CHAPTER
5

SOURCES, TYPES, AND PROPERTIES OF HAZARDOUS WASTES FOUND IN MUNICIPAL SOLID WASTE

As concern over the disposal of industrially derived hazardous waste has spread, concern has also grown over the disposal of MSW, which may contain small amounts of hazardous wastes from households and commercial facilities. What is unknown is the fate of hazardous materials found in MSW when products such as compost are produced from MSW, when MSW is combusted, and when MSW is placed in landfills. The long-term effects, if any, on public health and the environment from the presence of these materials also are unknown.

The purposes of this chapter are (1) to consider the properties and classification of hazardous wastes, (2) to review the sources and significance of hazardous wastes found in municipal waste, (3) to review the occurrence of hazardous wastes in various activities associated with the management of municipal solid waste, (4) to review the nature of the physical, chemical, and biological transformations that these wastes undergo, and (5) to consider the management of hazardous wastes in MSW. Because so much more needs to be known, the material in this chapter is only intended to serve as an introduction to this subject.

5-1 PROPERTIES AND CLASSIFICATION OF HAZARDOUS WASTES

Before discussing the sources, occurrences, and transformations associated with the hazardous wastes found in MSW, it will be helpful to define what constitutes a
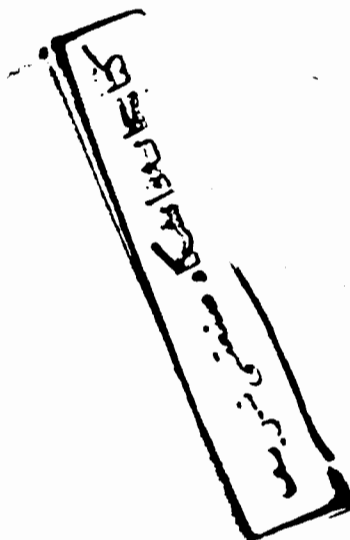
hazardous waste. Hazardous wastes have been defined as wastes or combinations of wastes that pose a substantial present or potential hazard to humans or other living organisms because (1) such wastes are nondegradable or persistent in nature, (2) they can be biologically magnified, (3) they can be lethal, or (4) they may otherwise cause or tend to cause detrimental cumulative effects [14]. Properties of waste materials that have been used to assess whether a waste is hazardous are related to questions of safety and health.

Safety-related properties

> Corrosivity
> Explosivity
> Flammability
> Ignitability
> Reactivity

Health-related properties

> Carcinogenicity
> Infectivity
> Irritant (allergic response)
> Mutagenicity
> Toxicity (poisons)
> > Acute toxicity
> > Chronic toxicity
> Radioactivity
> Teratogenicity

When dealing with the hazardous waste materials found in MSW, municipalities have most commonly used the following properties to define a hazardous waste:

> Ignitability
> Corrosivity
> Reactivity
> Toxicity
> Carcinogenicity

At present, a variety of classification systems and priority lists have been adopted by different regulatory agencies to define a hazardous waste. For this reason, all of the current operative classification systems must be considered in any assessment.

Definitions Given by the U.S. Environmental Protection Agency

In developing regulations for the implementation of legislation related to solid waste and wastewater, the U.S. Environmental Protection Agency has published

TABLE 5-1
Categories of RCRA hazardous wastes

Listed	Characteristic	Other
Nonspecific sources	Ignitable	Mixtures (hazardous and nonhazardous)
Specific sources	Corrosive	Residues derived from treatment of wastes
Commercial chemical products (acutely hazardous)	Reactive	Materials containing listed hazardous wastes
Commercial chemical products (nonacutely hazardous)	Toxic	

and refined definitions for (1) RCRA hazardous waste, and (2) priority pollutants. These definitions are reviewed briefly below.

RCRA Hazardous Wastes. The U.S. EPA has defined RCRA hazardous wastes in three general categories: (1) listed wastes, (2) characteristic hazardous wastes, and (3) other hazardous wastes (see Table 5-1). Based on criteria defined in the Code of Federal Regulations (40 CFR 261.11), the U.S. EPA has prepared a list of specific hazardous wastes. If a waste meets these criteria, it is presumed toxic regardless of the concentration. Characteristic hazardous wastes are established on the basis of their ignitability, corrosivity, reactivity, and toxicity (see Table 5-2). Toxicity is determined by an analysis of the constituents derived from an extraction test. Using "Acute hazardous waste" and "Toxic waste" classifications in addition to those reported in columns 1 and 2 of Table 5-1, more than 1200 compounds have been listed as hazardous wastes in the *Federal Register* since 1976.

Other RCRA hazardous wastes (column 3 of Table 5-1) include mixtures of hazardous and nonhazardous wastes; wastes derived from the management of other wastes, such as treatment plant residues (Derived-From Rule); and hazardous materials contained in nonhazardous wastes (Contained-In Rule) [14]. Medical wastes and low-level radioactive mixed wastes are considered special hazardous wastes. Because medical and low-level radioactive mixed wastes are regulated and managed separately, they are not considered further in this text.

Priority Pollutants. In 1979, pursuant to the Federal Water Pollution Control Act as amended by the Clean Water Act of 1977, the U.S. EPA was required to prepare a list of toxic pollutants proven to be harmful to human health. Four criteria were used to classify the pollutants.

