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Transport, Behavior, and Fate of Volatile Organic Compounds in Streams

By R.E. RATHBUN

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CONVERSION FACTORS

Multiply	By	To obtain
nanometer (nm)	3.937×10^{-8}	inch
millimeter (mm)	3.937×10^{-2}	inch
centimeter (cm)	3.937×10^{-1}	inch
meter (m)	3.281	foot
kilometer (km)	6.214×10^{-1}	mile
meter per meter (m/m)	1.00	foot per foot
meter per second (m/s)	3.281	foot per second
meter per second per second (m/s/s)	3.281	foot per second per second
meter per day (m/day)	3.281	foot per day
day per meter (day/m)	3.048×10^{-1}	day per foot
square meter (m^2)	10.76	square foot
square meter per second (m^2/s)	10.76	square foot per second
square meter per day (m^2/day)	10.76	square foot per day
cubic meter (m^3)	35.31	cubic foot
cubic meter per second (m^3/s)	35.31	cubic foot per second
liter (L)	3.531×10^{-2}	cubic foot
gram (g)	2.205×10^{-3}	pound
gram per square meter (g/m^2)	2.048×10^{-4}	pound per square foot
gram mole per square meter per second (g mol/m^2/s)	2.048×10^{-4}	pound mole per square foot per second
gram mole per square meter per day (g mol/m^2/day)	2.048×10^{-4}	pound mole per square foot per day
photon per square centimeter per second (photon/cm^2/s)	9.29×10^{2}	photon per square foot per second
nanogram per liter (ng/L)	6.243×10^{-11}	pound per cubic foot
microgram per liter (µg/L)	6.243×10^{-8}	pound per cubic foot
milligram per liter (mg/L)	6.243×10^{-5}	pound per cubic foot
kilogram per liter (kg/L)	6.243×10^{1}	pound per cubic foot
gram mole per cubic meter (g mol/m^3)	6.243×10^{-5}	pound mole per cubic foot
gram per liter (g/L)	6.243×10^{-2}	pound per cubic foot
gram millimole (g mmol)	2.205×10^{-6}	pound mole
gram micromole (g µmol)	2.205×10^{-9}	pound mole
gram per gram mole (g/g mol)	1.00	pound per pound mole
nanogram per kilogram (ng/kg)	1.00×10^{-12}	pound per pound
gram per kilogram (g/kg)	1.00×10^{-3}	pound per pound
milliliter per gram (mL/g)	1.60×10^{-2}	cubic foot per pound
liter per kilogram (L/kg)	1.60×10^{-2}	cubic foot per pound
cubic centimeter per gram mole (cm^3/g mol)	1.60×10^{-2}	cubic foot per pound mole
liter per gram mole per centimeter (L/g mol/cm)	4.88×10^{2}	cubic foot per pound mole per foot
pascal (Pa)	1.01×10^{5}	standard atmosphere
pascal cubic meter per gram mole (Pa m^3/g mol)	1.58×10^{-1}	standard atmosphere cubic foot per pound mole
pascal cubic meter per gram mole per kelvin (Pa m^3/g mol/K)	8.78×10^{-2}	standard atmosphere cubic foot per pound mole per degree rankine
kilojoule per gram mole (kJ/g mol)	1.08×10^{2}	kilocalorie per pound mole
kilojoule per gram mole per kelvin (kJ/g mol/K)	6.02×10^{1}	kilocalorie per pound mole per degree rankine

Temperature in kelvins (K) may be converted to degrees Celsius (°C) using

$$°C = K - 273.15$$

Temperature in kelvins (K) may converted to degrees rankine (°R) using

$$°R = (K - 273.15)(1.8) + 491.7$$

Temperature in kelvins (K) may be converted to degrees Fahrenheit (°F) using

$$°F = (K - 273.15)(1.8) + 32.0$$

TRANSPORT, BEHAVIOR, AND FATE OF VOLATILE ORGANIC COMPOUNDS IN STREAMS

By R.E. Rathbun

ABSTRACT

Volatile organic compounds (VOCs) are compounds with chemical and physical properties that allow the compounds to move freely between the water and air phases of the environment. VOCs are widespread in the environment because of this mobility. Many VOCs have properties making them suspected or known hazards to the health of humans and aquatic organisms. Consequently, understanding the processes affecting the concentration and distribution of VOCs in the environment is necessary.

The transport, behavior, and fate of VOCs in streams are determined by combinations of chemical, physical, and biological processes. These processes are volatilization, absorption, wet and dry deposition, microbial degradation, sorption, hydrolysis, aquatic photolysis, oxidation, chemical reaction, bioconcentration, advection, and dispersion. The relative importance of each of these processes depends on the characteristics of the VOC and the stream.

The U.S. Geological Survey National Water-Quality Assessment Program selected 55 VOCs for study. This report reviews the characteristics of the various processes that could affect the transport, behavior, and fate of these VOCs in streams.

INTRODUCTION

Many organic compounds have chemical and physical properties that allow the compounds to move freely between the water and air phases of the environment. These compounds commonly are called volatile organic compounds (VOCs). VOCs in general have low molecular weights, high vapor pressures, and low-to-medium water solubilities. Many VOCs are toxic and are the focus of Federal regulations related to water quality (Leahy and Thompson, 1994). Consequently, VOCs were designated for a national synthesis study under the National Water-Quality Assessment (NAWQA) Program of the U.S. Geological Survey (USGS).

THE NATIONAL WATER-QUALITY ASSESSMENT PROGRAM

The USGS began the NAWQA Program in 1991. The objectives of this program are to describe current water-quality conditions for a large part of the water resources of the United States, to define long-term trends or the absence of trends in water quality, and to identify and describe the primary factors affecting the observed water-quality conditions and trends (Hirsch and others, 1988). The NAWQA Program consists of two parts. These are investigations of the water quality of river basins and aquifer systems and national synthesis assessments (Leahy and Thompson, 1994). The synthesis assessments focus on high-priority water-quality issues. Initial national synthesis assessments were on the occurrences of nutrients and pesticides in surface water and ground water. In 1994, a national synthesis project on VOCs was initiated because of the widespread occurrence of these compounds in the waters of the environment and the lack of information on factors related to their occurrence and behavior. The objectives of the VOC project are to determine the occurrence of VOCs in surface water and ground water, to determine trends or absence of trends in the concentrations, to identify probable sources of VOCs, and to describe the primary processes affecting the concentrations of VOCs in waters of the United States.

PURPOSE AND SCOPE

The purpose of this report is to present a review of the characteristics of the various processes that affect the transport, behavior, and fate of VOCs in streams. Among these processes, volatilization is the one likely to be most important for VOCs. Other processes such as absorption, dry deposition with particles, wet deposition, microbial degradation, sorption, hydrolysis, aquatic photolysis, oxidation, chemical reaction, and bioconcentration may be important for some compounds under certain environmental conditions. Also, all VOCs in streams are subject to advective and dispersive mixing processes. Fundamentals of these processes are presented, and where appropriate, estimates of first-order rate coefficients for streams are given. This report emphasizes specific VOCs selected for study by the NAWQA Program. These target VOCs cover a wide range of chemical and physical properties. Consequently, much of this discussion also will be directly applicable to other VOCs.

TARGET VOLATILE ORGANIC COMPOUNDS

The NAWQA Program selected 55 target analytes for study. Details of the procedure used in the selection of these analytes have been described previously (J.S. Zogorski, U.S. Geological Survey, written commun., 1994). Briefly, the procedure began with 125 compounds regulated under the Safe Drinking Water Act and the Clean Water Act that could be considered to be volatile on the basis of their chemical and physical properties. This list was reduced to only VOCs that occurred frequently in natural waters, or were either known or possible human carcinogens, or were of non-cancer human-health concerns, or were likely to have detrimental effects on the health of aquatic ecosystems. A few compounds were included because of special uses and/or environmental effects, such as those compounds used as additives in reformulated automotive gasolines, those suspected of deteriorating the ozone layer, and those which can undergo significant bioconcentration.

The 55 VOCs selected as target analytes are listed in table 1. The International Union of Pure and Applied Chemistry (IUPAC) names of the compounds will be used in this report. Also given in table 1 are alternative names or abbreviations sometimes used in the literature for 34 of the analytes. The Chemical Abstracts Services (CAS) numbers and the USGS parameter codes are presented for identification purposes. The two dimethylbenzene compounds (1,3-dimethylbenzene and 1,4-dimethylbenzene) have the same USGS parameter code because these isomers cannot be separated by the analytical technique used by the USGS National Water-Quality Laboratory. Consequently, concentrations under this parameter code are for the sum of the concentrations of these two compounds.

Table 1. Volatile organic compound target analytes

[CAS, Chemical Abstracts Services; USGS, U.S. Geological Survey; IUPAC, International Union of Pure and Applied Chemistry]

CAS number	USGS parameter code	IUPAC name	Alternative name
		Halogenated alkanes	
74–87–3	34418	chloromethane	methyl chloride
75–09–2	34423	dichloromethane	methylene chloride
67–66–3	32106	trichloromethane	chloroform
56–23–5	32102	tetrachloromethane	carbon tetrachloride
74–83–9	34413	bromomethane	methyl bromide
75–25–2	32104	tribromomethane	bromoform
75–27–4	32101	bromodichloromethane	
124–48–1	32105	chlorodibromomethane	
75–00–3	34311	chloroethane	ethyl chloride
75–34–3	34496	1,1-dichloroethane	ethylidenedichloride
107–06–2	32103	1,2-dichloroethane	ethylenedichloride

Table 1. Volatile organic compound target analytes—Continued

[CAS, Chemical Abstracts Services; USGS, U.S. Geological Survey; IUPAC, International Union of Pure and Applied Chemistry]

CAS number	USGS parameter code	IUPAC name	Alternative name
		Halogenated alkanes—Continued	
71–55–6	34506	1,1,1-trichloroethane	methyl chloroform
79–00–5	34511	1,1,2-trichloroethane	
67–72–1	34396	hexachloroethane	
106–93–4	77651	1,2-dibromoethane	EDB
78–87–5	34541	1,2-dichloropropane	
96–18–4	77443	1,2,3-trichloropropane	
96–12–8	82625	1,2-dibromo-3-chloropropane	DBCP
75–69–4	34488	trichlorofluoromethane	Freon 11, CFC11
75–71–8	34668	dichlorodifluoromethane	Freon 12, CFC12
76–13–1	77652	1,1,2-trichloro-1,2,2-trifluoroethane	Freon 113, CFC113
		Halogenated alkenes	
75–01–4	39175	chloroethene	vinyl chloride
75–35–4	34501	1,1-dichloroethene	
156–59–2	77093	*cis*-1,2-dichloroethene	
156–60–5	34546	*trans*-1,2-dichloroethene	
79–01–6	39180	trichloroethene	TCE
127–18–4	34475	tetrachloroethene	perchloroethylene, PCE
593–60–2	50002	bromoethene	vinyl bromide
10061–01–5	34704	*cis*-1,3-dichloropropene	
10061–02–6	34699	*trans*-1,3-dichloropropene	
87–68–3	39702	hexachlorobutadiene	
		Aromatic hydrocarbons	
71–43–2	34030	benzene	
100–42–5	77128	styrene	vinyl benzene
91–20–3	34696	naphthalene	
		Alkyl benzenes	
108–88–3	34010	methylbenzene	toluene
100–41–4	34371	ethylbenzene	
103–65–1	77224	n-propylbenzene	
98–82–8	77223	iso-propylbenzene	cumene
104–51–8	77342	n-butylbenzene	
95–47–6	77135	1,2-dimethylbenzene	o-xylene
108–38–3	85795	1,3-dimethylbenzene	m-xylene
106–42–3	85795	1,4-dimethylbenzene	p-xylene
95–63–6	77222	1,2,4-trimethylbenzene	
		Halogenated aromatics	
108–90–7	34301	chlorobenzene	
95–50–1	34536	1,2-dichlorobenzene	o-dichlorobenzene
541–73–1	34566	1,3-dichlorobenzene	m-dichlorobenzene
106–46–7	34571	1,4-dichlorobenzene	p-dichlorobenzene
87–61–6	77613	1,2,3-trichlorobenzene	
120–82–1	34551	1,2,4-trichlorobenzene	
		Ethers	
1634–04–4	78032	methyl tertiary-butyl ether	MTBE
637–92–3	50004	ethyl tertiary-butyl ether	ETBE
994–05–8	50005	tertiary-amyl methyl ether	TAME
108–20–3	81577	diisopropyl ether	DIPE
		Others (aldehydes and nitriles)	
107–02–8	34210	2-propenal	acrolein
107–13–1	34215	2-propenenitrile	acrylonitrile

PROCESSES AFFECTING THE TRANSPORT, BEHAVIOR, AND FATE OF VOLATILE ORGANIC COMPOUNDS IN STREAMS

The transport, behavior, and fate of VOCs in streams are determined by the effects of combinations of various chemical, physical, and biological processes. These processes are depicted schematically in figure 1. Among these processes, volatilization is the one most important for VOCs. However, in some instances, the other processes shown in figure 1 may affect the fate of VOCs in streams.

Some of these processes such as volatilization, absorption, wet and dry deposition, bioconcentration, and sorption involve movement of VOCs between different parts of the environment. Other processes such as microbial degradation, hydrolysis, aquatic photolysis, oxidation, and chemical reaction result in changes of the chemical compounds to other compounds. Complete mineralization by microbial degradation results in the conversion of the compounds to water and carbon dioxide or methane, depending on whether the degradation is under aerobic or anaerobic conditions. Transport within the same water parcel or to other parts of the stream system occurs by advective and dispersive transport of the dissolved VOCs with the water and movement of sorbed VOCs with the suspended particulates.

The relative importance of the various processes shown in figure 1 depends on the characteristics of the VOC and the stream under consideration. In the case of microbial degradation, previous occurrences of the VOC in the stream reach also may affect the ability of the bacterial community in the stream to degrade the compound. In subsequent sections of this report, each of these processes is discussed, and experimental values of first-order rate coefficients for the processes are presented when appropriate.

The term "stream" will be used in this report to describe all natural open-channel flows, regardless of size. In some examples, the terms "deep, low-velocity," "intermediate-depth, high-velocity," and "shallow, medium-velocity" will be used to describe qualitatively streams with these combinations of flow depth and water velocity. Tidally affected streams are not considered in this report.

VOLATILIZATION

Volatilization is the movement of a VOC from the bulk water phase of a stream across the water/air interface into the air. Volatilization of organic solutes from water is a first-order process. A first-order process is one in which the rate of reaction is directly proportional to the concentration of the species undergoing the process (Tinsley, 1979). Thus, the rate of volatilization, dC/dt, is given by

$$-\frac{dC}{dt} = K_v(C - C_e) \qquad (1)$$

where

C is the concentration (g mol/m^3) of the VOC in the water,

t is time (days),

K_V is the volatilization coefficient (day^{-1}), and

C_e is what the concentration (g mol/m^3) of the VOC in the water would be if the water were in equilibrium with the partial pressure of the VOC in the air.

In many environmental situations, the VOC concentrations in the air above the stream surface are negligible with respect to the concentrations in the water because of rapid dispersion in the atmosphere. Consequently, C_e in equation 1 can be neglected, and the equation can be integrated to give

$$C = C_o \exp(-K_v t) \qquad (2)$$

where

C_0 is the concentration (g mol/m^3) of the VOC in the water at time zero.

Times are commonly expressed as half-lives, where the half-life is the time required for the concentration to be reduced by volatilization to one-half of the initial concentration. It follows from equation 2 that the half-life, $t_{0.5V}$ (days), is given by

$$t_{0.5V} = \frac{0.693}{K_v} . \qquad (3)$$

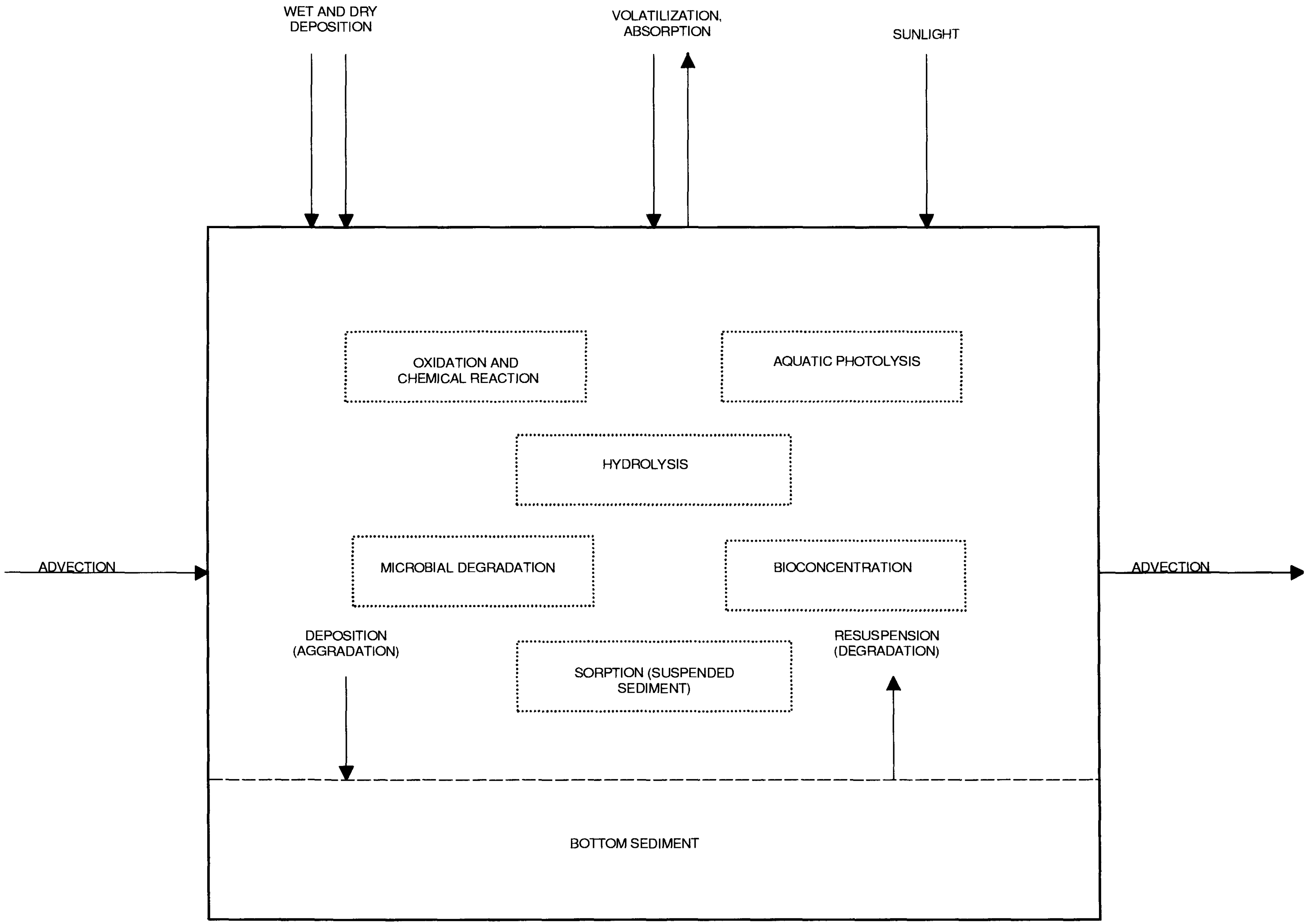
WET AND DRY DEPOSITION
VOLATILIZATION, ABSORPTION
SUNLIGHT
ADVECTION
OXIDATION AND CHEMICAL REACTION
AQUATIC PHOTOLYSIS
HYDROLYSIS
MICROBIAL DEGRADATION
BIOCONCENTRATION
ADVECTION
DEPOSITION (AGGRADATION)
SORPTION (SUSPENDED SEDIMENT)
RESUSPENSION (DEGRADATION)
BOTTOM SEDIMENT

Figure 1. Schematic diagram showing the processes affecting the transport, behavior, and fate of volatile organic compounds in streams.

Times can be converted to distances along a stream using the relationship

$$L = \frac{t\,U}{1.16\times10^{-5}} \qquad (4)$$

where

L is the distance (m) along the stream,
U is the mean water velocity (m/s), and
1.16×10^{-5} is the days-to-seconds conversion factor.

Concentration as a function of distance is obtained by combining equations 2 and 4 to give

$$C = C_0 \exp\left[(-K_v)(1.16\times10^{-5})\frac{L}{U}\right] . \qquad (5)$$

Equation 5 is somewhat simplified in that it neglects the effect of dispersion.

THE TWO-FILM MODEL

Equation 5 requires a value of the volatilization coefficient to permit prediction of the variation of the concentration of a VOC with distance along a stream. Various models are available for this purpose, one of them being the two-film model (Lewis and Whitman, 1924). This model assumes uniformly mixed water and air phases separated by thin films of water and air in which mass transfer is only by molecular diffusion. Figure 2 is a schematic representation of the two-film model depicting transfer from the water to the air phase. This figure indicates a constant concentration in the bulk water phase, a concentration gradient across the water film, a discontinuity at the interface, a concentration gradient across the air film, and a constant concentration in the bulk air phase. The discontinuity at the interface is because concentrations in water are usually expressed on a

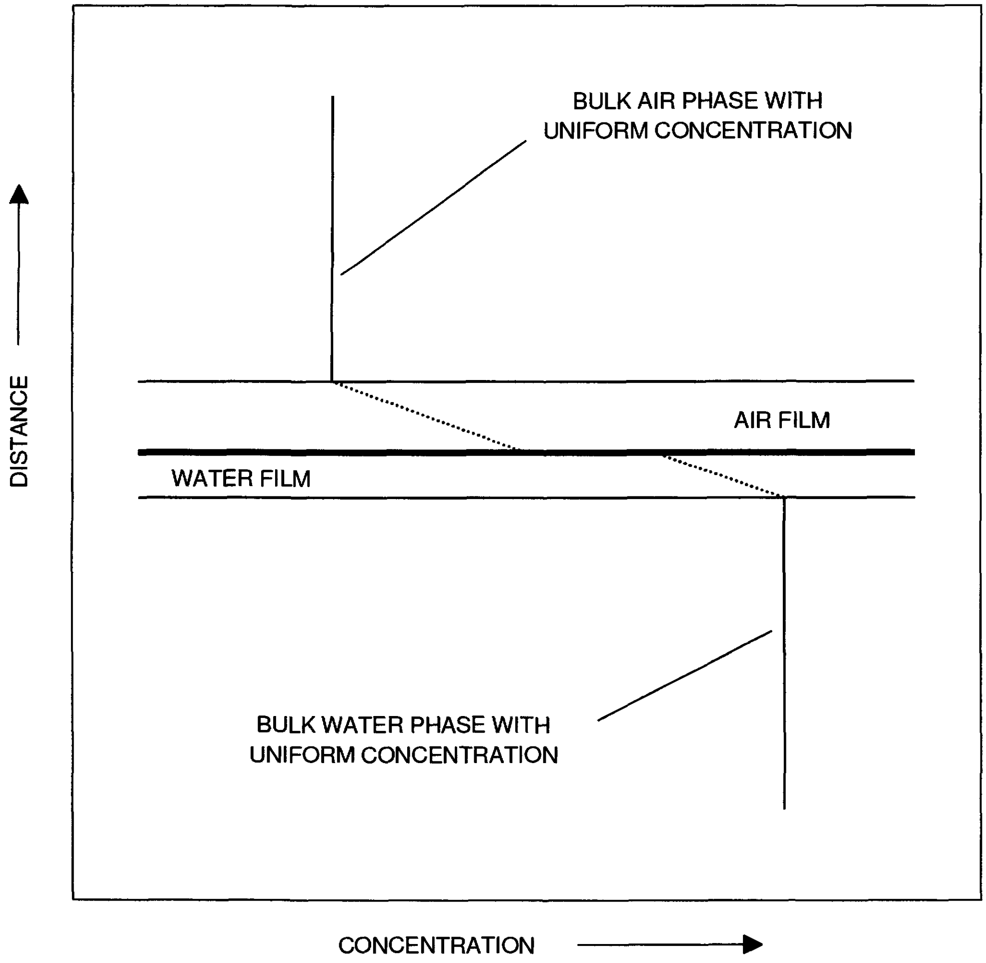

Figure 2. Schematic diagram showing the two-film model.

mass-per-unit-volume basis and concentrations in air are usually expressed on a partial pressure basis. The interface between the water and air films is assumed to have no resistance to mass transfer. A dynamic steady-state is assumed with equilibrium at the interface. The two-film model is a conceptual model in that the existence of a coherent stagnant film over the entire surface of a flowing stream seems unlikely.

The rate of mass transfer over the flow depth of a stream is generally large compared with the rate of mass transfer into or out of the stream. This difference in rates results in almost no gradient in concentration of dissolved solutes over most of the flow depth and a large gradient in concentration near the surface. Consequently, most of the resistance to mass transfer is in the films at the water/air interface as conceptualized in the two-film model (fig. 2). A discussion of resistances in the films and several examples of measurements of dissolved oxygen in streams, which provide experimental evidence in support of this phenomenon, have been presented previously (Bennett and Rathbun, 1972).

The basic equation of the two-film model can be developed as follows. Flux equations for the transfer of a solute through the water and air films (fig. 2) are

$$N_w = k_w(C - C_i) \tag{6}$$

$$N_a = \frac{k_a(p_i - p)}{RT} \tag{7}$$

where

N_w and N_a are the mass fluxes through the water and air films (g mol/m^2/day);

C_i is the concentration of the solute at the interface on the water side (g mol/m^3);

k_w is the mass-transfer coefficient for the water film (m/day);

k_a is the mass-transfer coefficient for the air film (m/day);

p_i is the partial pressure of the solute at the interface on the air side, in pascals;

p is the partial pressure of the solute in the uniformly mixed air phase, in pascals;

R is the ideal gas constant (Pa m^3/g mol/K); and

T is the temperature, in kelvins.

