

Appendix B

Harmful Properties of Chemical Agents

ESTIMATED SHORT-TERM SAFE DOSE AND AIRBORNE EXPOSURE LEVELS

Tables B-1 and B-2 list available short-term safe doses, EC_{50} , estimates of safe short-term doses, and current allowable exposure levels (AELs). The EC_{50} is the airborne concentration sufficient to produce severe effects in 50 percent of those exposed for 30 minutes (NRC, 1997a). An estimate of a short-term safe dose is obtained by dividing the incapacitating dose (ICt_{50}) by 480 minutes (eight hours) and then dividing by a safety factor of 10. The estimates are not considered recommendations but suggest concentration levels that would define an all-clear. The AEL is the maximum chemical concentration of an agent in air that is safe for continuous exposure during an eight-hour work day (ERDEC, 1996). The AEL is a general term indicating a level of exposure that is unlikely to result in adverse health effects.

LETHAL AGENTS

Nerve agents

Nerve agents are chemicals that disrupt the mechanism by which nerves transfer messages to organs. The disruption is caused by blocking the activity of acetylcholinesterase, an enzyme that normally destroys and stops the activity of acetylcholine, a neurotransmitter. Nerve agents, organophosphorus compounds originally developed by German scientists during the 1930s as

TABLE B-1 Lethal Chemical Warfare Agents

Agent	Code	Median Lethal Exposure, LCt_{50} (mg-min/m ³ except where noted)
Nerve Agents		
Tabun	GA	400 (resting inhalation) LD_{50} : 1 to 1.5 mg/person (dermal dose)
Sarin	GB	100 (resting inhalation) 70 (mildly active inhalation) 15,000 (dermal)
Soman	GD	70 (mildly active inhalation) 10,000 (dermal estimated)
Fluoride-containing organophosphate	GF	N/A for inhalation path LD_{50} : 16 to 400 µg/kg in mice
Standard V-agent	VX	100 (resting inhalation) 6 to 360 (dermal-clothed)
Vx or V-gas	Vx	Similar to VX
Binary nerve agents	GB2 VX2	Similar to GB Similar to VX
Pulmonary (Choking) Agents		
Phosgene	CG	3,200
Diphosgene	DP	3,000
Blood Agents		
Hydrogen cyanide	AC	Varies with concentration: 2,000 mg-min/m ³ at 200 mg/m ³ 4,500 mg-min/m ³ at 150 mg/m ³
Cyanogen chloride	CK	11,000
Arsine	SA	5,000

Sources: Boyle, 1998; ERDEC, 1996; NRC, 1997a; U.S. Army et al., 1990.

Median Incapacitating Exposure, ICt_{50} (mg-min/m ³ except where noted)	EC_{50} estimated short-term safe dose AEL (in mg/m ³)	Important Physical Properties
300 (resting inhalation) not known, ~ 30,000 (dermal)	13 0.06 0.0001	Colorless to brown liquid Colorless gas Persistence ~ days Volatility 1/20 H ₂ O
75 (resting inhalation) 35 (mildly active inhalation) 8,000 (dermal)	3 0.01 0.0001	Colorless liquid Colorless gas Persistence < GA Volatility ≈ H ₂ O
~ GB N/A (dermal)	2 0.01 0.00003	Colorless liquid Colorless gas Persistence ~ days Volatility 1/20 H ₂ O
N/A	N/A	Colorless liquid Colorless gas Persistence ~ days Volatility ≈ H ₂ O
50 (resting inhalation) LD_{50} : 10 mg/person (dermal)	3 0.01 0.00001	Amber oily liquid Persistence ~ weeks to months Volatility 1/1500 H ₂ O
Similar to VX	3 0.01 0.00001	Amber oily liquid Persistence ~ VX Volatility 1/150 H ₂ O
Similar to GB Similar to VX		Similar to GB Similar to VX
1,600	100 0.33 0.002	Colorless gas Volatile/not persistent
1,600	100 0.3 0.002	Colorless oily liquid Less volatile and more persistent than CG
Varies with concentration	150 N/A 0.003	Colorless liquid Evaporates quickly Rapid detoxification Highly volatile Not persistent Disperses rapidly in air
7,000	400 1.5 0.008	Colorless liquid Evaporates quickly Not persistent
2,500	200 0.5 0.004	Gas Ignites easily Not persistent

TABLE B-2 Debilitating and Incapacitating Chemical Warfare Agents

Agent	Code	Median Lethal Exposure, LCt_{50} (mg-min/m ³ except where noted)
Vesicants (Blister) Agents		
Levinstein mustard	H	Same as HD
Distilled mustard	HD	LD_{50} : (estimate) 7 gm/person 1,500 (respiratory) 10,000 (dermal)
Nitrogen mustard	HN-1	1,500 (respiratory) 20,000 (dermal)
Nitrogen mustard	HN-2	3,000 (respiratory)
Nitrogen mustard	HN-3	LD_{50} : (estimate) 0.7 gm/person (dermal) 1,500 (respiratory)
Mustard-T mixture	HT	None established, assume similar to HD
Lewisite	L	LD_{50} : 30 mg/kg 1,400 (respiratory) 100,000 (dermal)
Mustard-lewisite mixture	HL	~1,500 (respiratory) >10,000 (dermal)
Phenyl-dichloroarsine	PD	2,600 (respiratory)
Ethyl-dichloroarsine	ED	3,000 to 5,000 (respiratory) 100,000 (dermal)
Methyl-dichloroarsine	MD	No accurate data, likely similar to ED
Phosgene oxime	CX	3200 (estimated)

