boron tribromide (when spilled in water)	100	0.1	0.1	100	0.3	0.9
2740	n-Propyl chloroformate	100	0.1	0.2	200	0.4	0.7
2742	Chloroformates, poisonous, corrosive, flammable, n.o.s.	100	0.1	0.2	200	0.3	0.5
2742	Chloroformates, toxic, corrosive, flammable, n.o.s.	100	0.1	0.2	200	0.3	0.5
2743	n-Butyl chloroformate	100	0.1	0.1	100	0.2	0.3
2806	Lithium nitride (when spilled in water)	100	0.1	0.2	200	0.3	1
2826	Ethyl chlorothioformate	100	0.1	0.2	200	0.3	0.5
2845	Ethyl phosphonous dichloride, anhydrous	100	0.2	0.5	300	0.9	1.4
2845	Methyl phosphonous dichloride	100	0.3	0.7	600	1.6	2.6
2901	Bromine chloride	300	0.3	1.1	3000	3.5	7.0+
2927	Ethyl phosphonothioic dichloride, anhydrous	100	0.1	0.1	100	0.1	0.1
2927	Ethyl phosphorodichloridate	100	0.1	0.1	100	0.2	0.2
2965	Boron trifluoride dimethyl etherate (when spilled in water)	100	0.1	0.2	300	0.6	1.7
2977	Radioactive material, uranium hexafluoride, fissile (when spilled in water)	100	0.1	0.1	100	0.2	1
2977	Uranium hexafluoride, radioactive material, fissile (when spilled in water)	100	0.1	0.1	100	0.2	1
2978	Radioactive material, uranium hexafluoride, non-fissile or fissile-excepted (when spilled in water)	100	0.1	0.1	100	0.2	1
2978	Uranium hexafluoride, radioactive material, non fissile or fissile-excepted (when spilled in water)	100	0.1	0.1	100	0.2	1
2985	Chlorosilanes, flammable, corrosive, n.o.s. (when spilled in water)	100	0.1	0.1	200	0.3	1
2986	Chlorosilanes, corrosive, flammable, n.o.s. (when spilled in water)	100	0.1	0.1	200	0.3	1
2987	Chlorosilanes, corrosive, n.o.s. (when spilled in water)	100	0.1	0.1	200	0.3	1
2988	Chlorosilanes, water-reactive, flammable, corrosive, n.o.s. (when spilled in water)	100	0.1	0.1	200	0.3	1
3023	2-Methyl-2-heptanethiol	100	0.1	0.1	200	0.4	0.5

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3048	Aluminum phosphide pesticide (when spilled in water)	100	0.1	0.4	1250	1	2.8
3057	Trifluoroacetyl chloride	100	0.1	0.6	2500	3.1	7.0+
3079	Methacrylonitrile, stabilized	100	0.2	0.5	500	1.1	1.7
3083	Perchloryl fluoride	100	0.2	0.7	3000	3.4	6.8
3160	Liquefied gas, poisonous, flammable, n.o.s.	500	0.6	2.4	3000	3.9	6.5
3160	Liquefied gas, poisonous, flammable, n.o.s. (Inhalation Hazard Zone A)	500	0.6	2.4	3000	3.9	6.5
3160	Liquefied gas, poisonous, flammable, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.2	1000	0.9	1.9
3160	Liquefied gas, poisonous, flammable, n.o.s. (Inhalation Hazard Zone C)	100	0.1	0.2	500	0.6	1.7
3160	Liquefied gas, poisonous, flammable, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.2	500	0.6	1.7
3160	Liquefied gas, toxic, flammable, n.o.s.	500	0.6	2.4	3000	3.9	6.5
3160	Liquefied gas, toxic, flammable, n.o.s. (Inhalation Hazard Zone A)	500	0.6	2.4	3000	3.9	6.5
3160	Liquefied gas, toxic, flammable, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.2	1000	0.9	1.9
3160	Liquefied gas, toxic, flammable, n.o.s. (Inhalation Hazard Zone C)	100	0.1	0.2	500	0.6	1.7
3160	Liquefied gas, toxic, flammable, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.2	500	0.6	1.7
3162	Liquefied gas, poisonous, n.o.s.	500	0.6	2.4	3000	3.9	6.5
3162	Liquefied gas, poisonous, n.o.s. (Inhalation Hazard Zone A)	500	0.6	2.4	3000	3.9	6.5
3162	Liquefied gas, poisonous, n.o.s. (Inhalation Hazard Zone B)	100	0.2	0.7	1000	0.9	2.3
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	0.2	500	0.6	1.7
3162	Liquefied gas, toxic, n.o.s.	500	0.6	2.4	3000	3.9	6.5
3162	Liquefied gas, toxic, n.o.s. (Inhalation Hazard Zone A)	500	0.6	2.4	3000	3.9	6.5
3162	Liquefied gas, toxic, n.o.s. (Inhalation Hazard Zone B)	100	0.2	0.7	1000	0.9	2.3
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	0.2	500	0.6	1.7
3246	Methanesulfonyl chloride	100	0.2	0.2	200	0.5	0.6
3246	Methanesulphonyl chloride	100	0.2	0.2	200	0.5	0.6
3275	Nitriles, poisonous, flammable, n.o.s.	100	0.2	0.5	500	1.1	1.7

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)
3275	Nitriles, toxic, flammable, n.o.s.	100	0.2	0.5	500	1.1	1.7
3276	Nitriles, liquid, poisonous, n.o.s.	100	0.2	0.5	500	1.1	1.7
3276	Nitriles, liquid, toxic, n.o.s.	100	0.2	0.5	500	1.1	1.7
3276	Nitriles, poisonous, liquid, n.o.s.	100	0.2	0.5	500	1.1	1.7
3276	Nitriles, toxic, liquid, n.o.s.	100	0.2	0.5	500	1.1	1.7
3278	Organophosphorus compound, liquid, poisonous, n.o.s.	100	0.3	0.7	600	1.6	2.6
3278	Organophosphorus compound, liquid, toxic, n.o.s.	100	0.3	0.7	600	1.6	2.6
3279	Organophosphorus compound, poisonous, flammable, n.o.s.	100	0.3	0.7	600	1.6	2.6
3279	Organophosphorus compound, toxic, flammable, n.o.s.	100	0.3	0.7	600	1.6	2.6
3280	Organoarsenic compound, liquid, n.o.s.	100	0.1	0.5	500	1.1	2.2
3281	Metal carbonyls, liquid, n.o.s.	300	0.9	3.3	3000	7.0+	7.0+
3294	Hydrogen cyanide, solution in alcohol, with not more than 45% hydrogen cyanide	100	0.1	0.2	500	0.5	1.2
3300	Ethylene oxide and carbon dioxide mixture, with more than 87% ethylene oxide	100	0.1	0.2	500	0.5	1.2
3303	Compressed gas, poisonous, oxidizing, n.o.s.	300	0.3	1.6	2500	3.2	7.0+
3303	Compressed gas, poisonous, oxidizing, n.o.s. (Inhalation Hazard Zone A)	300	0.3	1.6	2500	3.2	7.0+
3303	Compressed gas, poisonous, oxidizing, n.o.s. (Inhalation Hazard Zone B)	100	0.2	0.7	1500	2.2	6.2
3303	Compressed gas, poisonous, oxidizing, n.o.s. (Inhalation Hazard Zone C)	100	0.1	0.4	300	0.4	1.4
3303	Compressed gas, poisonous, oxidizing, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.4	300	0.4	1.4
3303	Compressed gas, toxic, oxidizing, n.o.s.	300	0.3	1.6	2500	3.2	7.0+
3303	Compressed gas, toxic, oxidizing, n.o.s. (Inhalation Hazard Zone A)	300	0.3	1.6	2500	3.2	7.0+
3303	Compressed gas, toxic, oxidizing, n.o.s. (Inhalation Hazard Zone B)	100	0.2	0.7	1500	2.2	6.2
3303	Compressed gas, toxic, oxidizing, n.o.s. (Inhalation Hazard Zone C)	100	0.1	0.4	300	0.4	1.4
3303	Compressed gas, toxic, oxidizing, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.4	300	0.4	1.4
3304	Compressed gas, poisonous, corrosive, n.o.s.	600	0.7	2.1	2000	2.4	4.8
3304	Compressed gas, poisonous, corrosive, n.o.s. (Inhalation Hazard Zone A)	600	0.7	2.1	2000	2.4	4.8
3304	Compressed gas, poisonous, corrosive, n.o.s. (Inhalation Hazard Zone B)	100	0.2	0.7	1000	0.9	2.3
3304	Compressed gas, poisonous, corrosive, n.o.s. (Inhalation Hazard Zone C)	100	0.1	0.3	1000	1	2