With the assumption of steady-state conditions, the mass fluxes through the films must be equal. Consequently,

$$N = \frac{k_a(p_i - p)}{RT} = k_w(C - C_i) \tag{8}$$

where

N is the mass flux (g mol/m^2/day).

Equation 8 contains the concentration and partial pressure of the solute at the interface. These parameters, however, are difficult, if not impossible, to measure.

To eliminate these parameters, the flux equations are written in terms of overall mass-transfer coefficients and overall concentration-difference driving forces. The result is

$$N = \frac{K_{ao}(p_e - p)}{RT} = K_{wo}(C - C_e) \tag{9}$$

where

K_{ao} is the overall mass-transfer coefficient based on the air phase (m/day),

K_{wo} is the overall mass-transfer coefficient based on the water phase (m/day), and

p_e is the partial pressure, in pascals, of the solute in the air in equilibrium with the water concentration C.

Solute concentrations in environmental situations are almost always dilute enough such that ideal solution laws apply. Therefore, Henry's law can be used to describe the equilibrium conditions. This law is defined by

$$p = H\,C_e \tag{10}$$

$$p_e = H\,C \tag{11}$$

where

H is the Henry's law constant of the solute (Pa m^3/g mol).

Because equilibrium conditions are assumed at the interface, it follows that

$$p_i = H\,C_i\,. \tag{12}$$

By algebraic manipulation of equations 6, 7, 8, 10, 11, and 12 and comparison of the results with equation 9, it follows that

$$\frac{1}{K_{wo}} = \frac{1}{k_w} + \frac{RT}{Hk_a}\,. \tag{13}$$

Equation 13 is the basic equation of the two-film model, and it indicates that the overall mass-transfer coefficient for volatilization of a solute from a stream depends on the mass-transfer coefficients for the water and air films and the Henry's law constant of the solute.

The relationship between the volatilization coefficient, K_v, of equation 1 and the overall mass-transfer coefficient based on the water phase, K_{wo}, can be developed as follows. The rate of change of the concentration with time, dC/dt, and the mass flux, N, are related by

$$\frac{V}{A}\frac{dC}{dt} = N \tag{14}$$

where

V is the volume of the water phase (m^3), and

A is the water-surface area (m^2).

If the water surface is reasonably flat,

$$\frac{V}{A} = Y \tag{15}$$

where

Y is the water depth (m).

Comparing equations 1 and 9 and considering equations 14 and 15 gives

$$K_{wo} = K_v\,Y\,. \tag{16}$$

WATER-FILM AND AIR-FILM COEFFICIENTS AND RESISTANCES

In the general situation, the film coefficients, k_w and k_a are difficult, if not impossible, to measure because they involve the concentration and partial pressure of the solute at the interface. In two limiting cases, however, k_w and k_a can be measured directly. The first limiting case involves solutes with large values of the Henry's law constant such that the second term on the right-hand side of equation 13 is negligible with respect to the first. For these solutes,

$$\frac{1}{K_{wo}} \cong \frac{1}{k_w}\,. \tag{17}$$

Because the overall mass-transfer coefficient, K_{wo}, can be measured directly, the water-film coefficient, k_w, also can be measured for these solutes. The condition under which equation 17 applies is called water-film-controlled mass transfer, which means that virtually all the resistance to mass transfer is in the water film. Thus, volatilization in this case is controlled by mixing conditions in the water. Many of the VOCs of environmental significance have Henry's law constants such that most of the resistance to volatilization is in the water film.

The second limiting case involves solutes with small values of the Henry's law constant such that the first term on the right-hand side of equation 13 is negligible with respect to the second term. For these solutes,

$$\frac{1}{K_{wo}} \cong \frac{RT}{Hk_a}\,. \tag{18}$$

Because the overall mass-transfer coefficient, K_{wo}, can be measured directly, the air-film coefficient, k_a, also can be measured for these solutes. The condition under which equation 18 applies is called air-film-controlled mass transfer, which means that virtually all the resistance to mass transfer is in the air film. Thus, volatilization in this case is controlled by mixing processes in the air. Solutes with Henry's law constants small enough that equation 18 applies will have low potential to volatilize from water and, therefore, most likely would not be classified as VOCs.

Some solutes, however, will have Henry's law constants intermediate between the values of these limiting cases. Consequently, resistances of both the water and air films will be important. The resistances of the films are controlled primarily by the thicknesses of the films that, in turn, are controlled primarily by mixing conditions within the bulk water and air phases. Mixing within the water phase of streams is primarily the result of shear stresses at the bottom and banks of the stream. Mixing within the air phase above streams is primarily the result of wind shear. In some cases, shear stresses within one phase may affect mixing in the other phase. In a wide, shallow stream with low banks and a low water velocity, wind shear may significantly affect mixing in the water phase. An example of such an effect was unexpectedly high oxygen-absorption coefficients attributed to wind effects on a wide, shallow reach of the Rock River (Grant, 1978). Similarly, mixing within the water phase may have some effect on the air-film resistance. An example of such an effect is the observation that water-evaporation rates, which are in theory controlled completely by the air-film resistance, were larger for a canal than for a lake with comparable windspeeds (Jobson, 1980).

The relative importance of the resistances of the water and air films to volatilization of solutes from streams can be estimated from equation 13. The reciprocal of a mass-transfer coefficient is the resistance to that mass transfer. Therefore, equation 13 can be written as

$$r_t = r_w + r_a \qquad (19)$$

where

r is the resistance to mass transfer (day/m), and the t, w, and a subscripts indicate the total, water-film, and air-film resistances, respectively. It follows that the percentage resistance in the water film is given by

$$\frac{100\, r_w}{r_t} = \frac{100}{1 + \dfrac{RTk_w}{Hk_a}} \;. \qquad (20)$$

Thus, the percentage of the total resistance to mass transfer that is in the water film depends on the relative magnitudes of the mass-transfer coefficients for the water and air films and the Henry's law constant of the VOC.

The percentage resistance in the water film as a function of the Henry's law constant is presented in figure 3 for a temperature of 25°C. Three combinations of water-film and air-film mass-transfer coefficients were used to cover the range of coefficients that might be expected for streams. Minimum and maximum water-film and air-film coefficients were paired to obtain the maximum possible range of percentage resistances. The third combination was for values of the two film coefficients assumed appropriate for average conditions in a stream.

Values of 0.3, 3, and 6 m/day were used for the water-film coefficients. These values cover the range of water-film coefficients estimated for benzene, trichloromethane, dichloromethane, and methylbenzene for 12 streams of the United States (Rathbun and Tai, 1981). Values of 400, 800, and 1,200 m/day were used for the air-film coefficients. These values cover the range of air-film coefficients determined for evaporation of water from a canal in southern California (Jobson and Sturrock, 1979; Jobson, 1980), the open ocean (Liss and Slater, 1974), and three lakes in the United States (Smith and others, 1981).

Figure 3 indicates that as the Henry's law constant increases, the percentage resistance in the water film increases, and the increase is fastest for the smallest water-film coefficient. This observation is consistent with a thicker water film for the lower water-mixing intensity, as indicated by the low water-film coefficient. Conversely, for the highest water-mixing intensity, as indicated by the highest water-film coefficient, the percentage resistance in the water film approaches 100 percent more slowly.

Stated another way, for a specific Henry's law constant, the percentage resistance in the water film is largest for the combination of the small water-film coefficient and the large air-film coefficient. Conversely, the percentage resistance in the water film is smallest for the combination of the high water-film coefficient and the small air-film coefficient. Percentage resistances for the average film coefficients are intermediate between these extremes.

Figure 3 indicates that for solutes with Henry's law constants larger than 300 Pa m^3/g mol, at least 90 percent of the resistance to volatilization will be in the water film for all three combinations of film coefficients. Conversely, for solutes with Henry's law constants smaller than about 0.07 Pa m^3/g mol, less than 10 percent of the resistance to volatilization will

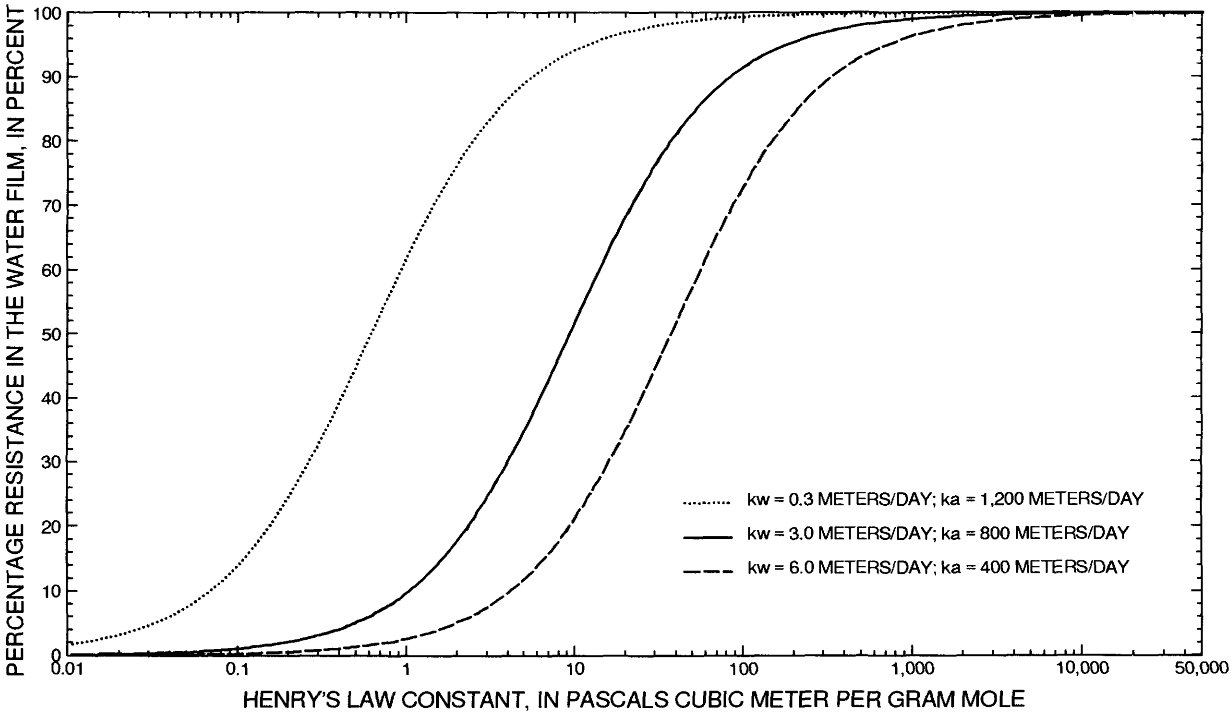

Figure 3. Percentage resistance to volatilization in the water film as a function of the Henry's law constant at 25 degrees Celsius.

be in the water film for the three combinations of film coefficients. For solutes with intermediate values of the Henry's law constant, both resistances will be significant for volatilization from water.

A useful lower limit is the Henry's law constant of water at 25°C, which is 0.057 Pa m^3/g mol. Solutes with constants less than this value are considered nonvolatile because the tendency to partition into the air phase is less than that of water. Consequently, the concentration of the solute would actually increase with time because the water would evaporate faster than the solute would volatilize.

The previous discussion used air-film coefficients that were about two orders of magnitude larger than the water-film coefficients. The air-film coefficients are larger that the water-film coefficients because molecular diffusion in gases is faster than molecular diffusion in liquids. In the case of no mixing in the bulk water and air phases, mass transfer is solely by molecular diffusion and the flux equations (eqs. 6 and 7) become

$$N_w = \frac{D_w}{\delta_w}\left[C - C_i\right] \qquad (21)$$

$$N_a = \frac{D_a}{\delta_a}\left[\frac{p_i - p}{RT}\right] \qquad (22)$$

where

D is the molecular-diffusion coefficient of the solute being transferred (m^2/day), δ is the thickness of the film (m), and the w and a subscripts refer to the water and air phases. Comparing equations 6 and 21 and equations 7 and 22, it follows that

$$k_w = \frac{D_w}{\delta_w} \qquad (23)$$

and

$$k_a = \frac{D_a}{\delta_a}\,. \qquad (24)$$

Equations 23 and 24 indicate that the film coefficients are proportional to the molecular-diffusion coefficients to the 1.0 power for the no-mixing case. Other theoretical values for this exponent range from 0.5 for the penetration model (Danckwerts, 1951) to a value for the film-penetration model that depends on the mixing intensity (Dobbins, 1956). The film-penetration model exponent varies from 0.5 for a high-mixing intensity to 1.0 for the low-mixing intensity characteristic of the molecular-diffusion limit of the film model. Experimental values of the exponent generally range between 0.50 and 0.67, and these are the values generally used to express dependence of the mass-transfer coefficient on the molecular-diffusion coefficient.

Molecular-diffusion coefficients of benzene in water and air can be used to illustrate the differences between water-film and air-film coefficients. In air, benzene has a molecular-diffusion coefficient at 25°C of 0.805 m^2/day (Lugg, 1968), and in water, the value is 9.50×10^{-5} m^2/day (Tominaga and others, 1984). Taking ratios of these values and raising the ratio to the 0.50 power and the 0.67 power results in values of 92 and 430, respectively. These numbers indicate that the air-film coefficients for benzene are likely to exceed the water-film coefficients by these factors, depending on the value assumed for the power dependence of the film coefficient on the diffusion coefficient. The large range is indicative of the sensitivity to the value of the exponent defining the dependence of the film coefficient on the molecular-diffusion coefficient. Finally, these values are qualitatively consistent with the ratios of the film coefficients used as representative values in figure 3.

REFERENCE-SUBSTANCE CONCEPT

The two-film model (eq. 13) describes the relative importance of the water-film and air-film resistances to volatilization of organic solutes from water. The model does not, however, give any information on the magnitudes of the water-film and air-film mass-transfer coefficients. These coefficients can be estimated using the reference-substance concept.

The reference-substance concept assumes that the film mass-transfer coefficients for an organic solute are directly proportional to the film mass-transfer coefficients for a reference substance and that the proportionality constants are independent of mixing conditions within the water and air phases. These relationships are

$$k_{worg} = \Phi \, k_{wref} \qquad (25)$$

$$k_{aorg} = \Psi \, k_{aref} \qquad (26)$$

where Φ and Ψ are the water and air reference-substance constants, the w and a subscripts indicate the water and air phases, and the org and ref subscripts indicate the organic solute and the reference substance, respectively. Values of the reference-substance constants are measured under controlled conditions in the laboratory. If the reference substances then are selected so that there is information on the values of the film coefficients for these substances for streams, equations 25 and 26 can be used to estimate film coefficients for organic solutes for the same streams.

Oxygen commonly is used as the reference substance for the water film for two reasons. First, the Henry's law constant for oxygen at 20.0°C, computed from the water solubility data of Benson and Krause (1980), is 74,900 Pa m^3/g mol. From figure 3, it is apparent that, for practical purposes, all the resistance to the absorption of oxygen by water is in the water film for all three combinations of film coefficients. Consequently, equation 17 applies, and the water-film mass-transfer coefficient for oxygen absorption can be measured directly.

The second reason for using oxygen as the reference substance for the water film is that considerable information exists on the oxygen-absorption coefficient, commonly called the reaeration coefficient, for streams. Tracer techniques (Tsivoglou and others, 1968; Kilpatrick and others, 1989) exist for measuring the oxygen-absorption coefficient, and numerous equations (Rathbun, 1977) exist for predicting the oxygen-absorption coefficient as a function of the hydraulic and physical characteristics of streams.

Equation 25 has been verified in the laboratory for 25 organic solutes (Rathbun, 1990), most of them VOCs commonly used and observed in the environment. These verifications were done by measuring simultaneously the rates of absorption of oxygen and the desorption of the organic solute from water in a tank stirred at a constant rate and maintained at a constant temperature. The absorption coefficient for oxygen and the desorption coefficient for the organic solute changed as the mixing rate was varied from one experiment to the next, but the ratio of the coefficients was constant, within experimental error, thus verifying the underlying assumption of equation 25. Experiments at different temperatures also showed that the ratio was independent of temperature.

Water commonly is used as the reference substance for the air film because there is no liquid-film resistance in the evaporation of a pure liquid; consequently, evaporation of a pure liquid is controlled 100 percent by the air-film resistance. Little information exists on the evaporation of water from streams. However, equations have been developed (Rathbun and Tai, 1983) for predicting the air-film coefficient as a function of windspeed and temperature for evaporation of water from a canal, which can be used as a reasonable approximation for streams.

Equation 26 has been verified in the laboratory for 1,2-dibromoethane and water (Rathbun and Tai, 1986). This verification was done by measuring, under identical experimental conditions, the evaporation rates of pure 1,2-dibromoethane and pure water as a function of windspeed. These measurements showed that the mass-transfer coefficients for both of these compounds increased as the windspeed increased, but that the ratio of the coefficients was constant, within experimental error, thus verifying equation 26. Evaporation measurements for 23 other organic solutes and water (Rathbun, 1990) permit computation of the reference-substance parameter for these solutes; these measurements, however, were limited to a single windspeed.

The large number of VOCs in use and detected in the waters of the environment precludes the experimental measurement of the reference-substance parameters for all these VOCs. However, prediction equations have been developed (Rathbun, 1990). Theoretical, semiempirical, and empirical approaches were used. Theoretical approaches were based on Graham's law and the mass-transfer models discussed previously. Graham's law (Glasstone, 1946) states that the diffusion coefficient of a solute is inversely proportional to the square root of the molecular weight. The mass-transfer models indicate that the mass-transfer coefficient of a solute is dependent on the molecular-diffusion coefficient raised to a power, usually between 0.50 and 0.67. Semiempirical approaches consisted of using the mass-transfer models with empirical equations for predicting the molecular-diffusion coefficients of solutes in water and air as a function of molecular weight and the molal volume at the normal boiling temperature. Empirical approaches consisted of computing log-log fits of the experimental values of the reference-substance parameters as a function of molecular weight and the molal volume.

Various combinations of these approaches resulted in five predictive equations for the water-film reference-substance parameter and four predictive equations for the air-film reference-substance parameter. Equations based on the empirical models had the smallest mean absolute percentage errors. These equations were

$$\Phi = 2.52\,V_m^{-0.301} \tag{27}$$

$$\Psi = 4.42\,M^{-0.462} \tag{28}$$

where

V_m is the molal volume at the normal boiling temperature (cm^3/g mol), and

M is the molecular weight (g/g mol).

The molal volume can be computed from the molecular structure by using the LeBas procedure (Reid and others, 1987).

HENRY'S LAW CONSTANT

The two-film model and figure 3 indicate that the Henry's law constant is important in determining the partitioning of organic solutes between water and air. Various defining equations for the Henry's law constant have been presented in the literature. These defining equations have resulted in Henry's law constants with a variety of dimensional units and also a nondimensional form. Also, in some studies, a Henry's law constant equal to the reciprocal of the one commonly used has been defined. Consequently, care should be exercised in using Henry's law constants from the literature. The following paragraphs present a discussion of these various forms of the Henry's law constant.

Henry's law applies to dilute solutions and describes the distribution of a solute between water and air phases at equilibrium. If these phases are in equilibrium, then the fugacities, f, must be equal:

$$f_a = f_w \,. \tag{29}$$

For the air phase,

$$f_a = y\,F\,P_t \tag{30}$$

where

y is the mole fraction of the solute in the air,

F is the fugacity coefficient, and

P_t is the total pressure, in pascals.

The fugacity coefficient, F, characterizes the degree of nonideality in the air phase. For the low concentrations characteristic of environmental situations and environmental pressures, ideal mixtures can be assumed, and F will equal 1.0. By Dalton's law, the product of the mole fraction y and the total pressure, P_t, is the partial pressure of the solute, p. Consequently, it follows that

$$f_a = y\,P_t = p\ . \tag{31}$$

For the water phase,

$$f_w = \gamma\ mf\ f_r \tag{32}$$

where

γ is the activity coefficient of the solute in water,

mf is the mole fraction of the solute in water, and

f_r is the reference fugacity.

The activity coefficient characterizes the degree of non-ideality between the solute and water, and it is defined on the convention that when the mole fraction, mf, is 1.0, the activity coefficient is 1.0. It follows from equation 32 that the reference fugacity is the fugacity of the pure solute in the liquid state at the system temperature. Thus, for typical environmental pressures, this reference fugacity is the vapor pressure of the pure solute. Therefore, combining equations 29, 31, and 32 gives

$$p = \gamma\ mf\ p^o \tag{33}$$

where

p^o is the vapor pressure, in pascals, of the solute at the system temperature.

Henry's law commonly is written

$$p = H\,C \tag{34}$$

where H, the Henry's law constant, is the proportionality constant between the concentration of the solute in the water, C, and the partial pressure, p, of the solute in the air above the water. Combining equations 34 and 33 gives

$$H = \frac{\gamma\ mf\ p^o}{C}\ . \tag{35}$$

Equation 35 indicates that the Henry's law constant has units of pressure divided by concentration, for example, Pa m^3/g mol.

However, the Henry's law constant has not always been defined in this manner. In early mass-transfer studies (Lewis and Whitman, 1924; Sherwood and Holloway, 1940; Whitney and Vivian, 1949) and in some textbooks (Prutton and Maron, 1951; Rich, 1973), the relation C = Hp was used, so that the Henry's law constant was the reciprocal of the one defined by equation 34, which is the one now used in most studies. Also, in some studies where distribution coefficients were determined (Hine and Mookerjee, 1975; Ioffe and Vitenberg, 1982) and in studies where Bunsen coefficients were determined (Park and others, 1982; Warner and Weiss, 1985; Bu and Warner, 1995), the coefficients are the reciprocal of the commonly used Henry's law coefficient defined by equation 34.

Various forms of equation 35 have appeared in the literature. The solute mole fraction, mf, is given by

$$mf = \frac{C V_s}{C V_s + M_w V_s} \tag{36}$$

where

V_s is the volume of the water (m^3), and

M_w is the gram moles of water per cubic meter (g mol/m^3).

For dilute aqueous solutions, the $M_w V_s$ term in the denominator of equation 36 is much larger than the CV_s term, and it follows that

$$mf \cong \frac{C}{M_w} = \frac{C}{10^6/18} \tag{37}$$

where

$10^6/18$ is the gram moles of water per cubic meter.

Combining equations 37 and 35 gives

$$H = (18)(10^{-6})\ \gamma\ p^{o}\ . \qquad (38)$$

Equation 38 was presented by Mackay and Shiu (1975).

An expression for the activity coefficient of a solute in a dilute aqueous solution can be developed as follows. Consider an aqueous solution of the solute in equilibrium with the pure organic solute. At equilibrium, the fugacities are equal, or

$$f_{org} = f_{aq} \qquad (39)$$

and

$$mf_{org}\gamma_{org}f_r = mf_{aq}\gamma_{aq}f_r \qquad (40)$$

where the org and aq subscripts indicate the organic and aqueous phases. If the solubility of water in the organic compound is small, it follows that

$$mf_{org} \cong 1.0 \text{ and } \gamma_{org} \cong 1.0 \qquad (41)$$

and

$$\gamma_{aq} = \frac{1}{mf_{aq}} \qquad (42)$$

where

mf_{aq} is the mole fraction solubility of the organic solute in water.

Assuming again that the aqueous solution is dilute, which is true for most environmental conditions, it follows that

$$mf_{aq} \cong \frac{18\ S}{10^6\ M} \qquad (43)$$

where

S is the solubility of the organic solute (mg/L), and

M is the molecular weight (g/g mol).

Combining equations 42, 43, and 38 gives

$$H = \frac{M\ p^{o}}{S}\ . \qquad (44)$$

Equation 44 commonly is used to compute Henry's law constants from solubility and vapor-pressure data for the solute of interest (Mackay and Shiu, 1981).

Another form of the Henry's law constant that commonly is used in the literature is the nondimensional Henry's law constant. This constant is obtained by dividing by RT, where R is the ideal gas constant (8.314 Pa m^3/g mol/K) and T is the absolute temperature, in kelvins. Equation 44 thus becomes

$$H_d = \frac{0.120\ M\ p^{o}}{ST} \qquad (45)$$

where

H_d is the nondimensional Henry's law constant.

Equation 45 with the numerical constant replaced by 16.04 to accommodate vapor pressures in mm Hg was used by Dilling (1977).

The defining equation for the Henry's law constant (eq. 34) also can be converted to the nondimensional form by dividing the partial pressure, p, by RT. The result is

$$H_d = \frac{p/RT}{C} = \frac{\text{gmol}/\text{m}^3}{\text{gmol}/\text{m}^3}\ . \qquad (46)$$

Equation 46 indicates that the nondimensional Henry's law constant is the ratio of the air concentration to the water concentration at equilibrium. Thus, the nondimensional Henry's law constant provides a direct measure of the partitioning of the solute between the water and air phases.

Finally, the Henry's law constant is sometimes expressed on a mole fraction basis, or

$$p = H_{mf}\ mf \qquad (47)$$

where H_{mf} has units of pressure, usually pascals. References containing Henry's law constants with units of pressure have constants on a mole fraction basis, for example, Keeley and others (1988). For dilute aqueous solutions, equation 37 applies, and combining this equation with equation 47 gives

$$p = \frac{H_{mf}\,C}{M_w}\,. \tag{48}$$

Comparing equations 48 and 34 indicates that

$$H = \frac{H_{mf}}{M_w}\,. \tag{49}$$

TECHNIQUES FOR MEASURING THE HENRY'S LAW CONSTANT

Several techniques are available for measuring Henry's law constants. The multiple equilibration (ME) technique (McAuliffe, 1971; Munz and Roberts, 1986) depends on the determination of the concentration of the organic compound in either the gas or liquid phase after repeated equilibrations of an inert gas with an aqueous sample containing the organic compound of interest. McAuliffe (1971) used measurements of the gas-phase concentration, and Munz and Roberts (1986) used measurements of the liquid-phase concentration. This technique assumes that the gas and liquid phases are in equilibrium at the end of each equilibration step.

