ANL/DIS-05-2

Development of the Table of Initial Isolation and Protective Action Distances for the *2004 Emergency Response Guidebook*

Decision and Information Sciences Division
Argonne National Laboratory

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by
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NOTATION

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

ACRONYMS AND ABBREVIATIONS

ABL	atmospheric boundary layer
ACGIH	American Conference of Governmental Industrial Hygienists
AEGL	Acute Exposure Guidance Level (National Advisory Committee)
AIHA	American Industrial Hygiene Association
CAS	Chemical Abstracts Services
CASRAM	Chemical Accident Statistical Risk Assessment Model
CBL	convective boundary layer
CFR	*Code of Federal Regulations*
CWIC	crosswind-integrated concentration
DOT	U.S. Department of Transportation
EEGL	Emergency Exposure Guidance Level (National Research Council)
EEL	Emergency Exposure Level (*AIHA Journal*)
EPA	U.S. Environmental Protection Agency
ERG	Emergency Response Guidebook
ERPG	Emergency Response Planning Guideline (AIHA)
ERPG-1	ERPG Level 1
ERPG-2	ERPG Level 2
ERPG-3	ERPG Level 3
GDP	gross domestic product
GLB	Great Lakes Buoy
HCl	hydrogen chloride
HF	hydrogen fluoride
HMIS	Hazardous Materials Information System
HSE	Health and Safety Executive
IDLH	immediately dangerous to life and health (NIOSH level)
LC_{50}	median lethal concentration; concentration lethal to 50% of an exposed population
LC_{LO}	lowest reported lethal concentration
LOC	level of concern (EPA)
NIOSH	National Institute for Occupational Safety and Health
n.o.s.	not otherwise specified
OSHA	Occupational Safety and Health Administration
PAD	Protective Action Distance
PEL	permissible exposure limit (OSHA)
RD_{50}	concentration producing a 50% respiratory rate decrease in test animals; used to estimate severe respiratory irritation
SBL	stratified boundary layer
SEB	surface energy budget

SEBMET	Surface Energy Budget Meteorological (model)
SLOT	specified level of toxicity (HSE)
STEL	short-term exposure limit (ACGIH)
TIH	toxic by inhalation
TIHWR	toxic by inhalation by water reactivity
TLV	threshold limit value (ACGIH)
TLV-C	ceiling TLV
TLV-TWA	time-weighted average TLV
UN	United Nations
USGS	U.S. Geological Survey
WQN	Water Quality Network

UNITS OF MEASURE

atm	atmosphere (1.01×10^5 Pa)
°C	degree(s) Celsius
cm	centimeter(s)
ft	foot (feet)
g	gram(s)
gal	gallon(s)
h	hour(s)
K	degree(s) Kelvin
kg	kilogram(s)
kPa	kilopascal(s)
m	meter(s)
m^2	square meter(s)
m^3	cubic meter(s)
µm	micrometer(s)
mi	mile(s)
min	minute(s)
mL	milliliter(s)
mmol	millimole(s)
Pa	Pascal(s)
ppm	part(s) per million
s	second(s)

DEVELOPMENT OF THE TABLE OF INITIAL ISOLATION AND PROTECTIVE ACTION DISTANCES FOR THE *2004 EMERGENCY RESPONSE GUIDEBOOK*

by

D.F. Brown, W.A. Freeman,* R.A. Carhart,* M. Krumpolc*

ABSTRACT

This report provides technical documentation for values in the Table of Initial Isolation and Protective Action Distances (PADs) in the *2004 Emergency Response Guidebook* (ERG2004). The objective for choosing the PADs specified in the ERG2004 is 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. To quantify this balance, a statistical approach is adopted, whereby the best available information is used to conduct an accident scenario analysis and develop a set of up to 1,000,000 hypothetical incidents. The set accounts for differences in containers types, incident types, accident severity (i.e., amounts released), locations, times of day, times of year, and meteorological conditions. Each scenario is analyzed using detailed emission rate and atmospheric dispersion models to calculate the downwind chemical concentrations from which a "safe distance" is determined. The safe distance is defined as the distance downwind from the source at which the chemical concentration falls below health protection criteria. The American Industrial Hygiene Association's Emergency Response Planning Guideline Level 2 (ERPG-2) or equivalent is the health criteria used. The statistical sample of safe distance values for all incidents considered in the analysis are separated into four categories: small spill/daytime release, small spill/nighttime release, large spill/daytime release, and large spill/nighttime release. The 90th-percentile safe distance values for each of these groups became the PADs that appear in the ERG2004.

EXECUTIVE SUMMARY

Chemical spills resulting from the transport of toxic materials can pose substantial hazards to the general public and to first responders. To address these hazards, first responders can consult the Emergency Response Guidebook (ERG), which helps them determine whether a spill is potentially hazardous and what actions to take. The 2004 edition of this guidebook, entitled *2004 Emergency Response Guidebook* (i.e., ERG2004), was prepared by the

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U.S. Department of Transportation (DOT), Transport Canada, and the Secretariat of Transport and Communications of Mexico.

The ERG provides information on fire-fighting and mitigation strategies as well as on potential health effects associated with various chemicals, which it lists under their proper shipping names and four-digit United Nations (UN) identification numbers. The ERG also provides Initial Isolation Distances and Protective Action Distances (PADs) for a subset of the chemicals that are toxic by inhalation (TIH) or that react with water to produce TIH gases (TIHWR). The Initial Isolation Distance identifies the radius of a zone around the release from which all people not directly involved in emergency response are to be kept away. The PAD is the downwind distance from the release that defines a zone in which persons should be either evacuated or sheltered in place, depending on the nature of the population at risk (e.g., density, age, health) and the severity of the incident.

This report provides the technical documentation for the values in the ERG2004 Table of Initial Isolation and Protective Action Distances (hereafter referred to as the Table). The objective for choosing the PADs specified in the ERG2004 was 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. To quantify this balance, a "level of protection" is defined. This level represents the probability that the listed PAD will allow sufficient protection of the public. A 90% level of protection was selected for the ERG2004.

Quantitative analysis of the level of protection requires a statistical approach to specify the PAD. To achieve this objective, we use the best available information to conduct accident scenario analyses, resulting in a set of up to 1,000,000 hypothetical incidents for each material. The set accounts for differences in the container types, incident types, accident severities (i.e., amounts released), accident locations, times of day, times of year, and meteorological conditions involved. Each scenario is analyzed using detailed emission rate and atmospheric dispersion models to calculate the downwind chemical concentrations from which a "safe distance" is determined. The safe distance is defined as the distance downwind from the source at which the chemical concentration falls below the health protection criteria. The health criteria used are the American Industrial Hygiene Association's Emergency Response Planning Guideline Level 2 (ERPG-2) or equivalent. The ERPG-2 criteria denote the highest chemical concentration at which persons will suffer no irreversible or other serious health effects that could impair their ability to take protective action. The statistical sample of safe distance values for all incidents for each material is separated into four categories: small spill/daytime release, small spill/nighttime release, large spill/daytime release, and large spill/nighttime release. The 90th-percentile safe distance values for each of these groups are the PADs that appear in the Table.

This report presents the entire methodology used to produce the Table, much of which is unchanged from the ERG2000 and companion report. Specific improvements and changes in the methodology from the ERG2000 are noted below.

1. The experimental program for evaluating water reactive materials initiated for the ERG2000 were continued for the ERG2004. These experiments covered 35 materials in addition to the 21 evaluated for the ERG2000. As a result of

the experiments, 14 new materials were added to the TIHWR list and 5 were deleted.

2. We reanalyzed the Hazardous Materials Information System (HMIS) database to incorporate accident records from recent years. The biggest change resulting from this reanalysis was development of a different method for treating shipments with multiple package freight containers (e.g., 25 cylinders, etc.) that is a more detailed and consistent system as compared to the previous approach. The overall result of this is a reduction of the predicted frequency of incidents where large numbers of package freight containers fail simultaneously. This had the net effect of causing the large spill distance estimates to increase slightly, since fewer package freight incidents had releases large enough to fall into the large spill category. Our new system for treating package freight also increased large spill distances for the Hazard Zone A gases. Changes in discharge fractions for bulk containers were fairly minor.

3. We developed several new shipment profiles for the ERG2004 tailored specifically to individual chemicals based on our analysis of HMIS and American Association of Railroads rail waybill data. Some adjustment was also made to existing profiles, most notably those for Hazard Zone A gases. (The shipment profiles specified the bulk and package freight containers typically used to transport the material, as well as the relative frequency at which each type of container is involved in incidents.)

1 INTRODUCTION

Transportation of hazardous materials creates numerous opportunities for the release of toxic substances into the environment due to traffic accidents, train derailments, equipment failures, and human error. Such releases can pose serious acute hazards to the general public and to emergency response personnel who are the first to arrive at the scene. To help first responders determine whether a shipment is potentially hazardous and decide what actions should be taken if a toxic spill does occur, the Emergency Response Guidebook (ERG) is published by the U.S. Department of Transportation (DOT), Transport Canada, and Secretariat of Transport and Communications of Mexico. The most recent version is the 2004 edition of the ERG (DOT et al. 2004), titled *2004 Emergency Response Guidebook* (hereafter referred to as ERG2004). The ERG provides essential information on fire-fighting, spill response, and potential public health effects. For chemicals that are toxic by inhalation (TIH) and chemicals that produce TIH gases upon reaction with water (TIHWR), the ERG provides Initial Isolation Distances and Protective Action Distances. The Initial Isolation Distance defines the radius of the zone around the spill that should be accessed solely by people who are directly involved in emergency response. The protective action distance (PAD) is the distance downwind from the source of the release to which persons should be either evacuated or sheltered-in-place, depending on the severity of the incident and the nature of the population (e.g., density, age, health).

This report was prepared to document the methodology used to prepare the ERG2004 Table of Initial Isolation and Protective Action Distances (hereafter referred to as “the Table”). The PADs in the Table were calculated to balance the need to adequately protect the public from exposure to potentially harmful substances against the risks and expenses that could result from overreacting to a spill. In determining the PADs, this balance was quantified in terms of a level of protection; namely, the probability that the listed PAD will allow sufficient protection of the public. The level of protection adopted for the ERG was 90%. Clearly, a quantitative analysis of the level of protection requires a statistical approach, the underlying technical basis of which is described in this report.

1.1 OVERVIEW OF THE EMERGENCY RESPONSE GUIDEBOOK

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

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

- United Nations (UN) identification number and/or proper shipping name of the material being transported,
- Direction of the prevailing wind,
- Whether the spill is small (60 gal or less) or large (more than 60 gal),
- Whether it is day or night, and
- Any special conditions that could preclude the use of the values given in the Table (e.g., releases of multiple tank cars, topographical anomalies, etc.).

As depicted in Figure 1.1, releases of TIH materials result in downwind concentrations of vapor that decrease with distance from the release point (assuming that the release is not buoyant). At some downwind distance, the concentration decreases to a level below which no protective action is necessary. This distance is the *Protective Action Distance* (PAD). The *Protective Action Zone* (PAZ) is defined as a square region having a side dimension equal to the PAD and lying downwind and symmetrically about the accident location. Note that since the PAZ lies downwind of the source, 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.

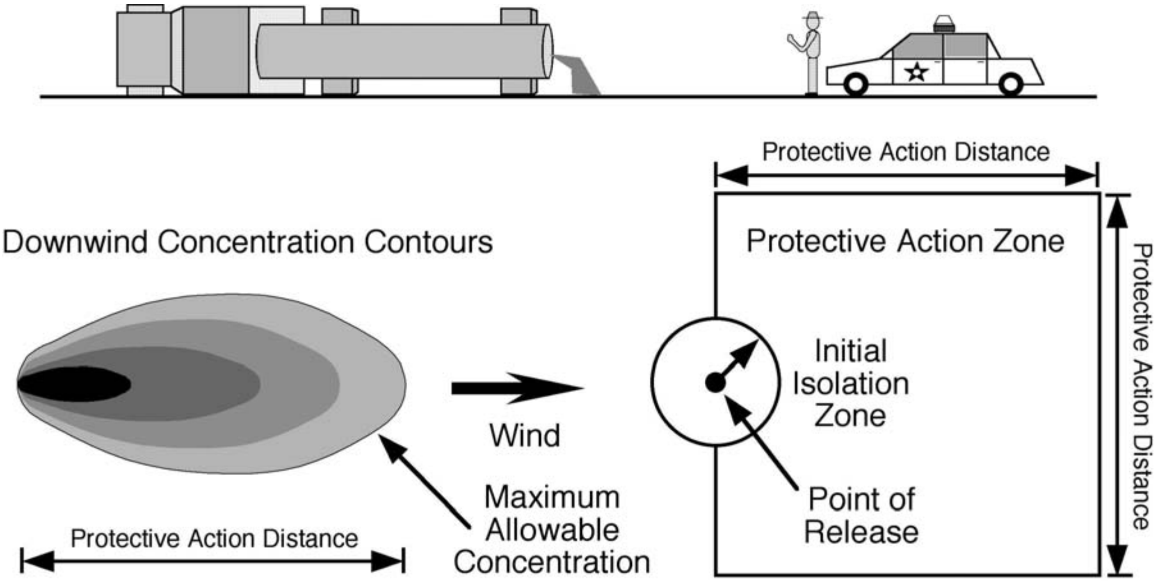

FIGURE 1.1 Illustration Showing How the ERG2004 Defines the Initial Isolation and Protective Action Zones for Use by a First Responder

The *Initial Isolation Distance* specifies a circular zone surrounding the accident site. Persons not involved with the response should be kept clear of this zone. Persons in the Initial Isolation Zone may be exposed to potentially life-threatening health effects downwind of the accident site and dangerous concentrations upwind due to wind direction variability. Specification of the Initial Isolation Distances is treated in a method analogous to that for the PADs.

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

1.2 ORGANIZATION OF THIS REPORT

Section 2 presents a detailed overview of the methodology used to calculate the Initial Isolation Distances and PADs. Included in this discussion is an examination of issues related to the TIH list; treatment of generic compounds, mixtures, and solutions; treatment of chemical warfare agents; and treatment of water-reactive materials. Section 3 provides details on the statistical scenario analysis applied to materials in the Table, as well as technical details on the consequence models used. Section 4 documents the health criteria, or threshold chemical concentrations, used to specify the Initial Isolation 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. Appendix A presents the Table (DOT et al. 2004). Appendixes B–D contain chemical data and details of the experiments conducted to identify and quantify TIH gas emission rates from water-reactive materials.

2 GENERAL METHODOLOGY

The methodology used in preparing the Table for the ERG2004 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 a few additions to and deletions from the ERG2000 list, with most additions being water reactive materials. 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 information, which takes into account 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 from transportation-related hazardous materials releases cataloged in the Hazardous Materials Information System (HMIS) database maintained by the DOT Research and Special Programs Administration.

Each scenario is then analyzed using detailed emission rate and atmospheric dispersion models to calculate an airborne chemical concentration footprint. The safe distance for a specific scenario is then chosen as the greatest downwind distance where the concentration exceeds the health criteria for the chemical involved in the incident. The health criteria, which are exposure-time-dependent threshold concentrations, are based on American Industrial Hygiene Association (AIHA) Emergency Response Planning Guideline Level 2 (ERPG-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. Incidents are then categorized by time (day, night) and spill size (60 gal or less = small, more than 60 gal = large). The PADs appearing in the ERG2004 are then selected as the 90th percentile values for these individual categories. The Initial Isolation Zones are calculated in a similar manner on the basis of health criteria for life-threatening effects.

2.1 TIH LIST

2.1.1 Background

For the purposes of our analysis, we classify materials on this TIH list into several different categories as follows: (1) pure chemicals, (2) mixtures, (3) solutions, and (4) generics (e.g., UN 1953: liquefied gas, toxic, flammable, n.o.s.). As is explained later, generic

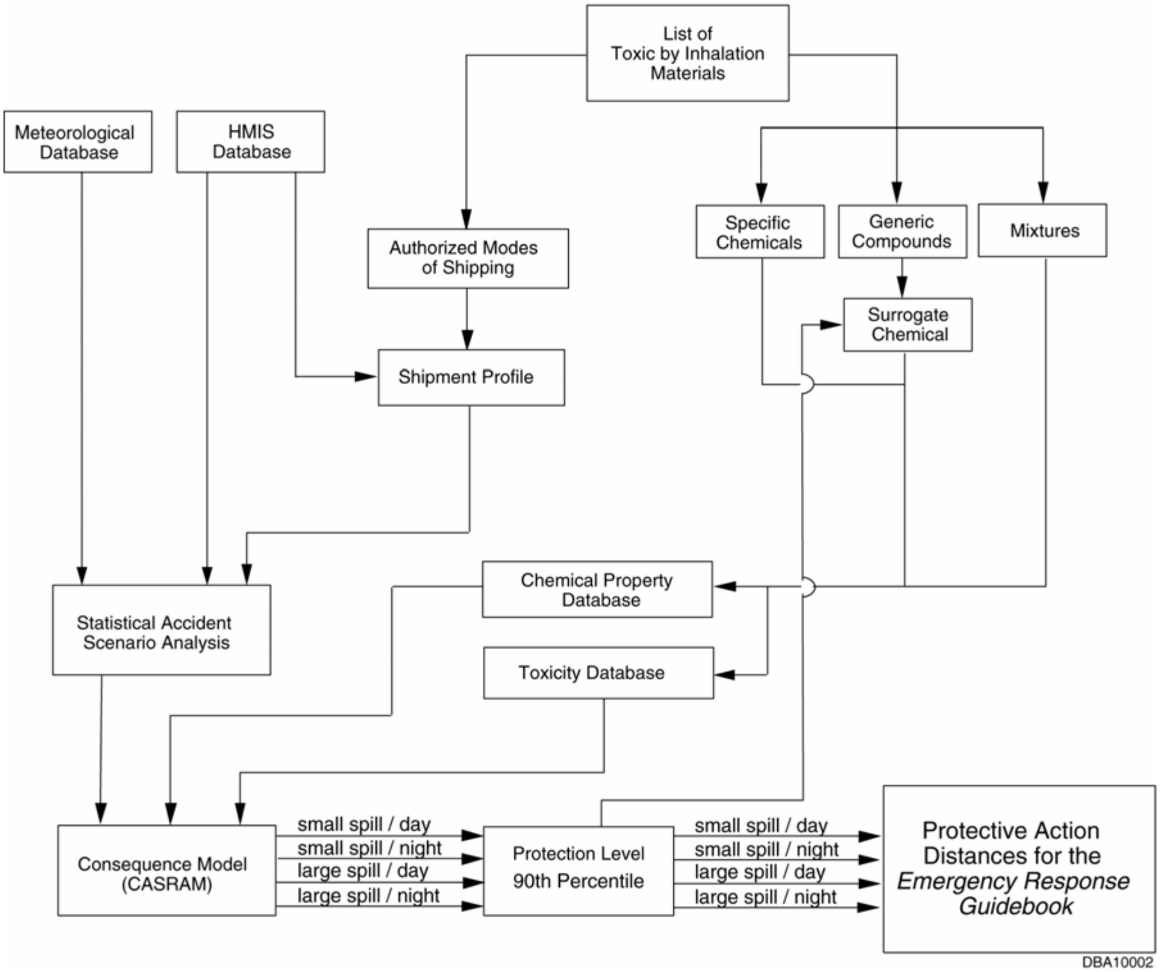

FIGURE 2.1 Schematic of the Methodology Used to Prepare the ERG2004 Table of Initial Isolation and Protective Action Distances

compounds are further divided into subcategories on the basis of Hazard Zone designation, as defined in Title 49, Part 173, Section 133 of the CFR (49 CFR 173.133). TIH materials fall into 4 Hazard Zones for gases (A, B, C, and D) and 2 for liquids (A and B). The ERG2004 lists PADs for 156 single compounds, 15 mixtures, and 26 generics. In addition, 70 water-reactive materials, defined here as materials that emit a TIH gas upon contact with water, are also included in the TIH list. Of the 70 water-reactive materials in the Table, several are also TIH compounds that produce a secondary, sometimes more toxic TIH gas upon reaction with water.

Each category is handled individually. Single chemicals are specified according to a Chemical Abstracts Services (CAS) number, which is a unique numerical identifier for each chemical compound. A unique identifier is necessary to avoid problems with chemical name synonyms. It is important to note that the UN number is not a unique identifier, in that two or more chemicals may be associated with a particular UN number. One example is UN 1076, which is used for both phosgene (CAS 75-44-5) and diphosgene (503-38-8), materials with structural similarities but markedly different physical properties. Mixtures are treated by considering the individual components in the mixture. Generics are modeled by using a surrogate compound, with the surrogate being the worst case of the materials considered for the particular generic description and hazard zone. Mixtures and generics are discussed in Section 2.3. Water-reactive materials are treated in a manner similar to that for regular TIH materials with modifications to the physical models for determining source emission rate. The treatment of water reactivity is discussed in Section 2.4 and Appendixes C and D.

2.1.2 Changes in the TIH List for the ERG2004

In contrast to the numerous changes in the TIH list that occurred between 1996 and 2000, there were relatively few substantive changes made in the TIH list for the 2004 Table, with the exception of (1) the addition of several new TIHWR materials and (2) the removal of all nerve and blister warfare agents that are Hazard Zone A and B liquids[1] for transportation-related releases. Considering water-reactive materials, 14 new materials were added to the TIHWR list, and 5 materials were removed. The additions and removals were based on experimental studies conducted for the ERG2004 analysis, which built on the experimental program initiated for the ERG2000. The treatment of water-reactive materials is discussed in depth in Section 2.4 and Appendixes C and D. The nerve and blister agents were removed because these materials do not appear in 49 CFR 172.101 (Hazardous Materials Table). Note that all these materials were retained for weapons-related releases, as discussed in Section 2.2.2. Wording revisions and synonym entry additions and deletions resulted in the addition of about 25 entries and removal of 6, thus bringing the names in the Table into agreement with current UN naming conventions.

For future editions of the ERG, we recommend deletion of coal gas (UN 1023) and oil gas (UN 1071). These are officially TIH materials; however, our analysis of the mixture constituents for these materials indicate the median lethal concentration (LC_{50}) is well above 10,000 ppm. We also recommend the addition of acrylonitrile (UN 1093) and methylamine (UN 1061). Acrylonitrile is a liquid with a vapor pressure of 11.9 kPa at 20°C, so in order to fit the criteria as a Hazard Zone B liquid, the LC_{50} would need to be below 1,000 ppm per 49 CFR 173.333. Several references cited in development of National Institute for Occupational Safety and Health (NIOSH) immediately dangerous to life and health (IDLH) values indicate the 1-h LC_{50} may be below 1,000 ppm (see www.cdc.gov/niosh/idlh). Methylamine is a gas. The reference used to set the IDLH value indicates the 1-h LC_{50} is below 5,000 ppm, the necessary criterion to become a Hazard Zone D gas. For reference, if acrylonitrile and methylamine were included in the Table, the large night spill protective action distances for them would be 0.37 and 1.45 mi, respectively.

2.2 SHIPMENT AND RELEASE SCENARIOS

To specify a level of protection as defined previously, we constructed a set of representative accident scenarios for each material on the TIH list. The first step in this process

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[1] Prior to this decision, Tris-(2-chloroethyl) amine (the warfare agent HN-3; UN 2810) was removed since investigation of the vapor pressure and LC_{50} values for this material showed it to be a Hazard Zone C liquid.

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

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

A special case within the shipment profile concept is the treatment of chemical warfare agents. These materials were first considered in the ERG2000. In 2000, entries were given for two release scenarios: (1) transportation-related release scenarios and (2) weapons-related release scenarios whereby the material is released in a criminal or terrorist act. However, the transportation-related release scenario was removed in 2004 as discussed in Section 2.1. The treatment of chemical warfare agents is outlined in Section 2.2.2.

TABLE 2.1 Ratio of En Route/Nonaccident Releases to Accident-Related Releases for Various Container Types as Derived from the HMIS Database for 1990–2002

Container Type	Ratio of En Route/Nonaccident Releases to Accident-Related Releases
111AW tank car	13
112JW and 105A tank car	23[a]
MC306 cargo tank	0.2
MC307 cargo tank	2.2
MC312 cargo tank	3.3
MC330/331 cargo tank	0.5
Small and medium drums	20
Large drums and portable tanks	7
Package freight cylinders	5

[a] For the ERG2004 analysis, the ratio for 111A tank cars is used for TIH liquids transported in Type 112JW and 105A tank cars.

2.2.1 Shipment Profiles

The starting point for the development of shipment profiles is 49 CFR 172.101 and associated subsections that specify the authorized shipping modes and packaging for hazardous materials. These specifications substantially influence the amount of material that could be released in a transport-related accident and other important factors that govern the release hazard, such as the relative frequencies of each container type being involved in a release and the discharge fractions resulting from releases (the amount of material released in an incident relative to the container capacity). For example, most Division 2.3 gases under Hazard Zone A cannot be transported in bulk form. Consequently, such materials are shipped only in package freight containers (drums, cylinders). The resultant total shipping volumes are thus much less than those associated with a typical bulk shipment even though there can be many package freight containers in a single shipment.

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

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

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

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

For 2004, we developed several new shipment profiles tailored specifically to several high-volume chemicals, such as chlorine and ammonia, based on our analysis of HMIS, rail waybill data from the American Association of Railroads, and other commodity flow information together with 49 CFR information. In addition, we created several additional profiles for materials called out for specific treatment in 49 CFR, such as diborane, fluorine, methyl mercaptin, and tetranitromethane. Some adjustment was made to existing profiles, most notably those for Hazard Zone A gases based on discussions with Compressed Gas Association members and analysis of HMIS incidents.

Examples of mixed rail and highway shipment profiles are provided in Tables 2.2 and 2.3 for liquids and gases, respectively. Three classes of shipments are listed for each profile: bulk rail transportation, bulk highway transportation, and package freight transportation. To provide some perspective on the relative influence of the shipment classes and release types on releases modeled in the ERG2004 analysis, the percentage of total releases represented by each type is listed for all releases, releases of 5–60 gal, and releases of more than 60 gal. When all releases are considered, en route/nonaccident incidents make up the majority of releases modeled for the shipment profiles given in Tables 2.2 and 2.3. However, in considering releases of more than 60 gal (i.e., "large spills" in the Table), accident-related incidents make up the majority of cases. For such releases, package freight incidents were the most common and bulk highway incidents the least. Because PADs are set by the 90th-percentile value, incidents involving bulk containers had a far greater influence on PAD values than did incidents involving package freight containers, since bulk containers usually involved larger release amounts.

2.2.2 Treatment of Chemical Agents

The 1995 Tokyo subway sarin attack and the events on and following September 11, 2001, have made the first-response community more aware of the threat from the malicious use of chemical and biological agents. For this reason, the ERG includes Initial Isolation Distances and PADs for various chemical agents that could be used as weapons. In addition, a separate section entitled Criminal/Terrorist Use of Chemical/Biological/Radiological Agents (page 354 of the ERG2004) 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 Initial Isolation and Protective Action Distances were calculated for cases in which they would be used as a weapon. (The table shows 36 chemical warfare agent names for the 26 compounds.) Accordingly, entries in the ERG2004 Table for these materials include the statement "when used as a weapon." Several of these materials are also industrial chemicals that appear separately in ERG2004 as transportation-related releases. Entries for weapons-related use of chemical agents, however, are listed under the common or military name for the compound, not the chemical name. For example, for

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	5–60 gal[b]	>60 gal[b]
1	Rail	DOT Class 112 tank car	80,000 kg	A	3.2	1.1	24.9
				E	41.6	23.0	21.7
2	Highway	DOT 312 cargo tank	20,000 kg	A	1.6	0.7	13.6
				E	5.0	6.4	6.2
3	Highway	Ten 55-gal 5C drums	550 gal	A	2.3	3.0	14.0
				E	46.2	65.8	19.6

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

[b] Data provided 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]

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

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

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

TABLE 2.4 Chemical Warfare Agents listed in the ERG2004 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	60	30,000	SH
1076	DP	Diphosgene	30	500	AL
1076	CG	Phosgene	60	1,500	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)	10	500	AS
1698	Adamsite				
1699	DA	Diphenylchloroarsine	10	500	AS
1892	ED	Ethyldichloroarsine	30	500	AL
2188	SA	Arsine	60	1,500	SH
2810	H	Bis-(2-chloroethyl) sulfide	2	100	SP
2810	HD				
2810	Mustard				
2810	HN-1	Bis-(2-chloroethyl) ethylamine	2	100	SP
2810	HN-2	Bis-(2-chloroethyl) methylamine	2	100	SP
2810	HN-3	Tris-(2-chloroethyl) amine	2	100	SP
2810	L	Dichloro-(2-chlorovinyl) arsine	2	100	SP
2810	Lewisite				
2810	HL[b]				
2810	Mustard lewisite[b]				
2810	BZ	3-Quinuclidinyl benzilate	10	500	AS
2810	Buzz				
2810	CS	o-Chlorobenzylidene malononitrile	10	500	AS
2810	DC	Diphenylcyanoarsine	10	500	AS
2810	GA	Ethyl N,N-dimethylphosphoramidocyanidate	2	100	SP
2810	Tabun				
2810	GB	Isopropyl methylphosphonofluoridate	2	100	SP
2810	Sarin				
2810	GD	Pinacolyl methylphosphonofluoridate	2	100	SP
2810	Soman				
2810	GF	Cyclohexyl methylphosphonofluoridate	2	100	SP
2810	VX	O-Ethyl S-(2-diisopropylaminoethyl) methylphosphonothiolate	2	100	SP
2811	CX	Phosgene oxime	10	500	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).

weapons-related entries, the first compound in Table 2.4 is listed as AC, whereas for transportation-related entries, this same compound is listed as hydrogen cyanide (UN 1051). These two terms refer to the same compound but with very different release scenarios.

The release scenarios for weapons-related incidents differ from those for transportation-related incidents because they involve deliberate releases. Two maximum release sizes were used for each material considered in the analysis. In the statistical analysis, release amounts were uniformly distributed between 50 and 100% of these maximum release amounts. Various release types were modeled, depending on the material being released. The release types are denoted in Table 2.4 by two-letter codes. The codes AL and AS refer to aerosolized liquid and aerosolized solid release mechanisms, respectively. It is assumed that AL and AS would be dispersed in aerosolized form with a 2- to 5-μm particle size. This release mechanism is used for solid materials or for materials that have very slow evaporation rates; thus, aerosolization is the only way to disseminate them effectively. The code SP refers to a spray or explosive release. This release mechanism is considered the most likely one to be used to disperse nerve and blister agents, since they are typically thick liquids not readily amenable to direct aerosolization. In the scenario used in this analysis, the spray quickly settles on the ground to a depth up to 0.25 mm and then evaporates. The evaporation rate for these materials is limited by their low vapor pressures. The code SH refers to releases by shipment sabotage. This release mechanism is used for volatile TIH materials. For example, the large release scenario for hydrogen cyanide involves the sabotage of a large bulk container such as a small rail car. Small release amounts for these materials correspond to the release of a standard gas cylinder.

2.3 GENERICS, MIXTURES, AND SOLUTIONS

The Table lists a variety of compounds that are generic in nature. Two examples are liquefied gas, flammable, poisonous, n.o.s. (Inhalation Hazard Zone B) (UN 3160) and toxic liquid, corrosive, organic, n.o.s. (UN 2927). (The abbreviation n.o.s. stands for not otherwise specified.) Each generic compound can represent many independent chemicals that fit that description but are not individually listed in the ERG2004 or the Table. In the ERG2004, Initial Isolation and Protective Action Distances for generic compounds are based on the worst-case compound from the pool of chemicals in the overall analysis that matches that generic description. As an example of this process, the generic compound described as liquefied gas, flammable, poisonous, n.o.s. (Inhalation Hazard Zone B) (UN 1953), which is also listed in the Table as liquefied gas, toxic, flammable, n.o.s. (Inhalation Hazard Zone B) (UN 3160), is considered below. The six chemicals analyzed for the ERG2004 that are included in this category are listed in Table 2.5. Phosphorus pentafluoride (UN 2198) yields the maximum distances for large spills, whereas dichlorosilane (UN 2189) yields the maximum distances for small spills (shown in bold in Table 2.5). Also provided are eight entries for this generic category that reflect the variations in wording in the Table. These entries are rounded up to the nearest 0.1 mi (100 ft for Initial Isolation Zones) to reflect their appearance in the Table.

Table 2.6 lists all the generic compounds included in the Table and provides the subset of chemicals from which their distances were calculated. Synonyms are not listed in Table 2.6, so

TABLE 2.5 Chemicals Used to Determine Initial Isolation and Protective Action Distances for the Generic Material Described as Liquefied Gas, Poisonous, Flammable, n.o.s. (Inhalation Hazard Zone B) (UN 1953, UN 3160)[a]

		Small Spills			Large Spills		
			Then Protect Persons Downwind during			Then Protect Persons Downwind during	
UN No.	Name of Material	First Isolate in All Directions (ft)	Day (mi)	Night (mi)	First Isolate in All Directions (ft)	Day (mi)	Night (mi)
Potential Surrogate Compounds							
1026	Cyanogen	58	0.11	0.71	348	0.66	2.63
1053	Hydrogen sulfide	16	0.03	0.17	681	1.29	3.84
2189	Dichlorosilane	53	0.1	0.56	**1,309**	**2.48**	**6.66**
2192	Germane	42	0.08	0.58	232	0.44	1.86
2198	Phosphorus pentafluoride	**79**	**0.15**	**0.99**	507	0.96	2.84
2204	Carbonyl sulfide	32	0.06	0.32	977	1.85	4.99
Synonymous Entries for Generic Compound Categories							
1953	Compressed gas, flammable, poisonous, n.o.s. (Inhalation Hazard Zone B)	100	0.2	0.8	1,400	2.5	6.7
1953	Compressed gas, flammable, toxic, n.o.s. (Inhalation Hazard Zone B)	100	0.2	0.8	1,400	2.5	6.7
1953	Compressed gas, poisonous, flammable, n.o.s. (Inhalation Hazard Zone B)	100	0.2	0.8	1,400	2.5	6.7
1953	Compressed gas, toxic, flammable, n.o.s. (Inhalation Hazard Zone B)	100	0.2	0.8	1,400	2.5	6.7
1953	Liquefied gas, flammable, poisonous, n.o.s. (Inhalation Hazard Zone B)	100	0.2	0.8	1,400	2.5	6.7
1953	Liquefied gas, flammable, toxic, n.o.s. (Inhalation Hazard Zone B)	100	0.2	0.8	1,400	2.5	6.7
3160	Liquefied gas, poisonous, flammable, n.o.s. (Inhalation Hazard Zone B)	100	0.2	0.8	1,400	2.5	6.7
3160	Liquefied gas, toxic, flammable, n.o.s. (Inhalation Hazard Zone B)	100	0.2	0.8	1,400	2.5	6.7

[a] This table provides distance estimates for all applicable entries in the ERG2004 Table of Initial Isolation and Protective Action Distances (DOT et al. 2004). The worst-case (maximum) distances for small spills and large spills for each column are shown in bold.

TABLE 2.6 Summary of Generic Compounds on DOT TIH List and Corresponding Surrogates Employed for the ERG2004. Note that a different surrogate material may by used for each release category.

UN Number	Proper Shipping Name	Surrogate
1953	Liquefied gas, poisonous, flammable, n.o.s.	Worst cases among all TIH, flammable gases
1953	Liquefied gas, poisonous, flammable, n.o.s. (Inhalation Hazard Zone A)	Worst cases among all TIH, flammable Hazard Zone A gases
1953	Liquefied gas, poisonous, flammable, n.o.s. (Inhalation Hazard Zone B)	Worst cases among all TIH, flammable Hazard Zone B gases
1953	Liquefied gas, poisonous, flammable, n.o.s. (Inhalation Hazard Zone C)	Worst cases among all TIH, flammable Hazard Zone C gases
1953	Liquefied gas, poisonous, flammable, n.o.s. (Inhalation Hazard Zone D)	Worst cases among all TIH, Hazard Zone D gases
1955	Liquefied gas, poisonous, n.o.s.	Worst cases among all TIH gases
1955	Liquefied gas, poisonous, n.o.s. (Inhalation Hazard Zone A)	Worst cases among all TIH, Hazard Zone A gases
1955	Liquefied gas, poisonous, n.o.s. (Inhalation Hazard Zone B)	Worst cases among all TIH, Hazard Zone B gases
1955	Liquefied gas, poisonous, n.o.s. (Inhalation Hazard Zone C)	Worst cases among all TIH, Hazard Zone C gases
1955	Liquefied gas, poisonous, n.o.s. (Inhalation Hazard Zone D)	Worst cases among all TIH, Hazard Zone D gases
1955	Organic phosphate mixed with compressed gas	Parathion and compressed gas mixture
1967	Insecticide gas, poisonous, n.o.s.	Parathion and compressed gas mixture
2810	Poisonous liquid, n.o.s.	Worst cases among all TIH liquids
2810	Poisonous liquid, n.o.s. (Inhalation Hazard Zone A)	Worst cases among all TIH Hazard Zone A liquids
2810	Poisonous liquid, n.o.s. (Inhalation Hazard Zone B)	Worst cases among all TIH Hazard Zone B liquids
2810	Poisonous liquid, organic, n.o.s.	Worst cases among all TIH organic liquids
2810	Poisonous liquid, organic, n.o.s. (Inhalation Hazard Zone A)	Worst cases among all TIH, organic, Hazard Zone A liquids
2810	Poisonous liquid, organic, n.o.s. (Inhalation Hazard Zone B)	Worst cases among all TIH, organic, Hazard Zone B liquids
2927	Poisonous liquid, corrosive, n.o.s.	Worst cases among all TIH corrosive liquids
2927	Poisonous liquid, corrosive, n.o.s. (Inhalation Hazard Zone A)	Worst cases among all TIH, corrosive, Hazard Zone A liquids
2927	Poisonous liquid, corrosive, n.o.s. (Inhalation Hazard Zone B)	Worst cases among all TIH, corrosive, Hazard Zone B liquids
2927	Toxic liquid, corrosive, organic, n.o.s.	Worst cases among all TIH corrosive, organic liquids
2927	Toxic liquid, corrosive, organic, n.o.s. (Inhalation Hazard Zone A)	Worst cases among all TIH, corrosive, organic Hazard Zone A liquids
2927	Toxic liquid, corrosive, organic, n.o.s. (Inhalation Hazard Zone B)	Worst cases among all TIH, corrosive, organic, Hazard Zone B liquids
2929	Poisonous liquid, flammable, n.o.s.	Worst cases among all TIH flammable liquids
2929	Poisonous liquid, flammable, n.o.s. (Inhalation Hazard Zone A)	Worst cases among all TIH, flammable, Hazard Zone A liquids
2929	Poisonous liquid, flammable, n.o.s. (Inhalation Hazard Zone B)	Worst cases among all TIH, flammable, Hazard Zone B liquids
2929	Poisonous liquid, flammable, organic, n.o.s.	Worst cases among all TIH flammable, organic, liquids
2929	Poisonous liquid, flammable, organic, n.o.s. (Inhalation Hazard Zone A)	Worst cases among all TIH, flammable, organic, Hazard Zone A liquids
2929	Poisonous liquid, flammable, organic, n.o.s. (Inhalation Hazard Zone B)	Worst cases among all TIH, flammable, organic, Hazard Zone B liquids
3122	Poisonous liquid, oxidizing, n.o.s.	Worst cases among all TIH, flammable, liquids
3122	Poisonous liquids, oxidizing, n.o.s. (Inhalation Hazard Zone A)	Worst cases among all TIH, flammable, Hazard Zone A liquids
3122	Poisonous liquids, oxidizing, n.o.s. (Inhalation Hazard Zone B)	Worst cases among all TIH, oxidizing, Hazard Zone B liquids
3123	Poisonous liquid, water-reactive, n.o.s.	Worst cases among all TIH liquids
3123	Poisonous liquid, water-reactive, n.o.s. (Inhalation Hazard Zone A)	Worst cases among all TIH Hazard Zone A liquids
3123	Poisonous liquid, water-reactive, n.o.s. (Inhalation Hazard Zone B)	Worst cases among all TIH Hazard Zone B liquids
3123	Poisonous liquid, which in contact with water emits flammable gases, n.o.s.	Worst cases among all TIH flammable liquids

TABLE 2.6 (Cont.)

UN Number	Proper Shipping Name	Surrogate
3123	Poisonous liquid, which in contact with water emits flammable gases, n.o.s. (Inhalation Hazard Zone A)	Worst cases among all TIH, flammable, Hazard Zone A liquids
3123	Poisonous liquid, which in contact with water emits flammable gases, n.o.s. (Inhalation Hazard Zone B)	Worst cases among all TIH, flammable, Hazard Zone B liquids
3160	Liquefied gas, poisonous, flammable, n.o.s.	Worst cases among all TIH, flammable gases
3160	Liquefied gas, poisonous, flammable, n.o.s. (Inhalation Hazard Zone A)	Worst cases among all TIH, flammable Hazard Zone A gases
3160	Liquefied gas, poisonous, flammable, n.o.s. (Inhalation Hazard Zone B)	Worst cases among all TIH, flammable Hazard Zone B gases
3160	Liquefied gas, poisonous, flammable, n.o.s. (Inhalation Hazard Zone C)	Worst cases among all TIH, flammable Hazard Zone C gases
3160	Liquefied gas, poisonous, flammable, n.o.s. (Inhalation Hazard Zone D)	Worst cases among all TIH, flammable Hazard Zone D gases
3162	Liquefied gas, poisonous, n.o.s.	Worst cases among all TIH gases
3162	Liquefied gas, poisonous, n.o.s. (Inhalation Hazard Zone A)	Worst cases among all TIH Hazard Zone A gases
3162	Liquefied gas, poisonous, n.o.s. (Inhalation Hazard Zone B)	Worst cases among all TIH Hazard Zone B gases
3162	Liquefied gas, poisonous, n.o.s. (Inhalation Hazard Zone C)	Worst cases among all TIH Hazard Zone C gases
3162	Liquefied gas, poisonous, n.o.s. (Inhalation Hazard Zone D)	Worst cases among all TIH Hazard Zone D gases
3275	Nitriles, poisonous, flammable, n.o.s.	Methacrylonitrile
3276	Nitriles, poisonous, n.o.s.	Methacrylonitrile
3278	Organophosphorus compound, poisonous, n.o.s.	Methyl phosphonous dichloride
3279	Organophosphorus compound, poisonous, flammable, n.o.s.	Methyl phosphonous dichloride
3280	Organoarsenic compound, n.o.s.	Tert-butylarsine
3281	Metal carbonyls, n.o.s.	Nickel carbonyl
3287	Poisonous liquid, inorganic, n.o.s.	Worst cases among all TIH inorganic liquids
3287	Poisonous liquid, inorganic, n.o.s. (Inhalation Hazard Zone A)	Worst cases among all TIH, inorganic, Hazard Zone A liquids
3287	Poisonous liquid, inorganic, n.o.s. (Inhalation Hazard Zone B)	Worst cases among all TIH, inorganic, Hazard Zone B liquids
3289	Poisonous liquid, corrosive, inorganic, n.o.s.	Worst cases among all TIH, corrosive, inorganic liquids
3289	Poisonous liquid, corrosive, inorganic, n.o.s. (Inhalation Hazard Zone A)	Worst cases among all TIH, corrosive, inorganic, Hazard Zone A liquids
3289	Poisonous liquid, corrosive, inorganic, n.o.s. (Inhalation Hazard Zone B)	Worst cases among all TIH, corrosive, inorganic, Hazard Zone B liquids
3303	Compressed gas, poisonous, oxidizing, n.o.s.	Worst cases among all TIH, oxidizing gases
3303	Compressed gas, poisonous, oxidizing, n.o.s. (Inhalation Hazard Zone A)	Worst cases among all TIH, Hazard Zone A, oxidizing gases
3303	Compressed gas, poisonous, oxidizing, n.o.s. (Inhalation Hazard Zone B)	Worst cases among all TIH, Hazard Zone B, oxidizing gases
3303	Compressed gas, poisonous, oxidizing, n.o.s. (Inhalation Hazard Zone C)	Worst cases among all TIH, Hazard Zone C gases
3303	Compressed gas, poisonous, oxidizing, n.o.s. (Inhalation Hazard Zone D)	Worst cases among all TIH, Hazard Zone D gases
3304	Compressed gas, poisonous, corrosive, n.o.s.	Worst cases among all TIH, corrosive gases
3304	Compressed gas, poisonous, corrosive, n.o.s. (Inhalation Hazard Zone A)	Worst cases among all TIH, corrosive, Hazard Zone A gases
3304	Compressed gas, poisonous, corrosive, n.o.s. (Inhalation Hazard Zone B)	Worst cases among all TIH, corrosive, Hazard Zone B gases
3304	Compressed gas, poisonous, corrosive, n.o.s. (Inhalation Hazard Zone C)	Worst cases among all TIH, corrosive, Hazard Zone C gases
3304	Compressed gas, poisonous, corrosive, n.o.s. (Inhalation Hazard Zone D)	Worst cases among all TIH, corrosive, Hazard Zone D gases
3305	Compressed gas, poisonous, flammable, corrosive, n.o.s.	Worst cases among all TIH, corrosive gases
3305	Compressed gas, poisonous, flammable, corrosive, n.o.s. (Inh. Hazard Zone A)	Worst cases among all TIH, corrosive, Hazard Zone A gases

TABLE 2.6 (Cont.)

UN Number	Proper Shipping Name	Surrogate
3305	Compressed gas, poisonous, flammable, corrosive, n.o.s. (Inh. Hazard Zone B)	Worst cases among all TIH, corrosive, Hazard Zone B gases
3305	Compressed gas, poisonous, flammable, corrosive, n.o.s. (Inh. Hazard Zone C)	Worst cases among all TIH, corrosive, Hazard Zone C gases
3305	Compressed gas, poisonous, flammable, corrosive, n.o.s. (Inh. Hazard Zone D)	Worst cases among all TIH, corrosive, Hazard Zone D gases
3306	Compressed gas, poisonous, oxidizing, corrosive, n.o.s.	Worst cases among all TIH, oxidizing, corrosive gases
3306	Compressed gas, poisonous, oxidizing, corrosive, n.o.s. (Inh. Hazard Zone A)	Worst cases among all TIH, oxidizing, corrosive, Hazard Zone A gases
3306	Compressed gas, poisonous, oxidizing, corrosive, n.o.s. (Inh. Hazard Zone B)	Worst cases among all TIH, oxidizing, corrosive, Hazard Zone B gases
3306	Compressed gas, poisonous, oxidizing, corrosive, n.o.s. (Inh. Hazard Zone C)	Worst cases among all TIH, corrosive, Hazard Zone C gases
3306	Compressed gas, poisonous, oxidizing, corrosive, n.o.s. (Inh. Hazard Zone D)	Worst cases among all TIH, corrosive, Hazard Zone D gases
3307	Liquefied gas, poisonous, oxidizing, n.o.s.	Worst cases among all TIH, oxidizing gases
3307	Liquefied gas, poisonous, oxidizing, n.o.s. (Inhalation Hazard Zone A)	Worst cases among all TIH, Hazard Zone A, oxidizing gases
3307	Liquefied gas, poisonous, oxidizing, n.o.s. (Inhalation Hazard Zone B)	Worst cases among all TIH, Hazard Zone B, oxidizing gases
3307	Liquefied gas, poisonous, oxidizing, n.o.s. (Inhalation Hazard Zone C)	Worst cases among all TIH, Hazard Zone C, oxidizing gases
3307	Liquefied gas, poisonous, oxidizing, n.o.s. (Inhalation Hazard Zone D)	Worst cases among all TIH, Hazard Zone D, oxidizing gases
3308	Liquefied gas, poisonous, corrosive, n.o.s.	Worst cases among all TIH, corrosive gases
3308	Liquefied gas, poisonous, corrosive, n.o.s. (Inhalation Hazard Zone A)	Worst cases among all TIH, corrosive, Hazard Zone A gases
3308	Liquefied gas, poisonous, corrosive, n.o.s. (Inhalation Hazard Zone B)	Worst cases among all TIH, corrosive, Hazard Zone B gases
3308	Liquefied gas, poisonous, corrosive, n.o.s. (Inhalation Hazard Zone C)	Worst cases among all TIH, corrosive, Hazard Zone C gases
3308	Liquefied gas, poisonous, corrosive, n.o.s. (Inhalation Hazard Zone D)	Worst cases among all TIH, corrosive, Hazard Zone D gases
3309	Liquefied gas, poisonous, flammable, corrosive, n.o.s.	Worst cases among all TIH, corrosive gases
3309	Liquefied gas, poisonous, flammable, corrosive, n.o.s. (Inhalation Hazard Zone A)	Worst cases among all TIH, corrosive, Hazard Zone A gases
3309	Liquefied gas, poisonous, flammable, corrosive, n.o.s. (Inhalation Hazard Zone B)	Worst cases among all TIH, corrosive, Hazard Zone B gases
3309	Liquefied gas, poisonous, flammable, corrosive, n.o.s. (Inhalation Hazard Zone C)	Worst cases among all TIH, corrosive, Hazard Zone C gases
3309	Liquefied gas, poisonous, flammable, corrosive, n.o.s. (Inhalation Hazard Zone D)	Worst cases among all TIH, corrosive, Hazard Zone D gases
3310	Liquefied gas, poisonous, oxidizing, corrosive, n.o.s.	Worst cases among all TIH, oxidizing, corrosive gases
3310	Liquefied gas, poisonous, oxidizing, corrosive, n.o.s. (Inhalation Hazard Zone A)	Worst cases among all TIH, oxidizing, corrosive, Hazard Zone A gases
3310	Liquefied gas, poisonous, oxidizing, corrosive, n.o.s. (Inhalation Hazard Zone B)	Worst cases among all TIH, oxidizing, corrosive, Hazard Zone B gases
3310	Liquefied gas, poisonous, oxidizing, corrosive, n.o.s. (Inhalation Hazard Zone C)	Worst cases among all TIH, corrosive, Hazard Zone C gases
3310	Liquefied gas, poisonous, oxidizing, corrosive, n.o.s. (Inhalation Hazard Zone D)	Worst cases among all TIH, corrosive, Hazard Zone D gases
3355	Insecticide gas, poisonous, flammable, n.o.s	Worst cases among all flammable, insecticide gases
3355	Insecticide gas, poisonous, flammable, n.o.s. (Inhalation Hazard Zone A)	Worst cases among all flammable, insecticide, Hazard Zone A gases
3355	Insecticide gas, poisonous, flammable, n.o.s. (Inhalation Hazard Zone B)	Worst cases among all flammable, insecticide, Hazard Zone B gases
3355	Insecticide gas, poisonous, flammable, n.o.s. (Inhalation Hazard Zone C)	Worst cases among all flammable, insecticide, Hazard Zone C gases
3355	Insecticide gas, poisonous, flammable, n.o.s. (Inhalation Hazard Zone D)	Worst cases among all flammable, insecticide, Hazard Zone D gases

TABLE 2.7 Summary of Mixtures and Solutions on DOT TIH List and How They Were Treated for the ERG2004

UN Number	Category	Proper Shipping Name	Modeled as
Mixtures and Solutions Modeled as Single Toxic Species			
1040	Mixture	Ethylene oxide with nitrogen	100% ethylene oxide
1051	Solution	Hydrocyanic acid, aqueous solutions, with more than 20% hydrogen cyanide	100% hydrogen cyanide
1911	Mixture	Diborane	7% diborane
1955	Mixture	Methyl bromide and nonflammable, nonliquified compressed gas mixtures	100% methyl bromide
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
1703	Mixture	Tetraethyl dithiopyrophosphate and gases, in solution	20% tetraethyl dithiopyrophosphate
1705	Mixture	Tetraethyl pyrophosphate and compressed gas mixtures	20% tetraethyl pyrophosphate
1744	Solution	Bromine solutions	100% bromine
1754	Mixture	Chlorosulfonic acid and sulfur trioxide mixture	100% sulfur trioxide
1967	Mixture	Parathion and compressed gas mixtures	20% parathion
1975	Mixture	Nitric oxide and dinitrogen tetroxide mixtures	100% nitric oxide
2600	Mixture	Carbon monoxide and hydrogen mixtures	100% carbon monoxide
3294	Solution	Hydrogen cyanide, solution in alcohol, with not more than 45% hydrogen cyanide	45% hydrogen cyanide solution in alcohol
3300	Mixture	Carbon dioxide and ethylene oxide mixture, with more than 87% ethylene oxide	100% ethylene oxide
3318	Solution	Ammonia solution, with more than 50% ammonia	100% ammonia
Mixtures Modeled with Multiple Toxic Chemical Species			
1581	Mixture	Chloropicrin and methyl bromide mixtures	(i) 5% chloropicrin, and (ii) 95 % methyl bromide
1582	Mixture	Chloropicrin and methyl chloride mixtures	(i) 2% chloropicrin, and (ii) 98 % methyl chloride
1023	Mixture	Coal gas	48% hydrogen, (ii) 27% methane, (iii) 10% carbon monoxide, (iv) 5% carbon dioxide, and (v) 6% nitrogen,
1071	Mixture	Oil gas	(i) 55% hydrogen, (ii) 25% methane, (iii) 11% carbon monoxide, (iv) 3% carbon dioxide, (v) 2% ethylene, and (vi) 2 % benzene

each entry may have several corresponding entries in the Table. For categories that had fewer than three chemicals from which to pick the worst-case example, the selection pool was enlarged to include materials from the next less restrictive designation. For instance, the pool for the generic category described as compressed gas, poisonous, oxidizing, corrosive, n.o.s. (Inhalation Hazard Zones C and D) included all corrosive gases in Hazard Zones C and D, respectively, because no corrosive, *oxidizing* gases with those hazard zone designations were identified in the analysis pool.

Table 2.7 lists the mixtures and solutions treated in the ERG2004 analysis and indicates how they were modeled. In general, the distances for mixtures were determined by (1) selecting a surrogate compound, (2) considering the toxic effects of a single hazardous constituent, or (3) considering the toxic effects of multiple hazardous constituents. Surrogates were chosen when the mixture composition was not specified. For these cases, the surrogate was chosen as the worst-case chemical or potential composition in that mixture. As an example, consider chlorosulfonic acid and sulfur trioxide mixtures (UN 1754). In these mixtures, sulfur trioxide is the more hazardous component, primarily because of its higher vapor pressure. The addition of chlorosulfonic acid will act to lower the vapor pressure, so a 100% sulfur trioxide mixture is the worst case and was chosen for analysis. A single hazardous constituent was modeled for several cases involving mixtures in compressed gases and solutions (e.g., diborane, tetraethyl pyrophosphate, hydrocyanic acid solutions). For each case, the worst case as specified in 49 CFR or by the description was modeled. The third class of mixtures involves compounds with more than one hazardous component. For instance, in chloropicrin and methyl bromide mixtures (UN 1581), chloropicrin is dissolved in methyl bromide up to 5% by volume. Therefore, toxic effects of both constituents are taken into account. The result is a mixture that behaves almost identically to pure methyl bromide in terms of release rate and dispersion. However, the mixture is much more toxic than pure methyl bromide as a result of the high toxicity of chloropicrin, so the PAD is longer than that for pure methyl bromide.