1. Actual or potential damage that a water discharge of these materials may create by virtue of certain toxicological properties. These properties include bioaccumulation, carcinogenicity, mutagenicity, teratogenicity, or high acute toxicity.
2. Seriousness of discharge or potential discharge of the pollutant by point sources. Factors include the nature and extent of toxic effects associated

TABLE 5-2
EPA listed wastes based on hazardous characteristics

Characteristic	40 CRF subpart[a]	Considerations	Hazard code
Ignitability	261.21	1. Liquids with flashpoints of less than 140°F (60°C) 2. Nonliquids liable to cause fires through friction, spontaneous chemical change, etc. 3. Ignitable compressed gas 4. Is an oxidizer	I
Corrosivity	261.22	1. Aqueous wastes exhibiting a pH of <3 or >12.5 2. Liquid wastes capable of corroding steel at a rate greater than 0.250 in/year	C
Reactivity	261.23	1. Instability and readiness to undergo violent change 2. Violent reactions when mixed with water 3. Formation of potentially explosive mixtures when mixed with water 4. Generation of toxic fumes when mixed with water 5. Cyanide or sulfide-bearing material that generates toxic fumes when exposed to acidic conditions 6. Ease of detonation or explosive reaction when exposed to pressure or heat 7. Ease of detonation or explosive decomposition or reaction at standard temperature and pressure 8. Defined as a forbidden explosive or a Class A or B explosive by U.S. Department of Transportation	R
Toxicity characteristic (TC), as defined by the toxicity characteristics leaching procedure test (TCLP)	261.24	The following steps are required in the TCLP test: 1. If the waste is liquid (i.e., contains less than 0.5% solids), after it is filtered the waste itself is considered the extract (simulated leachate). 2. If the waste contains greater than 0.5% solid material, the solid phase is separated from the liquid phase, if any. If required, the particle size of the solid phase is reduced until it passes through a 9.5 mm sieve. 3. For analysis other than for volatiles, the solid phase is then placed in an acidic solution and rotated at 30 rev/min for 18 hours. The pH of the solution is approximately 5, unless the solid is more basic, in which case a solution with a pH of approximately 3 is used. After extraction (rotation), solids are filtered from the liquid extract and discarded. 4. For volatiles analysis a solution of pH 5 is used, and a zero headspace extraction vessel is used for liquid/solid separation, agitation, and filtration. 5. Liquid extracted from the solid/acid mixture is combined with any original liquid separated from the solid material and is analyzed for the presence of specified contaminants. 6. If *any* of the contaminants in the extract meets or exceeds any of the maximum concentration levels allowed for the specified contaminants, the waste is classified as a TC hazardous waste.	E

[a] Adapted from the Code of Federal Regulations (CFR) and Ref. 14.

with the pollutant; extent that discharges have been identified; production and distribution; and use pattern of the pollutant.

3. The setting of effluent standards for point source dischargers.
4. Overall environmental effect of the control measures available.

The initial list of priority pollutants contained 65 classes of pollutants, comprising a total of 129 specific substances.

Other Hazardous Waste Classifications

Other hazardous waste classifications have been proposed by the following agencies:

- International Agency for Research on Cancer
- National Cancer Institute
- Environmental Protection Agency—Carcinogen Assessment Group

5-2 SOURCES, TYPES, AND QUANTITY OF HAZARDOUS WASTES FOUND IN MSW

The purpose of this section is to introduce the reader to the sources and types of hazardous wastes found in municipal solid wastes. The significance of these wastes is considered in the following section. Information on the quantities of hazardous waste found in municipal solid waste is presented in Chapter 6.

Typical Hazardous Wastes from Residential Sources

Many of the products used around the home every day such as household cleaners, personal products, automotive products, paint products, and garden products are toxic and can be hazardous to health and the environment (see Fig. 5-1). Typical

FIGURE 5-1
Typical household hazardous wastes found in small amounts in residential MSW.

TABLE 5-3
Typical hazardous household products[a]

Product	Concern	Disposal
Household cleaners		
Abrasive scouring powders	Corrosive	Hazardous waste facility
Aerosols	Flammable	Hazardous waste facility
Ammonia and ammonia-based cleaners	Corrosive[b]	Hazardous waste facility, or dilute small amounts
Chlorine bleach	Corrosive[c]	Hazardous waste facility, or dilute small amounts
Drain openers	Corrosive	Hazardous waste facility
Furniture polish	Flammable	Hazardous waste facility
Glass cleaners	Irritant	Dilute small amounts
Outdated medicines	Hazardous to others in family	Dilute small amounts and flush down toilet
Oven cleaner	Corrosive	Hazardous waste facility
Shoe polish	Flammable	Hazardous waste facility
Silver polish	Flammable	Hazardous waste facility
Spot remover	Flammable	Hazardous waste facility
Toilet bowl cleaner	Corrosive	Hazardous waste facility
Upholstery and carpet cleaner	Flammable and/or corrosive	Hazardous waste facility
Personal care products		
Hair-waving lotions	Poison	Dilute small amounts and flush down toilet
Medicated shampoos	Poison	Dilute small amounts and flush down toilet
Nail polish remover	Poison, flammable	Hazardous waste facility
Rubbing alcohol	Poison	Dilute small amounts and flush down toilet

(continued)

household hazardous products are identified in Table 5-3. These products are of concern owing to their corrosive, flammable, irritant, and poisonous properties.

A survey was conducted to assess the presence of household hazardous wastes in residential MSW; the distribution of hazardous wastes that was found is reported in Table 5-4. These data can be compared with data on hazardous wastes that were received in several Bay Area cities in California on days specified for hazardous waste collection (see Table 5-5). In comparing the data reported in Tables 5-4 and 5-5, it is clear that the relative distribution of hazardous wastes will be quite variable depending on time of year (e.g., greater during the spring cleanup)

TABLE 5-3 (*continued*)

Product	Concern	Disposal
Automotive products		
Antifreeze	Poison	Hazardous waste facility
Brake and transmission fluid	Flammable	Hazardous waste facility
Car batteries	Corrosive	Recycling center/repair
Diesel fuel	Flammable	Recycling center
Kerosene	Flammable	Recycling center
Gasoline	Flammable, poison	Hazardous waste facility
Waste oil	Flammable	Recycling center
Paint products		
Enamel, oil-based, latex or water-based paints	Flammable	Donate or hazardous waste facility
Paint solvents and thinners	Flammable	Reuse or hazardous waste facility
Miscellaneous products		
Batteries	Corrosive	Recycling center or hazardous waste facility
Photographic chemicals	Corrosive, poison	Hazardous waste facility, or donate to photo shop
Pool acids and chlorine	Corrosive	Hazardous waste facility
Pesticides, herbicides, and fertilizers		
Including garden insecticides, ant and roach killers, weed killers, etc.	Poison: some are flammable	Hazardous waste facility or County Department of Agriculture
Chemical fertilizers	Poison	Hazardous waste facility or County Department of Agriculture
Houseplant insecticide	Poison	Hazardous waste facility

*Adapted from Ref. 1.