The batch-stripping (BS) technique (Mackay and others, 1979) involves stripping the organic compound of interest from a water solution by bubbling an inert gas through the water. The Henry's law constant is determined from the slope of a plot of the liquid or gas concentration as a function of time. An advantage of the BS technique is that only relative concentrations are needed. This technique assumes that the concentration of the solute in the gas phase leaving the stripping chamber is in equilibrium with the liquid phase. The BS technique has been used for polychlorinated biphenyl compounds (PCBs) with Henry's law constants as small as 91 Pa m^3/g mol at 25°C (Dunnivant and others, 1988).

The equilibration cell (EC) technique (Leighton and Calo, 1981; Tancrede and Yanagisawa, 1990) depends on the measurement of the concentrations of the organic compound in the air and water phases of a mixture in a closed container. This technique assumes that the air and water phases are homogeneous, in equilibrium, and that there are no temperature gradients. Nonattainment of equilibrium is most likely to be important for those compounds with the largest Henry's law constants. Equilibrium techniques such as the EC technique are generally applicable only to compounds with Henry's law constants larger than 250 Pa m^3/g mol at 25°C because of the limited sizes of the headspace and water sample and limited analytical sensitivities (Fendinger and Glotfelty, 1988).

The equilibrium-partitioning-in-closed-systems (EPICS) technique (Lincoff and Gossett, 1984) is based on the measurement of the gas phase concentrations of the organic compound of interest in two closed bottles that contain different water volumes. This technique has the advantage that only relative rather than absolute concentrations are necessary. The EPICS technique assumes that the gas and liquid phases are in equilibrium. The coefficient of variation of Henry's law constants measured with the EPICS technique increased rapidly for constants less than about 500 Pa m^3/g mol at 25°C (Gossett, 1987). Consequently, the technique is not useful for low values of the Henry's law constant.

The wetted-wall-column (WWC) technique (Fendinger and Glotfelty, 1990) involves equilibrating the organic compound of interest in a thin water film on the wall of a vertical column with a concurrent flow of air. The organic compound can be introduced either as a vapor for air-to-water transfer or in solution for water-to-air transfer. The technique was used (Fendinger and Glotfelty, 1988) for three pesticides with Henry's law constants in the range from 0.2 to 0.6×10^{-4} Pa m^3/g mol.

The static-headspace (SH) technique (Robbins and others, 1993) involves determining the relative headspace concentration of one or more organic compounds of interest from aliquots of the same solution in three closed containers with different headspace-to-liquid volume ratios. This technique has the advantage that absolute concentrations are not needed, and the composition of the liquid matrix also is not needed. The essential assumptions are that the compositions of the solutions in the three containers are the same and that equilibrium is attained before the headspace samples are collected. The SH technique has been applied to the measurement of Henry's law constants as small as 53.5 Pa m^3/g mol at 25°C (Robbins and others, 1993).

The multiple-injection-interrupted-flow (MIIF) technique (Keeley and others, 1988) is a headspace technique based on comparative analyses of bottles containing vapor only with bottles containing the organic compound of interest and water. This technique has the advantage that little manipulation of the samples is required. However, the technique is limited to compounds with appreciable vapor pressure.

EXPERIMENTAL VALUES OF THE HENRY'S LAW CONSTANT

Experimental values of the Henry's law constant in Pa m^3/g mol for 43 of the 55 target analytes (table 1) are presented in table 2 for temperatures of 20°C and 25°C. Some of these values were experimentally determined at these temperatures; others are interpolated values calculated at these temperatures from Henry's law constant-versus-temperature relations. These interpolated values were used whenever the experimental temperatures were not at precisely 20°C or 25°C. The temperature relations were not used to extrapolate outside the reported temperature range of each study. The temperature relations are discussed in more detail in the section on the temperature dependence of the Henry's law constant.

When two or more experimental values existed at a temperature, an arithmetic mean Henry's law constant was computed. These mean values are given in table 2. Experimental values for four compounds were excluded from table 2 because they differed substantially from other values and were believed to be in error. These values are summarized in table 3. Three of the six excluded values are from McConnell and others (1975), and it was previously noted (Leighton and Calo, 1981) that some of their results appeared to be in error. The large differences shown in table 3 indicate the difficulties of measuring accurate values of the Henry's law constant.

Only two values were available for hexachlorobutadiene at 20°C, and those two values differ substantially (table 2). The larger of the two values was from McConnell and others (1975). Because values from this study were large for three of the other compounds for which values were excluded (table 3) and because the one value at 25°C (table 2) is intermediate between the 20°C values, the smaller value may be more representative of the true value at 20°C. There is, however, insufficient basis to exclude the 20°C value of McConnell and others (1975).

EQUATIONS FOR CALCULATING THE HENRY'S LAW CONSTANT

Experimental values of the Henry's law constant were not available for 12 of the target analytes. Constants for these compounds can be computed from equations 44 and 38. Mackay and Shiu (1981) used equation 44 for their extensive compilation of Henry's law constants. The development of relatively simple gas-chromatographic techniques (Tse and others, 1992; Li and others, 1993) for the measurement of activity coefficients has resulted in the use of equation 38 to compute Henry's law constants from these activity coefficients and vapor-pressure data.

Errors from using these equations result from failure to meet the assumptions in the derivations discussed previously and from errors in vapor pressures, solubilities, and activity coefficients. The equations assume that the mutual solubilities of the organic compound and water are small. Thus, this assumption is most valid for hydrophobic compounds and less valid for the more water-soluble compounds. Errors in vapor-pressure data in the literature have been noted, for example, by Hoffman (1984) and Rathbun and Tai (1987). Nirmalakhandan and Speece (1988) noted that errors in vapor-pressure data could range from 6 to 200 or 300 percent, with the error increasing as the molecular weight increases and the vapor pressure decreases. Also, vapor-pressure data often are measured at high temperatures that require extrapolation to temperatures appropriate for environmental conditions, and such extrapolation could introduce errors.

Errors in solubility data in the literature also have been noted, for example, by Mackay and Shiu (1981), Bharath and others (1984), and Rathbun and Tai (1988). Many of these errors result from the shake-flask method used in early solubility determinations. This method involves mixing an excess of the organic solute with water, followed by separation of the phases and analysis of the water phase for the organic compound. This method, however, frequently results in the dispersion and retention of compound molecules in the water by the process of accommodation (Peake and Hodgson, 1966; 1967) that are not truly in solution. Consequently, the measured solubilities are larger than the true solubilities, with this source of error likely to be most important for the least soluble compound. The generator column technique (May and others, 1978) now used for solubility determinations does not have this problem and also eliminates several other sources of error common in the shake-flask method. Nirmalakhandan and Speece (1988) indicated that experimental errors in solubility data are likely to be in the range of ±3 to 5 percent. They also noted that, unlike vapor-pressure data, the temperature dependence of water solubilities has not been studied extensively.

Table 2. Experimental and interpolated values of Henry's law constants at 20° Celsius and 25° Celsius for 43 target analytes

[USGS, U.S. Geological Survey; °C, degrees Celsius; H, Henry's law constant, in pascals cubic meter per gram mole; e, experimental value; i, interpolated value calculated from the Henry's law constant-temperature relationship; NS, not specified; EPICS, equilibrium partitioning in closed systems; EC, equilibrium cell; BS, batch stripping; ME, multiple equilibration; MIIF, multiple injection interrupted flow; SH, static headspace; WWC, wetted-wall column; av, arithmetic mean]

USGS parameter code	Compound	Temperature (°C)	H	e, i	Experimental technique	Reference
34418	chloromethane	20	816	e	NS	Glew and Moelwyn-Hughes (1953)
		20	739	e	NS	McConnell and others (1975)
		20	665	i	EPICS	Gossett (1987)
			20°C av = 740			
		25	957	e	NS	Glew and Moelwyn-Hughes (1953)
		25	845	i	EPICS	Gossett (1987)
			25°C av = 901			
34423	dichloromethane	20	301	e	NS	McConnell and others (1975)
		20	263	i	EC	Leighton and Calo (1981)
		20	229	i	EPICS	Lincoff and Gossett (1984)
		20	201	i	BS	Lincoff and Gossett (1984)
		20	173	i	EPICS	Gossett (1987)
		20	188	e	EPICS	Yurteri and others (1987)
		20	247	e	EPICS	Ashworth and others (1988)
			20°C av = 229			
		25	324	i	EC	Leighton and Calo (1981)
		25	291	i	EPICS	Lincoff and Gossett (1984)
		25	260	i	BS	Lincoff and Gossett (1984)
		25	215	i	EPICS	Gossett (1987)
		25	323	e	BS	Warner and others (1987)
		25	300	e	EPICS	Ashworth and others (1988)
			25°C av = 286			
32106	trichloromethane	20	283	e	NS	McConnell and others (1975)
		20	317	i	EC	Leighton and Calo (1981)
		20	337	i	EPICS	Lincoff and Gossett (1984)
		20	313	i	BS	Lincoff and Gossett (1984)
		20	332	e	BS	Lalezary and others (1984)
		20	312	e	BS	Nicholson and others (1984)
		20	305	e	ME	Munz and Roberts (1986)
		20	279	i	EPICS	Gossett (1987)
		20	301	i	ME	Munz and Roberts (1987)
		20	336	e	EPICS	Ashworth and others (1988)
		20	294	i	EPICS	Dewulf and others (1995)
			20°C av = 310			
		25	398	i	EC	Leighton and Calo (1981)
		25	428	i	EPICS	Lincoff and Gossett (1984)
		25	401	i	BS	Lincoff and Gossett (1984)
		25	399	i	BS	Nicholson and others (1984)
		25	363	i	EPICS	Gossett (1987)
		25	384	i	ME	Munz and Roberts (1987)

Table 2. Experimental and interpolated values of Henry's law constants at 20° Celsius and 25° Celsius for 43 target analytes—Continued

[USGS, U.S. Geological Survey; °C, degrees Celsius; H, Henry's law constant, in pascals cubic meter per gram mole; e, experimental value; i, interpolated value calculated from the Henry's law constant-temperature relationship; NS, not specified; EPICS, equilibrium partitioning in closed systems; EC, equilibrium cell; BS, batch stripping; ME, multiple equilibration; MIIF, multiple injection interrupted flow; SH, static headspace; WWC, wetted-wall column; av, arithmetic mean]

USGS parameter code	Compound	Temperature (°C)	H	e, i	Experimental technique	Reference
32106	trichloromethane (Continued)	25	343	e	BS	Warner and others (1987)
		25	427	e	EPICS	Ashworth and others (1988)
		25	378	i	EPICS	Dewulf and others (1995)
			25°C av = 391			
32102	tetrachloromethane	20	2,220	e	NS	McConnell and others (1975)
		20	2,140	i	EC	Leighton and Calo (1981)
		20	2,450	e	BS	Munz and Roberts (1982)
		20	2,030	i	ME	Hunter-Smith and others (1983)
		20	2,380	e	ME	Munz and Roberts (1986)
		20	2,390	i	ME	Munz and Roberts (1987)
		20	2,350	i	EPICS	Gossett (1987)
		20	2,280	e	EPICS	Yurteri and others (1987)
		20	2,350	e	EPICS	Ashworth and others (1988)
		20	2,000	i	EPICS	Dewulf and others (1995)
			20°C av = 2,260			
		25	2,750	i	EC	Leighton and Calo (1981)
		25	2,440	i	ME	Hunter-Smith and others (1983)
		25	3,050	i	ME	Munz and Roberts (1987)
		25	3,020	i	EPICS	Gossett (1987)
		25	3,060	e	BS	Warner and others (1987)
		25	2,990	e	EPICS	Ashworth and others (1988)
		25	2,980	e	BS	Ashworth and others (1988)
		25	2,880	e	EC	Tancrede and Yanagisawa (1990)
		25	2,560	i	EPICS	Dewulf and others (1995)
			25°C av = 2,860			
34413	bromomethane	20	532	e	NS	Glew and Moelwyn-Hughes (1953)
		25	631	e	NS	Glew and Moelwyn-Hughes (1953)
32104	tribromomethane	20	44.2	e	BS	Nicholson and others (1984)
		20	43.9	i	ME	Munz and Roberts (1987)
			20°C av = 44.0			
		25	61.1	i	BS	Nicholson and others (1984)
		25	54.1	i	ME	Munz and Roberts (1987)
		25	53.9	e	BS	Warner and others (1987)
			25°C av = 56.4			
32101	bromodichloromethane	20	157	e	BS	Nicholson and others (1984)
		25	212	i	BS	Nicholson and others (1984)
		25	215	e	BS	Warner and others (1987)
			25°C av = 214			
32105	chlorodibromomethane	20	83.4	e	BS	Nicholson and others (1984)
		20	104	e	EPICS	Ashworth and others (1988)
			20°C av = 93.7			

Table 2. Experimental and interpolated values of Henry's law constants at 20° Celsius and 25° Celsius for 43 target analytes—Continued

[USGS, U.S. Geological Survey; °C, degrees Celsius; H, Henry's law constant, in pascals cubic meter per gram mole; e, experimental value; i, interpolated value calculated from the Henry's law constant-temperature relationship; NS, not specified; EPICS, equilibrium partitioning in closed systems; EC, equilibrium cell; BS, batch stripping; ME, multiple equilibration; MIIF, multiple injection interrupted flow; SH, static headspace; WWC, wetted-wall column; av, arithmetic mean]

USGS parameter code	Compound	Temperature (°C)	H	e, i	Experimental technique	Reference
32105	chlorodibromomethane (Continued)	25	116	i	BS	Nicholson and others (1984)
		25	79.3	e	BS	Warner and others (1987)
		25	120	e	EPICS	Ashworth and others (1988)
			25°C av = 105			
34311	chloroethane	20	946	i	EPICS	Gossett (1987)
		20	1,110	e	EPICS	Ashworth and others (1988)
			20°C av = 1,030			
		25	1,130	i	EPICS	Gossett (1987)
		25	1,230	e	EPICS	Ashworth and others (1988)
			25°C av = 1,180			
34496	1,1-dichloroethane	20	435	i	EPICS	Gossett (1987)
		20	570	e	EPICS	Ashworth and others (1988)
		20	390	i	EPICS	Dewulf and others 1995)
			20°C av = 465			
		25	551	i	EPICS	Gossett (1987)
		25	552	e	BS	Warner and others (1987)
		25	633	e	EPICS	Ashworth and others (1988)
		25	502	i	EPICS	Dewulf and others (1995)
			25°C av = 560			
32103	1,2-dichloroethane	20	92.3	e	NS	McConnell and others (1975)
		20	127	i	EC	Leighton and Calo (1981)
		20	149	e	EPICS	Ashworth and others (1988)
		20	78.3	i	EPICS	Dewulf and others (1995)
			20°C av = 112			
		25	155	i	EC	Leighton and Calo (1981)
		25	111	e	BS	Warner and others (1987)
		25	143	e	EPICS	Ashworth and others (1988)
		25	63.6	e	BS	Ashworth and others (1988)
		25	99.2	i	EPICS	Dewulf and others (1995)
			25°C av = 114			
34506	1,1,1-trichloroethane	20	1,540	i	EC	Leighton and Calo (1981)
		20	1,510	e	BS	Munz and Roberts (1982)
		20	1,100	i	ME	Hunter-Smith and others (1983)
		20	1,340	i	EPICS	Lincoff and Gossett (1984)
		20	1,370	i	BS	Lincoff and Gossett (1984)
		20	1,360	i	ME	Munz and Roberts (1987)
		20	1,340	i	EPICS	Gossett (1987)
		20	1,570	e	EPICS	Yurteri and others (1987)
		20	1,480	e	EPICS	Ashworth and others (1988)
		20	1,190	i	EPICS	Dewulf and others (1995)
			20°C av = 1,380			

Table 2. Experimental and interpolated values of Henry's law constants at 20° Celsius and 25° Celsius for 43 target analytes—Continued

[USGS, U.S. Geological Survey; °C, degrees Celsius; H, Henry's law constant, in pascals cubic meter per gram mole; e, experimental value; i, interpolated value calculated from the Henry's law constant-temperature relationship; NS, not specified; EPICS, equilibrium partitioning in closed systems; EC, equilibrium cell; BS, batch stripping; ME, multiple equilibration; MIIF, multiple injection interrupted flow; SH, static headspace; WWC, wetted-wall column; av, arithmetic mean]

USGS parameter code	Compound	Temperature (°C)	H	e, i	Experimental technique	Reference
34506	1,1,1-trichloroethane	25	1,970	i	EC	Leighton and Calo (1981)
		25	1,320	i	ME	Hunter-Smith and others (1983)
		25	1,710	i	EPICS	Lincoff and Gossett (1984)
		25	1,740	i	BS	Lincoff and Gossett (1984)
		25	1,690	i	EPICS	Gossett (1987)
		25	1,720	i	ME	Munz and Roberts (1987)
		25	1,760	e	EPICS	Ashworth and others (1988)
		25	1,780	e	BS	Ashworth and others (1988)
		25	1,780	e	SH	Robbins and others (1993)
		25	1,520	i	EPICS	Dewulf and others (1995)
			25°C av = 1,700			
34511	1,1,2-trichloroethane	20	67.0	i	EC	Leighton and Calo (1981)
		20	75.0	e	EPICS	Ashworth and others (1988)
			20°C av = 71.0			
		25	82.5	i	EC	Leighton and Calo (1981)
		25	92.2	e	EPICS	Ashworth and others (1988)
		25	113	e	BS	Ashworth and others (1988)
			25°C av = 95.9			
34396	hexachloroethane	20	290	e	ME	Munz and Roberts (1986)
		20	285	i	ME	Munz and Roberts (1987)
		20	599	e	EPICS	Ashworth and others (1988)
			20°C av = 391			
		25	393	i	ME	Munz and Roberts (1987)
		25	998	e	BS	Warner and others (1987)
		25	846	e	EPICS	Ashworth and others (1988)
			25°C av = 746			
77651	1,2-dibromoethane	20	61.8	e	EPICS	Ashworth and others (1988)
		25	65.9	e	EPICS	Ashworth and others (1988)
34541	1,2-dichloropropane	20	224	i	EC	Leighton and Calo (1981)
		20	193	e	EPICS	Ashworth and others (1988)
			20°C av = 208			
		25	286	i	EC	Leighton and Calo (1981)
		25	286	e	BS	Warner and others (1987)
		25	362	e	EPICS	Ashworth and others (1988)
			25°C av = 311			
77443	1,2,3-trichloropropane	20	28.2	i	EC	Leighton and Calo (1981)
		25	34.3	i	EC	Leighton and Calo (1981)
34488	trichlorofluoromethane	20	7,770	i	ME	Hunter-Smith and others (1983)
		20	7,400	i	EC	Warner and Weiss (1985)
		20	8,150	e	EPICS	Ashworth and others (1988)
			20°C av = 7,770			

Table 2. Experimental and interpolated values of Henry's law constants at 20° Celsius and 25° Celsius for 43 target analytes—Continued

[USGS, U.S. Geological Survey; °C, degrees Celsius; H, Henry's law constant, in pascals cubic meter per gram mole; e, experimental value; i, interpolated value calculated from the Henry's law constant-temperature relationship; NS, not specified; EPICS, equilibrium partitioning in closed systems; EC, equilibrium cell; BS, batch stripping; ME, multiple equilibration; MIIF, multiple injection interrupted flow; SH, static headspace; WWC, wetted-wall column; av, arithmetic mean]

USGS parameter code	Compound	Temperature (°C)	H	e, i	Experimental technique	Reference
34488	trichlorofluoromethane (Continued)	25	9,790	e	EC	Park and others (1982)
		25	9,040	i	ME	Hunter-Smith and others (1983)
		25	9,230	i	EC	Warner and Weiss (1985)
		25	5,910	e	BS	Warner and others (1987)
		25	10,200	e	EPICS	Ashworth and others (1988)
			25°C av = 8,830			
34668	dichlorodifluoromethane	20	40,600	e	NS	McConnell and others (1975)
		20	27,000	i	EC	Warner and Weiss (1985)
		20	26,600	i	ME	Munz and Roberts (1987)
			20°C av = 31,400			
		25	37,200	e	EC	Park and others (1982)
		25	32,900	i	EC	Warner and Weiss (1985)
		25	32,500	i	ME	Munz and Roberts (1987)
			25°C av = 34,200			
77652	1,1,2-trichloro-1,2,2-trifluoroethane	20	24,800	e	EPICS	Ashworth and others (1988)
		20	25,300	i	EC	Bu and Warner (1995)
			20°C av = 25,000			
		25	32,300	e	EPICS	Ashworth and others (1988)
		25	32,500	i	EC	Bu and Warner (1995)
			25°C av = 32,400			
39175	chloroethene	20	2,200	i	EPICS	Gossett (1987)
		20	2,200	e	EPICS	Ashworth and others (1988)
			20°C av = 2,200			
		25	2,660	i	EPICS	Gossett (1987)
		25	2,690	e	EPICS	Ashworth and others (1988)
			25°C av = 2,680			
34501	1,1-dichloroethene	20	2,850	i	EC	Leighton and Calo (1981)
		20	2,090	i	EPICS	Gossett (1987)
		20	2,210	e	EPICS	Ashworth and others (1988)
			20°C av = 2,380			
		25	3,700	i	EC	Leighton and Calo (1981)
		25	2,590	i	EPICS	Gossett (1987)
		25	1,520	e	BS	Warner and others (1987)
		25	2,620	e	EPICS	Ashworth and others (1988)
		25	2,840	e	BS	Ashworth and others (1988)
			25°C av = 2,650			
77093	*cis*-1,2-dichloroethene	20	299	i	EPICS	Gossett (1987)
		20	441	e	EPICS	Yurteri and others (1987)
		20	365	e	EPICS	Ashworth and others (1988)
			20°C av = 368			

Table 2. Experimental and interpolated values of Henry's law constants at 20° Celsius and 25° Celsius for 43 target analytes—Continued

[USGS, U.S. Geological Survey; °C, degrees Celsius; H, Henry's law constant, in pascals cubic meter per gram mole; e, experimental value; i, interpolated value calculated from the Henry's law constant-temperature relationship; NS, not specified; EPICS, equilibrium partitioning in closed systems; EC, equilibrium cell; BS, batch stripping; ME, multiple equilibration; MIIF, multiple injection interrupted flow; SH, static headspace; WWC, wetted-wall column; av, arithmetic mean]

USGS parameter code	Compound	Temperature (°C)	H	e, i	Experimental technique	Reference
77093	*cis*-1,2-dichloroethene (Continued)	25	380	i	EPICS	Gossett (1987)
		25	460	e	EPICS	Ashworth and others (1988)
			25°C av = 420			
34546	*trans*-1,2-dichloroethene	20	731	i	EPICS	Gossett (1987)
		20	914	e	EPICS	Yurteri and others (1987)
		20	868	e	EPICS	Ashworth and others (1988)
			20°C av = 838			
		25	929	i	EPICS	Gossett (1987)
		25	539	e	BS	Warner and others (1987)
		25	958	e	EPICS	Ashworth and others (1988)
			25°C av = 809			
39180	trichloroethene	20	890	e	NS	McConnell and others (1975)
		20	757	i	EC	Leighton and Calo (1981)
		20	999	e	BS	Munz and Roberts (1982)
		20	688	i	EPICS	Lincoff and Gossett (1984)
		20	777	i	BS	Lincoff and Gossett (1984)
		20	793	i	ME	Munz and Roberts (1987)
		20	716	i	EPICS	Gossett (1987)
		20	1,050	e	EPICS	Yurteri and others (1987)
		20	853	e	EPICS	Ashworth and others (1988)
		20	654	i	EPICS	Dewulf and others (1995)
			20°C av = 818			
		25	984	i	EC	Leighton and Calo (1981)
		25	1,030	i	EPICS	Lincoff and Gossett (1984)
		25	881	i	BS	Lincoff and Gossett (1984)
		25	984	e	EPICS	Garbarini and Lion (1985)
		25	1,190	e	BS	Warner and others (1987)
		25	1,040	i	ME	Munz and Roberts (1987)
		25	944	i	EPICS	Gossett (1987)
		25	1,030	e	EPICS	Ashworth and others (1988)
		25	768	e	EC	Tancrede and Yanagisawa (1990)
		25	1,050	e	SH	Robbins and others (1993)
		25	864	i	EPICS	Dewulf and others (1995)
			25°C av = 979			
34475	tetrachloroethene	20	2,000	e	NS	McConnell and others (1975)
		20	1,230	i	EC	Leighton and Calo (1981)
		20	1,530	e	BS	Munz and Roberts (1982)
		20	1,320	i	EPICS	Lincoff and Gossett (1984)
		20	1,190	i	BS	Lincoff and Gossett (1984)

Table 2. Experimental and interpolated values of Henry's law constants at 20° Celsius and 25° Celsius for 43 target analytes—Continued

[USGS, U.S. Geological Survey; °C, degrees Celsius; H, Henry's law constant, in pascals cubic meter per gram mole; e, experimental value; i, interpolated value calculated from the Henry's law constant-temperature relationship; NS, not specified; EPICS, equilibrium partitioning in closed systems; EC, equilibrium cell; BS, batch stripping; ME, multiple equilibration; MIIF, multiple injection interrupted flow; SH, static headspace; WWC, wetted-wall column; av, arithmetic mean]