Median Incapacitating Exposure, ICt_{50} (mg-min/m ³ except where noted)	EC_{50} estimated short-term safe dose AEL (in mg/m ³)	Important Physical Properties
Same as HD	50 0.03 0.003	Same as HD
150 (respiratory) 100–200 (eye injury) 2,000 (dermal))	50 0.03 0.003	Oily liquid Colorless gas 4–6 hour delay for effects Very persistent
200 (eye injury) 9,000 (dermal))	50 0.03 0.003	Oily liquid Colorless gas ~12 hour delay for effects Very persistent, but < HD
100 (eye injury) ~ 6,000 (dermal)	50 0.03 0.003	Dark liquid ~12 hour delay for effects Similar to HD
200 (eye injury) 2,500 (dermal)	50 0.03 0.003	Oily liquid ~4–6 hour delay for effects Longer than HD
None established, assume similar to HD	50 0.03 0.003	Yellow liquid Delayed action but not well known More persistent than HD
< 300 (eye injury) > 1,500 (dermal)	50 0.06 0.003	Colorless to brown liquid Rapid acting Less persistent than HD
~200 (eye injury) 1,500 to 2,000 (dermal)	50 0.04 0.003	Liquid Rapid acting skin irritation, blisters in 13 hours Less persistent than HD
0.9 mg/m ³ (respiratory irritation) 16 (as vomit agent) 0 (as vesicant) 5 to 10 (respiratory)	100 0.003 0.003 N/A	Liquid Rapid acting Persists days to weeks Colorless liquid Rapid acting nose/throat irritation, blisters in 12 hours
25 (respiratory)	N/A	Not persistent Liquid Rapid acting nose/throat irritation, blisters in several hours
Becomes unbearable to the eyes at ~ 3 mg/m ³	N/A	Not persistent Solid (liquid above 39°C) Rapid acting Persists for hours in soil

TABLE B-2 Debilitating and Incapacitating Chemical Warfare Agents (continued)

Agent	Code	Median Lethal Exposure, $LC_{t_{50}}$ (mg-min/m ³ except where noted)
Sternutators (Vomiting Compounds)		
Diphenyl-chloroarsine	DA	15,000 (estimated)
Diphenyl-cyanoarsine	DC	10,000
Adamsite	DM	~ 11,000 (variable)
Lacrimators (Tearing Compounds, Riot-Control Agents)		
Bromobenzyl-cyanide	CA	8,000 to 11,000 (estimated)
Chloroaceto-phenone	CN	~ 11,000
CN + chloroform	CNC	11,000
CN + carbon tetrachloride + benzene	CNB	< 11,000
CN + chloropicrin + chloroform	CNS	11,400
o-chloro-benzylidene malonitrile	CS CS-1 CS-2 CSX	61,000
Dibenz-(b,f)-1,4-oxazepine)	CR	None reported
Chloropicrin	PS	2,000
Psychochemical (Incapacitating Agents)		
3-quinuclidine-dinyl benzilate	BZ	200,000

Median Incapacitating Exposure, ICt_{50} (mg-min/m ³ except where noted)	EC_{50} estimated short-term safe dose AEL (in mg/m ³)	Important Physical Properties
12	N/A	Solid (crystals) Not persistent
30 (30-sec exposure)	N/A	Solid (crystals)
20 (5-min exposure)	N/A	Not persistent
22 to 150	N/A	Yellow/green solid (crystals) Not persistent
30	N/A	Yellow solid or liquid Can persist 1-2 days
N/A	Solid powder	Not persistent
~ 80	N/A	Liquid Not persistent
~ 80	N/A	Liquid Not persistent
60	N/A	Liquid Not persistent
10-20 1 to 5 mg/m ³ (eye effects)	N/A	Solid, powder, or liquid Persistence depends on form
P0.15 mg/m ³ 0.002 mg/m ³ (respiratory threshold)	N/A	Yellow powder in solution Persists up to 60 days
0.004 mg/m ³ (eye threshold) 9 (irritation threshold)	N/A	Colorless, oily liquid Not persistent
112 2 mg/m ³ (inhalation threshold)	N/A	White crystalline solid Very persistent in soil and water

insecticides, were developed into chemical weapons by the Nazi military. Since then, nerve agents have been the main chemicals stockpiled as chemical weapons. The physiological symptoms associated with nerve agents begin seconds or minutes after skin contact or exposure to the vapors or aerosols of these compounds. At lower levels of exposure, symptoms range from dripping nose, tightness in the chest, and pinpoint pupils to excessive salivation, sweating, and nausea. At higher levels, symptoms range from vomiting, cramps, twitching/jerking, staggering, headache, confusion, and loss of muscle control to coma, convulsions, and death. When liquid agents are applied to the skin, the onset time is longer (up to 18 hours) than with inhalation (10 minutes) (Boyle, 1998).

The primary military nerve agents are tabun (GA), sarin (GB), soman (GD), GF, and VX. Vx is similar to VX, but 10 times more volatile. The binary nerve agents GB2 and VX2 are forms of GB and VX formed in binary reactions. A summary description of nerve agents is provided in Table B-1. In general, it is assumed that an area exposed to G agents will decontaminate itself in a few days because of the agents' volatility, which is about equal to the volatility of water (the volatility of GA and GF is about 1/20 that of water). However, V agents, the most potent nerve agents, are more stable and less volatile and thus can remain on the ground for several weeks. V agents are also rapidly absorbed by plants. VX, for example, can remain on materiel, equipment, and terrain for long periods. The uptake of V agents is mainly through the skin but also through inhalation of the gas or aerosol. Uptake of G agents is primarily through inhalation.

Pulmonary (Choking) Agents

A pulmonary agent, or choking agent, is a chemical that damages the membranes separating the alveolus (air sac) of the lung from the capillaries. A number of common chemicals can cause this type of damage. Phosgene (CG), the prototype of this class, is a common industrial chemical with a moderately lethal dose. Diphosgene has a toxicity similar to CG but is less volatile. Choking agents were the most commonly used agents during World War I, but they have lost much of their advantage since the advent of nerve gases. A summary description of pulmonary agents is provided in Table B-1.