*b*Never mix ammonia and chlorine-based products—a deadly gas can be produced.

*c*Never mix with toilet bowl cleaner.

and the number of hazardous waste collection days that have been completed in a given community.

Typical Hazardous Wastes from Commercial Sources

The hazardous wastes produced by commercial establishments (often identified as small-quantity generators) are related primarily to the services provided. Typical examples include inks from print shops, solvents from dry cleaning

TABLE 5-4
Distribution of hazardous waste materials found in residential and commercial MSW[a,b]

Item	Percent
Household and cleaning products	40.0
Personal care products	16.4
Automotive products	30.1
Paint and related products	7.5
Pesticides, insecticides, and herbicides	2.5
Other	3.5

[a] From Ref. 5.
[b] Note that the amount of hazardous waste material found in residential and commercial MSW is on the order of 0.1 percent.

TABLE 5-5
Distribution of hazardous waste materials collected during days specified for the collection of hazardous wastes[a]

Hazardous waste	Percent of total
Oil-based paint	31.9
Solvents	15.4
Latex paint	12.1
Pesticides	9.9
Empty oil cans	8.8
Cleaners	8.3
Waste oil	5.0
Acids/bases	4.0
Petroleum products	1.7
Other	2.9

[a] From Ref. 5.

establishments, cleaning solvents from auto repair shops, and paints and thinners from painting contractors. Typical compounds from commercial, industrial, and agricultural sources are presented in Table 5-6.

The U.S. EPA has defined a *small-quantity generator* as one which produces in a calendar month:

- More than 100 kg but less than 1000 kg of nonacutely hazardous waste
- Less than 100 kg of waste resulting from the cleanup of any residue or contaminated soil, water, or other debris involving the cleanup of an acutely hazardous waste
- Less than 1 kg of an acutely hazardous waste

TABLE 5-6
Hazardous waste compounds produced by commercial, industrial, and agricultural activities that are typically found in MSW[a]

Name	Formula or symbol	Use	Concern
Nonmetals			
Arsenic	As	Alloying additive for metals, especially lead and copper as shot, battery grids, cable sheaths, boiler tubes	Carcinogen and mutagen. Long-term: Sometimes can cause fatigue and loss of energy; dermatitis
Selenium	Se	Electronics, xerographic plates, TV cameras, photocells, magnetic computer cores, solar batteries, rectifiers, relays, ceramics (colorant for glass), steel and copper, vulcanizing agent, catalyst, trace element in animal feeds	Long-term: Red staining of fingers, teeth, and hair; general weakness; depression; irritation of nose and mouth
Metals			
Barium	Ba	Getter alloys in vacuum tubes, deoxidizer for copper, Frary's metal, lubricant for anode rotors in x-ray tubes, spark plug alloys	Flammable at room temperature in powder form. Long-term: Increased blood pressure and nerve block
Cadmium	Cd	Electrodeposited and dipped coatings on metals, bearing and low-melting alloys, brazing alloys, fire protection system, nickel-cadmium storage batteries, power transmission wire, TV phosphors, basis of pigments used in ceramic glazes, machinery enamels, fungicide, photography and lithography, selenium rectifiers, electrodes for cadmium-vapor lamps and photoelectric cells	Flammable in powder form. Toxic by inhalation of dust or fume. A carcinogen. Soluble compounds of cadmium are highly toxic. Long-term: Concentrates in the liver, kidneys, pancreas, and thyroid; hypertension suspected effect
Chromium	Cr	Alloying and plating element on metal and plastic substrates for corrosion resistance, chromium-containing and stainless steels, protective coating for automotive and equipment accessories, nuclear and high-temperature research, constituent of inorganic pigments	Hexavalent chromium compounds are carcinogenic and corrosive on tissue. Long-term: Skin sensitization and kidney damage
Lead	Pb	Storage batteries, gasoline additive, paint pigments, cable covering, ammunition, piping, tank linings, solder and fusible alloys, vibration damping in heavy construction, foil, babbitt, and other bearing alloys	Toxic by ingestion or inhalation of dust or fumes. Long-term: Brain, nervous system, and kidney damage; birth defects

TABLE 5-6 (continued)