USGS parameter code	Compound	Temperature (°C)	H	e, i	Experimental technique	Reference
34475	tetrachloroethene (Continued)	20	1,440	i	ME	Munz and Roberts (1987)
		20	1,330	i	EPICS	Gossett (1987)
		20	1,300	e	EPICS	Yurteri and others (1987)
		20	1,430	e	EPICS	Ashworth and others (1988)
		20	1,120	i	EPICS	Dewulf and others (1995)
			20°C av = 1,390			
		25	1,610	i	EC	Leighton and Calo (1981)
		25	1,770	i	EPICS	Lincoff and Gossett (1984)
		25	1,550	i	BS	Lincoff and Gossett (1984)
		25	1,860	i	ME	Munz and Roberts (1987)
		25	1,760	i	EPICS	Gossett (1987)
		25	2,910	e	BS	Warner and others (1987)
		25	1,730	e	EPICS	Ashworth and others (1988)
		25	1,880	e	BS	Ashworth and others (1988)
		25	1,360	e	EC	Tancrede and Yanagisawa (1990)
		25	1,790	e	SH	Robbins and others (1993)
		25	1,480	i	EPICS	Dewulf and others (1995)
			25°C av = 1,790			
39702	hexachlorobutadiene	20	2,510	e	NS	McConnell and others (1975)
		20	429	e	BS	Oliver (1985)
		25	1,040	e	BS	Warner and others (1987)
34030	benzene	20	441	i	EC	Leighton and Calo (1981)
		20	501	i	ME	Ioffe and Vitenberg (1982)
		20	746	e	EPICS	Yurteri and others (1987)
		20	458	e	EPICS	Ashworth and others (1988)
		20	387	i	EPICS	Dewulf and others (1995)
			20°C av = 507			
		25	562	e	BS	Mackay and others (1979)
		25	552	i	EC	Leighton and Calo (1981)
		25	612	i	ME	Ioffe and Vitenberg (1982)
		25	562	e	BS	Warner and others (1987)
		25	585	e	MIIF	Keeley and others (1988)
		25	535	e	EPICS	Ashworth and others (1988)
		25	588	e	BS	Ashworth and others (1988)
		25	535	e	SH	Robbins and others (1993)
		25	483	i	EPICS	Dewulf and others (1995)
			25°C av = 557			
34696	naphthalene	20	36.6	e	EPICS	Yurteri and others (1987)
		25	48.9	e	BS	Mackay and others (1979)

Table 2. Experimental and interpolated values of Henry's law constants at 20° Celsius and 25° Celsius for 43 target analytes—Continued

[USGS, U.S. Geological Survey; °C, degrees Celsius; H, Henry's law constant, in pascals cubic meter per gram mole; e, experimental value; i, interpolated value calculated from the Henry's law constant-temperature relationship; NS, not specified; EPICS, equilibrium partitioning in closed systems; EC, equilibrium cell; BS, batch stripping; ME, multiple equilibration; MIIF, multiple injection interrupted flow; SH, static headspace; WWC, wetted-wall column; av, arithmetic mean]

USGS parameter code	Compound	Temperature (°C)	H	e, i	Experimental technique	Reference
34696	naphthalene (Continued)	25	56.0	e	BS	Southworth (1979)
		25	44.6	e	BS	Mackay and others (1982)
		25	74.4	e	WWC	Fendinger and Glotfelty (1990)
			25°C av = 56.0			
34010	methylbenzene	20	519	i	EC	Leighton and Calo (1981)
		20	530	i	ME	Ioffe and Vitenberg (1982)
		20	595	e	EPICS	Yurteri and others (1987)
		20	562	e	EPICS	Ashworth and others (1988)
		20	440	i	EPICS	Dewulf and others (1995)
			20°C av = 529			
		25	673	e	BS	Mackay and others (1979)
		25	642	i	EC	Leighton and Calo (1981)
		25	682	i	ME	Ioffe and Vitenberg (1982)
		25	647	e	EPICS	Garbarini and Lion (1985)
		25	601	e	BS	Warner and others (1987)
		25	605	e	MIIF	Keeley and others (1988)
		25	651	e	EPICS	Ashworth and others (1988)
		25	674	e	SH	Robbins and others (1993)
		25	563	i	EPICS	Dewulf and others (1995)
			25°C av = 638			
34371	ethylbenzene	20	609	e	EPICS	Ashworth and others (1988)
		20	509	i	EPICS	Dewulf and others (1995)
			20°C av = 559			
		25	854	e	BS	Mackay and others (1979)
		25	653	e	BS	Warner and others (1987)
		25	798	e	EPICS	Ashworth and others (1988)
		25	793	e	SH	Robbins and others (1993)
		25	681	i	EPICS	Dewulf and others (1995)
			25°C av = 756			
77224	n-propylbenzene	20	893	e	EPICS	Ashworth and others (1988)
		25	1,090	e	EPICS	Ashworth and others (1988)
77135	1,2-dimethylbenzene	20	426	e	EPICS	Yurteri and others (1987)
		20	480	e	EPICS	Ashworth and others (1988)
		20	322	i	EPICS	Dewulf and others (1995)
			20°C av = 409			
		25	493	e	EPICS	Ashworth and others (1988)
		25	534	e	SH	Robbins and others (1993)
		25	426	i	EPICS	Dewulf and others (1995)
			25°C av = 484			

Table 2. Experimental and interpolated values of Henry's law constants at 20° Celsius and 25° Celsius for 43 target analytes—Continued

[USGS, U.S. Geological Survey; °C, degrees Celsius; H, Henry's law constant, in pascals cubic meter per gram mole; e, experimental value; i, interpolated value calculated from the Henry's law constant-temperature relationship; NS, not specified; EPICS, equilibrium partitioning in closed systems; EC, equilibrium cell; BS, batch stripping; ME, multiple equilibration; MIIF, multiple injection interrupted flow; SH, static headspace; WWC, wetted-wall column; av, arithmetic mean]

USGS parameter code	Compound	Temperature (°C)	H	e, i	Experimental technique	Reference
85795	1,3-dimethylbenzene	20	430	i	ME	Ioffe and Vitenberg (1982)
		20	606	e	EPICS	Ashworth and others (1988)
		20	481	i	EPICS	Dewulf and others (1995)
			20°C av = 506			
		25	547	i	ME	Ioffe and Vitenberg (1982)
		25	754	e	EPICS	Ashworth and others (1988)
		25	615	i	EPICS	Dewulf and others (1995)
			25°C av = 639			
85795	1,4-dimethylbenzene	20	654	e	EPICS	Ashworth and others (1988)
		20	456	i	EPICS	Dewulf and others (1995)
			20°C av = 555			
		25	754	e	EPICS	Ashworth and others (1988)
		25	762	e	BS	Ashworth and others (1988)
		25	605	i	EPICS	Dewulf and others (1995)
			25°C av = 707			
77222	1,2,4-trimethylbenzene	20	475	e	EPICS	Yurteri and others (1987)
34301	chlorobenzene	20	269	i	EC	Leighton and Calo (1981)
		20	319	e	EPICS	Yurteri and others (1987)
		20	346	e	EPICS	Ashworth and others (1988)
			20°C av = 311			
		25	328	i	EC	Leighton and Calo (1981)
		25	382	e	BS	Mackay and others (1979)
		25	315	e	BS	Mackay and Shiu (1981)
		25	398	e	BS	Warner and others (1987)
		25	365	e	EPICS	Ashworth and others (1988)
			25°C av = 358			
34536	1,2-dichlorobenzene	20	119	e	BS	Oliver (1985)
		20	170	e	EPICS	Ashworth and others (1988)
			20°C av = 144			
		25	193	e	BS	Mackay and Shiu (1981)
		25	197	e	BS	Warner and others (1987)
		25	159	e	EPICS	Ashworth and others (1988)
			25°C av = 183			
34566	1,3-dichlorobenzene	20	179	e	BS	Oliver (1985)
		20	298	e	EPICS	Ashworth and others (1988)
			20°C av = 238			
		25	266	e	BS	Warner and others (1987)
		25	289	e	EPICS	Ashworth and others (1988)
			25°C av = 278			

Table 2. Experimental and interpolated values of Henry's law constants at 20° Celsius and 25° Celsius for 43 target analytes—Continued

[USGS, U.S. Geological Survey; °C, degrees Celsius; H, Henry's law constant, in pascals cubic meter per gram mole; e, experimental value; i, interpolated value calculated from the Henry's law constant-temperature relationship; NS, not specified; EPICS, equilibrium partitioning in closed systems; EC, equilibrium cell; BS, batch stripping; ME, multiple equilibration; MIIF, multiple injection interrupted flow; SH, static headspace; WWC, wetted-wall column; av, arithmetic mean]

USGS parameter code	Compound	Temperature (°C)	H	e, i	Experimental technique	Reference
34571	1,4-dichlorobenzene	20	149	e	BS	Oliver (1985)
		20	190	e	EPICS	Yurteri and others (1987)
		20	262	e	EPICS	Ashworth and others (1988)
			20°C av = 200			
		25	240	e	BS	Mackay and Shiu (1981)
		25	276	e	BS	Warner and others (1987)
		25	321	e	EPICS	Ashworth and others (1988)
			25°C av = 279			
77613	1,2,3-trichlorobenzene	20	88.7	e	BS	Oliver (1985)
		25	127	e	BS	Mackay and Shiu (1981)
34551	1,2,4-trichlorobenzene	20	119	e	BS	Oliver (1985)
		20	185	e	EPICS	Ashworth and others (1988)
			20°C av = 152			
		25	144	e	BS	Warner and others (1987)
		25	195	e	EPICS	Ashworth and others (1988)
			25°C av = 170			
78032	methyl tertiary-butyl ether	25	64.3	e	SH	Robbins and others (1993)

Table 3. Henry's law constants excluded from the results presented in table 2 because they differed substantially from the average constants

[USGS, U.S. Geological Survey; °C, degrees Celsius; H, Henry's law constant, in pascals cubic meter per gram mole; av, arithmetic mean]

USGS parameter code	Compound	Temperature (°C)	H		Reference
			Table 2 av	Excluded value	
32106	trichloromethane	20	310	546	Munz and Roberts (1982)
34506	1,1,1-trichloroethane	20	1,380	3,430	McConnell and others (1975)
34506	1,1,1-trichloroethane	25	1,700	499	Warner and others (1987)
34488	trichlorofluoromethane	20	7,770	81,200	McConnell and others (1975)
34501	1,1-dichloroethene	20	2,380	15,200	McConnell and others (1975)
34501	1,1-dichloroethene	20	2,380	7,530	Yurteri and others (1987)

CALCULATED VALUES OF THE HENRY'S LAW CONSTANT

Details regarding the calculation of the Henry's law constant for the 12 target analytes for which experimental values were not available are given in the following paragraphs. Some of the values are for 20°C, others are for 25°C. The temperature selected usually depended upon the temperature at which solubility data were available.

1. Bromoethene: No solubility data were available for this compound (Mackay and others, 1993). The logarithm of the octanol-water partition coefficient, log K_{ow}, for this compound was estimated from the log K_{ow} value for chloroethene from Hansch and Leo as cited by Mackay and others (1993). The estimation procedure described by Lyman (1990a) was used. This procedure consisted of subtracting the value for the fragment factor for attachment of chlorine to a vinyl carbon atom and adding the corresponding factor for bromine. The result was a log K_{ow} value for bromoethene of 1.52. Solubilities computed from equations 2–9 and 2–19 of Lyman (1990b) and this estimated log K_{ow} were 10,100 and 11,700 mg/L, respectively. Using the geometric mean of these values as suggested by Lyman (1990b), the estimated solubility for bromoethene at 25°C was 10,900 mg/L. Bromoethene has a boiling point of 15.8°C (Mackay and others, 1993). Consequently, it is a gas at 25°C. Solubilities for gases should be considered as under 1.0 atmosphere of the pure gas (Roberts, 1984) rather than the corresponding vapor pressure of the pure gas. Thus, the Henry's law constant can be calculated from the estimated solubility and a pressure of 1.0 atmosphere. The resultant Henry's law constant was 994 Pa m^3/g mol.
2. 1,2-dibromo-3-dichloropropane: No data were available for this compound in Mackay and others (1993). Verschueren (1983) reported a vapor pressure of 107 Pa at 21°C and a solubility of 1,000 mg/L at room temperature, resulting in a calculated Henry's law constant of 25.3 Pa m^3/g mol. Howard (1991) reported a vapor pressure of 77.3 Pa at 20°C and a solubility of 1,230 mg/L, resulting in a calculated Henry's law constant of 14.8 Pa m^3/g mol.
3. *cis*-1,3-dichloropropene: Weber and others (1981) reported a vapor pressure of 4,000 Pa at 20°C, and Dilling (1977) reported a solubility of 2,700 mg/L at 20°C for this compound, resulting in a calculated Henry's law constant of 165 Pa m^3/g mol.
4. *trans*-1,3-dichloropropene: Weber and others (1981) reported a vapor pressure of 2,900 Pa at 20°C, and Dilling (1977) reported a solubility of 2,800 mg/L at 20°C for this compound, resulting in a calculated Henry's law constant of 115 Pa m^3/g mol.
5. iso-propylbenzene: Four vapor pressures for this compound at 25°C (Mackay and others, 1992a) ranged from 605 to 613 Pa and averaged 610 Pa. Eight water solubilities at 25°C (Mackay and others, 1992a) ranged from 48.3 to 80.4 mg/L and averaged 60.2 mg/L. The calculated Henry's law constant based on these average values was 1,220 Pa m^3/g mol. Li and others (1993) measured the infinite dilution-activity coefficient of iso-propylbenzene in water at 25°C, and the result was 1.02×10^5. Using this value in equation 38, the calculated Henry's law constant was 1,120 Pa m^3/g mol.
6. n-butylbenzene: A vapor pressure of 137 Pa at 25°C was reported for this compound by Mackay and others (1992a). Solubility values determined using the shake-flask method at 25°C ranged from 11.8 to 50.5 mg/L (Mackay and others, 1992a). Three values determined using the generator column technique were all 13.8 mg/L (Mackay and others, 1992a). Using this latter solubility, the calculated Henry's law constant was 1,340 Pa m^3/g mol. Using the infinite dilution-activity coefficient of n-butylbenzene in water (Li and others, 1993) and equation 38, the calculated Henry's law constant was 1,240 Pa m^3/g mol. Using vapor pressures from Stull (1947) and solubility values from Owens and others (1986), calculated values were 1,100 and 1,520 Pa m^3/g mol at 20° and 25°C.

7. styrene: The vapor pressure for this compound at 25°C calculated from an equation from Jordan (1954) was 864 Pa. Solubility values at 25°C (Mackay and others, 1993) ranged from 160 to 330 mg/L and averaged 264 mg/L. The calculated Henry's law constant was 340 Pa m^3/g mol.
8. ethyl tertiary-butyl ether: No data were available for this compound in either Mackay and others (1993) or Verschueren (1983). The vapor pressure for this compound was estimated from a logarithm vapor pressure-versus-normal boiling temperature regression for seven ethers using vapor-pressure data from Stull (1947). The boiling temperature of ethyl tertiary-butyl ether is 73.1°C (Weast, 1985), and boiling temperatures for the seven ethers were such that they bracketed the boiling temperature of ethyl tertiary-butyl ether. The vapor pressure at 20°C estimated by this procedure was 13,100 Pa. The water solubility at 20° was 12,000 mg/L (Evan and Edlund, 1936). The calculated Henry's law constant was 112 Pa m^3/g mol.
9. tertiary-amyl methyl ether: No data were available for this compound in either Mackay and others (1993) or Verschueren (1983). The normal boiling temperature for tertiary-amyl methyl ether is 86.3°C (Weast, 1985). The vapor pressure at 20°C estimated using the same relationship as used for ethyl tertiary-butyl ether was 7,760 Pa. The water solubility at 19.9°C was 11,000 mg/L (Stephenson, 1992). The calculated Henry's law constant was 72.1 Pa m^3/g mol.
10. diisopropyl ether: An experimental Henry's law constant for this compound was determined at 23°C using the batch stripping procedure (Nielsen and others, 1994). The resultant value of 209 Pa m^3/g mol was adjusted to values of 167 and 243 Pa m^3/g mol at 20° and 25°C using vapor-pressure data from Stull (1947), solubility data from Stephenson (1992), and equation 44.
11. 2-propenal: A logarithm vapor pressure-versus-reciprocal absolute temperature relationship was computed for vapor-pressure data for this compound from Stull (1947). The vapor pressure calculated from this relationship at 20°C was 29,400 Pa. The water solubility at 20°C was 208,000 mg/L (Verschueren, 1983). The calculated Henry's law constant was 7.92 Pa m^3/g mol.
12. 2-propenenitrile: A logarithm vapor pressure-versus-reciprocal absolute temperature relationship was computed for vapor-pressure data for this compound from Stull (1947). The vapor pressure at 25°C calculated from this relationship was 14,600 Pa. The water solubility at about 25°C was 80,000 mg/L (Lyman, 1990b). The calculated Henry's law constant was 9.72 Pa m^3/g mol.

TEMPERATURE DEPENDENCE OF THE HENRY'S LAW CONSTANT

The temperature dependence of the Henry's law constant usually is expressed with a form of the Arrhenius equation. The equation used is

$$\log_e H = A - \frac{B}{T} \tag{50}$$

where

A and B are constants; and

T is the absolute temperature, in kelvins.

Values of the A and B constants for 39 of the target analytes are given in table 4. For 30 of the target analytes, two or more temperature-dependence studies were available, and constants for each of these studies are given in table 4. The correlation coefficients also are given in table 4 to provide a measure of the degree of fit of the data to equation 50 and a measure of the internal consistency of the data for each isotherm. The trichloromethane isotherm of Tancrede and Yanagisawa (1990) was excluded because the predicted value at 25°C differed by more than three standard deviations of the mean value given in table 2.

Correlation coefficients were available for 114 isotherms. Of these isotherms, 94 had correlation coefficients greater than or equal to 0.980, indicating good fits of the experimental Henry's law constants to equation 50. Only two correlation coefficients were less than 0.900. These were the 0.876 value for hexachloroethane and the 0.681 value for 1,2-dichlorobenzene (Ashworth and others, 1988). These investigators attributed the low value for 1,2-dichlorobenzene to a strong dependence of the activity coefficient on temperature for aromatic compounds in water and, therefore, deviations from the temperature dependence expressed by equation 50.

Table 4. Constants in the equation for the temperature dependence of the Henry's law constants of 39 target analytes

[USGS, U.S. Geological Survey; A, B, constants in the temperature dependence equation; °C, degrees Celsius; R, correlation coefficient; EPICS, equilibrium partitioning in closed systems; BS, batch stripping; nd, not determined]

USGS parameter code	Compound	A	B	Temperature range (°C)	R	Reference
34418	chloromethane	16.68	2,931	4.1–39.9	0.999	Glew and Moelwyn-Hughes (1953)
		20.79	4,190	10.3–34.6	.995	Gossett (1987)
34423	dichloromethane	17.86	3,602	1.9–24.9	.984	Leighton and Calo (1981)
		19.73	4,191	10–30	.994	Lincoff and Gossett (1984) (EPICS)
		20.56	4,472	10–30	.994	Lincoff and Gossett (1984) (BS)
		18.24	3,836	9.6–34.6	.971	Gossett (1987)
		20.01	4,268	10–30	.994	Ashworth and others (1988)
32106	trichloromethane	19.40	3,998	1.9–24.9	.996	Leighton and Calo (1981)
		20.08	4,180	10–30	.994	Lincoff and Gossett (1984) (EPICS)
		20.49	4,322	10–30	.997	Lincoff and Gossett (1984) (BS)
		23.43	5,200	10–30	.999	Nicholson and others (1984)
		20.28	4,274	10–30	.997	Munz and Roberts (1987)
		21.35	4,608	9.6–34.6	.998	Gossett (1987)
		22.94	5,030	10–30	.998	Ashworth and others (1988)
		20.63	4,382	2.0–25.0	.997	Dewulf and others (1995)
32102	tetrachloromethane	22.63	4,385	1.0–27.2	.997	Leighton and Calo (1981)
		18.57	3,211	5–33	nd	Hunter-Smith and others (1983)
		22.28	4,250	10–30	.998	Munz and Roberts (1987)
		22.78	4,404	10.0–34.6	.998	Gossett (1987)
		21.27	3,951	10–30	.998	Ashworth and others (1988)
		22.57	4,363	25–47.2	.952	Tancrede and Yanagisawa (1990)
		22.41	4,341	2.0–25.0	.986	Dewulf and others (1995)
34413	bromomethane	17.32	3,248	5.0–40.1	.998	Glew and Moelwyn-Hughes (1953)
32104	tribromomethane	23.13	5,670	10–30	1.000	Nicholson and others (1984)
		19.68	4,679	10–30	.999	Munz and Roberts (1987)
32101	bromodichloromethane	22.83	5,210	10–30	.999	Nicholson and others (1984)
32105	chlorodibromomethane	22.23	5,210	10–30	1.000	Nicholson and others (1984)
		26.15	6,373	10–30	.956	Ashworth and others (1988)
34311	chloroethane	17.51	3,124	10.3–34.6	1.000	Gossett (1987)
		15.80	2,580	10–30	.992	Ashworth and others (1988)
34496	1,1-dichloroethane	20.17	4,131	9.6–34.6	.997	Gossett (1987)
		17.01	3,137	10–30	.996	Ashworth and others (1988)
		20.99	4,404	2.0–25.0	.983	Dewulf and others (1995)
32103	1,2-dichloroethane	16.83	3,513	1.0–27.2	.998	Leighton and Calo (1981)
		10.16	1,522	10–30	.937	Ashworth and others (1988)
		18.49	4,141	2.0–25.0	.975	Dewulf and others (1995)
34506	1,1,1-trichloroethane	22.09	4,324	1.0–26.1	.998	Leighton and Calo (1981)
		17.95	3,207	5–33	nd	Hunter-Smith and others (1983)
		21.74	4,262	10–30	.999	Lincoff and Gossett (1984) (EPICS)
		21.50	4,186	10–30	.999	Lincoff and Gossett (1984) (BS)
		21.07	4,061	10–30	1.000	Munz and Roberts (1987)
		21.29	4,130	9.6–34.6	.997	Gossett (1987)
		18.88	3,399	10–30	.999	Ashworth and others (1988)
		18.12	3,169	25–50	.985	Robbins and others (1993)
		21.74	4,299	2.0–25.0	.996	Dewulf and others (1995)

Table 4. Constants in the equation for the temperature dependence of the Henry's law constants of 39 target analytes—Continued

[USGS, U.S. Geological Survey; A, B, constants in the temperature dependence equation; °C, degrees Celsius; R, correlation coefficient; EPICS, equilibrium partitioning in closed systems; BS, batch stripping; nd, not determined]

USGS parameter code	Compound	A	B	Temperature range (°C)	R	Reference
34511	1,1,2-trichloroethane	16.65	3,647	2.5–26.1	0.996	Leighton and Calo (1981)
		20.85	4,843	10–30	.984	Ashworth and others (1988)
34396	hexachloroethane	24.88	5,637	10–30	.987	Munz and Roberts (1987)
		15.27	2,550	10–30	.876	Ashworth and others (1988)
77651	1,2-dibromoethane	17.23	3,876	10–30	.963	Ashworth and others (1988)
34541	1,2-dichloropropane	20.02	4,282	1.9–24.9	.998	Leighton and Calo (1981)
		21.37	4,708	10–30	.906	Ashworth and others (1988)
77443	1,2,3-trichloropropane	15.07	3,438	13.6–24.9	.944	Leighton and Calo (1981)
		16.77	4,070	26.5–45.0	.989	Tancrede and Yanagisawa (1990)
34488	trichlorofluoromethane	18.05	2,665	5–33	nd	Hunter-Smith and others (1983)
		22.13	3,875	0.85–40.8	.997	Warner and Weiss (1985)
		21.01	3,513	10–30	.999	Ashworth and others (1988)
34668	dichlorodifluoromethane	22.18	3,515	10–30	.999	Munz and Roberts (1987)
		21.91	3,432	0.85–40.8	.997	Warner and Weiss (1985)
77652	1,1,2-trichloro-1,2,2-trifluoroethane	21.18	3,243	10–30	.965	Ashworth and others (1988)
		24.97	4,348	0.04–39.6	.997	Bu and Warner (1995)
39175	chloroethene	18.89	3,281	10.3–34.6	.994	Gossett (1987)
		17.67	2,931	10–30	.985	Ashworth and others (1988)
34501	1,1-dichloroethene	23.52	4,564	2.5–26.1	.981	Leighton and Calo (1981)
		20.38	3,734	10.0–34.6	.997	Gossett (1987)
		17.65	2,907	10–30	.987	Ashworth and others (1988)
77093	*cis*-1,2-dichloroethene	20.01	4,196	10.3–34.6	.990	Gossett (1987)
		16.69	3,143	10–30	.987	Ashworth and others (1988)
34546	*trans*-1,2-dichloroethene	20.92	4,198	10.0–34.6	.997	Gossett (1987)
		16.86	2,964	10–30	.992	Ashworth and others (1988)
39180	trichloroethene	22.29	4,592	1.0–26.1	.998	Leighton and Calo (1981)
		23.47	4,929	10–30	.996	Lincoff and Gossett (1984)(EPICS)
		21.23	4,308	10–30	.990	Lincoff and Gossett (1984)(BS)
		22.67	4,690	10–30	.998	Munz and Roberts (1987)
		23.02	4,821	9.6–34.6	.998	Gossett (1987)
		19.38	3,702	10–30	.999	Ashworth and others (1988)
		18.73	3,510	25–50	.989	Robbins and others (1993)
		22.92	4,856	25–47.2	.942	Tancrede and Yanagisawa (1990)
		23.05	4,857	2.0–25.0	.994	Dewulf and others (1995)
34475	tetrachloroethene	23.08	4,679	1.0–26.1	.997	Leighton and Calo (1981)
		24.65	5,119	10–30	.997	Lincoff and Gossett (1984) (EPICS)
		22.85	4,622	10–30	1.000	Lincoff and Gossett (1984) (BS)
		22.43	4,443	10–30	.998	Munz and Roberts (1987)
		24.01	4,931	9.6–34.6	.998	Gossett (1987)
		22.18	4,368	10–30	.993	Ashworth and others (1988)
		26.10	5,566	25–47.2	.926	Tancrede and Yanagisawa (1990)
		19.50	3,580	25–45	.987	Robbins and others (1993)
		24.05	4,993	2.0–25.0	.999	Dewulf and others (1995)

Table 4. Constants in the equation for the temperature dependence of the Henry's law constants of 39 target analytes—Continued

[USGS, U.S. Geological Survey; A, B, constants in the temperature dependence equation; °C, degrees Celsius; R, correlation coefficient; EPICS, equilibrium partitioning in closed systems; BS, batch stripping; nd, not determined]

USGS parameter code	Compound	A	B	Temperature range (°C)	R	Reference
34030	benzene	19.45	3,918	1.0–27.2	0.998	Leighton and Calo (1981)
		18.22	3,518	10–30	.998	Ioffe and Vitenberg (1982)
		17.06	3,194	10–30	.984	Ashworth and others (1988)
		18.92	3,768	25–50	.990	Robbins and others (1993)
		19.22	3,887	2.0–25.0	.996	Dewulf and others (1995)
34010	methylbenzene	18.90	3,707	1.0–23.0	.996	Leighton and Calo (1981)
		21.31	4,408	10–30	.999	Ioffe and Vitenberg (1982)
		16.66	3,024	10–30	.991	Ashworth and others (1988)
		17.86	3,382	25–50	.994	Robbins and others (1993)
		20.81	4,317	2.0–25.0	.996	Dewulf and others (1995)
34371	ethylbenzene	23.45	4,994	10–30	1.000	Ashworth and others (1988)
		22.19	4,624	25–40	1.000	Robbins and others (1993)
		23.60	5,092	2.0–25.0	.989	Dewulf and others (1995)
77224	n-propylbenzene	19.36	3,681	10–30	.998	Ashworth and others (1988)
77135	1,2-dimethylbenzene	17.07	3,220	10–30	.983	Ashworth and others (1988)
		17.68	3,398	25–50	.961	Robbins and others (1993)
		22.40	4,872	2.0–25.0	.960	Dewulf and others (1995)
85795	1,3-dimethylbenzene	20.37	4,193	10–30	.981	Ioffe and Vitenberg (1982)
		17.81	3,337	10–30	.999	Ashworth and others (1988)
		20.89	4,315	2.0–25.0	.978	Dewulf and others (1995)
85795	1,4-dimethylbenzene	18.46	3,520	10–30	.994	Ashworth and others (1988)
		22.88	4,912	2.0–25.0	.966	Dewulf and others (1995)
34301	chlorobenzene	17.28	3,424	1.0–23.0	.986	Leighton and Calo (1981)
		15.00	2,689	10–30	.982	Ashworth and others (1988)
34536	1,2-dichlorobenzene	10.01	1,422	10–30	.681	Ashworth and others (1988)
34566	1,3-dichlorobenzene	14.41	2,564	10–30	.922	Ashworth and others (1988)
34571	1,4-dichlorobenzene	14.90	2,720	10–30	.970	Ashworth and others (1988)
34551	1,2,4-trichlorobenzene	18.89	4,028	10–30	.904	Ashworth and others (1988)
78032	methyl tertiary-butyl ether	30.06	7,721	25–50	.981	Robbins and others (1993)

This hypothesis is supported by the fact that 1,3-dichlorobenzene and 1,2,4-trichlorobenzene also had relatively low correlation coefficients (table 4). Conversely, chlorobenzene and 1,4-dichlorobenzene in the same study had high correlation coefficients.