Cyanide ("Blood") Agents

Cyanide-based compounds are the main components of blood agents. A characteristic of cyanide poisoning is red skin, which is caused by blood going through the capillary bed without unloading oxygen. Cyanide in moderate amounts can produce nausea and feelings of dizziness,

weakness, and anxiety. Blood agents are highly volatile and nonpersistent even at low temperatures.

Hydrogen cyanide is a slightly more lethal than CG but is less effective because of its rapid rate of evaporation and its rapid rate of detoxification. Loss of consciousness and death can occur after even very brief exposures to high concentrations of hydrogen cyanide, but because of rapid detoxification, the toxicity of hydrogen cyanide varies with the exposure concentration. Because of its high volatility, the large doses required, and the fact that it is lighter than air, hydrogen cyanide is a less-than-ideal compound in ambient air, although it can be very effective in enclosed spaces. Cyanogen chloride has strong irritating and choking effects and slows breathing and is not as toxic as hydrogen cyanide. Arsine is used as a delayed-action casualty agent. Arsine is lethal at relatively high doses; at lower doses, it damages the liver and kidneys, can cause anemia, and is a carcinogen. A summary description of blood agents is provided in Table B-1.

OTHER TYPES OF HARMFUL WARFARE AGENTS

Vesicants (Blister Agents)

Blister agents, or vesicants, are intended to cause injury by blistering rather than cause death. Levinstein mustard (H) was used extensively during World War I. Vesicants attack and burn the eyes, mucous membranes, respiratory tract, and skin, causing the formation of blisters. When absorbed through the lung, gut, or skin, they cause vomiting and diarrhea. The severity of vesicant damage is directly related to exposure levels, that is, the duration of contact and the concentration in the contact medium (air, water, food, surfaces, etc.). All of the blister agents are persistent, and all of them can be used as gases or liquids. Blister agents can be used to poison food and water supplies and to make other supplies dangerous to handle. A summary description of the blister agents is provided in Table B-2.

There are three categories of blister agents—mustards, arsenicals, and urticants. Mustards include the sulfur mustards (H, distilled mustard [HD]), and nitrogen mustards (HN-1, HN-2, HN-3). The mustards penetrate well into skin and other materials, such as wood, clothing, rubber, and paints, and are very persistent in cold and temperate climates. Because mustards have delayed effects (4 to 6 hours or more), unprotected individuals can be exposed to large doses without immediate response.

Arsenical vesicants have delayed action, but, unlike mustards, they tend to produce immediate pain to whatever part of the body they contact. The principal arsenical of military interest is lewisite (L). Other arsenicals

are the mustard-lewisite mixture (HL) and the substituted double-chlorinated arsines (phenyldichloroarsine, ethyldichloroarsine, and methyl-dichloroarsine). Urticants are vesicants with disagreeable and penetrating odors that cause an immediate and severe burning sensation, as well as intense pain, numbness, and swelling. The only urticant of current military interest is phosgene oxime (CX).

Sternutators and Lacrimators

Vomiting compounds, or sternutators, and tear-producing compounds, or lacrimators (known as riot-control agents), are used for short-term incapacitation. Unless used indoors or where ventilation is extremely poor, these compounds are not fatal. The effects are short lived, and therefore do not incapacitate troops for very long.

Chemical vomiting agents produce strong, pepper-like irritations in the upper respiratory tract and eyes, which results in uncontrolled sneezing, coughing, nausea, and vomiting. Military sternutator agents include diphenylchloroarsine, diphenylcyanoarsine, and adamsite. A summary description of vomiting agents is provided in Table B-2. Sternutators, which are solids at ambient conditions, vaporize when heated into aerosols that are dispersed in the air. Sternutators are not persistent, but the aerosols can be rapidly dispersed and deposit slowly out of the air. The median incapacitating concentrations, ICt_{50} , for these agents vary from 12 mg-min/m for diphenylchloroarsine and 30 mg-min/m for diphenylcyanoarsine to 22-150 mg-min/m for adamsite. Outdoors these agents are debilitating; indoors they can cause serious illness and even death.

Tear-producing compounds, or lacrimators, cause a large flow of tears and some irritation to the skin and respiratory tract. Because the effects are only transient, lacrimators are used for training and riot control. The principal tear-producing agents are bromobenzylcyanide (CA), chloroacetophenone (CN, also used as mace), o-chlorobenzylidenmalonitrile (CS), dibenz-(b,f)-1,4-oxazepine (CR), and chloropicrin (PS). There are three CN solutions—CNC (CN with chloroform), CNB (CN with carbon tetrachloride and benzene), and CNS (CN mixed with chloropicrin and chloroform). There are also different forms of CS—CS-1 (CS blended with silica aerogel), CS-2 (CS blended with silicone-treated silica aerogel), and CSX (a liquid form of CS). The lacrimators currently in use by the U.S. military are CS, CS1, CS2, CSX, and CR. However, any of the lacrimators could be used against U.S. troops. These agents are not persistent, with the exception of CR, which can persist for up to 60 days under some circumstances. A summary description of the many tear-producing agents is provided in Table B-2.

Psychochemical (Incapacitating) Agents

Psychochemical, or incapacitating, agents are chemicals that cause temporary, reversible physiological or mental effects. Unlike the effects of riot-control agents that last only a few minutes, the effect of psychochemical agents last for hours or days. Psychochemical agents include both central nervous system (CNS) depressants and CNS stimulants.

CNS depressants block the activity of the CNS and disrupt the transmission of information across nerve synapses. An example of this class of compounds is 3-quinuclidinyl benzilate, which affects the ability to remember, solve problems, pay attention, and listen to instructions. Cannabinols and phenothiazines lead to sedation and lack of motivation rather than impeding the ability to think. Fenyls are opiates that act like morphine but are 10,000 times as potent.