2.4 ANALYSIS OF WATER-REACTIVE MATERIALS

2.4.1 Background

Trucks and rail cars 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 byproducts. 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, or TIHWR[2]. 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

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[2] Note that we explicitly exclude from our definition and discussions that follow materials that evolve flammable gases that do not otherwise pose a toxic hazard.

Chicago spill of silicon tetrachloride from a storage tank in 1976 is an example. At one point in the eight-day episode, heavy rainfall led to a significant increase in emissions and sudden damage to the surroundings because additional HCl was released into the atmosphere. The same problem, though of less magnitude (due to a smaller release amount), would occur if a truck or tank car spilled silicon tetrachloride into water or had an accident during a rainstorm.

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

This section provides a description of our program for identifying and classifying TIHWR materials, as well as a companion experimental program instituted to provide a quantitative basis for the TIHWR analysis. 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 ERG2004 study are detailed in Section 3.3.2.3, and additional detail on the experiments and the parameters employed in the TIHWR modeling appear in Appendixes C and D.

2.4.2 Identification and Evaluation of Candidates

To compile the list of water-reactive materials for the Guidebook from the large pool of potential TIH emitters, we first screened materials by applying general principles of chemical reactivity, seeking specific reactivity information from the chemical literature and comparing such information among related compounds. Screening started with the 208 chemically distinct materials previously found by Carhart et al. (1996) to be capable of producing TIH gases if spilled into a river, lake, or other body of surface water. The 37 materials that make up the 1996 North American ERG “List of Dangerous Water-Reactive Materials” are a subset of these 208. In the analysis for the ERG2000, 16 more materials were added to this list based on 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 (1966).

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

Steps 1 through 3 were used to generate the 1996 TIHWR list. For the ERG2000, the experimental program outlined in Step 4 was initiated. This program was expanded for the ERG2004 to include over half of the TIHWR list. The need for such experimental data is underscored by the fact that quantitative observations of TIH gas evolution from hazardous chemicals added to water do not exist in the chemical literature. The experimental program is outlined below.

2.4.3 Experimental Program

The experimental program consisted of a series of small-scale experiments with candidate materials. The materials were tested for the generation of gases by mixing small amounts (about 1 millimole [mmol]) with water in a closed system. The release of gas was measured over time by observing the displacement of a suitable liquid in a manometer. Experiments were conducted using two different amounts of water (the stoichiometric equivalent amount and fivefold molar excess) for each material considered. The experimental procedure and resulting data and analysis are fully described in Appendixes C and D.

Experiments were conducted for 21 candidate materials for the ERG2000 or about one-quarter of the total TIHWR list. Heavy emphasis was placed on members of the large class of HCl emitters. An additional 35 materials were considered for the ERG2004 analysis, bringing the proportion of materials on the TIHWR list for which we have experimental data to over 50%.

The experimental program not only gave useful quantitative information on the rates of evolution of TIH gases, but it also allowed us to delete several chemicals from the TIHWR list because no evolution of gas was observed. In a few such cases, a reaction did actually 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, and additional experiments will be required to establish whether significant amounts of TIH gases would escape under such conditions.

2.4.4 Additional Selection Criteria

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

- Some potential TIHWR materials, especially generic materials, are not sufficiently described chemically to allow a complete assessment of their behavior when spilled into water. Such materials are not included on the TIHWR list unless there is a positive indication that a TIH gas might develop in a spill into water. Examples of materials that are not included on the

TIHWR list at this time include: pyrophoric organometallic compound n.o.s. (UN 3203); organometallic compound solution water-reactive, flammable, n.o.s (UN 3207); water-reactive substances, liquid, corrosive, n.o.s. (UN 3129); water-reactive solid, corrosive, n.o.s. (UN 3131); water-reactive substances, liquid, n.o.s, (UN 3148); water-reactive liquid, toxic, n.o.s. (UN 3130); and substances which in contact with water emit flammable gases, solid, poisonous, n.o.s. (UN 3134).

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

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

- Liquids boiling in the range of ordinary environmental temperature (0–20°C) presented problems, because they occur as a liquid or a gas depending on water temperature. Cyanogen chloride was rejected because it is a gas at temperatures above most of this range (boiling point 13.1°C) and because it does not require a spill into water to pose a TIH hazard. Chlorine trifluoride (boiling point 11.8°C) was rejected on similar grounds. On the other hand, 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. Also, since its boiling point is 12.5°C, the material can remain in the liquid state when spilled into cold water. In addition, BCl_3 is frequently purveyed in solution in an organic solvent.

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

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

- Thermal decomposition of calcium hypochlorite (UN 1748) and lithium hypochlorite (UN 1471) generates chlorine and/or HCl (Lewis 1966, p. 707), which are TIH gases. These two hypochlorites appeared as TIHWR materials in the ERG1996 but were removed as TIHWR materials in the ERG2000 and ERG2004 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 as TIHWR in ERG2004 on the basis of the behavior of sodium hydrosulfite in a serious plant accident in New Jersey April 21, 1995 (EPA and OHSA 1997).

2.4.5 Summary

As a result of the steps and considerations detailed above, 37 new materials were proposed for inclusion in the ERG2000 and 14 new materials were added to the TIHWR list for 2004, while 5 materials were removed for 2004. The full list of TIHWR materials considered in the ERG2004 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 Initial Isolation Distance is the length of the radius of a circular Initial Isolation Zone around the accident site from which people are to be kept away. Establishment of an Initial Isolation Zone serves two purposes. First, it provides a protective barrier upwind to protect against exposures due to wind direction variations. Second, it defines a zone downwind where life-threatening effects might be expected. The latter is generally a more stringent requirement, so that purpose is used to define the Initial Isolation Distance.

The Initial Isolation Distance is calculated in an identical manner to the PAD except that lethality is the health end point. As such, distances are evaluated using the 1-h LC_{50}. The 1-h value is used in all cases (no time adjustment is made) even though exposure times will be generally be 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 ERPG-3 (or surrogate) yielded slightly longer distances, although the methods are comparable for most materials. We use LC_{50} values because they are experimentally derived and available for nearly all materials on the TIH list.

It is important to note that many TIH materials are also flammable or oxidizers. The Initial Isolation Distance does not account for the explosive or flammable nature of the material, so there may be large differences between the Initial Isolation Distance and corresponding isolation distance guidelines in the orange guide pages in the ERG2004. In some cases, the Initial Isolation Distance can be less than the suggested evacuation distance based on flammability or explosion concerns.

3 STATISTICAL ACCIDENT SCENARIO ANALYSIS AND CASRAM

CASRAM (Chemical Accident Statistical Risk Assessment Model) lies at the core of the analysis for PAD determination for the ERG2004 and is the key tool we employ for both constructing accident scenarios and executing the 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 utilizes 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 (Reynolds 1992) and HPAC/SCIPUFF (Sykes et al. 1998). Rather than specifying a deterministic measure of risk, CASRAM determines the distribution of possible outcomes, thus allowing identification of the probability of a particular consequence within the limits of the statistical data.

CASRAM is primarily a routing-based risk assessment model that requires shipment attributes (e.g., materials, containers) and shipment routes as inputs. It provides distributions of affected persons as outputs (e.g., Brown et al. 2001). However, it is equally applicable to a geographically based incident distribution system. A geographically based system is required for the ERG analysis because the Table must reflect releases that occur anywhere in North America. The statistical accident scenario analysis (see Figure 2.1) combines the shipment profile information discussed in Section 2.2, meteorological observations from a preprocessed meteorological database, and statistical information from the HMIS database to provide a large distribution of incidents. These incidents are then modeled 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 Protective Action and Initial Isolation Distances 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 ERG2004 study. The emission rate and dispersion modeling within CASRAM, which makes up the consequence modeling effort to determine PADs, is then outlined.

3.1 STATISTICAL SCENARIO ANALYSIS

3.1.1 Overview of Analysis Steps

For each material in the Table, we use CASRAM to model between 200,000 and 1,000,000 separate incidents distributed between highway and rail transportation, relevant container types (e.g., DOT class 105 tank car, MC 330 cargo tank, 1A1 drums, etc), and release types (i.e., accident-related and en route/nonaccident). The distribution of the incidents within the categories above are specified in the shipment profiles discussed in Section 2.2. Incidents are also distributed geographically and temporally on the basis of transportation mode and release type. Geographic and temporal effects have a large influence on meteorology, which in turn directly affects the safe distance calculation. The location of the incident affects the general climate and land use (e.g., dry desert, temperate farmland), whereas the time of day and month affect the weather at that locale.

Each release modeled in the analysis is assigned a random date, time, and location. The locations for U.S.-based accidents are chosen probabilistically on the basis of state distributions of accidents in the HMIS database. Separate distributions are used for accident-related and en route/nonaccident releases for both highway and rail. Locations for Canada and Mexico are based on population density. Date and time are assigned on the basis of month-of-year and time-of-day distributions for incidents in the HMIS database as outlined in Section 3.1.4, where the year is assigned in a five-year window that corresponds to observations in the meteorological database (1985–1989[3]).

The emission rate model in CASRAM uses the shipment information and meteorology as specified above to determine the rate at which specific materials are released into the atmosphere. The first step is to estimate the discharge fraction on the basis of historical statistical distributions generated from analysis of incidents in the HMIS database. The emission rates of the material to the atmosphere are then calculated 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 pool size are treated stochastically.

Using the emission rates for the chemical(s) involved and the ambient meteorology, the dispersion model within CASRAM then determines the affected areas. We view the dispersion calculation as a two-step process. Step 1 involves characterizing the meteorology from the available surface observations, and step 2 involves estimating the transport and dispersion from the applicable meteorological parameters. Step 1 is accomplished with a *meteorological preprocessor*, which is a series of algorithms that take raw meteorological data (e.g., wind speed, temperature, humidity, cloud cover) and site information (e.g., land cover type, roughness length) and calculate parameters necessary for estimating dispersion. While this analysis is usually closely associated with dispersion modeling, the atmospheric parameters calculated are

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[3] More current meteorological data are not employed since the 1985–1989 window is the last 5-year period in which manual observations are available. Current NWS observations are made with automated equipment which has difficulty discerning cloud amounts and precipitation type.

also used in estimating source emission rates. Often, these parameters are represented as stability classes; however, in this analysis, the turbulence and structure of the atmospheric boundary layer were represented by more fundamental turbulence measures, such as friction velocity, surface heat flux, and inversion height. Step 2 is accomplished in CASRAM with a Lagrangian integral dispersion model for passive releases, coupled with a dense gas dispersion model to address large releases of liquefied gases where heavier-than-air plumes form. The physical relationships that make up the emission rate and dispersion models are outlined in Sections 3.3 and 3.4, respectively.

3.1.2 The HMIS database

The Hazardous Materials Information System (HMIS) database, maintained by DOT, catalogues transportation-related incidents involving the release of hazardous materials. In latter years, about 15,000 incidents per year are catalogued for highway, rail, air, and waterway transportation. In general, 80–85% of the incidents are highway-related, and about 11–14% are rail-related. Air accidents (mainly luggage-related) comprise almost all of the rest. Incidents in the database can occur (1) during an accident (i.e., during a vehicular mishap or a train derailment), (2) en route but not during an accident (e.g., due to a cargo shift or valve failure), or (3) during loading or unloading operations. For highway transportation, about 80% of the incidents in the HMIS database occur during loading and unloading; for rail, about 85% are en route/nonaccident releases.

For each incident catalogued in the HMIS database, information pertaining directly to the hazardous material release is provided, including: (1) name of chemical shipped, (2) container type and capacity, (3) number of containers shipped, (4) number of containers that fail, and (5) 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 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 comprised of data from actual hazardous materials incidents, it is an invaluable tool in statistical analyses of hazardous material transportation incidents and the best publicly available source of information concerning container failure statistics and release amount. For the ERG2004 analysis, as well as other risk assessments, we use HMIS data to specify geographical incident distributions, temporal incident distributions, and discharge fraction distributions as described in the subsections below. Further information on the HMIS database and our previous analyses can be found in (Brown et al. 2001).

3.1.3 Geographic Incident Distributions

In the ERG2004 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 1985–2002, and separate geographic distributions are used for highway and rail. The distribution of accidents between U.S., Canada, and Mexico is based on the relative Gross Domestic Products (GDP) for 2002. GDP was selected as a measure for hazard materials incidents because of the unavailability of detailed hazardous materials incident data 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, 89% of incidents modeled in the ERG2004 analysis occurred in the United States, 7% occurred in Canada, and 4% 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 and 22°N latitude), and Southern (below 18°N latitude, including the Yucatan Peninsula). A breakdown of the geographic distribution of incidents in the ERG2004 analysis for highway and rail transportation is provided in Table 3.1.

3.1.4 Temporal Incident Distributions

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

Temporal incident statistics in CASRAM and used in the ERG2004 analysis are based on HMIS database records for 1990–2002 and are updated from the distributions used for the ERG2000. These are shown in Figures 3.1 and 3.2. The figures show the percent of incidents broken into time of day as shown in Figure 3.1 and month of year Figure 3.2. Data are shown for accident-related and en route/nonaccident releases for both highway and rail. The number of incidents in the statistical samples is provided in the figure legends. The incident sample is slightly different between the figures, due to missing data fields (i.e., hour or month) in a small percentage of HMIS incident records.

3.1.5 Discharge Fraction Distributions

In the CASRAM emission model, the discharge fraction is estimated using statistical distributions developed from an analysis of the HMIS database. HMIS records list container type, number of containers shipped, number of containers that fail, and the amount of material

TABLE 3.1 Geographic Distribution of Highway and Rail Transportation Incidents Modeled in the ERG2004 Analysis, by Percentage

State	Rail	Highway	State/Province	Rail	Highway
Alabama	2.49	2.13	New Mexico	1.06	1.26
Alaska	0.18	0.10	New York	0.86	2.13
Arizona	1.34	1.37	North Carolina	2.23	2.71
Arkansas	2.57	2.87	North Dakota	0.17	0.18
California	10.63	4.25	Ohio	4.37	5.53
Colorado	1.54	1.49	Oklahoma	0.76	1.63
Connecticut	0.06	0.79	Oregon	1.49	0.93
District of Columbia	0.00	0.03	Pennsylvania	1.54	5.10
Delaware	0.12	0.20	Rhode Island	0.02	0.15
Florida	1.54	2.36	South Carolina	0.71	1.58
Georgia	2.42	2.65	South Dakota	0.02	0.20
Hawaii	0.00	0.05	Tennessee	2.35	3.29
Idaho	0.73	0.39	Texas	12.18	7.89
Illinois	5.06	4.98	Utah	2.40	1.24
Indiana	1.57	2.70	Vermont	0.01	0.14
Iowa	0.77	1.15	Virginia	1.26	1.83
Kansas	1.96	1.87	Washington	1.44	1.22
Kentucky	1.68	2.20	West Virginia	0.61	0.90
Louisiana	6.05	3.22	Wisconsin	0.29	1.50
Massachusetts	0.23	1.20	Wyoming	2.59	0.54
Maryland	0.63	1.40	Canada and Mexico		
Maine	0.12	0.27	British Columbia, Can.	0.82	0.82
Michigan	3.14	1.91	Alberta	0.63	0.63
Minnesota	0.50	1.45	Saskatchewan	0.25	0.25
Mississippi	0.86	1.60	Manitoba	0.27	0.27
Missouri	2.37	3.04	Ontario	2.51	2.51
Montana	0.54	0.30	Quebec	1.71	1.71
Nebraska	1.65	0.57	Atlantic Provinces	0.58	0.58
Nevada	0.97	0.40	Northern Mexico	1.03	1.03
New Hampshire	0.01	0.23	Central Mexico	2.69	2.69
New Jersey	0.68	1.67	Southern Mexico	0.76	0.76

released, allowing us to statistically characterize the release amount for containers of various types and sizes. In this process, we found that the fraction of the container capacity that is released proved a robust statistic in terms of both collapsing data from a wide variety of containers and ease of use in subsequent risk assessment studies. This fraction of the total container capacity that is released is defined here as the *discharge fraction*. Since the amount of material actually shipped is not currently provided in the HMIS database, the container capacity provides the best estimate of the amount shipped. As an example, consider a vehicular accident that involves the shipment of chlorine in a 17,000-gal Type 105A300W rail car and in which 240 gal is released. The discharge fraction would be 240/17,000 or 0.014. As is discussed later, this incident would be grouped with all other incidents involving releases from pressurized rail cars (Types 105 and 112) to construct the discharge fraction distributions for accident-related releases.

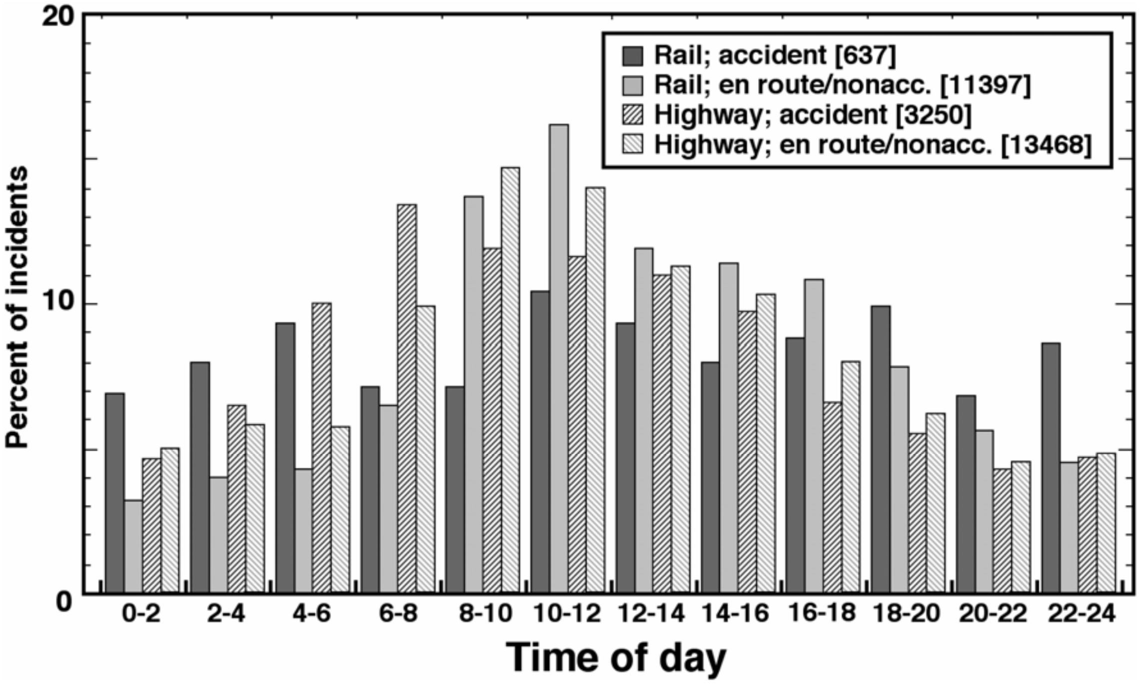

FIGURE 3.1 Hourly Distributions of Rail and Highway Transportation-Related Hazardous Material Releases Occurring During Accident-Related and En Route/Nonaccident Incidents from the HMIS Database, 1990-2002

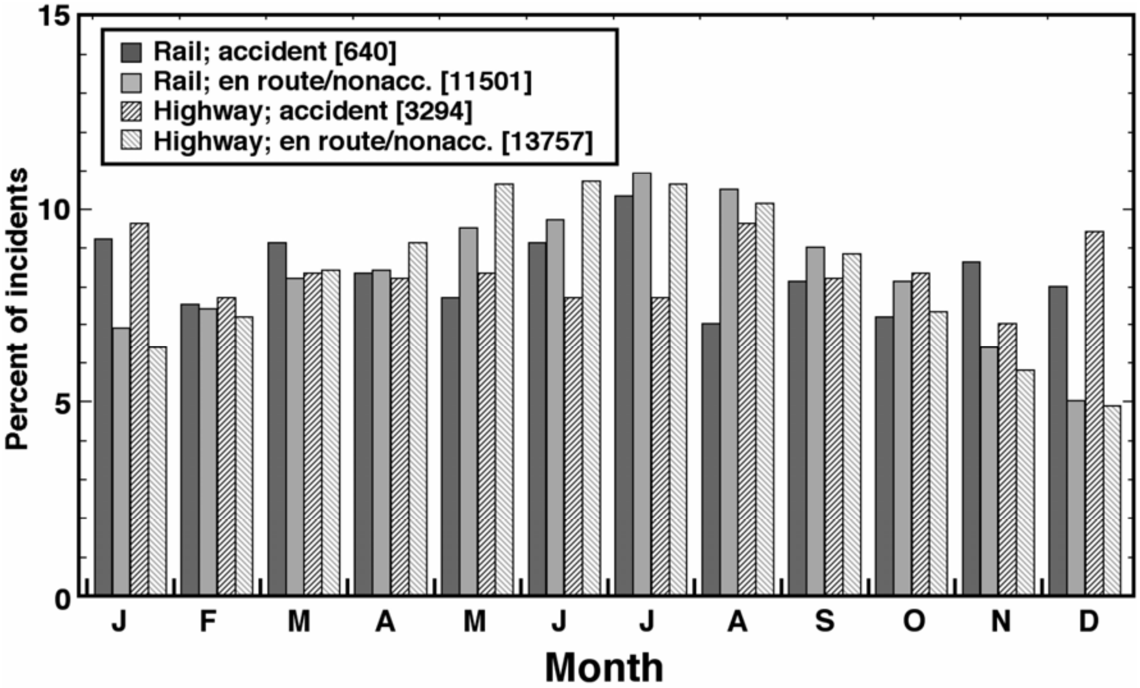

FIGURE 3.2 Monthly Distributions of Rail and Highway Transportation-Related Hazardous Material Releases Occurring During Accident-Related and En Route/Nonaccident Incidents from the HMIS Database, 1990-2002

In the CASRAM source model, discharge fraction statistics are segregated according to container type. In general, these container types can be classified according to whether they are used for bulk or package freight. As part of the analysis for the ERG2004, we re-evaluated our previously published discharge-fraction distributions (Brown et al. 2001) using HMIS data through 2002. Our basic methodology for organizing bulk container discharge fractions is unchanged our from ERG2000 analysis, although the distributions are slightly different due to the longer window of HMIS data employed, and the distributions are now represented with continuous equations. Substantial changes have been made in the organization of package freight statistics, however, which have had a moderate impact on PAD estimates for some materials, especially those authorized only for package freight transportation. We shall discuss bulk and package freight separately below.

3.1.5.1 Bulk Containers

Discharge fraction statistics for bulk containers are shown in Figures 3.3 and 3.4. Figure 3.3 shows discharge fraction distributions for containers that are used for nonpressurized and low-pressure materials. Figure 3.4 shows the distributions for containers that are used for high-pressure materials. Note that not all container types shown are authorized for transport of TIH materials; these are provided for comparison and for use in risk assessments involving other types of hazardous materials. Discharge fraction distributions are provided for the two transportation-related phases considered in the ERG2004 analysis: accident-related and en route/nonaccident releases. Discharge fraction statistics for bulk package freight were developed for a specific container type (Type 111A tank cars, MC/DOT 312 tanks, etc.) when sufficient statistical data were available (i.e., data on at least 25 incidents). In practice, discharge fractions for other container types for which data are insufficient could be estimated using a surrogate for a similar container type for which data do exist. For example, the surrogate discharge fraction distribution for Type 103 tank cars would be that for Type 111A tank cars, and the surrogate for MC/DOT 338 cargo tanks would be MC/DOT 331 cargo tanks.

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

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

where

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

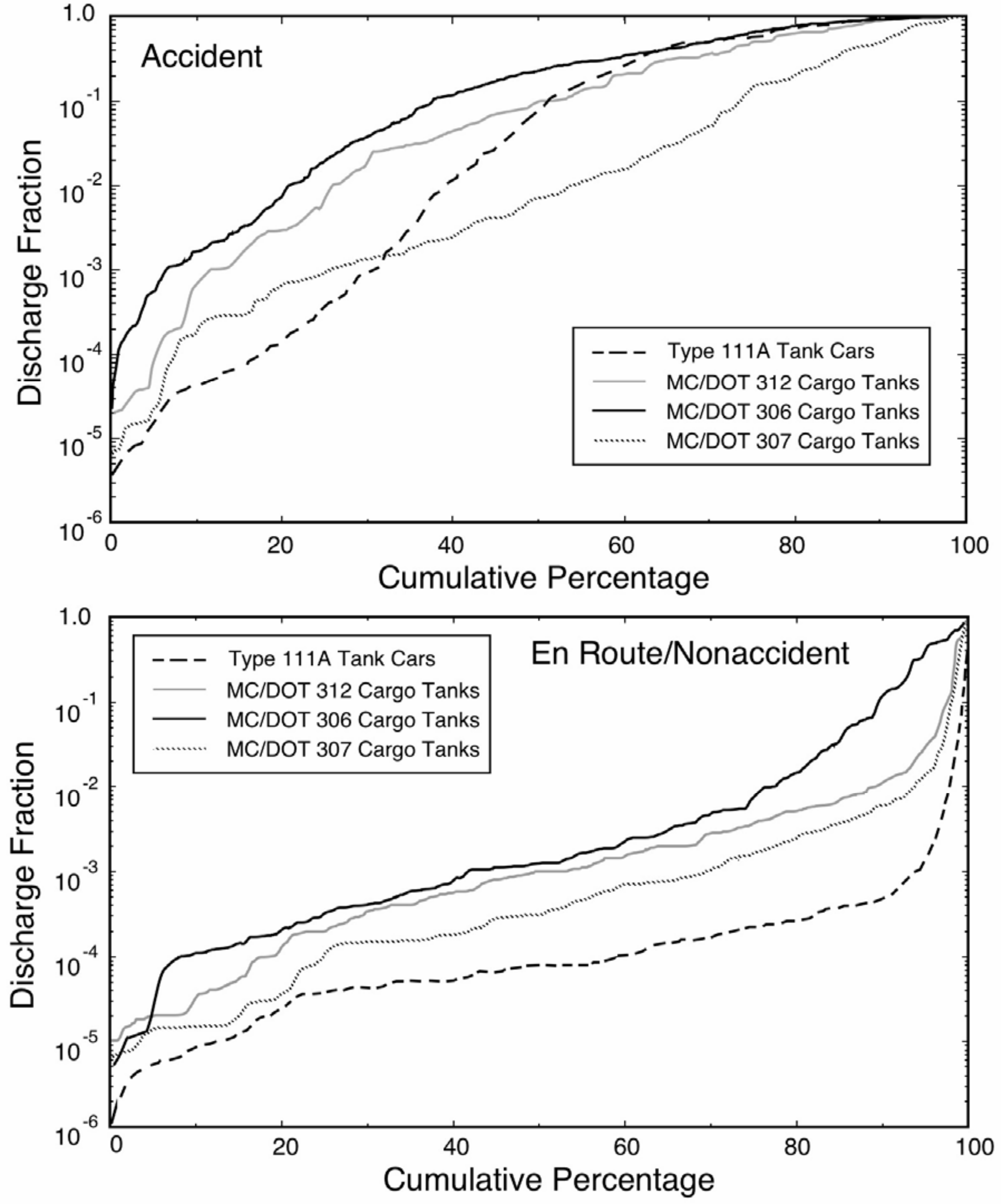

FIGURE 3.3 Discharge Fraction Cumulative Probability for Bulk Nonpressurized and Low-Pressure Containers as Derived from the Analysis of the HMIS Database (1990-2002) for the ERG2004 Analysis. Results are shown for accident-related releases (upper) and en route/nonaccident releases (lower).

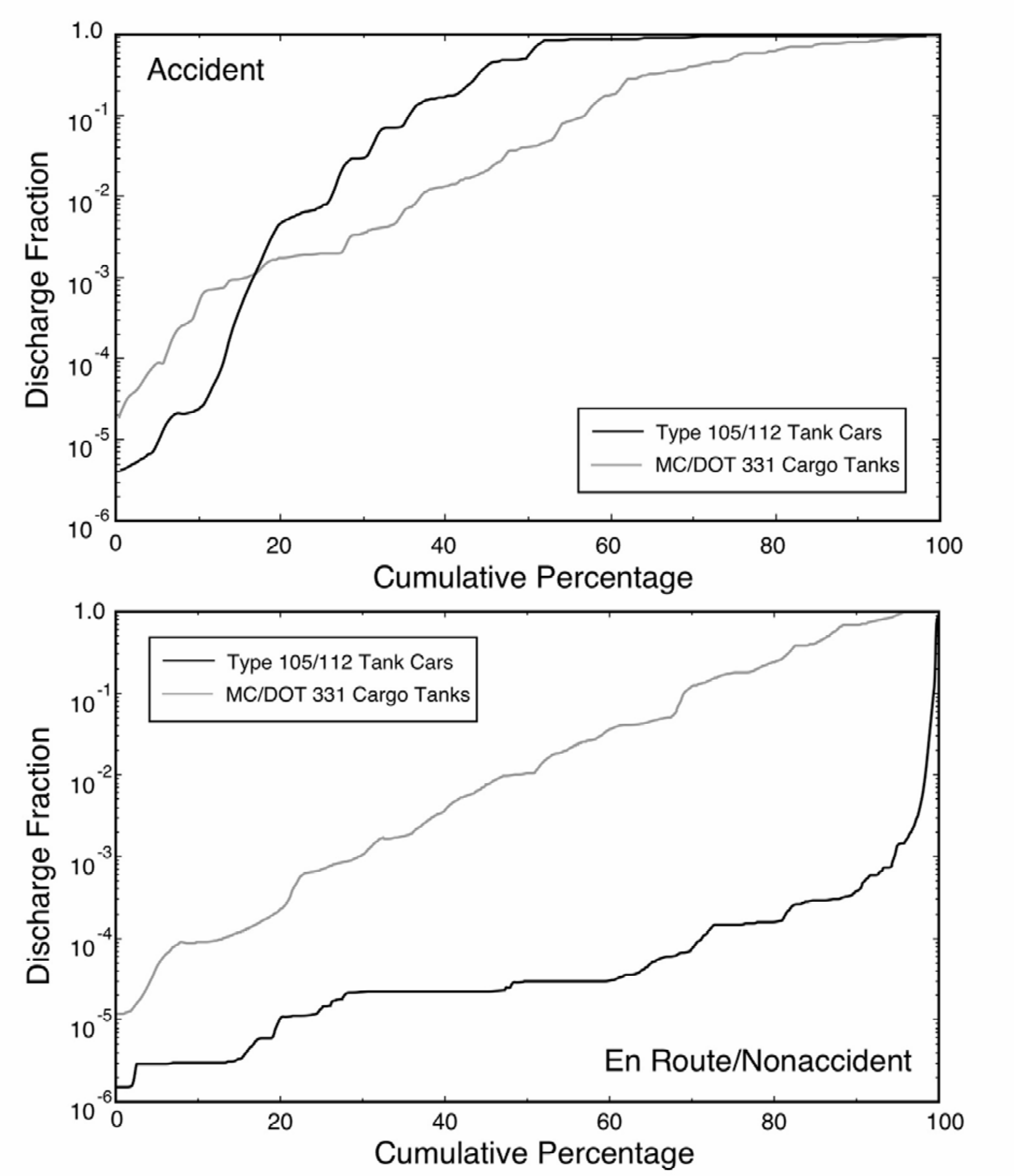

FIGURE 3.4 Discharge Fraction Cumulative Probability for Bulk Pressurized Containers as Derived from the Analysis of the HMIS Database (1990-2002) for the ERG2004 Analysis. Results are shown for accident-related releases (upper) and en route/nonaccident releases (lower).

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) 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, $b < 0.5$. The coefficients for Eq. 3.1 for accident and en route/nonaccident events are listed in Tables 3.2 and 3.3, respectively.

3.1.5.2 Package Freight Containers

For package freight containers, we 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 containing only a few containers. For the ERG2004 analysis, we revised this framework for drums and cylinders based on our re-analysis of HMIS data through 2002 to specify both (1) the percentage of containers that leaked or failed and (2) the 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 to these two classes of containers.

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

Accident-Related Releases

The first step in the analysis framework is to determine the percentage of cases in which the entire shipment amount is released. Typically, only a few containers of a multiple-container shipment are compromised in a traffic accident. However, in more serious accident-related events, the entire shipment can be released. A complicating factor, 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 cataloged in HMIS from 1990-2002 involving metal drums and shows the number of these cases in which over 90% of the total shipment amount was released. Over half of the incidents involving a single metal drum involved the release of the entire shipment contents, whereas for shipments containing multiple drums, the percentage of such incidents decreases to 10%. Table 3.5 shows the identical information for cylinders indicating a similar trend. Note that the total incident counts are rather low, especially for cylinders, so there is significant statistical noise in these data.

TABLE 3.2 Coefficients for Calculating Discharge Fraction Cumulative Probability Distributions for Accident-related Releases for a Variety of Containers. Coefficients were Developed from the analysis of the HMIS Database (1990-2002) for the ERG2004 Analysis.

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. Coefficients were Developed from the analysis of the HMIS Database (1990-2002) for the ERG2004 Analysis.

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) Shown with the Number of Which Involved Over 90% of the Total Shipment Amount Being 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) Shown with the Number of Which Involved Over 90% of the Total Shipment Amount Being 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 where over 90% of the shipment is released that occurs for shipments involving small numbers of containers is accounted for in the second analysis step detailed below.

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

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

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

The total amount of material released is then written as

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

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

En Route/Nonaccident Releases

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

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

3.2 METEOROLOGICAL DATABASE USED TO PREPARE THE GUIDEBOOK

The meteorological database is a critical component of the ERG2004 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 five years of observational data from 105 cities in the United States and with supplemental data from several stations in Canada and Mexico. The data were first preprocessed with the Surface Energy Budget Meteorological (SEBMET) model (Brown 1997; Brown and Dunn 1998). This meteorological preprocessor was designed for use with statistical dispersion studies such as the

TABLE 3.6 Coefficients for Calculating Discharge Fraction Cumulative Probability Distributions in Eq. 3.3 for Accident-related Releases Involving Drums and Cylinders. Coefficients were developed from the analysis of the HMIS Database (1990–2002) for the ERG2004 analysis.

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

TABLE 3.7 Incident Counts Involving Drums In En Route/Nonaccident Releases in the HMIS Database (1990–2002) Shown with the Number that Involved Only One Container and the Number with Over 90% of the Total Shipment Amount Being 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) Shown with the Number that Involved Only One Container and the Number with Over 90% of the Total Shipment Amount Being Released (for comparison with Table 3.4)

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

TABLE 3.9 Coefficients for Calculating Discharge Fraction Cumulative Probability Distributions in Eq. 3.3 for En Route/Nonaccident Releases Involving Drums and Cylinders. Coefficients were developed from analysis of the HMIS Database (1990–2002) for the ERG2004 analysis.

Container Type	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

ERG2004 analysis. A meteorological preprocessor contains a series of algorithms that use routinely measured observations of wind speed, temperature, humidity, and cloud cover, along with upper-air temperature soundings, to calculate the key atmospheric-boundary-layer parameters necessary for modeling 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 TIHWR materials.

3.2.1 Meteorological and Site Data

For the ERG2004 analysis, CASRAM uses a meteorological database that includes hourly meteorological parameters from 105 U.S. cities from 1985 through 1989 (as illustrated in Figure 3.5) and supplemental data from several stations in Canada and Mexico. The stations were chosen to provide a roughly uniform coverage area. Raw meteorological data included yearly surface files listing hourly values of wind speed, temperature, cloud cover (height and fraction), dew point temperature, pressure, and visibility, among other variables. In addition, upper air data from 80 stations across North America were employed to evaluate the atmospheric temperature profile up to the 7,000-m altitude necessary for determining the daytime mixing height. Site characteristics determined for each station included land cover, vegetative types, the monthly leaf area index (a measure of the canopy density) for each vegetative type, roughness length, albedo, and soil types. These site-specific parameters were determined through a climatological study of the areas surrounding each site.

3.2.2 Meteorological Preprocessor

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

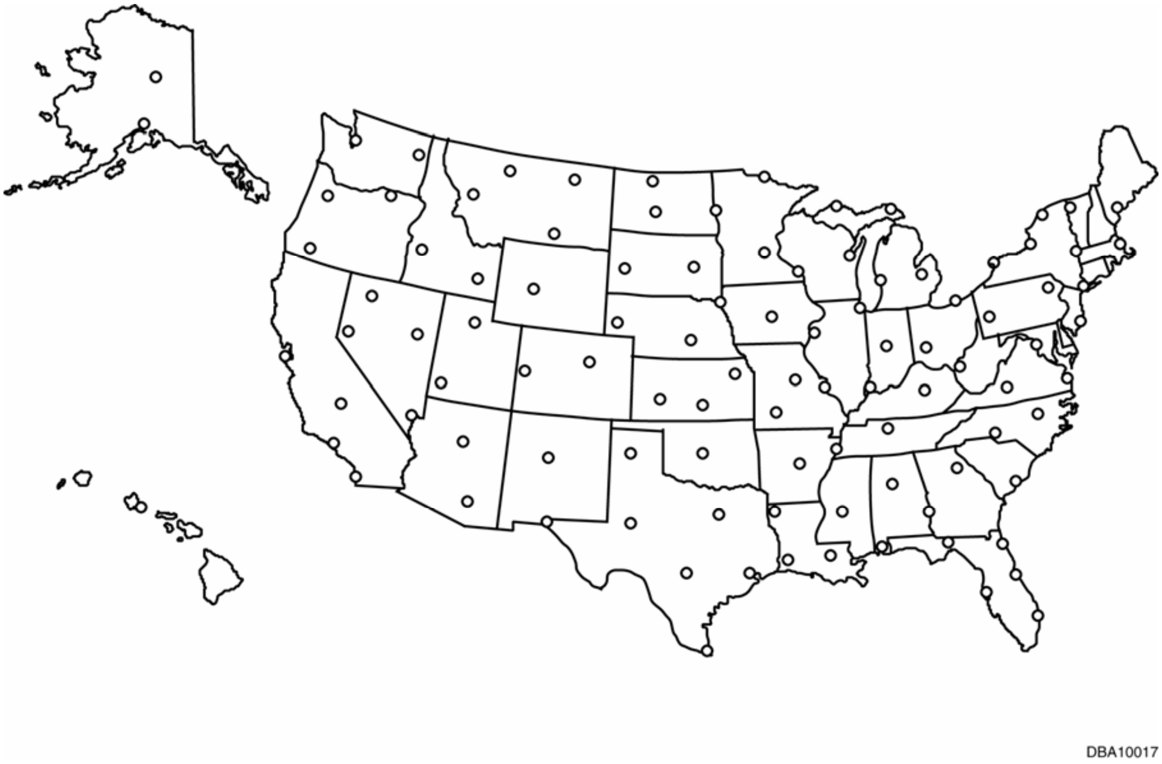

FIGURE 3.5 Locations of the 105 National Weather Service Stations Used for Statistical Meteorological Characterization

3.2.2.1 Surface Turbulence Parameters

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

$$Q^* = H + \lambda E_w + G + Q_a \, , \qquad (3.4)$$

where

Q^* = net surface radiative heat flux,

G = conductive soil heat flux,

λ = heat of vaporization for water,

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

Q_a = anthropogenic heat flux.

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

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

where

α_s = surface albedo,

ε_s = surface emissivity,

σ = Boltzmann constant, and

T_s = surface temperature.

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

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

Net long-wave radiation at the surface is determined from 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 using ground and foliage temperatures that are derived in the model.

At the surface, the solar radiation and incoming long-wave radiation are balanced against the (1) sensible heat transfer, (2) latent heat transfer, (3) ground conduction heat transfer, and (4) outgoing long-wave radiation. To provide a physical, unified treatment valid under both daytime and nighttime conditions, SEBMET employs a two-layer canopy model that evaluates energy transfer components from both the ground and the vegetative layer. The model is formulated by writing separate energy-balance relationships for the ground and the vegetative canopy similar to Eqs 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 using a numerical, finite-difference algorithm that allows the dependence of soil properties and the insulating effect of overlying vegetation and snow to be explicitly treated. Such a scheme allows the ground temperature profile to be saved for use in pool evaporation calculations in the CASRAM emission rate model.

3.2.2.2 Inversion Height and Boundary Layer Height

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

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

3.2.3 Water Temperature for TIHWR Reaction Rates

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

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

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

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

In the ERG2004 analysis, we added 10 more land-based (WQN) stations to bring the total to 45 land-based and 8 GLB stations, the locations of which are shown in Figure 3.6. These 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 desired data from a period of 20 yr to permit meaningful climatological modeling. While the target was about 240 temperature values, we chose stations that had recorded between about 150 and 450 values.

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

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

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

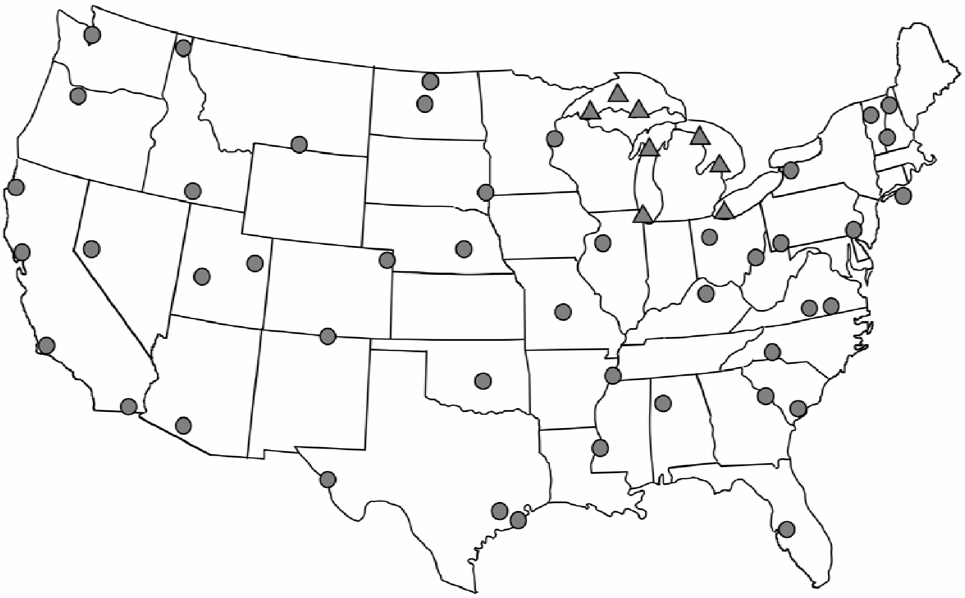

FIGURE 3.6 Water Quality Network Stations Used to Determine Variations of Average Water Temperature by Julian Day and Location (circles = 45 land-based sampling sites; triangles = 8 GLBs)

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 (1) solids, (2) ordinary liquids, (3) compressed gases, or (4) liquefied gases. The emission rate of a chemical to the atmosphere is largely dependent on the shipment state. Due to 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 (2–4 above), together with water-reactive materials, are illustrated in Figure 3.7 and discussed next.

Liquid materials are emitted to the atmosphere through pool evaporation as illustrated in Figure 3.7, panel a. As shall be discussed shortly, the pool evaporation rate is dependent on many factors, in particular the vapor pressure of the material. For volatile liquids (high vapor pressure) the evaporation rate is often limited by the available energy, whereas for low-volatility liquids, wind speed and atmospheric stability become very important. Highly volatile liquids evaporate very quickly, sometimes cooling the pool in excess of 30°C below the ambient temperature. For certain materials, the evaporating pool can cool so much that it freezes.

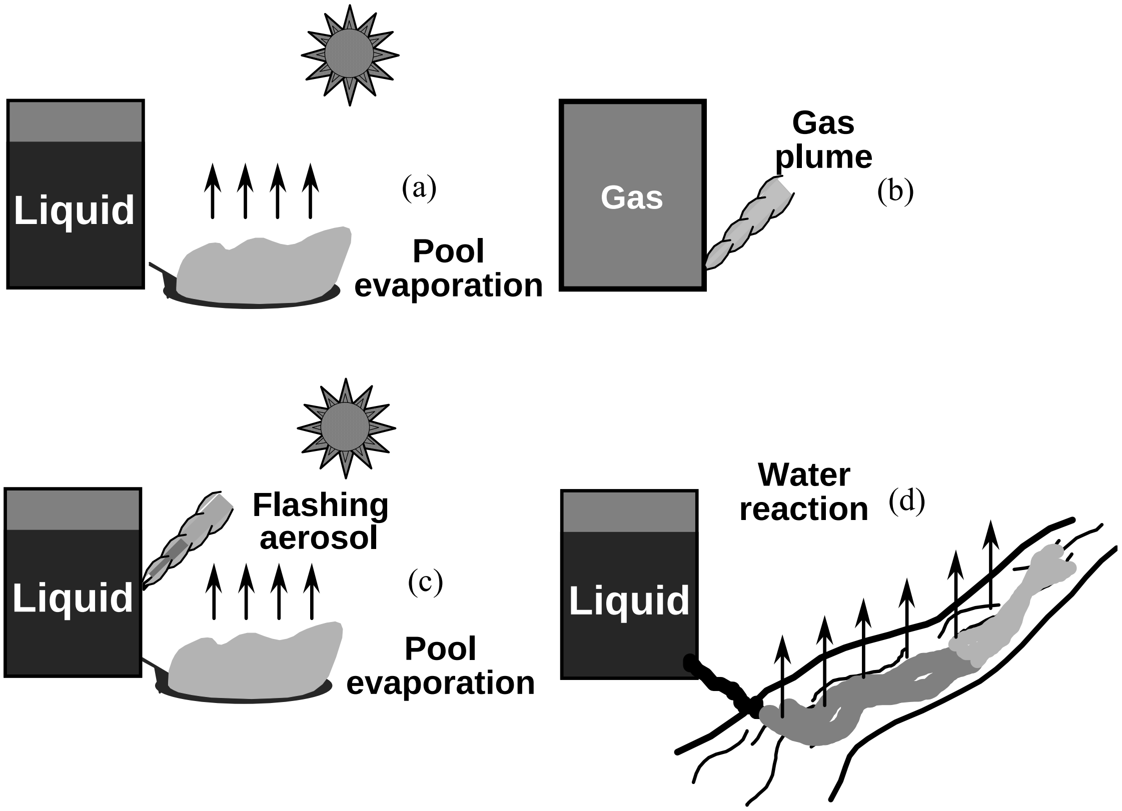

FIGURE 3.7 Important Source Types for Inhalation Risk Considered in the ERG2004 Analysis (a = ordinary liquids, b = compressed gases, c = liquefied gases, d = water-reactive materials)

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

The most catastrophic releases involve liquefied gases as is illustrated in Figure 3.7, panel c. These materials are gases at atmospheric pressure, but are liquefied through pressurization and, in some cases, refrigeration. For these materials, the release is broken into two phases. In the initial phase, denoted as the flashing and entrainment phase, a fraction of the material (up to 30% of the total) is instantaneously vaporized upon exiting the vessel due to the sudden reduction of pressure. Due to 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 (Figure 3.7, panel d). These materials release toxic gases to the atmosphere through the reaction of a parent chemical with water. Therefore, a water-way entry or an additional water exposure mechanism is required for them to become an inhalation hazard. The release rate of the toxic by-product to the atmosphere depends primarily on chemical reactivity, although many other factors can also influence the reaction rate. Key among these is water temperature, for higher water temperatures can greatly accelerate the reaction rate. Evidence also suggests water acidity may be important. Mixing rates also have a clear effect, for 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 increase 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 mists (typically acidic), which can be very corrosive and toxic.

3.3.2 CASRAM Emission Model and Its Application to the ERG2004 Analysis

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

3.3.2.1 Assumptions Used to Develop Accident Scenarios

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

- For accident-related releases from rail tank cars involving a container breach (60% of total set of such releases), the release rate of material from the container is regulated by the size of the hole, which is specified statistically according to hole size distributions presented by Raj and Turner (1993). Since no comparable data exist for highway transportation, the hole size distributions for highway bulk containers are set to those for tank car types having similar specifications (wall thickness, insulation). Total release amounts are limited to conform with 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 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 on the ground that expands and contracts in response to gravity-driven fluid flow and evaporation. 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 pavement or roadbed. 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 solid 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. The time-dependent emission rate of the TIH by-product 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 by-products, chemical transformation is not considered.

- The temperature of the material upon release is taken as a weighted average of the air temperature and 290 K, with the exact weight depending on the container type.

3.3.2.2 Physical Considerations

Discharge from Tanks

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

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

where

Q_l = liquid release rate (kg/s),

c_o = discharge coefficient,

A_h = hole area (m^2),

ρ_l = liquid density (kg/m^3),

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

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

P_t = tank pressure (Pa), and

P_a = atmospheric pressure (Pa).

Equation 3.7 is used to calculate the discharge rates from all bulk containers in CASRAM, where A_h is provided by the hole size distributions given by Raj and Turner (1993). Concerning the discharge coefficient c_o, experimental data show that c_o depends on the exit velocity, fluid viscosity, and hole characteristics (Perry et al. 1984). However, at high exit velocities, characteristic of the incidents modeled in CASRAM, $c_o \approx 0.6$. 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.

Pool Evaporation

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

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

where

A_p = pool area (m^2) and

E_c = evaporation rate from the pool (kg/s·m^2).

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

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

where h_m is the mass transfer coefficient, P_v is the chemical vapor pressure at the pool temperature T_p, and R is the ideal gas constant for air. The mass transfer coefficient h_m is a function of pool size, meteorology, and chemical properties. The key variable in Eq. 3.9 is the pool temperature, for the vapor pressure on which the evaporation rate depends usually varies exponentially with temperature. Pool temperature, and hence the evaporation rate, is determined 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 often the dominant source for available energy, especially for very volatile liquids. Treating the conduction correctly, especially the initial and boundary conditions, was a principal motivation in the development of the CASRAM evaporation model.

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

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

where Q_p^* is the net radiation given by

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

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

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

In these relationships, m is the pool mass per unit area, t is time, z is depth into the ground, ε_p is the pool emissivity, α_p is the pool albedo, k_g is the ground heat conductivity, and σ is the Boltzmann constant (5.67×10^{-8}). The necessary transfer coefficients for evaporation are provided by a chemical property database and the preprocessed meteorological database. In particular, the meteorological quantities of interest include aerodynamic resistances based on stability and wind speed, air temperature, incoming solar and longwave radiation, and the initial ground temperature profile. The relative importance of the terms in Eq. 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 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.

Compressed Gas Releases

In CASRAM, compressed gas releases are modeled 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 c_p is constant).

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

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

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

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

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

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

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

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

Liquefied Gas Releases

Liquefied gas releases are treated by first calculating the liquid release rate from the container given by Eq. 3.7. As discussed previously, this material either flashes to vapor, is aerosolized and entrained with the vapor, or remains liquid and falls to the ground. The flash fraction *f* is given by

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

where T_t is the tank temperature and T_b is the normal boiling point. This fraction of remaining material that is aerosolized and entrained into the flashed vapor is calculated using empirical relationships based on the discharge kinetic energy of the two-phase mixture provided by Johnson and Woodward (1999). Released material that does not flash to vapor or become entrained in the vapor clouds is deposited on the ground. Evaporation of the remaining material is then estimated using the pool evaporation algorithms.

3.3.2.3 Water-Reactive Materials

For water-reactive materials, a different method is needed to estimate TIH emission rates to the atmosphere. Because of the myriad of water body types, reaction scenarios, and release mechanisms; the general lack of historical data on water entry releases; the inadequate characterizations of water body turbulence and mixing; and the lack of experimental data to validate sophisticated water reactivity models, treatment of all possible incident scenarios is not possible. It was therefore necessary to develop a simplified general approach for assessing the level of public protection required for each spill. This effort was started in the ERG1996 analysis and supplemented with an experimental program begun in the ERG2000 analysis to provide quantitative data. We added experiments on many more materials for the ERG2004.

The basic formula employed to compute the release rate of TIHWR gases for most materials assumes the reaction rate exponentially decreases with time such that

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

where

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

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

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

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

λ = first-order rate coefficient (per second).

In the CASRAM source model, Eq. 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 Eq. 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. Experimental data for β and λ are not available in the chemical literature. In our past efforts, 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 to the TIHWR analysis, we conducted a series of direct experiments on about 50 water reactive chemicals beginning in 1999 (for the ERG2000 analysis). These experiments were small in scale, leading to some substantial issues in trying to scale the results up to the size of transportation spills. Nevertheless, the experiments greatly increased the accuracy of estimates for β and also provided a direct measure of λ, which is even more difficult to estimate from the qualitative descriptions.

In recent experiments, we found that Eq. 3.17 was not adequate to fully describe the reaction for a narrow class of silanes. For 5 of these materials in our experimental series, there appeared to be an initial induction period characterized by a constant release rate such that

$$Q(t) = M_o \frac{m_i}{T_{ind}}\ , \qquad (t \le T_{ind}) \qquad (3.18)$$

where m_i is an initial production coefficient and T_{ind} is the initial induction period. For these materials, the gas evolution starts slowly and then greatly accelerates after the initial induction period, indicating the reaction is likely autocatalytic. For times after T_{ind}, the reaction proceeds at an exponential rate and can be modeled using Eq. 3.17 with some minor modifications in β as discussed in Appendix D.

A review of 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, in addition to 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 acidity, however, and simpler to treat in a quantitative fashion. The reaction rate of many materials roughly doubles for every 10°C increase in temperature. Fortunately, the temperature of natural water bodies is well characterized by a network of water quality stations and buoys, as discussed in Section 3.2.3. The temperature dependence of the primary rate constant λ was included in the analysis via the Arrhenius equation, written as

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

where T_O is a reference temperature (20°C for our analysis) and T_W is 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 λ_o in Table D.1 in Appendix D.

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 (1) the release rate in the event of a continuous release or (2) 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 the ERG2004 is very similar to that employed in preparation of the ERG2000, with the only differences being minor adjustments to the horizontal dispersion coefficients. For passive dispersion, we use the vertical dispersion model of Brown (1997), which is applicable for calculating ground-level concentrations from near-ground releases. For heavier-than-air, or so-called *dense gas*, releases, we use relationships from the DEGADIS model. The dense gas model is employed for liquefied gas releases in which 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 does have a more substantial effect.