When several isotherms are available for a specific target analyte, the most logical choice is to use the one with the best fit as indicated by the largest correlation coefficient. However, consideration also should be given to the temperature range. Equation 50 assumes that the enthalpy of vaporization for the volatilization process is constant over the temperature range of interest. This is a reasonable assumption for the relatively short temperature ranges indicated in table 4. Extrapolation outside these temperature ranges, however, could lead to error. The enthalpy of vaporization, contained in the constant B of equation 50, decreases as the temperature increases (Reid and others, 1987). Consequently, extrapolation of an isotherm beyond the experimental temperature range will most likely result in predicted Henry's law constants that are larger than the true values. Such errors can be minimized by selecting an isotherm with a temperature range that brackets the temperature at which the Henry's law constant is being predicted.

Isotherms were not available for 16 of the target analytes. To estimate Henry's law constants for these analytes for temperatures other than the 20°C or 25°C considered in table 2 and the text, a procedure based on equation 44 can be used. Writing equation 44 for a base temperature, bT in kelvins, and the temperature at which the Henry's law constant is to be estimated, T in kelvins, and taking ratios gives

$$H_T = H_{bT} \frac{p_T S_{bT}}{p_{bT} S_T} \tag{51}$$

where

H_T and H_{bT} are the Henry's law constants (Pa m^3/g mol) at the temperature of interest and at the base temperature, respectively;

p_T and p_{bT} are the corresponding vapor pressures of the pure solute; and

S_T and S_{bT} are the corresponding water solubilities.

Vapor pressure data as a function of temperature are available for numerous compounds in several standard references such as Stull (1947), Jordan (1954), and Wilhoit and Zwolinski (1971). The temperature dependence of the water solubility has been studied much less extensively. However, some information exists, for example, in Stephen and Stephen (1963). This difference in effort is perhaps indicative of the fact that the vapor pressure is much more dependent on temperature than is the water solubility. If solubility data as a function of temperature are not available, equation 51 can be approximated as

$$H_T \cong H_{bT} \frac{p_T}{p_{bT}} \tag{52}$$

Equations 51 and 52 were evaluated by calculating the Henry's law constant at 10°C for six chlorinated aliphatic VOCs and for benzene, and comparing the results with the mean values computed from the isotherm constants given in table 4. The arithmetic means of the Henry's law constants at 25°C from table 2 were used as the base values. These particular compounds were selected because solubility data as a function of temperature were available for the chlorinated compounds in Stephenson (1992) and for benzene in May and others (1983). Vapor-pressure data for all compounds were from Stull (1947).

The results of the evaluation are presented in table 5. Comparisons are generally good, with the largest errors for 1,2-dichloroethane and 1,2-dichloropropane. The larger errors for these two compounds could be the result of the fact that there were few Henry's law constants available. Also, there was considerable variability among the four values for 1,2-dichloroethane at 25°C (table 2), with values ranging from 63.6 to 155 Pa m^3/g mol. Conversely, the three values available for 1,2-dichloropropane agreed reasonably well. The results in table 5 indicate that the predictive abilities of equations 51 and 52 are comparable, with equation 51 having a slightly smaller overall average absolute percent difference. This limited test indicates that equations 51 and 52 can be used to predict the temperature dependence of the Henry's law constant when isotherm data are not available.

DISTRIBUTION OF HENRY'S LAW CONSTANTS FOR THE TARGET ANALYTES

Henry's law constants at 25°C for the target analytes ranged from 9.72 Pa m^3/g mol for 2-propenenitrile to 34,200 Pa m^3/g mol for dichlorodifluoromethane. The median was 420 Pa m^3/g mol for *cis*-1,2-dichloroethene.

The distribution of the Henry's law constants is presented in figure 4. The largest number of Henry's law constants (33) was within the class between 100 and 1,000 Pa m^3/g mol, and 46 analytes had constants larger than 100 Pa m^3/g mol. The percentage of the total resistance to volatilization that is in the water film can be computed from equation 20. Calculation of this percentage resistance for the average film coefficients of 3 m/day for the water film and 800 m/day for the air film indicates that 90 percent of the total resistance will be in the water film for a solute with a Henry's law constant of 83.7 Pa m^3/g mol. A line corresponding to this Henry's law constant is plotted in figure 4; this line includes one value from the 10 to 100 Pa m^3/g mol class. Consequently, 47 of the 55 target analytes have 90 percent or more of the resistance to volatilization in the water film for average environmental conditions, indicating that mixing within the water phase will control volatilization for most of the target analytes.

Table 5. Evaluation of equations 51 and 52 for predicting the temperature dependence of the Henry's law constant

[USGS, U.S. Geological Survey; H_{10}, Henry's law constant at 10 degrees Celsius, in pascals cubic meter per gram mole; eq., equation; iso mean, mean Henry's law constant calculated from the isotherms in table 4; |av|, average absolute percent difference between eq. 51 or eq. 52 and the isotherm mean]

USGS parameter code	Compound	H_{10}			Percent difference	
		eq. 51	eq. 52	iso mean	eq. 51	eq. 52
34423	dichloromethane	136	150	135	0.74	11.1
32106	trichloromethane	170	196	179	–5.03	9.50
32102	tetrachloromethane	1,420	1,380	1,350	5.19	2.22
32103	1,2-dichloroethane	54.6	54.5	83.7	–34.8	–34.9
34541	1,2-dichloropropane	155	147	124	25.0	18.5
34475	tetrachloroethene	717	762	747	–4.02	2.01
34030	benzene	257	258	289	–11.1	–10.7
				|av| =	12.3	12.7

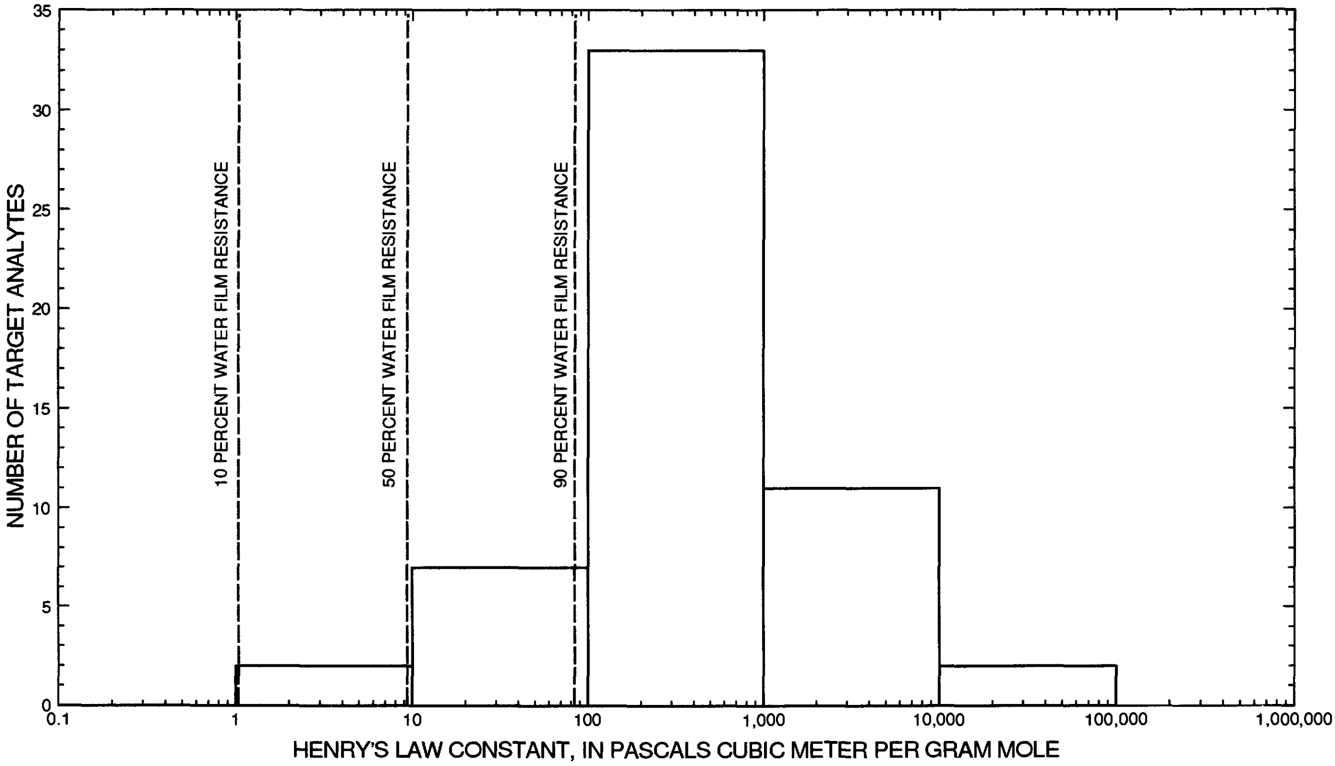

Figure 4. Frequency distribution of the Henry's law constants at 25 degrees Celsius for the target analytes.

Conversely, about 50 percent of the resistance to volatilization of 2-propenenitrile and 2-propenal will be in the air film for the same average environmental conditions. Between these limits, there are six target analytes for which mixing conditions in both the air and water phases are likely to be important in controlling volatilization. These six are the compounds with the higher molecular weights and/or the higher water solubilities. They are, in increasing order of Henry's law constant, 1,2-dibromo-3-chloropropane, 1,2,3-trichloropropane, naphthalene, tribromomethane, methyl tertiary-butyl ether, and 1,2-dibromoethane.

Deviation from the average environmental conditions can either increase or decrease the relative importance of the two film resistances to volatilization. Percentage resistance in the water film as a function of the water-film mass-transfer coefficient is shown in figure 5 for a temperature of 25°C for three of the target analytes, with the air-film mass-transfer coefficient as a parameter. The compound 2-propenenitrile has the lowest Henry's law constant of any of the target analytes, and figure 5 indicates that a significant fraction of the resistance to volatilization is in the air film for this compound. As the water-film mass-transfer coefficient increases from the zero condition of molecular diffusion only, the percentage resistance in the water film decreases rapidly and, correspondingly, the resistance in the air film increases. As would be expected, the air-film resistance for a specific water-film mass-transfer coefficient is least for the highest air-film mass-transfer coefficient. For most conditions, there are significant resistances to volatilization of 2-propenenitrile in both the water and air films.

Conversely, for tetrachloromethane, the lines for the three air-film mass-transfer coefficients are virtually indistinguishable from each other and from the 100-percent resistance line. Thus, volatilization of tetrachloromethane is water-film controlled, with virtually all the resistance in the water film. Methyl tertiary-butyl ether is intermediate between these extremes, with both films offering resistance to

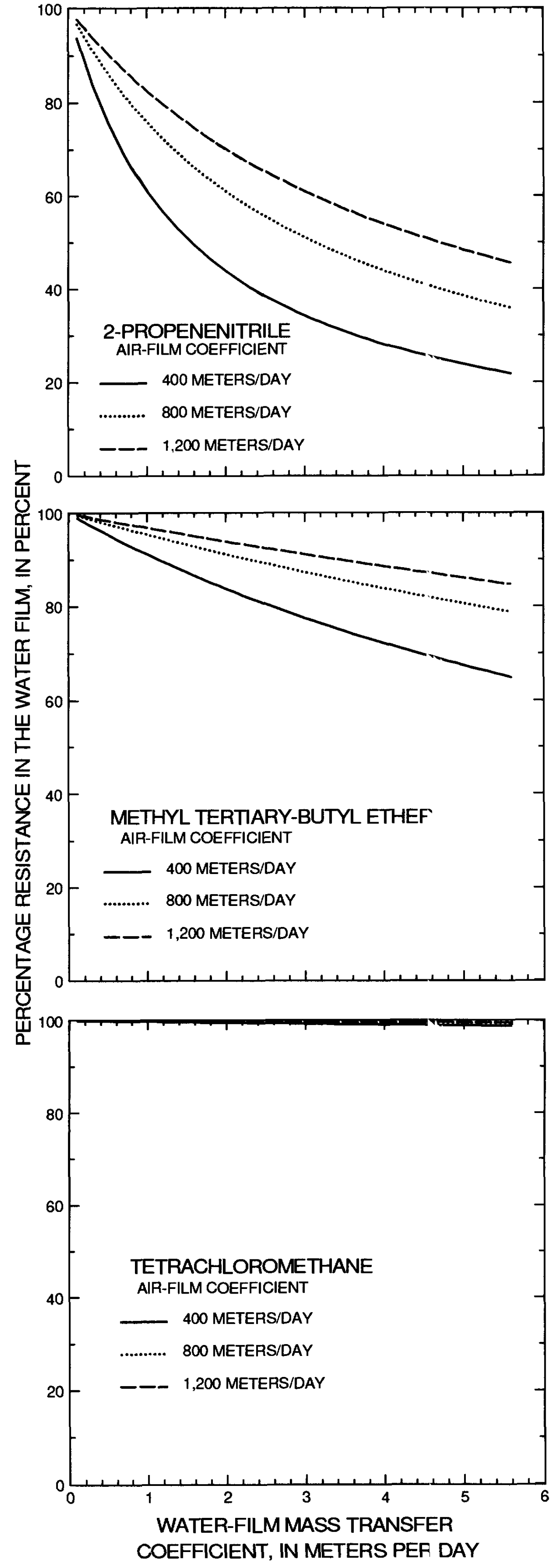

Figure 5. Percentage resistance in the water film for the volatilization of three target analytes as a function of the water-film and air-film mass-transfer coefficients at 25 degrees Celsius; Henry's law constants are 9.72, 64.3, and 2,860 pascals cubic meter per gram mole for 2-propenenitrile, methyl tertiary-butyl ether, and tetrachloromethane, respectively.

volatilization, but with the water film having more than 60 percent of the total resistance for the three combinations of film coefficients considered.

The change in the dependence of the percentage resistance on the film coefficients as the Henry's law constant increases is evident in figure 5. However, only six target analytes have Henry's law constants lower than methyl tertiary-butyl ether. Consequently, dependence of the percentage resistance on the film coefficients for most of the target analytes will be as indicated in figure 5 for methyl tertiary-butyl ether and tetrachloromethane. This again emphasizes the importance of the water-film mass-transfer coefficient for most of the target analytes.

PREDICTION OF VOLATILIZATION COEFFICIENTS

Volatilization coefficients and the corresponding half-lives (eq. 3) for the target analytes for a specific stream can be predicted from equation 16, the two-film model (eq. 13), the Henry's law constant (table 2 and/or table 4), and the reference-substance concept (eqs. 25 and 26). Use of the reference-substance concept requires a value of the oxygen-absorption (reaeration) coefficient and an estimate of the mass-transfer coefficient for water evaporation for the stream of interest.

The reaeration coefficient either can be measured using tracer techniques or predicted from the hydraulic and physical properties of the stream. If an accurate value of the volatilization coefficient for the target analyte is needed, then the reaeration coefficient should be measured using a tracer technique. Tracer measurements of the reaeration coefficient require much more effort than using empirical equations from the literature to predict the reaeration coefficient. However, the measured coefficient is much more likely to be an accurate representation of the oxygen-absorption characteristics of the stream. The radioactive tracer technique (Tsivoglou and others, 1968) uses krypton as the tracer for oxygen and tritium to adjust the krypton concentrations for the effects of dispersion and dilution. The hydrocarbon tracer technique (Kilpatrick and others, 1989) uses propane as the tracer for oxygen and rhodamine-WT dye as the dispersion-dilution tracer. Both steady-state and slug-injection versions of the hydrocarbon tracer technique are available.

If only an estimate of the volatilization coefficient for the target analyte is needed, then the reaeration coefficient can be estimated for the stream of interest by using one of the many reaeration-coefficient prediction equations from the literature. Several reviews of reaeration prediction equations have been done—for example, Bennett and Rathbun (1972); Bansal (1973); Zogorski and Faust (1973); Wilson and Macleod (1974); Covar (1976); and Rathbun (1977). The general consensus of these reviews is that prediction equations work reasonably well for the data upon which each equation is based. However, when used on other streams or other reaches of the same stream with hydraulic and physical properties outside the range of the data base used in equation development, large prediction errors may result. Thus, a prediction equation should be selected that is based on hydraulic and physical data covering the same range as the data for the stream of interest.

To assist in selecting the appropriate equation, a chart of the form of Covar (1976) can be used. This chart has three areas of predicted reaeration coefficients as a function of flow depth and water velocity, with the areas corresponding to the equations of Owens and others (1964) for shallow flows, Churchill and others (1962) for intermediate-depth flows, and O'Connor and Dobbins (1958) for deep flows. The approach used here differs somewhat from that used by Covar (1976) with regard to the equation for shallow flows. Covar used the equation of Owens and others (1964) based on a data base that included the data of Churchill and others (1962). These data, however, are for depths ranging from 0.646 to 3.48 m; thus, the shallow-flow data of Owens and others (1964) are biased toward deeper flows by the inclusion of the Churchill and others (1962) data. A more appropriate shallow-flow equation is that of Owens and others (1964) based solely on their data, with depths ranging from 0.119 to 0.744 m. This equation is

$$K_2^{20} = 6.92\ U^{0.73}\ Y^{-1.75} \qquad (53)$$

where

K_2^{20} is the base e reaeration coefficient at 20°C (day^{-1}),

U is the water velocity (m/s), and

Y is the flow depth (m).

Water velocities of the data base for equation 53 ranged from 0.040 to 0.558 m/s.

The intermediate-depth equation from Churchill and others (1962) is

$$K_2^{20} = 5.01\ U^{0.969}\ Y^{-1.673}. \qquad (54)$$

Equation 54 is based on a data base with water velocities ranging from 0.564 to 1.52 m/s and flow depths from 0.646 to 3.48 m.

The deep-flow equation from O'Connor and Dobbins (1958) is

$$K_2^{20} = 3.93\ U^{0.50}\ Y^{-1.50}. \qquad (55)$$

Equation 55 was verified using a data base with water velocities ranging from 0.058 to 1.28 m/s and flow depths ranging from 0.274 to 11.3 m.

A chart showing various combinations of water velocity and flow depth appropriate for each of these three equations is presented in figure 6, with the limits of the data bases for each of the three equations indicated by rectangles. Figure 6 indicates that the reaeration coefficient, K_2, can vary from approximately 100 day^{-1} to 0.05 day^{-1}, depending on the flow depth. Figure 6 can be used to determine which of equations 53, 54, or 55 should be used to compute reaeration coefficients for specific combinations of water velocity and flow depth. The K_2 lines for the O'Connor and Dobbins equation (eq. 55) match reasonably well with the lines for the Churchill and others equation (eq. 54), with the slope of the lines being somewhat higher for the latter equation. The lines for the O'Connor and Dobbins equation (eq. 55) do not match as well with the lines for the Owens and others equation (eq. 53). Such disagreement, however, is common in predicting reaeration coefficients for streams. If the water-velocity and flow-depth values fall outside the three rectangles in figure 6, two options are available. The first is to use whichever of equations 53, 54, or 55 is closest to the desired values and extrapolate, with the understanding that prediction errors are likely to be larger when an equation is used outside the range of the data upon which the equation was based. The second option is to search the literature—for example, Rathbun (1977)—for an equation based on data that encompass the values of interest. In general, however, water velocities and flow depths likely to be measured in streams of the United States will be within the ranges of water velocities and flow depths covered in figure 6.

Equations 53, 54, and 55 give reaeration coefficients at 20°C. To adjust to other temperatures, the temperature correction of Elmore and West (1961) can be used. This correction has the form

$$K_2^{\Theta} = K_2^{20}(1.0241)^{\Theta - 20} \qquad (56)$$

where
K_2^{Θ} is the reaeration coefficient (day^{-1}) at temperature Θ (°C).

The mass-transfer coefficient for evaporation of water from a stream can be estimated from the equation (Rathbun and Tai, 1983)

$$k_a^{26.1} = 416 + 156\ V_a \qquad (57)$$

where
k_a is the mass-transfer coefficient at 26.1°C (m/day), and
V_a is the windspeed (m/s).

Any temperature could have been used as the base temperature. The temperature of 26.1°C was chosen because this was the average water temperature of the data base used to establish the dependence of the gas-film coefficient on windspeed. The mass-transfer coefficient at 26.1°C can be adjusted to the desired temperature by using the equation (Rathbun and Tai, 1983)

$$k_a^{\Theta} = k_a^{26.1} \exp[0.00934(\Theta - 26.1)] \qquad (58)$$

where
k_a^{Θ} is the mass-transfer coefficient (m/day) at temperature Θ (°C).

Reference-substance parameters, Φ and Ψ, for the water- and air-film coefficients can be computed from equations 27 and 28. Equation 27 requires the molal volume at the normal boiling temperature. This volume can be computed from the molecular structure using the LeBas procedure (Reid and others, 1987).

