Section 2
General Methodology

The methodology used in preparing the Table for the 2000ERG is illustrated schematically in Figure 2.1. The starting point for the analysis of the methodology is a list of TIH materials developed by DOT (see discussion in Section 2.1). This list was modified slightly from the 1996 ERG in that it now includes various chemical agents that are either transported by the U.S. Department of Defense (DOD) or could be used as weapons. 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

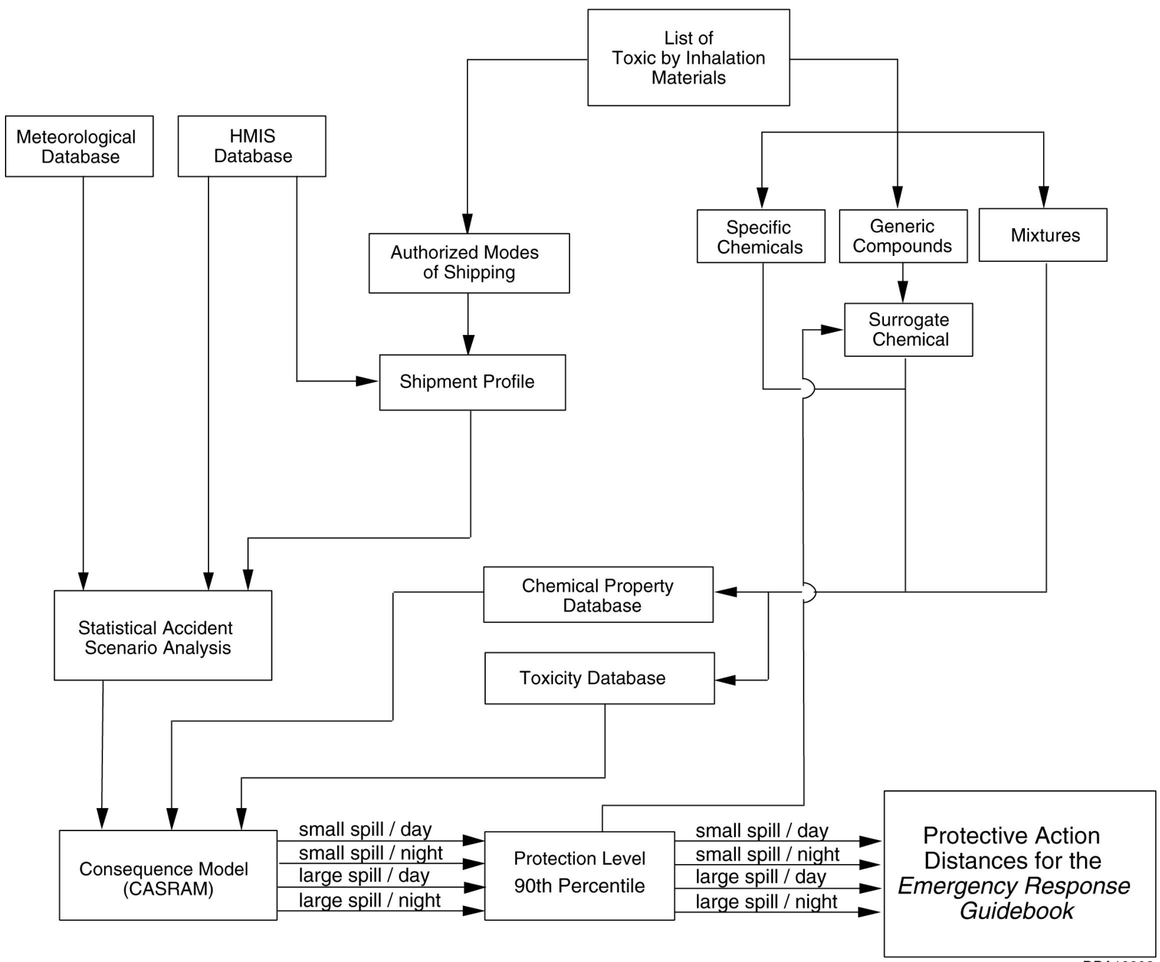

Figure 2.1 Schematic of the Methodology Used to Prepare the 2000ERG Table of Initial Isolation and Protective Action Distances