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

3.4.1 Overview of Atmospheric Dispersion

3.4.1.1 Diurnal Aspects of Plume Dispersion

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

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

An example of a dispersing plume in a typical CBL is pictured in Figure 3.8, panel b. 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 3.9, panel a. 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.

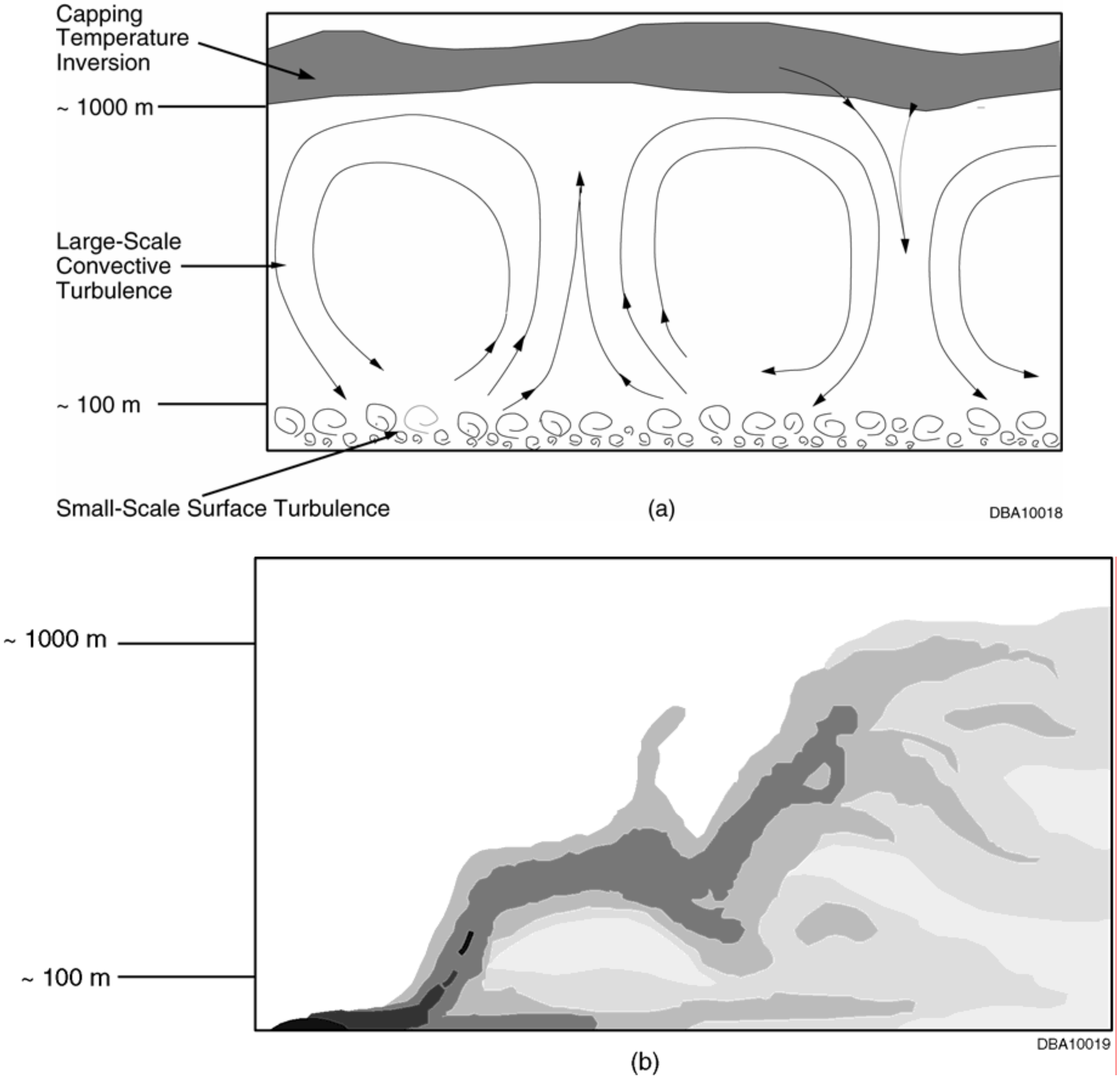

FIGURE 3.8 Typical Daytime Convective Boundary Layer Showing (a) an Instantaneous Wind Field and (b) an Instantaneous Material Concentration Field from a Ground-Level Release (characteristic height of about 1,000 m for the boundary layer and about 100 m for the surface layer provided for reference)

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

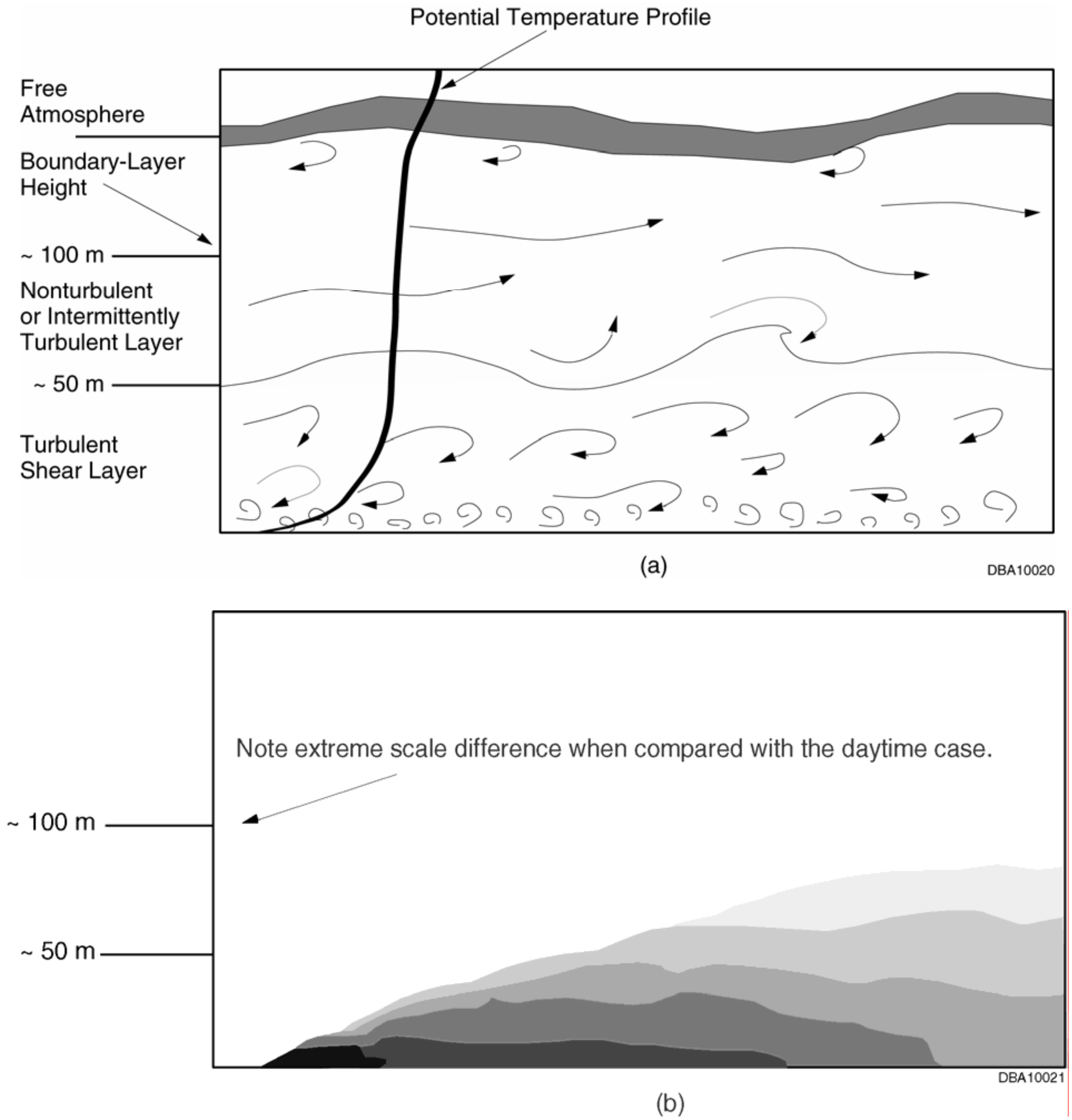

FIGURE 3.9 Typical Nighttime Stable Boundary Layer Showing (a) an Instantaneous Wind Field and (b) an Instantaneous Material Concentration Field from a Ground-Level Release (characteristic height of about 50 m for the surface shear layer and about 100 m for the boundary layer provided for reference)

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, in many cases of practical interest, the effect of a high density (relative to air) of the hazardous chemical discharge becomes important in considering impacts within 1–2 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 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., greater than 1 kg/s);

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

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

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

Several 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. One 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. Another is the presence of gravity-induced flow resulting from horizontal density gradients. These two effects result in a much shallower and wider cloud than a cloud that results from an analogous neutral density release. In addition, the movement of the dense gas cloud on uneven terrain can follow a 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 released.

As the dense plume travels downwind, the plume warms through ambient heating (e.g., from sunlight, ground heating, etc.) 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 a traditional Gaussian expression for the horizontal plume spread. The ground-level concentration distribution is represented as follows:

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

where

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

σ_y = lateral plume spread, and

y = lateral distance from the plume centerline.

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

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

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

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

where

M = total release amount,

T = averaging time, and

U = 10-m wind speed.

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

Vertical Dispersion

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

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

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

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

and

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

where u_o and k_o are constants representing the wind speed and diffusivity at 1 m. The advection-diffusion equation subject to the above power-law relationships yields an exact solution (see Roberts 1923; Calder 1949). The work of van Ulden (1978) extends this analysis by using the power-law coefficients to determine the concentration profile shape *a priori* (from the Roberts analysis) and then formulates integral relationships for the mean plume height and average advection velocity in terms of the more physically correct similarity functions for wind speed and diffusivity. The van Ulden (1978) solution reads:

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

where

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

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

and s is a shape parameter given by $1 - m - n$. In Eqs. 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 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 Eq. 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 Eq. 3.26.

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

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

where z_u is defined such that

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

and

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

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

The main departure of this approach from the models of van Ulden (1978) and Gryning et al. (1983) 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 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, to treat dispersion throughout the entire ABL.

Brown (1997) developed relationships for z_u, $\tilde{s}$, and F through 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 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 Eq. 3.24 and ultimately Eq. 3.20, 3.21, or 3.22.

Horizontal Dispersion

Under horizontally 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 using relationships originally proposed by Draxler (1976). Here, σ_y is given by

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

where

σ_v = standard deviation of transverse velocity,

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

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

f_y = a nondimensional function of travel time.

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

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

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

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

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

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

$$\sigma_v = 1.92\, u_* \tag{3.35}$$

during stable conditions.

In very stable conditions, Eq. 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. One kilometer from the source, this value of σ_v yields σ_y = 36 m from Eq. 3.32. Considering the 2,000-s travel time, such a narrow plume width at ground level is not realistic when the meandering nature of stable boundary layer flows is considered. To overcome this problem, we assign a minimum value of 0.15 m/s for σ_v on the basis of observations presented by Hanna and Chang (1992).

3.4.2.2 Dense Gas Dispersion

A dense gas algorithm was added to the CASRAM methodology as part of the ERG2000 study after a detailed review of available dense gas models. The review identified five dense gas models that were well documented and would be applicable within the CASRAM framework: DEGADIS (Havens 1988), HEGADAS (Post 1994), SLAB (Ermak 1990), SCIPUFF (Defense Threat Reduction Agency 1999), and TSCREEN (U.S. Environmental Protection Agency [EPA] 1992). Based on many considerations, most importantly accuracy and ease of incorporation into the CASRAM framework, we opted to rely on the empirical entrainment parameterizations within the DEGADIS formulation for the CASRAM heavy gas dispersion model, although future modifications to the CASRAM dense gas dispersion model may involve incorporation of the HEGADAS formulation since it was being revised when this work was completed.

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

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

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

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

where β_{ei} is the entrainment parameter at the source, taken as 2. This is a rough estimate that depends on many factors. However, the model results at distances more than 10–20 m from the source are not sensitive to β_{ei}.

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

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

where

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

4 HEALTH CRITERIA

Over the past 15 years, various health criteria have been used to develop Initial Isolation Zones and PADs. Early efforts employed occupational exposure guidelines, such as threshold limit values (TLVs) established by the American Conference of Governmental Industrial Hygienists (ACGIH). Beginning in 1990, the ERPGs developed by the AIHA were identified as the best available health criteria for evaluating the health significance of accidental releases and hence formed the basis for defining PADs. This preference was based on a number of factors, including the high quality of documentation, the consensus approach with which the values are derived, and the consideration of exposure to the general population. In the last few years, Acute Exposure Guidance Levels (AEGLs), which are defined similar to ERPGs but for a variety of exposure times, have emerged on the scene.

In 1995, as part of a continuing effort to improve the ERG, an analysis of the various health criteria used to develop PADs was performed because ERPGs were only available for a limited number of chemicals on the TIH list. This analysis indicated that certain health criteria were stratified when compared with ERPG-2 values. This stratification had a significant influence on the PADs calculated with these health criteria. As a result, efforts were undertaken to further identify and minimize sources of stratification. These efforts are described in Section 4.1 and included: (1) reviewing published studies on health criteria used to evaluate accidental releases, (2) performing an independent analysis of the ERPG values, and (3) convening an independent panel of expert toxicologists to recommend uses for health criteria and ways to minimize stratification. This effort led to the development of a solid peer-reviewed framework for specifying health criteria for PAD estimation and was first used in the ERG1996.

For the ERG2000 and ERG2004 analyses, we left this basic framework unchanged. The limited changes included incorporating several new ERPGs that became available between 1996 and 2003. In addition, we studied several new materials that had been added to the TIH list to determine appropriate health criteria. We also performed an extensive literature search to determine if any new acute toxicity information was published for the materials on the TIH list in the past several years that would be relevant to our analysis. Except for the ERPG values noted above, however, no new studies relevant to our analysis were identified.

As part of the ERG2004 analysis, we also began considering the issues involved with incorporating the new AEGLs developed by the Federal Advisory Committee, a collaborative effort of the public and private sectors. Since few final AEGLs were available when the ERG2004 was prepared, we decided to postpone the addition of AEGLs to the ERG methodology until work commences on the next edition of the ERG (expected to be published in 2008). The potential issues involved with their inclusion are discussed in Section 4.4.

4.1 REVIEW OF PAST DEVELOPMENT EFFORTS

4.1.1 ERPGs

Emergency Response Planning Guideline (ERPG) concentrations, in particular the ERPG-2, have been the basis for estimating PADs in the ERG since 1990. 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, since human exposure data are rarely available except for low-level exposures, animal exposure data, generally from acute inhalation toxicity studies, are most often employed as the basis for the ERPG concentrations. ERPGs are given for three levels:

- 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.

- 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-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.

As of July 2004, the AIHA has published ERPG concentrations for 111 different chemicals. Typically the AIHA adds about 7–10 chemicals per year to their list and modifies previously published values for another 7–10 materials.

4.1.2 Comparisons of ERPGs with other Health Criteria

A number of published studies compare alternative health criteria for use in evaluating accidental releases. These studies have helped to resolve several questions on the relationship between ERPGs and alternative values, which include NIOSH IDLH levels, National Research Council Emergency Exposure Guidance Levels (EEGLs), and occupational health guidelines.

Craig et al. (1995) calculated the ratios of ERPG-2 values to other health criteria and examined the statistical relationship between them. The mean, coefficient of variation, and coefficient of determination of these ratios were calculated. The analysis included ERPG data for 35 chemicals. None of the existing values adequately estimated ERPG-3 values. For example, National Research Council 30-min EEGLs substantially underestimated ERPG-3 values (mean ratio = 0.55), while NIOSH IDLH values overestimated ERPG-2 values (mean ratio = 2.48).

A good correlation was observed between ERPG-2 values and National Research Council 60-min EEGLs and EPA levels of concern (LOCs) (mean ratios of 0.99 and 0.82, respectively). Similarly, good correlations were observed between ERPG-2 and Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) ceiling values and 5 times the ACGIH 8-hour TLVs (mean ratios = 1.09 and 1.05, respectively). A poor correlation was observed between ERPG-2 and ACGIH TLV ceiling (TLV-C) values (mean ratio = 0.2). Data were not presented for the ratio of ERPG-2 to TLV values. However, on the basis of the good correlation with 5 times the 8-h TLVs, the correlation between ERPG-2 and unadjusted 8-h TLVs is probably very poor.

The study by Craig et al. (1995) confirms the stratification observed when unadjusted ACGIH TLV-C values, unadjusted 8-h TLV values, or 3 times the 8-h TLV values are used as surrogates for ERPG-2 values. Also, on the basis of the good correlation between the EPA LOC and ERPG-2 values, and since many EPA LOC values were derived by dividing the IDLH value by 10 and many IDLH values were derived by dividing an LC_{50} value by 10, a relationship between the ERPG-2 and $LC_{50}/100$ is inferred.

Woudenberg and Van Der Torn (1992) performed a number of nonparametric and parametric comparisons of various exposure limits, including ERPGs (3, 2, and 1), IDLH values, ACGIH short-term exposure limits (STELs), 50% decrease in mean respiratory rate (RD_{50}) values, Health and Safety Executive (HSE) specified levels of toxicity (SLOTs), and National Research Council EEGLs. Woudenberg and Van Der Torn also calculated ratios of ERPG-3 to ERPG-2. At the time these analyses were performed, ERPG values were available for only 25 chemicals.

For ERPG-2, the nonparameteric comparison procedure identified a cluster with only EEGLs. This trend was confirmed by using parametric procedures. The ratio of mean EEGL to mean ERPG-2 was 1, with a range of 0.1 to 3.3 (N = 7). For ERPG-3, the nonparametric procedure identified a cluster with IDLH values. When the limits were scaled to a common time period, the RD_{50} value was included in this cluster. The mean ERPG-3/IDLH ratio was 0.92, with a range of 0.125 to 5 (N = 16). The mean RD_{50}/ERPG-3 ratio was 2, with a range of 0.1 to 7.8 (N = 12). In the above ratios, the values are not scaled to a common time period. The ratio ERPG-2/ERPG-3 was 0.2, with a range of 0.01 to 0.4, indicating a fivefold difference between ERPG-2 and ERPG-3.

Two additional analyses were performed as part of ERG1996 study to further improve the values used in the ERG. Data from 65 ERPGs were used in the analyses (N = 65). The relationship between the ratio of the key LC_{50} value and the ERPG-3 was analyzed. The key LC_{50} values were selected from the ERPG documentation, except where noted. With the exception of one chemical, dimethylamine, the LC_{50} values were for 30-min to 4-h exposure durations. Non-1-h values were adjusted to 1 h. In this study, the ranking order described in Section 4.2 was used. The ratio of mean LC_{50} to mean ERPG-3 was 25.7, with a median of 17 and range of 3 to 168. The ratio of ERPG-3 to ERPG-2 was also analyzed. The ratio of mean ERPG-3 to mean ERPG-2 was 6.6, with a median of 5 and range of 1–50.

For both ratios, the median values are slightly lower than the mean values, indicating that a few high values are influencing the means. For such data, the median values, which minimize the influence of extreme values, are the best estimate of central tendency. Considering the median value, the 1-h LC_{50}/20 value (i.e., $0.05 \times LC_{50}$) is a reasonable approximation for the ERPG-3 value. Since ERPG-3 values are based on protection from life-threatening health effects, the relationship between LC_{50} and ERPG-3 has biological relevance. The product of the ratio of LC_{50}/ERPG-3 and ERPG-3/ERPG-2 is calculated as $17 \times 5 = 85$. Therefore, 1-h LC_{50}/100 values appear to be a reasonable and slightly conservative approximation for ERPG-2 values. Note that this relationship is empirical, since ERPG-2 values are based on a variety of serious health effects rather than lethality.

4.1.3 Expert Panel Review

On May 4, 1995, an independent panel of expert toxicologists convened to make recommendations on the use of health criteria for the 1996 version of the ERG (Dunn et al. 1996). The panel made a number of recommendations for improving the consistency of criteria and for reducing stratification. They are presented below.

- Avoid using occupational health guidelines based on cancer since their use results in significant stratification.

- Avoid using occupational health guidelines based on effects other than irritation since their use introduces a similar bias.

- Using acute inhalation toxicity data (e.g., LC_{50} values) in place of occupational health guidelines probably improves the consistency of the health criteria. However, the inconsistent use of these data has a high potential for introducing bias. To increase consistency, a scheme that considers species, exposure duration differences, and data sources should be developed and uniformly applied to data on individual chemicals.

In addition, the panel recommended identifying new potential sources of information for developing the health criteria. For example, additional acute toxicity data may be found in the documentation of the AIHA ERPGs. These documents cite proprietary data not included in the open literature. Also, the panel recommended making more use of ERPG values by using existing ERPGs for closely related analogs that have limited toxicity data and no ERPGs.

The recommendations from the expert panel, and information gained from the studies and analyses described above, were incorporated into an updated procedure for developing the health criteria used to calculate Initial Isolation and PADs.

4.2 PROCEDURE USED TO DEVELOP HEALTH CRITERIA

Modeling considerations indicated a need for three values for each chemical. These values were a 1-h life-threatening value for determining the Initial Isolation Distances, and 1-h and 15-min protective action values for determining PADs. The procedure used to derive these values is described below.

4.2.1 Use of ERPGs

When published or approved ERPGs were available for the chemical of interest, ERPG-2 was used as the 1-h protective action criteria. ERPG-2 × 2 was used to estimate 15-min protective criteria. Use of the twofold factor is explained in Section 4.2.2 below. If ERPGs were available for a closely related structural analog, the ERPG-2 value for the structural analog was used for the chemical of interest, as described above.

4.2.2 Use of Acute Inhalation Lethality Data in Animals

When ERPGs were not available, health criteria were derived by using LC_{50} data and lowest reported lethal concentration (LC_{LO}) data from acute inhalation studies on animals. When such data were not available for a chemical of interest, we used corresponding data for a structural analog. For example, for certain isocyanates for which there were no acute lethality data, data for methyl or butyl isocyanate could be used. Similarly, data for boron trichloride could be used for boron tribromide.

Several factors were considered in selecting and using the LC_{50} and LC_{LO} data. These factors included species, time, data source, and structure activity considerations. These factors are discussed below and the resulting ranking of studies appears in Table 4.1.

4.2.2.1 Species Considerations

Data from studies using rats and mice were 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, when such data were available, they were generally included after the data for rats and mice but before data for other species, as presented in Table 4.1. The amount of comparative data on rabbits is limited. Results on this species are not as representative as data on primates, and so they appear lower in the ranking scheme.

TABLE 4.1 Order of Acute Lethality Data for Estimating Health Criteria

Rank	Data	Rank	Data
1	1-h LC_{50} in rats	14	2- to 4-h LC_{50} in dogs
2	2- to 4-h LC_{50} in rats	15	30 min LC_{50} in dogs
3	30-min LC_{50} in rats	16	6- to 8-h LC_{50} in dogs
4	1-h LC_{50} in mice	17	1-h LC_{50} in guinea pigs
5	2- to 4-h LC_{50} in mice	18	2- to 4-h LC_{50} in guinea pigs
6	30-min LC_{50} in mice	19	30 min LC_{50} in guinea pigs
7	6- to 8-h LC_{50} in rats	20	6- to 8-h LC_{50} in guinea pigs
8	6- to 8-h LC_{50} in mice	21	1-h LC_{50} in rabbits
9	1-h LC_{50} in primates	22	2- to 4-h LC_{50} rabbits
10	2- to 4-h LC_{50} in primates	23	30-min LC_{50} in rabbits
11	30-min LC_{50} in primates	24	6- to 8-h LC_{50} in rabbits
12	6- to 8-h LC_{50} in primates	25	1-h LC_{LO} in rats[a]
13	1-h LC_{50} in dogs	26	2- to 4-h LC_{LO} in rats, etc.[a]

[a] Rank 25 through 50 for LC_{LO} data follow the same order as Rank 1 through 24 for LC_{50} data shown.

4.2.2.2 Exposure Duration Considerations

Data from 1-h exposures were preferred, since data from this duration require no adjustments. The most commonly reported acute lethality studies are for 1-h and 4-h exposure durations. Therefore, use of data from studies of this duration 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 exposures less than 30 min long, concerns over chamber equilibration time (T_{99}) increased. For exposures more than 4 h long, concerns that effects other than acute lethal effects might influence the study results increased. Limited confidence was placed on data reported as LC_{LO}. In these studies, no information was available concerning the slope of the dose response curve. Also, in some studies that used LC_{LO} values, 100% mortality was observed.

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

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

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

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

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

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

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

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

$$LC_{50}(T_1) = LC_{50}(T_o)\left(\frac{T_1}{T_o}\right)^{1/n}, \tag{4.3}$$

where

T_1 = actual exposure time,

T_o = experimental exposure time, and

n = constant.

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

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

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

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

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

4.2.2.3 Data Source Considerations

The source of the data is critical. Information from main-stream, peer-reviewed toxicology and industrial hygiene journals is preferable to information from ancillary, 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 NIOSH Registry of Toxic Effects of Chemical Substances.

4.2.2.4 Adjustment Factors

As described in Section 4.1, the 1-h LC_{50} or adjusted 1-h $LC_{50}/100$ is a reasonable estimate of ERPG-2. Also, a fivefold factor is a reasonable central tendency adjustment factor between ERPG-2 and ERPG-3. Therefore, 1-h or adjusted 1-h LC_{50} or LC_{LO} values were divided by 100 to estimate 1-h protective health criteria, and this value was multiplied by 5 to estimate the 1-h life-threatening health criteria.

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

4.2.3 Use of Alternative Health Criteria

For a few select chemicals, National Research Council EEGLs, Emergency Exposure Levels (EELs) published in the *AIHA Journal* were used to develop health criteria. For one chemical, data on oral LD_{50} in animals were used to estimate an LC_{50} value and to derive health criteria. Standard assumptions of animal inhalation rate and body weight were used.

4.2.4 Summary

By building on past efforts, an updated procedure was developed to provide health criteria for use in determining Initial Isolation and Protective Action Distances. The new procedure incorporated additional ERPG values published since 1992 and expanded the use of existing ERPGs by applying them to structural analogs that otherwise had limited or no available acute toxicity data. A strategy was developed to reduce the stratification of PADs according to health criteria. The strategy involved minimizing the use of occupational health criteria through increased use of acute lethality data and more consistent selection and use of acute lethality data.

A summary of the basis for health criteria of the 166 primary chemicals in the ERG analysis appears in Table 4.2. Documentation of the health criteria for individual chemicals is

TABLE 4.2 Summary of the Basis for Health Criteria Used to Prepare the ERG2004

Basis of Health Criteria	No. of Materials	Percentage
ERPG for chemical of concern	44	27
ERPG for structurally similar chemical	20	12
Subtotal for ERPGs	64	39
LC_{50} for chemical of concern	80	49
LC_{50} for structurally similar chemical	10	6
Subtotal for LC_{50}s	90	54
LC_{LO} for chemical of concern	9	5
AIHA EEL	2	1
Oral toxicity data	1	1
Total	166	100

presented in Appendix B. For 64 chemicals (39% of them), ERPGs or ERPGs for a structurally similar chemical formed the basis of the health criteria. For 90 chemicals (54%), LC_{50} values or LC_{50} values for a structurally similar chemical were used to develop the health criteria. For 9 chemicals (5%), LC_{LO} values for the chemical or a structurally similar chemical formed the basis of the health criteria. National Research Council EELs were employed for 2 chemicals, and for 1 chemical, oral toxicity data were used to estimate an inhalation LC_{50} and to derive the health criteria.

4.3 COMPARISON TO OTHER PROCEDURES

A number of other procedures have been developed for deriving health criteria used in evaluating accidental releases of chemicals. These include procedures developed by the EPA for deriving LOCs to evaluate releases of extremely hazardous substances (EPA 1991) and other procedures developed by the EPA for performing consequence analyses to comply with requirements of Section 112 R of the Clean Air Act (EPA 1996).

In the EPA LOC procedure, the NIOSH/OSHA IDLH/10 is the preferred value for deriving the LOC. Since IDLH values were developed during the Standards Completion Program 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 IDLH values are unavailable, estimated IDLH values based on $LC_{50}/100$, LC_{LO}, $LD_{50}/100$, or $LD_{LO}/100$ are used. As a third choice, ACGIH TLVs (8-h time-weighted average TLVs [TLV-TWA], STEL, and TLV-C values) and National Research Council EEGLs are also used to derive a number of LOCs. 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 developed, ERPGs did not form the basis for any LOC.

In the procedure described by NIOSH to develop IDLH values, human data are preferred. However, since reliable human data are rarely available, many of the IDLH values are based on adjusting the results of acute inhalation lethality data in animals to a 30-min exposure duration by using the calculation LC_{50} (30 min) = LC_{50} (T) × $(T/0.5)^{1/3}$, then dividing by 10. Therefore, many LOCs are based on adjusted LC_{50} or LC_{LO} data divided by 100.

Several similarities exist between the procedure used by the EPA to develop LOCs and the procedure used by DOT to develop health criteria for deriving Initial Isolation and Protection Action Distances. Many LOC and DOT 1-h protective levels are based on adjusted LC_{50} or LC_{LO} values divided by 100. Also, various alternative values such as National Research Council EEGLs and ACGIH TLVs are considered as “last resort” criteria.

There are also several important differences in these two procedures. In the DOT approach, AIHA ERPGs are the preferred choice for deriving health criteria. We believe this to be a sounder approach, since ERPG 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 produced a significant percentage of mortality, including 100% mortality.

In the approach described in the guidance document for off-site consequence analysis (EPA 1996), ERPGs are recommended as the preferred values, followed by LOC values. Since ERPGs are recommended 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.

4.4 FUTURE MODIFICATIONS

4.4.1 Additions of New ERPG Values

Through continued efforts of the AIHA ERPG Committee, ERPGs for additional chemicals are being provided at a rate of 7–10 per year, and already published values are occasionally revised. Not all of the chemicals on the ERPG list appear in the Table of Initial Isolation and Protective Action Distances, since many of the ERPG chemicals do not meet the specific toxicity and physical criteria for listing in the Table. However, when new ERPGs are available for chemicals on the Table, the values will be incorporated into the development of Isolation and Protective Action Distances in future additions of the ERG.

4.4.2 Acute Exposure Guidance Levels

A Federal Advisory Committee for Acute Exposure Guidance Levels (AEGLs) was approved in 1995. This committee is composed of scientists representing federal, state, and local agencies and organizations from the private sector with an interest in emergency planning, prevention, and response programs for acutely toxic chemicals. The purpose of the committee is to develop AEGLs that will meet the needs of various organizations (EPA, NIOSH, OSHA, DOT, U.S. Department of Defense, U.S. Department of Energy, Agency for Toxic Substances Disease Registry, and private industry). AEGLs represent threshold exposure limits for the general public and are applicable to emergency exposure periods ranging from 10 min to 8 h. AEGL-1 and AEGL-2 levels, and AEGL-3 levels as appropriate, are developed for each of five exposure periods (10 and 30 min, 1 h, 4 h, and 8 h) and are distinguished by varying degrees of severity of toxic effects. It is believed that the recommended exposure levels are applicable to the general population, including infants, children, and other individuals who may be sensitive and susceptible. The definitions of AEGL-1, AEGL-2 and AEGL-3 are very close to those for the ERPG values:

- 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, non-sensory effects. However, the effects are not disabling and are transient and reversible upon cessation of exposure.

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

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

As these are extensively peer reviewed acute health criteria applicable to emergency response situations, they are directly applicable for use in the ERG analysis for chemicals that do not have ERPGs. A few final AEGL values and many draft values of AEGLs were available at the time of the ERG2004 analysis; however, the AEGLs available at the time repeated already published ERPG values, and since the values were substantially different in some cases, the decision was made to postpone inclusion of AEGLs. AEGLs are being finalized at a rate of 10–20 chemicals a year, so by the time the analysis for the next ERG edition commences, many final AEGL values will be available. We anticipate that many of these will be for chemicals for which no ERPG exists, so it is likely that AEGLs will be incorporated in the ERG analysis framework in the future. However, there are a few questions that will need to be resolved for a seamless integration.

The main question is whether the AEGL-2 is exactly comparable to the ERPG-2. The ERG analysis was developed based on ERPG-2 levels. While the definitions of the ERPG-2 and

AEGL-2 appear very similar, the final AEGL-2 values are often lower than their ERPG-2 counterparts. This could have a marked effect on PAD values. Table 4.3 shows 8 TIH materials for which both ERPG and final AEGL values were available in February 2005, and the percent change in the nighttime, large spill PAD if the AEGL is used in place of the ERPG. For 4 of the materials the AEGL values were substantially lower, for 3 they were slightly higher, and for 1 they were the same. The percent changes in the nighttime, large spill PAD ranges from a decrease of 16% to an increase of 106%, with the average being an increase of 21%. The reason for this increase may indeed be a slight difference in their definitions, since the AEGL-2 definition contains the statement "…general population, including susceptible individuals …", whereas the ERPG-2 values are valid for "nearly all" individuals.

If this trend continues, incorporating large numbers of AEGLs could significantly raise the PAD values if the rest of the analysis is unchanged. This issue will be thoroughly examined as part of the next ERG analysis. A related question will be whether to use the AEGL or ERPG if both values exist for the same chemical.

4.5 GLOSSARY FOR SECTION 4

ACGIH 8-hour TLV: American Conference of Governmental Industrial Hygienists 8-h threshold limit value (ACGIH 1995). This is a time-weighted average concentration to which nearly all workers may be repeatedly exposed, day after day, without adverse effect.

TABLE 4.3 Comparison of ERPG-2 Values with Final AEGL-2 Values for 8 TIH Materials and the % Change in Large Spill Nighttime Distance if the AEGL-2 Value Replaced the ERPG-2 Value in the ERG Analysis

Chemical	1-h ERPG-2	15-min ERPG-2	1-h AEGL-2	15-min AEGL-2[a]	% Change in Large Spill Nighttime Distance
Hydrogen cyanide	10	20	7.1	14.2	+21
Phosgene	0.2	0.4	0.3	0.6	-16
Methyl isocyanate	0.5	1.0	0.067	0.26	+106
Hydrogen chloride	20	40	22	86	-7.3
Hydrogen fluoride	20	40	24	48	-10
Chlorine	3	6	2	2.8	+29
Arsine	0.5	1	0.17	0.26	+47
Diborane	1	2	1	2	0
Average change					+21

[a] 15-min AEGL-2 values were estimated using the published 10- and 30-min values.

ACGIH TLV STEL: ACGIH short-term exposure limit (ACGIH 1995). The concentration to which workers can be exposed continuously for a short period of time without suffering from (1) irritation, (2) chronic or irreversible tissue damage, or (3) narcosis of sufficient degree to increase the likelihood of accidental injury, impair self-rescue, or materially reduce work efficiency, provided that the daily TLV-TWA is not exceeded.

ACGIH TLV Ceiling: ACGIH threshold limit value ceiling (ACGIH 1995). This is the concentration that should not be exceeded during any part of the workday.

AEGL: Acute Exposure Guidance Levels (AEGLs) — described in detail in Section 4.4.2.

AIHA EEL: Emergency Exposure Level published in the *AIHA Journal* (Frawley et al. 1964). This is the concentration of 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.

AIHA ERPGs: AIHA Emergency Response Planning Guidelines (AIHA 2004) — described in detail in Section 4.1.1.

EPA LOC: U.S. Environmental Protection Agency level of concern (EPA 1991). 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.

HSE SLOT: Health and Safety Executive (England) specified level of toxicity (Turner and Fairhurst 1989).

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

LC_{LO}: lowest reported lethal concentration, i.e., that will produce a fatality in an exposed population.

NIOSH IDLH: NIOSH immediately dangerous to life and health level (NIOSH 1994). The maximum concentration from which, in the event of respirator failure, one could escape within 30 min without experiencing any escape-impairing (e.g., severe eye irritation) or irreversible health effects.

NRC EEGL: National Research Council Emergency Exposure Guidance Level (NRC 1984–1987). This level 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 1–24 h.

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

RD_{50}: concentration producing a 50% respiratory rate decrease in test animals; used to estimate severe respiratory irritation.

5 SUMMARY

Sections 2–4 of this report detail the statistical methodology for developing safe distance distributions, the consequence models used in the analysis, and the health criteria that define the safe distance. In this section, we summarize the results, discuss the appearance of the numbers in the Table (which is contained in Appendix A), and then conclude with some potential extensions of this analysis for situations where more information is immediately available besides gross spill size and whether it is day or night.

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 the Table. This set of incidents accounts for variability in container type, incident type, accident severity (i.e., release amount), location, time of day, time of year, and meteorology. Each of these scenarios was evaluated using detailed emission rate and atmospheric dispersion models to calculate downwind chemical concentration footprints with the safe distance for each incident defined as the distance downwind from the source at which the chemical concentration falls below the health protection criteria. The safe distance estimates for the entire set of hypothetical incidents considered in the analysis provide a safe-distance distribution corresponding 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 at night and whether they involve small (≤ 60 gal) or large (> 60 gal) spills.

Examples of safe distance distributions for two chemicals are given in Figures 5.1–5.8. The first four figures show safe distance distributions for chlorine, a Hazard Zone B gas. Distributions are separated according to spill size (large or small) and time of day (day or night). Figures 5.5–5.8 provide corresponding results for a water-reactive material, trichlorosilane, which emits HCl when spilled into water. In all eight figures, the 50th, 70th, 80th, 90th, and 95th percentiles are identified. The PADs in the guidebook correspond with the 90th-percentile values for the individual categories. Tables 5.1 and 5.2 provide safe distance estimates at several percentiles for the chlorine and trichlorosilane distributions shown in the figures. Tables 5.3 and 5.4 provide corresponding data for two additional chemicals, phosphorous chloride (a Hazard Zone B liquid) and ethylene oxide (a Hazard Zone D gas). Results for phosphorous chloride in Table 5.3 are for land-based releases only. A separate set of safe distance distributions was developed for spills of phosphorous chloride into water.

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

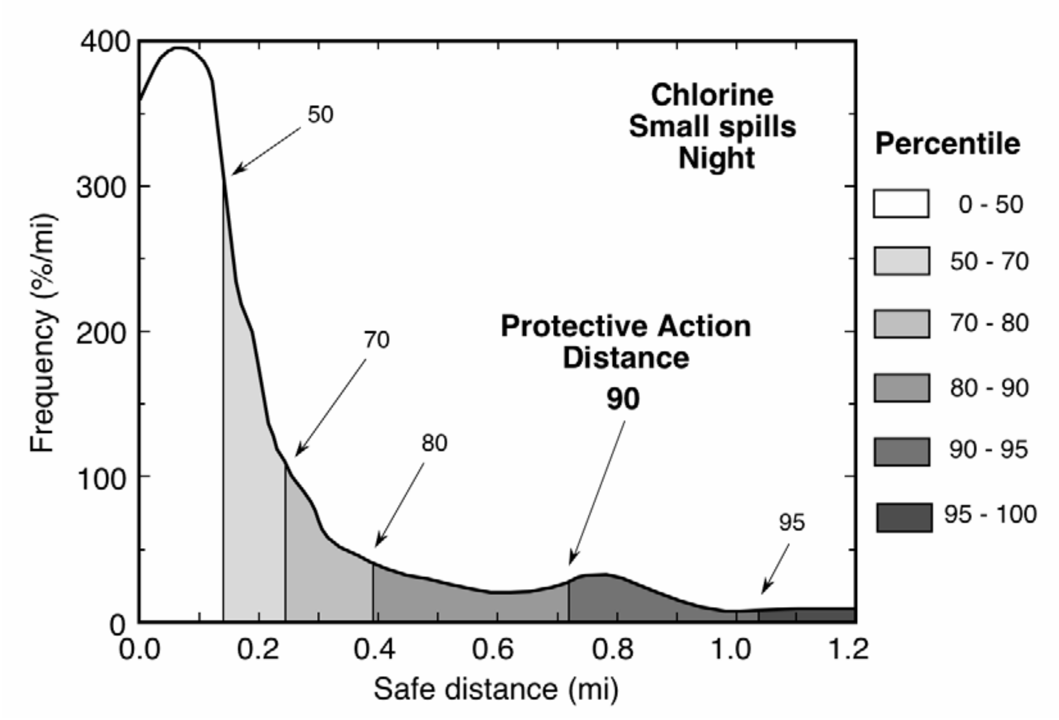

FIGURE 5.1 Frequency of Safe Distances for Small Nighttime Chlorine Spills as Determined in the ERG2004 Analysis

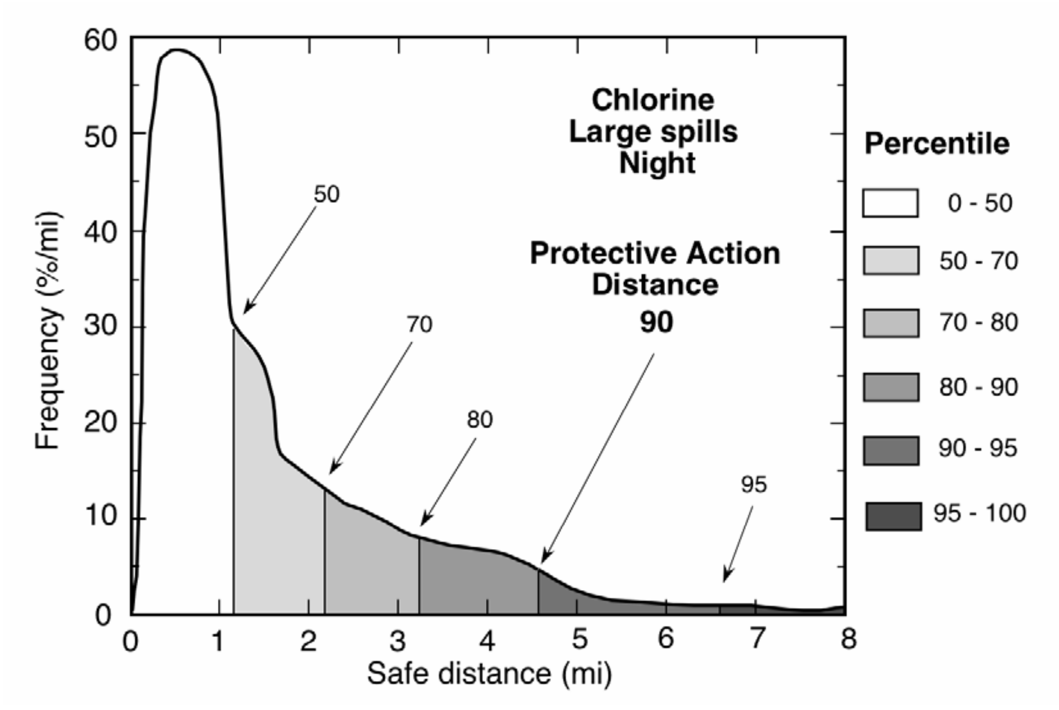

FIGURE 5.2 Frequency of Safe Distances for Large Nighttime Chlorine Spills as Determined in the ERG2004 Analysis

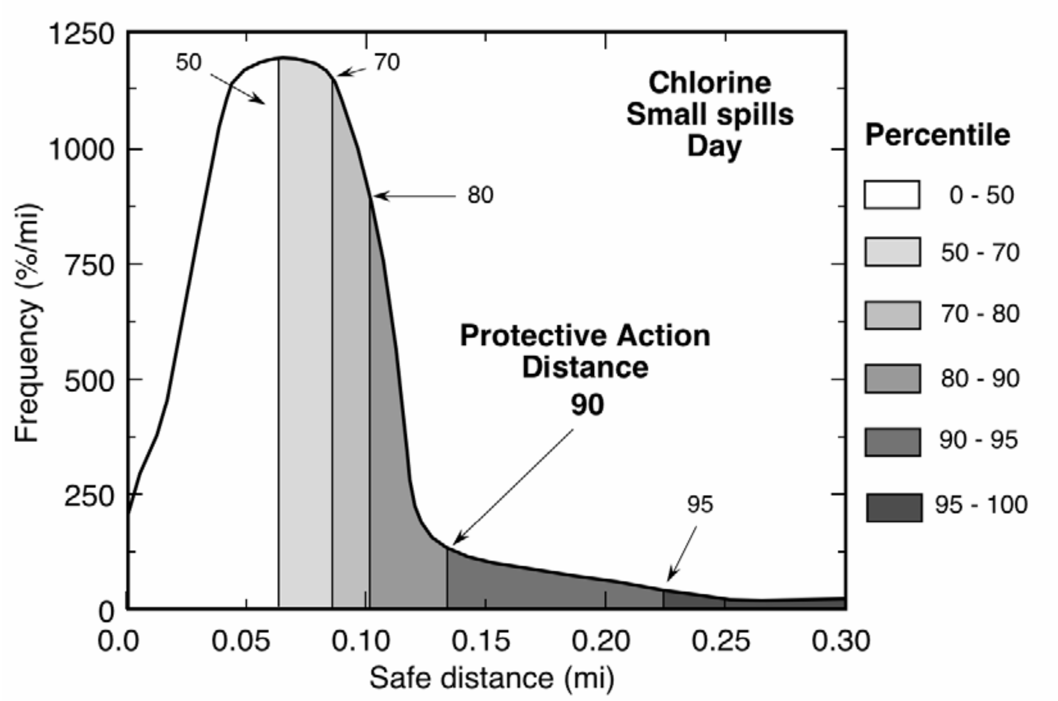

FIGURE 5.3 Frequency of Safe Distances for Small Daytime Chlorine Spills as Determined in the ERG2004 Analysis

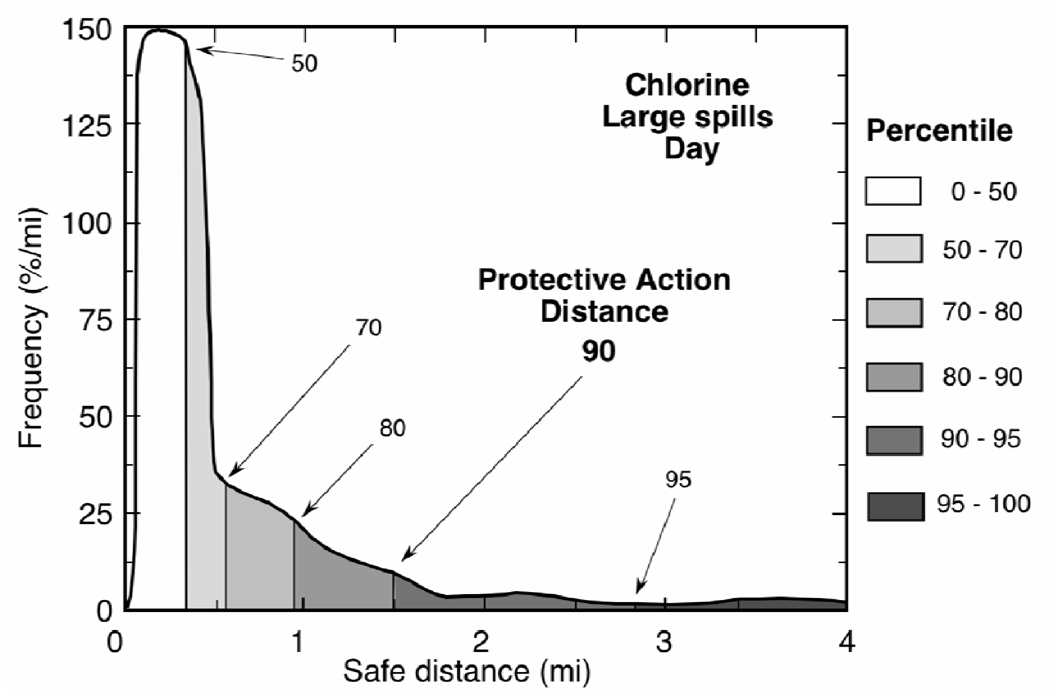

FIGURE 5.4 Frequency of Safe Distances for Large Daytime Chlorine Spills as Determined in the ERG2004 Analysis

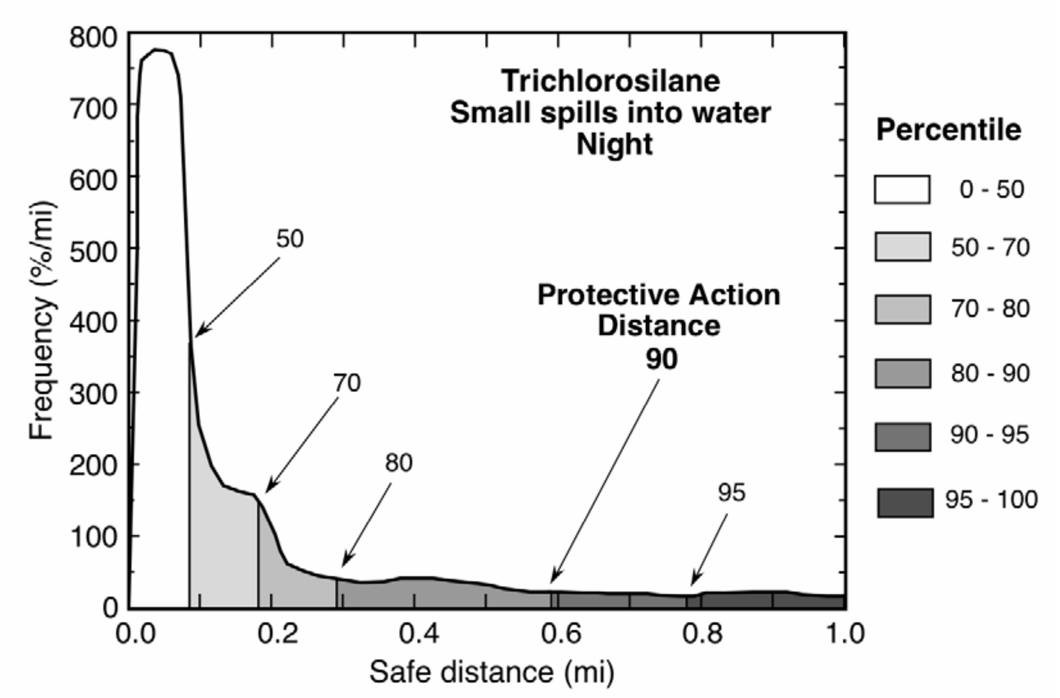

FIGURE 5.5 Frequency of Safe Distances for Small Nighttime Trichlorosilane Spills into Water as Determined in the ERG2004 Analysis

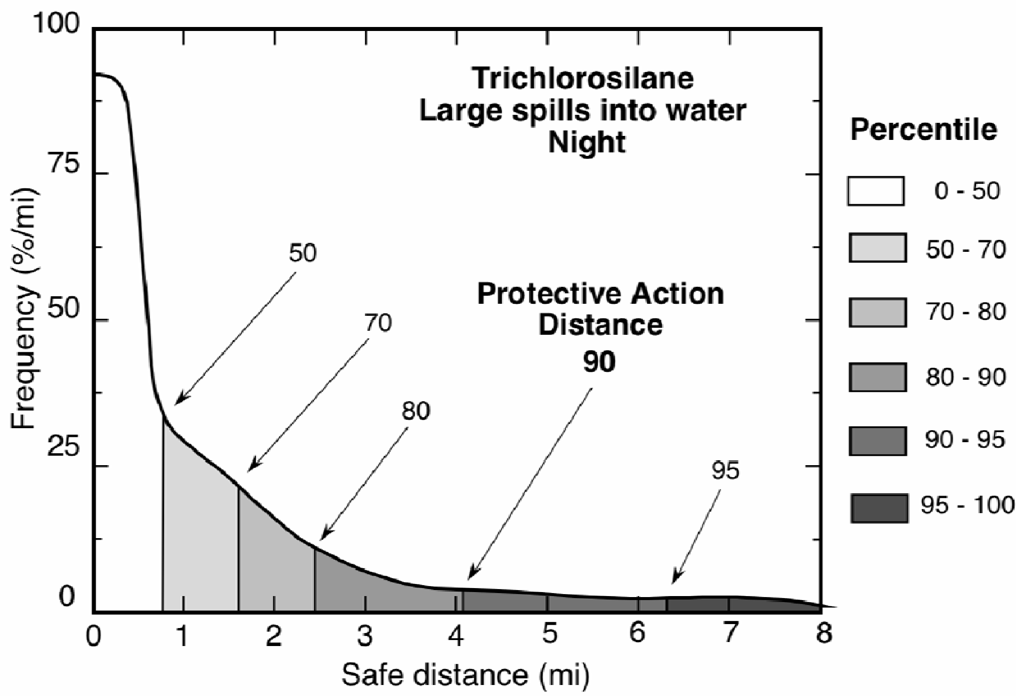

FIGURE 5.6 Frequency of Safe Distances for Large Nighttime Trichlorosilane Spills into Water as Determined in the ERG2004 Analysis

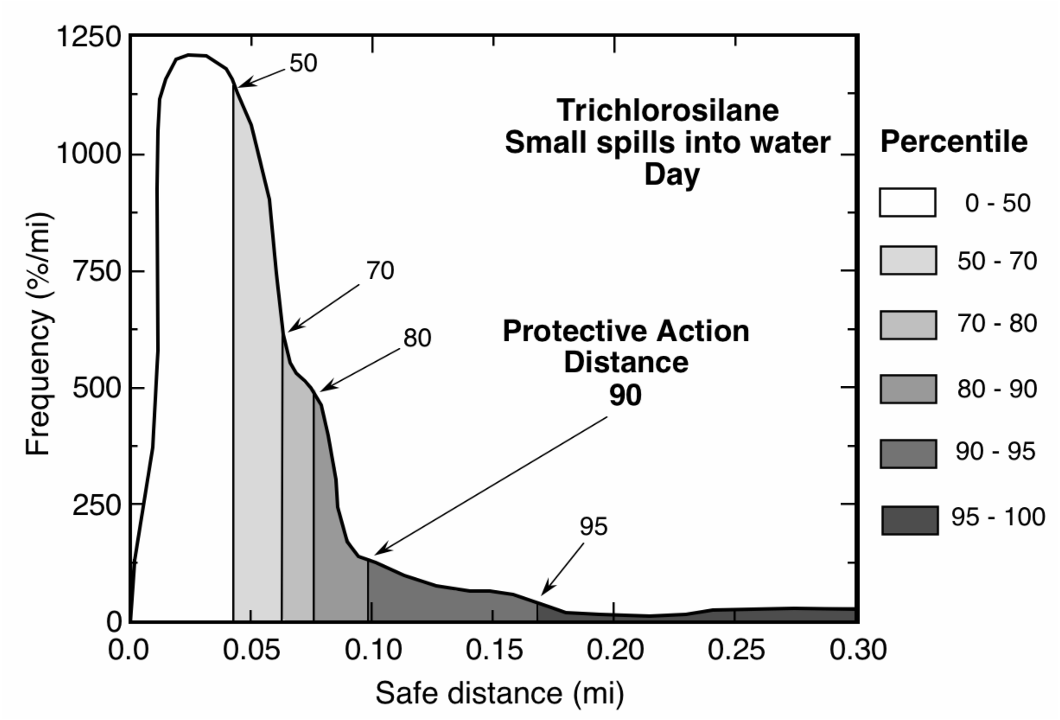

FIGURE 5.7 Frequency of Safe Distances for Small Daytime Trichlorosilane Spills into Water as Determined in the ERG2004 Analysis

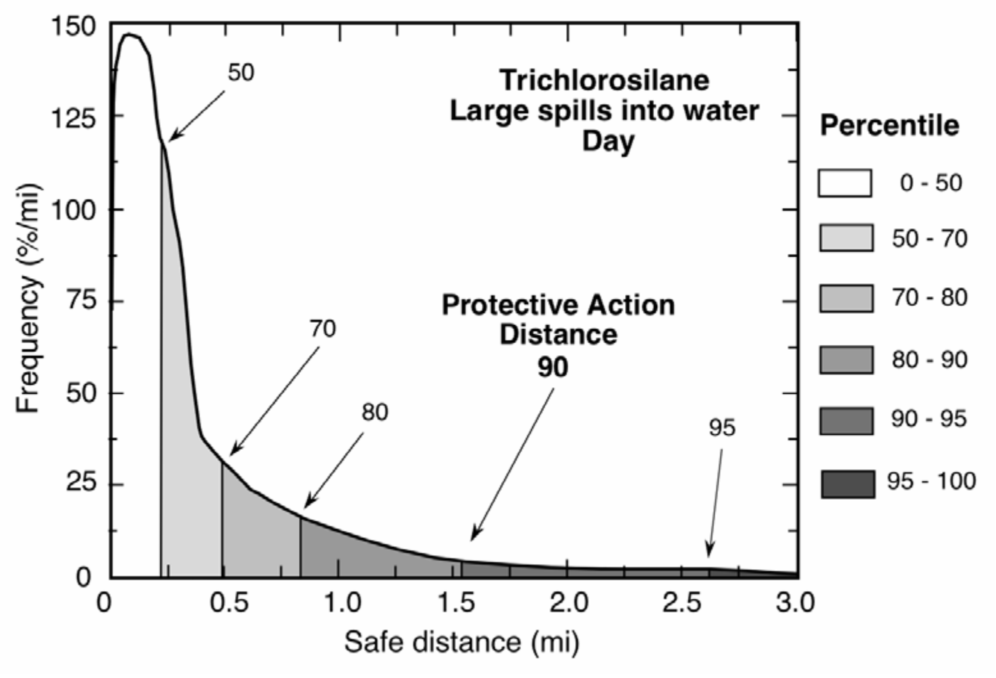

FIGURE 5.8 Frequency of Safe Distances for Large Daytime Trichlorosilane Spills into Water as Determined in the ERG2004 Analysis

TABLE 5.1 Safe Distances at Several Percentiles for Chlorine (UN 1017) Releases as Determined in the ERG2004 Analysis

		Safe Distance (mi) for Given Percentile					
Release Size	Time	50	70	80	90	95	99
Small	Day	0.06	0.08	0.10	**0.13**	0.22	0.72
	Night	0.13	0.23	0.39	**0.72**	1.03	1.71
Large	Day	0.32	0.53	0.95	**1.49**	2.83	8.22
	Night	1.03	2.13	3.12	**4.55**	6.56	12.5

TABLE 5.2 Safe Distances at Several Percentiles for Trichlorosilane (UN 1295) Releases into Water as Determined in the ERG2004 Analysis

		Safe Distance (mi) for Given Percentile					
Release Size	Time	50	70	80	90	95	99
Small	Day	0.04	0.06	0.07	**0.10**	0.16	0.72
	Night	0.08	0.16	0.28	**0.59**	0.86	1.29
Large	Day	0.22	0.49	0.83	**1.53**	2.62	6.51
	Night	0.81	1.71	2.45	**4.02**	6.36	11.55

TABLE 5.3 Safe Distances at Several Percentiles for Land-based Phosphorous Trichloride (UN 1809) Releases as Determined in the ERG2004 Analysis

		Safe Distance (mi) for Given Percentile					
Release Size	Time	50	70	80	90	95	99
Small	Day	0.01	0.03	0.05	**0.07**	0.10	0.27
	Night	0.04	0.07	0.13	**0.22**	0.34	0.73
Large	Day	0.32	0.54	0.71	**0.92**	1.41	3.46
	Night	0.67	1.17	1.57	**2.12**	3.26	6.56

TABLE 5.4 Safe Distances at Several Percentiles for Ethylene Oxide (UN 1040) Releases as Determined in the ERG2004 Analysis

		Safe Distance (mi) for Given Percentile					
Release Size	Time	50	70	80	90	95	99
Small	Day	0.01	0.01	0.02	**0.02**	0.03	0.09
	Night	0.02	0.04	0.06	**0.08**	0.13	0.22
Large	Day	0.11	0.21	0.39	**0.49**	0.81	2.04
	Night	0.36	0.79	1.04	**1.49**	2.80	6.00

to worst-case releases in worst-case meteorology, can result in safe distances exceeding the PAD by a factor of 2–4. However, using the 99th-percentile criterion to define the PAD would result in extreme overreaction to the vast majority of incidents first responders face. The 90th-percentile criterion was selected to strike a reasonable balance between adequately protecting the public from exposure to potentially harmful substances and avoiding the needless risks and expense associated with overreaction.