CNS stimulants cause excessive nervous activity, usually by increasing or facilitating the transfer of nerve impulses that might otherwise not cross certain nerve synapses. The effect is to flood the brain with too much information, which makes concentration difficult and results in indecisiveness and the inability to sustain actions.

EMERGING CHEMICAL WARFARE THREATS

The types and chemical properties of agents currently being developed or likely to be developed in the next five to ten years should be a subject of inquiry:

There are thousands, maybe even tens of thousands, of “chemical compounds” in existence or proposed that could be considered for use in war depending upon the action required of them from the military point of view, including all the various drugs that are prescribed and taken and those that are not prescribed and taken. Many of these are lethal and incapacitating, even in small doses (Boyle, 1998, p. 7).

Bioregulator chemicals, for example, could be a threat in future deployments. These chemicals mimic or disrupt hormone signals and could be effective at very low doses.

OTHER POTENTIALLY HARMFUL CHEMICAL AGENTS

Toxic Industrial Chemicals

In addition to warfare agents, a large and growing number of potentially harmful chemical compounds can be found in or introduced into

the environments of deployed forces. For example, troops could be exposed to propellents, explosives, and pyrotechnic (PEP) hazards, a growing number of toxic industrial chemicals (TICs) and chemicals associated with military materiel. TICs are now a common component of military deployment and military training.

An extensive literature is available on the identification, evaluation, and control of human exposures to harmful industrial/commercial chemicals in both occupational and nonoccupational settings. The number of chemical substances in these categories is large and growing. About 20 million chemical compounds have been identified; 80,000 industrially and commercially used chemicals, 600 pesticides, and 100 new chemicals being introduced each year (Chemical and Engineering News, 1999; GEO-CENTERS and Life Systems, 1997; NTP, 1999). Not all of these are harmful chemicals. Approximately 400 chemical substances have been identified by regulatory agencies as potentially toxic and requiring some limitations on exposures. Currently, only 188 substances are listed by the Environmental Protection Agency (EPA) as hazardous air pollutants (EPA, 1998), and 85 chemicals have federal and/or state health-based concentration standards (NRC, 1999). However, these lists continue to expand. Thousands of chemicals have not yet undergone even a screening-level analysis of their potential toxicity, and thousands more have only undergone limited toxicity studies.

TICs can be organized according to their chemical properties and sources. Table B-3 provides a list of categories of chemical compounds containing chemicals that have been labeled toxic to humans. The list is not complete, but it gives a sense of the types of substances that should be detected and monitored and the concentrations that should be measured. In each category, examples of toxic chemicals are listed along with the chronic oral reference safe dose (*RfD*) in mg/kg/day, the chronic reference concentration (*RfC*) in mg/m, and (if available) the cancer potency (kg-day/mg). These measures indicate the chemical concentrations that should be detected and monitored to protect troops from low-dose health effects.

The last column of Table B-3 provides concentrations of the substance in water and air corresponding to the safety factor and/or potency factor. For water, an *RfD*-based concentration is calculated based on the assumption that a 70-kg adult drinking 2 L¹ of water per day should be at or below the *RfD*. Water concentration based on the cancer potency is based on the assumption that a 70-kg adult drinking 2 L of water per day will

¹ Two liters per day may be low, however, because TB Med 577 assumes military consumption of water as either 5 L/day or 15 L/day, depending on heat stress.

TABLE B-3 Chemical Categories of Toxic Industrial Chemicals

CAS ID	Pollutant	<i>RfD</i> (mg/kg/day) <i>RfC</i> (mg/m ³)	Cancer Potency ^a	Corresponding Concentrations mg/l water mg/m ³ air
Volatile Halogenated Hydrocarbons				
56-23-5	carbon tetrachloride	<i>RfD</i> 7E-4 <i>RfC</i> N/A	0.13	0.02 mg/L 0.04 mg/m ³
67-66-3	chloroform	<i>RfD</i> 0.02 <i>RfC</i> N/A	0.0061	0.7 mg/L 0.8 mg/m ³
87-68-3	hexachlorobutadiene	<i>RfD</i> N/A <i>RfC</i> N/A	0.078	0.6 mg/L 0.06 mg/m ³
Alkenes				
106-99-0	1,3-Butadiene	<i>RfD</i> N/A <i>RfC</i> N/A	0.28 per mg/m ³ air risk	N/A 0.005 mg/m ³
Mono-Aromatic Hydrocarbons				
71-43-2	benzene	<i>RfD</i> N/A N/A	0.029 oral	1.7 mg/L 0.17 mg/m ³
100-42-5	styrene	<i>RfD</i> 0.2 <i>RfC</i> 1.0	N/A	7.0 mg/L 1 mg/m ³
108-88-3	toluene	<i>RfD</i> 0.2 <i>RfC</i> 0.4	N/A	7 mg/L 0.4 mg/m ³
Polycyclic Aromatic Hydrocarbons (PAHS)				
50-32-8	benzo(a)pyrene	<i>RfD</i> N/A <i>RfC</i> N/A	7.3 oral	0.007 mg/L 0.0007 mg/m ³
206-44-0	flouranthene	<i>RfD</i> 0.04 <i>RfC</i> N/A	None	1.4 mg/L N/A
Halogenated Aromatics				
108-90-7	chlorobenzene	<i>RfD</i> 0.02 <i>RfC</i> N/A	None	0.7 mg/L N/A
106-46-7	1,4-dichlorobenzene	<i>RfD</i> N/A <i>RfC</i> 0.8	None	N/A 0.8 mg/m ³
118-74-1	hexachlorobenzene	<i>RfD</i> 0.0008 <i>RfC</i> N/A	1.6	0.03 mg/L 0.003 mg/m ³
Biphenyls and Halogenated Biphenyls				
92-52-4	biphenyl	<i>RfD</i> 0.05 <i>RfC</i> N/A	None	2 mg/L N/A
1336-36-3	polychlorinated biphenyls (aroclor)	<i>RfD</i> N/A <i>RfC</i> N/A	1 to 2	0.03 mg/L 0.003 mg/m ³
Chlorinated Dibenzo-p-dioxins and Dibenzofurans				
1746-01-6	2,3,7,8-tetrachlorodibenzo- p-dioxin	<i>RfD</i> N/A <i>RfC</i> N/A	130,000	4E-7 mg/L 4E-8 mg/m ³