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 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 100,000 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 by using detailed emission rate and atmospheric dispersion models to calculate an estimated downwind chemical concentration footprint. The safe distance for a specific scenario is then chosen as the furthest downwind distance that the health criteria for the chemical involved in the incident is exceeded. 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 (see 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 (55 gal or less = small, more than 55 gal = large). The PADs provided in the 2000ERG are then selected as the 90^{th} 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

The analysis begins with the TIH list provided by DOT. The materials in the TIH list are designated by UN number and proper shipping name, although the UN numbers are not unique. The list can be divided into several categories of chemicals: (1) single chemicals, (2) mixtures, (3) solutions, and (4) generics. Altogether, the TIH list for 2000ERG includes 152 single chemicals, 16 mixtures, 5 solutions, and 24 generics. As is explained later, generic compounds are 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). Hazard Zones A, B, C, and D are for gases; Hazard Zones A and B are for liquids). In addition, 70 water-reactive materials, defined here as materials that emit a TIH gas upon contact with water, are included. Of the water-reactive materials in the Table, 12 are also TIH compounds, which 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. 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. Water-reactive materials are treated in a manner similar to regular TIH materials, with the water reactivity being treated in the emission rate analysis. The treatment of water reactivity is discussed in Section 2.4 and Appendixes C and D.

2.1.2 Changes in the Table for the 2000ERG

New materials were added to the Table for the 2000ERG. Twenty of the new materials are classified as chemical warfare agents and were included in the Table because they could be released as weapons (see Section 2.2.2). Ten of the new materials also have entries for standard transportation-related releases associated with legal activities. In addition, weapons-related entries were added for several other industrial TIH chemicals already on the TIH list (e.g., hydrocyanic acid, phosgene). Some of these materials have several synonyms for which entries were also added. The list of new materials is included in Section 2.2.2 in the discussion related to the treatment of chemical warfare agents.

The other substantial change made to the Table was to include materials that emit a TIH gas upon reaction with water throughout the table where appropriate; previously, these materials had been listed separately at the end of the Table. To make this change, individual distances were calculated for these materials by using a methodology similar to that employed for land-based spills. In addition, 37 new materials were added to the TIH by water reactivity (TIHWR) list, and 4 materials were removed, partially on the basis of results from experimental studies conducted for the 2000ERG analysis. The treatment of water-reactive materials is discussed in depth in Section 2.4 and Appendixes C and D.

In addition to the variety of new materials added to the Table, 17 new entries that are synonymous with materials already listed were added to the Table.

The two chemicals listed in Table 2.1 were removed from the TIH list because of their low volatility. These chemicals are liquids that fall into Hazard Zone C per the definitions in 49 CFR 173.133. The calculated PADs for these materials are less than 0.2 mi. Acetone cyanohydrin, however, is a water-reactive material and therefore is retained in the Table, but only for spills into water.

Table 2.1 Chemicals Removed from the TIH List to Prepare the 2000ERG[a]

Chemical	UN No.	LC_{50} (ppm)	P_{vap} at 20°C (Pa)
Acetone cyanohydrin	1541	126	29.4
Phenylcarbylamine chloride	1672	300 est.	41.4 est.

[a] LC_{50} = lethal concentration to 50% the population; ppm = parts per million; est. = estimated.

2.2 Shipment and Release Scenarios

Associated with each entry in the TIH list are authorized modes of shipping as specified in 49 CFR 172.101 and associated subsections. These specifications substantially influence the amount of material that could be released in a transport-related accident. For example, many 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. Packaging authorizations also govern container type. This factor is important to remember when considering not only shipping volumes but also discharge fractions (the amount of material released in an incident relative to the container capacity).