5.2 PRESENTATION OF THE TABLE IN THE GUIDEBOOK

Appendix A provides the Table of Initial Isolation and Protective Action Distances as it appears in the ERG2004 (DOT et al. 2004) with one important modification discussed below. The PADs in the Table are the 90th percentiles of the safe distance distributions presented in the previous section. As discussed in Section 2, three distinct types of materials are listed in the Table. The first are TIH materials released in transportation-related incidents. The second are water-reactive materials that emit TIH gases when spilled into water. These entries are denoted by the phrase “when spilled in water.” For TIH materials that emit a secondary TIH product when spilled in water, two entries are listed; they correspond to spills in water and on land. The third type of materials is chemical warfare agents released in a malicious manner. These entries are denoted by the phrase “when used as a weapon.” Some chemical warfare agents, such as arsine and hydrogen cyanide, are TIH industrial chemicals as well and contain additional entries for transportation-related releases.

In all cases, the PADs have been rounded up the next 0.1 mi. Appendix A differs from the presentation in the ERG2004 in that distances are not limited to 7 mi (or 11 km). These “unclipped” values are provided to more accurately show the relative risk of the high-hazard materials for which PADs can exceed 7 mi. Initial Isolation Distances are rounded up to the next 100 ft for distances shorter than 2,000 ft and to the next 500 ft for distances longer than 2,000 ft. Initial Isolation Distances are limited to 3,000 ft.

5.3 EXTENSIONS OF THE ERG ANALYSIS

One key limitation of PAD estimates in the ERG is that the only information taken into account is the spill size (large or small) and whether it is day or night. Clearly, the distributions in Figures 5.1–5.8 show wide variability in PAD estimates, and the data used to construct them contain a great amount of additional information that could be very useful in emergency response situations as well as a wide variety of other analyses. Factors that could be easily ascertained by emergency response personnel are whether they are dealing with a highway or rail incident, whether a vehicular accident or derailment is involved (as opposed to an en route/nonaccident event), general wind conditions (e.g., high or low wind speed), month of year, temperature, and cloud cover (clear or overcast). Each of these factors can affect the safe-distance estimate by a factor of 3 or more.

Examples of additional information that can considerably narrow the safe-distance distributions are shown in Figures 5.9–5.12. Figures 5.9 and 5.10 are for chlorine and are actually subsets of the distribution shown in Figure 5.4. In these figures, the distributions are shown with the ordinate on a log scale to emphasize differences at higher percentiles. The percentiles of the distributions are shown as circles superimposed on the curves. Figure 5.9 compares safe-distance distributions for large, daytime chlorine spills from rail transported tank cars and highway transported cargo tanks. Since rail cars contain approximately four times the quantity of chlorine as highway vehicles, safe-distance estimates are higher at all percentiles for tank cars than highway cargo tanks. At the 50th, 70th, 80th, and 90th percentiles, safe distances for rail releases falling into the large spill definition in the ERG (>60 gal) are about double that for corresponding highway cargo tank releases.

Figure 5.10 shows a comparison for two different wind-speed cases representing low winds (2–3 m/s) and high winds (7–9 m/s), demonstrating the profound influence of wind speed on atmospheric dispersion and, consequently, safe distances. Above the 70th percentile, safe distances for low-wind-speed cases greatly exceed those for high-wind-speed cases. For high-wind-speed cases, a 5-mi safe distance would provide protection 99.5% of the time, whereas it would only be sufficient 65% of the time for low-wind-speed cases.

Figure 5.11 compares safe-distance distributions for two different times of year. Here, we show results for a volatile liquid, fuming nitric acid. Higher temperatures characteristic of summer increase the pool evaporation rate and therefore increase safe distances. Again, we see about factor-of-2 differences between percentiles for summer and winter cases. These distributions could be refined much further if we consider a particular location rather than the full range of locations in the ERG analysis.

The last example we consider is in Figure 5.12. Here we show the effect of increased information on safe-distance estimates for a rail chlorine spill over 1,000 gal. Each of the factors listed in the figure could be easily determined by personnel arriving at the accident scene. The first curve shown is the large spill daytime distribution illustrated in Figure 5.3. This distribution comprises over 422,451 safe-distance estimates from our statistical analysis. Next, we narrow this to tank car spills over 1,000 gal. These incidents comprise 4.45% of the original distribution

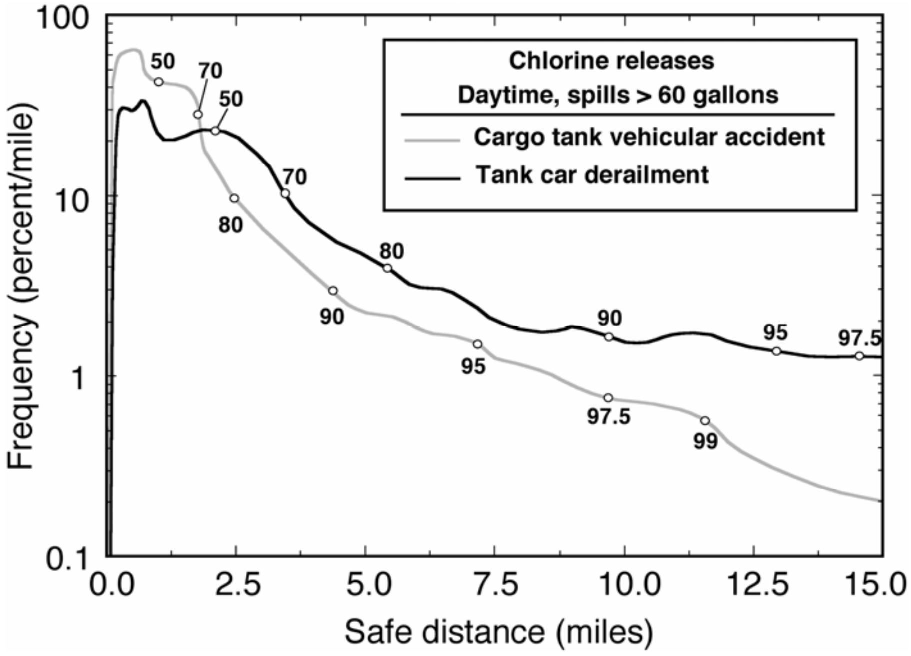

FIGURE 5.9 Frequency of Safe Distances for Large Daytime Chlorine Spills Occurring as a Result of Vehicular Accidents and Tank Car Derailments. Percentiles are denoted by open circles superimposed on the curves. These are a subset of cases shown in Figure 5.3.

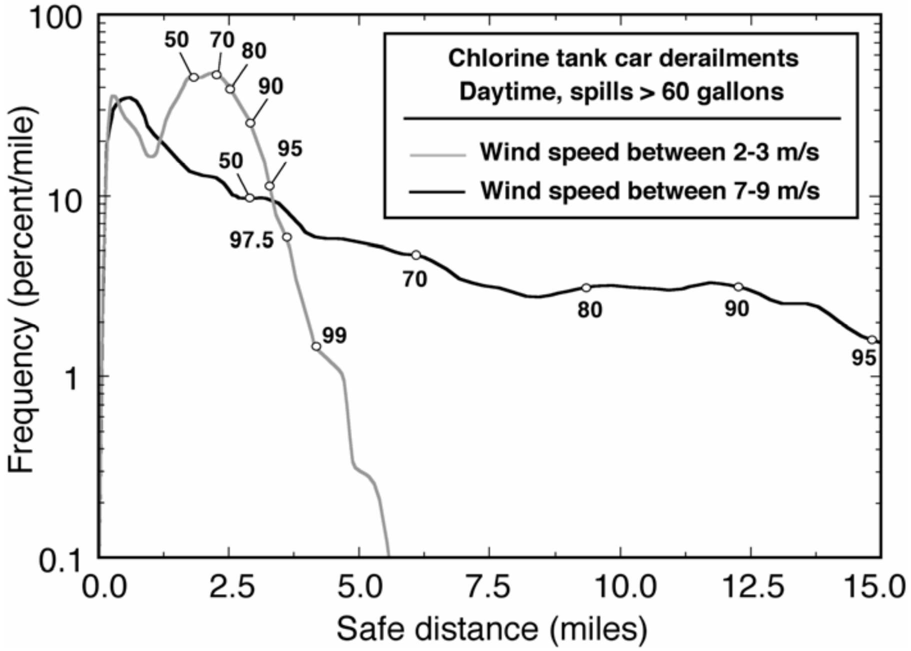

FIGURE 5.10 Frequency of Safe Distances for Large Daytime Chlorine Spills for Different Wind Speed Ranges. Percentiles are denoted by open circles superimposed on the curves. These are a subset of cases shown in Figure 5.9.

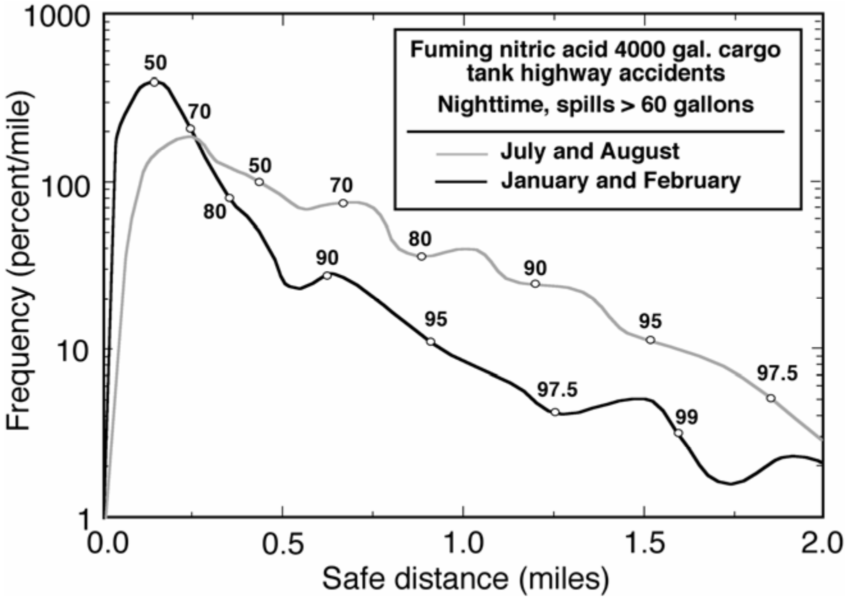

FIGURE 5.11 Frequency of Safe Distances for Highway Accidents Involving Fuming Nitric Acid 4,000-gal Cargo Tanks for Summer and Winter Conditions, Illustrating the Effects of Seasonal Climatology. Percentiles are denoted by open circles superimposed on the curves.

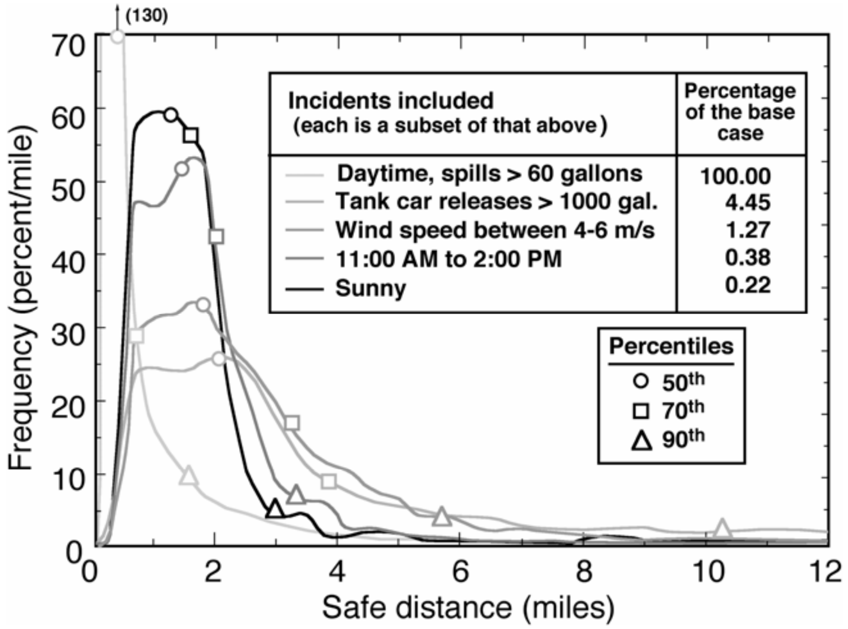

FIGURE 5.12 Frequency of Safe Distances for a Chlorine Tank Car Release Greater than 1,000 gal, Occurring from 11 a.m. to 2 p.m. on a Sunny Day with the Wind Between 4 and 6 m/s, Showing the Effect on the Safe-distance Distribution as Each Constraint Is Imposed. Percentiles are denoted as shown in the legend. The percentage of the base case (as given in Figure 5.3) is also provided.

(18,786 cases). These cases are among the worst cases of the original distribution in terms of spill amount, as evidenced by the fact that the 90th-percentile value is more than a factor of 5 greater than that for the original distribution. The next three curves refine this distribution using easily determined meteorology and time-of-day variables. The final case is that for a tank car release above 1,000 gal, occurring from 11 a.m. to 2 p.m. on a sunny day with the wind between 4 and 6 m/s. This combination of conditions represents only 0.22% of the cases comprising the original distribution for chlorine daytime large spills.

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APPENDIX A:

TABLE OF INITIAL ISOLATION AND PROTECTIVE ACTION DISTANCES IN THE *2004 EMERGENCY RESPONSE GUIDEBOOK*

APPENDIX A:

TABLE OF INITIAL ISOLATION AND PROTECTIVE ACTION DISTANCES IN THE *2004 EMERGENCY RESPONSE GUIDEBOOK*

Table A.1 provides the Table of Initial Isolation and Protective Action Distances for the 2004 Emergency Response Guidebook (in English units only). Table values are identical to those appearing in ERG2004, except that distances are not truncated at 7 mi (11 km).

TABLE A.1 Table of Initial Isolation and Protective Action Distances

UN ID 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)
1005	Ammonia, anhydrous	100	0.1	0.1	200	0.4	1.4
1005	Ammonia, anhydrous, liquefied	100	0.1	0.1	200	0.4	1.4
1005	Ammonia, solution, with more than 50% ammonia	100	0.1	0.1	200	0.4	1.4
1005	Anhydrous ammonia	100	0.1	0.1	200	0.4	1.4
1005	Anhydrous ammonia, liquefied	100	0.1	0.1	200	0.4	1.4
1008	Boron trifluoride	100	0.1	0.4	600	1.1	3.0
1008	Boron trifluoride, compressed	100	0.1	0.4	600	1.1	3.0
1016	Carbon monoxide	100	0.1	0.1	300	0.4	1.5
1016	Carbon monoxide, compressed	100	0.1	0.1	300	0.4	1.5
1017	Chlorine	100	0.2	0.8	800	1.5	4.6
1023	Coal gas	100	0.1	0.1	200	0.2	0.3
1023	Coal gas, compressed	100	0.1	0.1	200	0.2	0.3
1026	Cyanogen	100	0.2	0.8	400	0.7	2.7
1026	Cyanogen, liquefied	100	0.2	0.8	400	0.7	2.7
1026	Cyanogen gas	100	0.2	0.8	400	0.7	2.7
1040	Ethylene oxide	100	0.1	0.1	300	0.5	1.5
1040	Ethylene oxide with Nitrogen	100	0.1	0.1	300	0.5	1.5
1045	Fluorine	100	0.1	0.3	300	0.5	2.2
1045	Fluorine, compressed	100	0.1	0.3	300	0.5	2.2
1048	Hydrogen bromide, anhydrous	100	0.1	0.3	600	1.1	3.6
1050	Hydrogen chloride, anhydrous	100	0.1	0.3	1,200	2.2	6.5
1051	AC (when used as a weapon)	200	0.1	0.3	1,500	1.0	2.4
1051	Hydrocyanic acid, aqueous solutions, with more than 20% Hydrogen cyanide	100	0.1	0.3	500	0.8	2.3
1051	Hydrocyanic acid, liquefied	100	0.1	0.3	500	0.8	2.3
1051	Hydrogen cyanide, anhydrous, stabilized	100	0.1	0.3	500	0.8	2.3
1051	Hydrogen cyanide, stabilized	100	0.1	0.3	500	0.8	2.3
1052	Hydrogen fluoride, anhydrous	100	0.1	0.3	700	1.2	2.7
1053	Hydrogen sulfide	100	0.1	0.2	700	1.3	3.9
1053	Hydrogen sulfide, liquefied	100	0.1	0.2	700	1.3	3.9
1053	Hydrogen sulphide	100	0.1	0.2	700	1.3	3.9
1053	Hydrogen sulphide, liquefied	100	0.1	0.2	700	1.3	3.9
1062	Methyl bromide	100	0.1	0.1	300	0.5	1.4
1064	Methyl mercaptan	100	0.1	0.2	500	0.8	2.8
1067	Dinitrogen tetroxide	100	0.1	0.3	500	1.0	2.5
1067	Dinitrogen tetroxide, liquefied	100	0.1	0.3	500	1.0	2.5
1067	Nitrogen dioxide	100	0.1	0.3	500	1.0	2.5
1067	Nitrogen dioxide, liquefied	100	0.1	0.3	500	1.0	2.5
1069	Nitrosyl chloride	100	0.1	0.6	1,500	2.7	6.9
1071	Oil gas	100	0.1	0.1	200	0.2	0.3

TABLE A.1 (Cont.)

UN ID 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)
1071	Oil gas, compressed	100	0.1	0.1	200	0.2	0.3
1076	CG (when used as a weapon)	500	0.8	2.0	2,500	4.5	7.1
1076	Diphosgene	300	0.6	2.6	2,500	4.1	9.1
1076	DP (when used as a weapon)	200	0.2	0.6	600	1.0	2.8
1076	Phosgene	300	0.6	2.6	2,500	4.1	9.1
1079	Sulfur dioxide	100	0.2	0.8	700	1.3	3.9
1079	Sulfur dioxide, liquefied	100	0.2	0.8	700	1.3	3.9
1079	Sulphur dioxide	100	0.2	0.8	700	1.3	3.9
1079	Sulphur dioxide, liquefied	100	0.2	0.8	700	1.3	3.9
1082	Trifluorochloroethylene	100	0.1	0.1	200	0.3	0.5
1082	Trifluorochloroethylene, inhibited	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, inhibited	200	0.3	1.1	1,600	3.0	6.3
1092	Acrolein, stabilized	200	0.3	1.1	1,600	3.0	6.3
1098	Allyl alcohol	100	0.1	0.1	200	0.2	0.4
1135	Ethylene chlorohydrin	100	0.1	0.2	300	0.5	1.0
1143	Crotonaldehyde, inhibited	100	0.1	0.1	200	0.3	0.5
1143	Crotonaldehyde, stabilized	100	0.1	0.1	200	0.3	0.5
1162	Dimethdichlorosilane (when spilled in water)	100	0.2	0.7	1,000	1.9	4.9
1163	1,1-Dimethylhydrazine	100	0.1	0.1	200	0.4	0.8
1163	Dimethylhydrazine, unsymmetrical	100	0.1	0.1	200	0.4	0.8
1182	Ethyl chloroformate	100	0.1	0.2	300	0.6	1.1
1185	Ethyleneimine, inhibited	100	0.2	0.5	600	1.2	2.5
1185	Ethyleneimine, stabilized	100	0.2	0.5	600	1.2	2.5
1196	Ethyltrichlorosilane (when spilled in water)	100	0.2	0.7	1,000	1.9	4.9
1238	Methyl chloroformate	100	0.2	0.5	600	1.1	2.4
1239	Methyl chloromethyl ether	100	0.2	0.6	900	1.6	3.5
1242	Methyldichlorosilane (when spilled in water)	100	0.1	0.4	600	1.0	3.0
1244	Methylhydrazine	100	0.2	0.3	500	0.9	1.8
1250	Methyltrichlorosilane (when spilled in water)	100	0.1	0.3	500	0.8	2.5
1251	Methyl vinyl ketone	500	0.8	2.1	3,000	9.9	12.4
1251	Methyl vinyl ketone, stabilized	500	0.8	2.1	3,000	9.9	12.4
1259	Nickel carbonyl	300	0.5	2.2	1,600	2.9	6.1
1295	Trichlorosilane (when spilled in water)	100	0.1	0.6	900	1.6	4.1
1298	Trimethchlorosilane (when spilled in water)	100	0.1	0.2	300	0.5	1.7
1305	Vinyltrichlorosilane (when spilled in water)	100	0.1	0.5	600	1.1	3.1
1305	Vinyltrichlorosilane, inhibited (when spilled in water)	100	0.1	0.5	600	1.1	3.1
1305	Vinyltrichlorosilane, stabilized (when spilled in water)	100	0.1	0.5	600	1.1	3.1
1340	Phosphorus pentasulfide, free from yellow or white Phosphorous (when spilled in water)	100	0.1	0.4	500	0.6	2.4

TABLE A.1 (Cont.)

UN ID 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)
1340	Phosphorus pentasulphide, free from yellow or white Phosphorous (when spilled in water)	100	0.1	0.4	500	0.6	2.4
1360	Calcium phosphide (when spilled in water)	200	0.3	1.3	2,500	3.9	10.1
1380	Pentaborane	300	0.6	2.1	1,800	3.3	6.9
1384	Sodium dithionite (when spilled in water)	100	0.1	0.1	200	0.3	0.8
1384	Sodium hydrosulfite (when spilled in water)	100	0.1	0.1	200	0.3	0.8
1384	Sodium hydrosulphite (when spilled in water)	100	0.1	0.1	200	0.3	0.8
1397	Aluminum phosphide (when spilled in water)	300	0.4	1.7	3,000	5.6	12.2
1412	Lithium amide (when spilled in water)	100	0.1	0.2	100	0.2	1.0
1419	Magnesium aluminum phosphide (when spilled in water)	200	0.4	1.6	3,000	4.9	11.5
1432	Sodium phosphide (when spilled in water)	200	0.2	1.1	1,600	2.9	8.5
1510	Tetranitromethane	100	0.2	0.4	300	0.5	1.0
1541	Acetone cyanohydrin (when spilled in water)	100	0.1	0.2	800	0.5	1.9
1556	MD (when used as a weapon)[a]	100	0.2	0.5	400	0.8	2.2
1556	Methyldichloroarsine[a]	100	0.1	0.2	200	0.4	0.7
1556	PD (when used as a weapon)	100	0.1	0.1	100	0.1	0.2
1560	Arsenic chloride	100	0.2	0.2	300	0.6	1.1
1560	Arsenic trichloride	100	0.2	0.2	300	0.6	1.1
1569	Bromoacetone	100	0.1	0.4	300	0.5	1.5
1580	Chloropicrin	200	0.3	0.5	700	1.2	2.2
1581	Chloropicrin and Methyl bromide mixture	100	0.1	0.4	700	1.3	3.7
1581	Methyl bromide and Chloropicrin mixture	100	0.1	0.4	700	1.3	3.7
1582	Chloropicrin and Methyl chloride mixture	100	0.1	0.3	100	0.2	1.1
1582	Methyl chloride and Chloropicrin mixture	100	0.1	0.3	100	0.2	1.1
1583	Chloropicrin mixture, n.o.s.	200	0.3	0.5	700	1.2	2.2
1589	CK (when used as a weapon)	200	0.4	1.5	1,300	2.5	5.0
1589	Cyanogen chloride, inhibited	200	0.4	1.8	1,400	2.7	6.3
1589	Cyanogen chloride, stabilized	200	0.4	1.8	1,400	2.7	6.3
1595	Dimethyl sulfate	100	0.1	0.1	200	0.3	0.5
1595	Dimethyl sulphate	100	0.1	0.1	200	0.3	0.5
1605	Ethylene dibromide	100	0.1	0.1	100	0.2	0.4
1612	Hexaethyl tetraphosphate and compressed gas mixture	300	0.5	1.7	1,200	2.2	5.1
1613	Hydrocyanic acid, aqueous solution, with not more than 20% Hydrogen cyanide	100	0.1	0.1	400	0.3	0.8
1613	Hydrogen cyanide, aqueous solution, with not more than 20% Hydrogen cyanide	100	0.1	0.1	400	0.3	0.8
1614	Hydrogen cyanide, anhydrous, stabilized (absorbed)	100	0.1	0.4	200	0.3	1.1
1614	Hydrogen cyanide, stabilized (absorbed)	100	0.1	0.4	200	0.3	1.1
1647	Ethylene dibromide and Methyl bromide mixture, liquid	100	0.1	0.1	100	0.2	0.4
1647	Methyl bromide and Ethylene dibromide mixture, liquid	100	0.1	0.1	100	0.2	0.4

TABLE A.1 (Cont.)

UN ID 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)
1660	Nitric oxide	100	0.1	0.5	200	0.4	1.7
1660	Nitric oxide, compressed	100	0.1	0.5	200	0.4	1.7
1670	Perchloromethyl mercaptan	100	0.1	0.2	200	0.4	0.8
1680	Potassium cyanide (when spilled in water)	100	0.1	0.3	1,000	0.6	2.4
1680	Potassium cyanide, solid (when spilled in water)	100	0.1	0.3	1,000	0.6	2.4
1689	Sodium cyanide (when spilled in water)	200	0.1	0.4	1,300	0.8	3.0
1689	Sodium cyanide, solid (when spilled in water)	200	0.1	0.4	1,300	0.8	3.0
1694	CA (when used as a weapon)	100	0.1	0.3	500	1.0	2.6
1695	Chloroacetone, stabilized	100	0.1	0.2	300	0.5	0.9
1697	CN (when used as a weapon)	100	0.1	0.3	400	0.7	2.0
1698	Adamsite (when used as a weapon)	200	0.2	0.7	600	1.4	3.2
1698	DM (when used as a weapon)	200	0.2	0.7	600	1.4	3.2
1699	DA (when used as a weapon)	200	0.2	0.7	600	1.4	3.2
1703	Tetraethyl dithiopyrophosphate and gases, in solution	200	0.2	1.2	1,300	2.5	5.1
1703	Tetraethyl dithiopyrophosphate and gases, mixtures	200	0.2	1.2	1,300	2.5	5.1
1703	Tetraethyl dithiopyrophosphate and gases, mixtures, or in solution (LC_{50} more than 200 ppm but not more than 5,000 ppm)	100	0.1	0.6	600	1.1	2.8
1703	Tetraethyl dithiopyrophosphate and gases, mixtures, or in solution (LC_{50} not more than 200 ppm)	200	0.2	1.2	1,300	2.5	5.1
1705	Tetraethyl pyrophosphate and compressed gas mixtures	100	0.2	1.2	1,400	2.5	5.2
1705	Tetraethyl pyrophosphate and compressed gas mixtures (LC_{50} more than 200 ppm but not more than 5,000 ppm)	100	0.1	0.6	500	1.0	2.8
1705	Tetraethyl pyrophosphate and compressed gas mixtures (LC_{50} not more than 200 ppm)	100	0.2	1.2	1,400	2.5	5.2
1716	Acetyl bromide (when spilled in water)	100	0.1	0.2	300	0.5	1.4
1717	Acetyl chloride (when spilled in water)	100	0.1	0.3	400	0.7	2.2
1722	Allyl chlorocarbonate	100	0.2	0.5	700	1.2	2.4
1722	Allyl chloroformate	100	0.2	0.5	700	1.2	2.4
1724	Allyltrichlorosilane, stabilized (when spilled in water)	100	0.1	0.5	600	1.2	3.4
1725	Aluminum bromide, anhydrous (when spilled in water)	100	0.1	0.3	300	0.4	1.6
1726	Aluminum chloride, anhydrous (when spilled in water)	100	0.1	0.5	400	0.7	2.8
1728	Amyltrichlorosilane (when spilled in water)	100	0.1	0.1	200	0.3	1.2
1732	Antimony pentafluoride (when spilled in water)	100	0.1	0.6	600	1.2	3.4
1741	Boron trichloride	100	0.1	0.2	200	0.4	1.1
1744	Bromine	200	0.3	1.1	1,100	2.1	4.6
1744	Bromine, solution	200	0.3	1.1	1,100	2.1	4.6
1745	Bromine pentafluoride (when spilled on land)	100	0.2	0.9	900	1.7	4.3
1745	Bromine pentafluoride (when spilled in water)	100	0.1	0.6	800	1.4	4.1
1746	Bromine trifluoride (when spilled on land)	100	0.1	0.4	600	1.1	3

TABLE A.1 (Cont.)

UN ID 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)
1746	Bromine trifluoride (when spilled in water)	100	0.1	0.6	700	1.2	3.6
1747	Butyltrichlorosilane (when spilled in water)	100	0.1	0.2	200	0.4	1.3
1749	Chlorine trifluoride	200	0.3	1.3	1,000	1.8	5.1
1752	Chloroacetyl chloride (when spilled on land)	100	0.2	0.4	500	0.9	1.6
1752	Chloroacetyl chloride (when spilled in water)	100	0.1	0.1	200	0.3	1.0
1754	Chlorosulfonic acid (when spilled on land)	100	0.1	0.1	100	0.2	0.3
1754	Chlorosulfonic acid (when spilled in water)	100	0.1	0.4	300	0.5	1.7
1754	Chlorosulfonic acid and Sulfur trioxide mixture (when spilled on land)	100	0.1	0.1	100	0.2	0.3
1754	Chlorosulfonic acid and Sulfur trioxide mixture (when spilled in water)	100	0.1	0.4	300	0.5	1.7
1754	Chlorosulphonic acid (when spilled on land)	200	0.2	0.6	1,000	1.5	4.0
1754	Chlorosulphonic acid (when spilled in water)	100	0.1	0.4	300	0.5	1.7
1754	Chlorosulphonic acid and Sulphur trioxide mixture (when spilled on land)	200	0.2	0.6	1,000	1.5	4.0
1754	Chlorosulphonic acid and Sulphur trioxide mixture (when spilled in water)	100	0.1	0.4	300	0.5	1.7
1754	Sulfur trioxide and Chlorosulfonic acid mixture (when spilled on land)	200	0.2	0.6	1,000	1.5	4.0
1754	Sulfur trioxide and Chlorosulfonic acid mixture (when spilled in water)	100	0.1	0.4	300	0.5	1.7
1754	Sulphur trioxide and Chlorosulphonic acid mixture (when spilled on land)	200	0.2	0.6	1,000	1.5	4.0
1754	Sulphur trioxide and Chlorosulphonic acid mixture (when spilled in water)	100	0.1	0.4	300	0.5	1.7
1758	Chromium oxychloride (when spilled in water)	100	0.1	0.1	100	0.2	0.8
1763	Cyclohexyltrichlorosilane (when spilled in water)	100	0.1	0.2	300	0.5	1.9
1766	Dichlorophenyltrichlorosilane (when spilled in water)	100	0.1	0.6	700	1.3	3.6
1767	Diethlydichlorosilane (when spilled in water)	100	0.1	0.1	200	0.3	0.8
1769	Diphenyldichlorosilane (when spilled in water)	100	0.1	0.1	100	0.2	0.8
1771	Dodecyltrichlorosilane (when spilled in water)	100	0.1	0.1	200	0.3	1.2
1777	Fluorosulfonic acid (when spilled in water)	100	0.1	0.3	400	0.6	2.1
1777	Fluorosulphonic acid (when spilled in water)	100	0.1	0.3	400	0.6	2.1
1784	Hexyltrichlorosilane (when spilled in water)	100	0.1	0.3	400	0.7	2.4
1799	Nonyltrichlorosilane (when spilled in water)	100	0.1	0.2	200	0.4	1.6
1800	Octadecyltrichlorosilane (when spilled in water)	100	0.1	0.2	300	0.5	1.8
1801	Octyltrichlorosilane (when spilled in water)	100	0.1	0.2	200	0.4	1.6
1804	Phenyltrichlorosilane (when spilled in water)	100	0.1	0.6	800	1.4	4.0
1806	Phosphorus pentachloride (when spilled in water)	100	0.1	0.3	300	0.5	1.9
1809	Phosphorus trichloride (when spilled on land)	100	0.1	0.3	500	1.0	2.2
1809	Phosphorus trichloride (when spilled in water)	100	0.1	0.4	600	1.0	3.0

TABLE A.1 (Cont.)

UN ID No.	Name of Material	Small Spills			Large Spills		
		First Isolate in All Directions (ft)	Then Protect Persons Downwind during Day (mi)	Then Protect Persons Downwind during Night (mi)	First Isolate in All Directions (ft)	Then Protect Persons Downwind during Day (mi)	Then Protect Persons Downwind during Night (mi)
1810	Phosphorus oxychloride (when spilled on land)	100	0.2	0.3	400	0.7	1.4
1810	Phosphorus oxychloride (when spilled in water)	100	0.1	0.6	800	1.5	3.9
1816	Propyltrichlorosilane (when spilled in water)	100	0.1	0.3	400	0.8	2.6
1818	Silicon tetrachloride (when spilled in water)	100	0.1	0.4	500	1.0	2.9
1828	Sulfur chlorides (when spilled on land)	100	0.1	0.1	300	0.6	1.1
1828	Sulfur chlorides (when spilled in water)	100	0.1	0.4	500	0.9	3.0
1828	Sulphur chlorides (when spilled on land)	100	0.1	0.1	300	0.6	1.1
1828	Sulphur chlorides (when spilled in water)	100	0.1	0.4	500	0.9	3.0
1829	Sulfur trioxide	200	0.2	0.6	1,000	1.5	4.0
1829	Sulfur trioxide, inhibited	200	0.2	0.6	1,000	1.5	4.0
1829	Sulfur trioxide, stabilized	200	0.2	0.6	1,000	1.5	4.0
1829	Sulfur trioxide, uninhibited	200	0.2	0.6	1,000	1.5	4.0
1829	Sulphur trioxide	200	0.2	0.6	1,000	1.5	4.0
1829	Sulphur trioxide, inhibited	200	0.2	0.6	1,000	1.5	4.0
1829	Sulphur trioxide, stabilized	200	0.2	0.6	1,000	1.5	4.0
1829	Sulphur trioxide, uninhibited	200	0.2	0.6	1,000	1.5	4.0
1831	Sulfuric acid, fuming	200	0.2	0.6	1,000	1.5	4.0
1831	Sulfuric acid, fuming, with not less than 30% free Sulfur trioxide	200	0.2	0.6	1,000	1.5	4.0
1831	Sulphuric acid, fuming	200	0.2	0.6	1,000	1.5	4.0
1831	Sulphuric acid, fuming, with not less than 30% free Sulphur trioxide	200	0.2	0.6	1,000	1.5	4.0
1834	Sulfuryl chloride (when spilled on land)	100	0.1	0.1	100	0.2	0.5
1834	Sulfuryl chloride (when spilled in water)	100	0.1	0.2	300	0.5	1.8
1834	Sulphuryl chloride (when spilled on land)	100	0.1	0.1	100	0.2	0.5
1834	Sulphuryl chloride (when spilled in water)	100	0.1	0.2	300	0.5	1.8
1836	Thionyl chloride (when spilled on land)	100	0.2	0.5	300	0.6	1.4
1836	Thionyl chloride (when spilled in water)	200	0.2	1.1	1,500	2.8	6.5
1838	Titanium tetrachloride (when spilled on land)	100	0.1	0.1	200	0.3	0.5
1838	Titanium tetrachloride (when spilled in water)	100	0.1	0.3	400	0.7	2.3
1859	Silicon tetrafluoride	100	0.1	0.1	200	0.3	0.5
1859	Silicon tetrafluoride, compressed	100	0.1	0.1	200	0.3	0.5
1892	ED (when used as a weapon)	100	0.2	0.5	400	0.8	1.6
1892	Ethyldichloroarsine	100	0.1	0.2	200	0.4	0.7
1898	Acetyl iodide (when spilled in water)	100	0.1	0.2	200	0.4	1.1
1911	Diborane	200	0.2	1.0	600	1.1	3.4
1911	Diborane, compressed	200	0.2	1.0	600	1.1	3.4
1923	Calcium dithionite (when spilled in water)	100	0.1	0.1	200	0.3	0.8
1923	Calcium hydrosulfite (when spilled in water)	100	0.1	0.1	200	0.3	0.8
1923	Calcium hydrosulphite (when spilled in water)	100	0.1	0.1	200	0.3	0.8

TABLE A.1 (Cont.)

UN ID No.	Name of Material	Small Spills: First Isolate in All Directions (ft)	Small Spills: Then Protect Persons Downwind during Day (mi)	Small Spills: Then Protect Persons Downwind during Night (mi)	Large Spills: First Isolate in All Directions (ft)	Large Spills: Then Protect Persons Downwind during Day (mi)	Large Spills: Then Protect Persons Downwind during Night (mi)
1931	Zinc dithionite (<u>when spilled in water</u>)	100	0.1	0.1	200	0.3	0.8
1931	Zinc hydrosulfite (<u>when spilled in water</u>)	100	0.1	0.1	200	0.3	0.8
1931	Zinc hydrosulphite (<u>when spilled in water</u>)	100	0.1	0.1	200	0.3	0.8
1953	Compressed gas, flammable, poisonous, n.o.s. (Inhalation Hazard Zone A)	400	0.8	3.2	3,000	5.4	9.6
1953	Compressed gas, flammable, poisonous, n.o.s. (Inhalation Hazard Zone B)	100	0.2	0.8	1,400	2.5	6.7
1953	Compressed gas, flammable, poisonous, n.o.s. (Inhalation Hazard Zone C)	100	0.1	0.5	800	1.5	4.0
1953	Compressed gas, flammable, poisonous, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.1	300	0.5	1.5
1953	Compressed gas, flammable, toxic, n.o.s. (Inhalation Hazard Zone A)	400	0.8	3.2	3,000	5.4	9.6
1953	Compressed gas, flammable, toxic, n.o.s. (Inhalation Hazard Zone B)	100	0.2	0.8	1,400	2.5	6.7
1953	Compressed gas, flammable, toxic, n.o.s. (Inhalation Hazard Zone C)	100	0.1	0.5	800	1.5	4.0
1953	Compressed gas, flammable, toxic, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.1	300	0.5	1.5
1953	Compressed gas, poisonous, flammable, n.o.s.	400	0.8	3.2	3,000	5.4	9.6
1953	Compressed gas, poisonous, flammable, n.o.s. (Inhalation Hazard Zone A)	400	0.8	3.2	3,000	5.4	9.6
1953	Compressed gas, poisonous, flammable, n.o.s. (Inhalation Hazard Zone B)	100	0.2	0.8	1,400	2.5	6.7
1953	Compressed gas, poisonous, flammable, n.o.s. (Inhalation Hazard Zone C)	100	0.1	0.5	800	1.5	4.0
1953	Compressed gas, poisonous, flammable, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.1	300	0.5	1.5
1953	Compressed gas, toxic, flammable, n.o.s.	400	0.8	3.2	3,000	5.4	9.6
1953	Compressed gas, toxic, flammable, n.o.s. (Inhalation Hazard Zone A)	400	0.8	3.2	3,000	5.4	9.6
1953	Compressed gas, toxic, flammable, n.o.s. (Inhalation Hazard Zone B)	100	0.2	0.8	1,400	2.5	6.7
1953	Compressed gas, toxic, flammable, n.o.s. (Inhalation Hazard Zone C)	100	0.1	0.5	800	1.5	4.0
1953	Compressed gas, toxic, flammable, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.1	300	0.5	1.5
1953	Liquefied gas, flammable, poisonous, n.o.s.	400	0.8	3.2	3,000	5.4	9.6
1953	Liquefied gas, flammable, poisonous, n.o.s. (Inhalation Hazard Zone A)	400	0.8	3.2	3,000	5.4	9.6
1953	Liquefied gas, flammable, poisonous, n.o.s. (Inhalation Hazard Zone B)	100	0.2	0.8	1,400	2.5	6.7

TABLE A.1 (Cont.)

		Small Spills			Large Spills		
		First Isolate in All Direc-tions (ft)	Then Protect Persons Downwind during		First Isolate in All Direc-tions (ft)	Then Protect Persons Downwind during	
UN ID No.	Name of Material		Day (mi)	Night (mi)		Day (mi)	Night (mi)
1953	Liquefied gas, flammable, poisonous, n.o.s. (Inhalation Hazard Zone C)	100	0.1	0.5	800	1.5	4.0
1953	Liquefied gas, flammable, poisonous, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.1	300	0.5	1.5
1953	Liquefied gas, flammable, toxic, n.o.s.	400	0.8	3.2	3,000	5.4	9.6
1953	Liquefied gas, flammable, toxic, n.o.s. (Inhalation Hazard Zone A)	400	0.8	3.2	3,000	5.4	9.6
1953	Liquefied gas, flammable, toxic, n.o.s. (Inhalation Hazard Zone B)	100	0.2	0.8	1,400	2.5	6.7
1953	Liquefied gas, flammable, toxic, n.o.s. (Inhalation Hazard Zone C)	100	0.1	0.5	800	1.5	4.0
1953	Liquefied gas, flammable, toxic, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.1	300	0.5	1.5
1955	Compressed gas, poisonous, n.o.s.	2,000	3.7	7.9	3,000	16.9	18.2
1955	Compressed gas, poisonous, n.o.s. (Inhalation Hazard Zone A)	2,000	3.7	7.9	3,000	16.9	18.2
1955	Compressed gas, poisonous, n.o.s. (Inhalation Hazard Zone B)	200	0.3	1.3	3,000	4.9	11.5
1955	Compressed gas, poisonous, n.o.s. (Inhalation Hazard Zone C)	100	0.2	0.8	800	1.5	4.0
1955	Compressed gas, poisonous, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.4	400	0.8	2.4
1955	Compressed gas, toxic, n.o.s.	2,000	3.7	7.9	3,000	16.9	18.2
1955	Compressed gas, toxic, n.o.s. (Inhalation Hazard Zone A)	2,000	3.7	7.9	3,000	16.9	18.2
1955	Compressed gas, toxic, n.o.s. (Inhalation Hazard Zone B)	200	0.3	1.3	3,000	4.9	11.5
1955	Compressed gas, toxic, n.o.s. (Inhalation Hazard Zone C)	100	0.2	0.8	800	1.5	4.0
1955	Compressed gas, toxic, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.4	400	0.8	2.4
1955	Liquefied gas, poisonous, n.o.s.	2,000	3.7	7.9	3,000	16.9	18.2
1955	Liquefied gas, poisonous, n.o.s. (Inhalation Hazard Zone A)	2,000	3.7	7.9	3,000	16.9	18.2
1955	Liquefied gas, poisonous, n.o.s. (Inhalation Hazard Zone B)	200	0.3	1.3	3,000	4.9	11.5
1955	Liquefied gas, poisonous, n.o.s. (Inhalation Hazard Zone C)	100	0.2	0.8	800	1.5	4.0
1955	Liquefied gas, poisonous, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.4	400	0.8	2.4
1955	Liquefied gas, toxic, n.o.s.	2,000	3.7	7.9	3,000	16.9	18.2
1955	Liquefied gas, toxic, n.o.s. (Inhalation Hazard Zone A)	2,000	3.7	7.9	3,000	16.9	18.2
1955	Liquefied gas, toxic, n.o.s. (Inhalation Hazard Zone B)	200	0.3	1.3	3,000	4.9	11.5
1955	Liquefied gas, toxic, n.o.s. (Inhalation Hazard Zone C)	100	0.2	0.8	800	1.5	4.0
1955	Liquefied gas, toxic, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.4	400	0.8	2.4
1955	Organic phosphate compound mixed with compressed gas	400	0.7	2.1	1,500	2.7	6.0
1955	Organic phosphate mixed with compressed gas	400	0.7	2.1	1,500	2.7	6.0
1955	Organic phosphorus compound mixed with compressed gas	400	0.7	2.1	1,500	2.7	6.0
1967	Insecticide gas, poisonous, n.o.s.	400	0.7	2.1	1,500	2.7	6.0
1967	Insecticide gas, toxic, n.o.s.	400	0.7	2.1	1,500	2.7	6.0

TABLE A.1 (Cont.)

UN ID 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)
1967	Parathion and compressed gas mixture	400	0.7	2.1	1,500	2.7	6.0
1975	Dinitrogen tetroxide and Nitric oxide mixture	100	0.1	0.5	200	0.4	1.7
1975	Nitric oxide and Dinitrogen tetroxide mixture	100	0.1	0.5	200	0.4	1.7
1975	Nitric oxide and Nitrogen dioxide mixture	100	0.1	0.5	200	0.4	1.7
1975	Nitric oxide and Nitrogen tetroxide mixture	100	0.1	0.5	200	0.4	1.7
1975	Nitrogen dioxide and Nitric oxide mixture	100	0.1	0.5	200	0.4	1.7
1975	Nitrogen tetroxide and Nitric oxide mixture	100	0.1	0.5	200	0.4	1.7
1994	Iron pentacarbonyl	100	0.2	0.4	500	1.0	1.9
2004	Magnesium diamide (when spilled in water)	100	0.1	0.3	300	0.4	1.8
2011	Magnesium phosphide (when spilled in water)	200	0.4	1.5	3,000	4.7	11.2
2012	Potassium phosphide (when spilled in water)	200	0.3	1.1	1,600	2.9	8.6
2013	Strontium phosphide (when spilled in water)	200	0.2	1.1	1,600	2.9	8.3
2032	Nitric acid, fuming	100	0.1	0.2	200	0.4	0.8
2032	Nitric acid, red fuming	100	0.1	0.2	200	0.4	0.8
2186	Hydrogen chloride, refrigerated liquid	100	0.1	0.3	1,200	2.2	6.5
2188	Arsine	200	0.4	1.9	1,400	2.6	5.9
2188	SA (when used as a weapon)	200	0.5	1.5	1,300	2.5	5.0
2189	Dichlorosilane	100	0.1	0.6	1,400	2.5	6.7
2190	Oxygen difluoride	2,000	3.7	7.9	3,000	16.9	18.2
2190	Oxygen difluoride, compressed	2,000	3.7	7.9	3,000	16.9	18.2
2191	Sulfuryl fluoride	100	0.1	0.2	400	0.8	2.4
2191	Sulphuryl fluoride	100	0.1	0.2	400	0.8	2.4
2192	Germane	100	0.1	0.6	300	0.5	1.9
2194	Selenium hexafluoride	300	0.5	2.0	1,500	2.7	5.6
2195	Tellurium hexafluoride	300	0.6	2.5	2,000	3.7	7.1
2196	Tungsten hexafluoride	100	0.1	0.7	400	0.6	2.3
2197	Hydrogen iodide, anhydrous	100	0.1	0.2	400	0.8	2.3
2198	Phosphorus pentafluoride	100	0.2	1.0	600	1.0	2.9
2198	Phosphorus pentafluoride, compressed	100	0.2	1.0	600	1.0	2.9
2199	Phosphine	200	0.4	1.9	1,400	2.7	6.0
2202	Hydrogen selenide, anhydrous	400	0.8	3.2	3,000	5.4	9.6
2204	Carbonyl sulfide	100	0.1	0.4	1,000	1.9	5.0
2204	Carbonyl sulphide	100	0.1	0.4	1,000	1.9	5.0
2232	Chloroacetaldehyde	100	0.1	0.2	300	0.5	1.0
2232	2-Chloroethanal	100	0.1	0.2	300	0.5	1.0
2334	Allylamine	100	0.1	0.3	400	0.7	1.5
2337	Phenyl mercaptan	100	0.1	0.1	200	0.2	0.4
2382	1,2-Dimethylhydrazine	100	0.1	0.1	200	0.4	0.8
2382	Dimethylhydrazine, symmetrical	100	0.1	0.1	200	0.4	0.8
2407	Isopropyl chloroformate	100	0.1	0.2	300	0.5	0.9

TABLE A.1 (Cont.)