TABLE B-3 Chemical Categories of Toxic Industrial Chemicals
(continued)

CAS ID	Pollutant	RfD (mg/kg/day) RfC (mg/m ³)	Cancer Potency ^a	Corresponding Concentrations mg/l water mg/m ³ air
Alcohols and Phenols				
95-48-7	methylphenol (o-Cresol)	RfD 0.05 N/A	None	2 mg/L N/A
67-56-1	methanol	RfD 0.5 N/A	N/A	18 mg/L N/A
Halogenated Phenols				
87-86-5	pentachlorophenol	RfD 0.03 N/A	0.12	0.4 mg/L N/A
95-95-4	2,4,5-trichlorophenol	RfD 0.1 N/A	N/A	4 mg/L 0.4 mg/m ³
88-06-2	2,4,6-trichlorophenol	RfD N/A RfC N/A	0.011	0.44 mg/L N/A
Nitrophenols, Nitrotoluenes and Related Compounds				
51-28-5	2,4-dinitrophenol	RfD 0.002 RfC N/A	N/A	0.07 mg/L N/A
121-14-2	2,4-dinitrotoluene	RfD 0.002 RfC N/A	N/A	0.07 mg/L N/A
Nitrogen and Sulfur Compounds				
107-13-1	acrylonitrile	RfD N/A RfC 0.002	0.54	0.09 mg/L 0.009 mg/m ³
91-94-1	3,3'-dichlorobenzidine	RfD N/A RfC N/A	0.45	0.1 mg/L 0.01 mg/m ³
96-45-7	ethylene thiourea	RfD 8E-5 RfC N/A	N/A	0.003 mg/L N/A
Acids				
79-10-7	acrylic acid	RfD 0.5 RfC 0.001	N/A	18 mg/L 0.001 mg/m ³
79-43-6	dichloroacetic acid	RfD N/A RfC	Under review	
Ethers, Ketones, Aldehydes, and Related Compounds				
75-07-0	acetaldehyde	RfD N/A RfC 0.009	0.0022 per mg/m ³	N/A 0.009 mg/m ³
542-88-1	bis(chloromethyl) ether	RfD N/A RfC N/A	222	0.0002 mg/L 0.00002 mg/m ³
78-93-3	methyl ethyl ketone (2-butanone)	RfD 0.6 RfC 1.0	N/A	20 mg/L 1 mg/m ³

TABLE B-3 Chemical Categories of Toxic Industrial Chemicals (continued)

CAS ID	Pollutant	<i>RfD</i> (mg/kg/day) <i>RfC</i> (mg/m ³)	Cancer Potency ^a	Corresponding Concentrations mg/l water mg/m ³ air
Phthalate Esters				
117-81-7	bis(2-ethylhexyl)phthalate (DEHP)	<i>RfD</i> 0.02 <i>RfC</i> N/A	0.014	0.7 mg/L 0.4 mg/m ³
84-74-2	dibutyl phthalate	<i>RfD</i> 0.1 <i>RfC</i> N/A	N/A	4 mg/L N/A
Pesticides				
57-74-9	chlordane	<i>RfD</i> 0.0005 <i>RfC</i> 0.0007	0.35	0.018 mg/L 0.0007 mg/m ³
62-73-7	dichlorvos	<i>RfD</i> 0.0005 <i>RfC</i> 0.0005	0.29	0.018 mg/L 0.0005 mg/m ³
58-89-9	gamma-hexachlorocyclo- hexane (lindane)	<i>RfD</i> 0.0003 <i>RfC</i> N/A	N/A	0.01 mg/L N/A
Metals				
7440-38-2	arsenic	<i>RfD</i> 0.0003 <i>RfC</i> N/A	1.5	0.01 mg/L 0.003 mg/m ³
7440-43-9	cadmium	<i>RfD</i> 0.0005 <i>RfC</i> N/A	1.8 m ³ /mg	0.02 mg/L 0.0008 mg/m ³
Others				
123-91-1	1,4-dioxane	<i>RfD</i> N/A <i>RfC</i> N/A	0.011	5 mg/L 0.5 mg/m ³
	particulate matter (diesel exhaust)	<i>RfD</i> N/A <i>RfC</i> 0.005	N/A	N/A 0.005 mg/m ³

^a [mg/(kg-d)]-1 is the cancer slope factor, the result of a low-dose extrapolation procedure and is presented as the risk (mg/kg)/day. It expresses the lifetime increase in cancer risk as a result of a unit increase in lifetime equivalent dose, expressed as mg/kg-d—that is, the low-dose rate averaged over a lifetime.

not exceed a lifetime (70 years) equivalent risk of 10 during a six-month deployment. The lesser of these water concentrations is listed in the last column. Air concentration for the cancer potency is based on the assumption that a 70-kg adult breathing 20 m of air per day will not exceed a lifetime (70 years) equivalent risk of 10⁻⁵ during a six-month deployment. The lesser of potency-derived air concentration and the *RfC* is listed in the last column. *RfD*, *RfC*, and potency values were obtained from the EPA's IRIS database (EPA, 1999).