Name	Formula or symbol	Use	Concern
Metals (cont)			
Mercury	Hg	Amalgams, catalyst, electrical apparatus, cathodes for production of chlorine and caustic soda, instruments, mercury-vapor lamps, mirror coating, arc lamps, boilers	Highly toxic by skin absorption and inhalation of fume or vapor. Long-term: Toxic to central nervous system; may cause birth defects
Silver	Ag	Manufacture of silver nitrate, silver bromide, photo chemicals; lining vats and other equipment for chemical reaction vessels, water distillation, etc.; mirrors, electric conductors, silver plating, electronic equipment; sterilant; water purification; surgical cements; hydration and oxidation catalyst, special batteries, solar cells, reflectors for solar towers; low-temperature brazing alloys; table cutlery; jewelry; dental, medical, and scientific equipment; electrical contacts; bearing metal; magnet windings; dental amalgams. Colloidal silver is used as a nucleating agent in photography and medicine, often combined with protein	Toxic metal. Long-term: Permanent grey discoloration of skin, eyes, and mucous membranes
Organic compounds			
Benzene[b] (Benzol)	C_6H_6	Manufacturing of ethylbenzene (for styrene monomer); dodecylbenzene (for detergents); cyclohexane (for nylon); phenol; nitrobenzene (for aniline); maleic anhydride; chlorobenzene hexachloride; benzene sulfonic acid; as a solvent	A carcinogen. Highly toxic. Flammable; dangerous fire risk
Ethylbenzene[b] (Phenylethane)	$C_6H_5C_2H_5$	Intermediate in production of styrene; solvent	Toxic by ingestion, inhalation, and skin absorption; irritant to skin and eyes. Flammable, dangerous fire risk
Toluene[b] (Methylbenzene)	$C_6H_5CH_3$	Aviation gasoline and high-octane blending stock; manufacture of benzene, phenol, and caprolactam; solvent for paints and coatings, gums, resins, most oils, rubber, vinyl organosols; diluent and thinner in nitrocellulose lacquers; adhesive solvent in plastic toys and model airplanes; chemicals (benzoic acid, benzyl and benzoyl derivatives, saccharine, medicines, dyes, perfumes); source of toluenediisocyanates (polyurethane resins); explosives (TNT); toluene sulfonates (detergents); scintillation counters	Flammable, dangerous fire risk. Toxic by ingestion, inhalation, and skin absorption

Compound	Formula	Uses	Hazards
Halogenated compounds			
Chlorobenzene (Phenylchloride)	C_6H_5Cl	Phenol, chloronitrobenzene, aniline, solvent carrier for methylene diisocyanate, solvent, pesticide intermediate, heat transfer	Moderate fire risk. Toxic by inhalation and skin contact
Chloroethene[b] (Vinyl chloride)	CH_2CHCl	Polyvinyl chloride and copolymers, organic synthesis, adhesives for plastics	Extremely toxic and hazardous by all avenues of exposure. A carcinogen
Dichloromethane[b] (Methylene chloride)	CH_2Cl_2	Paint removers, solvent degreasing, plastics processing, blowing agent in foams, solvent extraction, solvent for cellulose acetate	Toxic. A carcinogen, narcotic
Tetrachloroethene (Tetrachloroethylene, perchloroethylene)	CCl_2CCl_2	Dry-cleaning solvent, vapor-degreasing solvent, drying agent for metals and certain other solids, vermifuge, heat transfer medium, manufacture of fluorocarbons	Irritant to eyes and skin
Pesticides, herbicides, insecticides[c]			
Endrin™	$C_{12}H_8OCl_6$	Insecticide and fumigant	Toxic by inhalation and skin absorption, carcinogen
Lindane™	$C_6H_6Cl_6$	Pesticide	Toxic by inhalation, ingestion, skin absorption
Methoxychlor™	$Cl_3CCH(C_6H_4OCH_3)_2$	Insecticide	Toxic material
Toxaphene™	$C_{10}H_{10}Cl_8$, approximately	Insecticide and fumigant	Toxic by ingestion, inhalation, skin absorption
Silvex	$Cl_3C_6H_2OCH(CH_3)COOH$	Herbicide, plant growth regulator	Toxic material; use has been restricted

a From Ref. 11.

b The five trace organic compounds footnoted are most common in landfill gas.

c Pesticides, herbicides, and insecticides are listed by trade name. The compounds listed are also halogenated organic compounds.

Generators who produce more than these quantities are considered to be *large generators*. Generators who produce less than these quantities are considered *conditionally exempt generators*. Of the three types of waste generators, conditionally exempt generators are subject to the fewest regulatory controls [9]. Under federal regulations and in a few states, conditionally exempt generators are permitted to dispose of small amounts of waste in sanitary landfills that would otherwise be regulated as hazardous waste. It should be noted that many states do not have a lower threshold for small-quantity or conditionally exempt generators and do not allow any hazardous materials to be commingled with MSW.

Quantity of Hazardous Wastes in MSW

To put the issue of hazardous wastes in MSW in perspective, it is estimated that the amount of hazardous waste found in MSW (1992) varies from 0.01 to 1 percent by weight, with a typical value of 0.1 percent. These percentages do not account for the HHW that are illegally disposed of onto land and into sewers and storm drains. The reported range is wide because the methods used to identify and classify the hazardous wastes found in MSW are quite variable and the sampling periods are not consistent between studies. For example, measured values are higher in late spring, when many residents clean their garages of materials such as small amounts of paint, unused cleaning products, and garden products including pesticides and herbicides. The authors have measured values in the range of 0.075 to 0.2 percent by weight for residential and commercial MSW. Although the exact distribution between residential and commercial sources is quite variable, approximately 75 to 85 percent of the hazardous wastes found in MSW are from residential sources. (See Section 6-6.)

5-3   SIGNIFICANCE OF HAZARDOUS WASTES IN MSW

The small amounts of hazardous wastes found in MSW are of significance because of their occurrence in all solid waste management facilities and their persistence when discharged to the environment.

Occurrence of Hazardous Wastes in Solid Waste Management Facilities

The occurrence in MSW of small amounts of solid, semisolid, and liquid hazardous wastes and gaseous compounds derived from these wastes influences the recovery of materials, conversion products (e.g., compost), combustion products, and landfills.

Hazardous Waste Constituents in Conversion Products. Trace amounts of hazardous organic constituents had been found in waste components that had been separated mechanically from commingled MSW. Trace contaminants have

also been found in the compost produced from MSW. In both cases, the presence of trace amounts of hazardous constituents has rendered the materials and products unusable. Source separation is being encouraged to eliminate these constituents from solid waste–processing operations.

Hazardous Waste Constituents in Combustion Products. Hazardous waste constituents have been measured in the gaseous emissions and in the residual materials resulting from the combustion of solid wastes. Toxic heavy metals such as barium, cadmium, chromium, lead, mercury, and silver are especially troublesome.