		Small Spills			Large Spills		
			Then Protect Persons Downwind during			Then Protect Persons Downwind during	
UN ID No.	Name of Material	First Isolate in All Directions (ft)	Day (mi)	Night (mi)	First Isolate in All Directions (ft)	Day (mi)	Night (mi)
2417	Carbonyl fluoride	100	0.1	0.7	300	0.6	2.3
2417	Carbonyl fluoride, compressed	100	0.1	0.7	300	0.6	2.3
2418	Sulfur tetrafluoride	200	0.4	2.0	1,600	2.9	6.6
2418	Sulphur tetrafluoride	200	0.4	2.0	1,600	2.9	6.6
2420	Hexafluoroacetone	100	0.2	0.8	2,500	4.5	10.1
2421	Nitrogen trioxide	100	0.1	0.3	200	0.3	1.2
2437	Methylphenyldichlorosilane (when spilled in water)	100	0.1	0.1	100	0.2	0.7
2438	Trimethylacetyl chloride	100	0.1	0.1	200	0.3	0.5
2442	Trichloroacetyl chloride	100	0.2	0.5	400	0.8	1.4
2474	Thiophosgene	300	0.5	1.5	1,200	2.3	4.2
2477	Methyl isothiocyanate	100	0.1	0.1	200	0.3	0.7
2480	Methyl isocyanate	200	0.3	1.2	1,800	3.3	7.0
2481	Ethyl isocyanate	200	0.4	1.3	2,500	3.9	7.5
2482	n-Propyl isocyanate	400	0.7	1.6	3,000	5.6	8.6
2483	Isopropyl isocyanate	400	0.7	1.8	3,000	7.4	9.8
2484	tert-Butyl isocyanate	300	0.6	1.5	3,000	5.2	8.6
2485	n-Butyl isocyanate	300	0.5	1.0	1,600	2.9	5.0
2486	Isobutyl isocyanate	300	0.5	1.0	1,600	3.0	4.8
2487	Phenyl isocyanate	100	0.2	0.3	600	1.0	1.8
2488	Cyclohexyl isocyanate	100	0.2	0.2	300	0.6	1.0
2495	Iodine pentafluoride (when spilled in water)	100	0.1	0.6	700	1.2	3.6
2521	Diketene, inhibited	100	0.1	0.1	100	0.2	0.3
2521	Diketene, stabilized	100	0.1	0.1	100	0.2	0.3
2534	Methylchlorosilane	100	0.1	0.5	800	1.5	4.0
2548	Chlorine pentafluoride	100	0.2	1.1	800	1.5	4.6
2600	Carbon monoxide and Hydrogen mixture	100	0.1	0.1	300	0.4	1.5
2600	Carbon monoxide and Hydrogen mixture, compressed	100	0.1	0.1	300	0.4	1.5
2600	Hydrogen and Carbon monoxide mixture	100	0.1	0.1	300	0.4	1.5
2600	Hydrogen and Carbon monoxide mixture, compressed	100	0.1	0.1	300	0.4	1.5
2605	Methoxymethyl isocyanate	200	0.2	0.4	600	1.0	1.6
2606	Methyl orthosilicate	100	0.1	0.1	200	0.3	0.4
2644	Methyl iodide	100	0.1	0.1	100	0.2	0.5
2646	Hexachlorocyclopentadiene	100	0.1	0.1	200	0.3	0.3
2668	Chloroacetonitrile	100	0.1	0.1	100	0.2	0.3
2676	Stibine	200	0.3	1.4	900	1.7	4.7
2691	Phosphorus pentabromide (when spilled in water)	100	0.1	0.4	300	0.4	1.7
2692	Boron tribromide (when spilled on land)	100	0.1	0.3	200	0.4	0.8
2692	Boron tribromide (when spilled in water)	100	0.1	0.3	300	0.5	1.6
2740	n-Propyl chloroformate	100	0.1	0.2	300	0.5	0.9
2742	sec-Butyl chloroformate	100	0.1	0.1	200	0.3	0.4

TABLE A.1 (Cont.)

UN ID No.	Name of Material	Small Spills			Large Spills		
		First Isolate in All Directions (ft)	Then Protect Persons Downwind during Day (mi)	Then Protect Persons Downwind during Night (mi)	First Isolate in All Directions (ft)	Then Protect Persons Downwind during Day (mi)	Then Protect Persons Downwind during Night (mi)
2742	Isobutyl chloroformate	100	0.1	0.1	100	0.2	0.3
2743	n-Butyl chloroformate	100	0.1	0.1	100	0.2	0.3
2806	Lithium nitride (when spilled in water)	100	0.1	0.2	200	0.4	1.6
2810	Buzz (when used as a weapon)	100	0.1	0.3	200	0.3	1.2
2810	BZ (when used as a weapon)	100	0.1	0.3	200	0.3	1.2
2810	CS (when used as a weapon)	200	0.2	0.7	800	1.6	3.5
2810	DC (when used as a weapon)	100	0.1	0.5	800	1.4	3.3
2810	GA (when used as a weapon)	100	0.2	0.4	500	1.0	1.9
2810	GB (when used as a weapon)	500	1.0	2.1	3,000	7.1	7.1
2810	GD (when used as a weapon)	300	0.5	1.1	2,500	4.2	6.5
2810	GF (when used as a weapon)	100	0.2	0.4	800	1.4	3.2
2810	H (when used as a weapon)	100	0.1	0.1	200	0.4	0.7
2810	HD (when used as a weapon)	100	0.1	0.1	200	0.4	0.7
2810	HL (when used as a weapon)	100	0.1	0.2	300	0.6	1.1
2810	HN-1 (when used as a weapon)	100	0.1	0.1	200	0.4	0.8
2810	HN-2 (when used as a weapon)	100	0.1	0.1	200	0.3	0.7
2810	HN-3 (when used as a weapon)	100	0.1	0.1	100	0.1	0.2
2810	L (Lewisite) (when used as a weapon)	100	0.1	0.2	300	0.6	1.1
2810	Lewisite (when used as a weapon)	100	0.1	0.2	300	0.6	1.1
2810	Mustard (when used as a weapon)	100	0.1	0.1	100	0.1	0.2
2810	Mustard lewisite (when used as a weapon)	100	0.1	0.2	300	0.6	1.1
2810	Poisonous liquid, n.o.s.	500	0.8	2.2	3,000	9.9	12.4
2810	Poisonous liquid, n.o.s. (Inhalation Hazard Zone A)	500	0.8	2.2	3,000	9.9	12.4
2810	Poisonous liquid, n.o.s. (Inhalation Hazard Zone B)	200	0.3	1.1	1,100	2.1	4.6
2810	Poisonous liquid, organic, n.o.s.	500	0.8	2.1	3,000	9.9	12.4
2810	Poisonous liquid, organic, n.o.s. (Inhalation Hazard Zone A)	500	0.8	2.1	3,000	9.9	12.4
2810	Poisonous liquid, organic, n.o.s. (Inhalation Hazard Zone B)	200	0.2	0.6	900	1.6	3.5
2810	Sarin (when used as a weapon)	500	1.0	2.1	3,000	7.1	7.1
2810	Soman (when used as a weapon)	300	0.5	1.1	2,500	4.2	6.5
2810	Tabun (when used as a weapon)	100	0.2	0.4	500	1.0	1.9
2810	Thickened GD (when used as a weapon)	300	0.5	1.1	2,500	4.2	6.5
2810	Toxic liquid, n.o.s.	500	0.8	2.2	3,000	9.9	12.4
2810	Toxic liquid, n.o.s. (Inhalation Hazard Zone A)	500	0.8	2.2	3,000	9.9	12.4
2810	Toxic liquid, n.o.s. (Inhalation Hazard Zone B)	200	0.3	1.1	1,100	2.1	4.6
2810	Toxic liquid, organic, n.o.s.	500	0.8	2.1	3,000	9.9	12.4
2810	Toxic liquid, organic, n.o.s. (Inhalation Hazard Zone A)	500	0.8	2.1	3,000	9.9	12.4
2810	Toxic liquid, organic, n.o.s. (Inhalation Hazard Zone B)	200	0.2	0.6	900	1.6	3.5
2810	VX (when used as a weapon)	100	0.1	0.1	200	0.4	0.6
2811	CX (when used as a weapon)	100	0.1	0.3	300	0.6	1.9
2826	Ethyl chlorothioformate	100	0.1	0.1	200	0.4	0.6

TABLE A.1 (Cont.)

		Small Spills			Large Spills		
			Then Protect Persons Downwind during			Then Protect Persons Downwind during	
UN ID No.	Name of Material	First Isolate in All Directions (ft)	Day (mi)	Night (mi)	First Isolate in All Directions (ft)	Day (mi)	Night (mi)
2845	Ethyl phosphonous dichloride, anhydrous	100	0.2	0.5	700	1.2	2.2
2845	Methyl phosphonous dichloride	200	0.3	0.8	1,000	1.9	3.7
2901	Bromine chloride	100	0.2	0.6	800	1.5	3.9
2927	Ethyl phosphonothioic dichloride, anhydrous	100	0.1	0.1	100	0.1	0.2
2927	Ethyl phosphorodichloridate	100	0.1	0.1	100	0.2	0.2
2927	Poisonous liquid, corrosive, n.o.s.	300	0.5	1.5	2,500	3.9	7.5
2927	Poisonous liquids, corrosive, n.o.s. (Inhalation Hazard Zone A)	300	0.5	1.5	2,500	3.9	7.5
2927	Poisonous liquids, corrosive, n.o.s. (Inhalation Hazard Zone B)	200	0.3	1.1	1,100	2.1	4.6
2927	Toxic liquid, corrosive, organic, n.o.s.	200	0.4	1.3	2,500	3.9	7.5
2927	Toxic liquid, corrosive, organic, n.o.s. (Inhalation Hazard Zone A)	200	0.4	1.3	2,500	3.9	7.5
2927	Toxic liquid, corrosive, organic, n.o.s. (Inhalation Hazard Zone B)	100	0.2	0.4	600	1.0	1.8
2929	Poisonous liquid, flammable, n.o.s.	500	0.8	2.2	3,000	9.9	12.4
2929	Poisonous liquid, flammable, n.o.s. (Inhalation Hazard Zone A)	500	0.8	2.2	3,000	9.9	12.4
2929	Poisonous liquid, flammable, n.o.s. (Inhalation Hazard Zone B)	200	0.2	0.6	900	1.6	3.5
2929	Poisonous liquid, flammable, organic, n.o.s.	500	0.8	2.1	3,000	9.9	12.4
2929	Poisonous liquid, flammable, organic, n.o.s. (Inhalation Hazard Zone A)	500	0.8	2.1	3,000	9.9	12.4
2929	Poisonous liquid, flammable, organic, n.o.s. (Inhalation Hazard Zone B)	200	0.2	0.6	900	1.6	3.5
2929	Toxic liquid, flammable, n.o.s.	500	0.8	2.2	3,000	9.9	12.4
2929	Toxic liquid, flammable, n.o.s. (Inhalation Hazard Zone A)	500	0.8	2.2	3,000	9.9	12.4
2929	Toxic liquid, flammable, n.o.s. (Inhalation Hazard Zone B)	200	0.2	0.6	900	1.6	3.5
2929	Toxic liquid, flammable, organic, n.o.s.	500	0.8	2.1	3,000	9.9	12.4
2929	Toxic liquid, flammable, organic, n.o.s. (Inhalation Hazard Zone A)	500	0.8	2.1	3,000	9.9	12.4
2929	Toxic liquid, flammable, organic, n.o.s. (Inhalation Hazard Zone B)	200	0.2	0.6	900	1.6	3.5
2977	Radioactive material, Uranium hexafluoride, fissile (when spilled in water)	100	0.1	0.4	300	0.5	2.1
2977	Uranium hexafluoride, fissile containing more than 1% Uranium-235 (when spilled in water)	100	0.1	0.4	300	0.5	2.1
2978	Radioactive material, Uranium hexafluoride (when spilled in water)	100	0.1	0.4	300	0.5	2.1
2978	Radioactive material, Uranium hexafluoride, non fissile or fissile-excepted (when spilled in water)	100	0.1	0.4	300	0.5	2.1
2978	Uranium hexafluoride (when spilled in water)	100	0.1	0.4	300	0.5	2.1

TABLE A.1 (Cont.)

UN ID 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)
2978	Uranium hexafluoride, fissile-excepted (when spilled in water)	100	0.1	0.4	300	0.5	2.1
2978	Uranium hexafluoride, low specific activity (when spilled in water)	100	0.1	0.4	300	0.5	2.1
2978	Uranium hexafluoride, non-fissile (when spilled in water)	100	0.1	0.4	300	0.5	2.1
2985	Chlorosilanes, flammable, corrosive, n.o.s. (when spilled in water)	100	0.1	0.3	500	0.8	2.4
2985	Chlorosilanes, n.o.s.(when spilled in water)	100	0.1	0.3	500	0.8	2.4
2986	Chlorosilanes, corrosive, flammable, n.o.s. (when spilled in water)	100	0.1	0.3	500	0.8	2.4
2986	Chlorosilanes, n.o.s. (when spilled in water)	100	0.1	0.3	500	0.8	2.4
2987	Chlorosilanes, corrosive, n.o.s. (when spilled in water)	100	0.1	0.3	500	0.8	2.4
2987	Chlorosilanes, n.o.s. (when spilled in water)	100	0.1	0.3	500	0.8	2.4
2988	Chlorosilanes, n.o.s. (when spilled in water)	100	0.1	0.3	500	0.8	2.4
2988	Chlorosilanes, water-reactive, flammable, corrosive, n.o.s. (when spilled in water)	100	0.1	0.3	500	0.8	2.4
3023	2-Methyl-2-hepthanethiol	100	0.1	0.1	200	0.3	0.5
3023	tert-Octyl mercaptan	100	0.1	0.1	200	0.3	0.5
3048	Aluminum phosphide pesticide (when spilled in water)	300	0.4	1.7	3,000	5.6	12.2
3049	Metal alkyl halides, n.o.s. (when spilled in water)	100	0.1	0.1	100	0.2	0.8
3049	Metal alkyl halides, water-reactive, n.o.s. (when spilled in water)	100	0.1	0.1	100	0.2	0.8
3049	Metal aryl halides, n.o.s. (when spilled in water)	100	0.1	0.1	100	0.2	0.8
3049	Metal aryl halides, water-reactive, n.o.s. (when spilled in water)	100	0.1	0.1	100	0.2	0.8
3052	Aluminum alkyl halides (when spilled in water)	100	0.1	0.1	100	0.2	0.8
3052	Aluminum alkyl halides, liquid (when spilled in water)	100	0.1	0.1	100	0.2	0.8
3052	Aluminum alkyl halides, solid (when spilled in water)	100	0.1	0.1	100	0.2	0.8
3057	Trifluoroacetyl chloride	100	0.2	0.8	3,000	4.9	11.5
3079	Methacrylonitrile, inhibited	100	0.1	0.2	300	0.5	1.0
3079	Methacrylonitrile, stabilized	100	0.1	0.2	300	0.5	1.0
3083	Perchloryl fluoride	100	0.1	0.4	1,200	2.2	5.5
3122	Poisonous liquid, oxidizing, n.o.s.	500	0.8	2.2	3,000	9.9	12.4
3122	Poisonous liquids, oxidizing, n.o.s. (Inhalation Hazard Zone A)	500	0.8	2.2	3,000	9.9	12.4
3122	Poisonous liquids, oxidizing, n.o.s. (Inhalation Hazard Zone B)	100	0.2	0.9	900	1.7	4.3
3122	Toxic liquid, oxidizing, n.o.s.	500	0.8	2.2	3,000	9.9	12.4
3122	Toxic liquid, oxidizing, n.o.s. (Inhalation Hazard Zone A)	500	0.8	2.2	3,000	9.9	12.4
3122	Toxic liquid, oxidizing, n.o.s. (Inhalation Hazard Zone B)	100	0.2	0.9	900	1.7	4.3
3123	Poisonous liquid, water-reactive, n.o.s.	500	0.8	2.2	3,000	9.9	12.4

TABLE A.1 (Cont.)

UN ID No.	Name of Material	Small Spills			Large Spills		
		First Isolate in All Directions (ft)	Then Protect Persons Downwind during Day (mi)	Then Protect Persons Downwind during Night (mi)	First Isolate in All Directions (ft)	Then Protect Persons Downwind during Day (mi)	Then Protect Persons Downwind during Night (mi)
3123	Poisonous liquid, water-reactive, n.o.s. (Inhalation Hazard Zone A)	500	0.8	2.2	3,000	9.9	12.4
3123	Poisonous liquid, water-reactive, n.o.s. (Inhalation Hazard Zone B)	200	0.3	1.1	1,100	2.1	4.6
3123	Poisonous liquid, which in contact with water emits flammable gases, n.o.s.	500	0.8	2.2	3,000	9.9	12.4
3123	Poisonous liquid, which in contact with water emit flammable gases, n.o.s. (Inhalation Hazard Zone A)	500	0.8	2.2	3,000	9.9	12.4
3123	Poisonous liquid, which in contact with water emit flammable gases, n.o.s. (Inhalation Hazard Zone B)	200	0.3	1.1	1,100	2.1	4.6
3123	Toxic liquid, water-reactive, n.o.s.	500	0.8	2.2	3,000	9.9	12.4
3123	Toxic liquid, water-reactive, n.o.s. (Inhalation Hazard Zone A)	500	0.8	2.2	3,000	9.9	12.4
3123	Toxic liquid, water-reactive, n.o.s. (Inhalation Hazard Zone B)	200	0.3	1.1	1,100	2.1	4.6
3123	Toxic liquid, which in contact with water emits flammable gases, n.o.s.	500	0.8	2.2	3,000	9.9	12.4
3123	Toxic liquids, which in contact with water emit flammable gases, n.o.s. (Inhalation Hazard Zone A)	500	0.8	2.2	3,000	9.9	12.4
3123	Toxic liquids, which in contact with water emit flammable gases, n.o.s. (Inhalation Hazard Zone B)	200	0.3	1.1	1,100	2.1	4.6
3160	Liquefied gas, poisonous, flammable, n.o.s.	400	0.8	3.2	3,000	5.4	9.6
3160	Liquefied gas, poisonous, flammable, n.o.s. (Inhalation Hazard Zone A)	400	0.8	3.2	3,000	5.4	9.6
3160	Liquefied gas, poisonous, flammable, n.o.s. (Inhalation Hazard Zone B)	100	0.2	0.8	1,400	2.5	6.7
3160	Liquefied gas, poisonous, flammable, n.o.s. (Inhalation Hazard Zone C)	100	0.1	0.5	800	1.5	4.0
3160	Liquefied gas, poisonous, flammable, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.1	300	0.5	1.5
3160	Liquefied gas, toxic, flammable, n.o.s.	400	0.8	3.2	3,000	5.4	9.6
3160	Liquefied gas, toxic, flammable, n.o.s. (Inhalation Hazard Zone A)	400	0.8	3.2	3,000	5.4	9.6
3160	Liquefied gas, toxic, flammable, n.o.s. (Inhalation Hazard Zone B)	100	0.2	0.8	1,400	2.5	6.7
3160	Liquefied gas, toxic, flammable, n.o.s. (Inhalation Hazard Zone C)	100	0.1	0.5	800	1.5	4.0
3160	Liquefied gas, toxic, flammable, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.1	300	0.5	1.5
3162	Liquefied gas, poisonous, n.o.s.	2,000	3.7	7.9	3,000	16.9	18.2
3162	Liquefied gas, poisonous, n.o.s. (Inhalation Hazard Zone A)	2,000	3.7	7.9	3,000	16.9	18.2
3162	Liquefied gas, poisonous, n.o.s. (Inhalation Hazard Zone B)	200	0.3	1.3	3,000	4.9	11.5
3162	Liquefied gas, poisonous, n.o.s. (Inhalation Hazard Zone C)	100	0.2	0.8	800	1.5	4.0

TABLE A.1 (Cont.)

UN ID 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)
3162	Liquefied gas, poisonous, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.4	400	0.8	2.4
3162	Liquefied gas, toxic, n.o.s.	2,000	3.7	7.9	3,000	16.9	18.2
3162	Liquefied gas, toxic, n.o.s. (Inhalation Hazard Zone A)	2,000	3.7	7.9	3,000	16.9	18.2
3162	Liquefied gas, toxic, n.o.s. (Inhalation Hazard Zone B)	200	0.3	1.3	3,000	4.9	11.5
3162	Liquefied gas, toxic, n.o.s. (Inhalation Hazard Zone C)	100	0.2	0.8	800	1.5	4.0
3162	Liquefied gas, toxic, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.4	400	0.8	2.4
3246	Methanesulfonyl chloride	200	0.2	0.4	500	1.0	1.6
3246	Methanesulphonyl chloride	200	0.2	0.4	500	1.0	1.6
3275	Nitriles, poisonous, flammable, n.o.s.	100	0.1	0.2	300	0.5	1.0
3275	Nitriles, toxic, flammable, n.o.s.	100	0.1	0.2	300	0.5	1.0
3276	Nitriles, poisonous, liquid n.o.s.	100	0.1	0.2	300	0.5	1.0
3276	Nitriles, poisonous, n.o.s.	100	0.1	0.2	300	0.5	1.0
3276	Nitriles, toxic, liquid, n.o.s.	100	0.1	0.2	300	0.5	1.0
3276	Nitriles, toxic, n.o.s.	100	0.1	0.2	300	0.5	1.0
3278	Organophosphorus compound, poisonous, liquid, n.o.s.	200	0.3	0.8	1,000	1.9	3.7
3278	Organophosphorus compound, poisonous, n.o.s.	200	0.3	0.8	1,000	1.9	3.7
3278	Organophosphorus compound, toxic, liquid, n.o.s.	200	0.3	0.8	1,000	1.9	3.7
3278	Organophosphorus compound, toxic, n.o.s.	200	0.3	0.8	1,000	1.9	3.7
3279	Organophosphorus compound, poisonous, flammable, n.o.s.	200	0.3	0.8	1,000	1.9	3.7
3279	Organophosphorus compound, toxic, flammable, n.o.s.	200	0.3	0.8	1,000	1.9	3.7
3280	Organoarsenic compound, liquid, n.o.s.	100	0.1	0.4	700	1.3	3.2
3280	Organoarsenic compound, n.o.s.	100	0.1	0.4	700	1.3	3.2
3281	Metal carbonyls, liquid, n.o.s.	300	0.5	2.2	1,600	2.9	6.1
3281	Metal carbonyls, n.o.s.	300	0.5	2.2	1,600	2.9	6.1
3287	Poisonous liquid, inorganic, n.o.s.	300	0.6	2.2	1,800	3.3	6.9
3287	Poisonous liquid, inorganic, n.o.s. (Inhalation Hazard Zone A)	300	0.6	2.2	1,800	3.3	6.9
3287	Poisonous liquid, inorganic, n.o.s. (Inhalation Hazard Zone B)	200	0.3	1.1	1,100	2.1	4.6
3287	Toxic liquid, inorganic, n.o.s.	300	0.6	2.2	1,800	3.3	6.9
3287	Toxic liquid, inorganic, n.o.s. (Inhalation Hazard Zone A)	300	0.6	2.2	1,800	3.3	6.9
3287	Toxic liquid, inorganic, n.o.s. (Inhalation Hazard Zone B)	200	0.3	1.1	1,100	2.1	4.6
3289	Poisonous liquid, corrosive, inorganic, n.o.s.	300	0.6	2.2	1,800	3.3	6.9
3289	Poisonous liquid, corrosive, inorganic, n.o.s. (Inhalation Hazard Zone A)	300	0.6	2.2	1,800	3.3	6.9
3289	Poisonous liquid, corrosive, inorganic, n.o.s. (Inhalation Hazard Zone B)	200	0.3	1.1	1,100	2.1	4.6
3289	Toxic liquid, corrosive, inorganic, n.o.s.	300	0.6	2.2	1,800	3.3	6.9
3289	Toxic liquid, corrosive, inorganic, n.o.s. (Inhalation Hazard Zone A)	300	0.6	2.2	1,800	3.3	6.9

TABLE A.1 (Cont.)

UN ID 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)
3289	Toxic liquid, corrosive, inorganic, n.o.s. (Inhalation Hazard Zone B)	200	0.3	1.1	1,100	2.1	4.6
3294	Hydrogen cyanide, solution in alcohol, with not more than 45% Hydrogen cyanide	100	0.1	0.2	700	0.4	1.3
3300	Carbon dioxide and Ethylene oxide mixture, with more than 87% Ethylene oxide	100	0.1	0.1	300	0.5	1.5
3300	Ethylene oxide and Carbon dioxide mixture, with more than 87% Ethylene oxide	100	0.1	0.1	300	0.5	1.5
3303	Compressed gas, poisonous, oxidizing, n.o.s.	2,000	3.7	7.9	3,000	16.9	18.2
3303	Compressed gas, poisonous, oxidizing, n.o.s. (Inhalation Hazard Zone A)	2,000	3.7	7.9	3,000	16.9	18.2
3303	Compressed gas, poisonous, oxidizing, n.o.s. (Inhalation Hazard Zone B)	200	0.3	1.3	1,200	2.2	5.5
3303	Compressed gas, poisonous, oxidizing, n.o.s. (Inhalation Hazard Zone C)	100	0.2	0.8	800	1.5	4.0
3303	Compressed gas, poisonous, oxidizing, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.4	400	0.8	2.4
3303	Compressed gas, toxic, oxidizing, n.o.s.	2,000	3.7	7.9	3,000	16.9	18.2
3303	Compressed gas, toxic, oxidizing, n.o.s. (Inhalation Hazard Zone A)	2,000	3.7	7.9	3,000	16.9	18.2
3303	Compressed gas, toxic, oxidizing, n.o.s. (Inhalation Hazard Zone B)	200	0.3	1.3	1,200	2.2	5.5
3303	Compressed gas, toxic, oxidizing, n.o.s. (Inhalation Hazard Zone C)	100	0.2	0.8	800	1.5	4.0
3303	Compressed gas, toxic, oxidizing, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.4	400	0.8	2.4
3304	Compressed gas, poisonous, corrosive, n.o.s.	2,000	3.7	7.9	3,000	16.9	18.2
3304	Compressed gas, poisonous, corrosive, n.o.s. (Inhalation Hazard Zone A)	2,000	3.7	7.9	3,000	16.9	18.2
3304	Compressed gas, poisonous, corrosive, n.o.s. (Inhalation Hazard Zone B)	200	0.3	1.3	2,500	4.5	10.1
3304	Compressed gas, poisonous, corrosive, n.o.s. (Inhalation Hazard Zone C)	100	0.2	0.8	800	1.5	4.0
3304	Compressed gas, poisonous, corrosive, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.4	200	0.4	1.4
3304	Compressed gas, toxic, corrosive, n.o.s.	2,000	3.7	7.9	3,000	16.9	18.2
3304	Compressed gas, toxic, corrosive, n.o.s. (Inhalation Hazard Zone A)	2,000	3.7	7.9	3,000	16.9	18.2
3304	Compressed gas, toxic, corrosive, n.o.s. (Inhalation Hazard Zone B)	200	0.3	1.3	2,500	4.5	10.1
3304	Compressed gas, toxic, corrosive, n.o.s. (Inhalation Hazard Zone C)	100	0.2	0.8	800	1.5	4.0
3304	Compressed gas, toxic, corrosive, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.4	200	0.4	1.4

TABLE A.1 (Cont.)

UN ID No.	Name of Material	Small Spills			Large Spills		
		First Isolate in All Direc-tions (ft)	Then Protect Persons Downwind during		First Isolate in All Direc-tions (ft)	Then Protect Persons Downwind during	
			Day (mi)	Night (mi)		Day (mi)	Night (mi)
3305	Compressed gas, poisonous, flammable, corrosive, n.o.s.	2,000	3.7	7.9	3,000	16.9	18.2
3305	Compressed gas, poisonous, flammable, corrosive, n.o.s. (Inhalation Hazard Zone A)	2,000	3.7	7.9	3,000	16.9	18.2
3305	Compressed gas, poisonous, flammable, corrosive, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.6	1,400	2.5	6.7
3305	Compressed gas, poisonous, flammable, corrosive, n.o.s. (Inhalation Hazard Zone C)	100	0.1	0.5	800	1.5	4.0
3305	Compressed gas, poisonous, flammable, corrosive, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.1	300	0.5	1.5
3305	Compressed gas, toxic, flammable, corrosive, n.o.s.	2,000	3.7	7.9	3,000	16.9	18.2
3305	Compressed gas, toxic, flammable, corrosive, n.o.s. (Inhalation Hazard Zone A)	2,000	3.7	7.9	3,000	16.9	18.2
3305	Compressed gas, toxic, flammable, corrosive, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.6	1,400	2.5	6.7
3305	Compressed gas, toxic, flammable, corrosive, n.o.s. (Inhalation Hazard Zone C)	100	0.1	0.5	800	1.5	4.0
3305	Compressed gas, toxic, flammable, corrosive, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.1	300	0.5	1.5
3306	Compressed gas, poisonous, oxidizing, corrosive, n.o.s.	2,000	3.7	7.9	3,000	16.9	18.2
3306	Compressed gas, poisonous, oxidizing, corrosive, n.o.s. (Inhalation Hazard Zone A)	2,000	3.7	7.9	3,000	16.9	18.2
3306	Compressed gas, poisonous, oxidizing, corrosive, n.o.s. (Inhalation Hazard Zone B)	200	0.3	1.3	1,200	2.2	5.5
3306	Compressed gas, poisonous, oxidizing, corrosive, n.o.s. (Inhalation Hazard Zone C)	100	0.2	0.8	800	1.5	4.0
3306	Compressed gas, poisonous, oxidizing, corrosive, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.4	200	0.4	1.4
3306	Compressed gas, toxic, oxidizing, corrosive, n.o.s.	2,000	3.7	7.9	3,000	16.9	18.2
3306	Compressed gas, toxic, oxidizing, corrosive, n.o.s. (Inhalation Hazard Zone A)	2,000	3.7	7.9	3,000	16.9	18.2
3306	Compressed gas, toxic, oxidizing, corrosive, n.o.s. (Inhalation Hazard Zone B)	200	0.3	1.3	1,200	2.2	5.5
3306	Compressed gas, toxic, oxidizing, corrosive, n.o.s. (Inhalation Hazard Zone C)	100	0.2	0.8	800	1.5	4.0
3306	Compressed gas, toxic, oxidizing, corrosive, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.4	200	0.4	1.4
3307	Liquefied gas, poisonous, oxidizing, n.o.s.	2,000	3.7	7.9	3,000	16.9	18.2
3307	Liquefied gas, poisonous, oxidizing, n.o.s. (Inhalation Hazard Zone A)	2,000	3.7	7.9	3,000	16.9	18.2
3307	Liquefied gas, poisonous, oxidizing, n.o.s. (Inhalation Hazard Zone B)	200	0.3	1.3	1,200	2.2	5.5
3307	Liquefied gas, poisonous, oxidizing, n.o.s. (Inhalation Hazard Zone C)	100	0.2	0.8	800	1.5	4.0

TABLE A.1 (Cont.)

UN ID 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)
3307	Liquefied gas, poisonous, oxidizing, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.4	400	0.8	2.4
3307	Liquefied gas, toxic, oxidizing, n.o.s.	2,000	3.7	7.9	3,000	16.9	18.2
3307	Liquefied gas, toxic, oxidizing, n.o.s. (Inhalation Hazard Zone A)	2,000	3.7	7.9	3,000	16.9	18.2
3307	Liquefied gas, toxic, oxidizing, n.o.s. (Inhalation Hazard Zone B)	200	0.3	1.3	1,200	2.2	5.5
3307	Liquefied gas, toxic, oxidizing, n.o.s. (Inhalation Hazard Zone C)	100	0.2	0.8	800	1.5	4.0
3307	Liquefied gas, toxic, oxidizing, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.4	400	0.8	2.4
3308	Liquefied gas, poisonous, corrosive, n.o.s.	2,000	3.7	7.9	3,000	16.9	18.2
3308	Liquefied gas, poisonous, corrosive, n.o.s. (Inhalation Hazard Zone A)	2,000	3.7	7.9	3,000	16.9	18.2
3308	Liquefied gas, poisonous, corrosive, n.o.s. (Inhalation Hazard Zone B)	200	0.3	1.3	2,500	4.5	10.1
3308	Liquefied gas, poisonous, corrosive, n.o.s. (Inhalation Hazard Zone C)	100	0.2	0.8	800	1.5	4.0
3308	Liquefied gas, poisonous, corrosive, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.4	200	0.4	1.4
3308	Liquefied gas, toxic, corrosive, n.o.s.	2,000	3.7	7.9	3,000	16.9	18.2
3308	Liquefied gas, toxic, corrosive, n.o.s. (Inhalation Hazard Zone A)	2,000	3.7	7.9	3,000	16.9	18.2
3308	Liquefied gas, toxic, corrosive, n.o.s. (Inhalation Hazard Zone B)	200	0.3	1.3	2,500	4.5	10.1
3308	Liquefied gas, toxic, corrosive, n.o.s. (Inhalation Hazard Zone C)	100	0.2	0.8	800	1.5	4.0
3308	Liquefied gas, toxic, corrosive, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.4	200	0.4	1.4
3309	Liquefied gas, poisonous, flammable, corrosive, n.o.s.	2,000	3.7	7.9	3,000	16.9	18.2
3309	Liquefied gas, poisonous, flammable, corrosive, n.o.s. (Inhalation Hazard Zone A)	2,000	3.7	7.9	3,000	16.9	18.2
3309	Liquefied gas, poisonous, flammable, corrosive, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.6	1,400	2.5	6.7
3309	Liquefied gas, poisonous, flammable, corrosive, n.o.s. (Inhalation Hazard Zone C)	100	0.1	0.5	800	1.5	4.0
3309	Liquefied gas, poisonous, flammable, corrosive, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.1	300	0.5	1.5
3309	Liquefied gas, toxic, flammable, corrosive, n.o.s.	2,000	3.7	7.9	3,000	16.9	18.2
3309	Liquefied gas, toxic, flammable, corrosive, n.o.s. (Inhalation Hazard Zone A)	2,000	3.7	7.9	3,000	16.9	18.2
3309	Liquefied gas, toxic, flammable, corrosive, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.6	1,400	2.5	6.7

TABLE A.1 (Cont.)

		Small Spills			Large Spills		
			Then Protect Persons Downwind during			Then Protect Persons Downwind during	
UN ID No.	Name of Material	First Isolate in All Directions (ft)	Day (mi)	Night (mi)	First Isolate in All Directions (ft)	Day (mi)	Night (mi)
3309	Liquefied gas, toxic, flammable, corrosive, n.o.s. (Inhalation Hazard Zone C)	100	0.1	0.5	800	1.5	4.0
3309	Liquefied gas, toxic, flammable, corrosive, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.1	300	0.5	1.5
3310	Liquefied gas, poisonous, oxidizing, corrosive, n.o.s.	2,000	3.7	7.9	3,000	16.9	18.2
3310	Liquefied gas, poisonous, oxidizing, corrosive, n.o.s. (Inhalation Hazard Zone A)	2,000	3.7	7.9	3,000	16.9	18.2
3310	Liquefied gas, poisonous, oxidizing, corrosive, n.o.s. (Inhalation Hazard Zone B)	200	0.3	1.3	1,200	2.2	5.5
3310	Liquefied gas, poisonous, oxidizing, corrosive, n.o.s. (Inhalation Hazard Zone C)	100	0.2	0.8	800	1.5	4.0
3310	Liquefied gas, poisonous, oxidizing, corrosive, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.4	200	0.4	1.4
3310	Liquefied gas, toxic, oxidizing, corrosive, n.o.s.	2,000	3.7	7.9	3,000	16.9	18.2
3310	Liquefied gas, toxic, oxidizing, corrosive, n.o.s. (Inhalation Hazard Zone A)	2,000	3.7	7.9	3,000	16.9	18.2
3310	Liquefied gas, toxic, oxidizing, corrosive, n.o.s. (Inhalation Hazard Zone B)	200	0.3	1.3	1,200	2.2	5.5
3310	Liquefied gas, toxic, oxidizing, corrosive, n.o.s. (Inhalation Hazard Zone C)	100	0.2	0.8	800	1.5	4.0
3310	Liquefied gas, toxic, oxidizing, corrosive, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.4	200	0.4	1.4
3318	Ammonia solution, with more than 50% ammonia	100	0.1	0.1	200	0.4	1.4
3355	Insecticide gas, poisonous, flammable, n.o.s	400	0.8	3.2	3,000	5.4	9.6
3355	Insecticide gas, poisonous, flammable, n.o.s. (Inhalation Hazard Zone A)	400	0.8	3.2	3,000	5.4	9.6
3355	Insecticide gas, poisonous, flammable, n.o.s. (Inhalation Hazard Zone B)	100	0.2	0.8	1,400	2.5	6.7
3355	Insecticide gas, poisonous, flammable, n.o.s. (Inhalation Hazard Zone C)	100	0.1	0.5	800	1.5	4.0
3355	Insecticide gas, poisonous, flammable, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.1	300	0.5	1.5
3355	Insecticide gas, toxic, flammable, n.o.s	400	0.8	3.2	3,000	5.4	9.6
3355	Insecticide gas, toxic, flammable, n.o.s. (Inhalation Hazard Zone A)	400	0.8	3.2	3,000	5.4	9.6
3355	Insecticide gas, toxic, flammable, n.o.s. (Inhalation Hazard Zone B)	100	0.2	0.8	1,400	2.5	6.7
3355	Insecticide gas, toxic, flammable, n.o.s. (Inhalation Hazard Zone C)	100	0.1	0.5	800	1.5	4.0
3355	Insecticide gas, toxic, flammable, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.1	300	0.5	1.5
3381	Poisonous by inhalation liquid, n.o.s. (Inhalation Hazard Zone A)	500	0.8	2.2	3,000	9.9	12.4

TABLE A.1 (Cont.)

UN ID No.	Name of Material	Small Spills: First Isolate in All Directions (ft)	Small Spills: Then Protect Persons Downwind during Day (mi)	Small Spills: Then Protect Persons Downwind during Night (mi)	Large Spills: First Isolate in All Directions (ft)	Large Spills: Then Protect Persons Downwind during Day (mi)	Large Spills: Then Protect Persons Downwind during Night (mi)
3381	Toxic by inhalation liquid, n.o.s. (Inhalation Hazard Zone A)	500	0.8	2.2	3,000	9.9	12.4
3382	Poisonous by inhalation liquid, n.o.s. (Inhalation Hazard Zone B)	200	0.3	1.1	1,100	2.1	4.6
3382	Toxic by inhalation liquid, n.o.s. (Inhalation Hazard Zone B)	200	0.3	1.1	1,100	2.1	4.6
3383	Poisonous by inhalation liquid, flammable, n.o.s. (Inhalation Hazard Zone A)	500	0.8	2.2	3,000	9.9	12.4
3383	Toxic by inhalation liquid, flammable, n.o.s. (Inhalation Hazard Zone A)	500	0.8	2.2	3,000	9.9	12.4
3384	Poisonous by inhalation liquid, flammable, n.o.s. (Inhalation Hazard Zone B)	200	0.2	0.6	900	1.6	3.5
3384	Toxic by inhalation liquid, flammable, n.o.s. (Inhalation Hazard Zone B)	200	0.2	0.6	900	1.6	3.5
3385	Poisonous by inhalation liquid, water-reactive, n.o.s. (Inhalation Hazard Zone A)	500	0.8	2.2	3,000	9.9	12.4
3385	Toxic by inhalation liquid, water-reactive, n.o.s. (Inhalation Hazard Zone A)	500	0.8	2.2	3,000	9.9	12.4
3386	Poisonous by inhalation liquid, water-reactive, n.o.s. (Inhalation Hazard Zone B)	200	0.3	1.1	1,100	2.1	4.6
3386	Toxic by inhalation liquid, water-reactive, n.o.s. (Inhalation Hazard Zone B)	200	0.3	1.1	1,100	2.1	4.6
3387	Poisonous by inhalation liquid, oxidizing, n.o.s. (Inhalation Hazard Zone A)	500	0.8	2.2	3,000	9.9	12.4
3387	Toxic by inhalation liquid, oxidizing, n.o.s. (Inhalation Hazard Zone A)	500	0.8	2.2	3,000	9.9	12.4
3388	Poisonous by inhalation liquid, oxidizing, n.o.s. (Inhalation Hazard Zone B)	100	0.2	0.9	900	1.7	4.3
3388	Toxic by inhalation liquid, oxidizing, n.o.s. (Inhalation Hazard Zone B)	100	0.2	0.9	900	1.7	4.3
3389	Poisonous by inhalation liquid, corrosive, n.o.s. (Inhalation Hazard Zone A)	300	0.5	1.5	2,500	3.9	7.5
3389	Toxic by inhalation liquid, corrosive, n.o.s. (Inhalation Hazard Zone A)	300	0.5	1.5	2,500	3.9	7.5
3390	Poisonous by inhalation liquid, corrosive, n.o.s. (Inhalation Hazard Zone B)	200	0.3	1.1	1,100	2.1	4.6
3390	Toxic by inhalation liquid, corrosive, n.o.s. (Inhalation Hazard Zone B)	200	0.3	1.1	1,100	2.1	4.6
3413	Potassium cyanide, solution (when spilled in water)	100	0.1	0.3	1,000	0.6	2.4
3414	Sodium cyanide, solution (when spilled in water)	200	0.1	0.4	1,300	0.8	3.0
3461	Aluminum alkyl halides, solid (when spilled in water)	100	0.1	0.1	100	0.2	0.8
9191	Chlorine dioxide, hydrate, frozen (when spilled in water)	100	0.1	0.1	100	0.1	0.4
9192	Fluorine, refrigerated liquid (cryogenic liquid)	100	0.1	0.3	300	0.5	2.2
9202	Carbon monoxide, refrigerated liquid (cryogenic liquid)	100	0.1	0.1	300	0.4	1.5
9206	Methyl phosphonic dichloride	100	0.1	0.1	100	0.1	0.1

TABLE A.1 (Cont.)

UN ID No.	Name of Material	Small Spills: First Isolate in All Directions (ft)	Small Spills: Then Protect Persons Downwind during Day (mi)	Small Spills: Then Protect Persons Downwind during Night (mi)	Large Spills: First Isolate in All Directions (ft)	Large Spills: Then Protect Persons Downwind during Day (mi)	Large Spills: Then Protect Persons Downwind during Night (mi)
9263	Chloropivaloyl chloride	100	0.1	0.1	100	0.2	0.3
9264	3,5-Dichloro-2,4,6-trifluoropyridine	100	0.1	0.1	100	0.2	0.3
9269	Trimethoxysilane	100	0.1	0.3	400	0.7	1.4

[a] The distances for MD (when used as a weapon) and methyldichloroarsine are transposed in the 2004 Emergency Response Guidebook. They are reported correctly in this document.

APPENDIX B:

CHEMICALS ANALYZED FOR THE ERG2004

APPENDIX B:

CHEMICALS ANALYZED FOR THE ERG2004

Table B.1 lists the chemicals analyzed for the *2004 Emergency Response Guidebook* (ERG2004), in alphabetical order by DOT name. Most of these materials are TIH materials; however, several are surrogates for generic table entries (e.g., 2-amino-2-methylpropanenitrile) or mildly toxic components of mixtures (e.g., benzene, methyl chloride, etc). For reference, the 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, and melting point and the temperature-dependent properties heat of vaporization, liquid density, specific heat of the liquid, viscosity, and surface tension.

TABLE B.1 Chemicals Analyzed for the ERG2004 (see table endnotes for explanation of abbreviations)

DOT Name	CAS #	Mol. Weight	Boiling Point (°C)	Vapor Pressure at 20°C (kPa)	LC$_{50}$ or LC$_{LO}$ (ppm)	1-hr Protective (ppm)	15-min Protective (ppm)	Basis
Acrolein	107-02-8	56.1	52.7	29.69	62	0.5	1	ERPG
Acrylonitrile	107-13-1	53	77.4	11.4	666	35	70	ERPG
Aldicarb	116-06-3	N/A	N/A	N/A	1	0.01	0.02	LC$_{50}$
Allyl alcohol	107-18-6	58.1	97.1	2.491	1,060	10	20	LC$_{50}$
Allyl chloroformate	2937-50-0	120.5	112.9	6.194	5	0.05	0.2	LC$_{50}$
Allyl isothiocyanate	57-06-7	99.2	150.7	0.5 16	28-S	1	2	ERPG-S
Allylamine	107-11-9	57.1	53.4	25.69	572	5	10	LC$_{50}$
2-Amino-2-methylpropanenitrile	19355-69-2	84.1	159.5	0.099	112	1	2	LC$_{50}$
Ammonia	7664-41-7	17	-33.5	854.5	7,338	150	300	ERPG
Arsenic trichloride	7784-34-1	181.2	130.1	1.113	56	0.5	1.0	LC$_{LO}$
Arsine	7784-42-1	77.9	-62.5	1475	30	0.5	0.6	ERPG
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	3.6	0.036	0.144	LC$_{50}$
Bis-(2-chloroethyl) methylamine	51-75-2	156.1	174.9	0.039	7.8	0.078	0.312	LC$_{50}$
Bis-(2-chloroethyl) sulfide	505-60-2	159.1	216.9	0.010	2.3	0.023	0.092	LC$_{50}$
Boron tribromide	10294-33-4	251.5	89.0	7.336	387-S	3	6	LC$_{50}$-S
Boron trichloride	10294-34-5	117.2	12.5	132.2	2541	25	50	LC$_{50}$
Boron trifluoride	7637-07-2	67.8	-99.8	4,264	387	3	6	ERPG
Bromine	7726-95-6	159.8	58.8	22.87	310	1	2	ERPG
Bromine chloride	13863-41-7	115.4	4.9	220.0	290	3	6	LC$_{50}$-S
Bromine pentafluoride	7789-30-2	174.9	40.9	42.88	299-S	1	2	ERPG-S
Bromine trifluoride	7787-71-5	136.9	125.9	0.774	299-S	1	2	ERPG-S
Bromoacetone	598-31-2	137	135.9	11.431	95	1	2	LC$_{LO}$
n-Butyl chloroformate	592-34-7	136.6	137.9	0.765	323-S	3	6	LC$_{50}$
sec-Butyl chloroformate	17462-58-7	136.6	127.9-E	1.051-E	323	3	6	LC$_{50}$-S
n-Butylisocyanate	111-36-4	99.1	115.0-S	1.755-S	28	0.05	0.1	ERPG
tert-Butyl-isocyanate	1609-86-5	99.1	86.0	4.888-E	22	0.05	0.1	ERPG-S
tert-Butylarsine	117791-53-4	134	44.4-E	40.35-E	140	1.5	3	LC$_{50}$
Carbon monoxide	630-08-0	28	-191.5	2792	4,590	350	700	ERPG
Carbon tetrachloride	56-23-5	153.8	76.7	12.138	19,000	100	200	ERPG
Carbonyl fluoride	353-50-4	66	-84.6	5211	360	3	6	LC$_{50}$
Carbonyl sulfide	463-58-1	60.1	-50.2	1124	924	10	20	LC$_{50}$
Chlorine	7782-50-5	70.9	-34.1	679.7	293	3	6	ERPG
Chlorine pentafluoride	13637-63-3	130.4	-13.9	332.1	122	1	2	ERPG-S
Chlorine trifluoride	7790-91-2	92.4	11.8	148.0	299	1	2	ERPG

TABLE B.1 (Cont.)

DOT Name	CAS #	Mol. Weight	Boiling Point (°C)	Vapor Pressure at 20°C (kPa)	LC_{50} or LC_{LO} (ppm)	1-hr Protective (ppm)	15-min Protective (ppm)	Basis
Chloroacetaldehyde	107-20-0	78.5	84.9	3.522	200	2	4	LC_{50}
Chloroacetone	78-95-5	92.5	120.1	1.567	262	2	4	LC_{50}
Chloroacetonitrile	107-14-2	75.5	126.0	1.087	500	5	10	LC_{50}
Chloroacetyl chloride	79-04-9	112.9	106.0	2.522	660	0.5	1	ERPG
Chloromethyl methyl ether	107-30-2	80.5	59.5	21.14	441	1	2	ERPG
p-Chlorophenyl isocyanate	104-12-1	153.6	199.0	0.069	18	0.3	0.6	ERPG
Chloropicrin	76-06-2	164.4	111.9	3.190	28	0.2	0.4	ERPG
Chloropivaloyl chloride	4300-97-4	155	147.9	0.189-E	126	1	2	LC_{50}
Chlorosulfonic acid	7790-94-5	116.5	153.9	0.309	929 mg/m^3	10 mg/m^3	20 mg/m^3	ERPG
Crotonaldehyde	4170-30-3	70.1	104.9	3.121	380	10	20	ERPG
Cyanogen	460-19-5	52	-21.2	489.7	350	3	6	LC_{50}
Cyanogen chloride	506-77-4	61.5	12.9	135.0	80	0.4	1.0	ERPG
Cyclohexyl isocyanate	3173-53-3	125.2	169.0	0.094	15	0.05	0.1	ERPG-S
Cyclohexyl methylphosphonofluoridate	329-99-7	180.2	238.9	0.006	0.08	0.0008	0.0032	LC_{50}
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	2	ERPG
Dichlorosilane	4109-96-0	101	8.4	154.2	215	2	4	LC_{50}
3,5-Dichloro-2,4,6-trifluoropyridine	1737-93-5	202	177.5-S	0.104-S	62	0.5	1	LC_{50}
Diketene	674-82-8	84.1	126.1	1.064	612	5	10	ERPG
1,1-Dimethyl hydrazine	57-14-7	60.1	63.4	16.38	1,410	15	30	LC_{50}
1,2-Dimethyl hydrazine	540-73-8	60.1	87.1	7.230	680	7	15	LC_{50}
Dimethyl sulfate	77-78-1	126.1	188.9	0.069	17	0.15	0.3	LC_{50}
Diphosgene	503-38-8	197.8	127.9	0.553	50-S	0.1	0.2	ERPG-S
Ethyl chloroformate	541-41-3	108.5	92.9	2.121	145	1	2	LC_{50}-S
Ethylchlorothioformate	2812-73-9	124.6	131.9	0.685-E	138-S	1	2	LC_{50}-S
Ethylchlorothiolformate	2941-64-2	124.6-S	131.9-S	0.685-S	138-S	1	2	LC_{50}-S
Ethyl dichloroarsine	598-14-1	174.9	155.9	0.281	36	0.3	0.6	LC_{50}
Ethyl N,N-dimethylphosphoramidocyanidate	77-81-6	162.3	239.9-E	0.005-E	0.18	0.0018	0.0072	LC_{50}
Ethyl isocyanate	109-90-0	71.1	61.6	24.50	28-S	0.5	1	ERPG-S
Ethyl phosphonothionic dichloride	993-43-1	162.9	176.9	0.026-E	62-S	0.5	1	LC_{50}
Ethyl phosphonous dichloride	1498-40-4	130.9	113.0-E	4.762-E	62	0.5	1	LC_{LO}
Ethyl phosphorodichloridate	1498-51-7	162.9	166.9	0.040-E	43	0.3	0.6	LC_{50}
Ethylacrolein	922-63-4	84.1	92.9	5.392-E	578	5	10	LC_{50}
Ethylene chlorohydrin	107-07-3	80.5	128.7	0.699	74	0.5	1	LC_{50}
Ethylene dibromide	106-93-4	187.9	131.4	1.357	691	5	10	LC_{50}

TABLE B.1 (Cont.)

DOT Name	CAS #	Mol. Weight	Boiling Point (°C)	Vapor Pressure at 20°C (kPa)	LC_{50} or LC_{LO} (ppm)	1-hr Protective (ppm)	15-min Protective (ppm)	Basis
Ethylene oxide	75-21-8	44.1	10.5	146.3	5,840	50	100	ERPG
Ethylenimine	151-56-4	43.1	55.9	22.18	250	2	4	LC_{50}
Fluorine	7782-41-4	38	-188.3	4160	185	5	15	ERPG
Germanium tetrachloride	10038-98-9	214.4	83.9	9.51	150	1	2	LC_{LO}
Germanium tetrahydride	7782-65-2	76.6	-88.2	3870	622	5	10	LC_{50}
Hexachlorocyclopentadiene	77-47-4	272.8	239.1	0.0052	3	0.03	0.06	LC_{50}
Hexaethyltetraphosphate	757-58-4	506.2	GS	GS	24-E	0.5	1	LC_{50}-E
Hexafluoroacetone	684-16-2	166	-27.3	584.19	476	1	2	ERPG
Hydrogen bromide	10035-10-6	80.9	-66.8	2182	2,860	20	40	ERPG-S
Hydrogen chloride	7647-01-0	36.5	-85.1	4206	3,124	20	40	ERPG
Hydrogen cyanide	74-90-8	27	25.8	81.63	71	10	20	ERPG
Hydrogen fluoride	7664-39-3	20	19.6	102.7	1,300	20	40	ERPG
Hydrogen iodide	10034-85-2	127.9	-35.6	691.0	2,860	20	40	ERPG-S
Hydrogen selenide	7783-07-5	81	-42.1	911.1	5	0.2	0.4	ERPG
Hydrogen sulfide	7783-06-4	34.1	-60.4	1781	712	30	60	ERPG
Iron pentacarbonyl	13463-40-6	195.9	102.8	3.142	57	0.5	1	LC_{50}
Isobutyl chloroformate	543-27-1	136.6	128.1	0.751	299	3	6	LC_{50}
Isobutyl isocyanate	1873-29-6	99.1	115.0	1.755	28-S	0.05	0.1	ERPG-S
Isopropyl chloroformate	108-23-6	122.6	104.9-S	4.698-S	299	3	6	LC_{50}
Isopropyl isocyanate	1795-48-8	85.1	82.9	7.372	28-S	0.05	0.1	ERPG-S
Isopropyl methylphosphonofluoridate	107-44-8	140.1	157.9	0.283	0.1	0.001	0.004	LC_{50}
Methacrylonitrile	126-98-7	67.1	90.4	7.541	656	5	10	LC_{50}
Methanesulfonyl monochloride	124-63-0	114.6	162.4	0.190	5-S	0.05	0.01	LC_{50}-S
Methoxymethyl isocyanate	6427-21-0	87.1	165.7-E	0.250-E	28-S	0.05	0.1	ERPG-S
Methyl bromide	74-83-9	94.9	3.6	184.3	1007	50	100	ERPG
Methyl chloride	74-87-3	50.5	-24.3	495.4	11,040	400	1,500	ERPG
Methyl chloroformate	79-22-1	94.5	70.9	11.20	88	1	2	LC_{50}
Methyl hydrazine	60-34-4	46.1	87.6	4.997	148	1	2	LC_{50}
Methyl iodide	74-88-4	141.9	42.5	44.33	1,600	50	100	ERPG
Methyl isocyanate	624-83-9	57.1	38.9	50.18	41	0.5	1	ERPG
Methyl isothiocyanate	556-61-6	73.1	118.9	3.205	635	5	10	LC_{50}
Methyl mercaptan	74-93-1	48.1	6.0	169.8	1,340	25	50	ERPG
Methyl phosphonic dichloride	676-97-1	132.9	162.9-E	0.040-E	52	0.5	1.0	LC_{50}
Methyl phosphonous dichloride	676-83-5	116.9	81.9-E	11.89-E	52-S	0.5	1.0	LC_{50}-S
Methyl silicate	681-84-5	152.2	120.9	1.613	300	3	6	LC_{LO}

TABLE B.1 (Cont.)