Sources of chemically toxic agents for deployed troops include smokes and obscurants, solvents, products of combustion, metals and metal products, pesticides, fuels, and other industrial and/or military compounds. The sections below provide examples of the types of chemical substances associated with these sources and examples of the sources and emissions of these chemicals.

Smokes and Obscurants

Smokes and obscurants are used in military operations to create diversions and to conceal troop movements. The National Research Council Committee on Toxicology has carried out studies on the health effects of exposures to commonly used smokes and obscurants (NRC, 1997b). White phosphorus is presented here as an example of a smoke/obscurant compound, although the smoke rises in a pillar, and is one of the less toxic smokes in use. Other examples are hexachloroethane and Russian anthracene-based smokes.

White phosphorus is a colorless, white, or yellow waxy solid with a garlic-like odor; it does not occur naturally but is derived from phosphate rocks. White phosphorus reacts rapidly with oxygen, easily catching fire at temperatures of only 4 to 8°C above room temperature. White phosphorus is used by the military in various types of ammunition and to produce smoke for concealing troop movements and identifying targets. It is also used by industry to produce phosphoric acid and other chemicals used in fertilizers, food additives, and cleaning compounds. White phosphorus can enter the environment through deliberate deployment or through accidental spills during transport or storage. In the air, white phosphorus reacts rapidly with oxygen to produce relatively harmless chemicals within minutes. In water, it reacts with oxygen within hours or days. In soil, it may stick to particles and be changed within a few days to less harmful compounds. On the skin, burning white phosphorus particles not only cause severe thermal injury, but the phosphorus pentoxide formed by oxidation reacts with water in the blood to form phosphoric acid, which causes death by reacting with ionized calcium, thus depleting the blood of this essential element.

Solvents

Trichloroethylene

Trichloroethylene (TCE), an example of a volatile halogenated hydrocarbon of the chemical family of chlorinated alkenes, is commercially produced by chlorination and dehydrochlorination of 1,2-dichloroethane.

A major use of TCE is in the vapor degreasing of fabricated metal parts. It is also used as a carrier solvent in textile cleaning and solvent extraction processes, as a lubricant and adhesive, and as a low-temperature heat transfer fluid. TCE is also used in the production of polyvinyl chloride, paints, coatings, and some miscellaneous chemical syntheses. An estimated 60 to 90 percent of the TCE produced in the world is released into the environment; the primary transport process for removal is volatilization (WHO, 1984a).

Tetrachloroethylene

Tetrachloroethylene (PCE), an example of a volatile halogenated hydrocarbon, is a commercially important chlorinated hydrocarbon solvent used as a dry cleaning agent and degreasing agent. PCE is used as a solvent for fats, greases, waxes, rubber, and the decaffeination process; to remove soot from industrial boilers; and as a heat-transfer medium. PCE is used in the manufacture of fluorocarbon refrigerants, paint removers, and printing inks. PCE is a primary source for the preparation of trichloroacetic acid (WHO, 1984b). PCE typically enters the atmosphere as a fugitive industrial emission. It reaches water supplies and the soil through the disposal of sewage sludge and factory waste and from leakages from storage and waste sites.

1,4-dichlorobenzene

This compound is a halogenated aromatic produced commercially by the direct chlorination of benzene in the liquid phase. Approximately 30 to 50 percent of the 1,4-dichlorobenzene (p-DCB) produced is used as a space deodorant for toilets and refuse containers or a fumigant for moths, molds, and mildews. A significant amount of p-DCB is used in the production of resins and as an intermediate for the production of other chemicals. p-DCB is also used as a solvent for various applications, such as paint and gums (Howard et al., 1990).

Products of Combustion

Benzo(a)pyrene

Benzo(a)pyrene (B(a)P), a polycyclic aromatic hydrocarbon (PAH), is produced ubiquitously as the result of incomplete combustion. Formation occurs when gasoline, garbage, or any animal or plant material is burned. B(a)P is often found in the smoke and soot of tar-production plants, coking plants, asphalt-production plants, and facilities that burn

organic material, such as wood, coal, and oil. B(a)P is also in cigarette smoke, charcoal-broiled meat, and smoked foods. When released into the atmosphere, smoke and soots combine with dust particles in the air and are carried into water, soil, and crops (WHO, 1983). Other sources of B(a)P are coal tar pitch used to cement electrical parts and the wood preservative, creosote.

2,3,7,8 tetrachloro-dibenzo-p-dioxin

Sources of 2,3,7,8 tetrachloro-dibenzo-p-dioxin (TCDD), a chlorinated dibenzo-p-dioxin, are pulp and paper manufacturing, incineration of municipal and industrial wastes, accidental transformer fires, and accidental industrial explosions (Sittig, 1985). TCDD is a trace contaminant of chlorophenols and products synthesized from chlorophenols. It has been associated with the manufacture of hexachlorophene, 2,4,5-T, and 2,4-D, and other pesticides having these compounds as precursors. Similar to some of the chlorinated hydrocarbon insecticides, TCDD is persistent and immobile in soil.

Metals and Metal Compounds

Arsenic

More than 100 minerals and ores contain arsenic (Bodek et al., 1988). In nature, arsenic (As) is usually associated with sulfide ores. Arsenic has valence states of -3, 0, +3, or +5. The principal arsenic-bearing minerals include arsenopyrite (FeAsS), niccolite (NiAsS), cobaltite (CoAsS), tennantite (Cu₁₂As₄S₁₃), enargite (Cu₃AsS₄), and native arsenic. The principal arsenic compounds produced for industrial use are arsenic trioxide (As₂O₃) and arsenic metal. From these, other arsenic compounds are made. About 70 percent of all arsenic consumed by industry is used in pesticides. Other uses include wood preservatives, glass manufacturing processes, alloys, electronics, catalysts, feed additives, and veterinary chemicals (Bodek et al., 1988).