2.2.1 Shipment Profiles

For the ERG2000 analysis, we used packaging authorizations together with data on commodity flow and hazardous material incidents to develop shipment profiles for each material considered. 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. In this method, each chemical is assigned a set of representative shipments that reflect its transportation in the United States, Canada, and Mexico. For almost all chemicals, the shipment profile fell into one of the following nine general classes:

1. Gases dominated by rail transportation,
2. Gases with mixed rail and highway transportation,
3. Gases dominated by highway transportation,
4. Liquids dominated by rail transportation,
5. Liquids with mixed rail and highway transportation,

6. Liquids dominated by highway transportation,

7. Bulk-forbidden gases and liquids authorized under 49 CFR 173.192,

8. Bulk-forbidden gases and liquids authorized under 49 CFR 173.302, and

9. Organophosphates authorized under 49 CFR 173.334.

Chemicals with a 49 CFR 173.245 authorization for bulk transportation are included in the bulk-forbidden classes. For these chemicals (and the ones for which bulk is forbidden), the PADs for large spills were estimated from shipments containing up to 25 cylinders or drums. A release from this number of package freight containers is equivalent to a release from a small bulk cargo tank (e.g., 1,500 g). 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.

A shipment was designated as being either rail- or highway-dominated on the basis of available commodity flow data (these data are available for a few 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. 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. (1999).

For each class of shipment, analyses were conducted for releases that occurred (1) during a traffic accident or train derailment and (2) during transport en route from the point of origin to the destination but not during an accident or derailment. These release types are referred to as *accident-related* releases and *en route/nonaccident* releases, respectively. Nonaccident releases include releases that occur as a result of cargo shifts, valve failures, corrosion-induced container failure, and so forth. Nonaccident releases are much more common than accident-related releases, as shown by the HMIS incident data summarized in Table 2.2. However, most en route/nonaccident releases are minor.

An example of a mixed rail and highway shipment profile is provided in Table 2.3 for liquids and in Table 2.4 for gases. 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 2000ERG analysis, the percentage of total releases represented by each type is listed for all releases, releases of 5 through 55 gal, and releases of more than 55 gal. When all releases are considered, en route/nonaccident incidents makeup the majority of releases modeled for the shipment profiles given in Tables 2.3 and 2.4. However, in considering releases of more than 55 gal (i.e., “large spills” in the Table), accident-related incidents makeup the majority of cases. For such

Table 2.2 Ratio of En Route/Nonaccident Releases to Accident-Related Releases for Various Container Types as Derived from the HMIS Database for 1990–1995

Container Type	Ratio of En Route/Nonaccident Releases to Accident-Related Releases
111AW tank car	25
112JW and 105A tank car	40
MC306 cargo tank	0.25
MC307 cargo tank	2.5
MC312 cargo tank	3.5
MC330/331 cargo tank	0.5
Portable tank	10
Small and medium drum	25
Large drum	7
Cylinder	7
Miscellaneous package freight	50

Source: Brown et al. (1999).

releases, package freight incidents contributed the most releases, whereas bulk highway incidents contributed the least. Because PADs are set by the 90-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

One of the major changes in the Table in the 2000ERG from previous versions is that it now includes chemical warfare agents. Entries are given for two release scenarios: (1) transportation-related release scenarios, which are for other materials in the Table, and (2) weapons-related release scenarios, which model a criminal or terrorist act. Each scenario is analyzed in the following sections.

2.2.2.1 Transportation-Related Releases

Previous editions of the ERG listed various industrial chemicals that are classic chemical warfare agents, including hydrogen cyanide, phosgene, diphosgene, cyanogen chloride, arsine, methyldichloroarsine, and ethyldichloroarsine. Because these materials

Table 2.3 Mixed Rail and Highway Shipment Profile Data for Liquids[a]

Shipment	Transport Mode	Container	Shipment Amount	Release Type	Percent of Total Releases by Type, Listed by Release Amount: All Releases	5–55 gal[b]	>55 gal[b]
1	Rail	DOT Class 112 tank car	80,000 kg	A	1.5	0.6	19.8
				E	30.5	6.8	14.6
2	Highway	MC312 cargo tank	25,000 kg	A	0.8	0.3	11.2
				E	3.1	2.9	2.5
3	Highway	Ten 55-gal 5C drums	550 gal	A	3.1	3.7	27.9
				E	61.0	85.7	24.0

[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 through 55 gal, and releases of more than 55 gal.

[b] Data provided for allylamine (UN 2334). Other materials with this profile would have similar results.