DOT Name	CAS #	Mol. Weight	Boiling Point (°C)	Vapor Pressure at 20°C (kPa)	LC_{50} or LC_{LO} (ppm)	1-hr Protective (ppm)	15-min Protective (ppm)	Basis
Methyl vinyl ketone	78-94-4	70.1	81.5	9.274	5	0.05	0.1	LC_{50}
Methylamine	74-89-5	31.1	-6.3	295.7	5,000	100	200	ERPG
Methylchlorosilane	993-00-0	80.6	8.8	149.6	1547-S	3	6	ERPG-S
Methyldichloroarsine	593-89-5	160.9	135.9	1.034	68	0.5	1	LC_{50}
Nickel carbonyl	13463-39-3	170.8	42.5	43.50	18	0.15	0.3	LC_{50}
Nitric acid	7697-37-2	63	83.0	6.401	67	6	12	ERPG
Nitric oxide	10102-43-9	30	-151.8	5093	1,708	15	30	LC_{50}
Nitrogen dioxide	10102-44-0	46	21.0	96.04	115	10	20	EEL
Nitrogen fluoride oxide	13847-65-9	87.1	-129.1-E	3979-E	48	0.5	1.0	LC_{50}
Nitrogen trioxide	10544-73-7	76	2.0	218.3	115-S	10	20	EEL
Nitrosyl chloride	2696-92-6	65.5	-5.3	270.4	293-S	3	6	ERPG-S
tert-octyl mercaptan	141-59-3	146.3	155.9	0.488	102	1	2	LC_{50}
O-Ethyl S-(2-diisopropylaminoethyl) methylphosphonothiolate	50782-69-9	267.4	297.9	.00005	0. 023	0.00023	0.0009	LC_{50}
Oxygen difluoride	7783-41-7	54	-145.0	2789	2.6	0.03	0.06	LC_{50}
Parathion	56-38-2	291.3	GS	GS	14	0.15	0.3	LC_{50}
Pentaborane	19624-22-7	63.2	58.4	22.70-E	10	0.1	0.2	LC_{50}
Perchloromethyl mercaptan	594-42-3	185.9	148.0	0.642	69	0.5	1.0	LC_{50}
Perchloryl fluoride	7616-94-6	102.4	-46.7	1060	770	5	10	LC_{50}
Phenyl isocyanate	103-71-9	119.1	165.7	0.250	16	0.05	0.1	ERPG-S
Phenyl mercaptan	108-98-5	110.2	169.2	0.142	66	0.5	1.0	LC_{50}
Phosgene	75-44-5	98.9	7.6	159.3	5	0.2	0.4	ERPG
Phosphine	7803-51-2	34	-87.8	3517	22	0.5	1	ERPG
Phosphorous oxychloride	10025-87-3	153.3	105.5	3.273	96	1	2	LC_{50}
Phosphorous pentafluoride	7647-19-0	126	-84.6	56888	260	2	4	LC_{50}-S
Phosphorous trichloride	7719-12-2	137.3	76.1	12.82	208	2	4	LC_{50}
Phosphorous trifluoride	7783-55-3	88	-101.3	6902	433	3	6	LC_{50}
Pinacolyl methylphosphonofluoridate	96-64-0	182.2	197.9	0.037	0.08	0.0008	0.0032	LC_{50}
n-Propyl chloroformate	109-61-5	122.6	104.9	4.698	319	3	2	LC_{50}
n-Propyl isocyanate	110-78-1	85.1	82.9	5.274	44	0.05	0.1	ERPG-S
Selenium hexafluoride	7783-79-1	193	-34.7	2854	50	0.5	1	LC_{50}
Silicon tetrafluoride	7783-61-1	104.1	-95.2	3205	922	10	20	LC_{50}
Stibine	7803-52-3	124.8	-18.5	286.1-E	20	0.5	1	ERPG
Sulfur chloride pentafluoride	13780-57-9	162.5	-21.2	442.0-S	100	1	2	LC_{LO}
Sulfur dioxide	7446-09-5	64.1	-10.1	336.5	2,520	3	6	ERPG
Sulfur monochloride	10025-67-9	135	137.9	0.944	150	1	2	LC_{50}

TABLE B.1 (Cont.)

DOT Name	CAS #	Mol. Weight	Boiling Point (°C)	Vapor Pressure at 20°C (kPa)	LC_{50} or LC_{LO} (ppm)	1-hr Protective (ppm)	15-min Protective (ppm)	Basis
Sulfur tetrafluoride	7783-60-0	108.1	-40.4	1785	40	0.4	0.8	LC_{50}
Sulfur trioxide	7446-11-9	80.1	44.8	25.73	106 mg/m^3	10 mg/m^3	20 mg/m^3	ERPG
Sulfuryl chloride	7791-25-5	135	69.4	14.811	3,020-S	30	60	LC_{50}-S
Sulfuryl fluoride	2699-79-8	102.1	-55.4	1964	3,020	30	60	LC_{50}
Tellurium hexafluoride	7783-80-4	241.6	-38.2	709.6	20	0.2	0.4	LC_{LO}
Tetraethyl dithiopyrophosphate	3689-24-5	322.3	GS	GS	1.5	0.015	0.02	LC_{50}
Tetraethyl pyrophosphate	107-49-3	290.1	GS	GS	1.5-S	0.015	0.02	LC_{50}-S
Tetrafluorohydrazine	10036-47-2	104	-74.3	2515	950	10	20	LC_{50}
Tetramethyl tin	594-27-4	178.8	77.9	17.92-E	58	0.6	1.2	LC_{LO}
Tetranitromethane	509-14-8	196	125.8	1.121	36	0.3	0.6	LC_{50}
Thionyl chloride	7719-09-7	119	75.7	12.77	500	2	4	ERPG
Thiophosgene	463-71-8	115	72.9	15.04	25-S	0.2	0.4	ERPG-S
Titanium tetrachloride	7550-45-0	189.7	135.9	1.253	1,300 mg/m^3	20 mg/m^3	40 mg/m^3	ERPG
Trichloroacetyl chloride	76-02-8	181.8	118.0	2.189	128	1	2	ERPG-S
Trifluoroacetyl chloride	354-32-5	132.5	-17.9	356.2-S	208	1	2	ERPG-S
Trifluorochloroethylene	79-38-9	116.5	-27.9	531.4	8,568	100	200	ERPG
Trimethoxy silane	2487-90-3	122.3	80.9	20.40-E	84	2	4	ERPG
Trimethylacetyl chloride	3282-30-2	120.6	106.9	2.866	250	5	10	LC_{50}
Tris-(2-chloroethyl) amine	817-09-4	204.5	255.9	0.00094	3	0.03	0.12	LC_{50}
Tungsten hexafluoride	7783-82-6	297.8	17.4	111.8	207	2	4	LC_{50}

Abbreviations

ERPG	Emergency Response Planning Guideline, established by the AIHA
EEL	Emergency Exposure Level, published in the *AIHA Journal*
LC_{50}	Median lethal concentration; lethal to 50% of a population exposed via inhalation
LC_{LO}	Lowest lethal concentration reported in an animal study
LC_{50}-E	LC_{50} estimated from oral toxicity data
E	Estimated value
GS	Solid or liquid in solution with gas
S	Data are for a structurally similar chemical

APPENDIX C:

EXPERIMENTAL PROGRAM CONDUCTED TO SUPPORT THE WATER REACTIVITY ANALYSIS

APPENDIX C:

EXPERIMENTAL PROGRAM CONDUCTED TO SUPPORT THE WATER REACTIVITY ANALYSIS

Few data exist in the chemical literature on the rate of evolution of TIH gases from the reactions between water and different substances. In 1999, we began a program of gas-evolution experiments to create a basis for estimates of how fast different water-reactive substances emit TIH gases when they are spilled into water. Two series of experiments have been performed. The 1999 series covered 21 substances in support of the ERG2000. Some of these experiments were intended to rule out certain substances as TIHWR substances. The 2003 series covered 35 additional substances in support of the ERG2004 and repeated and extended the observations on 10 substances from the first group.

C.1 GENERAL DESCRIPTION

C.1.1 Apparatus and Experimental Method

A small amount of a substance was mixed with water in a closed system. If a reaction occurred and generated a gas, the system expanded. Changes in the volume of the system were noted as functions of time. From these data, the mass of the gas that the reaction generated and the percentage yield of the gas could be calculated as functions of time. The first of these results required only the chemical formula of the gas; the second required a balanced chemical equation representing the gas-generating reaction.

Figure C.1 provides a diagram of the experimental apparatus. The system was first purged with dry nitrogen. Reactions were performed using 1.00-mmol (millimole) or 2.00-mmol samples of the water-reactive substances as received from vendors. Liquid chemicals of known density were measured out by volume. Different orders of mixing and amounts of waters were used (see method A and method B below), but the sample/water mixtures were in every case stirred continuously at a constant rate (using a magnetic stirrer). The evolution of gases in the closed apparatus displaced a manometric liquid (octane in Figure C.1) upward into the burette, and the increase in volume was noted at appropriate intervals of time. The burette was canted upward from the horizontal at an angle of about 15 degrees. This arrangement allowed the volume of the system to increase substantially while limiting the increase in the interior pressure to a negligible amount (less than 10–15 cm of manometric liquid, or about 0.015 atm). Care was taken to use a manometric liquid that did not react with the TIH gas. When gaseous HCl was evolved, for example, the manometric liquid was octane saturated with HCl. This precaution prevented loss of a TIH gas by dissolution in the manometric liquid or reaction with it. The experiments were carried out at room temperature (24°C). Although the reactions were all exothermic, the small volume of the reaction mixture favored fast cooling; the temperature of the system generally remained close to room temperature.

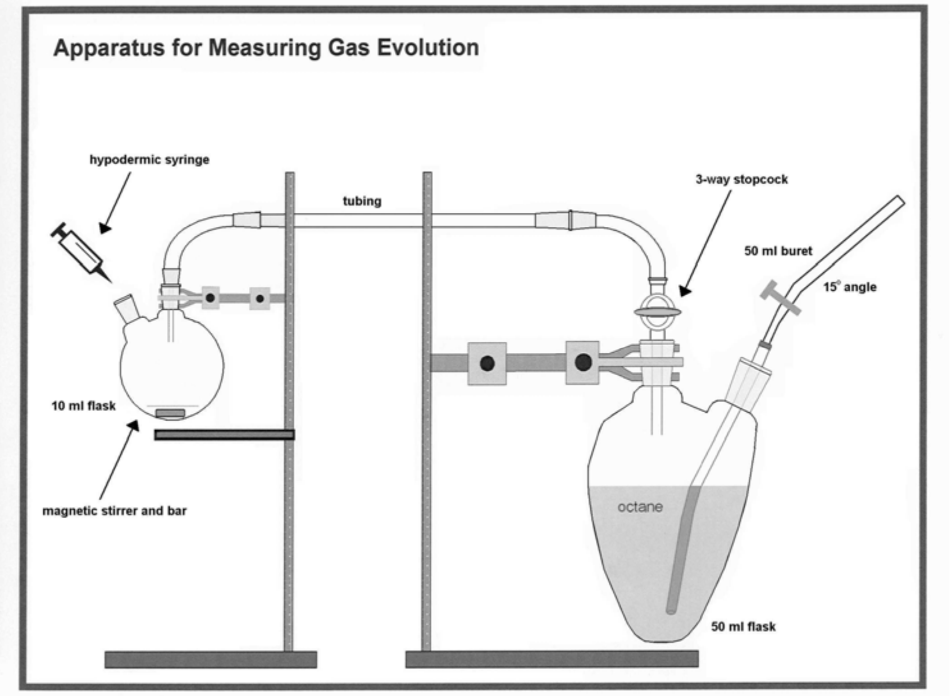

FIGURE C.1 Apparatus Used to Measure the Amounts and Rates of Evolution of Gases When Substances React with Water

The gas-evolution apparatus was calibrated by reacting 0.149 g (2.00 mmol) of potassium chloride (KCl) with excess 98% sulfuric acid (H_2SO_4).

$$2\ KCl(s) + H_2SO_4(aq) \longrightarrow 2\ HCl(g) + K_2SO_4(aq)$$

The final volume of HCl(g) (gaseous hydrogen chloride) generated in the apparatus equaled 32.0 mL at 24°C and 1.0 atm. This volume was taken as equivalent to 2.00 mmol of gas, which is the theoretical yield of HCl(g) according to the above equation.

The masses of the gases that were produced in the apparatus at various times after the first mixing of the reactants were calculated using this equivalence and the molar masses of the gases. The calculations thus assumed that during the course of the experiments the gases were confined under the same temperature and pressure as HCl(g) was confined at the end of the calibration run. The calculations also assumed that all gases (actually, gas mixtures) in the apparatus behaved ideally.

The experiments were carried out in two different ways:

- Method A: After the nitrogen purge, 1.00 mmol (typically) of substance was injected into the reaction flask through a side-arm covered with a rubber cap. The stirrer was started, and a chemically equivalent amount of water, as determined from the chemical equation written to represent the anticipated reaction, was rapidly injected. The clock was started when the water was first added. For example, 1.00 mmol (0.170 g) of tetrachlorosilane ($SiCl_4$) was charged into the flask, and 0.036 g (2.00 mmol) of H_2O was added. This 1:2 molar ratio ensured that both reactants would be consumed entirely if the reaction

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

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

- Method B: The substance 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.

C.1.2 Notes on Hydrogen Chloride

Hydrogen chloride (HCl) is a TIH gas that is evolved from reactions between water and a number of commercially important substances. Some of its physical properties and its interactions with water accordingly merit discussion.

Hydrogen chloride has a normal boiling point of –85.05°C and is therefore gaseous under ambient conditions of temperature and pressure. It dissolves readily in water to give HCl(aq), or aqueous hydrogen chloride, more commonly called hydrochloric acid. The solubility of HCl in water is large but not unlimited. It depends upon the temperature and also upon on the partial pressure of gaseous HCl (symbolized P_{HCl}) above the solution as described by Henry's law

$$X_{HCl} = K_H\, P_{HCl} \tag{C.1}$$

where K_H is a temperature-dependent constant (the Henry's law constant) and X_{HCl} is the mole fraction of HCl in the solution

$$X_{HCl} = \frac{n_{HCl}}{n_{HCl} + n_{H_2O}}\ . \tag{C.2}$$

The Henry's law constant for HCl in H_2O at 25°C is 0.258 atm^{-1}. This constant changes with temperature: from 0.289 at 0°C to 0.217 at 60°C, for example. The decrease in K_H with increasing temperature means that HCl is *less* soluble in hot H_2O than in cold. This solubility behavior is typical of gases.

It can be shown that the mass fraction (symbolized w_{HCl}) of HCl in saturated binary HCl/H_2O mixtures is related to the mole fraction X_{HCl} as follows

$$\frac{1}{w_{\mathrm{HCl}}} = \left(1 - \frac{18.02}{36.46}\right) + \left(\frac{18.02}{36.46}\right) \bullet \frac{1}{X_{\mathrm{HCl}}} , \tag{C.3}$$

where 36.46 and 18.02 are the relative molar masses of HCl and H_2O, respectively. If H_2O is saturated with HCl at a partial pressure of 1 atm at 25°C, then

$$X_{\mathrm{HCl}} = (0.258\ \mathrm{atm}^{-1})(1\ \mathrm{atm}) = 0.258 \text{ and}$$
$$w_{\mathrm{HCl}} = 0.413.$$

At 24°C, the temperature at which the experiments described in this report were performed, the result is essentially the same.

The concentrated hydrochloric acid of commerce contains somewhat less than 41% HCl by mass. It has a nominal composition of 37.5% HCl and varies between about 36.5 and 38%. Closed bottles of concentrated HCl(aq) emit fumes of HCl(g) when they are opened to the air because the partial pressure of HCl(g) in the atmosphere is 0. A 41% aqueous solution of HCl fumes heavily when opened to the air. The fumes appear white in moist air because the escaping HCl(g) interacts with the water vapor to give HCl(aq) droplets of colloidal size. Fumes of HCl(g) are colorless in dry air.

Water and HCl form a non-ideal solution. The attractions between HCl and H_2O molecules in the mixture are stronger than either the HCl-to-HCl or H_2O-to-H_2O attractions. One consequence is the existence of a high-boiling-point azeotrope. (An azeotrope is a liquid solution for which the equilibrium composition of vapors confined above the solution is the same as the composition of the solution itself.) Experiments show that the composition of the HCl/H_2O binary azeotrope is $w_{\mathrm{HCl}} = 0.2022$ (corresponding to $X_{\mathrm{HCl}} = 0.1113$). Evaporative loss from an azeotrope does not change the composition of the remaining solution. When HCl/H_2O solutions in which w_{HCl} exceeds 0.2022 evaporate at 25°C, they lose HCl(g), the more volatile component, preferentially until w_{HCl} falls to 0.2022. Then, w_{HCl} stays at 0.2022 until the whole of the solution has evaporated. When HCl/H_2O solutions in which w_{HCl} is less than 0.2022 evaporate, they lose H_2O preferentially, despite the fact that H_2O is less volatile than HCl at all temperatures, until w_{HCl} *rises* to 0.2022.

In Method B in our experiments on HCl-generating chlorosilanes, the equilibrium composition of the aqueous phase should lie between $w_{\mathrm{HCl}} = 0.20$ and $w_{\mathrm{HCl}} = 0.41$ *if* the additional components in the system can be neglected. These components are the nitrogen in the gaseous phase above the solution and the by-products of the HCl-producing reaction. The latter are often, but not always, insoluble polymeric materials. Dissolution of these materials in the aqueous phase would in principle influence the amount of HCl that is co-dissolved.

C.2 EXPERIMENTAL RESULTS

The following tables give the observed changes in the volume of the experimental system as functions of the time after different water-reactive substances were mixed with water. The tables also include the yields of the TIH gases as functions of time, both in terms of their mass and as percentages of the theoretical yield. The computations of this last quantity required a balanced chemical equation, which is given. Notes on variations in procedures and particular observations and some brief discussion are also given.

For ease of reference, the chemicals are presented in order of UN identification number and correspond to those chemicals listed in Table D.1 for which experiments were conducted.

UN 1162 — Dimethydichlorosilane, $(CH_3)_2SiCl_2$

Dimethydichlorosilane is a liquid with a relative molar mass of 129.06 and a room-temperature density of 1.064 g/cm^3. In method A, 1.00 mmol of it was mixed with 1.00 mmol of water. In method B, 1.00 mmol of it was mixed with 5.00 mmol of water. Reaction according to the equation

$$(CH_3)_2SiCl_2 + H_2O \longrightarrow 2\ HCl + [(CH_3)_2SiO]_n \text{ polymer}$$

was taken as the source of HCl(g). The theoretical yield of HCl(g) was 2.00 mmol, which corresponded to 32.0 mL of gas in the calibrated experimental apparatus.

1999 Experimental Results for Dimethydichlorosilane

Method A				Method B			
Time (min)	Volume of Gas (mL)	Mass of HCl (g)	Yield (%)	Time (min)	Volume of Gas (mL)	Mass of HCl (g)	Yield (%)
0	0	0	0	0	0	0	0
1	5	0.0113	16	1	8	0.0182	25
5	19	0.043	59	5	12	0.027	37
10	30	0.068	94	10	13	0.030	40
20	32	0.073	100	20	13	0.030	40

2003 Experimental Results for Dimethydichlorosilane

Method A				Method B			
Time (min)	Volume of Gas (mL)	Mass of HCl (g)	Yield (%)	Time (min)	Volume of Gas (mL)	Mass of HCl (g)	Yield (%)
0	0	0	0	0	0	0	0
-	-	-	-	0.5	5.9	0.0134	18.4
1	5.0	0.0114	15.6	1	7.8	0.0178	24.4
2	9.2	0.0210	28.8	2	9.6	0.0219	30.0
3	12.9	0.0294	40.3	3	10.6	0.024	33.1
4	16.3	0.037	50.9	4	11.3	0.026	35.3
5	19.4	0.044	60.6	5	11.8	0.027	36.9
7	24.2	0.055	75.6	7	12.5	0.028	39.1
10	29.7	0.068	92.8	10	12.8	0.029	40.0
20	31.6	0.072	98.8	20	13.2	0.030	41.3
30	32.0	0.073	100.0	30	13.3	0.030	41.6

Comments: The experiments were repeated in 2003 to obtain more data on the early course of the reaction. In method A, the full theoretical amount of HCl(g) formed in 30 min; in method B, a solid by-product formed immediately upon mixing the reactants. This by-product might have sequestered some of the test substance, some of the water, or both. If, however, we suppose that the reaction was complete after 30 min in method B, then (1 – 0.416) × 2.00 mmol of HCl was dissolved in 4.00 mmol of excess water. Such a solution has a mole fraction of HCl (X_{HCl}) of 1.17 ÷ (1.17 + 4.00), or 0.226. This is fairly close to but still somewhat less than the concentration of HCl in saturated HCl/H_2O solutions at 24°C (see Section C.1.2).

UN 1196 —Ethyltrichlorosilane,$CH_3CH_2SiCl_3$

Ethyltrichlorosilane is a liquid with a relative molar mass of 163.51 and a room-temperature density of 1.238 g/cm^3. In method A, 1.00 mmol of it was mixed with 1.50 mmol of water. In method B, 1.00 mmol of it was mixed with 7.50 mmol of water. The equation

$$CH_3CH_2SiCl_3 + 3/2\ H_2O \longrightarrow 3\ HCl + [CH_3CH_2SiO_{3/2}]_n \text{ polymer}$$

was taken to represent the evolution of gas. The theoretical yield of HCl(g) (3.00 mmol) corresponded to 48.0 mL of gas in the calibrated experimental apparatus.

2003 Experimental Results for Ethyltrichlorosilane

Method A				Method B			
Time (min)	Volume of Gas (mL)	Mass of HCl (g)	Yield (%)	Time (min)	Volume of Gas (mL)	Mass of HCl (g)	Yield (%)
1	5.1	0.012	10.6	1	12.5	0.028	26.0
2	11.2	0.026	23.3	2	21.2	0.048	44.2
3	19.	0.044	40.2	3	28.1	0.064	58.5
4	27.5	0.063	57.3	4	32.1	0.073	66.9
5	33.6	0.077	70.0	5	31.5	0.072	65.6
6	40.5	0.106	84.0	6	28.6	0.065	59.6
11	48.0	0.109	100	11	26.7	0.061	55.6
15	48.0	0.109	100	15	24.0	0.055	50.0
				20	22.3	0.151	46.5
				30	18.5	0.042	38.5
				120	18.1	0.041	37.7

Comments: In method A, the theoretical amount of HCl(g) was evolved while a white solid by-product (a polysiloxane) formed. In method B, HCl(g) was evolved as a similar white solid formed. The amount of HCl(g) in method B went to a maximum and then diminished. This was caused by the dissolution of some of the HCl(g) in the excess water. The by-product might have sequestered some of the test substance, some of the water, or both. If, however, we suppose that the HCl-generating reaction was complete after 120 min in method B, then (1 – 0.377) × 3.00 mmol of HCl was dissolved in 6.00 mmol of excess water. Such a solution has a mole fraction of HCl (X_{HCl}) of 1.87 ÷ (1.87 + 6.00), or 0.237. This is fairly close to but still somewhat less than the concentration of HCl in saturated HCl/H_2O solutions at 24°C (see Section C.1.2).

UN 1242 — Methyldichlorosilane, $(CH_3)SiHCl_2$

Methyldichlorosilane is a liquid with relative molar mass of 115.04 and a room-temperature density of 1.105 g/cm^3. In method A, 1.00 mmol of it was mixed with 1.00 mmol of water. In method B, 1.00 mmol of it was mixed with 5.00 mmol of water. Reaction according to the equation

$$(CH_3)HSiCl_2 + H_2O \longrightarrow 2\,HCl + [(CH_3)HSiO]_n \text{ polymer}$$

was taken as the source of HCl(g). The theoretical yield of HCl(g) was 2.00 mmol, which corresponded to 32.0 mL of gas in the calibrated experimental apparatus.

2003 Experimental Data for Methyldichlorosilane

Method A				**Method B**			
Time (min)	Volume of Gas (mL)	Mass of HCl (g)	Yield (%)	Time (min)	Volume of Gas (mL)	Mass of HCl (g)	Yield (%)
0.33	10.1	0.023	31.6	0.33	18.3	0.042	57.2
0.67	14.5	0.033	45.3	0.67	19.2	0.044	60.0
1	18.9	0.043	59.1	1	18.5	0.042	57.8
2	19.8	0.045	61.9	2	18.1	0.041	56.6
3	21.6	0.049	67.5	3	17.5	0.040	54.7
5	21.8	0.05	68.1	5	16.8	0.038	52.5
10	21.9	0.050	68.4	7	16.5	0.038	51.6
				10	16.3	0.037	50.9
				20	16.2	0.037	50.6

Comments: In method A, an immediate reaction very rapidly formed a viscous liquid polysiloxane. This product might have sequestered some water and so restricted the yield of HCl(g). In method B, reaction was also quick; a viscous liquid polysiloxane formed as HCl(g) evolved. A maximum on the HCl(g) yield curve was apparent.

UN 1250 — Methyltrichlorosilane, CH_3SiCl_3

Methyltrichlorosilane is a liquid with a relative molar mass of 149.48 and a room-temperature density of 1.273 g/cm^3. In method A, 2.00 mmol (instead of 1.00 mmol) of it was mixed with 3.00 mmol of water. In method B, 2.00 mmol of it was mixed with 10.0 mmol of water. Reaction according to the equation

$$CH_3SiCl_3 + 3/2\ H_2O \longrightarrow 3\ HCl + [CH_3SiO_{3/2}]_n \text{ polymer}$$

was taken as the source of HCl(g). The theoretical yield of HCl(g) (6.00 mmol) corresponded to 96.0 mL of gas in the calibrated experimental apparatus.

1999 Experimental Results for Methyltrichlorosilane

Method A				**Method B**			
Time (min)	Volume of Gas (mL)	Mass of HCl (g)	Yield (%)	Time (min)	Volume of Gas (mL)	Mass of HCl (g)	Yield (%)
1	19	0.023	10	1	22	0.050	23
5	18	0.041	19	5	28	0.064	29
10	24	0.055	25	10	30	0.068	31
20	26	0.059	27	20	32	0.073	33

2003 Experimental Results for Methyltrichlorosilane

Method A				**Method B**			
Time (min)	Volume of Gas (mL)	Mass of HCl (g)	Yield (%)	Time (min)	Volume of Gas (mL)	Mass of HCl (g)	Yield (%)
0.5	5.8	0.0132	6.0	0.5	15.5	0.035	16.1
1	8.9	0.0203	9.3	1	22.0	0.050	22.9
2	11.7	0.0267	12.2	2	24.2	0.055	25.2
3	14.1	0.032	14.7	3	26.8	0.061	27.9
4	16.1	0.037	16.8	4	27.4	0.063	28.5
5	17.8	0.041	18.5	5	28.0	0.064	29.2
7	20.3	0.046	21.1	7	29.1	0.066	30.3
10	23.7	0.054	24.7	10	30.5	0.070	31.8
20	25.8	0.059	26.9	20	32.5	0.074	33.9
30	26.2	0.060	27.3	30	32.8	0.075	34.2
45	26.5	0.060	27.6	45	33.0	0.075	34.4

Comments: The 1999 experiments were repeated in 2003 to obtain more data on the early course of the reaction. Only 27–28% of the theoretical amount of HCl(g) was generated with method A. A white solid formed immediately after the reactants were mixed. This by-product, a polymeric siloxane, probably sequestered H_2O or unreacted methyltrichlorosilane. A similar white solid was observed with method B. No maxima were observed in the HCl(g) yield curves with method B. The absence of such maxima does not however imply that dissolution of HCl(g) fails to occur.

UN 1298 — Trimethylchlorosilane, $(CH_3)_3SiCl$

Trimethylchlorosilane is a liquid with a relative molar mass of 108.64 and a room-temperature density of 1.257 g/cm^3. In method A, 1.00 mmol of it was mixed with 1.00 mmol of water. In method B, 1.00 mmol was mixed with 5.00 mmol of water. Reaction according to the equation

$$(CH_3)_3SiCl + H_2O \longrightarrow HCl + [(CH_3)_3SiOH]_n$$

was taken as the source of HCl(g) for computations of mass and yield. The theoretical yield of HCl(g) was 1.00 mmol, which corresponded to 16.0 mL of gas in the calibrated experimental apparatus.

1999 Experimental Results for Trimethylchlorosilane

Method A				Method B			
Time (min)	Volume of Gas (mL)	Mass of HCl (g)	Yield (%)	Time (min)	Volume of Gas (mL)	Mass of HCl (g)	Yield (%)
1	2	0.0046	13	1	4.5	0.0102	28
5	4.5	0.0102	28	5	5.5	0.0125	34
10	5	0.0114	31	10	6	0.0137	38
20	5.5	0.0125	34	20	6	0.0137	38

2003 Experimental Results for Trimethylchlorosilane

Method A				Method B			
Time (min)	Volume of Gas (mL)	Mass of HCl (g)	Yield (%)	Time (min)	Volume of Gas (mL)	Mass of HCl (g)	Yield (%)
0.5	1.3	0.0030	8.1	0.5	3.1	0.0071	19.4
1	2.1	0.0048	13.1	1	4.2	0.0096	26.3
2	2.9	0.0066	18.1	2	5.1	0.0116	31.9
3	3.6	0.0082	22.5	3	5.3	0.0121	33.1
4	4.1	0.0093	25.6	4	5.6	0.0128	35.0
5	4.6	0.0105	28.8	5	5.8	0.0132	36.3
10	5.2	0.0118	32.5	10	6.2	0.0141	38.8
20	5.7	0.0130	35.6	20	6.4	0.0146	40.0
30	5.9	0.0134	36.9	30	6.5	0.0148	40.6
45	6.0	0.0137	37.5	45	6.6	0.0150	41.3

Comments: The 1999 experiments were repeated in 2003 to obtain more data on the early course of the reaction. In method A, the reaction produced a white solid by-product and only about one-third of the theoretical amount of HCl(g). In method B, the white solid by-product also appeared. The by-product might have sequestered some of the HCl in both cases. No dissolution of HCl(g) in excess water was observed towards the end of the reaction [i.e., there was no maximum on the HCl(g) yield curve].

UN 1305 — Vinyltrichlorosilane, $CH_2{=}CHSiCl_3$

Vinyltrichlorosilane is a liquid with a relative molar mass of 161.49 and a room-temperature density of 1.270 g/cm^3. In method A, 1.00 mmol of it was mixed with 1.50 mmol of water. In method B, 1.00 mmol of it was mixed with 7.50 mmol of water. The equation

$$CH_2CHSiCl_3 + 3/2\ H_2O \longrightarrow 3\ HCl + [CH_2CHSiO_{3/2}]_n \text{ polymer}$$

was taken to represent the evolution of gas. The theoretical yield of HCl(g) (3.00 mmol) corresponded to 48.0 mL of gas in the calibrated experimental apparatus.

2003 Experimental Results for Vinyltrichlorosilane							
Method A				**Method B**			
Time (min)	Volume of Gas (mL)	Mass of HCl (g)	Yield (%)	Time (min)	Volume of Gas (mL)	Mass of HCl (g)	Yield (%)
1	2.6	0.006	5.4	1	22.3	0.051	46.5
2	4.0	0.009	8.3	2	27.1	0.062	56.5
3	4.7	0.011	9.8	3	26.3	0.060	54.8
4	5.1	0.012	10.6	4	25.6	0.058	53.3
5	5.4	0.012	11.3	5	25.0	0.057	52.1
6	5.7	0.013	11.9	6	24.2	0.055	50.4
8	6.1	0.014	12.7	8	23.1	0.053	48.1
10	6.5	0.015	13.5	10	21.9	0.050	45.6
12	6.8	0.015	14.2	12	21.0	0.048	43.8
15	7.1	0.016	14.8	15	19.8	0.045	41.3
20	7.6	0.017	15.8	20	18.0	0.041	37.5
25	8.1	0.018	16.9	25	16.9	0.039	35.2
30	8.6	0.020	17.9	30	15.8	0.036	32.9
45	9.4	0.021	19.6	45	15.1	0.034	31.5
60	10.1	0.023	21.0	60	14.7	0.034	30.6
90	10.9	0.025	22.7	90	14.5	0.033	30.2
120	11.4	0.026	23.8	120	14.3	0.033	29.8
180	11.6	0.026	24.2	180	14.1	0.032	29.4

Comments: In method A, a white solid polysiloxane quickly formed. This by-product apparently sequestered some water and so prevented completion of the reaction. Some HCl was also conceivably consumed by a side-reaction involving the vinyl group. In method B, the less-than-theoretical yield of HCl(g) was ascribed to sequestration of some reactant by the polymeric by-product and dissolution of HCl(g) in the excess water.

UN 1360 — Calcium Phosphide, Ca_3P_2

Calcium phosphide is a solid with a relative molar mass of 182.18. In method A, 6.00 mmol of water was added to 1.00 mmol of it. In method B, 1.00 mmol of it was added to 30.0 mmol of water. The reaction

$$Ca_3P_2 + 6\ H_2O \longrightarrow 2\ PH_3 + 3\ Ca(OH)_2$$

was taken as the source of gaseous phosphine (PH_3). Generation of 2.00 mmol of PH_3(g) corresponded to an increase in volume of 32.0 mL in the calibrated apparatus. Pure octane was used as the manometric fluid.

1999 Experimental Results for Calcium Phosphide

Method A				Method B			
Time (min)	Volume of Gas (mL)	Mass of PH_3 (g)	Yield (%)	Time (min)	Volume of Gas (mL)	Mass of PH_3 (g)	Yield (%)
1	1.0	0.00212	3.1	1	1.9	0.00425	6.2
2	2.0	0.00425	6.2	2	4.9	0.0106	15.6
5	2.0	0.00425	6.2	5	8.0	0.0170	25.0
10	2.0	0.00425	6.2	10	9.0	0.0191	28.1
20	2.0	0.00425	6.2	20	9.0	0.0191	28.1

2003 Experimental Results for Calcium Phosphide

Method A				Method B			
Time (min)	Volume of Gas (mL)	Mass of PH_3 (g)	Yield (%)	Time (min)	Volume of Gas (mL)	Mass of PH_3 (g)	Yield (%)
0.33	4.8	0.0102	15.0	1	1.5	0.0032	4.7
0.67	5.5	0.0117	17.2	2	2.3	0.0049	7.2
1	6.2	0.0132	19.4	3	2.9	0.0062	9.1
2	6.6	0.0140	20.6	5	4.0	0.0085	12.5
3	6.7	0.0142	20.9	7	5.0	0.0106	15.6
5	6.9	0.0146	21.6	10	6.2	0.0132	19.4
10	6.9	0.0146	21.6	15	7.4	0.0157	23.1
				20	8.1	0.0172	25.3
				30	9.5	0.0202	29.7
				40	10.8	0.0229	33.8
				50	12.6	0.0267	39.4
				60	13.8	0.0293	43.1
				90	14.6	0.0310	45.6
				120	15.0	0.0318	46.9
				150	15.1	0.0320	47.2

Comments: The reaction was incomplete in all four experiments, although in 2003 a different sample of Ca_3P_2 was used, and the yields of PH_3 were higher than in 1999. In method A, the reaction mixture thickened and became difficult to stir. In method B, larger amounts of gas were evolved than in method A. The solubility of PH_3 is negligible in both water and octane. Dissolution in the excess water did not therefore remove any gas from the reaction system. Chemical events in the mixture were almost certainly more complex than suggested by the single equation given above. For example, gaseous diphosphine [$P_2H_4(g)$] might have formed. The extent of such a concurrent reaction cannot be determined in this experiment, which measures only the total volume of evolved gases. The yields and masses in the table are based on the assumption that the gaseous product was pure PH_3.

UN 1384 — Sodium Dithionite, $Na_2S_2O_4$

Sodium dithionite, also called sodium hydrosulfite, is a solid with a relative molar mass of 174.11. In method A, 1.00 mmol of it was mixed with 1.00 mmol of water. In method B, 1.00 mmol of it was mixed with 5.00 mmol of water.

Comments: The purpose was to check on the evolution of $H_2S(g)$ and/or $SO_2(g)$ by means of a disproportionation reaction. No measurable amounts of gas were evolved within 30 min using method A or within 300 min using method B. In separate test-tube experiments, the presence of both $H_2S(g)$ and $SO_2(g)$ was recognized by their odors. The amounts of these acidic gases were sufficient to change the color of moistened pH paper.

UN 1412 — Lithium Amide, $LiNH_2$

Lithium amide is a solid with a relative molar mass of 22.96. In method A, 1.00 mmol of water was added to 1.00 mmol of it. In method B, 1.00 mmol of it was mixed with 5.00 mmol of water. Reaction according to the equation

$$LiNH_2 + H_2O \longrightarrow NH_3 + LiOH$$

was taken as the source of $NH_3(g)$ for computations of mass and yield. The theoretical yield of $NH_3(g)$ was 1.00 mmol, which corresponded to 16.0 mL of gas in the calibrated experimental apparatus.

2003 Experimental Data for Lithium Amide

Method A				Method B			
Time (min)	Volume of Gas (mL)	Mass of NH_3 (g)	Yield (%)	Time (min)	Volume of Gas (mL)	Mass of NH_3 (g)	Yield (%)
0.33	2.4	0.0025	14.5	0.33	3.1	0.0032	18.8
0.67	3.0	0.0031	18.2	0.5	3.6	0.0037	21.8
1	3.2	0.0033	19.4	1	3.1	0.0032	18.8
2	3.5	0.0036	21.2	2	2.7	0.0028	16.4
3	3.7	0.0038	22.4	3	2.6	0.0027	15.8
5	3.9	0.0040	23.6	5	2.4	0.0025	14.5
7	4.1	0.0042	24.8	7	2.3	0.0024	13.9
10	4.3	0.0044	26.1	10	2.2	0.0023	13.3
15	4.6	0.0047	27.9	15	2.1	0.0022	12.7
20	4.7	0.0049	28.5	20	2.1	0.0022	12.7
30	4.8	0.0050	29.1				
40	4.8	0.0050	29.1				

Comments: In method A, the reaction was rapid at first but ultimately produced less than one third of the theoretical amount of NH_3(g). In method B, the reaction was apparently less productive of NH_3(g) but the maximum on the yield curve for NH_3(g) indicated that some NH_3(g) dissolved in the excess water.

UN 1433 — Stannic Phosphide, Sn_4P_3

Stannic phosphide, which has a relative molar mass of 567.70, is metallic. In method A, 0.567 g (1.00 mmol) of it was mixed with 0.144 g (8.0 mmol) of water. In method B, 1.00 mmol of it was mixed with 0.720 g (40.0 mmol) of water.

Comments: The purpose of the experiment was to check on the possible evolution of phosphine (PH_3). No measurable amount of gas was evolved within 20 min using either method. Also, no odor of PH_3 was detected.

UN 1541 — Acetone Cyanohydrin, Stabilized, $(CH_3)_2C(OH)CN$

Acetone cyanohydrin is a liquid with a relative molar mass of 85.11 and a density of 0.932 g/cm^3. In method A, 1.00 mmol of water was added to 1.00 mmol of it. In method B, 1.00 mmol of it was added to 5.00 mmol of water. The equilibrium reaction

$$(CH_3)_2C(OH)CN \longrightarrow HCN + (CH_3)_2CO$$

was considered as a source of evolved HCN. Generation of 1.00 mmol of gas corresponded to an increase in volume of 16.0 mL in the calibrated apparatus.

Comments: No measurable amount of gas was evolved within 30 min using either method. Contact of this substance with acidic aqueous solutions is known to cause evolution of HCN(g).

UN 1714 — Zinc Phosphide, Zn_3P_2

Zinc phosphide is a solid with a relative molar mass of 258.11. In method A, 0.258 g (1.00 mmol) of it was mixed with 6.00 mmol of water. In method B, 1.00 mmol of it was mixed with 30.0 mmol of water. The equation

$$Zn_3P_2 + 6\ H_2O \longrightarrow 2\ PH_3 + 3\ Zn(OH)_2$$

was taken to represent the evolution of gas. The theoretical yield of PH_3(g) (2.00 mmol) corresponded to 32.0 mL of gas in the calibrated experimental apparatus.

Comments: No measurable amount of gas was generated within 30 min using method A and within 20 minutes using method B. Also, the odor of PH_3 was not detected.

UN 1716 — Acetyl Bromide, CH_3COBr

Acetyl bromide is a colorless liquid with a relative molar mass of 122.95 and a room-temperature density of 1.663 g/cm^3. In method A, 1.00 mmol of water was added to 1.00 mmol of it. In method B, 1.00 mmol of it was mixed with 5.00 mmol of water. Reaction according to the equation

$$CH_3COBr + H_2O \longrightarrow HBr + CH_3COOH$$

was taken as the source of HBr(g) for computations of mass and yield. The theoretical yield of HBr(g) was 1.00 mmol, which corresponded to 16.0 mL of gas in the calibrated experimental apparatus.

2003 Experimental Data for Acetyl Bromide

Method A				**Method B**			
Time (min)	Volume of Gas (mL)	Mass of HBr (g)	Yield (%)	Time (min)	Volume of Gas (mL)	Mass of HBr (g)	Yield (%)
0.25	11.1	0.056	69.4	0.25	5.3	0.0268	33.1
0.5	15.5	0.078	96.9	0.5	1.2	0.0061	7.5
1	15.7	0.079	98.1	1	0.5	0.0025	3.1
2	16.2	0.082	101.3	2	0.2	0.0010	1.3
5	16.2	0.082	101.3	3	0.1	0.0005	0.6

Comments: In method A, the theoretical amount of HBr(g) was evolved rapidly. In method B, the reaction was faster than in method A. HBr(g) dissolved in the excess water throughout the gas-producing reaction. No maximum was found on the HBr(g) yield curve.

UN 1717 — Acetyl Chloride, CH_3COCl

Acetyl chloride is a colorless liquid with a relative molar mass of 78.50 and a room-temperature density of 1.104 g/cm^3. In method A, 1.00 mmol of water was added to 1.00 mmol of it. In method B, 1.00 mmol of it was mixed with 5.00 mmol of water. Reaction according to the equation

$$CH_3COCl + H_2O \longrightarrow HCl + CH_3COOH$$

was taken as the source of HCl(g) for computations of mass and yield. The theoretical yield of HCl(g) was 1.00 mmol, which corresponded to 16.0 mL of gas in the calibrated experimental apparatus.

2003 Experimental Data for Acetyl Chloride

Method A				Method B			
Time (min)	Volume of Gas (mL)	Mass of HCl (g)	Yield (%)	Time (min)	Volume of Gas (mL)	Mass of HCl (g)	Yield (%)
0.33	10.5	0.0239	65.6	0.33	6.0	0.0137	37.5
0.67	13.5	0.0308	84.4	0.67	4.5	0.010	28.1
1	14.7	0.0335	91.9	1	3.2	0.0073	20.0
2	15.7	0.0358	98.1	1.5	2.3	0.0052	14.4
3	15.9	0.0362	99.4	2	1.6	0.0036	10.0
5	15.9	0.0362	99.4	3	1.0	0.0023	6.3
				5	0.2	0.0005	1.3
				10	0.0	0.0000	0.0

Comments: In method A, the theoretical amount of HCl(g) evolved rapidly. In method B, the formation of HCl(g) was also rapid, but it dissolved in the water/acetic acid mixture almost as fast as it formed. All of the HCl(g) ultimately dissolved. No maximum was observed on the HCl(g) yield curve.

UN 1724 — Allyltrichlorosilane, $CH_2=CHCH_2SiCl_3$

Allyltrichlorosilane is a liquid with a relative molar mass of 175.52 and a room-temperature density of 1.211 g/cm^3. In method A, 1.00 mmol of it was mixed with 1.50 mmol of water. In method B, 1.00 mmol of it was mixed with 7.50 mmol of water. Reaction according to the equation

$$CH_2CHCH_2SiCl_3 + 3/2\ H_2O \longrightarrow 3\ HCl + [CH_2CHCH_2SiO_{3/2}]_n \text{ polymer}$$

was taken as the source of HCl(g). The theoretical yield of HCl(g) was 3.00 mmol, which corresponded to 48.0 mL of gas in the calibrated experimental apparatus.

2003 Experimental Data for Allyltrichlorosilane							
Method A				**Method B**			
Time (min)	Volume of Gas (mL)	Mass of HCl (g)	Yield (%)	Time (min)	Volume of Gas (mL)	Mass of HCl (g)	Yield (%)
0.33	2.7	0.0062	5.6	0.5	15.0	0.034	31.3
0.67	5.1	0.0116	10.6	1	23.8	0.054	49.6
1	8.4	0.0191	17.5	2	23.2	0.053	48.3
1.5	13.2	0.0301	27.5	3	21.6	0.049	45.0
2	16.7	0.038	34.8	4	20.2	0.046	42.1
2.5	19.2	0.044	40.0	5	19.1	0.044	39.8
3	20.9	0.048	43.5	6	18.5	0.042	38.5
4	24.6	0.056	51.3	8	17.5	0.040	36.5
5	28.8	0.066	60.0	10	16.5	0.038	34.4
6	41.4	0.094	86.3	12	15.9	0.036	33.1
7	43.4	0.099	90.4	15	15.3	0.035	31.9
8	43.5	0.099	90.6	20	15.0	0.034	31.3
10	43.6	0.099	90.8	30	14.9	0.034	31.0

Comments: With both methods, the reaction rapidly formed a viscous polymeric siloxane. In method B, the yield of gaseous HCl reached a maximum in less than 1 min. This was followed by the absorption of HCl(g) by the excess water.

UN 1725 — Aluminum Bromide (anhydrous), $AlBr_3$

Aluminum bromide, a solid, has a relative molar mass of 266.69. In method A, 1.00 mmol of it was mixed with 1.00 mmol of water. In method B, 1.00 mmol was mixed with 5.00 mmol of water. No equation was proposed for a reaction generating a TIH gas beyond the following:

$$AlBr_3 + n\,H_2O \longrightarrow AlBr_3\bullet(H_2O)_n \text{ (hydration)}$$

1999 Experimental Results for Aluminum Bromide (anhydrous)

Method A				**Method B**			
Time (min)	Volume of Gas (mL)	Mass of HBr (g)	Percent Yield	Time (min)	Volume of Gas (mL)	Mass of HBr (g)	Percent Yield
1	1	-	-	1	1	-	-
5	1	-	-	5	1	-	-
10	0.5	-	-	10	0.5	-	-
20	0.5	-	-	20	0.5	-	-

Comments: The hydration reaction was rapid and quite exothermic. The observed small changes in volume were attributed solely to this heating. The production of an acidic mist by the intense heating of a restricted quantity of water cannot be ruled out in a spill of a large amount of aluminum bromide into a restricted supply of water.

UN 1726 — Aluminum Chloride (anhydrous), $AlCl_3$

Aluminum chloride, a solid, has a relative molar mass of 133.34. In method A, 1.00 mmol of it was mixed with 1.00 mmol of water. In method B, 1.00 mmol was mixed with 5.00 mmol of water. No equation was proposed for a reaction generating a TIH gas beyond the following:

$$AlCl_3 + n\ H_2O \longrightarrow AlCl_3{\bullet}(H_2O)_n \text{ (hydration)}$$

1999 Experimental Results for Aluminum Chloride (anhydrous)

Method A				Method B			
Time (min)	Volume of Gas (mL)	Mass of HCl (g)	Yield (%)	Time (min)	Volume of Gas (mL)	Mass of HCl (g)	Yield (%)
1	1	-	-	1	1	-	-
5	1	-	-	5	1	-	-
10	0.5	-	-	10	0.5	-	-
20	0.5	-	-	20	0.5	-	-

Comments: The hydration reaction was rapid and quite exothermic. The observed small change in volume was attributed solely to this heating. The production of an acidic mist by intense heating of a restricted quantity of water should not be ruled out as the result of a spill of a large quantity of aluminum chloride into a restricted supply of water.

UN 1728 — Amyltrichlorosilane, $C_5H_{11}SiCl_3$

Amyltrichlorosilane, also known as (n-pentyl)trichlorosilane, is a liquid with a relative molar mass of 205.59 and a room-temperature density of 1.142 g/cm^3. In method A, 1.00 mmol of it was mixed with 1.50 mmol of water. In method B, 1.00 mmol of it was mixed with 7.50 mmol of water. The equation

$$C_5H_{11}SiCl_3 + 3/2\ H_2O \longrightarrow 3\ HCl + [C_5H_{11}SiO_{3/2}]_n \text{ polymer}$$

was taken to represent the evolution of HCl(g). The theoretical yield of HCl(g) was 3.00 mmol, which corresponded to 48.0 mL of gas in the calibrated experimental apparatus.

2003 Experimental Data for Amyltrichlorosilane							
Method A				**Method B**			
Time (min)	Volume of Gas (mL)	Mass of HCl (g)	Yield (%)	Time (min)	Volume of Gas (mL)	Mass of HCl (g)	Yield (%)
1	0.2	0.0005	0.4	1	0.3	0.0007	0.6
3	0.3	0.0007	0.6	3	0.7	0.0016	1.5
5	0.4	0.0009	0.8	5	1.7	0.0039	3.5
10	0.9	0.0021	1.9	10	3.5	0.0080	7.3
15	1.2	0.0027	2.5	15	5.7	0.0130	11.9
20	2.0	0.0046	4.2	20	6.6	0.0150	13.8
30	3.0	0.0068	6.3	25	7.3	0.0166	15.2
40	5.2	0.0119	10.8	30	8.1	0.0185	16.9
50	5.9	0.0134	12.3	35	8.8	0.0201	18.3
60	6.9	0.0157	14.4	40	9.3	0.0212	19.4
75	7.8	0.0178	16.3	50	10.0	0.0228	20.8
90	8.7	0.0198	18.1	60	10.3	0.0235	21.5
105	9.6	0.0219	20.0	90	10.4	0.0237	21.7
120	10.5	0.0239	21.9				
135	11.3	0.0258	23.5				
150	12.8	0.0292	26.7				
165	14.7	0.0335	30.6				
180	14.8	0.0337	30.8				

Comments: In method A, the reaction slowly formed a very viscous liquid polysiloxane. This product apparently sequestered a considerable amount of water because less than one-third of the stoichiometric amount of HCl(g) evolved. In method B, the viscous liquid by-product again was formed. The reaction was slow enough that the HCl(g) dissolved without a maximum on the yield curve.

UN 1732 — Antimony Pentafluoride, SbF_5

Antimony pentafluoride is a liquid with a relative molar mass of 216.74 and a room-temperature density of 2.99 g/cm^3. In method A, 1.00 mmol of it was mixed with 5.00 mmol of water. In method B, 1.00 mmol of it was mixed with 25.0 mmol of water. The equation

$$2\,SbF_5 + 5\,H_2O \longrightarrow 10\,HF + Sb_2O_5$$

was taken to represent the evolution of HF. The theoretical yield of HF(g) was 10.0 mmol, which corresponded to 160 mL of gas in the calibrated experimental apparatus.

Comments: No evolution of gas was observed with either method A or method B, even after 20–30 min. This experiment was the first attempt to measure the evolution of HF(g). Both

SbF_5 and HF are difficult to handle. This result cannot be regarded as conclusive because of the experimental difficulties.

UN 1736 — Benzoyl Chloride, C_6H_5COCl

Benzoyl chloride is a liquid with relative molar mass of 140.57 and a room-temperature density of 1.211 g/cm^3. In method A, 1.00 mmol of it was mixed with 1.00 mmol of water. In method B, 1.00 mmol of it was mixed with 5.00 mmol of water. Reaction according to the equation

$$C_6H_5COCl + H_2O \longrightarrow HCl + C_6H_5COOH$$

was taken as the source of HCl(g). The theoretical yield of HCl(g) was 1.00 mmol, which corresponded to 16.0 mL of gas in the calibrated experimental apparatus.

Comments: No measurable volume change was observed within 20 min using either method. Thus, within the observed time period the rate of hydrolysis of benzoyl chloride is negligible.

UN 1747 — Butyltrichlorosilane, $C_4H_9SiCl_3$

Butyltrichlorosilane is a liquid with a relative molar mass of 191.56 and a room-temperature density of 1.160 g/cm^3. In method A, 1.00 mmol of it was mixed with 1.50 mmol of water. In method B, 1.00 mmol of it was mixed with 7.50 mmol of water. The equation

$$C_4H_9SiCl_3 + 3/2\ H_2O \longrightarrow 3\ HCl + [C_4H_9SiO_{3/2}]_n \text{ polymer}$$

was taken to represent the evolution of HCl(g). The theoretical yield of HCl(g) was 3.00 mmol, which corresponded to 48.0 mL of gas in the calibrated experimental apparatus.

2003 Experimental Data for Butyltrichlorosilane

Method A				Method B			
Time (min)	Volume of Gas (mL)	Mass of HCl (g)	Yield (%)	Time (min)	Volume of Gas (mL)	Mass of HCl (g)	Yield (%)
1	0.2	0.0005	0.4	1	0.3	0.0007	0.6
2	0.5	0.0011	1.0	2	0.5	0.0011	1.0
3	0.7	0.0016	1.5	3	0.7	0.0016	1.5
5	1.0	0.0023	2.1	5	1.1	0.0025	2.3
7	1.5	0.0034	3.1	7	1.9	0.0043	4.0
10	2.3	0.0052	4.8	10	3.6	0.0082	7.5
15	3.6	0.0082	7.5	15	6.7	0.0153	14.0
20	4.9	0.0112	10.2	20	8.8	0.0201	18.3
25	6.1	0.0139	12.7	25	10.5	0.0239	21.9
30	7.2	0.0164	15.0	30	11.5	0.0262	24.0
35	8.0	0.0182	16.7	40	12.0	0.0274	25.0
40	8.8	0.0201	18.3	50	12.1	0.0276	25.2
50	10.0	0.0228	20.8	60	12.1	0.0276	25.2
60	11.2	0.0255	23.3				
75	12.3	0.0280	25.6				
90	14.2	0.032	29.6				
105	16.9	0.039	35.2				
120	18.4	0.042	38.3				
150	18.5	0.042	38.5				

Comments: In method A, the reaction slowly formed a very viscous liquid by-product that apparently sequestered a considerable amount of water. In method B, the reaction also formed the viscous by-product. The reaction was slow enough that the HCl(g) dissolved without a maximum on the yield curve.

UN 1748 — Calcium Hypochlorite, $Ca(OCl)_2$

Calcium hypochlorite, a solid, has a relative molar mass of 142.98. In method A, 1.00 mmol of the substance was mixed with 1.00 mmol of water. In method B, 1.00 mmol was mixed with 5.00 mmol of water. No equation was proposed for a reaction generating a TIH gas beyond the following

$$Ca(OCl)_2 + H_2O \longrightarrow Cl_2 + \text{other products}$$

1999 Experimental Results for Calcium Hypochlorite

Method A				Method B			
Time (min)	Volume of Gas (mL)	Mass of Gas (g)	Yield (%)	Time (min)	Volume of Gas (mL)	Mass of Gas (g)	Yield (%)
1	0	0	0	1	0	0	0
5	0.5	-	-	5	0.5	-	-
10	0.5	-	-	10	0.5	-	-
20	0.5	-	-	20	0.5	-	-

Comments: The substance is known to disproportionate in acidic water to give $Cl_2(g)$, along with $HClO_4(aq)$, $O_2(g)$, and other products. No gases formed when it was mixed with water under these conditions. The dissolution in water was exothermic enough to cause a slight increase (less than 0.5 mL) in the volume of the gas-evolution apparatus.