Cadmium

Cadmium (Cd) typically occurs naturally in association with zinc ores, such as sphalerite (ZnS). Greenockite (CdS) is the only mineral of any consequence that bears cadmium (CRC, 1991). Almost all cadmium used industrially is obtained as a by-product in the treatment of zinc, copper, and lead ores. Cadmium has only one valance state, +2. Cadmium forms a number of salts, including cadmium chloride (CdCl₂), cadmium sulfate

(CdSO_4), and cadmium sulfide (CdS). Cadmium sulfate is the most common salt. Cadmium has a relatively high bioavailability and is accumulated and retained in the human body.

Pesticide Formulations

Hexachlorobenzene

Hexachlorobenzene (HCB) is an example of a halogenated aromatic formed as a waste product in the production of several chlorinated hydrocarbons and is a contaminant in some pesticides. HCB is released to air as a fugitive emission from hydrocarbon production facilities and in flue gases and fly ash from waste incineration. HCB is persistent in the environment because of its chemical stability and resistance to biodegradation (Howard, 1989).

Chlorpyrifos

Chlorpyrifos, a pesticide, is a white crystal-like solid with a strong odor. Because it does not mix well with water, it is usually mixed with oily liquids before it is applied to crops or animals. It may also be applied to crops in a capsule form. In residences, chlorpyrifos is widely used to control cockroaches, fleas, and termites. In agriculture, it is used to control ticks on cattle and as a spray to control crop pests. Chlorpyrifos enters the environment through direct application to crops, homes, work spaces, and pets. It may also enter the environment through volatilization, spills, and the disposal of chlorpyrifos waste. Chlorpyrifos sticks tightly to soil particles, but because it does not mix well with water, it rarely enters local water systems.

Dichlorvos

Dichlorvos, a pesticide, is a sweetish smelling, dense, colorless liquid that mixes readily with water. When used for pest control, dichlorvos is diluted with other chemicals and used as a spray. It can also be incorporated into plastic that slowly releases the chemical. Dichlorvos is used for insect control in food storage areas, greenhouses, and barns, as well as directly on livestock. It is not generally used on outdoor crops. Dichlorvos is sometimes used for insect control in work places and residences. Veterinarians use it to control parasites on pests, and it used to be the active ingredient in No-Pest Strips®. Dichlorvos enters the environment during its manufacture and use, from landfills, and from accidental

spills during transport and leaks from storage containers. It evaporates easily into the air, where it is broken down into less harmful chemicals.

Hexachlorocyclohexane

Hexachlorocyclohexane (HCH), also a pesticide, is a manufactured chemical that exists in eight chemical forms (called isomers). One of these forms, gamma-HCH, also known as lindane, is a white solid substance that may evaporate into the air as a colorless vapor with a slightly musty odor. Although lindane has not been produced in the United States since 1977, it is still imported to and formulated in the United States. Prior to 1983, lindane was used widely as an insecticide on fruit and vegetable crops (including greenhouse vegetables and tobacco) and forest crops (including Christmas trees). It is still used in ointments to treat head and body lice and scabies, but its use is restricted by the EPA, and it can be applied only by a certified applicator. In air, alpha- , beta- , gamma- , and delta-HCH can be present as a vapor or attached to small particles, such as soil or dust. Lindane can remain in the air for up to 17 weeks and travel long distances. Particles with attached HCH may be removed from the air by rain. The length of time that HCH isomers remain in soil is not known. It can accumulate in the fatty tissue of fish.

Fuels

Benzene

Benzene, a mono-aromatic hydrocarbon, enters the atmosphere primarily from fugitive emissions and exhaust connected with its use in gasoline and as an industrial intermediate (WHO, 1982). Sources of benzene are the pyrolysis of gasoline, catalytic or thermal hydrodealkylation of toluene or xylenes, and transalkylation of toluene. Coking, liquefaction, and gasification of coal are also potential sources of benzene. Benzene is used primarily in the manufacture of other chemicals, such as ethylbenzene, styrene, cumene, phenolic resins, ketones, adipic acid, caprolactam, nylon, and various dyes (Clayton and Clayton, 1981).

Toluene

Toluene, a mono-aromatic hydrocarbon, is a colorless liquid with a distinctive sweet and pungent smell that occurs naturally in crude oil and in the tolu tree. One can smell toluene at 8 parts per million parts (ppm) of air and taste it in water at 0.04 ppm to 1 ppm. Toluene is produced during the process of making gasoline and other fuels from crude oil, in making

coke from coal, and as a by-product in the manufacture of styrene. It is also used in making paints, paint thinners, fingernail polish, lacquers, adhesives, and rubber, as well as in some printing and leather tanning processes.

Toluene has been found in waste sites and landfills when discarded as used solvent or in paints, paint thinners, and nail polish. It does not stay in the environment long. It is readily broken down by microorganisms in the soil, and it evaporates quickly from the soil and surface water into the air, where it combines with oxygen to form benzaldehyde and cresol, which can be harmful to people. However, this process is slow. Toluene is removed from air more rapidly by reacting with OH radicals.

Other Industrial Pollutants

Di-2-ethylhexylphthalate

Di-2-ethylhexylphthalate (DEHP), a phthalate ester, is used in large quantities in the organic chemical industry primarily as a plasticizer for PVCs and other polymeric materials (Howard, 1989). It is also used as organic pump fluid. DEHP is released to air and water during the production, disposal, incineration, and recycling of plastic materials in which it has been used. It is also continuously "volatilized" from PVC in which it is used as a plasticizer.

Vinyl chloride

Vinyl chloride (VC), a volatile halogenated hydrocarbon, is not known as a natural product but is commercially produced by halogenation of ethylene. About 96 percent of the vinyl chloride produced is used for the homopolymer and copolymer resins known as PVC. Environmental contamination of VC is reported to come from PVC and latex manufacturing plants that emit residual VC monomer into the air or in the effluent discharge. VC is also found in food and beverage packaging materials. When introduced into the environment, VC is quickly volatilized into the atmosphere (WHO, 1979).