Table 2.4 Mixed Rail and Highway Shipment Profile Data for Gases[a]

Shipment	Transport Mode	Container	Shipment Amount	Release Type	Percent of Total Releases by Type, Listed by Release Amount: All Releases	5–55 gal[b]	>55 gal[b]
1	Rail	DOT Class 105, 112 tank car	80,000 kg	A	1.7	0.70	21.7
				E	69.3	19.7	17.9
2	Highway	MC331 cargo tank	25,000 kg	A	0.8	0.7	8.8
				E	0.4	0.5	2.2
3	Highway	Fifteen 19-gal 3A or 4A cylinders	285 gal	A	3.5	7.1	34.0
				E	24.3	71.3	15.4

[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 through 55 gal, and releases of more than 55 gal.

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

are transported for industrial purposes, they are listed in 49 CFR 173.101 and were included in the standard shipment profile methodology.

For the 2000ERG, some nerve and blister agents transported in small quantities by military agencies were added to this list (see Table 2.5). Release scenarios for these materials are somewhat different than those for the other materials in the Table. Military agencies primarily ship these agents in very small quantities (less than 2 kg). In rare circumstances, small munitions are also transported for disposal. Because of overpacking, small leaks (primarily in en route/nonaccident incidents) are contained. As a result, only accident-related incidents were studied in this analysis. "Ton cylinders" however, were also included in the analysis. These containers are used to store blister and nerve agents at a few military bases. Although such containers have not been transported off site in the past several years, they were included to provide PAD values for large spills, because the other shipments fall well below this size limit, and ton cylinders would be a likely container to be involved in such a release. The containers and release amounts modeled for nerve and blister agents are summarized in Table 2.6.

It is important to note that although blister and nerve agents are extremely toxic, most are nonvolatile liquids (except for isopropyl methylphosphonofluoridate). Consequently, their PAD values are actually small relative to those of other highly hazardous materials in the Table.

Table 2.5 Chemical Agents Added to the 2000ERG Table of Initial Isolation and Protective Action Distances

UN No.	Chemical Name	Agent Synonym
2810	Bis-(2-chloroethyl) sulfide	H, HD, Mustard
2810	Bis-(2-chloroethyl) ethylamine	HN-1
2810	Bis-(2-chloroethyl) methylamine	HN-2
2810	Tris-(2-chloroethyl) amine	HN-3
2810	Dichloro-(2-chlorovinyl) arsine	L, Lewisite
2810	Ethyl N,N-dimethylphosphoramidocyanidate	GA, Tabun
2810	Isopropyl methylphosphonofluoridate	GB, Sarin
2810	Pinacolyl methylphosphonofluoridate	GD
2810	Cyclohexyl methylphosphonofluoridate	GF
2810	O-Ethyl S-(2-diisopropylaminoethyl) methylphosphonothiolate	VX

Table 2.6 Shipment Profile Data for Chemical Warfare Agents Transported by the Military

Shipment	Transport Mode	Container	Shipment Amount	Total Release by Category (%)
1	Highway	Glass vial overpacked with vermiculite	2 kg	90
2	Highway	Chemical munition overpacked with vermiculite	25 gal	5
3	Highway	Ton cylinder	200 gal	5

2.2.2.2 Weapons-Related Releases

The first-response community has become more aware of the potential threat from the malicious use of chemical and biological agents. For this reason, the 2000ERG now includes Initial Isolation and Protective Action Distances for various chemical agents that could be used as weapons. In addition, a separate new section entitled Criminal/Terrorist Use of Chemical/Biological Agents (page 368 of the 2000ERG) provides information on identification, response, and decontamination strategies for personnel who must respond to a suspected chemical or biological agent release.

Table 2.7 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 2000ERG Table for these materials include the statement "when used as a weapon." Many of these materials are also industrial chemicals that appear separately in 2000ERG as transportation-related releases. (In general, if the material represents a TIH hazard, it is also listed separately as a transportation-related release in 2000ERG.) 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 weapons-related entries, one compound is listed as sarin and GB, whereas for transportation-related entries, this same compound is listed as isopropyl methylphosphonofluoridate. All three terms refer to the same compound.