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		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)
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.	600	0.7	2.1	2000	2.4	4.8
3304	Compressed gas, toxic, corrosive, n.o.s. (Inhalation Hazard Zone A)	600	0.7	2.1	2000	2.4	4.8
3304	Compressed gas, toxic, corrosive, n.o.s. (Inhalation Hazard Zone B)	100	0.2	0.7	1000	0.9	2.3
3304	Compressed gas, toxic, corrosive, n.o.s. (Inhalation Hazard Zone C)	100	0.1	0.3	1000	1	2
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.	500	0.6	2.4	3000	3.9	6.5
3305	Compressed gas, poisonous, flammable, corrosive, n.o.s. (Inhalation Hazard Zone A)	500	0.6	2.4	3000	3.9	6.5
3305	Compressed gas, poisonous, flammable, corrosive, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.2	1000	0.9	1.9
3305	Compressed gas, poisonous, flammable, corrosive, n.o.s. (Inhalation Hazard Zone C)	100	0.1	0.2	500	0.6	1.7
3305	Compressed gas, poisonous, flammable, corrosive, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.2	500	0.6	1.7
3305	Compressed gas, toxic, flammable, corrosive, n.o.s.	500	0.6	2.4	3000	3.9	6.5
3305	Compressed gas, toxic, flammable, corrosive, n.o.s. (Inhalation Hazard Zone A)	500	0.6	2.4	3000	3.9	6.5
3305	Compressed gas, toxic, flammable, corrosive, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.2	1000	0.9	1.9
3305	Compressed gas, toxic, flammable, corrosive, n.o.s. (Inhalation Hazard Zone C)	100	0.1	0.2	500	0.6	1.7
3305	Compressed gas, toxic, flammable, corrosive, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.2	500	0.6	1.7
3306	Compressed gas, poisonous, oxidizing, corrosive, n.o.s.	300	0.3	1.6	2500	3.4	7.0+
3306	Compressed gas, poisonous, oxidizing, corrosive, n.o.s. (Inhalation Hazard Zone A)	300	0.3	1.6	2500	3.4	7.0+
3306	Compressed gas, poisonous, oxidizing, corrosive, n.o.s. (Inhalation Hazard Zone B)	100	0.2	0.7	3000	3.2	6.8
3306	Compressed gas, poisonous, oxidizing, corrosive, n.o.s. (Inhalation Hazard Zone C)	100	0.1	0.3	1000	1	2
3306	Compressed gas, poisonous, oxidizing, corrosive, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.1	500	0.5	1.3
3306	Compressed gas, toxic, oxidizing, corrosive, n.o.s.	300	0.3	1.6	2500	3.4	7.0+
3306	Compressed gas, toxic, oxidizing, corrosive, n.o.s. (Inhalation Hazard Zone A)	300	0.3	1.6	2500	3.4	7.0+

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		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)
3306	Compressed gas, toxic, oxidizing, corrosive, n.o.s. (Inhalation Hazard Zone B)	100	0.2	0.7	3000	3.2	6.8
3306	Compressed gas, toxic, oxidizing, corrosive, n.o.s. (Inhalation Hazard Zone C)	100	0.1	0.3	1000	1	2
3306	Compressed gas, toxic, oxidizing, corrosive, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.1	500	0.5	1.3
3307	Liquefied gas, poisonous, oxidizing, n.o.s.	300	0.3	1.6	2500	3.2	7.0+
3307	Liquefied gas, poisonous, oxidizing, n.o.s. (Inhalation Hazard Zone A)	300	0.3	1.6	2500	3.2	7.0+
3307	Liquefied gas, poisonous, oxidizing, n.o.s. (Inhalation Hazard Zone B)	100	0.2	0.7	1500	1.8	6.8
3307	Liquefied gas, poisonous, oxidizing, n.o.s. (Inhalation Hazard Zone C)	100	0.1	0.4	300	0.4	1.4
3307	Liquefied gas, poisonous, oxidizing, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.4	300	0.4	1.4
3307	Liquefied gas, toxic, oxidizing, n.o.s.	300	0.3	1.6	2500	3.2	7.0+
3307	Liquefied gas, toxic, oxidizing, n.o.s. (Inhalation Hazard Zone A)	300	0.3	1.6	2500	3.2	7.0+
3307	Liquefied gas, toxic, oxidizing, n.o.s. (Inhalation Hazard Zone B)	100	0.2	0.7	1500	1.8	6.8
3307	Liquefied gas, toxic, oxidizing, n.o.s. (Inhalation Hazard Zone C)	100	0.1	0.4	300	0.4	1.4
3307	Liquefied gas, toxic, oxidizing, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.4	300	0.4	1.4
3308	Liquefied gas, poisonous, corrosive, n.o.s.	600	0.7	2.1	2000	2.4	4.8
3308	Liquefied gas, poisonous, corrosive, n.o.s. (Inhalation Hazard Zone A)	600	0.7	2.1	2000	2.4	4.8
3308	Liquefied gas, poisonous, corrosive, n.o.s. (Inhalation Hazard Zone B)	100	0.2	0.7	1000	1	2.3
3308	Liquefied gas, poisonous, corrosive, n.o.s. (Inhalation Hazard Zone C)	100	0.1	0.3	1000	0.9	2
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.	600	0.7	2.1	2000	2.4	4.8
3308	Liquefied gas, toxic, corrosive, n.o.s. (Inhalation Hazard Zone A)	600	0.7	2.1	2000	2.4	4.8
3308	Liquefied gas, toxic, corrosive, n.o.s. (Inhalation Hazard Zone B)	100	0.2	0.4	1000	1	2.3
3308	Liquefied gas, toxic, corrosive, n.o.s. (Inhalation Hazard Zone C)	100	0.1	0.3	1000	0.9	2
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.	500	0.6	2.4	3000	3.9	6.5

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		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)
3309	Liquefied gas, poisonous, flammable, corrosive, n.o.s. (Inhalation Hazard Zone A)	500	0.6	2.4	3000	3.9	6.5
3309	Liquefied gas, poisonous, flammable, corrosive, n.o.s. (Inhalation Hazard Zone B)	100	0.2	0.4	1000	1.6	1.9
3309	Liquefied gas, poisonous, flammable, corrosive, n.o.s. (Inhalation Hazard Zone C)	100	0.1	0.2	500	0.6	1.7
3309	Liquefied gas, poisonous, flammable, corrosive, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.2	500	0.6	1.7
3309	Liquefied gas, toxic, flammable, corrosive, n.o.s.	500	0.6	2.4	3000	3.9	6.5
3309	Liquefied gas, toxic, flammable, corrosive, n.o.s. (Inhalation Hazard Zone A)	500	0.6	2.4	3000	3.9	6.5
3309	Liquefied gas, toxic, flammable, corrosive, n.o.s. (Inhalation Hazard Zone B)	100	0.2	0.4	1000	1.6	1.9
3309	Liquefied gas, toxic, flammable, corrosive, n.o.s. (Inhalation Hazard Zone C)	100	0.1	0.2	500	0.6	1.7
3309	Liquefied gas, toxic, flammable, corrosive, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.2	500	0.6	1.7
3310	Liquefied gas, poisonous, oxidizing, corrosive, n.o.s.	300	0.3	1.6	3000	3.2	7.0+
3310	Liquefied gas, poisonous, oxidizing, corrosive, n.o.s. (Inhalation Hazard Zone A)	300	0.3	1.6	3000	3.2	7.0+
3310	Liquefied gas, poisonous, oxidizing, corrosive, n.o.s. (Inhalation Hazard Zone B)	100	0.2	0.7	2500	2.8	6.8
3310	Liquefied gas, poisonous, oxidizing, corrosive, n.o.s. (Inhalation Hazard Zone C)	100	0.1	0.3	1000	1	2
3310	Liquefied gas, poisonous, oxidizing, corrosive, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.1	500	0.5	1.3
3310	Liquefied gas, toxic, oxidizing, corrosive, n.o.s.	300	0.3	1.6	3000	3.2	7.0+
3310	Liquefied gas, toxic, oxidizing, corrosive, n.o.s. (Inhalation Hazard Zone A)	300	0.3	1.6	3000	3.2	7.0+
3310	Liquefied gas, toxic, oxidizing, corrosive, n.o.s. (Inhalation Hazard Zone B)	100	0.2	0.7	2500	2.8	6.8
3310	Liquefied gas, toxic, oxidizing, corrosive, n.o.s. (Inhalation Hazard Zone C)	100	0.1	0.3	1000	1	2
3310	Liquefied gas, toxic, oxidizing, corrosive, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.1	500	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.	500	0.6	2.4	3000	3.9	6.5
3355	Insecticide gas, poisonous, flammable, n.o.s. (Inhalation Hazard Zone A)	500	0.6	2.4	3000	3.9	6.5
3355	Insecticide gas, poisonous, flammable, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.2	1000	0.9	1.9