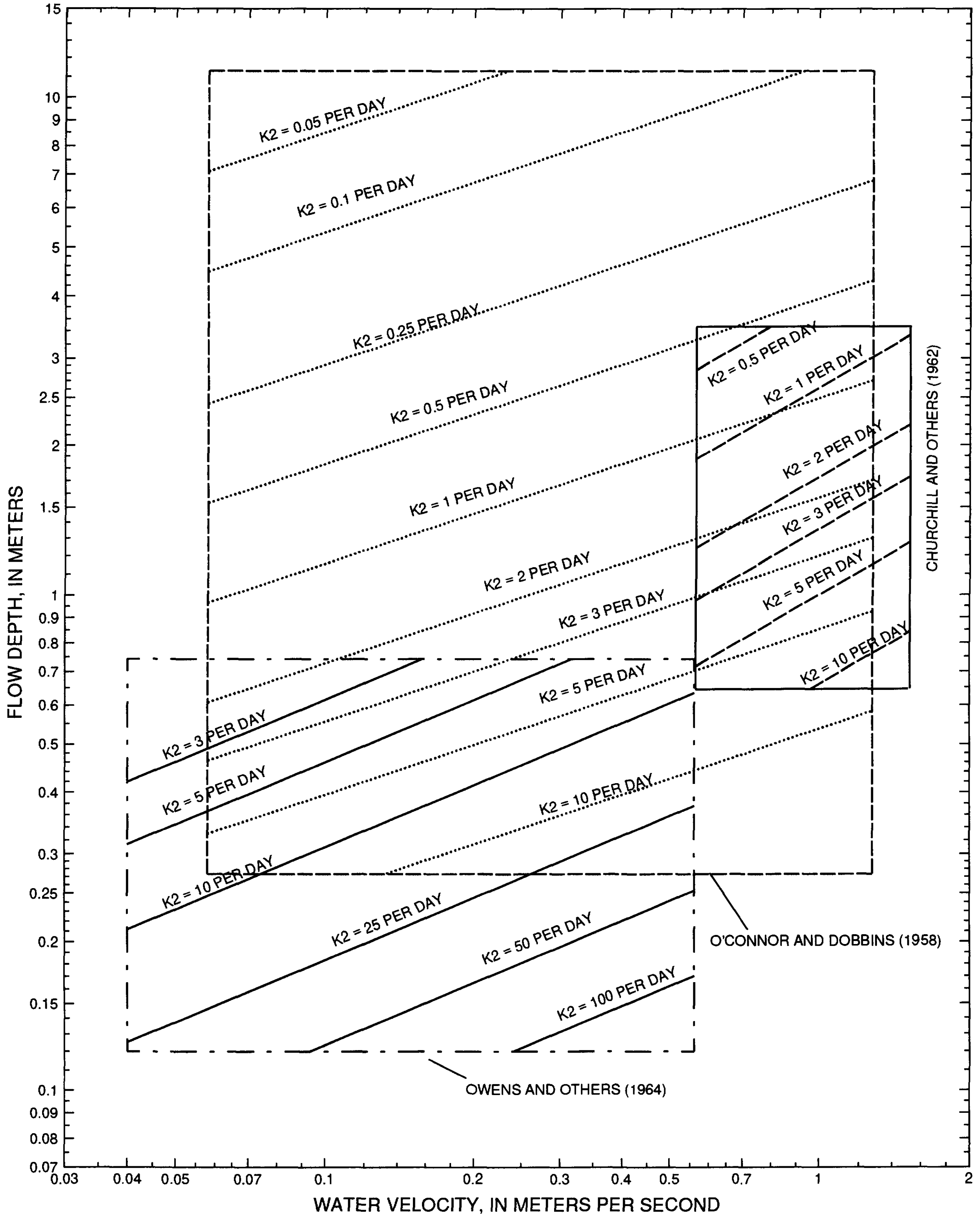

Figure 6. Oxygen-absorption (reaeration) coefficient (K_2) in per day at 20 degrees Celsius as a function of water velocity and flow depth for the equations of Owens and others (1964), Churchill and others (1962), and O'Connor and Dobbins (1958).

The reference-substance parameters for the target analytes are presented in table 6. The water-film reference-substance parameter, Φ, ranged from 0.506 for hexachlorobutadiene to 0.774 for chloromethane. This range indicates that the water-film mass-transfer coefficient for the volatilization of the target analytes from a stream will range from about 51 to 77 percent of the reaeration coefficient for absorption of oxygen by the same stream.

The air-film reference-substance parameter, Ψ, ranged from 0.338 for hexachlorobutadiene to 0.722 for chloromethane. This range indicates that the air-film mass-transfer coefficient for the volatilization of the target analytes from a stream will range from about 34 to 72 percent of the mass-transfer coefficient for evaporation of water from the same stream. However, the relative importance of these two mass-transfer coefficients is dependent on the Henry's law constant; as discussed previously, many of the target analytes have Henry's law constants large enough that the air-film mass-transfer coefficient will contribute little to the overall volatilization coefficient. If VOCs other than the 55 target analytes (table 1) prove to be important in some streams, the reference-substance parameters can be computed from equations 27 and 28.

Table 6. Water-film and air-film reference-substance parameters for the target analytes

[USGS, U.S. Geological Survey; Φ, water-film reference-substance parameter; Ψ, air-film reference-substance parameter]

USGS parameter code	Compound	Φ	Ψ
34418	chloromethane	0.774	0.722
34423	dichloromethane	.697	.568
32106	trichloromethane	.645	.485
32102	tetrachloromethane	.607	.432
34413	bromomethane	.763	.539
32104	tribromomethane	.631	.343
32101	bromodichloromethane	.640	.419
32105	chlorodibromomethane	.636	.375
34311	chloroethane	.694	.645
34496	1,1-dichloroethane	.643	.529
32103	1,2-dichloroethane	.643	.529
34506	1,1,1-trichloroethane	.605	.461
34511	1,1,2-trichloroethane	.605	.461
34396	hexachloroethane	.530	.354
77651	1,2-dibromoethane	.633	.393
34541	1,2-dichloropropane	0.603	0.498
77443	1,2,3-trichloropropane	.574	.440
82625	1,2-dibromo-3-chloropropane	.568	.354
34488	trichlorofluoromethane	.635	.455
34668	dichlorodifluoromethane	.670	.482
77652	1,1,2-trichloro-1,2,2-trifluoroethane	.583	.394
39175	chloroethene	.716	.654
34501	1,1-dichloroethene	.659	.534
77093	*cis*-1,2-dichloroethene	.659	.534
34546	*trans*-1,2-dichloroethene	.659	.534
39180	trichloroethene	.617	.464
34475	tetrachloroethene	.585	.417
50002	bromoethene	.709	.510
34704	*cis*-1,3-dichloropropene	.615	.502
34699	*trans*-1,3-dichloropropene	.615	.502
39702	hexachlorobutadiene	.506	.338
34030	benzene	.638	.590
77128	styrene	.578	.517
34696	naphthalene	.560	.470
34010	methylbenzene	.599	.547
34371	ethylbenzene	.569	.512
77224	n-propylbenzene	.544	.484
77223	iso-propylbenzene	.544	.484
77342	n-butylbenzene	.524	.460
77135	1,2-dimethylbenzene	.569	.512
85795	1,3-dimethylbenzene	.569	.512
85795	1,4-dimethylbenzene	.569	.512
77222	1,2,4-trimethylbenzene	.544	.484
34301	chlorobenzene	.601	.499
34536	1,2-dichlorobenzene	.572	.441
34566	1,3-dichlorobenzene	.572	.441
34571	1,4-dichlorobenzene	.572	.441
77613	1,2,3-trichlorobenzene	.548	.400
34551	1,2,4-trichlorobenzene	.548	.400
78032	methyl tertiary-butyl ether	.583	.558
50004	ethyl tertiary-butyl ether	.556	.521
50005	tertiary-amyl methyl ether	.556	.521
81577	diisopropyl ether	.556	.521
34210	2-propenal	.712	.688
34215	2-propenenitrile	.698	.706

The procedure for estimating volatilization coefficients and the corresponding half-lives can be demonstrated best with an example. Consider a wastewater containing tribromomethane, 1,2,4-trichlorobenzene, and chloromethane that is discharged into a stream which has a water velocity of 0.307 m/s and a flow depth of 0.557 m. Estimate the distance downstream at which the concentrations will be reduced to 10 percent of the initial concentration for windspeeds of 0.2, 3.0, and 6.0 m/s. The water and air temperatures are both 16.5°C. Steps in the estimation procedure are:

1. Estimate the reaeration coefficient. For a water velocity of 0.307 m/s and a flow depth of 0.557 m, figure 6 indicates that these values fall within the ranges of both the equation of Owens and others (1964) and the equation of O'Connor and Dobbins (1958). From equation 53, the calculated coefficient K_2^{20} is 8.14 day^{-1} and from equation 55, the calculated coefficient K_2^{20} is 5.24 day^{-1}. Use the smaller value because this will result in lower estimates of the mass-transfer coefficients and, therefore, possibly conservative estimates of the distances required for the concentrations to be reduced to 10 percent of the initial concentrations.
2. Adjust the estimated reaeration coefficient from 20°C to 16.5°C. From equation 56, $K_2^{16.5} = 4.82\ day^{-1}$.
3. Convert the reaeration coefficient to a film coefficient for the reference substance, oxygen, k_{wref}, by multiplying by the flow depth. The equation used for this conversion is analogous to equation 16 and can be written $k_{wref} = K_2\ Y$. The result is 2.68 m/day.
4. Calculate the water-film mass-transfer coefficients, k_w, for the three compounds being considered in this example. Use equation 25 and the water-film reference-substance parameters, Φ, from table 6. The results for the three compounds are presented in table 7.
5. Calculate the air-film mass-transfer coefficient for evaporation of water from equation 57. The results are 447, 884, and 1,350 m/day for the three windspeeds.
6. Adjust these air-film mass-transfer coefficients from the base temperature of 26.1°C to 16.5°C using equation 58. The results from this calculation are 409, 808, and 1,230 m/day.
7. Calculate the air-film mass-transfer coefficients for the three compounds being considered in this example by using equation 26 and the air-film reference parameters, Ψ, from table 6. The results for the three compounds for the three windspeeds are given in table 7.
8. Calculate the Henry's law constants at 16.5°C, using equation 50 and the constants from table 4. The two sets of constants for chloromethane give values of 558 and 707 Pa m^3/g mol. Use the average of 632 Pa m^3/g mol. The two sets of constants for tribromomethane give values of 35.0 and 34.0 Pa m^3/g mol. Use the average of 34.5 Pa m^3/g mol.
9. Calculate the overall mass-transfer coefficients based on the water phase by using the values in table 7 and equation 13. The results are given in table 7.
10. Calculate the volatilization coefficients, K_v, from equation 16 and the flow depth. The results are given in table 7.
11. Calculate the distances required for the concentration to be reduced to 10 percent of the initial concentration by using equation 5. The results are given in table 7.

The results in table 7 indicate that substantial distances are required for the concentration to be reduced to 10 percent of the initial concentration, even for chloromethane, which is a gas at normal environmental temperatures. The influence of the Henry's law constant is evident, with longer distances needed for tribromomethane, which has the lowest Henry's law constant of the three VOCs considered in this example. The distance required for the concentration of each VOC to be reduced to the target percentage decreased as the windspeed increased, with the effect of windspeed decreasing as the Henry's law constant increased. The windspeed had appreciable effect on the volatilization of tribromomethane, less effect on 1,2,4-trichlorobenzene, and little effect on chloromethane. These observations are in agreement with previous discussions of the relationships among windspeed, Henry's law constant, and volatilization.

Table 7. Prediction of the volatilization coefficients and distances downstream required for 90-percent loss by volatilization of three target analytes

[USGS, U.S. Geological Survey; k_w, water-film mass-transfer coefficient, in meters per day; k_a, air-film mass-transfer coefficient, in meters per day; H, Henry's law constant, in pascals cubic meter per gram mole; K_{wo}, overall mass-transfer coefficient based on the water phase, in meters per day; K_v, volatilization coefficient, in reciprocal days; L, distance, in kilometers]

USGS parameter code	Compound	k_w	k_a	H	K_{wo}	K_v	L
34418	chloromethane	2.07	295	632	2.02	3.63	16.8
			583		2.04	3.66	16.7
			888		2.05	3.68	16.6
32104	tribromomethane	1.69	140	34.5	.917	1.65	37.0
			277		1.19	2.14	28.5
			422		1.32	2.37	25.8
34551	1,2,4-trichlorobenzene	1.47	164	146	1.28	2.30	26.6
			323		1.37	2.46	24.8
			492		1.40	2.51	24.3

DEPENDENCE OF THE VOLATILIZATION HALF-LIFE ON WATER VELOCITY, FLOW DEPTH, AND WATER TEMPERATURE

Procedures similar to those in the previous example can be used to estimate the effects of water velocity, flow depth, and water temperature on the volatilization half-life. The volatilization half-life is the time required for the concentration of a VOC to be reduced to one-half by volatilization. The half-lives for tribromomethane, trichloromethane, and dichlorodifluoromethane are presented in figures 7, 8, and 9. These compounds represent low, middle, and high values of Henry's law constants (table 2) for the target analytes (fig. 4).

Figure 7 shows the effect of water velocity on the half-lives predicted from the equations of Owens and others (1964), Churchill and others (1962), and O'Connor and Dobbins (1958). These are equations 53, 54, and 55, and they were used in conjunction with equations 13, 25, 26, 16, and 3 to predict the volatilization half-lives. Values in figure 7 are for a water temperature of 20°C. An air-film mass-transfer coefficient of 800 m/day at a base temperature of 26.1°C was assumed, and this value was adjusted to a value of 756 m/day at 20°C by using equation 58. Computations for each of the three equations were for the ranges of water velocities and midpoints of the depth ranges of the data used to develop the equations. These depths were 0.4 m for the Owens and others (1964) equation, 2.0 m for the Churchill and others (1962) equation, and 6.0 m for the O'Connor and Dobbins (1958) equation.

The half-lives of the three VOCs decrease as the water velocity increases (fig. 7), which is consistent with much of the resistance to volatilization of the target analytes being in the water film. Consequently, as the water velocity increases, turbulent mixing within the water phase increases, the water-film thickness decreases, the mass-transfer coefficient for the water film increases, the volatilization coefficient increases, and the half-life decreases. Half-lives and the dependence of the half-life on water velocity are nearly the same for trichloromethane and dichlorodifluoromethane, despite the fact that the Henry's law constant for dichlorodifluoromethane (31,400 Pa m^3/g mol at 20°C) is about 100 times larger than the Henry's law constant for trichloromethane (310 Pa m^3/g mol at 20°C). Figure 3, however, indicates that the Henry's law constants for both of these compounds are large enough that most of the resistance to volatilization is in the water film. Consequently, half-lives for a given flow depth and water temperature depend mostly on water velocity because the second term on the right-hand side of equation 13 is negligible with respect to the first term. Because the Henry's law constant for tribromomethane is relatively small (44.0 Pa m^3/g mol at 20°C), the air film contributes some resistance to volatilization. The half-lives for all three compounds decrease considerably as the flow depth decreases, indicating that VOCs will persist much longer in deep, slow-flowing streams than in shallow, swift-flowing streams.

Figure 8 presents half-lives for the three target analytes as a function of flow depth for water velocities of 0.3 m/s for the equation of Owens and others (1964), 1.0 m/s for the equation of Churchill and others (1962), and 0.7 m/s for the equation of O'Connor and Dobbins (1958). These velocities were selected because they were near the midpoints of the velocity ranges of the data used to develop the equations. Half-life computations were over the flow-depth range appropriate for each of the equations.

Figure 8 indicates that the half-life increases as the flow depth increases. This again is consistent with much of the resistance to volatilization of the target analytes being in the water film. Consequently, for a specific water velocity, the effect of turbulent mixing on the water-film thickness decreases as the flow depth increases because of the greater water volume, the film thickness increases, the mass-transfer coefficient for the water film decreases, the volatilization coefficient decreases, and the half-life increases. The half-lives for trichloromethane and dichlorodifluoromethane are similar for the three equations; the half-life for tribromomethane is longer. As for water velocity, the Henry's law constants for trichloromethane and dichlorodifluoromethane are such that virtually all the resistance to volatilization is in the water film, whereas the air film contributes some resistance to the volatilization of tribromomethane.

Figures 7 and 8 indicate that flow depth probably has more of an effect on the half-life than water velocity. This observation is consistent with the previous observation (Rathbun, 1977) that, with one exception, the exponent on flow depth was larger than

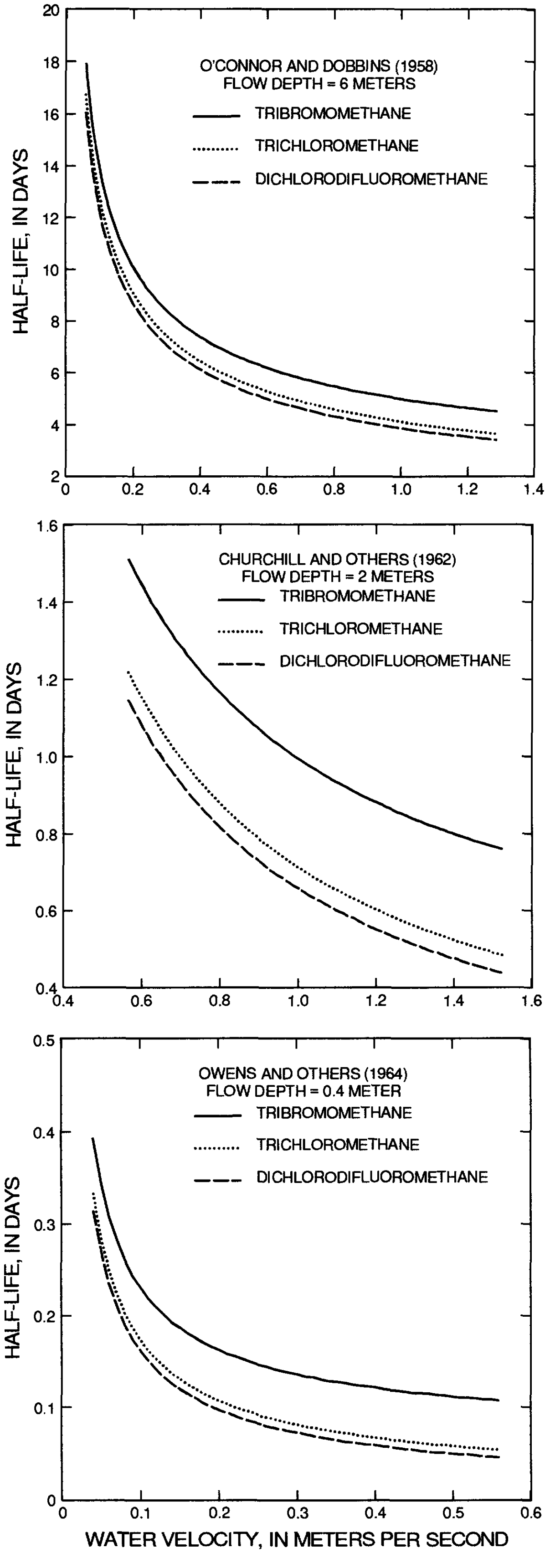

Figure 7. Variation of the volatilization half-life with water velocity for three target analytes at 20 degrees Celsius with flow depth as a parameter; Henry's law constants are 44.0, 310, and 31,400 pascals cubic meter per gram mole for tribromomethane, trichloromethane, and dichlorodifluoromethane, respectively.

the exponent on water velocity in semiempirical and empirical prediction equations for the reaeration coefficient.

Figure 9 presents half-lives as a function of water temperature. These half-lives were computed using equations 56 and 58 to define the temperature dependencies of the reaeration coefficient and the air-film mass-transfer coefficient. The constants from table 4 were used to define the temperature dependence of the Henry's law constants. Computations were for the combinations of water velocities and flow depths used for figures 7 and 8.

The results in figure 9 indicate that the half-lives for all three compounds decrease as the temperature increases. Such a decrease is consistent with increased molecular movement as the temperature increases, with correspondingly higher volatilization coefficients and, therefore, shorter half-lives. Half-lives for trichloromethane and dichlorodifluoromethane are similar, for reasons discussed previously. Half-lives for tribromomethane are considerably longer because the Henry's law constant for this compound is in the range where the air film contributes to the overall resistance to volatilization.

Results in figures 7, 8, and 9 for the three target analytes indicate that the volatilization half-lives decrease as the temperature increases and as the flow depth decreases. The half-lives also generally decrease as the water velocity increases, with the effect dependent on the Henry's law constant of the VOC of interest. Graphs similar to figures 7, 8, and 9 can be prepared for other VOCs as needed and/or for other water-velocity and flow-depth conditions.

This analysis of the effect of water velocity, flow depth, and water temperature on the half-lives of VOCs in streams is based on the two-film model. This model assumes thin films of water and air at the air-water interface in which mass transfer is by molecular diffusion alone. This is only a conceptual model, but it does provide a framework for analysis of the volatilization process and predictions are qualitatively consistent with observations.

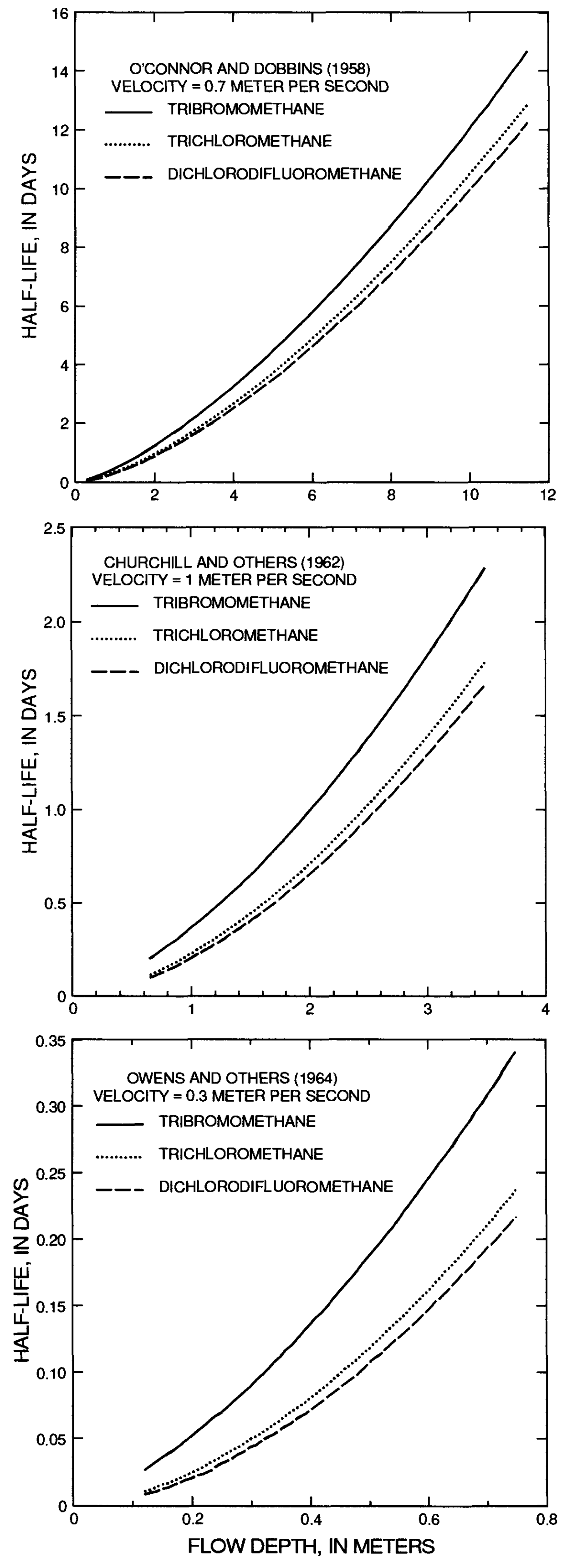

Figure 8. Variation of the volatilization half-life with flow depth for three target analytes at 20 degrees Celsius with water velocity as a parameter; Henry's law constants are 44.0, 310, and 31,400 pascals cubic meter per gram mole for tribromomethane, trichloromethane, and dichlorodifluoromethane, respectively.

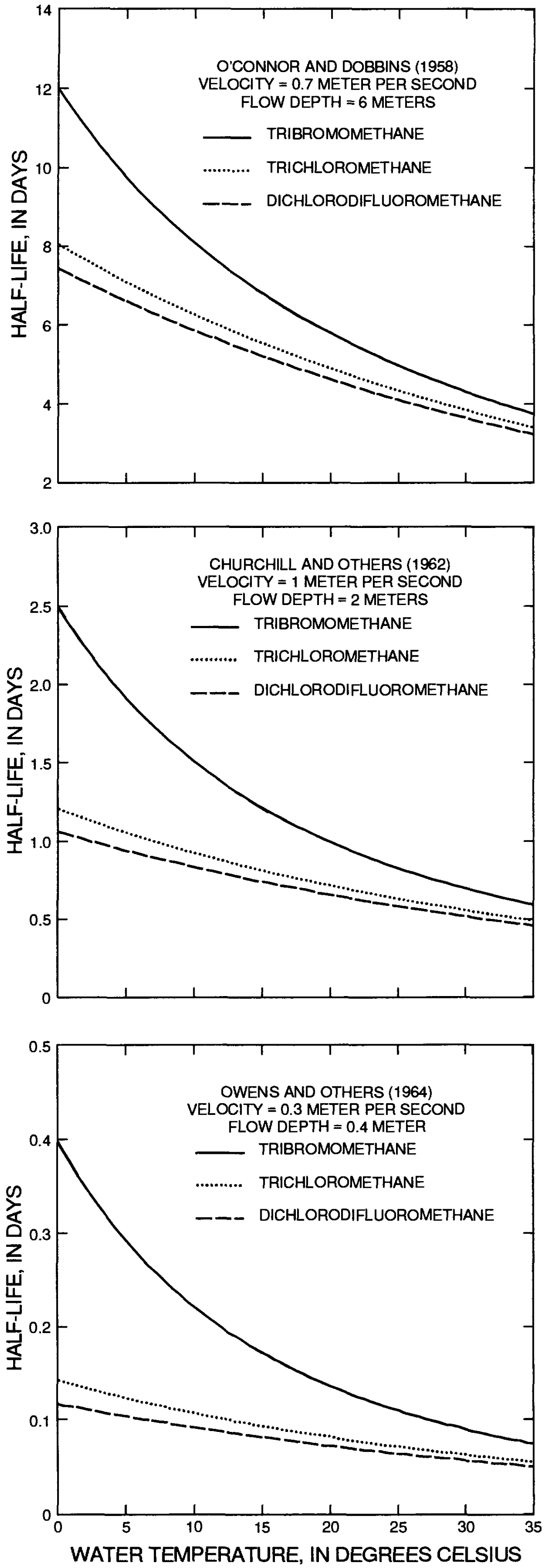

Figure 9. Variation of the volatilization half-life with water temperature for three target analytes; Henry's law constants at 20 degrees Celsius are 44.0, 310, and 31,400 pascals cubic meter per gram mole for tribromomethane, trichloromethane, and dichlorodifluoromethane, respectively.