The accident 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 (Table 2.7). 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 2.7 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

Table 2.7 Chemical Warfare Agents Added to the 2000ERG 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	Diphenylamine chloroarsine	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-Quinuclidinylbenzilate	10	500	AS
2810	Buzz				
2810	CS	o-Chlorobenzylidene malononitrile	10	500	AS
2810	DC	Diphenylcyanoarsine	10	500	AS
2810	GA	Ethyl N,N-dimethylphos-phoramidocyanidate	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	C X	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).

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 settled to the ground to a depth up to 0.25 mm and then evaporated. 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 chemicals that fit that description but are not individually listed in the 2000ERG or the Table. In the 2000ERG, 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 in the 2000ERG analysis that are included in this category are listed in Table 2.8. Cyanogen (UN 1026) yields the maximum distances for large spills, whereas phosphorus pentafluoride (UN 2198) yields the maximum distances for small spills (shown in bold in Table 2.8). 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 2.9 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 2.9; each entry in Table 2.9 may have several corresponding entries in the Table of Protective Action and Initial Isolation Distances. 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 2.8 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		
		First Isolate in All Directions (ft)	Then Protect Persons Downwind during		First Isolate in All Directions (ft)	Then Protect Persons Downwind during	
UN No.	Name of Material		Day (mi)	Night (mi)		Day (mi)	Night (mi)
Potential Surrogate Compounds							
1026	Cyanogen	58.1	0.11	0.61	**966**	**1.83**	**4.80**
1053	Hydrogen sulfide	31.6	0.04	0.19	644	0.82	2.63
2189	Dichlorosilane	58.1	0.11	0.56	787	1.49	3.84
2192	Germane	47.5	0.09	0.49	869	1.64	4.09
2198	Phosphorus pentafluoride	**68.6**	**0.13**	**0.63**	322	0.61	2.15
2204	Carbonyl sulfide	31.7	0.06	0.31	602	1.14	3.45
Synonymous Entries for Generic Compound Categories							
1953	Compressed gas, flammable, poisonous, n.o.s. (Inhalation Hazard Zone B)	100	0.2	0.7	1,000	1.9	4.8
1953	Compressed gas, flammable, toxic, n.o.s. (Inhalation Hazard Zone B)	100	0.2	0.7	1,000	1.9	4.8
1953	Compressed gas, poisonous, flammable, n.o.s. (Inhalation Hazard Zone B)	100	0.2	0.7	1,000	1.9	4.8
1953	Compressed gas, toxic, flammable, n.o.s. (Inhalation Hazard Zone B)	100	0.2	0.7	1,000	1.9	4.8
1953	Liquefied gas, flammable, poisonous, n.o.s. (Inhalation Hazard Zone B)	100	0.2	0.7	1,000	1.9	4.8
1953	Liquefied gas, flammable, toxic, n.o.s. (Inhalation Hazard Zone B)	100	0.2	0.7	1,000	1.9	4.8
3160	Liquefied gas, poisonous, flammable, n.o.s. (Inhalation Hazard Zone B)	100	0.2	0.7	1,000	1.9	4.8
3160	Liquefied gas, toxic, flammable, n.o.s. (Inhalation Hazard Zone B)	100	0.2	0.7	1,000	1.9	4.8

[a] This table provides distance estimates for all applicable entries in the 2000ERG Table of Initial Isolation and Protective Action Distances (DOT et al. 2000). The worst-case (maximum) distances for small spills and large spills for each column are shown in bold.

Table 2.9 Summary of Generic Compounds in the DOT TIH List and Corresponding Surrogates Used for 2000ERG (A different surrogate material can be used for each release category)

UN No.	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	Worst cases among all organic phosphate/gompressed gas mixtures
1967	Insecticide gas, poisonous, n.o.s.	Worst cases among all insecticide gases
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

Continued

Table 2.9 Summary of Generic Compounds in the DOT TIH List and Corresponding Surrogates Used for 2000ERG (A different surrogate material can be used for each release category) (Cont.)

UN No.	Proper Shipping Name	Surrogate
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
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

Continued

Table 2.9 Summary of Generic Compounds in the DOT TIH List and Corresponding Surrogates Used for 2000ERG (A different surrogate material can be used for each release category) (Cont.)