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		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)
3355	Insecticide gas, poisonous, flammable, n.o.s. (Inhalation Hazard Zone C)	100	0.1	0.2	500	0.6	1.7
3355	Insecticide gas, poisonous, flammable, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.2	500	0.4	1
3355	Insecticide gas, toxic, flammable, n.o.s.	500	0.6	2.4	3000	3.9	6.5
3355	Insecticide gas, toxic, flammable, n.o.s. (Inhalation Hazard Zone A)	500	0.6	2.4	3000	3.9	6.5
3355	Insecticide gas, toxic, flammable, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.2	1000	0.9	1.9
3355	Insecticide gas, toxic, flammable, n.o.s. (Inhalation Hazard Zone C)	100	0.1	0.2	500	0.6	1.7
3355	Insecticide gas, toxic, flammable, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.2	500	0.6	1.7
3361	Chlorosilanes, poisonous, corrosive, n.o.s. (when spilled in water)	100	0.1	0.1	200	0.3	1
3361	Chlorosilanes, toxic, corrosive, n.o.s. (when spilled in water)	100	0.1	0.1	200	0.3	1
3362	Chlorosilanes, poisonous, corrosive, flammable, n.o.s. (when spilled in water)	100	0.1	0.1	200	0.3	1
3362	Chlorosilanes, toxic, corrosive, flammable, n.o.s. (when spilled in water)	100	0.1	0.1	200	0.3	1
3381	Poisonous by inhalation liquid, n.o.s. (Inhalation Hazard Zone A)	200	0.4	1.1	600	1.4	2.6
3381	Toxic by inhalation liquid, n.o.s. (Inhalation Hazard Zone A)	200	0.4	1.1	600	1.4	2.6
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	0.3	1	1000	2.1	3.6
3383	Toxic by inhalation liquid, flammable, n.o.s. (Inhalation Hazard Zone A)	200	0.3	1	1000	2.1	3.6
3384	Poisonous by inhalation liquid, flammable, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.2	200	0.4	0.6
3384	Toxic by inhalation liquid, flammable, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.2	200	0.4	0.6
3385	Poisonous by inhalation liquid, water-reactive, n.o.s. (Inhalation Hazard Zone A)	200	0.4	1.1	600	1.4	2.6
3385	Toxic by inhalation liquid, water-reactive, n.o.s. (Inhalation Hazard Zone A)	200	0.4	1.1	600	1.4	2.6
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

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		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)
3387	Poisonous by inhalation liquid, oxidizing, n.o.s. (Inhalation Hazard Zone A)	200	0.3	1	1000	2.1	3.6
3387	Toxic by inhalation liquid, oxidizing, n.o.s. (Inhalation Hazard Zone A)	200	0.3	1	1000	2.1	3.6
3388	Poisonous by inhalation liquid, oxidizing, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.1	500	0.2	0.3
3388	Toxic by inhalation liquid, oxidizing, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.1	500	0.2	0.3
3389	Poisonous by inhalation liquid, corrosive, n.o.s. (Inhalation Hazard Zone A)	300	0.2	0.5	2500	1.1	1.8
3389	Toxic by inhalation liquid, corrosive, n.o.s. (Inhalation Hazard Zone A)	300	0.2	0.5	2500	1.1	1.8
3390	Poisonous by inhalation liquid, corrosive, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.1	200	0.3	0.4
3390	Toxic by inhalation liquid, corrosive, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.1	200	0.3	0.4
3456	Nitrosylsulfuric acid, solid (when spilled in water)	100	0.1	0.3	600	0.4	1.5
3456	Nitrosylsulphuric acid, solid (when spilled in water)	100	0.1	0.3	600	0.4	1.5
3488	Poisonous by inhalation liquid, flammable, corrosive, n.o.s. (Inhalation Hazard Zone A)	200	0.3	1	1000	2.1	3.6
3488	Toxic by inhalation liquid, flammable, corrosive, n.o.s. (Inhalation Hazard Zone A)	200	0.3	1	1000	2.1	3.6
3489	Poisonous by inhalation liquid, flammable, corrosive, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.2	200	0.4	0.6
3489	Toxic by inhalation liquid, flammable, corrosive, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.2	200	0.4	0.6
3490	Poisonous by inhalation liquid, water-reactive, flammable, n.o.s. (Inhalation Hazard Zone A)	200	0.3	1	1000	2.1	3.6
3490	Toxic by inhalation liquid, water-reactive, flammable, n.o.s. (Inhalation Hazard Zone A)	200	0.3	1	1000	2.1	3.6
3491	Poisonous by inhalation liquid, water-reactive, flammable, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.2	200	0.4	0.6
3491	Toxic by inhalation liquid, water-reactive, flammable, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.2	200	0.4	0.6
3492	Poisonous by inhalation liquid, corrosive, flammable, n.o.s. (Inhalation Hazard Zone A)	200	0.3	1	1000	2.1	3.6
3492	Toxic by inhalation liquid, corrosive, flammable, n.o.s. (Inhalation Hazard Zone A)	200	0.3	1	1000	2.1	3.6
3493	Poisonous by inhalation liquid, corrosive, flammable, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.2	200	0.4	0.6
3493	Toxic by inhalation liquid, corrosive, flammable, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.2	200	0.4	0.6

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		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)
3494	Petroleum sour crude oil, flammable, poisonous	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
3507	Uranium hexafluoride, radioactive material, excepted package, less than 0.1 kg per package, non-fissile or fissile-excepted (when spilled in water)	100	0.1	0.1	100	0.1	0.1
3512	Adsorbed gas, poisonous, n.o.s.	100	0.1	0.1	100	0.1	0.1
3512	Adsorbed gas, poisonous, n.o.s. (Inhalation hazard zone A)	100	0.1	0.1	100	0.1	0.1
3512	Adsorbed gas, poisonous, n.o.s. (Inhalation hazard zone B)	100	0.1	0.1	100	0.1	0.1
3512	Adsorbed gas, poisonous, n.o.s. (Inhalation hazard zone C)	100	0.1	0.1	100	0.1	0.1
3512	Adsorbed gas, poisonous, n.o.s. (Inhalation hazard zone D)	100	0.1	0.1	100	0.1	0.1
3512	Adsorbed gas, toxic, n.o.s.	100	0.1	0.1	100	0.1	0.1
3512	Adsorbed gas, toxic, n.o.s. (Inhalation hazard zone A)	100	0.1	0.1	100	0.1	0.1
3512	Adsorbed gas, toxic, n.o.s. (Inhalation hazard zone B)	100	0.1	0.1	100	0.1	0.1
3512	Adsorbed gas, toxic, n.o.s. (Inhalation hazard zone C)	100	0.1	0.1	100	0.1	0.1
3512	Adsorbed gas, toxic, n.o.s. (Inhalation hazard zone D)	100	0.1	0.1	100	0.1	0.1
3514	Adsorbed gas, poisonous, flammable, n.o.s.	100	0.1	0.1	100	0.1	0.1
3514	Adsorbed gas, poisonous, flammable, n.o.s. (Inhalation hazard zone A)	100	0.1	0.1	100	0.1	0.1
3514	Adsorbed gas, poisonous, flammable, n.o.s. (Inhalation hazard zone B)	100	0.1	0.1	100	0.1	0.1
3514	Adsorbed gas, poisonous, flammable, n.o.s. (Inhalation hazard zone C)	100	0.1	0.1	100	0.1	0.1
3514	Adsorbed gas, poisonous, flammable, n.o.s. (Inhalation hazard zone D)	100	0.1	0.1	100	0.1	0.1
3514	Adsorbed gas, toxic, flammable, n.o.s.	100	0.1	0.1	100	0.1	0.1
3514	Adsorbed gas, toxic, flammable, n.o.s. (Inhalation hazard zone A)	100	0.1	0.1	100	0.1	0.1
3514	Adsorbed gas, toxic, flammable, n.o.s. (Inhalation hazard zone B)	100	0.1	0.1	100	0.1	0.1
3514	Adsorbed gas, toxic, flammable, n.o.s. (Inhalation hazard zone C)	100	0.1	0.1	100	0.1	0.1
3514	Adsorbed gas, toxic, flammable, n.o.s. (Inhalation hazard zone D)	100	0.1	0.1	100	0.1	0.1
3515	Adsorbed gas, poisonous, oxidizing, n.o.s.	100	0.1	0.1	100	0.1	0.1