ABSORPTION

Absorption is the movement of a VOC from the bulk air phase above a stream across the air/water interface into the water. This process is sometimes called condensation or vapor deposition, and occurs when the air concentration is greater than the concentration that would be in equilibrium with the water concentration. Absorption is the reverse of volatilization, and can be described by the same equations, with the sign of the concentration-difference driving force reversed. Combining equations 9 and 10 gives

$$N = K_{wo}\left(C - \frac{p}{H}\right) \qquad (59)$$

where

C is greater than p/H for volatilization, and
p/H is greater than C for absorption.

The overall mass-transfer coefficient, K_{wo}, is assumed to be the same for both processes, and this coefficient can be estimated for VOCs by using procedures described previously in the section on volatilization. A laboratory study (Sherwood and Holloway, 1940) indicated that mass-transfer coefficients for absorption and desorption of gases from water were the same, within experimental error.

The importance of volatilization as a mechanism for the loss of VOCs from streams has been firmly established. The importance of the reverse process of absorption is less clear. Absorption of VOCs would be most important in areas of high air concentrations and low water concentrations such that the driving force is toward the water. Target analytes with small Henry's law constants would be most susceptible to absorption because of their preference for the water phase. However, demonstration of absorption for VOCs may be difficult because of generally low ambient air concentrations and the corresponding low water concentrations that may be below analytical detection limits available at the present time. Methods for concentrating air samples to lower the concentrations that can be measured are fairly standard. Concentration methods for water samples are less well developed. Some work has been done with PCBs in lakes. Doskey and Andren (1981) estimated that absorption could be a significant source of PCBs in Lake Michigan when the air film controlled the uptake process. Conversely, they estimated that volatilization was important when the water film controlled the mass-transfer process. The uncertainty in the estimation of the direction of transfer was the result of inaccuracies in the Henry's law constant for the PCBs, the determination of the controlling film resistance, and the resultant overall mass-transfer coefficients. Swackhamer and others (1988) determined from mass-balance calculations that the fluxes of 17 PCB congeners in Siskiwit Lake were from the lake to the atmosphere, indicating volatilization. The fluxes for four other congeners were small or negative. Lakes, however, are less dynamic than streams, and demonstration of absorption in streams is expected to be more difficult.

DRY DEPOSITION WITH PARTICLES

The dry deposition of organic compounds associated with particles onto a surface depends on the characteristics of the surface, mass-transfer resistance in the deposition layer above the surface, particle size and concentration, concentrations of the organic compound in the air, and meteorological conditions (Eisenreich and others, 1981). In simplified form, the deposition flux is defined by

$$N_d = V_d C_a \qquad (60)$$

where

N_d is the flux (g mol/m^2/s),

V_d is the deposition velocity (m/s), and

C_a is the concentration of the organic compound sorbed on the particles in the air (g mol/m^3).

The deposition velocity depends on the surface type, the distribution of the particle sizes, and the windspeed (Eisenreich and others, 1981) and also the near-surface turbulence (Swackhamer and others, 1988). There is considerable uncertainty in values of the deposition velocity, and this value is difficult to measure because of uncertainties in extrapolating from dry collector surfaces to water surfaces (Swackhamer and others, 1988).

The sorption of organic compounds to particles in the atmosphere depends on the vapor pressure of the compound and the size, surface area, and organic-carbon content of the particles. Eisenreich and others (1981) estimated for the range of expected atmospheric environments that organic compounds with vapor pressures greater than 10^{-4} mm Hg (1.3×10^{-2} Pa) should exist almost entirely in the gas phase, and those having vapor pressures less than 10^{-8} mm Hg (1.3×10^{-6} Pa) should exist almost entirely in the particulate phase. Vapor pressures at 25°C for the target analytes range from about 4,200 mm Hg (5.6×10^{5} Pa) for chloromethane to about 7.5×10^{-2} mm Hg (10 Pa) for naphthalene. Consequently, the target analytes will all be essentially 100 percent in the gas phase, and dry deposition with particles will not be a significant process for these compounds.

WET DEPOSITION

It is difficult, if not impossible, to separate experimentally the contributions to the removal of organic compounds from the air made by wet deposition with particles and gas scavenging. The total washout ratio, W_t, is given by (Pankow and others, 1984)

$$W_t = (W_g)(1-\phi) + W_p\phi \qquad (61)$$

where

W_g is the gas scavenging ratio,

W_p is the particle scavenging ratio, and

ϕ is the fraction of the organic compound in the air that is associated with the particulate phase.

Because ϕ is estimated to be small for the target analytes, equation 61 reduces to

$$W_t = W_g\,. \qquad (62)$$

Gas scavenging occurs when gaseous organic compounds partition into the precipitation and fall to a land or water surface. The gas scavenging ratio, W_g, can thus be defined as

$$W_g = \frac{C_p}{C_a} \quad (63)$$

where

C_p and C_a are the concentrations of the organic compound in the precipitation and the air.

It has been estimated (Slinn and others, 1978) that a falling raindrop reaches equilibrium with trace concentrations of organic compounds in the air in a fall distance of about 10 m. Consequently, it is generally assumed that equilibrium exists, and equation 63 can be combined with Henry's law (eq. 34) and the ideal gas law to give

$$W_g = \frac{RT}{H} \quad (64)$$

where

H is the Henry's law constant (Pa m^3/g mol).

Thus, W_g is equal to the reciprocal of the nondimensional Henry's law constant as defined by equation 46.

The temperature dependence of the gas scavenging ratio can be estimated from equation 64 and the temperature dependence of the Henry's law constant as given by equation 50. Using trichloroethene as an example, the constants of Dewulf and others (1995) from table 4 yield computed values of the gas scavenging ratio at 25°C and 8°C of 2.88 and 7.26, respectively. These values indicate that the ratio increases as the temperature decreases so that the trichloroethene concentration in the precipitation increases with decreasing temperature. The exponential dependence of the Henry's law constant on temperature has a much greater effect on the gas scavenging ratio than the explicit dependence on temperature in equation 64. The ratio of the gas scavenging ratios at 8°C and 25°C for trichloroethene is 2.5, which is generally consistent with the ratio of 3 to 6 found between experimental values at 8°C for a number of organic compounds and values calculated from the Henry's law constant at 25°C (Ligocki and others, 1985).

Gas scavenging ratios for organic compounds generally range between 1 and 10^4 (Eisenreich and others, 1981), with the ratio increasing as the Henry's law constant decreases (eq. 64). It was estimated previously that wet deposition with particulate matter was not likely to be important for the target analytes because of their very limited tendency to sorb to particulate matter in the atmosphere.

The most common forms of precipitation are rain and snow, and concentrations of organic compounds in these types of precipitation might be expected to be different because of different temperatures. However, Swackhamer and others (1988) noted that the concentrations of PCBs in rain and snow in the Siskiwit Lake region were similar, with a few exceptions. Conversely, Czuczwa and others (1988) noted significant seasonal differences in the concentrations of alkylbenzenes in precipitation, with snow and winter rain having the highest concentrations, autumn rain having intermediate concentrations, and spring and summer rain having the lowest concentrations. Possible explanations are seasonal temperature differences that affect the equilibria between the air and precipitation phases, and seasonal differences in the atmospheric mixing heights and atmospheric reactivities that affect the air concentrations. There also are indications that concentrations of organic compounds in fog are enriched relative to other types of precipitation. This enrichment results from the high specific surface area of the fog droplets, with adsorption of the organic compounds occurring at the air-water interface. Goss (1994) calculated an enrichment factor of 1.8 for 1,2,4-trichlorobenzene for 8-µm droplets.

EXPERIMENTAL VALUES OF THE GAS SCAVENGING RATIO

Experimental values of the gas scavenging ratio for 11 target analytes are presented in table 8. Most of the data are accompanied by values indicating ± one standard deviation of the mean value and, therefore, the variability in the data. The considerable variability in the data is indicative of the experimental difficulties in collecting and analyzing air and precipitation samples for small concentrations of VOCs.

CALCULATED VALUES OF THE GAS SCAVENGING RATIO

Gas scavenging ratios for the other 44 target analytes or for other VOCs that might be important in certain situations can be estimated using equation 64 and Henry's law constants from table 2. If ratios at a temperature other than 20°C or 25°C are needed, the Henry's law constant can be computed at the appropriate temperature using equation 50 and temperature parameters from table 4. If the temperature parameters are not available for the compound of interest, Henry's law constants at the appropriate temperature can be estimated from equation 51 or 52 and procedures discussed previously. The same procedures can be used to adjust the experimental ratios in table 8 to others temperatures.

ESTIMATION OF THE IMPORTANCE OF WET DEPOSITION

A mass balance about the surface of a stream during a storm event yields

$$C_{ww} = \frac{(W_g)(RF)(C_a)}{Y} \tag{65}$$

where

C_{ww} is the concentration (ng/L) of the organic compound in the stream resulting from gas scavenging from the atmosphere during the storm,

RF is the amount of rainfall (m),

C_a is the concentration (ng/L) of the compound in the air, and

Y is the flow depth (m) of the stream.

Equation 65 is a simplistic approach and assumes that the rainfall occurs instantaneously and is uniformly and instantaneously distributed over a stream reach of constant width and depth containing no background concentrations of the organic compounds of interest. Consequently, estimates of gas scavenging and the resultant wet deposition are likely to be upper bound estimates. The relative validity of equation 65 increases as the intensity of the precipitation event

Table 8. Experimental values of gas scavenging ratios for 11 target analytes

[USGS, U.S. Geological Survey; °C, degrees Celsius; W_g, mean value of the gas scavenging ratio; ±, one standard deviation; nd, not determined]

USGS parameter code	Compound	Temperature (°C)	W_g	Reference
39180	trichloroethene	8	3.7 ± 1.3	Ligocki and others (1985)
34475	tetrachloroethene	8	3.6 ± 1.1	Ligocki and others (1985)
34696	naphthalene	11	230 ± nd	Pankow and others (1984)
		8	250 ± 73	Ligocki and others (1985)
34010	methylbenzene	8	22 ± 5	Ligocki and others (1985)
		7	31 ± 9	Hart and others (1993)
		–1	42 ± 16	Hart and others (1993)
34371	ethylbenzene	8	27 ± 11	Ligocki and others (1985)
		7	32 ± 48	Hart and others (1993)
		–1	36 ± 34	Hart and others (1993)
77135	1,2-dimethylbenzene	8	35 ± 15	Ligocki and others (1985)
		7	69 ± 53	Hart and others (1993)
		–1	94 ± 66	Hart and others (1993)
85795	1,3-,1,4-dimethylbenzene	8	33 ± 17	Ligocki and others (1985)
		7	70 ± 70	Hart and others (1993)
		–1	67 ± 50	Hart and others (1993)
77222	1,2,4-trimethylbenzene	8	27 ± 9	Ligocki and others (1985)
		7	54 ± 44	Hart and others (1993)
		–1	52 ± 40	Hart and others (1993)
34536	1,2-dichlorobenzene	8	46 ± 13	Ligocki and others (1985)
34571	1,4-dichlorobenzene	11	44 ± nd	Pankow and others (1984)
		8	39 ± 10	Ligocki and others (1985)
34551	1,2,4-trichlorobenzene	8	66 ± 51	Ligocki and others (1985)

increases. On the other hand, the more intense the event, the less likely equilibrium is achieved between the precipitation and the air.

Naphthalene, methylbenzene, and tetrachloroethene were selected as examples to demonstrate the possible significance of wet deposition as a source of VOCs in streams..These three target analytes were chosen because they have been detected in urban air (Ligocki and others, 1985). Also, these three compounds have Henry's law constants that approximately span the range of Henry's law constants for the target analytes.

The concentrations of these three target analytes predicted to occur in a stream as result of gas scavenging were computed from equation 65. The concentrations are presented in figure 10 as a function of flow depth for temperatures of 5°C, 15°C, and 25°C. Gas scavenging ratios were computed from equation 64. The average Henry's law constants at 25°C from table 2 were used. Henry's law constants at 5°C and 15°C for methylbenzene and tetrachloroethene were computed from equation 50 and the constants of Dewulf and others (1995) as given in table 4. Henry's law constants at 5°C and 15°C for naphthalene were computed from equation 51 because temperature-dependent data were not available for this compound. Solubilities were from May and others (1983), and vapor pressures were estimated from an equation from Jordan (1954). A rainfall of 0.025 m was assumed, and air concentrations for the three compounds were from Ligocki and others (1985).

The results in figure 10 indicate that the concentrations of the three compounds in the water decrease rapidly as the flow depth increases because of the increasingly larger volume of water into which the scavenged compounds are mixed. The results also indicate that the concentrations decrease as the Henry's law constant increases, indicating a decreasing tendency to be scavenged. Decreasing the temperature results in increases of the concentrations of the three compounds in the stream water.

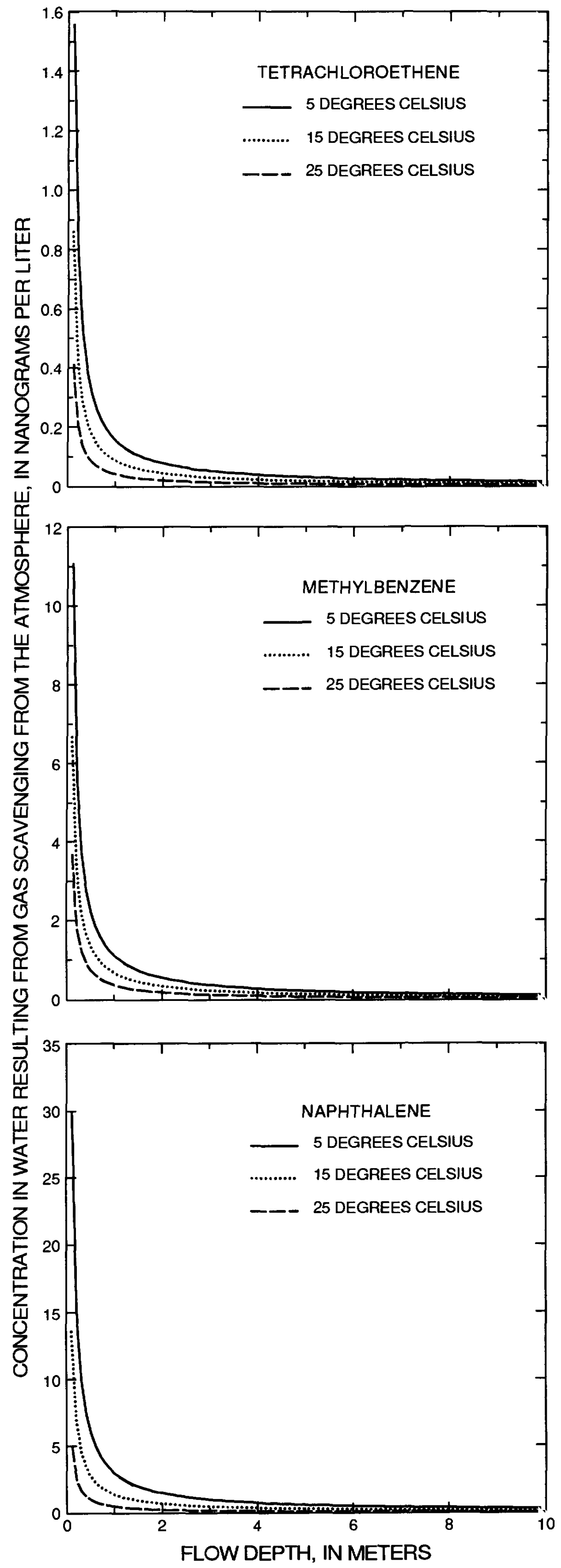

Figure 10. Concentrations of three target analytes in a stream resulting from gas scavenging from the atmosphere as a function of flow depth and water temperature; calculated Henry's law constants at 15 degrees Celsius are 19.6, 340, and 831 pascals cubic meter per gram mole for naphthalene, methylbenzene, and tetrachloroethene, respectively; air concentrations (Ligocki and others, 1985) are 0.450, 3.80, and 1.20 nanograms per liter for naphthalene, methylbenzene, and tetrachloroethene, respectively.

The concentrations in figure 10 for all three compounds are in the low nanogram-per-liter-concentration range. These concentrations are below the current analytical method reporting limits (MRLs) of 50 ng/L for methylbenzene and tetrachloroethene and 200 ng/L for naphthalene (J.S. Zogorski, U.S. Geological Survey, written commun., 1996). The fact that these concentrations are less than the MRLs does not, however, mean that these concentrations are not hazardous to humans or aquatic life. Indeed, little is known about the effects of long-term exposures of humans and aquatic life to low concentrations of organic compounds. Consequently, as MRLs are lowered, the question of what concentration levels are hazardous must be addressed. Conversely, long-term exposure to VOCs may be somewhat less of a problem than exposure to other nonvolatile organic compounds because VOCs generally will not persist in streams for long times because of their volatile nature. In the case of continuous discharges of VOCs, however, long-term exposures could occur because equilibrium concentrations of the VOCs would be established in the stream. These equilibrium concentrations would be the result of a balance of the processes depicted schematically in figure 1.

The concentrations in figure 10 indicate that scavenging of VOCs from the atmosphere is not likely to be a significant source for streams. However, equation 65 is simplistic, and other factors could result in both higher and lower concentrations in the stream water. For example, rainfall on the impervious part of an urban watershed could run off into the stream, resulting in higher concentrations than those resulting from rain falling directly onto the surface of the stream. Flushing of VOCs from the surface also could be another possible source of VOCs. However, much of this runoff would enter a stream as sheet flow over the land surface. Consequently, volatilization to the atmosphere could be rapid. Figure 10 indicates that the highest concentrations are predicted for the shallowest flows. However, volatilization is inversely proportional to the flow depth and would be rapid for these shallow flows. The relative importance of volatilization and scavenging depends on the directions and magnitudes of the concentration gradients driving each process, and the relative importance of these processes has not been studied. However, Czuczwa and others (1988) hypothesized that the net effect of scavenging on atmospheric concentrations of alkylbenzenes and tetrachloroethene is likely to be minor because of rapid volatilization back to the atmosphere. Volatilization from a water surface is likely to be slower than volatilization from a land surface because of shallower flows over the land surface. However, the relative rates of these processes have not been determined.

MICROBIAL DEGRADATION

Microbes such as bacteria, protozoa, fungi, and algae are present in almost all parts of the environment. Microbes use organic compounds as a source of food and energy. As a rule of thumb, about one-half of the organic carbon assimilated by microbes is used to form new biomass, with the other one-half used as an energy source for the synthesis process (Gaudy and Gaudy, 1980). The energy is obtained by oxidation of some of the organic matter that has been assimilated. Consequently, microbial degradation may be defined as the metabolism of organic compounds by microorganisms in which the organisms use the compound as sources of food and energy to form microbial biomass and inorganic and organic end products such as carbon dioxide, water, and methane (Larson and Cowan, 1995). The term biotransformation has been used by some researchers, for example, Lanzarone and McCarty (1990), who defined this process as one in which the structure of the organic compound is changed, but the change is something less than complete degradation to these simple end products.

The principle of microbial infallibility says that microbes can degrade all organic compounds, and microbes will eventually develop the ability to degrade whatever compounds humans develop (Richards and Shieh, 1986). However, the timeframe over which this occurs may be long for practical purposes, and some compounds may appear to be resistant to degradation (Alexander, 1975). Consequently, classifications of degradability have been developed.

CLASSIFICATIONS OF DEGRADABILITY

Grady (1985) classified organic compounds as biodegradable, persistent, or recalcitrant. Biodegradable, however, is a nonspecific term in that no extent of transformation is specified. Transformation may not always be beneficial to the environment because the transformation can be from a nontoxic compound to a toxic compound, or from a readily metabolized compound to a persistent or recalcitrant compound. A persistent compound is one that does not undergo biodegradation under a specific set of conditions, whereas a recalcitrant compound is one that is inherently resistant to biodegradation (Grady, 1985) or one that endures for long time periods in the environment because of the inability of the microbes to degrade it (Alexander, 1981). However, because of the many factors involved in the microbial degradation of organic compounds in the environment, recalcitrance may be difficult to prove (Grady, 1985). Also, persistence of a compound in the environment may result because the compound is actually recalcitrant or because conditions for degradation are unsatisfactory.

A somewhat more quantitative measure of biodegradability under aerobic conditions is the refractory index (RI), which is defined as the ratio of the ultimate biochemical oxygen demand (BOD_u) to the ultimate oxygen demand (UOD) (Hart and Helfgott, 1975; Helfgott and others, 1977). BOD_u is the oxygen consumed by a heterogeneous community of bacteria from domestic sewage during microbial degradation of a specific organic compound over an extended period of time in the absence of light. UOD is the oxygen consumed in the complete wet phase chemical oxidation of the compound to carbon dioxide, water, and nitrate.

RI values of approximately 1.0 indicate readily degradable compounds, with values between 0.3 and 0.7 indicating partial degradation. RI values approaching zero indicate refractory compounds for the specific conditions of the measurement, and a negative value indicates an inhibitory compound. The RI value is negative when the BOD_u is negative, which occurs when the oxygen uptake is greater for the bacteria alone than for the mixture of the bacteria and the specific organic compound being tested. Among VOCs, RIs of 0.2 were determined for benzene and gasoline, 0.0 for chloroethene, and trichloromethane was inhibitory (Helfgott and others, 1977).

Biodegradability also has been classified in terms of the ratio of the biodegradation half-life (BHL) and the retention time (RT) of the organic compound in a specific section of the environment (Larson and Cowan, 1995). Readily biodegradable compounds have BHL/RT ratios between 0.1 and 0.3, and they do not accumulate or persist in the environment. Practically biodegradable compounds have BHL/RT ratios less than or equal to 1.0, and they do not accumulate to steady-state concentrations above the input rate. Once the input is stopped, the concentration decreases rapidly and there is no accumulation or persistence in the environment. Slowly biodegradable compounds have BLH/RT ratios between 1.0 and 5.0, and these compounds can persist in the environment after the input is stopped. These compounds will not persist indefinitely, however, because finite degradation rates exist. Nonbiodegradable compounds have BHL/RT ratios greater than 5, and they persist more or less indefinitely in the environment (Larson and Cowan, 1995).

This discussion of the classification of biodegradability indicates that classification is at best qualitative. This limitation results from the fact that microbial degradation of organic compounds in the environment is a complex process with many variables affecting the process.

CHARACTERISTICS OF THE DEGRADATION PROCESS

Biodegradation of organic compounds in the environment is highly system-specific (Grady, 1985). A microbe capable of degrading the compound of interest must be present, conditions must exist for the necessary enzymes to be synthesized, and other system conditions such as nutrient, trace-metal, and oxygen concentrations, pH, and temperature must all be adequate and within acceptable ranges for degradation to occur at a measurable rate.

Microbial degradation of organic compounds is catalyzed by enzymes that, in most cases, are highly specific for the compound being degraded (Dugan, 1975). Consequently, a major factor in determining the susceptibility of an organic compound to microbial degradation is the time it has been in the environment and, therefore, the time available for the necessary enzymes to develop (Grady, 1985). Biogenic compounds have been in the environment for millions of years, and microbes and enzymes generally are likely to exist that can effect degradation of these naturally-occurring compounds. In comparison, many anthropogenic compounds have been in the environment for only an instant on the time scale of evolution, and microbes and enzymes may not exist that can degrade these compounds (Grady, 1985).

The time required for a microbial population to develop the ability to degrade specific organic compounds has been called the adaptation time (Aelion and others, 1989) or the acclimation time (Wiggins and others, 1987). The term adaptation will be used in this report. Adaptation assumes that the microbial population has the genetic capacity for degradation, but the population must adapt to the specific organic compound of interest. The time required for adaptation is the difference between the time when the specific organic compound is first introduced into the environment and the time when significant degradation of the compound begins. The extent of this adaptation time, also called the lag period, depends on many factors, including the time needed for the enzymes to be induced or to develop. Also, there must be sufficient time for small populations of microbes to become large enough to cause measurable degradation of the organic compound. Other factors that may affect the length of the adaptation time are concentrations of inorganic nutrients, preferential use of other organic compounds in the system before the use of the compound of interest, the time needed for the microbes to adapt to toxins or inhibitors present in the system, and predation by protozoa on the degrading microbes (Wiggins and others, 1987). Lag periods may vary from a few hours to days or weeks, depending on the organic compound, the microbes, and the system characteristics (Scow, 1990). In the case of recalcitrant compounds, adaptation does not occur within the timeframe of interest.

Degradation of some organic compounds also may occur by the process of cometabolism. This process is defined as the degradation of a compound that does not provide food or energy for the degrading microbes, but the compound is broken down during the degradation of other organic compounds in the system (Scow, 1990). Cometabolism probably occurs because of the lack of specificity of the microbial enzymes, and growth of the specific microorganisms does not occur (Battersby, 1990). The result is that the rate of transformation of a cometabolized compound is usually very slow because of the low population of organisms, in contrast to more rapid transformation that occurs with a growing population. Compounds with chlorine and nitro substituents sometimes are susceptible to cometabolism. An example of cometabolism is the aerobic degradation of trace concentrations of trichloroethene and 1,2-dichloroethane with the degradation of methane (Lanzarone and McCarty, 1990).

KINETICS OF THE DEGRADATION PROCESS

The classifications of biodegradability permit a qualitative estimate of the effect of microbial degradation on the concentrations of organic compounds in the environment. These classifications do not, however, permit quantitative comparison of the effect of microbial degradation with the effects of other processes acting on the concentrations of organic compounds in the environment, nor do they permit mathematical description of the microbial degradation process. This can be done, however, by considering the kinetics of the degradation process.