UN No.	Proper Shipping Name	Surrogate
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.	Worst case among TIH flammable nitriles
3276	Nitriles, poisonous, n.o.s.	Worst case among TIH nitriles
3278	Organophosphorus compound, poisonous, n.o.s.	Worst cases among all organophosphorus compounds
3279	Organophosphorus compound, poisonous, flammable, n.o.s.	Worst cases among all organophosphorus compounds
3280	Organoarsenic compound, n.o.s.	Worst cases among all organoarsenic compounds
3281	Metal carbonyls, n.o.s.	Worst cases among all metal carbonyls
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

Continued

Table 2.9 Summary of Generic Compounds in the DOT TIH List and Corresponding Surrogates Used for 2000ERG (A different surrogate material can be used for each release category) (Cont.)

UN No.	Proper Shipping Name	Surrogate
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

Continued

Table 2.9 Summary of Generic Compounds in the DOT TIH List and Corresponding Surrogates Used for 2000ERG (A different surrogate material can be used for each release category) (Cont.)

UN No.	Proper Shipping Name	Surrogate
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
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

Continued

Table 2.9 Summary of Generic Compounds in the DOT TIH List and Corresponding Surrogates Used for 2000ERG (A different surrogate material can be used for each release category) (Cont.)

UN No.	Proper Shipping Name	Surrogate
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

Continued

Table 2.9 Summary of Generic Compounds in the DOT TIH List and Corresponding Surrogates Used for 2000ERG (A different surrogate material can be used for each release category) (Cont.)

UN No.	Proper Shipping Name	Surrogate
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 2.10 lists the mixtures and solutions treated in the 2000ERG 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 at 2 or 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 Water-Reactive Materials

Trucks and rail cars that transport hazardous chemicals can have accidents in which their solid or liquid cargo spills into some body of water such as a water-filled roadside ditch, stream, river, pond, lake, or body of saline water connected to an ocean. A subset of the hazardous materials carried routinely on highways and railway lines can emit TIH gases that react with water (TIHWR gases). An example is silicon tetrachloride, which is not listed as a TIH material but produces airborne hydrogen chloride (HCl) and HCl mist upon water reaction. Even heavy rainfall at the time of an accident or airborne water vapor can cause the emission of TIHWR gases. The well-known Chicago spill of “siltet” 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, would occur if a truck or tank car spilled siltet into water or had an accident during a heavy 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.

Table 2.10 Summary of Mixtures and Solutions in the DOT TIH List and How They Were Modeled for 2000ERG

ID No.	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, nonliquefied 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	(a) 2% chloropicrin and (b) 98% methyl bromide
1581	Mixture	Methyl bromide and more than 2% chloropicrin mixture, liquid	(a) 5% chloropicrin and (b) 95% methyl bromide
1582	Mixture	Chloropicrin and methyl chloride mixtures	(a) 2% chloropicrin and (b) 98% methyl chloride

Continued

Table 2.10 Summary of Mixtures and Solutions in the DOT TIH List and How They Were Modeled for 2000ERG (Cont.)

ID No.	Category	Proper Shipping Name	Modeled as
1023	Mixture	Coal gas	(a) 48% hydrogen, (b) 27% methane, (c) 10% carbon monoxide, (d) 5% carbon dioxide, and (e) 6% nitrogen
1071	Mixture	Oil gas	(a) 55% hydrogen, (b) 25% methane, (c) 11% carbon monoxide, (d) 3% carbon dioxide, (e) 2% ethylene, and (f) 2% benzene

In the following discussions, materials are considered water-reactive if they are likely to generate substantial quantities of toxic gases fairly rapidly after a spill into water. To compile the recommended list of water-reactive materials for the 2000ERG, general principles of chemical reactivity, specific reactivity information from the chemical literature, and comparisons of such information among related compounds were considered. Experiments were also conducted in which 21 compounds were mixed with water and the evolution of TIH gases was measured as a function of time.

This section discusses the identification of the candidate chemicals and the evaluation of these materials with regard to their water-reactivity hazard. 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 2000ERG study are detailed in Section 3.3.2.3.