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)
3515	Adsorbed gas, poisonous, oxidizing, n.o.s. (Inhalation hazard zone A)	100	0.1	0.1	100	0.1	0.1
3515	Adsorbed gas, poisonous, oxidizing, n.o.s. (Inhalation hazard zone B)	100	0.1	0.1	100	0.1	0.1
3515	Adsorbed gas, poisonous, oxidizing, n.o.s. (Inhalation hazard zone C)	100	0.1	0.1	100	0.1	0.1
3515	Adsorbed gas, poisonous, oxidizing, n.o.s. (Inhalation hazard zone D)	100	0.1	0.1	100	0.1	0.1
3515	Adsorbed gas, toxic, oxidizing, n.o.s.	100	0.1	0.1	100	0.1	0.1
3515	Adsorbed gas, toxic, oxidizing, n.o.s. (Inhalation hazard zone A)	100	0.1	0.1	100	0.1	0.1
3515	Adsorbed gas, toxic, oxidizing, n.o.s. (Inhalation hazard zone B)	100	0.1	0.1	100	0.1	0.1
3515	Adsorbed gas, toxic, oxidizing, n.o.s. (Inhalation hazard zone C)	100	0.1	0.1	100	0.1	0.1
3515	Adsorbed gas, toxic, oxidizing, n.o.s. (Inhalation hazard zone D)	100	0.1	0.1	100	0.1	0.1
3516	Adsorbed gas, poisonous, corrosive, n.o.s.	100	0.1	0.1	100	0.1	0.1
3516	Adsorbed gas, poisonous, corrosive, n.o.s. (Inhalation hazard zone A)	100	0.1	0.1	100	0.1	0.1
3516	Adsorbed gas, poisonous, corrosive, n.o.s. (Inhalation hazard zone B)	100	0.1	0.1	100	0.1	0.1
3516	Adsorbed gas, poisonous, corrosive, n.o.s. (Inhalation hazard zone C)	100	0.1	0.1	100	0.1	0.1
3516	Adsorbed gas, poisonous, corrosive, n.o.s. (Inhalation hazard zone D)	100	0.1	0.1	100	0.1	0.1
3516	Adsorbed gas, toxic, corrosive, n.o.s.	100	0.1	0.1	100	0.1	0.1
3516	Adsorbed gas, toxic, corrosive, n.o.s. (Inhalation hazard zone A)	100	0.1	0.1	100	0.1	0.1
3516	Adsorbed gas, toxic, corrosive, n.o.s. (Inhalation hazard zone B)	100	0.1	0.1	100	0.1	0.1
3516	Adsorbed gas, toxic, corrosive, n.o.s. (Inhalation hazard zone C)	100	0.1	0.1	100	0.1	0.1
3516	Adsorbed gas, toxic, corrosive, n.o.s. (Inhalation hazard zone D)	100	0.1	0.1	100	0.1	0.1
3517	Adsorbed gas, poisonous, flammable, corrosive, n.o.s.	100	0.1	0.1	100	0.1	0.1
3517	Adsorbed gas, poisonous, flammable, corrosive, n.o.s. (Inhalation hazard zone A)	100	0.1	0.1	100	0.1	0.1
3517	Adsorbed gas, poisonous, flammable, corrosive, n.o.s. (Inhalation hazard zone B)	100	0.1	0.1	100	0.1	0.1
3517	Adsorbed gas, poisonous, flammable, corrosive, n.o.s. (Inhalation hazard zone C)	100	0.1	0.1	100	0.1	0.1
3517	Adsorbed gas, poisonous, flammable, corrosive, n.o.s. (Inhalation hazard zone D)	100	0.1	0.1	100	0.1	0.1

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)
3517	Adsorbed gas, toxic, flammable, corrosive, n.o.s.	100	0.1	0.1	100	0.1	0.1
3517	Adsorbed gas, toxic, flammable, corrosive, n.o.s. (Inhalation hazard zone A)	100	0.1	0.1	100	0.1	0.1
3517	Adsorbed gas, toxic, flammable, corrosive, n.o.s. (Inhalation hazard zone B)	100	0.1	0.1	100	0.1	0.1
3517	Adsorbed gas, toxic, flammable, corrosive, n.o.s. (Inhalation hazard zone C)	100	0.1	0.1	100	0.1	0.1
3517	Adsorbed gas, toxic, flammable, corrosive, n.o.s. (Inhalation hazard zone D)	100	0.1	0.1	100	0.1	0.1
3518	Adsorbed gas, poisonous, oxidizing, corrosive, n.o.s.	100	0.1	0.1	100	0.1	0.1
3518	Adsorbed gas, poisonous, oxidizing, corrosive, n.o.s. (Inhalation hazard zone A)	100	0.1	0.1	100	0.1	0.1
3518	Adsorbed gas, poisonous, oxidizing, corrosive, n.o.s. (Inhalation hazard zone B)	100	0.1	0.1	100	0.1	0.1
3518	Adsorbed gas, poisonous, oxidizing, corrosive, n.o.s. (Inhalation hazard zone C)	100	0.1	0.1	100	0.1	0.1
3518	Adsorbed gas, poisonous, oxidizing, corrosive, n.o.s. (Inhalation hazard zone D)	100	0.1	0.1	100	0.1	0.1
3518	Adsorbed gas, toxic, oxidizing, corrosive, n.o.s.	100	0.1	0.1	100	0.1	0.1
3518	Adsorbed gas, toxic, oxidizing, corrosive, n.o.s. (Inhalation hazard zone A)	100	0.1	0.1	100	0.1	0.1
3518	Adsorbed gas, toxic, oxidizing, corrosive, n.o.s. (Inhalation hazard zone B)	100	0.1	0.1	100	0.1	0.1
3518	Adsorbed gas, toxic, oxidizing, corrosive, n.o.s. (Inhalation hazard zone C)	100	0.1	0.1	100	0.1	0.1
3518	Adsorbed gas, toxic, oxidizing, corrosive, n.o.s. (Inhalation hazard zone D)	100	0.1	0.1	100	0.1	0.1
3519	Boron trifluoride, adsorbed	100	0.1	0.1	100	0.1	0.1
3520	Chlorine, adsorbed	100	0.1	0.1	100	0.1	0.1
3521	Silicon tetrafluoride, adsorbed	100	0.1	0.1	100	0.1	0.1
3522	Arsine, adsorbed	100	0.1	0.1	100	0.1	0.1
3523	Germane, adsorbed	100	0.1	0.1	100	0.1	0.1
3524	Phosphorus pentafluoride, adsorbed	100	0.1	0.1	100	0.1	0.1
3525	Phosphine, adsorbed	100	0.1	0.1	100	0.1	0.1
3526	Hydrogen selenide, adsorbed	100	0.1	0.1	100	0.1	0.1
3539	Articles containing toxic gas, n.o.s.	100	0.2	0.7	1000	0.9	2.3
9191	Chlorine dioxide, hydrate, frozen (when spilled in water)	100	0.1	0.1	100	0.1	0.3
9202	Carbon monoxide, refrigerated liquid (cryogenic liquid)	100	0.1	0.1	600	0.7	2.4
9206	Methyl phosphonic dichloride	100	0.1	0.1	200	0.3	0.4