Hazardous Waste Constituents at Landfills. Trace organic constituents have been found in the atmosphere near landfills, in extracted landfill gas, and in landfill leachate. The trace constituents that have been measured at landfills have two basic sources. They are derived from the hazardous wastes themselves and/or they may be produced by chemical and biological conversion reactions within the landfill.

Long-Term Persistence

As we noted in the introduction to this chapter, the fate of small quantities of hazardous wastes found in MSW is generally unknown. The environmental persistence of these hazardous compounds is one of the critical issues in their long-term management. Often, hazardous wastes are classified as either nonpersistent or persistent (see Table 5-7).

TABLE 5-7
Hazards associated with nonpersistent and persistent organic wastes[a]

Typical compounds	Hazards
Nonpersistent organic wastes Oil, low molecular-weight solvents, some biodegradable pesticides (organophosphates, carbamates, triazines, anilines, ureas), waste oils, most detergents	Toxicity problems primarily to environment and biota at the source or point of release. Toxic effects occur rapidly after exposure (acute and subacute).
Persistent organic wastes High molecular-weight chlorinated and aromatic hydrocarbons, some pesticides (chlorinated insecticides like hexachlorobenzene, DDT, DDE, lindane); PCBs, phthalates	Immediate toxic effects (acute and subacute) may occur at the source or point of release. Long-term chronic toxicity may result. Transport of organic waste from the source can result in widespread contamination and bioconcentration in the food chain. Environmental transport may expose biota to lower levels of the pollutant, resulting in chronic toxicity.

[a] Adapted from Ref 10.

The half-life concept can be used to characterize and compare the relative environmental persistence of various hazardous wastes [4, 13]. At the relatively low concentrations encountered in MSW, the decay (disappearance) of an individual hazardous waste constituent can be described adequately as a first-order function as follows:

$$\frac{d[C]}{dt} = -k_T C \tag{5-1}$$

where $[C]$ = concentration at time t
$\quad t$ = time
$\quad k_T$ = first order reaction rate constant

The integrated form of Eq. (5-1) is

$$\ln \frac{[C_o]}{[C]} = k_T t \tag{5-2}$$

where $[C_o]$ = concentration at time zero

When half of the initial material has decayed away, $[C_o]/[C]$ is equal to 2; the corresponding time is given by the following expression:

$$t_{1/2} = \frac{\ln 2}{k_T} = \frac{0.69}{k_T} \tag{5-3}$$

Example 5-1 illustrates the application of the half-life concept.

Example 5-1 Evaluation of contaminant persistence. Determine the time required for the concentrations of toluene and Dieldrin[*] spilled in a shallow leachate treatment pond to be reduced to one half their initial values. Assume the first-order removal constants for toluene and Dieldrin are 0.0665/hr and 2.665×10^{-5}/hr, respectively.

Solution. Use Eq.(5-3) to determine the time required for the concentrations in the treatment pond to reach one half their original values.

1. For toluene

$$t_{1/2} = \frac{0.69}{k_T} = \frac{0.069}{0.0665/\text{hr}}$$

$$= 10.4 \text{ hr}$$

2. For Dieldrin

$$t_{1/2} = \frac{0.69}{2.665 \times 10^{-5}/\text{hr}}$$

$$= 25,891 \text{ hr}$$

Comment. The time required for the concentration of dieldrin to reach one half of the initial value can be used as an argument for the development and use of agricultural chemicals that are more readily broken down in the environment.

5-4 PHYSICAL, CHEMICAL, AND BIOLOGICAL TRANSFORMATIONS OF HAZARDOUS WASTE CONSTITUENTS FOUND IN MSW

In general, hazardous wastes in MSW are either solids, semisolids, or liquids. In addition, trace chemical compounds can exist as a solute within a liquid solvent, as a gas adsorbed onto a solid, or as a component of the gaseous emissions from MSW, particularly MSW placed in landfills. Physical, chemical, and biological transformations that are important in determining the fate and dispersal of these materials are introduced in this and the following two sections.

Physical Transformations

The principal physical transformations that alter the form of the hazardous constituents found in MSW are volatilization and phase distribution.

Volatilization. The principal mechanisms leading to the production of the gaseous substances from MSW are volatilization, biodegradation, and chemical reaction. Of these, volatilization is thought to be the most important. Hazardous wastes can occur in the gaseous state as a result of three related processes: volatilization of chemical wastes, volatilization of liquid chemical wastes in water and leachate, and volatilization of chemical wastes adsorbed on soil or other solids [7]. The first process is a function of exposed surface area, time, diffusion coefficients, vapor pressures, molecular weight, and temperature. The second process is primarily affected by the Henry's law constant for the substance in question but also by temperature, liquid turbulence, trace constituent concentration in the gas phase, and wind speed. The important factors in the third process are surface area, strength of adsorption, vapor pressure, and type of soil or solid. Other factors affecting volatilization include pH, solubility, the amount and type of organics present, the size of particles, the density of the solid wastes, reactivity, and leaching [7].

Vapor pressure. In a closed container, part of which is filled by a substance in a liquid state, a portion of the liquid will evaporate so as to fill the remaining volume with this substance in the vapor state. The pressure exerted by the vapor on the liquid when the two phases are in equilibrium is defined as the *vapor pressure* of the compound. Vapor pressure is strongly affected by temperature, increasing as the temperature increases. When the boiling temperature of a liquid has been reached the vapor pressure is equal to the atmospheric pressure. Vapor pressure is a characteristic property of the substance and is important for several reasons. The vapor pressure can be used to determine the partial pressure of each component

TABLE 5-8
Relationship between Henry's law constants and the tendency of an organic compound to volatilize[a]

Henry's law constant (K_H), $m^3 \cdot$ atm/mol	Comments on transfer mechanism
$< 10^{-7}$	The substance is essentially nonvolatile.
$10^{-7} < K_H < 10^{-5}$	The gas phase resistance dominates the liquid phase resistance by a factor of 10 at least; therefore, the substance volatilizes slowly.
$10^{-5} < K_H < 10^{-3}$	Liquid phase and gas phase resistances are both important. Volatilization for compounds in this range is less rapid than for compounds in a higher range of K_H, but is still a significant transfer mechanism.
$> 10^{-3}$	The resistance of the liquid phase dominates. Thus, transfer is liquid-phase controlled and these substances are highly volatile.