2.4.1 Identification of Candidates

A large number of certain materials could emit TIH gases upon their reaction with water. For this reason, 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. The following materials were then considered as possible additions to this list of 208 candidates:

- Forty-nine materials produced by Nuessler were listed as dangerous water reactives in correspondence from Dieter Nuessler (Chief Fire Officer, Aachen Germany) to DOT. However, most of the materials on the list are active metals, metal alkyls, and metal hydrides (e.g., cesium, diethylzinc, calcium hydride) that generate flammable, low-toxicity gases, such as hydrogen or methane, when mixed with water. Although the gaseous products from the materials are generally serious fire or explosion hazards, they are not TIH hazards, so the materials were rejected as plausible candidates for the list.

  Fourteen water-reactive materials on Nuessler's list were found to be suitable TIHWR candidates, however. The reason most of these materials had been previously omitted from the Table is because they were incompletely chemically specified. The 14 suitable candidates are listed below:

UN1730	antimony pentachloride
UN1827	tin tetrachloride
UN 2985	chlorosilanes n.o.s.
UN 2986	chlorosilanes, flammable, corrosive n.o.s
UN 2987	chlorosilanes, corrosive n.o.s.
UN 3049	metal alkyl halides n.o.s.
UN 3052	aluminum alkyl halides
UN 3129	water-reactive substances, liquid, corrosive n.o.s.

UN 3130	water-reactive liquid, toxic n.o.s.
UN 3131	water-reactive solid, corrosive n.o.s.
UN 3134	substances which in contact with water emit flammable gases, solid, poisonous, n.o.s
UN 3148	water-reactive substances, liquid, n.o.s
UN 3203	pyrophoric organometallic compound n.o.s.
UN 3207	organometallic compound solution water-reactive, flammable n.o.s.

- Seven materials that did not appear in the 1996 North American ERG were proposed by DOT for inclusion.

UN1026	cyanogen chloride
UN1340	phosphorus pentasulfide
UN1394	aluminum carbide
UN1402	calcium carbide
UN1809	phosphorus trichloride
UN1827	titanium tetrachloride
UN1831	oleum

Two of these compounds, cyanogen chloride and titanium tetrachloride, were found to be suitable candidates. Three of the seven materials (phosphorus pentasulfide, phosphorus trichloride, and oleum) were already included in the starting set of 208. Calcium carbide and aluminum carbide were rejected because their reaction with water generates acetylene, a gas that is flammable but is not a TIH hazard.

2.4.2 Evaluation of Candidates

The final initial list of 224 candidate materials (208 + 14 + 2) 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. Consider general patterns of reactivity.
2. Examine the primary literature.
3. Examine standard secondary sources such as Kroschwitz (1991–1996) and Lewis (1966).
4. Perform experimental tests on 21 compounds at the University of Illinois at Chicago to estimate the yield and rate of production of toxic gases when mixed with water.

Steps 1 through 3 are similar to the process used to generate the 1996 TIHWR list. Step 4, however, is a new element in the overall analysis. In addition to qualitative descriptions and professional judgment, this experimental program was included in the TIHWR analysis framework to provide a more empirical basis for TIHWR hazard estimates. The program consisted of a series of small-scale experiments with representative materials. 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. Experiments were conducted for 21 substances. About one-quarter of the total TIHWR list was examined, with heavy emphasis on members of the large class of HCl emitters.

Water-reactive materials were tested for the generation of gases by mixing small amounts (about 1 millimole [mmol]) of the material with water in a closed system. A diagram of this apparatus is given in Figure C.1 in Appendix C. The release of gas was followed over time by observing the displacement of a manometer. For example, when gaseous HCl was generated, HCl vapor was displaced into a buret held at an angle of about 15 degrees from the horizontal. This arrangement allowed for substantial increases in the volume of the closed system while limiting the increase in the pressure within the system to less than 15 kPa. Two experiments that used different amounts of water (stoichiometric and five-fold molar excess) were conducted for each material considered. The experimental procedure and resulting data are more fully discussed in Appendix C.

Additional issues associated with the evaluation process are specifically discussed here.