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)
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	0.2	0.4	500	0.9	1.5

Table A. 2 Initial Isolation and Protective Action Distances for Chemical Warfare Agents in the *2024 Emergency Response Guidebook.*

Chemical warfare agents	Guide	Initial isolation Meters (Feet)	Small release Kilometers (Miles)	Large release Kilometers (Miles)
Blister agents	153	200 (600)	0.4 (0.3)	1.6 (1.0)
Blood agents	117	400 (1200)	0.9 (0.6)	3.2 (2.0)
Choking agents	125	100 (300)	0.3 (0.2)	1.1 (0.7)
Incapacitating agents	153	1000 (3000)	1.7 (1.1)	7.8 (4.8)
Nerve agents	153	400 (1200)	1.0 (0.6)	4.0 (2.5)
Tear gas agents	159	30 (100)	0.2 (0.1)	0.6 (0.4)
Vomiting agents	153	100 (300)	0.6 (0.4)	1.1 (0.7)

APPENDIX B:
INITIAL ISOLATION AND PROTECTIVE ACTION DISTANCES FOR SIX COMMON TIH GASES IN TABLE 3 OF ERG2024

Tables B.1–B.6 provide container specifics for six commonly transported TIH materials that appear in Table 3 of ERG2024. These six materials are anhydrous ammonia, chlorine, ethylene oxide/ethylene oxide mixed with nitrogen, hydrogen chloride, hydrogen fluoride, and sulfur dioxide. For each material, either three or four entries are provided for commonly employed transportation containers. Distances are provided for three wind speed ranges:

- Less than 6 mph
- Between 6 and 12 mph
- More than 12 mph

These tables are strictly for “large spills” from a bulk container or multiple small cylinders (i.e., releases over 55 gal), and are 90th percentile values as shown in Table 1 of the ERG (as listed in Appendix A).

Table B.1 Container-specific table for ammonia, anhydrous (UN 1005).

Transport container	First ISOLATE in all Directions m (ft)	Then PROTECT persons Downwind during					
		Day km (mi)			Night km (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	300 (1000)	1.6 (1.0)	1.2 (0.8)	1.0 (0.6)	4.1 (2.6)	2.1 (1.3)	1.3 (0.8)
Highway tank truck or trailer	150 (500)	0.8 (0.5)	0.5 (0.3)	0.4 (0.3)	1.8 (1.1)	0.7 (0.4)	0.6 (0.4)
Agricultural nurse tank	60 (200)	0.5 (0.3)	0.3 (0.2)	0.3 (0.2)	1.4 (0.9)	0.3 (0.2)	0.3 (0.2)
Multiple small cylinders	30 (100)	0.3 (0.2)	0.2 (0.1)	0.1 (0.1)	0.7 (0.5)	0.3 (0.2)	0.2 (0.1)

Table B.2 Container-specific table for chlorine (UN 1017).

Transport container	First ISOLATE in all Directions m (ft)	Then PROTECT persons Downwind during					
		Day km (mi)			Night km (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 (3000)	9.6 (6.0)	6.3 (3.9)	5.1 (3.2)	11+ (7+)	8.9 (5.6)	6.5 (4.1)
Highway tank truck or trailer	600 (2000)	5.6 (3.5)	3.3 (2.1)	2.5 (1.6)	6.4 (4.0)	4.7 (2.9)	3.8 (2.4)
Multiple ton cylinders	300 (1000)	1.9 (1.2)	1.3 (0.8)	1.0 (0.6)	3.5 (2.2)	2.3 (1.4)	1.3 (0.8)
Multiple small cylinders or single ton cylinder	150 (500)	1.3 (0.9)	0.7 (0.5)	0.5 (0.3)	2.4 (1.5)	1.2 (0.8)	0.6 (0.4)

Table B.3 Container-specific table for ethylene oxide (UN 1040) and ethylene oxide mixed with nitrogen (UN 1040).

Transport container	First ISOLATE in all Directions m (ft)						
		Day km (mi)			Night km (mi)		
		Low wind [< 6 mph]	Moderate wind [6-12 mph]	High wind [> 12 mph]	Low wind [< 6 mph]	Moderate wind [6-12 mph]	
Rail tank car	200 (600)	1.5 (1.0)	0.8 (0.5)	0.7 (0.4)	3.0 (1.8)	1.4 (0.9)	0.8 (0.5)
Highway tank truck or trailer	100 (300)	0.9 (0.6)	0.5 (0.3)	0.4 (0.3)	2.0 (1.3)	0.7 (0.4)	0.4 (0.3)
Multiple small cylinders or single ton cylinder	30 (100)	0.4 (0.3)	0.2 (0.1)	0.1 (0.1)	0.8 (0.5)	0.3 (0.2)	0.2 (0.1)

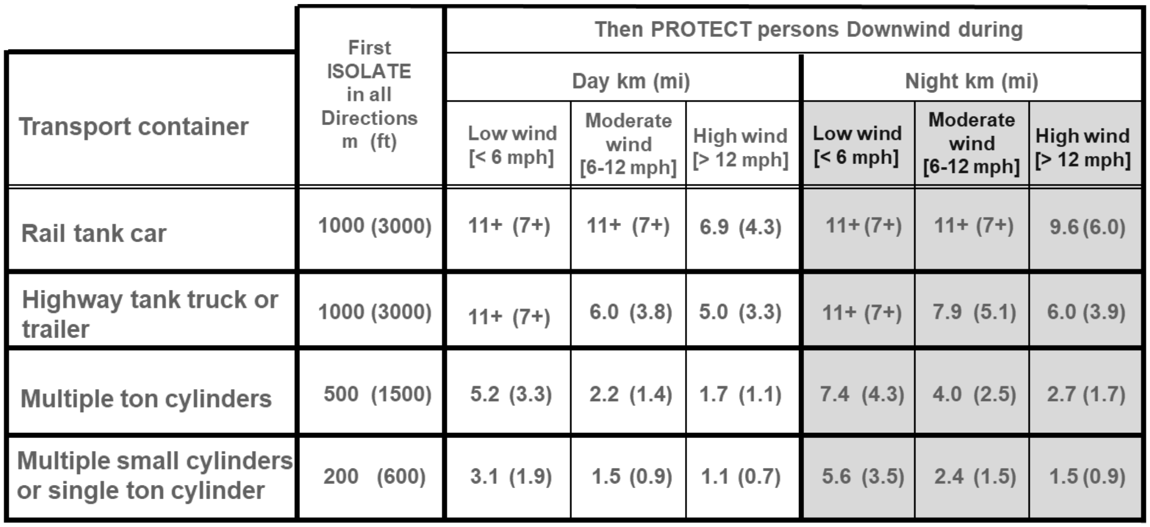
Table B.4 Container-specific table for hydrogen chloride, anhydrous (UN 1050) and hydrogen chloride, refrigerated (UN 2186).

Transport container	First ISOLATE in all Directions [ft]	Then PROTECT persons Downwind during					
		Day km (mi)			Night km (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	500 (1500)	3.7 (2.3)	2.0 (1.3)	1.7 (1.1)	9.7 (6.1)	3.3 (2.1)	2.2 (1.4)
Highway tank truck or trailer	200 (600)	1.5 (0.9)	0.8 (0.5)	0.6 (0.4)	3.7 (2.3)	1.5 (0.9)	0.8 (0.5)
Multiple ton cylinders	30 (100)	0.4 (0.3)	0.2 (0.1)	0.1 (0.1)	1.0 (0.6)	0.3 (0.2)	0.1 (0.1)
Multiple small cylinders or single ton cylinder	30 (100)	0.3 (0.2)	0.2 (0.1)	0.1 (0.1)	0.9 (0.6)	0.3 (0.2)	0.2 (0.1)

Table B.5 Container-specific table for hydrogen fluoride (UN 1052).