[a] Adapted from Ref. 8.

in a mixture of gases. The relative proportions of the individual components in a mixture can be determined when the partial pressure is known. The vapor pressure can also be used as a measure of the volatility of the substance. Liquids with a high vapor pressure will tend to evaporate easily, while liquids with a low vapor pressure will evaporate slowly. Compounds that are considered volatile have vapor pressures greater than 0.1 mm Hg at 20°C and/or boiling points less than 100°C [12].

Henry's law. With a dilute amount of trace constituent (TC) in a mixture of compounds, the Henry's law constant (K_H) relates the partial pressure of the solute in the vapor phase to the mole fraction of the constituent in solution. Henry's law is given in Appendix F. Values of the Henry's law constant for various volatile and semivolatile compounds are presented in Appendix H. Values of Henry's law constants for most hazardous waste compounds range from 10^{-7} to $> 10^{-3}$ $m^3 \cdot$ atm/mol (see Table 5-8). When the value of the Henry's law constant is high, the resistance of the liquid phase dominates over the gas phase and these compounds are highly volatile. For compounds with Henry's law constants between 10^{-5} and 10^{-3} $m^3 \cdot$ atm/mol, both the liquid- and gas-phase resistances are important. Volatilization for compounds with constants in this range is less rapid than for compounds in a higher range, but is still significant [8].

Example 5-2 Volatility of trace organic compounds found in MSW. Given the following hazardous waste compounds that may be found in MSW, arrange them in order of most volatile to least volatile, and discuss their relative volatility.

Benzene
Chloroethene
1,1,1,2-Tetrachloroethane
Tetrachloroethene
Tetrachloromethane
Toluene

Solution

1. Using the data from Appendix H arrange the compounds according to their boiling point, as in the table below.

Compounds	mw	bp, °C	vp, mm Hg	K_H, m³ · atm/mol
Chloroethene	62.5	−13.9	2548	$1.07\text{–}6.4 \times 10^{-2}$
Tetrachloromethane	153.82	76.7	90	2.86×10^{-2}
Benzene	78.11	80.1	76	$5.43\text{–}5.49 \times 10^{-3}$
Toluene	92.1	110.8	22	$5.94\text{–}6.44 \times 10^{-3}$
Tetrachloroethene	165.83	121	15.6	2.85×10^{-2}
1,1,1,2-Tetrachloroethane	167.86	146.2	14.74	$4.2\text{–}4.55 \times 10^{-4}$

2. Referring to the above table, the proposed arrangement according to boiling point corresponds to how the compounds would be arranged based on their vapor pressure. Based on their Henry's law constants, all of the compounds would be considered to be highly volatile.

3. Based on boiling points it can be concluded that chloroethene is significantly more volatile than any of the other compounds in this example.

Distribution of Waste between Phases. The distribution of a substance between two immiscible phases or liquids is defined by the distribution coefficient. Knowledge of the amount of a waste in each phase is important in developing waste management plans.

Distribution coefficient for two phases. When a substance that is soluble in each of two (immiscible) phases is added to a system of these two immiscible phases, the substance will be distributed in each in fixed proportions at a given temperature, independent of the quantity of the substance. This statement defines the distribution law. The ratio of the concentrations in each phase is called the distribution coefficient (or the partition coefficient). For dilute solutions, the preceding is also a working statement of Henry's law.

Distribution coefficient for two immiscible liquids. An identical relationship to that for two phases also holds for the distribution of a solute between two immiscible liquids. The coefficient is constant only when the given solute dissolves in both solvents in the same form and no association or dissociation takes

place. In practice, the distribution ratio for liquids is seldom strictly a constant. Stated mathematically, the distribution coefficient for two phases is

$$\frac{C_{X/A}}{C_{X/B}} = K_D \tag{5-4}$$

where $C_{X/A}$ = concentration of solute X in solvent A, g/m^3
   $C_{X/B}$ = concentration of solute X in solvent B, g/m^3
 K_D = distribution or partition coefficient

If the solute remains unchanged during its distribution between the two solvents, the distribution coefficient can be used to calculate the efficiency of an extraction process in which a given solvent is used to extract a solute from another solvent.

Octanol: water distribution coefficient. For the purposes of comparison and analysis, the octanol:water solvent system is used to characterize a variety of organic substances. Initially the octanol:water distribution coefficient of a compound was used to assess the bioaccumulation potential of a compound. Values of the octanol:water distribution coefficient are available in the literature [6, 7] but vary widely. Typical values for selected compounds are presented in Appendix H.

Chemical Transformations

The organic hazardous waste constituents in MSW can be transformed by a variety of chemical reactions, some of which are considered briefly below.

Chemical Reactions in Combustion. Under ideal conditions the combustion process is an effective means of destroying the hazardous organic constituents found in municipal solid waste. On the other hand, if the combustion process is not ideal, the products of incomplete combustion (PICs) can be quite varied and, in many cases, toxic. The stoichiometric combustion of chlorobenzene (C_6H_5Cl) with oxygen can be described by the following reaction:

$$C_6H_5Cl + 7O_2 \rightarrow 6CO_2 + 2H_2O + HCl \tag{5-5}$$
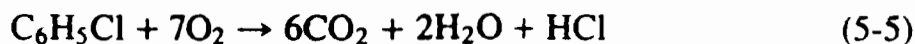
If the combustion is complete, then the chlorine in C_6H_5Cl will be converted to hydrochloric acid. If, however, the combustion is incomplete, then the formation of toxic trace constituents is possible. Similar reactions can occur with most hazardous waste compounds.