- In an independent study, Nuessler omitted 19 substances that appear in the 1996 North American ERG “List of Dangerous Water-Reactive Materials.” This difference occurred because the purposes of the two lists differed. Nuessler’s list focused on fire safety and omitted the 19 substances because the gases (such as ammonia or HCl) generated when these substances react with water are not very flammable. These 19 materials were retained for the 2000 TIHWR list because ammonia and HCl are TIH hazards.

- Materials that undergo highly exothermic reactions with water can generate mist when released into water. For such compounds, water in contact with the material boils violently, emitting a mist of fine particles of hydrated or partially hydrated material. For example, in contact with water, oleum (UN 1831) raises a toxic fume containing $SO_3 \cdot H_2O$, H_2SO_4, and other sulfur-containing species. Such mists present a clear toxic inhalation hazard. The possibility of acidic mists also exists for spills into water of phosphorus pentoxide (UN 1807), leading to a mist of phosphoric acid; sulfur trioxide (UN 1829), emitting a mist of $SO_3 \cdot H_2O$ and H_2SO_4; and sulfuryl chloride (UN 1834), generating a mist of $SO_3 \cdot H_2O$ and H_2SO_4, plus gaseous HCl.

- Some materials in 2000ERG are not sufficiently described chemically to allow a complete assessment of their behavior when spilled into water. Such materials were not recommended for inclusion unless there was a positive indication that a TIH gas might develop in a spill into water. Thus, pyrophoric organometallic compound n.o.s. (UN 3203) and organometallic compound solution water-reactive, flammable, n.o.s (UN 3207), which would almost certainly evolve only weakly toxic hydrocarbons or hydrogen when spilled into water, were not recommended. Similarly, 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) were not recommended for inclusion.

On the other hand, 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) were recommended for inclusion.

- Materials that are gases at ordinary conditions (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 cause a significant reaction with surface water under most atmospheric conditions.

- Liquids boiling in the range of ordinary environmental temperature (0 to 30°C) presented problems, in part because they can exist 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. 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 frequently remains in the liquid state when spilled in water. In addition, BCl_3 is frequently purveyed in solution in an organic solvent.

- DOT representatives proposed removing calcium hypochlorite (UN 1748), which appears in the 1996 North American ERG. Because of the uncertainties that are associated with both this material and lithium hypochlorite (UN 1471), the former was among the 21 materials chosen for experimental studies. Under the conditions of these experiments, no gases evolved when calcium hypochlorite was mixed with water. Therefore, a recommendation was made to remove both calcium hypochlorite and lithium hypochlorite from the TIHWR list. Calcium hypochlorite had previously been recommended for inclusion because instances of heating and subsequent decomposition to Cl_2 with some HCl upon mixing with a restricted quantity of water had been reported (Lewis [1966], p. 707). However, this scenario appeared too unlikely to justify continued inclusion of the material in the TIHWR list. The results of this analysis also concur with the DOT-proposed omission of nitrosylsulfuric acid (UN 2308) and ammonium hydrosulfide solution (UN 2638).

As a result of the steps and considerations detailed above, 37 new materials were proposed for inclusion in the 2000ERG. This list is presented in Appendix D, along with a brief summary of reasons for the inclusion of each material. Table D.1 provides the full list of TIHWR materials with these 37 additions. It also provides important parameters associated with each material such as the (1) state in which the material is shipped, (2) density of the material, (3) stoichiometric yield, (4) effectiveness factor, and (5) primary rate constant.

2.5 Determination of Initial Isolation Distances

The Initial Isolation Distance denotes 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 a more stringent requirement for most cases, so that purpose is used to define the Initial Isolation Distance. For TIH materials that are also flammable or oxidizers, the Initial Isolation Distance does not account for the explosive or flammable nature of the material. Therefore, the Initial Isolation Distance can be less than the suggested evacuation distances specified in the 2000ERG.

The Initial Isolation Distance is calculated in a manner similar to that used for the PAD. Here, the life-threatening health criterion is defined as an ERPG-3, together with a 5-min exposure time. For chemicals for which an ERPG-3 does not exist, the health criterion is $0.1 \times LC_{50}$. For such materials, this criterion is 10 times the health criterion used to define the PAD (i.e., the ERPG-2 surrogate). The 5-min exposure time accounts for both the meander of the plume close to the source and the fact that people would not remain in this zone unless they became incapacitated.