Transport container	First ISOLATE in all Directions m (ft)	Then PROTECT persons Downwind during					
		Day km (mi)			Night km (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	500 (1500)	3.4 (2.1)	2.1 (1.3)	1.8 (1.1)	6.4 (4.0)	3.0 (1.9)	1.9 (1.2)
Highway tank truck or trailer	200 (700)	2.0 (1.2)	1.0 (0.7)	0.9 (0.6)	3.6 (2.3)	1.5 (1.0)	0.9 (0.6)
Multiple small cylinders or single ton cylinder	100 (300)	0.8 (0.5)	0.4 (0.2)	0.3 (0.2)	1.7 (1.1)	0.5 (0.3)	0.3 (0.2)

Table B.6 Container-specific table for sulfur dioxide (UN 1079).



Transport container	First ISOLATE in all Directions m (ft)	Then PROTECT persons Downwind during					
		Day km (mi)			Night km (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 (3000)	11+ (7+)	11+ (7+)	6.9 (4.3)	11+ (7+)	11+ (7+)	9.6 (6.0)
Highway tank truck or trailer	1000 (3000)	11+ (7+)	6.0 (3.8)	5.0 (3.3)	11+ (7+)	7.9 (5.1)	6.0 (3.9)
Multiple ton cylinders	500 (1500)	5.2 (3.3)	2.2 (1.4)	1.7 (1.1)	7.4 (4.3)	4.0 (2.5)	2.7 (1.7)
Multiple small cylinders or single ton cylinder	200 (600)	3.1 (1.9)	1.5 (0.9)	1.1 (0.7)	5.6 (3.5)	2.4 (1.5)	1.5 (0.9)

APPENDIX C:
CHEMICALS ANALYZED IN THE ERG2024 ANALYSIS

Table C.1 lists the 164 chemicals analyzed in the *2024 Emergency Response Guidebook* (ERG2024) 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 ERG2024 (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
Acrylonitrile	107-13-1	53	77.4	11.4	392	35	70	AEGL-F
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	2	11	AEGL-F
Allyl chloroformate	2937-50-0	120.5	112.9	6.194	7	0.7	1.30	AEGL-F
Allyl isothiocyanate	57-06-7	99.2	150.7	0.516	635	6.4	12.7	LC_{50}
Allylamine	107-11-9	57.1	53.4	25.69	572	3.3	3.3	AEGL-F
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
Arsenic trichloride	7784-34-1	181.2	130.1	1.113	56	0.56	1.12	LC_{50}
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
Bis-(2-chloroethyl) methylamine	51-75-2	156.1	174.9	0.039	7.83	0.0034	0.0204	AEGL-I
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	13	83.0	AEGL-F
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
Bromine	7726-95-6	159.8	58.8	22.87	310	0.24	0.55	AEGL-F
Bromine chloride	13863-41-7	115.4	4.9	220.0	290	0.8	1.1	AEGL-F
Bromine pentafluoride	7789-30-2	174.9	40.9	42.88	299-S	0.2	0.7	AEGL-F
Bromine trifluoride	7787-71-5	136.9	125.9	0.774	299-S	2.0	8.1	AEGL-F
Bromoacetone	598-31-2	137	135.9	11.431	95	0.33	1.40	AEGL-F
n-Butyl chloroformate	592-34-7	136.6	137.9	0.765	323-S	2.2	4.0	AEGL-F
sec-Butyl chloroformate	17462-58-7	136.6	127.9-E	1.051-E	323	2.2	4.0	AEGL-F
n-Butylisocyanate	111-36-4	99.1	115.0-S	1.755-S	105	0.050	0.100	AEGL-F

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
tert-Butyl-isocyanate	1609-86-5	99.1	86.0	4.888-E	22	0.050	0.100	AEGL-FS
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
Carbonyl fluoride	353-50-4	66	–84.6	5,211	360	0.28	0.35	AEGL-F
Carbonyl sulfide	463-58-1	60.1	–50.2	1,124	924	55	69	AEGL-I
Chlorine	7782-50-5	70.9	–34.1	679.7	293	2.0	2.8	AEGL-F
Chlorine pentafluoride	13637-63-3	130.4	–13.9	332.1	122	0.2	0.7	AEGL-F
Chlorine trifluoride	7790-91-2	92.4	11.8	148.0	299	2.0	8.1	AEGL-F
Chloroacetaldehyde	107-20-0	78.5	84.9	3.522	200	2.2	9.8	AEGL-F
Chloroacetone	78-95-5	92.5	120.1	1.567	262	4.4	8.0	AEGL-F
Chloroacetonitrile	107-14-2	75.5	126.0	1.087	500	5	8	AEGL-F
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	AEGL-F
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	0.15	0.3	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
Cyanogen	460-19-5	52	–21.2	489.7	350	8.3	50.0	AEGL-F
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	0.2	0.3	AEGL-F
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
Dichlorosilane	4109-96-0	101	8.4	154.2	215	11	50	AEGL-F
3,5-Dichloro-2,4,6-trifluoropyridine	1737-93-5	202	177.5-S	0.104-S	62	0.62	1.24	LC_{50}

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
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
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
Ethylchlorothiolformate	2941-64-2	124.6-S	131.9-S	0.685-S	138-S	0.26	0.33	AEGL-I
Ethyl dichloroarsine	598-14-1	174.9	155.9	0.281	36	0.0041	0.0238	AEGL-I
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	0.034	0.2	AEGL-F
Ethyl phosphonothionic dichloride	993-43-1	162.9	176.9	0.026-E	52	0.52	1.04	LC_{50}
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	0.2	0.37	AEGL-F
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	1.2	2.1	AEGL-F
Ethylene dibromide	106-93-4	187.9	131.4	1.357	691	24	73	AEGL-I
Ethylene oxide	75-21-8	44.1	10.5	146.3	5,840	45	80	AEGL-F
Ethylenimine	151-56-4	43.1	55.9	22.18	80	4.6	33.0	AEGL-F
Fluorine	7782-41-4	38	–188.3	4,160	185	5.0	20.0	AEGL-F
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
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	0.2	0.4	AEGL-F
Hydrogen bromide	10035-10-6	80.9	–66.8	2,182	2,860	40	250	AEGL-F
Hydrogen chloride	7647-01-0	36.5	–85.1	4,206	3,124	22	100	AEGL-F

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
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
Hydrogen selenide	7783-07-5	81	–42.1	911.1	5	0.11	0.22	AEGL-F
Hydrogen sulfide	7783-06-4	34.1	–60.4	1781	712	27	41	AEGL-F
Iron pentacarbonyl	13463-40-6	195.9	102.8	3.142	57	0.060	0.077	AEGL-F
Isobutyl chloroformate	543-27-1	136.6	128.1	0.751	299	2.2	4.0	AEGL-F
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
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	1	1.3	AEGL-F
Methanesulfonyl monochloride	124-63-0	114.6	162.4	0.190	325	0.2	0.4	AEGL-F
Methanesulfonyl dichloride	3518-65-8	149	178	0.121	325-S	0.2	0.4	AEGL-FS
Methoxymethyl isocyanate	6427-21-0	87.1	165.7-E	0.250-E	28-S	0.067	0.400	AEGL-FS
Methyl bromide	74-83-9	94.9	3.6	184.3	1007	210	940	AEGL-F
Methyl chloride	74-87-3	50.5	–24.3	495.4	5,133	910	1100	AEGL-F
Methyl chloroformate	79-22-1	94.5	70.9	11.20	88	2.0	4.0	ERPG
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	17	21	AEGL-F
Methyl mercaptan	74-93-1	48.1	6.0	169.8	1340	23	40	AEGL-F
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	0.9	1.1	AEGL-F

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 vinyl ketone	78-94-4	70.1	81.5	9.274	5	1.2	1.5	AEGL-I
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-F
Methyldichloroarsine	593-89-5	160.9	135.9	1.034	68	0.0081	0.0958	AEGL-I
Nickel carbonyl	13463-39-3	170.8	42.5	43.50	18	0.036	0.100	AEGL-F
Nitric acid	7697-37-2	63	83.0	6.401	67	24	43	AEGL-F
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	12	20	AEGL-F
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-F
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	0.083	0.43	AEGL-F
Parathion	56-38-2	291.3	GS	GS	14	0.13	0.24	AEGL-I
Pentaborane	19624-22-7	63.2	58.4	22.70-E	12	0.14	0.56	AEGL-F
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	4.0	5.0	AEGL-F
Phenyl isocyanate	103-71-9	119.1	165.7	0.250	16	0.0096	0.012	AEGL-F
Phenyl mercaptan	108-98-5	110.2	169.2	0.142	66	0.53	1.00	AEGL-F
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
Phosphorous oxychloride[a]	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$_{50}$
Phosphorous trichloride	7719-12-2	137.3	76.1	12.82	208	2.0	2.5	AEGL-F
Phosphorous trifluoride	7783-55-3	88	–101.3	6,902	420	4.2	8.4	LC$_{50}$