Chemical Reactions in Landfills. The principal classes of chemical (abiotic) reactions that can occur to alter the composition of the hazardous waste compounds found in MSW include [13]:

1. Simple substitution
2. Dehydrogenation (hydrolysis)

3. Oxidation (Auto-oxidation)
4. Reduction

While these reactions can occur at any time, they typically occur during landfilling and in completed landfills. Most abiotic reactions involving the more persistent halogenated hazardous compounds are slow but may be significant in the time scales involved in the long-term management of landfills [13]. In an environment such as a landfill where active biological decomposition is occurring, the rates of abiotic reaction may be increased significantly by the activity of biologically produced enzymes. Typical half lives for abiotic dehydrohalogenation (hydrolysis) of halogenated compounds are indicated in Table 5-9. These abiotic half lives can vary from 20 days to 7000 years. In the absence of biotic reactions the half lives of some of the compounds reported in Table 5-9 are troublesome from the standpoint of the long-term management of these compounds in landfills.

Biological Transformations

The biological transformations of the major organic constituents, as discussed in Chapter 4, are relatively well established. Much less is known, however, about the chemical/biological transformations of the hazardous inorganic and organic wastes found in MSW. Because this subject is so complex and so many pathways are unknown, what is presented here is meant to serve as an introduction to this important subject.

TABLE 5-9
Typical half lives and products derived from the chemical hydrolysis or dehydrogenation of halogenated aliphatic compounds at 20°C

Compound	Half life, yr	Products
Methanes		
Bromomethane	0.10	
Bromodichloromethane	137	
Trichloromethane	1.3	
Tetrachloromethane	7000	
Ethanes		
Chloroethane	0.12	Ethanol
1,1,2-Trichloroethane	170	1,1-Dichloroethene
1,1,1,2-Tetrachloroethane	384	Trichloroethene
Ethenes		
Trichloroethene	0.9	
Tetrachlorethene	0.7	
Propanes		
1-Bromopropane	0.07	Bromopropene
1,2-Dibromopropane	0.88	

ᵃ Adapted from Ref. 13

Transformations Involving Metals. Many of the hazardous inorganic constituents present in MSW, such as chromium, lead, and mercury, can be converted biologically into a variety of compounds, some of which are extremely toxic. For example, toxic compounds that can be produced under anaerobic conditions, such as those in landfills, include methylmercury, dimethylarsine, and dimethylselenide. It is interesting to note that as the metallic covers (shells) on household and other batteries decompose with time and mercury is released under anaerobic conditions, the biological transformation of mercury will probably occur for years to come.

Transformations Involving Biodegradable (Nonpersistent) Organic Compounds. Based on both laboratory and field studies, it is also known that a number of the hazardous organic compounds found in municipal waste are biodegradable. Typically, biodegradable chemicals undergo reactions such as:

1. Simple substitution
2. Dehydrogenation (hydrolysis)
3. Oxidation
4. Reduction

Transformations Involving Persistent Organic Compounds. Again, based on both laboratory and field studies, it is also known that a number of the so-called persistent hazardous organic compounds found in municipal waste are biodegradable, but at extremely slow rates. The slowly biodegradable chemicals may undergo one or more of the following biologically mediated reactions:

1. Amide and ester hydrolysis
2. Dealkylation
3. Deamination
4. Dehalogenation
5. Double bond reduction
6. Hydroxylation
7. Oxidation (β-oxidation)
8. Reduction
9. Ring cleavage

Many of these reactions lead to the detoxification of the original compound. Unfortunately, many of these reactions also result in the formation of new toxic compounds, some of which may be more toxic than the original.

Combined Abiotic and Biotic Transformations. In addition to the abiotic and biotic transformations considered above, a number of hazardous waste compounds are transformed by a combination of abiotic/biotic reactions. The conversion of
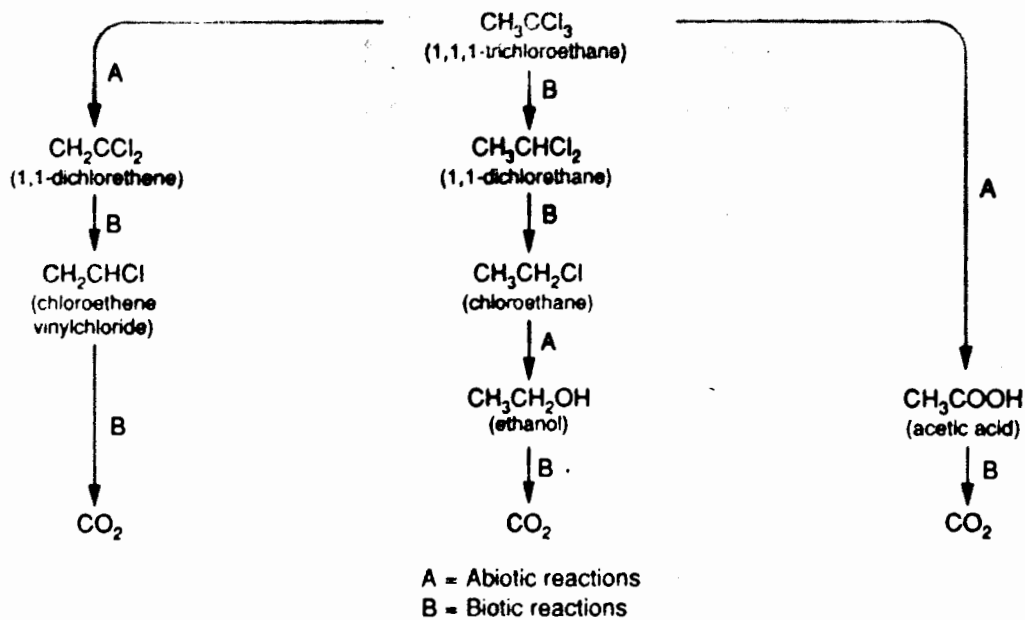
A = Abiotic reactions
B = Biotic reactions

FIGURE 5-2
Pathways for the transformation of TCA (1,1,1-trichloroethane, CH_3CCl_3) under methanogenic conditions (from Refs. 3 and 13).