UN 1752 — Chloroacetyl Chloride, $ClCH_2COCl$

Chloroacetyl chloride is a liquid with a relative molar mass of 112.94 and a room-temperature density of 1.418 g/cm^3. In method A, 1.00 mmol of water was added to 1.00 mmol of it. In method B, 1.00 mmol of the substance was added to 5.00 mmol of water. Reaction according to the equation

$$ClCH_2COCl + H_2O \longrightarrow HCl + ClCH_2COOH$$

was taken as the source of HCl. Generation of 1.00 mmol of gas corresponded to an increase in volume of 16.0 mL in the calibrated apparatus.

1999 Experimental Results for Chloroacetyl Chloride

Method A				**Method B**			
Time (min)	Volume of Gas (mL)	Mass of HCl (g)	Yield (%)	Time (min)	Volume of Gas (mL)	Mass of HCl (g)	Yield (%)
1	0.2	0.00046	1.2	1	0.2	0.00046	1.2
2	0.3	0.00068	1.9	2	0.5	0.00114	3.1
3	0.5	0.00114	3.1	3	1.0	0.00230	6.2
4	0.6	0.0014	3,7	4	0.5	0.00114	3.1
5	0.8	0.0018	5.0	5	0.2	0.00046	1.2
10	2.7	0.0062	17	10	0	0	0
20	6.2	0.014	39	20	0	0	0
30	10.2	0.023	64				
40	12.0	0.027	75				
50	13.2	0.030	82				
60	13.9	0.032	87				
90	15.4	0.035	96				
120	15.8	0.036	99				
150	15.9	0.036	99				

2003 Experimental Results for Chloroacetyl Chloride

Method A				**Method B**			
Time (min)	Volume of Gas (mL)	Mass of HCl (g)	Yield (%)	Time (min)	Volume of Gas (mL)	Mass of HCl (g)	Yield (%)
1	0.2	0.00046	1.3	0.5	0.3	0.00068	1.88
2	0.3	0.00068	1.9	1	0.5	0.00114	3.13
3	0.5	0.00114	3.1	1.5	0.7	0.00160	4.38
4	0.6	0.00137	3.8	2	0.9	0.00205	5.63
5	0.8	0.00182	5.0	2.5	1.0	0.00228	6.25
10	2.7	0.0062	16.9	3	1.1	0.00251	6.88
20	6.2	0.0141	38.8	3.5	1.0	0.00228	6.25
30	10.2	0.0232	63.8	4	0.5	0.00114	3.13
40	12.0	0.0273	75.0	5	0.2	0.00046	1.25
50	13.2	0.0301	82.5	6	0.1	0.00023	0.63
60	13.9	0.0317	86.9	7	0.00	0.0000	0.00
90	15.4	0.0351	96.3				
120	15.8	0.0360	98.8				
150	15.9	0.0362	99.4				

Comments: In method A, the reaction started slowly but picked up speed, suggesting autocatalysis (catalysis by one of the products). In method B, the reaction was fast, and dissolution of HCl(g) in the excess water was fairly fast; maxima on the HCl(g) yield curve are evident. In method B, all of the HCl eventually dissolved in the excess water, but in an open spill the duration of contact between HCl and the water would likely be lesser, and emission might be substantial.

UN 1754 — Chlorosulfonic Acid, $ClSO_2(OH)$

Chlorosulfonic acid is a liquid with relative molar mass of 116.52 and a room-temperature density of 1.753 g/cm^3. In method A, 1.00 mmol of it was mixed with 1.00 mmol of water. In method B, 1.00 mmol of it was mixed with 5.00 mmol of water. The equation

$$ClSO_2(OH) + H_2O \longrightarrow HCl + H_2SO_4$$

was taken to represent the evolution of HCl(g). The theoretical yield of HCl(g) was 1.00 mmol, which corresponded to 16.0 mL of gas in the calibrated experimental apparatus.

2003 Experimental Data for Chlorosulfonic Acid

Method A				Method B			
Time (min)	Volume of Gas (mL)	Mass of HCl (g)	Yield (%)	Time (min)	Volume of Gas (mL)	Mass of HCl (g)	Yield (%)
0.167	11.1	0.025	69.4	0.167	15.1	0.034	94.4
0.33	13.9	0.032	86.9	0.5	14.5	0.033	90.6
0.5	15.4	0.035	96.3	1	14.1	0.032	88.1
1	15.5	0.035	96.9	2	13.5	0.031	84.4
2	15.5	0.035	96.9	3	13.0	0.030	81.3
5	15.6	0.036	97.5	5	12.5	0.028	78.1
				7	12.2	0.028	76.3
				10	12.0	0.027	75.0
				15	11.8	0.027	73.8
				20	11.7	0.027	73.1

Comments: In method A, the reaction was rapid and yielded essentially the theoretical amount of HCl(g). In method B, hydrolysis was similarly rapid and was followed by a slower dissolution of HCl(g) in the excess water (as shown by the maximum on the yield curve). The acidic by-product H_2SO_4 that was co-dissolved in the excess water certainly lowered the solubility of the HCl and so raised the yield of HCl(g). In a real spill, the by-product H_2SO_4 would be diluted and the amount of HCl(g) would be less.

UN 1758 — Chromium Oxychloride, CrO_2Cl_2

Chromium oxychloride, also called chromyl chloride, is a dark-red liquid with a relative molar mass of 154.90 and a room-temperature density of 1.911 g/cm^3. In method A, 1.00 mmol of it was mixed with 1.00 mmol of water. In method B, 1.00 mmol of it was mixed with 3.00 mmol (rather than 5.00 mmol) of water. Reaction according to the equation

$$CrO_2Cl_2 + H_2O \longrightarrow 2\ HCl + CrO_3$$

was taken as the source of HCl(g). The theoretical yield of HCl(g) was 2.00 mmol, which corresponded to 32.0 mL of gas in the calibrated experimental apparatus.

2003 Experimental Data for Chromium Oxychloride

Method A				**Method B**			
Time (min)	Volume of Gas (mL)	Mass of HCl (g)	Yield (%)	Time (min)	Volume of Gas (mL)	Mass of HCl (g)	Yield (%)
2	0.2	0.00046	0.6	2	0.8	0.0014	1.9
5	0.3	0.00068	0.9	5	1.4	0.0018	2.5
10	0.3	0.00068	0.9	10	1.9	0.0032	4.4
20	0.3	0.00068	0.9	15	2.4	0.0043	5.9
				20	2.8	0.0055	7.5
				30	2.9	0.0064	8.8
				45	2.9	0.0066	9.1
				60	0	0.0066	9.1

Comments: In method A, the amount of gaseous HCl(g) that formed was negligibly small — less than 1% of the theoretical yield. In method B, the rate of hydrolysis of the substance was again very slow, but the yield of HCl was substantially higher, despite the possible loss of HCl(g) by dissolution.

UN 1763 — Cyclohexyltrichlorosilane, $C_6H_{11}SiCl_3$

Cyclohexyltrichlorosilane is a liquid with a relative molar mass of 217.60 and a room-temperature density of 1.232 g/cm^3. In method A, 1.00 mmol of it was mixed with 1.50 mmol of water. In method B, 1.00 mmol of it was mixed with 7.50 mmol of water. Reaction according to the equation

$$C_6H_{11}SiCl_3 + 3/2\ H_2O \longrightarrow 3\ HCl + [C_6H_{11}SiO_{3/2}]_n \text{ polymer}$$

was taken as the source of HCl(g). The theoretical yield of HCl(g) (3.00 mmol) corresponded to 48.0 mL of gas in the calibrated experimental apparatus.

2003 Experimental Results for Cyclohexyltrichlorosilane							
Method A				**Method B**			
Time (min)	Volume of Gas (mL)	Mass of HCl (g)	Yield (%)	Time (min)	Volume of Gas (mL)	Mass of HCl (g)	Yield (%)
1	0.2	0.00046	0.4	1	0.2	0.00046	0.4
2	0.3	0.00068	0.6	2	0.4	0.00091	0.8
3	0.4	0.00091	0.8	3	0.6	0.00137	1.3
4	0.6	0.00137	1.3	4	0.8	0.00182	1.7
5	1.0	0.0023	2.1	5	1.5	0.0034	3.1
6	1.4	0.0032	2.9	6	3.6	0.0082	7.5
7	2.0	0.0046	4.2	7	5.7	0.0130	11.9
8	2.5	0.0057	5.2	8	7.2	0.0164	15.0
9	3.0	0.0068	6.3	9	8.4	0.0191	17.5
10	3.7	0.0084	7.7	10	9.3	0.0212	19.4
12	4.9	0.0112	10.2	12	10.7	0.0244	22.3
15	6.6	0.0150	13.8	15	11.6	0.0264	24.2
20	9.2	0.0210	19.2	20	12.6	0.0287	26.3
25	11.7	0.027	24.4	25	13.2	0.030	27.5
30	13.8	0.031	28.8	30	13.5	0.031	28.1
40	17.8	0.041	37.1	35	13.7	0.031	28.5
50	21.7	0.049	45.2	40	13.8	0.031	28.8
60	25.8	0.059	53.8	45	13.8	0.031	28.8
70	29.8	0.068	62.1				
80	30.8	0.070	64.2				
90	30.9	0.070	64.4				
120	31.0	0.071	64.6				

Comments: In method A, the reaction slowly formed a white solid polysiloxane that sequestered water. In method B, the solid polysiloxane by-product apparently sequestered a large portion of the monomer, thus preventing it from contacting the water.

UN 1766 (Surrogate) — 4-(Chloromethyl)Phenyltrichlorosilane, $ClCH_2C_6H_4SiCl_3$

4-(Chloromethyl)phenyltrichlorosilane was studied as a surrogate for dichlorophenyltrichlorosilane (UN 1766). It is a liquid with a relative molar mass of 260.02 and a room-temperature density of 1.361 g/cm^3. In method A, 1.00 mmol of it was mixed with 1.50 mmol of water. In method B, 1.00 mmol of it was mixed with 7.50 mmol of water. Reaction according to the equation

$$ClCH_2C_6H_4SiCl_3 + 3/2\ H_2O \longrightarrow 3\ HCl + [ClCH_2C_6H_4SiO_{3/2}]_n \text{ polymer}$$

was taken as the source of HCl(g). The theoretical yield of HCl(g) (3.00 mmol) corresponded to 48.0 mL of gas in the calibrated experimental apparatus.

2003 Experimental Results for 4-(Chloromethyl)Phenyltrichlorosilane

Method A				**Method B**			
Time (min)	Volume of Gas (mL)	Mass of HCl (g)	Yield (%)	Time (min)	Volume of Gas (mL)	Mass of HCl (g)	Yield (%)
1	0.6	0.0014	1.3	1	24.8	0.057	51.7
2	1.2	0.0027	2.5	2	28.5	0.065	59.4
3	2.1	0.0048	4.4	3	28.4	0.065	59.2
4	2.9	0.0066	6.0	4	27.7	0.063	57.7
5	3.8	0.0087	7.9	5	26.9	0.061	56.0
6	4.8	0.0109	10.0	6	26.3	0.060	54.8
8	6.7	0.0153	14.0	8	25.1	0.057	52.3
10	8.5	0.0194	17.7	10	24.0	0.055	50.0
12	10.0	0.0228	20.8	12	23.5	0.054	49.0
15	11.9	0.0271	24.8	15	22.3	0.051	46.5
20	14.2	0.0324	29.6	20	21.0	0.048	43.8
25	15.9	0.0362	33.1	25	20.0	0.046	41.7
30	16.9	0.0385	35.2	30	19.3	0.044	40.2
45	17.6	0.0401	36.7	45	17.3	0.039	36.0
60	17.7	0.0403	36.9	60	15.8	0.036	32.9
75	17.8	0.0406	37.1	75	14.8	0.034	30.8
90	17.8	0.0406	37.1	90	14.1	0.032	29.4
				120	13.7	0.031	28.5

Comments: In method A, the reaction formed a solid white polysiloxane that sequestered water and so restricted the yield of HCl(g). In method B, the yield of HCl(g) that was evolved was less than the theoretical amount because of (1) sequestration of some water by the polysiloxane product and (2) dissolution of some HCl(g) in the excess water to produce HCl(aq). A maximum on the yield curve of HCl(g) was reached in 2 min.

UN 1767 — Diethyldichlorosilane, $(C_2H_5)_2SiCl_2$

Diethyldichlorosilane is a liquid with relative molar mass of 157.12 and a room-temperature density of 1.050 g/cm^3. In method A, 1.00 mmol of it was mixed with 1.00 mmol of water. In method B, 1.00 mmol of it was mixed with 5.00 mmol of water. Reaction according to the equation

$$(CH_3CH_2)_2SiCl_2 + H_2O \longrightarrow 2\ HCl + [(CH_3CH_2)_2SiO]_n \text{ polymer}$$

was taken as the source of HCl(g). The theoretical yield of HCl(g) was 2.00 mmol, which corresponded to 32.0 mL of gas in the calibrated experimental apparatus.

2003 Experimental Data for Diethyldichlorosilane

Method A				Method B			
Time (min)	Volume of Gas (mL)	Mass of HCl (g)	Yield (%)	Time (min)	Volume of Gas (mL)	Mass of HCl (g)	Yield (%)
1	0.4	0.0009	1.3	1	0.2	0.0005	0.6
2	0.7	0.0016	2.2	2	0.4	0.0009	1.3
3	0.9	0.0021	2.8	3	0.6	0.0014	1.9
5	1.3	0.0030	4.1	5	0.8	0.0018	2.5
10	2.4	0.0055	7.5	7	1.3	0.0030	4.1
15	3.4	0.0077	10.6	10	2.0	0.0046	6.3
20	4.3	0.0098	13.4	12	2.4	0.0055	7.5
25	5.2	0.0118	16.3	15	3.0	0.0068	9.4
30	5.9	0.0134	18.4	20	3.8	0.0087	11.9
40	7.2	0.0164	22.5	25	4.4	0.0100	13.8
50	8.3	0.0189	25.9	30	4.9	0.0112	15.3
60	9.2	0.0210	28.8	40	5.6	0.0128	17.5
90	10.9	0.0248	34.1	50	6.1	0.0139	19.1
120	12.0	0.0273	37.5	60	6.4	0.0146	20.0
150	12.5	0.0285	39.1	90	6.6	0.0150	20.6
180	12.7	0.0289	39.7				

Comments: In method A, the reaction formed a very viscous liquid by-product polysiloxane. This by-product sequestered a considerable amount of water so that less than half of the stoichiometric amount of HCl(g) was evolved. In method B, the polymer again formed and remained liquid throughout in the course of the reaction. The presence of this liquid may have accelerated the dissolution of HCl(g) in the excess water. No maximum on the HCl(g) yield curve was observed.

UN 1769 — Dichlorodiphenylsilane, $(C_6H_5)_2SiCl_2$

Dichlorodiphenylsilane is a liquid with a relative molar mass of 253.20 and a room-temperature density of 1.204 g/cm^3. In method A, 1.00 mmol of it was mixed with 1.00 mmol of water. In method B, 1.00 mmol of it was mixed with 5.00 mmol of water. Reaction according to the equation

$$(C_6H_5)_2SiCl_2 + H_2O \longrightarrow 2\ HCl + [(C_6H_5)_2SiO]_n \text{ polymer}$$

was taken as the source of HCl(g). The theoretical yield of HCl(g) was 2.00 mmol, which corresponded to 32.0 mL of gas in the calibrated experimental apparatus.

2003 Experimental Data for Dichlorodiphenylsilane

Method A				Method B			
Time (min)	Volume of Gas (mL)	Mass of HCl (g)	Yield (%)	Time (min)	Volume of Gas (mL)	Mass of HCl (g)	Yield (%)
1	0.0	0.0000	0.0	1	0.3	0.0007	0.9
3	0.1	0.0002	0.3	2	0.5	0.0011	1.6
5	0.6	0.0014	1.9	3	1.3	0.0030	4.1
8	2.3	0.0052	7.2	4	1.7	0.0039	5.3
10	3.3	0.0075	10.3	5	2.0	0.0046	6.3
12	4.4	0.0100	13.8	6	2.2	0.0050	6.9
15	5.8	0.0132	18.1	8	2.5	0.0057	7.8
20	7.5	0.0171	23.4	10	2.9	0.0066	9.1
30	9.1	0.0207	28.4	12	3.1	0.0071	9.7
40	10.0	0.0228	31.3	15	3.5	0.0080	10.9
50	10.5	0.0239	33.4	30	3.9	0.0089	12.2
90	10.8	0.0246	33.8	40	3.9	0.0089	12.2

Comments: In method A, the reaction slowly formed a solid polysiloxane in its early stages. This material apparently sequestered water, restricting the yield of HCl(g). In method B, the solid polymer trapped a substantial portion of the reactant. No dissolution of HCl(g) in the excess water was observed towards the end of the experiment [no maximum on the HCl(g) yield curve].

UN 1771 — Dodecyltrichlorosilane, $CH_3(CH_2)_{11}SiCl_3$

Dodecyltrichlorosilane is a liquid with a relative molar mass of 303.78 and a room-temperature density of 1.020 g/cm^3. In method A, 1.00 mmol of it was mixed with 1.50 mmol of water. In method B, 1.00 mmol of it was mixed with 7.50 mmol of water. Reaction according to the equation

$$CH_3(CH_2)_{11}SiCl_3 + 3/2\ H_2O \longrightarrow 3\ HCl + [CH_3(CH_2)_{11}SiO_{3/2}]_n \text{ polymer}$$

was taken as the source of HCl(g). The theoretical yield of HCl(g) (3.00 mmol) corresponded to 48.0 mL of gas in the calibrated experimental apparatus.

2003 Experimental Results for Dodecyltrichlorosilane							
Method A				**Method B**			
Time (min)	Volume of Gas (mL)	Mass of HCl (g)	Yield (%)	Time (min)	Volume of Gas (mL)	Mass of HCl (g)	Yield (%)
1	0.3	0.0007	0.62	1	1.1	0.00525	2.3
2	0.5	0.0011	1.0	2	2.3	0.0052	4.8
3	3.5	0.0080	7.3	3	4.0	0.0091	8.3
4	8.8	0.0201	18.3	4	4.7	0.0107	9.8
5	11.8	0.0269	24.6	5	5.2	0.0119	10.8
6	13.3	0.0303	27.7	6	5.8	0.0132	12.1
8	16.3	0.0372	34.0	8	7.2	0.0164	15.0
10	17.7	0.0403	36.9	10	8.1	0.0185	16.9
12	19.1	0.0435	39.8	12	9.1	0.0207	19.0
15	20.5	0.0467	42.7	15	10.4	0.0237	21.7
20	22.4	0.0511	46.7	20	12.3	0.0280	25.6
25	23.6	0.538	49.2	25	13.5	0.0308	28.1
30	24.4	0.0556	50.8	30	14.4	0.0328	30.0
45	25.8	0.0588	53.8	45	15.7	0.0358	32.7
60	26.3	0.0599	54.8	60	16.0	0.0365	33.3
90	26.6	0.0606	55.4	90	16.1	0.0367	33.5

Comments: In method, A the reaction slowly formed a white solid polysiloxane that sequestered some water and so restricted the yield of HCl(g). In method B, the lesser yield of HCl(g) (as compared to method A) was caused by dissolution of HCl(g) in the excess water.

UN 1780 — Fumaryl Chloride, ClOCCH=CHCOCl

Fumaryl chloride is a liquid with a relative molar mass of 152.96 and a room-temperature density of 1.41 g/cm^3. In method A, 2.00 mmol of water was added to 1.00 mmol of it. In method B, 1.00 mmol of it was added to 10.0 mmol of water. Reaction according to the equation

$$\mathrm{ClOCCH{=}CHCOCl} + 2\ \mathrm{H_2O} \longrightarrow 2\ \mathrm{HCl} + \mathrm{HOOCCH{=}CHCOOH}$$

was taken as the source of HCl. Generation of 2.00 mmol of gas corresponded to an increase in volume of 32.0 mL in the calibrated apparatus.

1999 Experimental Results for Fumaryl Chloride

Method A				Method B			
Time (min)	Volume of Gas (mL)	Mass of HCl (g)	Yield (%)	Time (min)	Volume of Gas (mL)	Mass of HCl (g)	Yield (%)
1	0	-	-	1	0.3	-	-
5	0.3	-	-	5	0.3	-	-
10	0.3	-	-	10	0	-	-
20	0.3	-	-	20	0	-	-

Comments: Essentially no gas formation was observed.

UN 1784 — Hexyltrichlorosilane, $C_6H_{13}SiCl_3$

Hexyltrichlorosilane is a liquid with a relative molar mass of 219.62 and a room-temperature density of 1.107 g/cm^3. In method A, 1.00 mmol of it was mixed with 1.50 mmol of water. In method B, 1.00 mmol of it was mixed with 7.50 mmol of water. Reaction according to the equation

$$C_6H_{13}SiCl_3 + 3/2\ H_2O \longrightarrow 3\ HCl + [C_6H_{13}SiO_{3/2}]_n \text{ polymer}$$

was taken as the source of HCl(g). The theoretical yield of HCl(g) (3.00 mmol) corresponded to 48.0 mL of gas in the calibrated experimental apparatus.

2003 Experimental Data for Hexyltrichlorosilane

Method A				Method B			
Time (min)	Volume of Gas (mL)	Mass of HCl (g)	Yield (%)	Time (min)	Volume of Gas (mL)	Mass of HCl (g)	Yield (%)
1	0.5	0.0011	1.0	1	0.6	0.0014	1.3
2	1.0	0.0023	2.1	2	1.0	0.0023	2.1
3	1.4	0.0032	2.9	3	1.3	0.0030	2.7
4	1.8	0.0041	3.8	4	1.9	0.0043	4.0
5	2.1	0.0048	4.4	5	2.7	0.0062	5.6
6	2.4	0.0055	5.0	6	4.1	0.0093	8.5
8	3.0	0.0068	6.3	7	5.7	0.0130	11.9
10	3.6	0.0082	7.5	8	7.8	0.0178	16.3
12	4.2	0.0096	8.8	9	10.0	0.0228	20.8
15	5.2	0.0119	10.8	10	13.0	0.0296	27.1
20	6.9	0.0157	14.4	11	15.0	0.0342	31.3
30	10.2	0.0232	21.3	12	16.3	0.0372	34.0
40	14.4	0.033	30.0	13	17.5	0.0399	36.5
50	18.3	0.042	38.1	15	19.1	0.0435	39.8
60	21.5	0.049	44.8	17	19.8	0.0451	41.3
70	24.8	0.057	51.7	20	20.0	0.0456	41.7
80	26.6	0.061	55.4	30	20.0	0.0456	41.7
90	27.3	0.062	56.9				
100	27.5	0.063	57.3				
120	27.6	0.063	57.5				
150	27.7	0.063	57.7				

Comments: In method A, The reaction slowly formed a solid polysiloxane that sequestered some water. In method B, the reaction also slowly formed a solid polysiloxane that sequestered some reactant. No maximum was observed on the HCl(g) yield curve.

UN 1799 — Nonyltrichlorosilane, $C_9H_{19}SiCl_3$

Nonyltrichlorosilane is a liquid with a relative molar mass of 261.70 and a room-temperature density of 1.050 g/cm^3. In method A, 1.00 mmol of it was mixed with 1.50 mmol of water. In method B, 1.00 mmol of it was mixed with 7.50 mmol of water. Reaction according to the equation

$$C_9H_{19}SiCl_3 + 3/2\ H_2O \longrightarrow 3\ HCl + [C_9H_{19}SiO_{3/2}]_n \text{ polymer}$$

was taken as the source of HCl(g). The theoretical yield of HCl(g) (3.00 mmol) corresponded to 48.0 mL of gas in the calibrated experimental apparatus.

2003 Experimental Data for Nonyltrichlorosilane

Method A				Method B			
Time (min)	Volume of Gas (mL)	Mass of HCl (g)	Yield (%)	Time (min)	Volume of Gas (mL)	Mass of HCl (g)	Yield (%)
1	0.9	0.0021	1.9	1	1.4	0.0032	2.9
2	2.0	0.0046	4.2	2	2.5	0.0057	5.2
3	2.8	0.0064	5.8	3	3.8	0.0087	7.9
4	3.4	0.0077	7.1	4	4.9	0.0112	10.2
5	3.8	0.0087	7.9	5	5.6	0.0128	11.7
7	4.6	0.0105	9.6	7	6.8	0.0155	14.2
10	5.5	0.0125	11.5	10	8.4	0.0191	17.5
15	6.8	0.0155	14.2	15	10.8	0.0246	22.5
20	7.6	0.0173	15.8	20	13.5	0.031	28.1
25	8.3	0.0189	17.3	25	16.2	0.037	33.8
30	9.0	0.0205	18.8	30	19.3	0.044	40.2
40	10.1	0.0230	21.0	35	22.7	0.052	47.3
50	11.0	0.0251	22.9	40	24.8	0.057	51.7
60	11.6	0.0264	24.2	45	25.7	0.059	53.5
75	12.3	0.0280	25.6	50	26.2	0.060	54.6
90	13.0	0.0296	27.1	60	26.4	0.060	55.0
120	13.9	0.0317	29.0	90	26.5	0.060	55.2
150	14.2	0.0324	29.6				
180	14.4	0.0328	30.0				

Comments: In method A, the reaction formed a viscous polymeric siloxane that apparently sequestered water. In method B, dissolution of HCl(g) in excess water was not observed towards the end of the reaction [no maximum on the HCl(g) yield curve].

UN 1800 — Octadecyltrichlorosilane, $C_{18}H_{37}SiCl_3$

Octadecyltrichlorosilane is a liquid with a relative molar mass of 387.94 and a room-temperature density of 0.984 g/cm^3. In method A, 1.00 mmol of it was mixed with 1.50 mmol of water. In method B, 1.00 mmol of it was mixed with 7.50 mmol of water. Reaction according to the equation

$$C_{18}H_{37}SiCl_3 + 3/2\ H_2O \longrightarrow 3\ HCl + [C_{18}H_{37}SiO_{3/2}]_n \text{ polymer}$$

was taken as the source of HCl(g). The theoretical yield of HCl(g) (3.00 mmol) corresponded to 48.0 mL of gas in the calibrated experimental apparatus.

2003 Experimental Data for Octadecyltrichlorosilane

Method A				Method B			
Time (min)	Volume of Gas (mL)	Mass of HCl (g)	Yield (%)	Time (min)	Volume of Gas (mL)	Mass of HCl (g)	Yield (%)
1	0.0	0.00	0.0	1	0.0	0.00	0.0
2	0.0	0.00	0.0	2	0.0	0.00	0.0
4	0.0	0.00	0.0	4	0.0	0.00	0.0
6	0.0	0.00	0.0	6	0.0	0.00	0.0
8	0.0	0.00	0.0	8	0.5	0.0011	1.0
10	0.0	0.00	0.0	9	3.0	0.0068	6.3
12	0.3	0.0007	0.6	10	6.9	0.0157	14.4
14	0.9	0.0021	1.9	11	11.2	0.0255	23.3
16	2.3	0.0052	4.8	12	14.7	0.034	30.6
18	3.9	0.0089	8.1	13	17.4	0.040	36.3
20	5.4	0.0123	11.3	14	19.3	0.044	40.2
22	6.6	0.0150	13.8	15	20.8	0.047	43.3
25	8.5	0.0194	17.7	16	22.0	0.050	45.8
30	11.0	0.0251	22.9	17	22.9	0.052	47.7
35	12.8	0.0292	26.7	18	23.6	0.054	49.2
40	14.5	0.033	30.2	20	24.0	0.055	50.0
45	15.5	0.035	32.3	22	24.1	0.055	50.2
50	16.4	0.037	34.2	25	24.2	0.055	50.4
60	18.4	0.042	38.3	30	24.2	0.055	50.4
75	19.8	0.045	41.3				
90	20.0	0.046	41.7				

Comments: In method A, the evolution of gas began only after an induction period, suggesting that the reaction was autocatalytic. A solid polysiloxane formed. Evidently, some water was prevented from reaction by being bound by this by-product. In method B, the reaction got under way slowly. No dissolution of HCl(g) in excess water was observed towards the end of the reaction [no maximum on the HCl(g) yield curve].

UN 1801 — Octyltrichlorosilane, $C_8H_{17}SiCl_3$

Octyltrichlorosilane is a liquid with a relative molar mass of 247.67 and a room-temperature density of 1.070 g/cm^3. In method A, 1.00 mmol of it was mixed with 1.50 mmol of water. In method B, 1.00 mmol of it was mixed with 7.50 mmol of water. Reaction according to the equation

$$C_8H_{17}SiCl_3 + 3/2\ H_2O \longrightarrow 3\ HCl + [C_8H_{17}SiO_{3/2}]_n \text{ polymer}$$

was taken as the source of HCl(g). The theoretical yield of HCl(g) was 3.00 mmol, which corresponded to 48.0 mL of gas in the calibrated experimental apparatus.

2003 Experimental Data for Octyltrichlorosilane

Method A				Method B			
Time (min)	Volume of Gas (mL)	Mass of HCl (g)	Yield (%)	Time (min)	Volume of Gas (mL)	Mass of HCl (g)	Yield (%)
1	2.8	0.0064	5.8	1	2.6	0.0059	5.4
2	4.4	0.0100	9.2	2	3.8	0.0087	7.9
3	5.3	0.0121	11.0	3	4.5	0.0103	9.4
4	6.5	0.0148	13.5	4	5.0	0.0114	10.4
5	7.2	0.0164	15.0	5	5.7	0.0130	11.9
7	8.7	0.0198	18.1	7	7.0	0.0160	14.6
10	10.6	0.0242	22.1	10	9.5	0.0217	19.8
15	13.2	0.0301	27.5	15	12.1	0.0276	25.2
20	15.5	0.035	32.3	20	13.4	0.031	27.9
25	17.5	0.040	36.5	30	14.2	0.032	29.6
30	19.3	0.044	40.2	40	14.3	0.033	29.8
45	22.6	0.052	47.1	50	14.3	0.033	29.8
60	24.9	0.057	51.9				
75	26.2	0.060	54.6				
90	29.1	0.066	60.6				
120	31.1	0.071	64.8				
150	31.1	0.071	64.8				

Comments: In method A, the substance slowly reacted to form a viscous polymeric siloxane that sequestered some water and about two-thirds of the theoretical amount of HCl(g). In method B, a solid polymer formed in the early stage of the reaction. This material trapped a portion of the monomer, preventing it from reacting with water. No absorption of HCl(g) in excess water was observed towards the end of the reaction [i.e., there was no maximum on the HCl(g) yield curve].

UN 1804 — Phenyltrichlorosilane, $C_6H_5SiCl_3$

Phenyltrichlorosilane is a liquid with a relative molar mass of 211.55 and a room-temperature density of 1.321 g/cm^3. In method A, 1.00 mmol of it was mixed with 1.50 mmol of water. In method B, 1.00 mmol of it was mixed with 7.50 mmol of water. Reaction according to the equation

$$C_6H_5SiCl_3 + 3/2\ H_2O \longrightarrow 3\ HCl + [C_6H_5SiO_{3/2}]_n \text{ polymer}$$

was taken as the source of HCl(g). The theoretical yield of HCl(g) (3.00 mmol) corresponded to 48.0 mL of gas in the calibrated experimental apparatus.

2003 Experimental Results for Phenyltrichlorosilane

Method A				Method B			
Time (min)	Volume of Gas (mL)	Mass of HCl (g)	Yield (%)	Time (min)	Volume of Gas (mL)	Mass of HCl (g)	Yield (%)
1	0.5	0.0011	1.0	1	7.1	0.016	14.8
2	0.9	0.0021	1.9	2	21.0	0.054	43.8
3	1.5	0.0034	3.1	3	23.8	0.109	49.6
4	2.1	0.0048	4.4	4	24.5	0.056	51.0
5	2.9	0.0066	6.0	5	24.5	0.056	51.0
6	3.6	0.0082	7.5	6	24.4	0.056	50.8
7	4.2	0.0096	8.8	7	24.2	0.055	50.4
8	4.9	0.0112	10.2	8	24.0	0.055	50.0
9	5.5	0.0125	11.5	9	23.9	0.054	49.8
10	6.2	0.0141	12.9	10	23.8	0.054	49.6
12	7.5	0.0171	15.6	12	23.2	0.053	48.3
15	9.3	0.0212	19.4	15	22.8	0.052	47.5
20	12.0	0.0274	25.0	20	21.9	0.050	45.6
25	16.0	0.0365	33.3	30	20.5	0.048	42.7
30	22.4	0.0511	46.7	45	18.5	0.042	38.5
35	39.5	0.0900	82.3	60	16.8	0.038	35.0
40	39.6	0.0903	82.5	90	14.1	0.032	29.4
50	39.6	0.0903	82.5	120	12.2	0.028	25.4
				180	10.5	0.024	21.9
				240	9.8	0.022	20.4

Comments: In method A, The reaction formed a voluminous white solid polysiloxane but also produced gaseous HCl(g) in good yield (82%). In the final stages, the rate of reaction suddenly increased, nearly doubling the amount of HCl(g) within a 5-min interval. In method B, the yield of HCl(g) was less than the theoretical amount because of sequestration of some reactant by the polysiloxane by-product and dissolution of HCl(g) in the excess water. A maximum on the yield curve of HCl(g) was reached in 5 min.

UN 1806 — Phosphorus Pentachloride, PCl_5

Phosphorus pentachloride is a solid with a relative molar mass of 208.24. In method A, 4.00 mmol of water was added to 1.00 mmol of it. In method B, 1.00 mmol of it was added to 20.0 mmol of water. The reaction

$$PCl_5 + 4\,H_2O \longrightarrow 5\,HCl + H_3PO_4$$

was taken as the source of evolved gas. Generation of 5.00 mmol of gas corresponded to an increase in volume of 80.0 mL in the calibrated apparatus.

2003 Experimental Data for Phosphorus Pentachloride

Method A				**Method B**			
Time (min)	Volume of Gas (mL)	Mass of HCl (g)	Yield (%)	Time (min)	Volume of Gas (mL)	Mass of HCl (g)	Yield (%)
0.17	30.0	0.068	37.5	0.17	18.0	0.0410	22.5
0.33	35.0	0.080	43.8	0.33	11.0	0.0251	13.8
1	38.2	0.087	47.8	0.5	9.6	0.0219	12.0
2	41.6	0.095	52.0	1	6.8	0.0155	8.5
3	43.0	0.098	53.8	1.5	4.8	0.0109	6.0
5	44.4	0.101	55.5	2	3.4	0.0077	4.3
7	45.6	0.104	57.0	3	2.1	0.0048	2.6
10	45.8	0.104	57.3	5	1.0	0.0023	1.3
15	45.9	0.105	57.4	10	0.0	0.0000	0.0

Comments: In method A, more than 1 mmol of HCl(g) appeared within seconds. This confirmed that more than one Cl hydrolyzed per PCl_5 molecule. The reaction, however, remained incomplete after 90 min with respect to the theoretical yield of 5.0 mmol of HCl(g). In method B, HCl(g) also formed very rapidly. Visible signs of reaction vanished within the first minute. This was followed by dissolution of HCl(g) in the excess water (as shown by the maximum on the yield curve).

UN 1808 — Phosphorus Tribromide, PBr_3

Phosphorus tribromide is a liquid with a relative molar mass of 270.68 and a room-temperature density of 2.85 g/cm^3. In method A, 3.00 mmol of water was added to 1.00 mmol of the substance. In method B, 1.00 mmol of it was added to 15.0 mmol of water. Reaction according to the equation

$$PBr_3 + 3\ H_2O \longrightarrow 3\ HBr + P(OH)_3$$

was taken as the source of HBr. Generation of 3.00 mmol of gas corresponded to an increase in volume of 48.0 mL in the calibrated apparatus.

1999 Experimental Results for Phosphorus Tribromide

Method A				Method B			
Time (min)	Volume of Gas (mL)	Mass of HBr (g)	Yield (%)	Time (min)	Volume of Gas (mL)	Mass of HBr (g)	Yield (%)
1	1.6	0.0081	3.3	1	0	0	0
2	4	0.0202	8.3	2	0	0	0
3	8	0.0405	17	3	0	0	0
5	16	0.0809	33	5	0	0	0
10	32	0.162	67	10	0	0	0
20	43	0.217	90	20	0	0	0
25	45	0.228	94	25	0	0	0
30	46	0.233	96	30	0	0	0
60	47	0.238	98	60	0	0	0

Comments: In method A, the reaction slowly generated HBr(g) and after an hour had liberated essentially the full theoretical amount. In method B, in the presence of excess water, the solubility of HBr in water was never exceeded, and the rate of solution of the HBr was so high that the gas dissolved before it could be released. Therefore, the substance was considered a non-TIHWR chemical, even though in the exothermic, violent conditions of a large spill, some HBr might well be released as a gas.

UN 1809 — Phosphorus Trichloride, PCl_3

Phosphorus trichloride is a liquid with a relative molar mass of 137.33. In method A, 3.00 mmol of water was added to 1.00 mmol of it. In method B, 1.00 mmol of it was added to 15.0 mmol of water. The reaction

$$PCl_3 + 3\ H_2O \longrightarrow 3\ HCl + P(OH)_3$$

was taken as the source of HCl. Generation of 2.00 mmol of HCl(g) corresponded to an increase in volume of 48.0 mL in the calibrated apparatus.

1999 Experimental Results for Phosphorus Trichloride

Method A				Method B			
Time (min)	Volume of Gas (mL)	Mass of HCl (g)	Yield (%)	Time (min)	Volume of Gas (mL)	Mass of HCl (g)	Yield (%)
1	26	0.059	54	1	16	0.036	33
2	40	0.091	83	2	9	0.021	19
3	44	0.100	92	3	5	0.0114	10
5	47	0.107	98	5	2	0.0046	4
10	48	0.109	100	10	1	0.0023	2
20	48	0.109	100	20	0.5	0.0011	1

2003 Experimental Results for Phosphorus Trichloride

Method A				Method B			
Time (min)	Volume of Gas (mL)	Mass of HCl (g)	Yield (%)	Time (min)	Volume of Gas (mL)	Mass of HCl (g)	Yield (%)
0.5	17.5	0.0399	36.5	0.5	11.8	0.0269	24.6
1	25.1	0.0572	52.3	1	16.8	0.0383	35.0
2	39.1	0.089	81.5	2	9.4	0.0214	19.6
3	43.2	0.098	90.0	3	5.2	0.0118	10.8
4	45.6	0.104	95.0	4	3.4	0.0077	7.1
5	46.7	0.106	97.3	5	2.2	0.0050	4.6
7	47.3	0.108	98.5	7	1.4	0.0032	2.9
10	48.0	0.109	100	10	1.1	0.0025	2.3
20	48.0	0.109	100	20	0.5	0.0011	1.0
				30	0.2	0.0005	0.4
				60	0.1	0.0002	0.2

Comments: The experiments were repeated in 2003 to obtain more data on the early stages of the reaction. In method A, the theoretical amount of the HCl(g) was generated in 10 min. In method B, essentially all of the HCl(g) that formed soon dissolved in the excess water to produce HCl(aq) (maxima on the yield curves). In the free atmosphere, probably close to one-third of the maximum yield of HCl would occur, because the gas would not remain in contact with the water for enough time (on the order of 1 min) to permit dissolution.

UN 1810 — Phosphorus Oxychloride, $POCl_3$

Phosphorus oxychloride, also called phosphoryl chloride, is a liquid with a relative molar mass of 153.33 and a room-temperature density of 1.675 g/cm^3. In method A, 3.00 mmol of water was added to 1.00 mmol of it. In method B, 1.00 mmol was added to 15.0 mmol of water. Reaction according to the equation

$$OPCl_3 + 3\ H_2O \longrightarrow 3\ HCl + OP(OH)_3$$

was taken as the source of evolved gas. Generation of 3.00 mmol of gas corresponded to an increase in volume of 48.0 mL in the calibrated apparatus.

1999 Experimental Results for Phosphorus Oxychloride

Method A				Method B			
Time (min)	Volume of Gas (mL)	Mass of HCl (g)	Yield (%)	Time	Volume of Gas	Mass of HCl (g)	Yield (%)
1	7	0.016	15	1	10	0.0228	21
2	7.5	0.0171	16	2	4.5	0.0103	9.4
3	8	0.0182	17	3	3	0.0068	6.3
5	8.5	0.0194	18	5	2	0.0046	4.2
10	9	0.0205	19	10	1.9	0.0043	4.0
20	10	0.0228	21	20	1.9	0.0043	4.0
30	11	0.0251	23				
60	12	0.0274	25				
180	13	0.0297	27				

2003 Experimental Results for Phosphorus Oxychloride

Method A				Method B			
Time (min)	Volume of Gas (mL)	Mass of HCl (g)	Yield (%)	Time (min)	Volume of Gas (mL)	Mass of HCl (g)	Yield (%)
				0.33	13.6	0.0310	28.3
0.5	6.2	0.0141	13	0.5	12.5	0.0285	26.0
1	7.3	0.0166	15	1	10.6	0.0242	22.1
2	7.8	0.0178	16	2	5.1	0.0116	11
3	8.2	0.0187	17	3	3.7	0.0084	7.7
				4	2.9	0.0066	6.0
5	8.9	0.0203	19	5	2.4	0.0055	5.0
10	9.5	0.0216	20	10	1.8	0.0041	3.8
20	10.7	0.0244	22	20	1.7	0.0039	3.5
30	11.6	0.0264	24				
60	12.7	0.0289	26				
120	13.3	0.0303	28				
180	13.8	0.0314	29				

Comments: The 1999 experiments were repeated in 2003 to obtain more data on the early stages of the reaction. In method A, about one-sixth of the HCl evolved as a gas in the first 2 min. Then the rate of evolution slowed dramatically. This suggested that hydrolysis of the first Cl atom according to the equation

$$\mathrm{OPCl_3 + H_2O \longrightarrow HCl + OPCl_2OH}$$

was substantially faster than hydrolysis of the second and third. In method B, HCl(g) formed rapidly and then dissolved quickly in the excess water [as indicated by the quick maxima in the HCl(g) yield curves]. In a spill into open water, air currents across the water's surface would sweep HCl(g) away and so reduce such dissolution.

UN 1816 — Propyltrichlorosilane, $CH_3CH_2CH_2SiCl_3$

Propyltrichlorosilane is a liquid with a relative molar mass of 177.53 and a room-temperature density of 1.195 g/cm^3. In method A, 1.00 mmol of it was mixed with 1.50 mmol of water. In method B, 1.00 mmol of it was mixed with 7.50 mmol of water. Reaction according to the equation

$$\mathrm{CH_3(CH_2)_2SiCl_3 + 3/2\ H_2O \longrightarrow 3\ HCl + [CH_3(CH_2)_2SiO_{3/2}]_n}\ \text{polymer}$$

was taken as the source of HCl(g). The theoretical yield of HCl(g) (3.00 mmol) corresponded to 48.0 mL of gas in the calibrated experimental apparatus.

2003 Experimental Results for Propyltrichlorosilane

Method A				**Method B**			
Time (min)	Volume of Gas (mL)	Mass of HCl (g)	Yield (%)	Time (min)	Volume of Gas (mL)	Mass of HCl (g)	Yield (%)
1	2.0	0.0046	4.2	1	7.2	0.016	15.0
2	4.8	0.0109	10.0	2	12.6	0.029	26.3
3	8.2	0.0187	17.1	3	15.7	0.036	32.7
4	12.2	0.0278	25.4	4	18.0	0.041	37.5
5	15.4	0.0351	32.1	5	19.1	0.044	39.8
6	17.8	0.0406	37.1	6	20.0	0.046	41.7
7	20.3	0.0463	42.3	7	20.4	0.046	42.5
8	22.4	0.0511	46.7	8	20.6	0.047	42.9
9	24.2	0.0552	50.4	9	20.7	0.047	43.1
10	25.8	0.0588	53.8	10	20.7	0.047	43.1
11	27.6	0.0629	57.5	15	20.4	0.046	42.5
12	29.7	0.0677	61.9	20	19.9	0.045	41.5
13	32.8	0.0748	68.3	25	19.3	0.044	40.2
14	36.6	0.0834	76.3	30	18.7	0.043	39.0
15	39.1	0.0891	81.5	40	18.1	0.041	37.7
16	40.5	0.0923	84.4	50	17.7	0.040	36.9
18	42.8	0.0975	89.2	60	17.3	0.039	36.0
20	44.1	0.1005	91.9	90	17.0	0.039	35.4
25	44.4	0.1012	92.5				
30	44.5	0.1014	92.7				

Comments: In method A, the reaction formed a white solid polymeric by-product. Despite this, the system eventually produced nearly 93% of the theoretical amount of HCl(g). In method B, the smaller yield of HCl(g) was ascribed to (1) sequestration of some monomer by the polysiloxane product and (2) dissolution of HCl(g) in the excess water to produce HCl(aq).

UN 1818 — Tetrachlorosilane, $SiCl_4$

Tetrachlorosilane, a liquid, has a relative molar mass of 169.90 and a room-temperature density of 1.483 g/cm^3. Reaction according to the equation

$$SiCl_4 + 2\ H_2O \longrightarrow 4\ HCl + (SiO_2)_n \text{ polymer}$$

was taken as the only source of evolved gas. In all experiments, 1.00 mmol (0.170 g) of $SiCl_4$ was used, so the theoretical yield of HCl(g) was 4.00 mmol (0.146 g). This amount of gas corresponded to 64.0 mL of gas in the calibrated experimental apparatus.

1999 Experimental Results for Tetrachlorosilane

Method A				**Method B**			
Time (min)	Volume of Gas (mL)	Mass of HCl (g)	Yield (%)	Time (min)	Volume of Gas (mL)	Mass of HCl (g)	Yield (%)
1	15	0.034	23	1	20	0.046	31
5	18	0.041	28	5	22	0.050	34
10	19	0.043	30	10	21	0.048	33
20	20	0.046	31	20	19	0.043	30

2003 Experimental Results for Tetrachlorosilane

Method A				**Method B**			
Time (min)	Volume of Gas (mL)	Mass of HCl (g)	Yield (%)	Time (min)	Volume of Gas (mL)	Mass of HCl (g)	Yield (%)
0.5	10.1	0.0230	15.8	0.5	14.7	0.0335	23.0
1	14.7	0.0335	23.0	1	20.9	0.048	32.7
2	16.4	0.0374	25.6	2	21.5	0.049	33.6
3	17.2	0.0392	26.9	3	22.3	0.051	34.8
4	17.8	0.0406	27.8	4	22.8	0.052	35.6
5	18.2	0.0415	28.4	5	23.1	0.053	36.1
7	18.8	0.0428	29.4	7	22.9	0.052	35.8
10	19.3	0.0440	30.2	10	22.1	0.050	34.5
20	20.5	0.0467	32.0	20	19.8	0.045	30.9
30	20.8	0.0474	32.5	30	19.4	0.044	30.3
45	21.1	0.0481	33.0	45	18.8	0.043	29.4
60	21.3	0.0485	33.3	60	18.4	0.042	28.8

Comments: The 1999 experiments were repeated in 2003 to obtain more information on the early course of the reaction. A white solid formed immediately upon mixing the reactants. This siliceous by-product almost certainly sequestered water, preventing productive contact between the reactants [its probable formula was $(SiO_2)_n \cdot xH_2O$]. The yield-versus-time curves for HCl(g) in method B had maxima. This indicated that the rate of dissolution of HCl(g) in the excess water exceeded its rate of production toward the end of the experiment. The yield of HCl(g) in the two method B runs settled to a final average of 29.4%, or 1.18 mmol. If the hydrolysis of the test substance was complete at this point, then 8.00 mmol of water was present and (4.00 – 1.18) mmol of HCl was dissolved in it. The mole fraction of HCl in this solution was

$$X_{\mathrm{HCl}} = \frac{n_{\mathrm{HCl}}}{n_{\mathrm{HCl}} + n_{\mathrm{H_2O}}} = \frac{(4.00-1.18)}{(4.00-1.18)+8.00} = 0.26$$

This value is quite close to the literature value for X_{HCl} in saturated aqueous solutions of HCl under the conditions of the experiments (see Section C.1.2).

UN 1827 — Tin Tetrachloride, $SnCl_4$

Tin tetrachloride, also called stannic chloride, is a liquid with a relative molar mass of 266.6 and a room-temperature density of 2.28 g/cm^3. In method A, 1.00 mmol of the substance was mixed with 4.00 mmol of water. In method B, 1.00 mmol was mixed with 20.0 mmol of water. Reaction according to the equation

$$SnCl_4 + 4\ H_2O \longrightarrow 4\ HCl + SnO_2 \cdot 2H_2O$$

was used for computations of mass and yield. The theoretical yield of HCl(g) was 4.00 mmol, which corresponded to 64.0 mL of gas in the calibrated experimental apparatus.

1999 Experimental Results for Tin Tetrachloride

Method A				Method B			
Time (min)	Volume of Gas (mL)	Mass of HCl (g)	Yield (%)	Time (min)	Volume of Gas (mL)	Mass of HCl (g)	Yield (%)
1	1	0.00057	1.6	1	1	0.00057	1.6
5	1	0.00057	1.6	5	0.5	0.0028	1
10	1	0.00057	1.6	10	0	0	0
20	1	0.00057	1.6	20	0	0	0

Comments: Less than 2% of the theoretical amount of HCl(g) was generated.

UN 1831 — Oleum (fuming sulfuric acid)

Oleum, a liquid, has an approximate relative molar mass of 122. In method A, 1.0 mmol of it was mixed with 1.00 mmol of water. In method B, 1.0 mmol was mixed with 5.00 mmol of water. No equation was proposed for a reaction generating a TIH gas beyond the following

$$H_2SO_4{\bullet}(SO_3)_n + n\ H_2O \longrightarrow H_2SO_4$$

1999 Experimental Results for Oleum

Method A				Method B			
Time (min)	Volume of Gas (mL)	Mass of Gas (g)	Yield (%)	Time (min)	Volume of Gas (mL)	Mass of Gas (g)	Yield (%)
1	1	-	-	1	1	-	-
5	1	-	-	5	1	-	-
10	0.5	-	-	10	0.5	-	-
20	0.5	-	-	20	0.5	-	-

Comments: Little evidence of a gaseous product was detected. The dissolution reaction in water produced a large amount of heat, which probably caused the slight volume change (on the order of 1 mL). The TIH concern associated with this material was the production of an acidic mist. However, neither method A nor B simulated conditions that might generate an acidic mist.

UN 1834 — Sulfuryl Chloride, SO_2Cl_2

Sulfuryl chloride is a liquid with a relative molar mass of 134.96 and a room-temperature density of 1.67 g/cm^3. In method A, 2.00 mmol of water was added to 1.00 mmol of it. In method B, 1.00 mmol of it was mixed with 10.0 mmol of water. The reaction

$$SO_2Cl_2 + 2\ H_2O \longrightarrow 2\ HCl + H_2SO_4$$

was taken as the source of evolved gas. Generation of 2.00 mmol of gas corresponded to an increase in volume of 32.0 mL in the calibrated apparatus.

1999 Experimental Results for Sulfuryl Chloride

Method A				Method B			
Time (min)	Volume of Gas (mL)	Mass of HCl (g)	Yield (%)	Time (min)	Volume of Gas (mL)	Mass of HCl (g)	Yield (%)
1	3	0.0068	9	1	4	0.0091	12
2	5	0.0114	16	2	5	0.0114	16
3	6.5	0.015	20	3	5.5	0.0125	17
5	10	0.023	31	5	6	0.0137	19
10	18	0.041	56	10	6.5	0.0148	20
15	24	0.055	75	15	5.5	0.0125	17
20	26	0.059	81	20	5	0.0114	16
30	28	0.064	88	30	5	0.0114	16
60	30	0.068	94				
90	31	0.071	97				
120	31	0.071	97				

Comments: In method A, essentially the stoichiometric amount of gaseous HCl was generated, but slowly. In method B, some HCl dissolved in the excess water after it was generated. The acidic by-product H_2SO_4 that was co-dissolved in the excess water certainty reduced the amount of HCl it could dissolve and so raised the yield of HCl(g). In a real spill, the by-product H_2SO_4 would be diluted and the amount of HCl(g) would be less.

UN 1836 — Thionyl Chloride, $SOCl_2$

Thionyl chloride, a liquid, has a relative molar mass of 118.97 and a room-temperature density of 1.64 g/cm^3. In method A, 1.00 mmol was mixed with 1.00 mmol of water. In method B, 1.00 mmol was added to 5.00 mmol of water. The reaction with water generates two TIH gases, hydrogen chloride and sulfur dioxide, according to the equation

$$SOCl_2 + H_2O \longrightarrow 2\ HCl + SO_2$$

The theoretical yield of TIH gases is 3.00 mmol, which corresponds to 48.0 mL of mixed gases (32.0 mL of HCl and 16.0 mL of SO_2) in the calibrated experimental apparatus.

1999 Experimental Results for Thionyl Chloride, Method A

Time (min)	Volume of Gases (mL)	Mass of HCl (g)	Yield of HCl (%)	Mass of SO_2 (g)	Yield of SO_2 (%)
1	15	0.023	31	0.020	31
2	35	0.053	73	0.047	73
3	46	0.070	96	0.061	96
5	48	0.073	100	0.064	100
10	46	0.073	100	0.056	87.5
20	45	0.073	100	0.052	81

1999 Experimental Results for Thionyl Chloride, Method B

Time (min)	Volume of Gases (mL)	Mass of HCl (g)	Yield of HCl (%)	Mass of SO_2 (g)	Yield of SO_2 (%)
1	33	0.041	56	0.060	94
2	35	0.043	59	0.064	100
3	33.5	0.040	55	0.064	100
5	32	0.039	53	0.060	94
10	30	0.039	53	0.052	81
20	29	0.039	53	0.048	75

Comments: The reaction generated two TIH gases, HCl and SO_2, concurrently in a 2:1 molar ratio, but the experiment measured only the total volume of gas, not their separate volumes. In method A, the theoretical yield of the mixed gases appeared within 5 min of mixing. The amounts of HCl(g) and SO_2(g) at 1, 2, and 3 min were calculated by assuming that the 2:1 molar ratio held at those points in time (that is, that no differential dissolution of gas occurred before the water was consumed by the reaction). At the end of the reaction some absorption of sulfur dioxide into the manometric fluid (octane saturated with HCl) was observed. In method B, the partition into mass of HCl(g) and mass of SO_2(g) was estimated by assuming that 40% of the total HCl dissolved instantly in the excess water.