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
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
n-Propyl isocyanate	110-78-1	85.1	82.9	5.274	44	0.034	0.2	AEGL-FS
Selenium hexafluoride	7783-79-1	193	–34.7	2,854	50	0.087	0.110	AEGL-I
Silicon tetrafluoride	7783-61-1	104.1	–95.2	3,205	922	3.3	6.3	AEGL-I
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
Sulfur monochloride	10025-67-9	135	137.9	0.944	150	6.4	8.1	AEGL-I
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
Sulfuryl fluoride	2699-79-8	102.1	–55.4	1,964	1,982	21	27	AEGL-I
Tellurium hexafluoride	7783-80-4	241.6	–38.2	709.6	10	0.018	0.032	AEGL-I
Tetraethyl dithiopyrophosphate	3689-24-5	322.3	GS	GS	6	0.06	0.12	AEGL-I
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
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-FS
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	0.8	2.9	AEGL-F

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
Trimethylacetyl chloride	3282-30-2	120.6	106.9	2.866	250	0.16	0.20	AEGL-F
Tris-(2-chloroethyl) amine	817-09-4	204.5	255.9	0.00094	2.99	0.0026	0.0156	AEGL-I
Tungsten hexafluoride	7783-82-6	297.8	17.4	111.8	217	2.2	4.3	LC_{50}

a Only 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 LC50 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
LC50 = median lethal concentration in animals exposed via inhalation
LC50-E = LC50 estimated from oral toxicity data
LC50-S = LC50 from structurally similar chemical used
LCLO = 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

This appendix provides detailed information on the water-reactive materials listed in the Table of Initial Isolation and Protective Action Distances. This information is identical to that prepared for the 2012, 2016, 2020, and 2024 ERGs. 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 ERG2000. Experiments in 2003–2004 in support of ERG2004 added 35 new materials and repeated or extended observations on 10 materials from the first group. The experiments in support of 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).

Section A is a description of the experiments. In Section D.2 we detail how these experimental data are used to determine the key parameters necessary to model toxic inhalation hazards by water-reaction (TIHWR) releases. The parameters for all TIHWR materials considered in ERG2024 are provided in Section D.3. Sections D.4 and D. 4.4 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.[12]

  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

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

ensured that both reactants would be consumed entirely if the following reaction went to completion:

$$SiCl_4 + 2\ H_2O \xrightarrow{\quad\quad} 4\ HCl + SiO_2 \qquad \text{(Eq. D.1)}$$

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:

$$M(t) = M_{st}\beta(1 - e^{-\lambda(t-T_{ind})}) \qquad \text{(Eq. D.2)}$$

where M_{st} is the stoichiometric mass that could evolve and $M(t)$ is the total mass of TIH gas that evolves from the water 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.2 as follows:

$$\beta = \frac{M_\infty}{M_{st}} \qquad \text{(Eq. D.3)}$$

where M_∞ is the maximum mass of TIH gas that evolves from the water during long periods, 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 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 D.2 with no induction time ($T_{ind} = 0$). Typical examples in which 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.

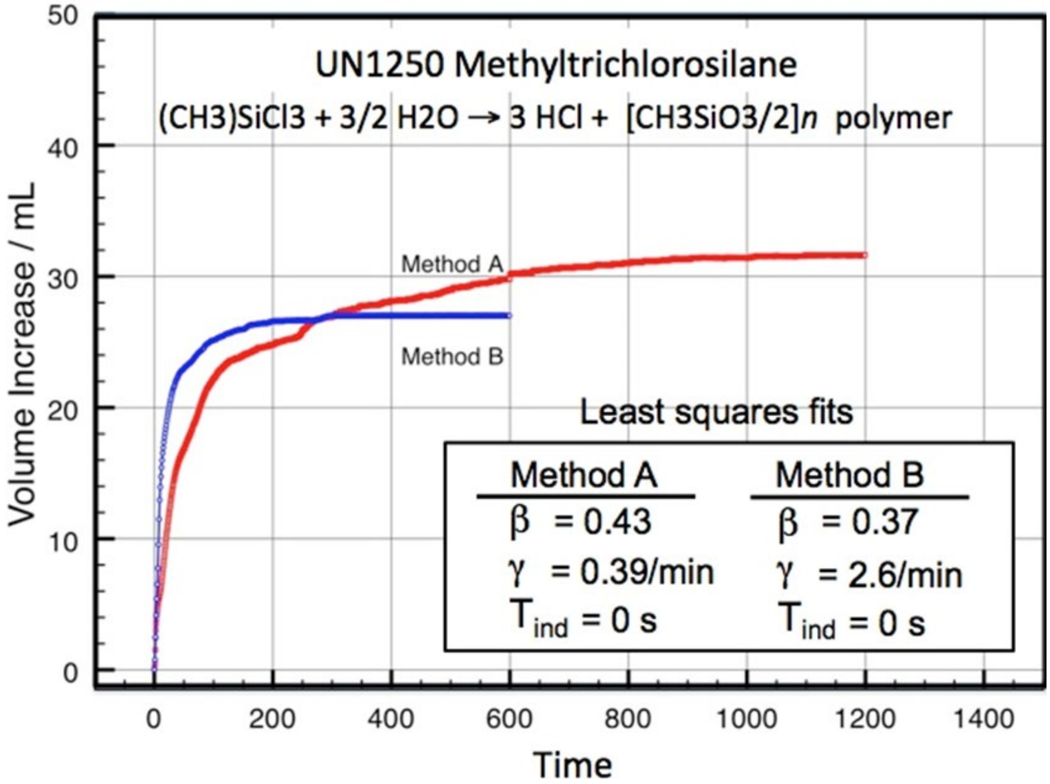

Figure D.1 Example of a first-order process from the experimental series in which dissolution of the TIH product competes with the evolution. Data are shown together with the derived parameters for Equation D.2. Results are shown for methyltrichlorosilane (UN 1250). The stoichiometric yield is 72.2 mL of HCl, equating to 0.732 g HCl per g of methyltrichlorosilane.

D. 2.3 First-Order Process with Dissolution

Several experiments showed an apparent first-order process in which the evolved TIH gas dissolved back into the water, which thus served as a removal mechanism. This process was especially apparent when Method B (fivefold molar excess of water) was used. Examples 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.