TCA (1,1,1-trichloroethane) to CO_2 and H_2O by a combination of abiotic and biotic reactions is illustrated in Fig. 5-2. There is some evidence that detoxification reactions, like those in Fig. 5-2, can be enhanced by successively creating an aerobic and anaerobic environment within a landfill. In the future, as these reactions become understood more clearly, it may be possible to accelerate the conversion of these compounds through more effective management of landfills.

5-5 MANAGEMENT OF HAZARDOUS WASTES IN MSW

The most effective way to eliminate the small quantities of hazardous wastes now found in municipal solid waste is to separate them at the point of generation. The number and types of hazardous components separated will depend on the hazardous waste storage, collection, treatment, and disposal facilities provided by the community.

Handling and Storage of Hazardous Wastes at Residential Dwellings

The handling and storage of household hazardous wastes (HHW) depend on the nature of the product. The principal categories of HHW were listed in Table 5-3. In reviewing the entries in Table 5-3, it is clear that HHW will be found (stored) in all parts of a residence. The disposal of HHW is, at present, unregulated in most states. As a consequence, many of the products within the various generic categories

are often stored and, once used, disposed of improperly. The only effective way to deal with HHW is to educate citizens about the proper use, storage, and disposal of HHW and to provide them with convenient options for the disposal of these wastes.

Household Hazardous Waste Collection Programs

To minimize the improper disposal of HHW, product exchange programs, special collection days and permanent collection sites have been established by a number of communities.

Product Exchange Programs. Because paint products form a major portion of HHW, paint exchange programs are being used in a number of communities to reduce the cost of HHW disposal. The reuse of latex-based paints has proven to be the most successful, with up to 50 percent recovery being reported [2]. Unrecoverable paint must be either combusted in a hazardous waste combustor or disposed of in a hazardous waste landfill.

Specific Collection Days. One of the most common approaches to HHW management is to hold one or more community waste collection days. On collection days, community members are invited to bring their HHW, at little or no charge, to a specified location for recycling, treatment, or disposal by professional waste handlers. In larger communities, several locations are used on successive days. For these collection days to be successful, adequate promotion and education are critical. Even though hazardous waste collection days are well attended when properly promoted, at present (1992) it is estimated that less than 5 to 10 percent of the total available HHW is collected through such programs.

Permanent Collection Sites. To increase the convenience of the HHW collection programs and, therefore, increase participation, more and more communities are establishing permanent collection sites (e.g., fire stations, landfills, city and corporation yards). Programs involving permanent collection facilities allow citizens to drop off wastes at their own convenience. For this reason, permanent collection sites have proven to be more effective for collecting HHW than the one-day collection programs.

Elimination of Hazardous Wastes from Commercial Sources

To reduce the toxicity of commingled MSW, most communities have sought to eliminate all discharges of hazardous wastes from commercial facilities. The key to the elimination of hazardous wastes from commercial activities is the availability of community or regional facilities for handling and processing hazardous wastes.

5-6 DISCUSSION TOPICS AND PROBLEMS

5-1. List potential sources of hazardous waste generated in a university environment. Indicate what properties make such substances hazardous (i.e., flammability, irritant, etc.).

5-2. Identify two or more sources of household radioactive waste that are common in the United States.

5-3. The allowable limit for the disposal of benzene contained in a mixed sludge from a treatment process is 5 ppb. Sixty days after disposing of some sludge waste, a sample was collected and analyzed for benzene. The concentration of benzene found in the sludge was 1.37 ppb. If the first-order removal rate constant for benzene is 0.00345/hr, determine whether the sludge could have been disposed of in the landfill if a sample had been analyzed at the time the sludge was brought to the landfill.

5-4. Solve Problem 5-3 assuming that the second-order removal rate constant for benzene is 0.0029/hr.

5-5. Assuming that the half-life time ($t_{1/2}$) for hazardous substance A is 15 hr,

(a) determine $t_{1/8}$, $t_{1/4}$, $t_{3/8}$, $t_{5/8}$, $t_{3/4}$, $t_{7/8}$ and tabulate your results,

(b) plot $1 - (C/C_o)$ versus time (where C_o is initial concentration),

(c) explain what $1 - (C/C_o)$ represents. According to the first-order model, how long would it take to achieve 99% decay?

5-6. What are the principal factors that affect the rate of decay of a hazardous substance? Could the first-order model given by Eq. (5-1) be used to account for such factors?

5-7. Rank the compounds listed below in order of decreasing volatility based on the following properties: molecular weight, vapor pressure, Henry's law constant, and boiling point.

Compound
Benzene
Toluene
Chloroethene
Bromodichloromethane
Ethylbenzene

5-8. Assume an ideal gas mixture is in contact with water. Determine the equilibrium concentration of the contaminant in the liquid if the gas stream is composed of: (a) 200 ppm of benzene in air, (b) 100 ppm of trichloromethane in air, and (c) 700 mg/m³ of chlorobenzene in air. Assume the air temperature is 20°C and the pressure is equal to 1 atm.

5-9. Referring to the literature on hazardous waste management, cite typical examples of (1) simple substitution, (2) dehydrogenation (hydrolysis), (3) oxidation, and (4) reduction reactions in the biological conversion of hazardous waste.

5-10. Referring to the literature on hazardous waste management, cite some typical reactions to illustrate six of the reactions given in Section 5-4 for the biological transformation of persistent organic compounds.

5-11. How are HHW now collected and disposed of in your community? What plans have been developed to reduce the toxicity of the commingled MSW from your community further?

5-12. What regulations and policies are currently in place in your community (or region) to reduce or eliminate the discharge of hazardous wastes with other solid wastes from commercial sources?

5-7 REFERENCES

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