Polychlorinated Biphenyls

Polychlorinated Biphenyls (PCBs) are a class of synthetic organic compounds, members of a family that contain 209 individual isomers. No PCBs have been manufactured in the United States since 1977. PCBs were widely used as coolants and lubricants in transformers, capacitors, hydraulic fluids, and vacuum pumps, and as plasticizers in rubbers and

synthetic resins. PCBs are used in adhesives, wax extenders, dedusting agents, inks, cutting oils, pesticide extenders, sealants, and caulking compounds (WHO, 1993).

Toluene-2,4-diisocyanate

Toluene-2,4-diisocyanate (2,4-TDI) is a white liquid used in the manufacture of polyurethane foams and other elastomers. 2,4-TDI constitutes roughly 80 percent of the commercial toluene diisocyanate (TDI) used in the United States, the other 20 percent being the isomer, 2,6-TDI (Howard, 1989). TDI is released to the environment as a fugitive emission from stack exhaust during the production, transport, and use of TDI in the manufacture of polyurethane foam products. Both 2,4- and 2,6-TDI are reactive with any compound having active hydrogens (i.e. water, acids, alcohols).

REFERENCES

- Bodek, I., W.J. Lyman, W.F. Reehl, and D.H. Rosenblat. 1988. *Environmental Inorganic Chemistry: Properties, Processes, and Estimation Methods*. New York: Pergamon Press.
- Boyle, R.E. 1998. *U.S. Chemical Warfare: A Historical Perspective*. Contract No. LG-1597. Albuquerque, N.M.: Sandia National Laboratories.
- Chemical and Engineering News. 1999. Flotsam and Jetsom. *Chemical and Engineering News* 77(43): 96.
- Clayton, G.D., and F.E. Clayton, eds. 1981. *Patty's Industrial Hygiene and Toxicology* (3rd ed.). New York: John Wiley and Sons.
- CRC (Chemical Rubber Company). 1991. *CRC Handbook of Chemistry and Physics* (72nd ed). Boston, Mass.: CRC Press, Inc.
- EPA. 1998. *National Air Quality and Emissions Trends Report, 1997*. Contract No. EPA 454/R-98-016. Research Triangle Park, N.C.: Environmental Protection Agency, Office of Air Quality Planning and Standards.
- EPA. 1999. Stand Alone (Downloadable) IRIS Database. Available on line at: <http://www.epa.gov/iris/stand-al.htm>
- ERDEC (Edgewood Research, Development and Engineering Center). 1996. *Military Unique Material Safety Data Sheets*. Available on line at: <http://www.sbcom.apgea.army.mil/RDA/ecbc/services/msds/index.htm>
- GEO-CENTERS and Life Systems. 1997. *Deployment Toxicology Research and Development Master Plan*. Contract No. DAMD 17-93-C-3006. Ft. Detrick, Md.: U.S. Army Center for Environmental Health Research.
- Howard, P.H. 1989. *Handbook of Fate and Exposure Data for Organic Chemicals*. Vol. 1. Large Production and Priority Pollutants. Chelsea, Mich.: Lewis Publishers.
- Howard, P.H., G.W. Sage, W.F. Jarvis, and D.A. Gray. 1990. *Handbook of Environmental Fate and Exposure Data for Organic Chemicals*. Vol. 2. Solvents. Chelsea, Mich.: Lewis Publishers.
- NRC. 1997a. *Review of Acute Human Toxicity Estimates for Selected Chemical Warfare Agents*. Board on Environmental Studies and Toxicology, National Research Council. Washington, D.C.: National Academy Press.

- NRC. 1997b. Toxicity of Smokes and Obscurants. Board on Environmental Studies and Toxicology, National Research Council. Washington, D.C.: National Academy Press.
- NRC. 1999. Drinking Water Contaminants. Board on Environmental Studies and Toxicology, National Research Council. Washington, D.C.: National Academy Press.
- NTP (National Toxicology Program). 1999. National Toxicology Program Fiscal Year 1998 Annual Plan. Rockville, Md.: U.S. Department of Health and Human Services, Public Health Service.
- Sittig, M. 1985. Handbook of Toxic and Hazardous Chemicals and Carcinogens (2nd ed). Park Ridge, N.J.: Noyes Publications.
- U.S. Army, U.S. Navy, and U.S. Air Force. 1990. Potential Military Chemical/Biological Agents and Compounds. Field Manual 3-9, Navy Publication P-467, and Air Force Manual 355-7. Washington, D.C.: Department of the Army/Department of the Navy/Department of the Air Force.
- WHO (World Health Organization IARC). 1979. Evaluation of the Carcinogenic Risk to Chemicals to Humans: Vinyl Chloride. Geneva: WHO/IARC.
- WHO. 1982. Evaluation of the Carcinogenic Risk of Chemicals to Humans: Some Industrial Chemicals and Dyestuffs. IARC Monographs Vol.29. Geneva: WHO/IARC.
- WHO. 1983. Evaluation of the Carcinogenic Risk of Chemicals to Humans: Polynuclear Aromatic Compounds. Part 1. Chemical, Environmental and Experimental Data. IARC Monographs Vol. 32. Geneva: World Health Organization.
- WHO. 1984a. Trichloroethylene. World Health Organization Environmental Health Criteria 50. Geneva: WHO/IPCS (International Programme on Chemical Safety).
- WHO. 1984b. World Health Organization Environmental Health Criteria 61: Tetrachloroethylene. Geneva: World Health Organization.
- WHO. 1993. Polychlorinated Biphenyls and Terphenyls. International Programme on Chemical Safety (IPCS). World Health Organization's Environmental Health Criteria 140 (2nd ed). Geneva: WHO/IPCS.