UN 1838 — Titanium Tetrachloride, $TiCl_4$

Titanium tetrachloride, a liquid, has a relative molar mass of 189.71 and a room-temperature density of 1.730 g/cm^3. In method A, 1.00 mmol of the substance was mixed with 2.00 mmol of water. In method B, 1.00 mmol was mixed with 10.0 mmol of water. Reaction according to the equation

$$TiCl_4 + 2\ H_2O \longrightarrow 4\ HCl + TiO_2$$

was taken as the source of HCl(g). The theoretical yield of HCl(g) was 4.00 mmol, which corresponded to 64.0 mL of gas in the calibrated experimental apparatus.

1999 Experimental Results for Titanium Tetrachloride

Method A				Method B			
Time (min)	Volume of Gas (mL)	Mass of HCl (g)	Yield (%)	Time (min)	Volume of Gas (mL)	Mass of HCl (g)	Yield (%)
1	10	0.023	16	1	10	0.0182	16
5	17	0.039	27	5	14	0.027	8
10	17	0.039	27	10	4	0.030	6
20	17	0.039	27	20	4	0.030	6

2003 Experimental Results for Titanium Tetrachloride

Method A				Method B			
Time (min)	Volume of Gas (mL)	Mass of HCl (g)	Yield (%)	Time (min)	Volume of Gas (mL)	Mass of HCl (g)	Yield (%)
0.5	7.2	0.0164	11.3	0.5	7.4	0.0169	11.6
1	11.3	0.0257	17.7	1	11.2	0.0255	17.5
2	15.7	0.0358	24.5	2	9.2	0.0210	14.4
3	17.1	0.0390	26.7	3	7.1	0.0162	11.1
4	18.2	0.0415	28.4	4	5.7	0.0130	8.9
5	18.6	0.0424	29.1	5	5.1	0.0116	8.0
7	18.9	0.0431	29.5	7	4.7	0.0107	7.3
10	19.1	0.0435	29.8	10	4.2	0.0096	6.6
20	19.2	0.0438	30.0	20	4.0	0.0091	6.3
30	19.3	0.0440	30.2	30	3.8	0.0087	5.9
60	19.4	0.0442	30.3	60	3.7	0.0084	5.8

Comments: The 1999 experiments were repeated in 2003 to obtain more data on the early course of the reaction. $TiCl_4$ reacts very vigorously with water. In method A, the injected water was immediately covered with a white crust, probably titanium dioxide. This might have prevented complete reaction of water with the remaining $TiCl_4$, despite the stirring. In method B, the yield of the gas peaked and then diminished. Apparently, some HCl(g) later dissolved in the excess water. In a spill into open water, air currents across the water's surface would probably reduce such dissolution by blowing the HCl(g) away.

According to the literature,[4] mixing $TiCl_4$ and a 50-fold excess of H_2O gives an immediate voluminous precipitate of $TiO_2 \cdot x(H_2O)$, but the yield of HCl(aq) is substantially less than the amount calculated on the basis of the preceding chemical equation.

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[4] Information obtained from an on-line commercial database, "Gmelin," through a multi-database portal provided by CAS. Additional information can be obtained at http://www.cas.org/ONLINE/DBSS/gmelinss.html.

UN 1939 — Phosphorus Oxybromide, $OPBr_3$

Phosphorus oxybromide, also called phosphoryl bromide, is a solid with a relative molar mass of 286.70. In method A, 3.00 mmol of water was added to 1.00 mmol of it. In method B, 1.00 mmol of it was added to 15.0 mmol of water. The reaction

$$OPBr_3 + 3\,H_2O \longrightarrow 3\,HBr + OP(OH)_3$$

was taken as the source of evolved gas. Generation of 3.00 mmol of gas corresponded to an increase in volume of 48.0 mL in the calibrated apparatus.

2003 Experimental Data for Phosphorus Oxybromide

Method A				Method B			
Time (min)	Volume of Gas (mL)	Mass of HBr (g)	Yield (%)	Time (min)	Volume of Gas (mL)	Mass of HBr (g)	Yield (%)
3	0.9	0.0046	1.9	1	0.0	0.00	0.0
5	1.5	0.0076	3.1	2	0.0	0.00	0.0
10	2.3	0.0116	4.8	3	0.0	0.00	0.0
15	3.4	0.0172	7.1	5	0.0	0.00	0.0
20	4.4	0.0223	9.2	10	0.0	0.00	0.0
30	5.7	0.0288	11.9	15	0.0	0.00	0.0
40	6.8	0.0344	14.2	20	0.0	0.00	0.0
50	7.6	0.038	15.8	30		0.00	0.0
60	8.4	0.042	17.5				
90	9.8	0.050	20.4				
120	11.4	0.058	23.8				
180	13.0	0.066	27.0				
240	13.3	0.067	27.7				

Comments: In method A, somewhat less than one-third of the theoretical amount of HBr evolved slowly. This suggests little hydrolysis of the second and third Br atoms. Because the amount of water used in the experiment was 3.00 mmol, water was effectively in excess and some HBr(g) dissolved in it. In method B, there was evidence of reaction, but the HBr evidently dissolved immediately in the excess water.

It was interesting to compare the hydrolysis of this compound to the hydrolysis of phosphorus oxychloride (UN 1810). In method A, the ultimate yields of HBr(g) and HCl(g) were nearly identical but HBr(g) formed much more slowly. The hydrolysis of phosphorus oxychloride in method B generated HCl(g) that subsequently mostly dissolved in the excess water. This contrasts to the hydrolysis of phosphorus oxybromide in method B, where the dissolution of HBr in the excess water was rapid enough, relative to the rate of formation of HBr, to prevent evolution of HBr(g).

UN 2308 — Nitrosylsulfuric Acid, HO_3SONO

Pure nitrosylsulfuric acid is a solid with a relative molar mass of 127.07. In method A, 1.00 mmol of water was added to 1.00 mmol of it. In method B, 1.00 mmol of it was added to 5.00 mmol of water. The generation of the TIH gas nitrogen dioxide (NO_2) was modeled by the equations:

$$3\ HO_3SONO + 3\ H_2O \longrightarrow 3\ H_2SO_4 + 3\ HONO$$
$$3\ HONO \longrightarrow 2\ NO + HNO_3 + H_2O$$
$$2\ NO + O_2 \longrightarrow 2\ NO_2$$

The sum of these equations is

$$3\ HO_3SONO + 3\ H_2O \longrightarrow 3\ H_2SO_4 + HNO_3 + H_2O + 2\ NO_2$$

Because the formation of NO_2 requires O_2, the nitrogen purge was omitted in the experiments.

1999 Experimental Results for Nitrosylsulfuric Acid

Method A				**Method B**			
Time (min)	Volume of Gas (mL)	Mass of NO_2 (g)	Yield (%)	Time (min)	Volume of Gas (mL)	Mass of NO_2 (g)	Yield (%)
1	3	0.0086	28	1	11	0.0316	103
5	1	0.0028	9.1	5	10.5	0.0302	98
10	0.5	0.0014	4.5	10	9.5	0.0273	89
20	0	0	0	20	8.5	0.0244	79

Comments: According to the chemical equations, 1 mmol of O_2 was consumed for every 2 mmol of NO_2 that was generated. For this reason, the true yield of $NO_2(g)$ exceeded the amount indicated by the observed changes in volume by a factor of 3/2. The chemical equations also indicated that the theoretical yield of NO_2 from 1.00 mmol of nitrosylsulfuric acid is 0.667 mmol (0.0307 g). These factors were taken into account in computing the masses and yields in the table.

The formation of red $NO_2(g)$ was observed immediately in both experiments. In method A, the amount of $NO_2(g)$ diminished after the first minute as the gas dissolved in the by-product water or otherwise interacted with the other products. The drop in the amount of $NO_2(g)$ after the first minute in method B had a similar cause. The amount of NO_2 produced at 1 min in method B slightly exceeded the theoretical maximum, possibly because of side-reactions not represented above.

UN 2437 — Methylphenyldichlorosilane, $CH_3(C_6H_5)SiCl_2$

Methylphenyldichlorosilane is a liquid with relative molar mass of 191.13 and a room-temperature density of 1.176 g/cm^3. In method A, 1.00 mmol of it was mixed with 1.00 mmol of water. In method B, 1.00 mmol of it was mixed with 5.00 mmol of water. Reaction according to the equation

$$CH_3(C_6H_5)SiCl_2 + H_2O \longrightarrow 2\ HCl + [(CH_3)(C_6H_5)SiO]_n \text{ polymer}$$

was taken as the source of HCl(g). The theoretical yield of HCl(g) was 2.00 mmol, which corresponded to 32.0 mL of gas in the calibrated experimental apparatus.

2003 Experimental Data for Methylphenyldichlorosilane

Method A				Method B			
Time (min)	Volume of Gas (mL)	Mass of HCl (g)	Yield (%)	Time (min)	Volume of Gas (mL)	Mass of HCl (g)	Yield (%)
2	0.5	0.0011	1.6	2	0.6	0.038	1.9
5	1.3	0.0030	4.1	5	1.0	0.063	3.1
10	2.3	0.0052	7.2	10	1.6	0.100	5.0
15	3.2	0.0073	10.0	15	1.8	0.113	5.6
20	4.0	0.0091	12.5	20	2.0	0.125	6.3
25	4.7	0.0107	14.7	30	2.1	0.131	6.6
30	5.3	0.0121	16.6	45	2.2	0.138	6.9
40	6.2	0.0141	19.4	60	2.3	0.144	7.2
50	6.9	0.0157	21.6	90	2.3	0.144	7.2
60	7.3	0.0166	22.8				
90	7.8	0.0178	24.4				
120	8.1	0.0185	25.3				
150	8.2	0.0187	25.6				

Comments: In method A, the reaction slowly formed a very viscous liquid polysiloxane that sequestered a considerable proportion of the water. In method B, the liquid polysiloxane also formed. The fact that polymer was a liquid probably aided to the smooth dissolution of the HCl(g) in the excess water. No maximum was observed on the HCl(g) yield curve. The reaction strongly resembled that of diethyldichlorosilane (UN 1767) in its rate and yield and in the appearance of polysiloxane in the by-product.

UN 2442 —Trichloroacetyl Chloride, Cl_3CCOCl

Trichloroacetyl chloride is a liquid with relative molar mass of 181.83 and a room-temperature density of 1.629 g/cm^3. In method A, 1.00 mmol of it was mixed with 1.00 mmol of water. In method B, 1.00 mmol of it was mixed with 5.00 mmol of water. Reaction according to the equation

$$Cl_3CCOCl + H_2O \longrightarrow HCl + Cl_3CCOOH$$

was taken as the source of HCl(g). The theoretical yield of HCl(g) was 1.00 mmol, which corresponded to 16.0 mL of gas in the calibrated experimental apparatus.

Comments: Neither method A nor B yielded a measurable amount of gaseous HCl within 20 min. Thus, the rate of hydrolysis of the substance was negligibly small within this period.

UN 2691 — Phosphorus Pentabromide, PBr_5

Phosphorus pentabromide is a solid with a relative molar mass of 430.49. In method A, 4.00 mmol of water was added to 1.00 mmol of it. In method B, 1.00 mmol of it was added to 20.0 mmol of water. Reaction according to the equation

$$PBr_5 + 4\ H_2O \longrightarrow 5\ HBr + OP(OH)_3$$

was taken as the source of HBr. Generation of 5.00 mmol of gas corresponded to an increase in volume of 80.0 mL in the calibrated apparatus.

1999 Experimental Results for Phosphorus Pentabromide

Method A				**Method B**			
Time (min)	Volume of Gas (mL)	Mass of HBr (g)	Yield (%)	Time (min)	Volume of Gas (mL)	Mass of HBr (g)	Yield (%)
1	25.9	0.131	32.4	1	24.9	0.126	31.1
2	24.9	0.126	31.1	2	3.0	0.015	3.7
5	24.9	0.126	31.1	5	0	0	0
10	24.9	0.126	31.1	10	0	0	0

2003 Experimental Results for Phosphorus Pentabromide

Method A				Method B			
Time (min)	Volume of Gas (mL)	Mass of HBr (g)	Yield (%)	Time (min)	Volume of Gas (mL)	Mass of HBr (g)	Yield (%)
0.5	20.5	0.104	25.6	0.5	20.1	0.102	25.1
1	27.2	0.138	34.4	1	26.2	0.133	32.8
1.5	26.5	0.134	33.1	1.5	10.5	0.053	13.1
2	26.2	0.133	32.8	2	4.1	0.021	5.1
3	26.2	0.133	32.8	3	0.0	0.000	0.0
5	26.1	0.132	32.6	5	0.0	0.000	0.0

Comments: In method A, the reaction was rapid and so violent that small droplets of water were spattered onto the walls of the container and out of contact with the PBr_5. This initial reaction quickly gave about 35% of the theoretical amount of HBr as a gas. This was roughly 2 mmol of HBr out of the theoretical yield of 5 mmol. The initial reaction is therefore better represented as

$$PBr_5 + H_2O \longrightarrow 2\ HBr + OPBr_3$$

Subsequent production of HBr(g) took place only slowly. In method B, HBr(g) also formed very rapidly but then dissolved in the excess water within the first 3 min. This indicated that no more than first 2/5 of the theoretical amount of HBr(g) is unlikely to contribute to a TIH in a real spill. The remaining 3/5 of the HBr would dissolve as rapidly as it formed.

UN 2692 — Boron Tribromide, BBr_3

Boron tribromide is a colorless liquid with a relative molar mass of 250.54 and a room-temperature density of 2.650 g/cm^3. In method A, 3.00 mmol of water was added to 1.00 mmol of it. In method B, 1.00 mmol of it was mixed with 15.0 mmol of water. Reaction according to the equation

$$2\ BBr_3 + 2\ H_2O \longrightarrow 3\ HBr + B(OH)_3$$

was taken as the source of HBr(g) for computations of mass and yield. The theoretical yield of HBr(g) was 1.00 mmol, which corresponded to 48.0 mL of gas in the calibrated experimental apparatus.

2003 Experimental Data for Boron Tribromide

Method A				Method B			
Time (min)	Volume of Gas (mL)	Mass of HBr (g)	Yield (%)	Time (min)	Volume of Gas (mL)	Mass of HBr (g)	Yield (%)
0.17	35.0	0.1770	72.9	0.17	9.0	0.0455	18.8
0.35	47.6	0.2407	99.2	0.35	3.5	0.0177	7.3
0.5	48.9	0.2473	102	0.5	1.5	0.0076	3.1
1	49.8	0.2519	104	1	0.6	0.0030	1.3
2	49.9	0.2524	104	2	0.2	0.0010	0.4
5	49.9	0.2524	104	5	0.0	0.0000	0.0

Comments: In method A, the reaction was explosively rapid and generated the full theoretical amount of HBr(g) within 5 s. In method B, the reaction was again very rapid. Essentially all of the HBr(g) that formed quickly dissolved in the excess water to produce HBr(aq) (note the quick maximum on the yield curve).

UN 2806 — Lithium Nitride, Li_3N

Lithium nitride is a solid with a relative molar mass of 34.82. In method A, 1.12 mmol of water was added to 0.373 mmol of it. In method B, 0.373 mmol of it was mixed with 5.60 mmol of water. Reaction according to the equation

$$Li_3N + 3\ H_2O \longrightarrow 3\ LiOH + NH_3$$

was taken as the source of NH_3(g) for computations of mass and yield. The theoretical yield of NH_3(g) was 0.373 mmol, which corresponded to 5.96 mL of gas in the calibrated experimental apparatus.

2003 Experimental Data for Lithium Nitride

Method A				Method B			
Time (min)	Volume of Gas (mL)	Mass of NH_3 (g)	Yield (%)	Time (min)	Volume of Gas (mL)	Mass of NH_3 (g)	Yield (%)
0.167	6.0	0.00619	97.4	0.167	6.0	0.00619	97.4
0.5	6.0	0.00619	97.4	0.5	6.0	0.00619	97.4
1	6.0	0.00619	97.4	1	5.9	0.00609	95.8
2	6.0	0.00619	97.4	2	5.8	0.00599	94.2
5	6.0	0.00619	97.4	5	5.7	0.00588	92.5
				10	5.70	0.00588	92.5

Comments: Less than 1.00 mmol of substance was used because of the violence of the reaction. The safe amount was established in preliminary tests. A flame-like flash occurred instantly upon mixing the Li_3N and water. This suggested that some air-oxidation [according to the equation: $2\ Li_3N + O_2 \longrightarrow 3\ Li_2O + 2\ NO_2(g)$, for example] might have occurred. However, the product gases were colorless, and $NO_2(g)$ is brown. Close to the theoretical amount of $NH_3(g)$ was generated very rapidly in both methods. When excess water was present (method B), some of the $NH_3(g)$ dissolved to give $NH_3(aq)$. However, the excess water in method B had a high concentration of dissolved by-product LiOH, which greatly limited the dissolution of the $NH_3(g)$.

UN2806 (Surrogate) — Magnesium Nitride, Mg_3N_2

Magnesium nitride was studied as a surrogate for lithium nitride (UN 2806). Magnesium nitride is a solid with a relative molar mass of 100.95. In method A, 6.00 mmol of water was added to 1.00 mmol of it. In method B, 1.00 mmol of it was mixed with 30.0 mmol of water. Reaction according to the equation

$$Mg_3N_2 + 6\ H_2O \longrightarrow 2\ NH_3 + 3\ Mg(OH)_2$$

was taken as the source of $NH_3(g)$ for computations of mass and yield. The theoretical yield of $NH_3(g)$ was 2.00 mmol, which corresponded to 32.0 mL of gas in the calibrated experimental apparatus.

2003 Experimental Data for Magnesium Nitride

Method A				Method B			
Time (min)	Volume of Gas (mL)	Mass of NH_3 (g)	Yield (%)	Time (min)	Volume of Gas (mL)	Mass of NH_3 (g)	Yield (%)
0.33	16.0	0.0168	49.2	0.33	22.0	0.0231	67.7
0.67	16.3	0.0171	50.2	0.5	26.4	0.0277	81.2
1	17.0	0.0178	52.3	1	20.6	0.0216	63.4
2	17.8	0.0187	54.8	2	15.8	0.0166	48.6
3	18.2	0.0191	56.0	3	13.0	0.0136	40.0
5	18.4	0.0193	56.6	5	10.0	0.0105	30.8
10	18.6	0.0195	57.2	7	8.4	0.0088	25.8
20	18.8	0.0197	57.8	10	7.0	0.0073	21.5
				15	5.8	0.0061	17.8
				20	5.2	0.0054	16.0
				30	5.0	0.0052	15.4

Comments: This substance, which does not have a UN number, was tested because it is chemically related to lithium nitride, which reacted explosively with water. The reaction in this case was less violent, although still quite rapid. In method A, the yield of $NH_3(g)$ was only about half of the theoretical yield. In method B, the maximum on the yield curve indicated that NH_3(g) that formed at the start of the reaction later dissolved to form NH_3(aq). In this case, the by-product of the hydrolysis reaction, $Mg(OH)_2$, is only sparingly soluble in water. The excess water was accordingly not as basic as it would have been if a soluble base had formed and more NH_3(g) had dissolved.

UN 3246 — Methanesulfonyl Chloride, CH_3SO_2Cl

Methanesulfonyl chloride is a yellow liquid with a relative molar mass of 114.54 and a room-temperature density of 1.485 g/cm^3. In method A, 1.00 mmol of it was mixed with 1.00 mmol of water. In method B, 1.00 mmol was mixed with 5.00 mmol of water. The reaction

$$CH_3SO_2Cl + H_2O \longrightarrow HCl + CH_3SO_2OH$$

was proposed as the source of HCl(g). The theoretical yield of HCl(g) was 1.00 mmol, which corresponded to 16.0 mL of gas in the calibrated experimental apparatus.

Comments: Neither method A nor B generated any measurable gases within 20 min.

APPENDIX D:

ADDITIONAL DETAILS ON WATER-REACTIVE MATERIALS

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This appendix provides detailed information on the water-reactive materials listed in the Table of Initial Isolation and Protective Action Distances. We begin in Section D.1 with a detailed discussion of how we reduce the experimental data listed in Appendix C to determine the key parameters necessary to model TIHWR releases. The parameters themselves for all TIHWR materials considered in the ERG2004 are then provided in Section D.2. Finally, Section D.3 explains why various materials were selected for the TIHWR list and reviews changes from previous recommendations.

D.1 ANALYSIS OF EXPERIMENTAL DATA: EXTRACTION OF KEY PARAMETERS

As discussed in Section 3.3, we assume that the evolution of a TIHWR gas can be modeled (for most materials) using the first-order rate equation

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

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

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

where M_{∞} is the maximum mass of TIH gas that is evolved from the water at long times. Note that more product may be formed than actually evolves from the water due to dissolution of the gas in the water, as discussed in Section D.1.3. 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 method B experiments.

Four types of behavior were observed in the 55 experiments performed in 1999 and 2003 (for the 2000 and 2004 ERGs, respectively). They are described in the following subsections.

D.1.1 No Emissions

Some experiments produced no TIH gases in either method (A or B), even though we had descriptive evidence that they were quite reactive with water. These numbered 13, or 24% of cases measured. An additional two materials (phosphorus tribromide and phosphorus oxybromide) exhibited slow emissions in method A but no emissions with method B due to sequestration of the evolved gas by the excess water. Null results for these chemicals illustrate the importance of actual experiments over anecdotal information from the chemistry literature.

D.1.2 Simple First-Order Process

Twelve experiments (22%) showed the simple first-order process described above. A typical example of these simple cases is shown in Figure D.1. As shown, 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.

D.1.3 First-Order Process with Dissolution

Many experiments showed an apparent first-order process where the evolved TIH gas dissolved back into the water, thus serving as a removal mechanism. Twenty-three out of the 55 experiments, or approximately 45%, showed this behavior, an example of which is shown in Figure D.2. Because the TIH gas was kept in a closed environment in contact with water in the experimental apparatus, dissolution was promoted. In the natural environment, the TIH gas produced would likely bubble out of the water quickly and dilute in the atmosphere, thus avoiding significant dissolution. For this reason, M_∞ was determined with a least-squares fit of the data to obtain the completion fraction β, rather than simply using the observed maximum that occurred as dissolution overcame the rate of evolution. This procedure may tend to overestimate the source term for atmospheric dispersion of the TIH gas. Three subcases of strong dissolution materials were identified and treated differently:

1. **Three or more rising points.** For 7 of the 23 dissolution cases, the data contained 3 or more points, as shown in Figure D.2. In these cases, the first-order rate curve resulting from fitting only the rising points is overdetermined and the goodness of fit confirms the appropriateness of a first-order model.

2. **Two rising points.** For 8 of the 23 dissolution cases, only two points were obtained on the rising portion of the $M(\mathrm{t})$ curve due to the rapidity with which dissolution occurred. The origin and these two points exactly determine the parameters M_∞ and λ, and the fit to the model is perfect. These cases were handled in the same way as those with 3 or more meaningful measurements. An example of such a case is given in Figure D.3.

3. **Only one rising point.** Finally, in Figure D.4 we show an example of the other 8 dissolution cases, for which only the first nontrivial measurement was higher and the second and subsequent evolved mass values had decreased. These represent cases in which dissolution of the gas competes strongly with production. These cases generally exhibited very fast reaction rates as well. For these chemicals, it is not possible to determine two parameters from a fit. Therefore, we determined the rate constant λ by fitting a first-order process to the data obtained in method A, in which

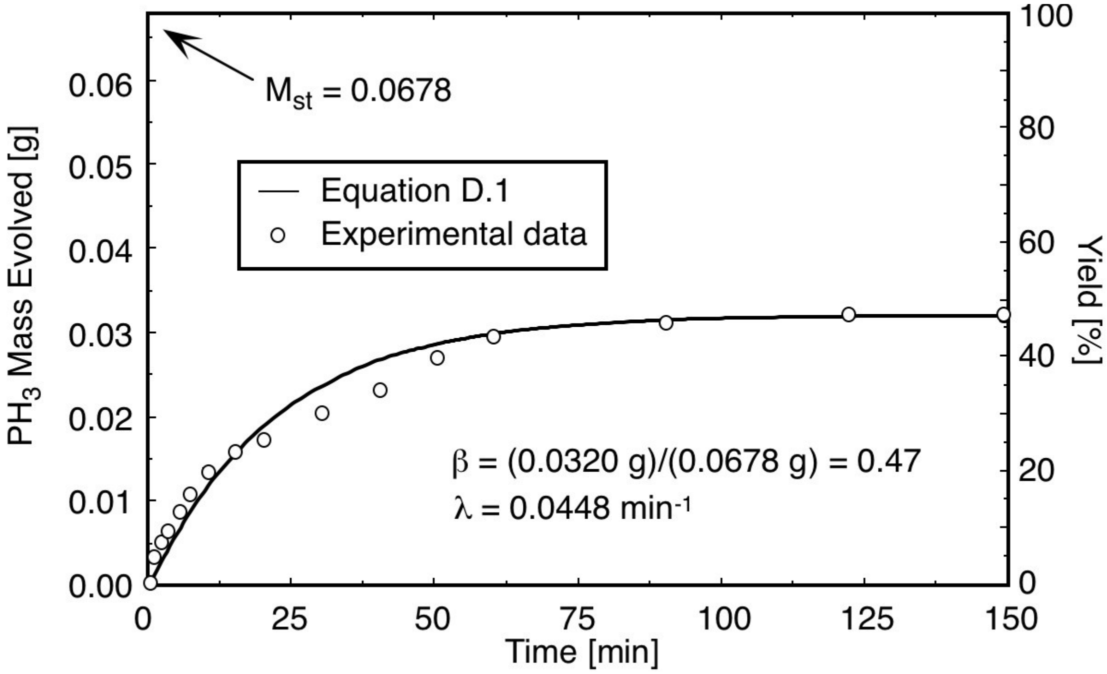

FIGURE D.1 Example of a Simple First-Order Process from the Experimental Series Together with the Derived Parameters for Eq. D.1. Results are shown for calcium phosphide (UN 1360).

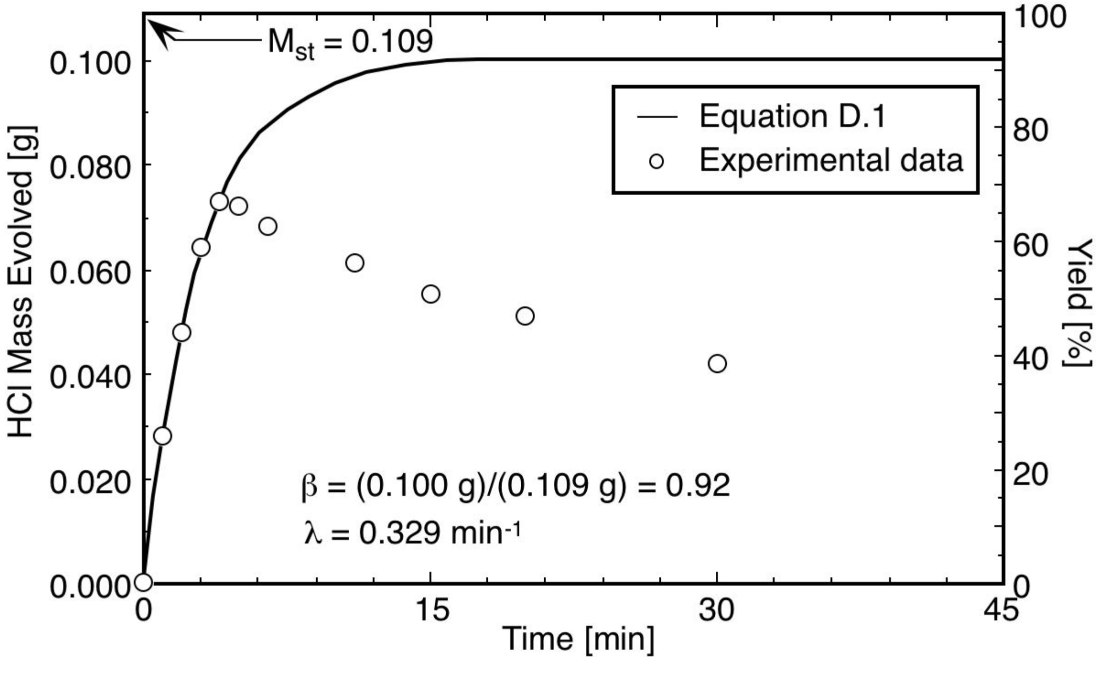

FIGURE D.2 Example of a First-Order Process from the Experimental Series where Dissolution of the TIH Product Competes with the Evolution. Data are shown together with the derived parameters for Eq. D.1. Results are shown for ethyltrichlorosilane (UN 1196).

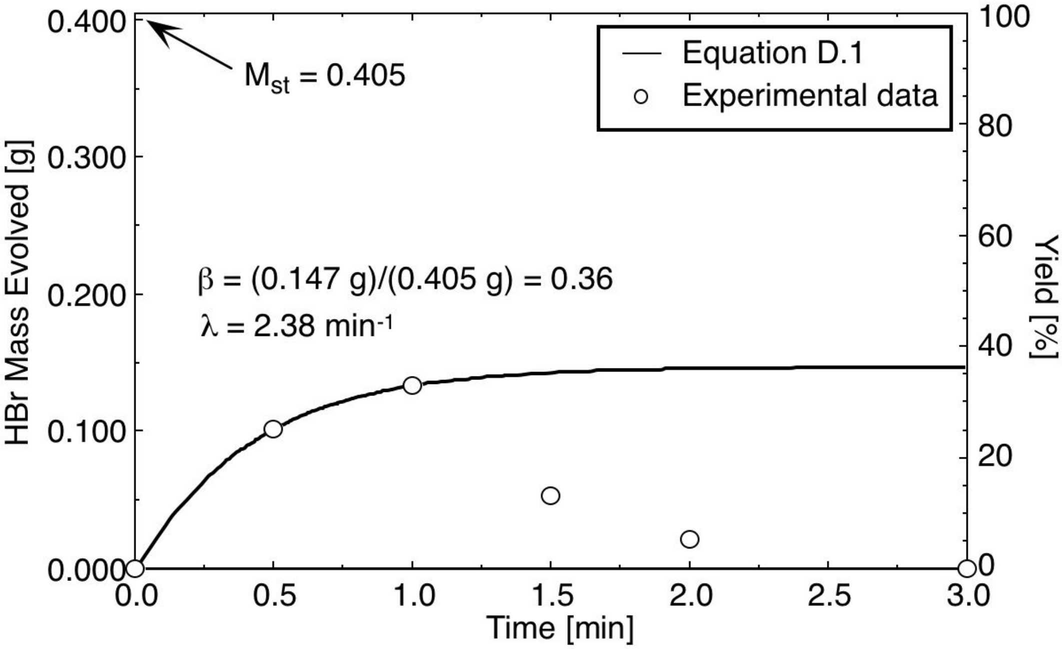

FIGURE D.3 Example of a First-Order Rate Process Competing with Dissolution of the TIH Gas for which only Two Rising Points were Measured. Data are shown together with the derived parameters for Eq. D.1. Results are shown for phosphorus pentabromide (UN 2691).

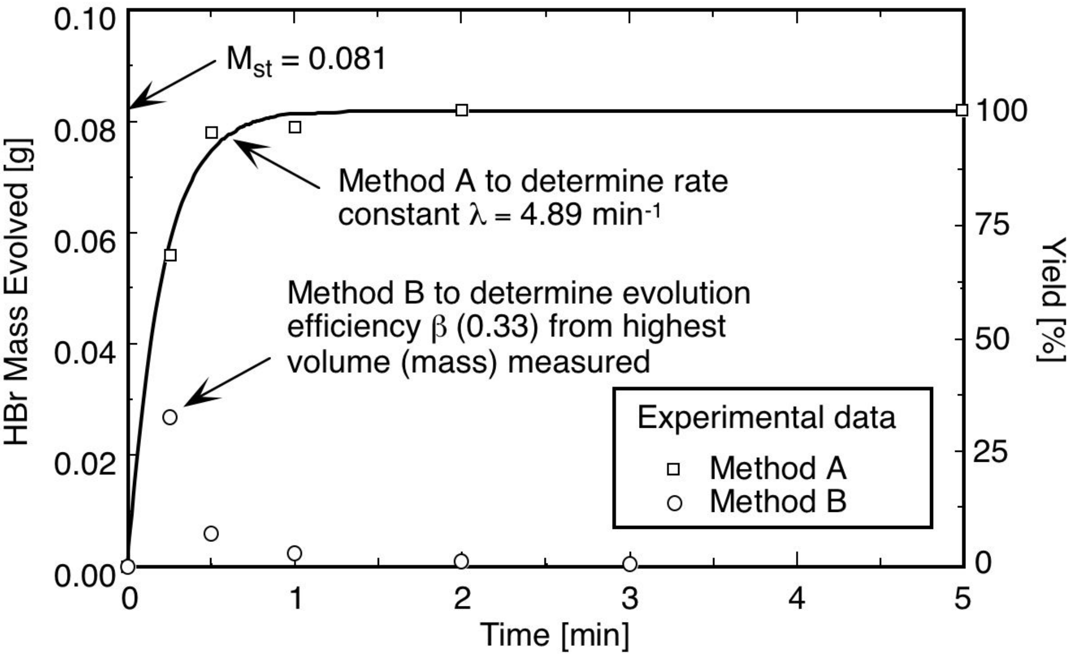

FIGURE D.4 Example of a First-Order Rate Process Competing with Dissolution of the TIH Gas for which only One Rising Point was Measured. Data are shown together with the derived parameters for Eq. D.1. Results are shown for acetyl bromide (UN 1716).

water was not in stoichiometric excess. Then, rather than using the known λ to fit the one nontrivial point to a first-order process and find M_∞, we used the largest evolved TIH gas mass actually observed, $M_{\max}$, to obtain β as the ratio $M_{\max}/M_{st}$. This procedure reflects the very rapid dissolution that occurs in these cases. To extrapolate an exponential fitted in this way to find M_∞ is probably too conservative.

Two exceptional cases were observed: nitrosylsulfuric acid (UN 2308) and lithium nitride (UN 2806). The nitrosylsulfuric acid experiment was performed in 1999 but not repeated in 2003. In this case, the method A experiment also gave a single high initial point followed by a rapid decrease of the gas volume to zero. Therefore, we could not fit the method A data to find λ, but had to estimate it based on the maximum observed gas volume, which occurred at $t = 1$ min. The lithium nitride experiment was performed in 2003, and produced 97% of the stoichiometric maximum amount of NO_2 after 10 s, in both methods A and B. Again, we could not use method A data to fit for a value of λ. We estimated it as 6 min^{-1}, the inverse of the smallest time studied.

D.1.4 Autocatalytic Reactions

In 5 of the 55 experiments, we observed a more complex pattern of reaction. These cases all involved silanes but represented only 23% of the 22 silanes studied. In these cases, a polymeric by-product formed during the first stages of the reaction apparently slowed the reaction of the remaining silane with water. A slow emission of gas at a constant rate ensued for a period of 2-10 min. At that point the reactions appeared to autocatalyze, and subsequently followed what appeared to be a normal first-order reaction process. In these cases, we used a four-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. The mass of gas that had evolved during the interval from $t = 0$ to $t = T_{ind}$ was also used as a parameter, called m_i. The formal relationships are as follows:

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

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

where

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

These formulas are continuous at $t = T_{ind}$, but their slopes are not. Nevertheless, they give a good fit to the time dependence of the data in these cases. Figure D.5 illustrates this behavior and the goodness of the fit.

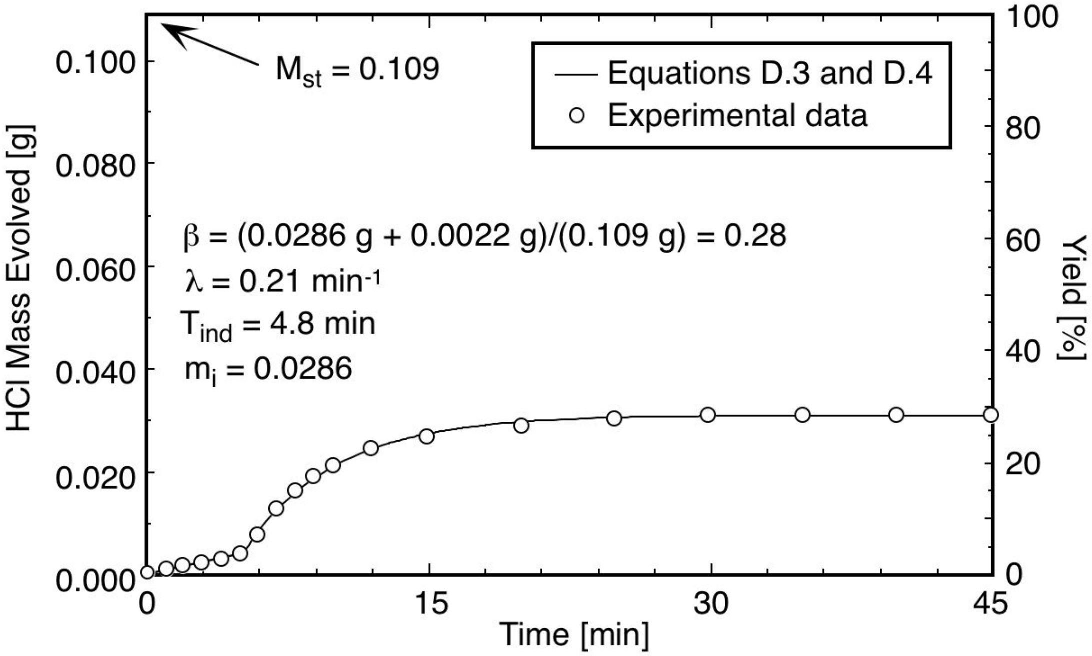

FIGURE D.5 Example of an Autocatalytic Reaction with an Initial By-Product Greatly Reducing Availability of Water for Subsequent Reaction. Data are shown together with the derived parameters for Eqs. D.3 and D.4. Results are shown for cyclohexyltrichlorosilane (UN 1763).

D.1.5 Summary

The four types of emission time dependence, along with the three in which dissolution and production competed significantly, describe all of the 55 cases studied experimentally. The parameters obtained by fitting the data were used in CASRAM to describe the time dependent emissions of TIH gas when a water-reactive substance is spilled into water. Larger-scale experiments in the future should verify that these millimole results do indeed give a good approximation of an actual large-scale spill.

D.2 KEY PARAMETERS EMPLOYED IN THE TIWHR ANALYSIS

Supplementary information on all water-reactive materials in the TIHWR list is provided in Tables D.1 and D.2.

TABLE D.1 Supplementary Information on Water-Reactive Materials in the ERG2004 for Materials Modeled by a Simple First-order Process[a]

UN No.	Name	ERG	Type	Prod.	St	Dens.	S.Y.	β	λ_o (min^{-1})
1162	Dimethyldichlorosilane	00/04	2	HCl	L	1.10	0.565	0.41	0.935
1196	Ethyltrichlorosilane	04	3.1	HCl	L	1.238	0.669	0.92	0.329
1242	Methyldichlorosilane	04	3.2	HCl	L	1.11	0.634	0.60	9.24
1250	Methyltrichlorosilane	00/04	2	HCl	L	1.27	0.732	0.33	1.31
1295	Trichlorosilane			HCl	L	1.34	0.808	0.41	1.14
1298	Trimethylchlorosilane	00/04	2	HCl	L	0.85	0.336	0.37	1.45
1305	Vinyltrichlorosilane	04	3.2	HCl	L	1.26	0.681	0.60	1.53
1340	Phosphorus pentasulfide			H_2S	S	2.09	0.766	0.6	0.2
1360	Calcium phosphide	00/04	2	PH_3	S	2.51	0.373	0.47	0.045
1384	Sodium hydrosulfite	00	1	H_2S	S	0.9	0.390	0.02	5
1397	Aluminum phosphide			PH_3	S	2.40	0.587	0.47	0.045
1412	Lithium amide	04	3.2	NH_3	S	1.18	0.740	0.24	4.51
1419	Magnesium aluminum phosphide			PH_3	S	2.20	0.529	0.47	0.05
1432	Sodium phosphide			PH_3	S	1.74	0.283	0.47	0.05
1541	Acetone cyanohydrin	04	1	HCN	L	0.93	0.317	0.3	0.1
1680	Potassium cyanide			HCN	S	1.52	0.415	0.4	0.1
1689	Sodium cyanide			HCN	S	1.52	0.552	0.4	0.1
1716	Acetyl bromide	04	3.3	HBr	L	1.66	0.658	0.33	4.89
1717	Acetyl chloride	04	3.3	HCl	L	1.11	0.464	0.38	3.15
1724	Allyl trichlorosilane, stabilized	04	3.2	HCl	L	1.21	0.623	0.76	1.06
1725	Aluminum bromide, anhydrous	00	1	HBr	S	2.54	0.910	0.5	0.1
1726	Aluminum chloride, anhydrous	00	2	HCl	S	2.44	0.820	0.5	0.2
1732	Antimony pentafluoride	04	1	HF	L	2.99	0.461	0.4	5
1745	Bromine pentafluoride[b]			Br_2	L	2.47	0.456	0.04	0.2
1745	Bromine pentafluoride[b]			HF	L	2.47	0.572	0.4	5
1746	Bromine trifluoride[b]			Br_2	L	2.80	0.591	0.02	0.2
1746	Bromine trifluoride[b]			HF	L	2.80	0.438	0.4	5
1752	Chloroacetyl chloride	00/04	3.1	HCl	L	1.50	0.323	0.1	0.391
1754	Chlorosulfonic acid	04	3.3	HCl	L	1.76	0.313	0.91	7.31
1758	Chromium oxychloride	04	2	HCl	L	1.91	0.471	0.09	0.067
1766	Dichlorophenyltrichlorosilane[c]	04	3.2	HCl	L	1.56	0.84	0.61	1.96
1767	Diethyldichlorosilane	04	2	HCl	L	1.05	0.464	0.21	0.0364
1769	Diphenyldichlorosilane	04	2	HCl	L	1.22	0.288	0.12	0.129
1771	Dodecyltrichlorosilane	04	2	HCl	L	1.03	0.359	0.33	0.0733
1777	Fluorosulfonic acid			HF	L	1.73	0.200	0.1	5
1799	Nonyltrichlorosilane	04	2	HCl	L	1.0	0.417	0.55	0.037
1801	Octyltrichlorosilane	04	2	HCl	L	1.33	0.442	0.3	0.109
1804	Phenyltrichlorosilane	04	3.1	HCl	L	1.321	1.035	0.68	0.399
1806	Phosphorus pentachloride	04	3.3	HCl	S	1.60	0.875	0.22	6.13
1809	Phosphorus trichloride	00	3.2	HCl	L	1.57	0.796	0.43	1.72
1810	Phosphorus oxychloride	00/04	3.3	HCl	L	1.67	0.713	0.85	1.90
1816	Propyltrichlorosilane	00/04	3.1	HCl	L	1.20	0.618	0.45	0.45
1818	Silicon tetrachloride	04	3.1	HCl	L	1.48	0.858	0.37	2.20
1828	Sulfur chlorides[b]			SO_2	L	1.62	0.252	0.12	0.2
1828	Sulfur chlorides[b]			HCl	L	1.62	0.540	0.4	5
1828	Sulfur chlorides[b]			H_2S	L	1.62	0.474	0.1	0.6
1834	Sulfuryl chloride[b]	00	3.1	HCl	L	1.66	0.540	0.2	0.92
1836	Thionyl chloride[b]	04	3.1	SO_2	L	1.63	0.538	1	2.75
1836	Thionyl chloride[b]	04	3.1	HCl	L	1.63	0.613	0.59	3.02
1838	Titanium tetrachloride[b]	00	3.1	HCl	L	1.73	0.769	0.24	1.35

TABLE D.1 (Cont.)

UN No.	Name	ERG	Type	Prod.	St	Dens.	S.Y.	β	λ_o (min^{-1})
1898	Acetyl iodide			HI	L	2.07	0.753	0.4	0.2
1923	Calcium hydrosulfite			H_2S	S	1.0	0.327	0.02	5
1931	Zinc hydrosulfite			H_2S	S	0.7	0.384	0.02	5
2004	Magnesium diamide			NH_3	S	1.39	0.604	0.97	6
2011	Magnesium phosphide			PH_3	S	2.06	0.504	0.47	0.05
2012	Potassium phosphide			PH_3	S	2.50	0.229	0.47	0.05
2013	Strontium phosphide			PH_3	S	2.68	0.209	0.47	0.05
2308	Nitrosylsulfuric acid	00	3.3	NO_2	L	1.890	0.724	1.00	1.0
2437	Methylphenyldichlorosilane	04	2	HCl	L	1.176	0.382	0.071	0.125
2495	Iodine pentafluoride			HF	L	3.75	0.450	0.4	5
2691	Phosphorus pentabromide	00/04	3.2	HBr	S	2.00	0.940	0.36	2.38
2692	Boron tribromide[b]	04	3.3	HBr	L	2.65	0.971	0.19	7.36
2806	Lithium nitride	04	3.3	NH_3	S	1.27	0.489	0.97	6
2977	Uranium hexafluoride, fissile			HF	S	4.68	0.341	0.2	5
2978	Uranium hexafluoride, non-fissile			HF	S	4.68	0.341	0.2	5
2985	Chlorosilanes, n.o.s.			HCl	L	1.10	0.565	0.43	1.01
2986	Chlorosilanes, flam., corr, n.o.s.			HCl	L	1.10	0.565	0.43	1.01
2987	Chlorosilanes, corrosive, n.o.s.			HCl	L	1.10	0.565	0.43	1.01
2988	Chlorosilanes, wtr-rctv, flam., corr., n.o.s.			HCl	L	1.10	0.565	0.43	1.01
3048	Aluminum phosphide pesticide			PH_3	S	2.40	0.587	0.47	0.05
3049	Metal alkyl halides n.o.s.			HCl	S	1.60	0.500	0.05	5
3049	Metal alkyl halides n.o.s.			HBr	S	1.60	0.500	0.05	5
3052	Aluminum alkyl halides			HCl	S	1.60	0.500	0.05	5
9191	Chlorine dioxide, hydrate, frozen			Cl_2	S	1.40	0.084	0.05	5

[a] ERG = ERG edition (2000 or 2004) for which experiment was performed, Type = type of analysis used to derive parameters from experimental data (numbers refer to section and paragraph numbers in Section D.1), St = normal state during shipment (solid, liquid), Dens = density (g/cm^3), S.Y. = stoichiometric yield of TIH gas (kg TIH gas/kg spilled parent), β = efficiency factor (average fraction of S.Y. produced), and λ_o = primary rate constant at 20°C.

[b] Parent chemical is TIH gas.

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

TABLE D.2 Supplementary Information on Water-Reactive Materials in the ERG2004 for 5 Liquid Chlorosilanes Modeled Using an Initial Induction Period Followed by Simple First-order Process[a]

UN No.	Chemical	Dens	S.Y.	m_i	β	λ_o (min^{-1})	T_{ind} (min)
1728	Amyltrichlorosilane	1.16	0.532	0.0205	0.22	0.054	5.3
1747	Butyltrichlorosilane	1.16	0.571	0.0233	0.26	0.099	8.6
1763	Cyclohexyltrichlorosilane	1.23	0.503	0.0286	0.28	0.21	4.8
1784	Hexyltrichlorosilane	1.0	0.496	0.0355	0.43	0.29	7.4
1800	Octadecyltrichlorosilane	0.984	0.281	0.0528	0.51	0.31	9.2

[a] Experiment performed on all materials, Dens = density (g/cm^3), S.Y. = stoichiometric yield of TIH gas (kg TIH gas/kg spilled parent), m_i = the initial production coefficient, β = total efficiency factor (average fraction of S.Y. produced), λ_o = primary rate constant at 20°C, and T_{ind} = initial induction period.

D.3 SUPPLEMENTARY DETAILS IN SUPPORT OF MATERIALS APPEARING IN TABLE D.1

Most materials appear in Tables D.1 and D.2 and the ERG either because they evolved TIH gases at reasonable rates in the experiments described in Appendix C or because they are described as evolving TIH gases in the chemical literature. Reasons for the inclusion of materials in the Table are listed in Sections D.3.1–D.3.3. We also briefly describe why materials were deleted from the list or otherwise not included in Section D.3.4.

D.3.1 Materials that Evolved TIH Gases During Experiments

The ERG Table contains 40 materials that were shown to evolve gas during the experimental program described in Appendix C. These are listed in Table D.1.

D.3.2 Materials Described as TIHWR in the Literature

The Table includes 29 materials because of descriptions of their water reactivity in the chemical literature. These are listed in Table D.3.

TABLE D.3 Chemicals Reported to Be Water-Reactive in the Scientific Literature

UN No.	Name	Comment	Reference
1295	Trichlorosilane	Reacts with water and steam to produce heat and toxic and corrosive fumes (of HCl).	Lewis (1993)
1340	Phosphorus pentasulfide	Readily liberates toxic hydrogen sulfide and phosphorus pentoxide and evolves heat on contact with moisture.	Lewis (1993)
1397	Aluminum phosphide	Slowly evolves PH_3 in contact with water.	Lewis (1993)
1419	Magnesium aluminum phosphide	Evolves PH_3 in contact with water.	Lewis (1993)
1432	Sodium phosphide	Is known to evolve PH_3 in contact with water.	Lewis (1993)
1680	Potassium cyanide	Included on the basis of its chemical similarity to sodium cyanide.	
1689	Sodium cyanide	A spill into a river (on May 20, 1998 in Kyrgyzstan) led to evolution of gaseous HCN despite the fact that sodium cyanide is soluble in water; the evolution of gaseous HCN is favored by acidic water and by higher temperatures; the PAD is greater for a spill into water because of the possibility of such evolution.	Cleven and van Bruggen (2000)
1745	Bromine pentafluoride	Explodes on contact with water; products of this rapid reaction include HF and possibly Br_2.	Lewis (1989)
1746	Bromine trifluoride	Smokes in air; decomposed violently in water; products of reaction include HF and possibly Br_2.	Budavari (1996); Lewis (1989)
1777	Fluorosulfonic acid	Fumes in moist air; reacts violently with water, although it is incompletely and reversibly hydrolyzed; products of reaction include HF.	Budavari (1996)
1828	Sulfur chlorides	Decomposes when contacted by water to produce heat and toxic/corrosive fumes.	Carson and Mumford (1994)
1898	Acetyl iodide	Included by analogy to acetyl chloride.	
1923	Calcium hydrosulfite	Included by analogy to sodium hydrosulfite.	
1931	Zinc hydrosulfite	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 (1989).
2012	Potassium phosphide	Phosphides tend to decompose to PH_3 upon contact with moisture or acids.	Lewis (1989).
2013	Strontium phosphide	Phosphides tend to decompose to PH_3 upon contact with moisture or acids.	Lewis (1989).
2495	Iodine pentafluoride	Violent reaction with water; products include HF.	Lewis and Sax (1992)
2977	Uranium hexafluoride, fissile	Is rapidly hydrolyzed by water. Reacts vigorously with water; products include HF.	Cotton and Wilkinson (1966); Lewis (1989).
2978	Uranium hexafluoride, non-fissile	Is rapidly hydrolyzed by water; reacts vigorously with water; products include HF.	Cotton and Wilkinson (1966); Lewis (1989).
2985	Chlorosilanes n.o.s.	Most chlorosilanes generate HCl at some rate on contact with water.	
2986	Chlorosilanes, flammable, corrosive n.o.s.	Most chlorosilanes generate HCl at some rate on contact with water.	
2987	Chlorosilanes, corrosive n.o.s.	Most chlorosilanes generate HCl at some rate on 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; included despite the fact that the coating applied to the particles in the pesticide application is likely to slow the hydrolysis.	Lewis (1993)

TABLE D.3 (Cont.)

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 (1989)

D.3.3 Materials Included Due to Special Concerns

Four materials appearing in Table D.1 did not evolve TIH gases during the Appendix C experiments. They were included because they might evolve TIH gases if spilled under the right circumstances.

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

2. **UN 1541 — acetone cyanohydrin.** Experiments found no evolution of gas when the chemical was mixed with room-temperature water. This material was retained on the basis 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 (Cleven and van Bruggen 2000).

3. **UN 1725 — aluminum bromide (anhydrous).** Experiments found no evolution of gas when the chemical was mixed with room-temperature water. It was retained on the basis of its chemical similarity to aluminum chloride.

4. **UN 1726 — aluminum chloride (anhydrous).** Experiments found no evolution of gas when the chemical was mixed with room-temperature water. It was retained because the small scale of the experiment might have masked its TIHWR character. Aluminum chloride is cited 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” (Carson and Mumford 1994).

D.3.4 Materials No Longer Recommended as TIHWR Materials

Eleven materials previously recommended by ANL and the University of Illinois at Chicago as TIWHR materials were removed from the current list. (Note that not all these materials actually appeared in the ERG2000).

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

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

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

4. **UN 1808 — phosphorus tribromide (solid).** This compound reacted with water, but no gaseous HBr was evolved when excess water was present; the excess water apparently dissolved the HBr as rapidly as it was formed

5. **UN 1939 — phosphorus oxybromide (solid).** Reacted with water, similarly to phosphorus tribromide; the excess water apparently dissolved the HBr as rapidly as it was formed.

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

7. **UN 1807 — phosphorus pentoxide.** This material reacts explosively with water to generate water-soluble phosphoric acid. Previously included by analogy to SO_3 because of the possibility that this very rapid, exothermic reaction might raise a toxic acidic mist in a spill. Since phosphoric acid is not a TIH material, DOT chose not to include phosphorus pentoxide.

8. **UN 1831 — oleum.** Oleum is a solution of sulfur trioxide in sulfuric acid. It fumes strongly in moist air (Lewis 1993) 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.

9. **UN 1829 — sulfur trioxide.** Like oleum, this compound reacts with water and water vapor to form sulfuric acid mists (NIOSH Substance Profile). Excluded for the same reasons as oleum.

10. **UN 2442 — trichloroacetyl chloride.** This compound was reacted with water in the experiments, but no evolution of gaseous HCl was observed (see Appendix C).

11. **Sodium methylcarbamodithioate (metam sodium) (no UN number).** This material has a known history of water reactivity but is excluded because it does not have a UN number.