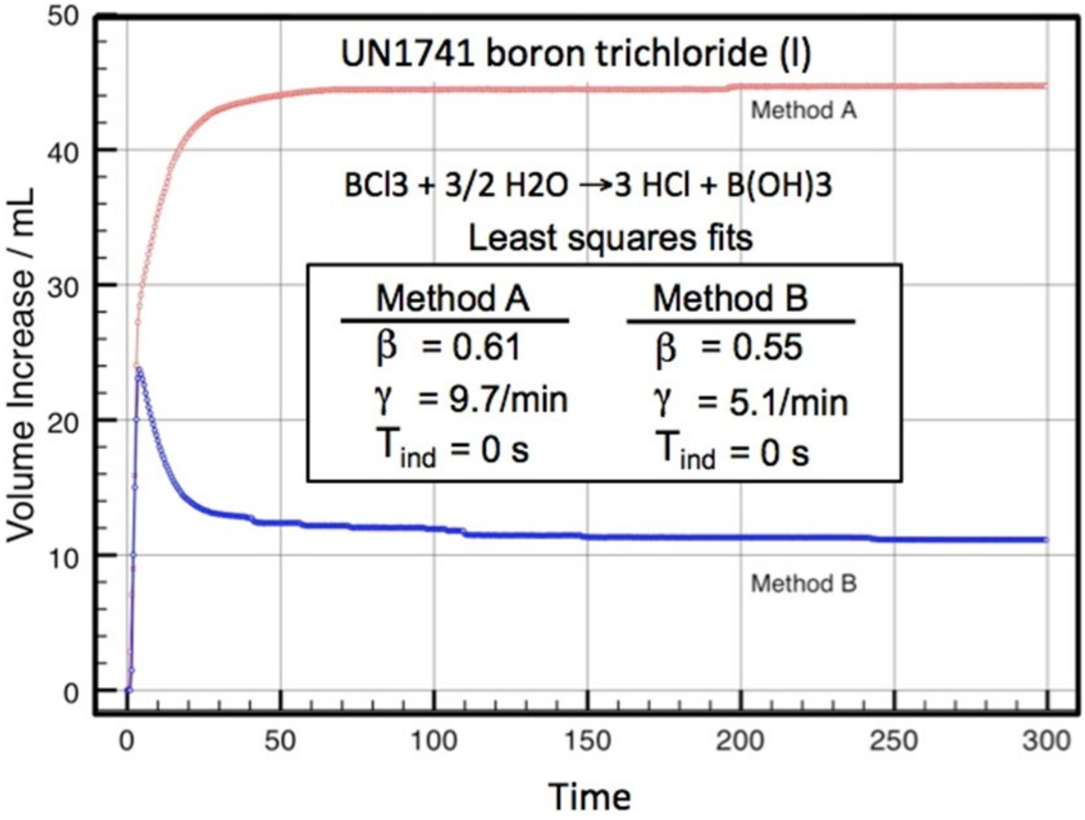

Figure D.2 Example of a first-order process from the experimental series where dissolution of the TIH product competes with the evolution. Data are shown together with the derived parameters for Equation D.2. Results are for boron trichloride (UN 1741). The stoichiometric yield is 72.2 mL of HCl, equating to 0.934 g HCl per g of boron trichloride.

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; examples include cyclohexyltrichlorosilane (UN 1763) and octadecyltrichlorosilane (UN 1800). In these reactions, slow emissions of gas at a constant rate ensued for a 2–10 min period. 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 to generate parameters for octadecyltrichlorosilane (UN 1800) is shown in Figure D.3.

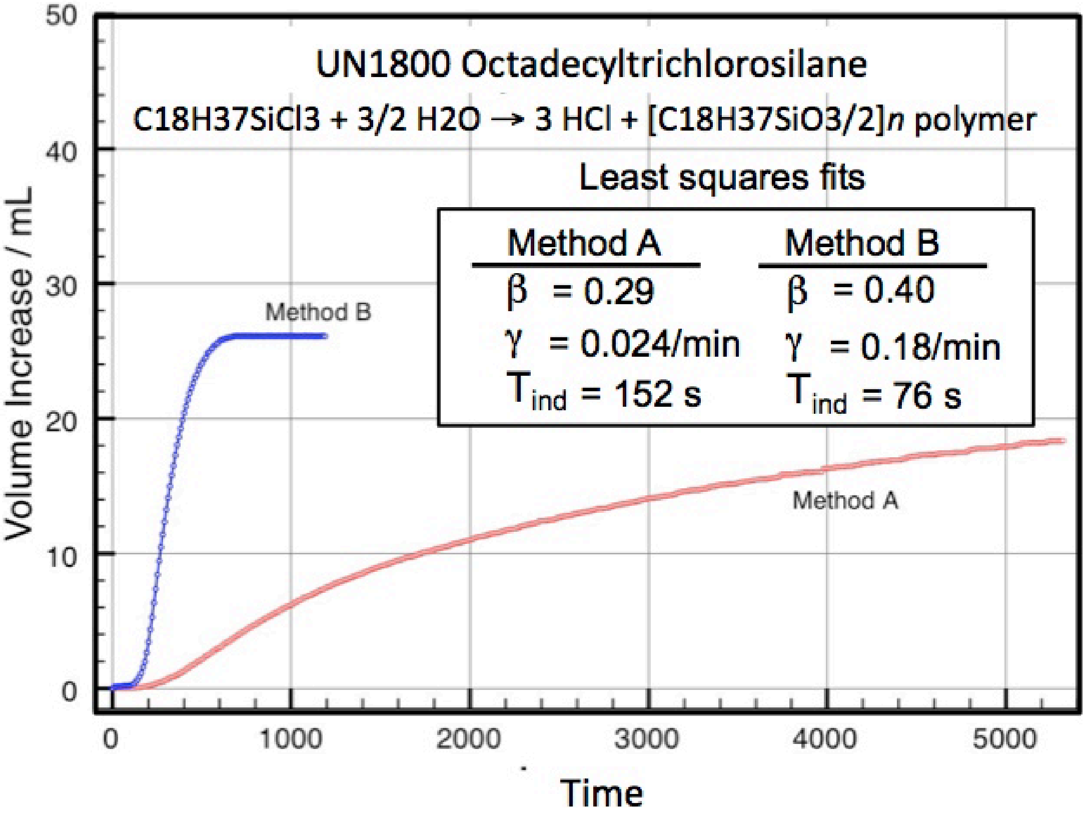

Figure D.3 Example of an autocatalytic reaction with an initial byproduct greatly reducing the availability of water for subsequent reaction. Data are shown together with the derived parameters for Equation D.2. Results are shown for octadecyltrichlorosilane (UN 1800). The stoichiometric yield is 72.2 mL of HCl, equating to 0.282 g HCl per g of octadecyltrichlorosilane.

In 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:

$$M(t) = m_i \frac{t}{T_{ind}} \qquad (t \le T_{ind}) \qquad \text{(Eq. D. 4)}$$

$$M(t) = m_i + M_{st}\beta'(1 - e^{-\lambda(t - T_{ind})}) \qquad (t > T_{ind}) \qquad \text{(Eq. D. 5)}$$

where

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

In compiling the experimental data for ERG2008, we found that we could simplify this analysis and the experimental data by ignoring the slow initial constant release described by Equation D.5 and instead simply use Equation D.3 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.3, for experimental trials of both Method A and Method B. These parameters were subsequently used in 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 were 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 ERG2024 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 ERG2008 because the experiments were conducted after February 2007, which was the cutoff for inclusion in 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 ERG2024 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 through D. 4.3 give the reasons why these materials are on the TIHWR list. Section D. 4.4 briefly describes why other materials were never on the list or were deleted from the list.

D. 4.1 Materials That Evolved TIH Gases During Experiments

The ERG2024 TIHWR list includes 62 materials from which TIH gases evolved during the experimental program described previously. These materials and the experimental studies used for analysis are listed in Table D.1.

D. 4.2 Materials Described as TIHWR in the Literature

The ERG2024 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 ERG2024.[a]

UN No.	Name	St.	Den.	Prod.	Experiments Conducted			S.Y.	Method A			Method B		
					00	04	08		β	λ (min^{-1})	T_{ind} (s)	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

					Experiments Conducted				Method A			Method B		
UN No.	Name	St.	Den.	Prod.	00	04	08	S.Y.	β	λ (min^{-1})	T_{ind} (s)	β	λ (min^{-1})	T_{ind} (s)
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
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

UN No.	Name	St.	Den.	Prod.	Experiments Conducted			S.Y.	Method A			Method B		
					00	04	08		β	λ (min^{-1})	T_{ind} (s)	β	λ (min^{-1})	T_{ind} (s)
1836	Thionyl chloride[c,d]	L	1.63	SO_2	X			0.538	1.00	2.75	0	1.00	2.75	0
1838	Titanium 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
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/cm3); 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), λo = primary rate constant at 20°C (min-1); and Tind = 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)

UN No.	Name	Comment	Reference
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 certain circumstances if they spilled.

- **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 of chemical 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” (EPA, 1997).
- **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 (Cleven and van Bruggen 2000).
- **UN 1689 — sodium cyanide.** Experiments conducted for 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.

- **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. 4.4 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 were 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.

- **UN 1433 — stannic phosphide.** No evolution of TIH gas was observed in the experiments (see Appendix C:).
- **UN 1714 — zinc phosphide.** No evolution of TIH gas was observed in the experiments (see Appendix C:).
- **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."
- **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.
- **UN 1807 — phosphorus pentoxide.** This material reacts explosively with water to generate water-soluble phosphoric acid. It was 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.
- **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 (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 PADs in excess of those already listed for land-based spills.

- **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.
- **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.
- **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:).
- **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 specific to the compound.

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