The kinetics of the microbial degradation process can be described by the Monod equation, which has the form (Herbert and others, 1956)

$$\mu = \mu_m \frac{C}{K_s + C} \qquad (66)$$

where

μ is the specific growth rate of the microbes expressed as rate of increase of the microbe concentration per unit of microbe concentration,

μ_m is the maximum growth-rate constant,

C is the concentration of the organic substrate, and

K_s is the saturation constant.

Analysis of equation 66 indicates that the constant K_s is numerically equal to the substrate concentration at which the specific growth rate μ is one-half the maximum growth rate. Equation 66 assumes that the compound being degraded sustains growth and is the only source of carbon (Howard and Banerjee, 1984), conditions not likely to be true in an environmental situation. Also, μ and K_s values apply to a specific bacteria, whereas in a mixed population typical of the environment, there may be a wide range of μ and K_s values.

Monod (Herbert and others, 1956) also indicated that the growth rate of the microbes, dB/dt, is a constant fraction, z, of the substrate utilization rate, dC/dt. Therefore, it follows that

$$\frac{dB}{dt} = -z\frac{dC}{dt} \qquad (67)$$

where

z is the yield of the reaction, equal to the mass of microbes formed per mass of substrate consumed.

Because the growth rate of the microbes is related to the specific growth rate by

$$\frac{dB}{dt} = \mu B \qquad (68)$$

it follows that

$$-\frac{dC}{dt} = \frac{B\mu_m C}{z(K_s + C)} \ . \qquad (69)$$

Equation 69 is the Michaelis-Menton equation, and it expresses the rate of change of the substrate concentration as a function of time.

There are, however, several assumptions in these equations that may not be completely valid in environmental systems with mixed populations of microbes and more than one substrate (Scow, 1990). First, the constant relation between the growth rate of the microbes and the substrate utilization rate expressed by equation 67 will most likely not be valid for systems containing several substrates because the population growth may be partly the result of degradation of substrates other than the one of interest. Also, yields may not necessarily be the same for different species of microbes. Finally, with the dilute solutions common in the environment, a significant amount of the energy obtained from the substrate may be necessary for maintenance of the population rather than growth.

Despite these limitations, equation 69 does serve as an empirical basis for describing the microbial degradation of organic compounds in natural systems. Values of K_s commonly range from 0.1 to 10 mg/L (Scow, 1990) and consequently are larger than concentrations of organic compounds present in many environmental situations. With this consideration, equation 69 reduces to

$$-\frac{dC}{dt} = \frac{B\mu_m C}{zK_s} = K_d BC \qquad (70)$$

where

K_d is a second-order rate coefficient for microbial degradation.

Equation 70 indicates that the degradation rate is dependent on the concentrations of the microbes and the compound being degraded.

Simplification of equation 70 is possible for certain situations. If an organic compound is being discharged continuously at low concentrations into a surface water such that the microbes are adapted to the compound, then the biomass concentration will likely be relatively constant so that equation 70 becomes

$$-\frac{dC}{dt} = K'_d C \qquad (71)$$

where the degradation process is now first order in the substrate concentration with pseudo first-order rate coefficient K'_d.

Equations 70 and 71 are empirical simplifications of a complex process. Observed changes in concentrations as a result of microbial degradation in natural systems are likely the sum effects of a number of different processes, given the specificity of enzyme processes and the number of different organic compounds that could be present. However, laboratory data for the microbial degradation of three compounds indicated good fits to equation 71, and the pseudo first-order rate constants were proportional to the microbial concentration, as indicated by equation 70 (Paris and others, 1981).

COMPARISON OF LABORATORY AND ENVIRONMENTAL DEGRADATION STUDIES

Various factors affect the microbial degradation process, and in the laboratory, many of these factors can be controlled to study the fundamentals of the process. The coefficient describing microbial degradation is not a fundamental property of an organic compound that can be quantified, such as water solubility or vapor pressure (Battersby, 1990), but is the coefficient describing a highly system-specific process (Grady, 1985) and site-specific process within a given system (Battersby, 1990). Such specificity is the result of differences in various factors such as the biomass concentration, population diversity, nutrient and trace-metal concentrations, temperature, and pH. Other variables such as vitamin and amino acid concentrations also may be important in some situations (Fewson, 1988). Effects of these variables as well as the effect of the organic-compound concentration on the degradation process have been determined in numerous laboratory studies. These studies generally have used high concentrations of single substrates in batch cultures of one strain of bacteria (Fewson, 1988), and results have been valuable in elucidating the fundamentals of the microbial degradation process and determining degradation products and pathways.

However, because of differences between laboratory and environmental conditions, various admonitions have been made regarding the application of laboratory degradation rate coefficients to field situations. Howard and others (1975; 1978) noted that the behavior of an organic compound in a laboratory test does not precisely predict the behavior of the compound in nature, and that laboratory simulations of nature are difficult because of varying conditions. Scow (1990) stated that using laboratory-derived rate coefficients to predict the persistence of an organic compound in the environment should be done with caution, and Kobayashi and Rittmann (1982) and Bedding and others (1983) noted that laboratory results cannot always be used to predict biodegradability or biotransformation in natural systems or wastewater-treatment processes. Howard and Banerjee (1984) concluded that the results of laboratory screening tests should not be applied to natural waters containing oligotrophic organisms because these organisms are active when organic carbon concentrations are low but are inactive when organic carbon concentrations are high. They noted that the application of screening-test results to environmental situations with easily degradable and resistant compounds gave good qualitative comparisons, but that application to compounds of intermediate degradability resulted in extremely variable comparisons. Smith and Dragun (1984) concluded that the high metabolic efficiency of laboratory cultures was unlikely in ground-water aquifers. Conversely, Battersby (1990) observed that the high concentrations of organic compounds used in laboratory biodegradability tests can result in underestimation of degradability in all natural waters except the most polluted. Similarly, Larson (1983) reported that results from biodegradability screening tests did not directly correlate with results in environmental tests for all compounds tested, but that degradation rates from the screening tests tended to underestimate the potential for degradation in the environment. Also, laboratory degradation rates for high compound concentrations underestimated the degradation rates at more realistic environmental concentrations. Boethling and Alexander (1979) cautioned against the extrapolation of laboratory coefficients to the environment because environmental concentrations usually are much lower than the concentrations used in laboratory experiments, and laboratory degradation rates at relatively high concentrations are much higher than rates at concentrations likely to be present in environmental waters. Similarly, Kuhn and others (1985) concluded that differences in concentration between the laboratory and field situations complicated the quantitative comparison of results. In summary, this discussion of applying the results of laboratory degradation studies to field situations and the differences of opinion expressed in these references indicate the difficulty of such applications.

The concentrations in laboratory degradation studies usually are higher than the concentrations in most environmental situations. The concentration of the organic compound can have several effects on the degradability in environmental situations. If the concentration is too low, then the mechanisms for uptake by the cells may be inadequate, the enzymes necessary for degradation may not be induced, and there may be insufficient energy, even for maintenance of the community population (Grady, 1985; Fewson, 1988). The existence of threshold concentrations below which microbial degradation does not occur has been established. Battersby (1990) pointed out that natural biodegradable compounds such as glucose, glycerol, and lactate have threshold concentrations below which they do not degrade. Typical threshold concentrations for many anthropogenic compounds are in the range of 0.1 to 1 mg/L (Kobayashi and Rittmann, 1982), although the threshold concentration may be dependent on the compound (Battersby, 1990). Also, Boethling and Alexander (1979) noted that the presence of other utilizable carbon sources in the system may lower the threshold concentration for the compound of interest. There also is evidence that organic compounds that are usually degradable are persistent at low concentrations (Scow, 1990). Conversely, high concentrations of the organic compound may be toxic or inhibitory to the microbial community (Grady, 1985; Fewson, 1988). The optimum concentration for microbial degradation is dependent on the characteristics of the organic compound and the microbial species, with the possibility of a shift in the order and rate of the kinetics as the organic compound is depleted during the degradation process (Scow, 1990).

The use of pure cultures in laboratory studies also may complicate application of the resultant rate coefficients in the environment. Mixed cultures may degrade organic compounds that are resistant to pure cultures (Smith and Dragun, 1984); consequently, lack of degradation in laboratory studies with pure cultures is not necessarily a good criterion for predicting behavior in the environment (Kobayashi and Rittmann, 1982; Grady, 1985). Examples of the importance of mixed cultures are cometabolism and sequential degradation where initial transformation products are degraded by another microbe or series of microbes (Bedding and others, 1983).

Other factors contribute to differences between laboratory and environmental degradation studies. Sediments in the environment are important because they affect the concentrations of bacteria and nutrients (Boethling and Alexander, 1979). Bacteria attached onto sediments often have a higher rate of growth and, therefore, a higher rate of degradation of organic compounds than free-floating bacteria (Battersby, 1990). This has been attributed to concentrations of nutrients sorbed on the sediments that are higher than concentrations in the accompanying water. The importance of nutrients was demonstrated by Bouwer (1989), who observed that the biotransformation of aromatic compounds in pond water increased markedly when acetate, nitrogen, and phosphorus were added. Swindol and others (1988) observed that the effect of nutrients varied among the compounds under study with different samples of sediment from the same horizon of an aquifer. They found, contrary to expectations, that the addition of ammonium sulfate decreased the biotransformation of 1,2-dibromoethane and methylbenzene.

Temperature also is important in microbial degradation. Growth of microbes has been observed from −12°C to 100°C, and organisms are sometimes classified into three groups according to temperature (Scow, 1990). Psychrophiles are active at temperatures less than 25°C, mesophiles are active between 25°C and 40°C, and thermophiles are active above 40°C. Most laboratory studies are done in the temperature range from 20°C to 25°C. Consequently, if psychrophilic bacteria are involved and laboratory degradation coefficients are extrapolated to lower environmental temperatures, errors will result because psychrophilic bacteria have an optimum growth rate at a temperature less than 15°C.

MICROBIAL DEGRADATION OF THE TARGET ANALYTES

Microbial degradation of VOCs in surface waters has not been studied extensively. Painter and King (1985) considered the problem of aerobic microbial degradation of VOCs possibly to be nonrelevant, presumably because volatilization rates will normally be much higher than microbial degradation rates. Grady (1985) noted that VOCs may appear to be recalcitrant because they are lost by volatilization before adaptation can occur and a microbial community capable of degrading the compounds can develop.

Two types of source conditions for VOCs in surface waters are important. The first type is the continuous discharge of a wastewater containing VOCs into a receiving stream. In this situation, microbial degradation of the VOCs may be a significant process because exposure to the VOCs may have been long enough that adaptation will have occurred. The second type is an instantaneous, short-term exposure where the microbial community most likely will not have sufficient time to develop the necessary enzymes for degradation and, therefore, will not be able to adapt to and degrade the VOCs. This type of exposure could result from an instantaneous spill, a short-term continuous discharge such as might occur with a leaking storage tank, stormwater runoff, or other types of intermittent nonpoint sources.

There have been some laboratory determinations of the first-order rate coefficients for microbial degradation of VOCs. One of the most comprehensive of these is the work of Tabak and others (1981), who determined the degradability of the 96 organic compounds on the Environmental Protection Agency (EPA) Consent Decree List. Of these compounds, 31 were target analytes (table 1). The test method was a static-culture-flask screening procedure using biochemical oxygen demand (BOD) dilution water containing 5 mg/L of yeast extract as the synthetic medium and concentrations of the test compounds of 5 and 10 mg/L. Incubation was at 25°C in the dark for 7 days, followed by three weekly subcultures to promote adaptation. Settled domestic wastewater was used as the microbial inoculum.

The results of Tabak and others (1981) indicated that biodegradation of naphthalene was rapid enough that it could be a dominant process determining the fate of this compound in aquatic systems. Significant biodegradation with rapid adaptation was observed for benzene and methylbenzene, with chlorobenzene and ethylbenzene exhibiting somewhat slower rates of adaptation and degradation. A gradual adaptation followed by significant biodegradation was observed for 1,2-, 1,3-, and 1,4-dichlorobenzene and 1,3,4-trichlorobenzene. However, subsequent subcultures for these compounds indicated declining degradation rates. These declining rates were attributed to possible changes in the original heterogeneous microbial population as a result of the subculturing process or accumulation of toxic byproducts during the metabolism process. The chlorinated aliphatics 1,1- and 1,2-dichloroethane and 1,1,1-trichloroethane potentially were degradable after a considerable adaptation period, whereas the tetrachloroethanes might be considered recalcitrant because very extensive adaptation periods appeared to be necessary for these compounds.

Dichloromethane and tetrachloromethane were rapidly degraded, and trichloromethane required adaptation. Bromodichloromethane and tribromomethane had significant losses at the end of the third subculture period, whereas chlorodibromomethane was recalcitrant for the four 7-day incubation periods. Trichloroethene and tetrachloroethene were degraded significantly, with gradual adaptation. The 1,1-dichloroethene compound degraded relatively rapidly, with the *cis*-1,2- and *trans*-1,2-dichloroethenes exhibiting somewhat slower rates of degradation. The 1,2-dichloropropane and 1,3-dichloropropene compounds were essentially biodegradable, with gradual adaptation and relatively high degradation rates. Also, hexachlorobutadiene had 100-percent loss at the end of the first 7-day incubation period. Both 2-propenal and 2-propenenitrile showed rapid adaptation and significant biodegradation.

The results presented by Tabak and others (1981) were qualitative in nature. Schnoor and others (1987) did a quantitative analysis of these data and presented first-order rate coefficients as defined by equation 71 for 24 target analytes. Coefficients ranged from 0 for 1,1,2-trichloroethane to 0.37 day^{-1} for 1,1,1-trichloroethane.

These results indicate that most of the VOCs were subject to microbial degradation. However, these measurements were for idealized conditions in the laboratory where extensive steps were taken to encourage adaptation to the compounds of interest. Also, the concentrations used were 5 and 10 mg/L, which are higher than most concentrations likely to be measured in the environment.

Other limited data on the microbial degradation of VOCs in surface water exist. Bouwer (1989) observed high rates of degradation of aromatic VOCs in water from a strip-pit pond formed as a result of coal-mining operations, but only after amendment with nutrients. Degradation-rate coefficients ranged from 3.6 day^{-1} for 1,2-dimethylbenzene to 6.7 day^{-1} for styrene. Without the nutrient amendment, significant concentrations of all compounds except styrene remained after 43 days of incubation. Lee and Ryan (1979) observed degradation of benzene and chlorobenzene in river water, after some unspecified adaptation period. Degradation-rate coefficients were 0.11 day^{-1} for benzene and 0.0045 day^{-1} for chlorobenzene. Vaishnav and Babeu (1987) determined degradation-rate coefficients for benzene and naphthalene in ground water, river water, and harbor water by using adapted microbial seeds and media supplemented with nutrients. Benzene had degradation-rate coefficients of 0.025 day^{-1} in ground water and 0.044 day^{-1} in river water, and insufficient concentration changes in the harbor water for computation of a rate coefficient. Naphthalene showed no significant changes in any of the water samples, in contrast to the results of Tabak and others (1981), who concluded that naphthalene was readily degradable. Bouwer and others (1981) studied the microbial degradation of halogenated 1- and 2-carbon organic compounds under aerobic and anaerobic conditions. None of the compounds indicated any degradation at initial concentrations from 8.8 to 85 µg/L after 25 weeks of aerobic incubation. Degradation was observed, however, in the deoxygenated anaerobic medium in the presence of methanogenic bacteria for trichloromethane, bromodichloromethane, and chlorodibromomethane, but not for trichloroethene or tetrachloroethene.

Anaerobic conditions are not likely to exist in the main flow of streams, but may exist in bottom sediments. If VOCs exist in the bottom sediments, then anaerobic degradation may be a significant fate-determining process, particularly if the VOCs are sorbed to sediments, which will minimize volatilization. Presence of VOCs in bottom sediments has been established for a river estuary (Pereira and others, 1988), a lake (Ferrario and others, 1985), and rivers (Gotoh and others, 1992). A study (Van Beelen and Van Keulen, 1990) of the anaerobic degradation of trichloromethane and benzene in the presence of river sediments indicated first-order rate coefficients of 0.058 day^{-1} and 0.27 day^{-1} at 10°C and 20°C for trichloromethane, but little degradation for benzene.

The lack of rate coefficients for the microbial degradation of VOCs in surface water is emphasized by the compilation of Howard and others (1991). They assembled environmental degradation rate coefficients expressed as half-lives for 331 chemicals, where the half-life ($t_{0.5md}$) is the time required for the concentration to be reduced by microbial degradation to one-half of the initial concentration. Half-lives were assembled for a number of biotic and abiotic processes including aerobic biodegradation in water and soil and anaerobic biodegradation. Half-lives for microbial degradation based on grab samples of surface water or river die-away studies were preferred to half-lives determined from screening tests or field studies under controlled conditions. A river die-away test involves collecting a sample of river water, adding the organic compound of interest, and determining in the laboratory the decrease with time of the concentration of the compound (Burns, 1982). Temperature and bacterial population densities are maintained at ambient levels.

However, data were not available for a substantial number of compounds. In the absence of the preferred type of data, screening tests were evaluated, and high and low values of the half-lives were estimated. When there were few data or conflicting data, scientific judgment was used to adjust and/or estimate the high and low values of the half-lives. In the absence of data for a specific compound, half-lives for related compounds were used in some cases.

Of the 331 compounds included in the compilation of Howard and others (1991), 45 were VOC target analytes (table 1). High and low values of the half-lives for these target analytes for aerobic and anaerobic microbial degradation were converted to first-order rate coefficients by using

$$K'_d = \frac{0.693}{t_{0.5md}} \qquad (72)$$

where

K'_d is the pseudo first-order rate coefficient (day^{-1}) for microbial degradation defined by equation 71, and

$t_{0.5md}$ is half-life (days) for microbial degradation previously defined.

Because of the general lack of the preferred type of experimental data and the subsequent scientific judgment used in estimating half-lives, the values of the half-lives for aerobic microbial degradation fall into the general categories of 6 months to 1 year, 4 weeks to 6 months, and 7 days to 4 weeks. Target analytes having these half-lives are presented in tables 9, 10, and 11. High and low values of the rate coefficients for anaerobic microbial degradation of these target analytes are presented in the tables also. Half-lives for 13 target analytes did not fall into these three general classifications for aerobic degradation, and first-order rate coefficients for both aerobic and anaerobic degradation for these 13 analytes are presented in table 12.

Table 9. Estimated rate coefficients for anaerobic microbial degradation of six target analytes with estimated half-lives for aerobic microbial degradation between 6 months ($K'_d = 0.0038$ day^{-1}) and 1 year ($K'_d = 0.0019$ day^{-1})

[K'_d, pseudo first-order rate coefficient for microbial degradation; USGS, U.S. Geological Survey]

USGS parameter code	Compound	Anaerobic rate coefficient (day^{-1})	
		High	Low
32102	tetrachloromethane	0.099	0.025
34511	1,1,2-trichloroethane	.00096	.00048
34488	trichlorofluoromethane	.0010	.00048
77652	1,1,2-trichloro-1,2,2-trifluoroethane	.00096	.00048
39180	trichloroethene	.0071	.00042
34475	tetrachloroethene	.0071	.00042

Table 10. Estimated and experimental rate coefficients for anaerobic microbial degradation of 15 target analytes with estimated half-lives for aerobic microbial degradation between 4 weeks ($K'_d = 0.025$ day^{-1}) and 6 months ($K'_d = 0.0038$ day^{-1})

[K'_d, pseudo first-order rate coefficient for microbial degradation; USGS, U.S. Geological Survey; *, indicates experimental value]

USGS parameter code	Compound	Anaerobic rate coefficient (day^{-1})	
		High	Low
32106	trichloromethane	0.099	0.025
32104	tribromomethane	.0062	.00096
32105	chlorodibromomethane	.025	.0038
34396	hexachloroethane	.0062	.00096
77651	1,2-dibromoethane	.35*	.046*
82625	1,2-dibromo-3-chloropropane	.0058	.00096
34668	dichlorodifluoromethane	.0062	.0010
39175	chloroethene	.0062	.00096
34501	1,1-dichloroethene	.0086	.0040
50002	bromoethene	.0058	.00096
34536	1,2-dichlorobenzene	.0058	.00096
34566	1,3-dichlorobenzene	.0058	.00096
34571	1,4-dichlorobenzene	.0062	.00096
34551	1,2,4-trichlorobenzene	.0062	.00096
78032	methyl tertiary-butyl ether	.0062	.00096

Table 11. Estimated rate coefficients for anaerobic microbial degradation of eight target analytes with estimated half-lives for aerobic microbial degradation between 7 days ($K'_d = 0.099$ day^{-1}) and 4 weeks ($K'_d = 0.025$ day^{-1})

[K'_d, pseudo first-order rate coefficient for microbial degradation; USGS, U.S. Geological Survey]

USGS parameter code	Compound	Anaerobic rate coefficient (day^{-1})	
		High	Low
34418	chloromethane	0.025	0.0062
34423	dichloromethane	.025	.0062
34413	bromomethane	.025	.0062
34311	chloroethane	.025	.0062
77135	1,2-dimethylbenzene	.0038	.0019
85795	1,3-dimethylbenzene	.025	.0013
85795	1,4-dimethylbenzene	.025	.0062
77222	1,2,4-trimethylbenzene	.025	.0062

Analysis of tables 9, 10, 11, and 12 indicates that the rate coefficients for anaerobic microbial degradation are smaller than the rate coefficients for aerobic degradation for all compounds, with the exception of several halogenated compounds. High and low anaerobic coefficients for tetrachloromethane, trichloromethane, and 1,2-dibromoethane were larger than the corresponding aerobic coefficients. Coefficients for trichloroethene, tetrachloroethene, and 1,1-dichloroethene were mixed, in that some anaerobic coefficients were larger than the corresponding aerobic coefficients and some were smaller. Anaerobic and aerobic coefficients for chlorodibromomethane were the same, within experimental error.

Scientific judgment was required in the estimation of most of the microbial degradation coefficients in tables 9, 10, 11, and 12. The only coefficients not requiring such judgment were the anaerobic coefficients for 1,2-dibromoethane and naphthalene and the aerobic coefficients for benzene, naphthalene, and iso-propylbenzene; these values are marked with an asterisk in tables 10 and 12 to differentiate them from the estimated values. The small number of experimental values indicates the general lack of suitable microbial degradation coefficient data and also that the coefficients in tables 9, 10, 11, and 12 and the accompanying discussion should be considered very qualitative in nature.

All the rate coefficients in tables 9, 10, 11, and 12 are for an unadapted microbial community. Rate coefficients for an adapted microbial community are likely to be larger, but it is difficult, if not impossible, to estimate how much larger because of the great number of variables affecting the degradation process. Tabak and others (1981), in the work discussed previously, used procedures designed specifically to develop adapted communities. Rate coefficients from their work for aerobic degradation ranged from 0 to 0.37 day^{-1}, and this maximum is within the range of coefficients in tables 9, 10, 11, and 12.

PREDICTION OF MICROBIAL DEGRADATION COEFFICIENTS

Some research has been directed toward the development of structure-activity relationships and group contribution calculations that would permit the prediction of microbial degradation coefficients in the absence of experimental data. Desai and others (1990) developed such a model and applied it to first-order degradation coefficients from the literature for 11 compounds, one of which was a target analyte (n-butylbenzene). The percentage differences between the experimental and predicted $\log_e K'_d$ values ranged from −3.39 to 27.4 percent, and the percentage

Table 12. Estimated and experimental rate coefficients for aerobic and anaerobic microbial degradation of 13 target analytes

[USGS, U.S. Geological Survey; *, indicates experimental value]

USGS parameter code	Compound	Aerobic rate coefficient (day^{-1})		Anaerobic rate coefficient (day^{-1})	
		High	Low	High	Low
34496	1,1-dichloroethane	0.022	0.0045	0.0054	0.0011
32103	1,2-dichloroethane	.0069	.0038	.0017	.00096
34506	1,1,1-trichloroethane	.0050	.0025	.0012	.00063
34541	1,2-dichloropropane	.0042	.00054	.0010	.00013
34030	benzene	.14*	.043*	.0062	.00096
77128	styrene	.050	.025	.012	.0062
34696	naphthalene	1.39*	.035*	.028*	.0027*
34010	methylbenzene	.17	.032	.012	.0033
34371	ethylbenzene	.23	.069	.0039	.0030
77223	iso-propylbenzene	.35*	.087*	.087	.022
34301	chlorobenzene	.010	.0046	.0025	.0012
34210	2-propenal	.099	.025	.025	.0058
34215	2-propenenitrile	.55	.030	.14	.0075

differences for the experimental and predicted K'_d values ranged from 10.7 to −44.7 percent. In general, these techniques are in the early stages of development. Because of the complex nature of the microbial degradation process, degradation coefficients predicted by using these procedures should be considered as qualitative estimates only, and therefore, should be used with caution. Also, much of this work has been directed toward the higher molecular weight compounds rather than the lower molecular weight VOC compounds.

Attempts to develop structure-activity relationships have resulted, however, in certain generalizations regarding the biodegradability of organic compounds. Compounds with highly branched structures are usually more resistant to degradation than the corresponding straight-chain structures because branching hinders β-oxidation, which is the process by which straight chains usually are degraded (Howard and others, 1975). Long-chain molecules are degraded more readily than short-chain molecules, and unsaturated aliphatic molecules are more readily degraded than the corresponding saturated aliphatic molecules (Scow, 1990). Substitutions on aromatic rings have different effects, with carboxyl and hydroxyl groups having a tendency to increase degradability and halogens and nitro groups having a tendency to reduce degradability (Howard and others, 1975). Substitutions in the meta position of aromatic rings result in increased resistance to degradation (Kobayashi and Rittmann, 1982). Ether functions are sometimes particularly resistant to microbial degradation (Howard and others, 1975). Finally, highly oxidized compounds such as halogenated compounds may be resistant to further oxidation under aerobic conditions but may be degraded under anaerobic conditions (Scow, 1990). This observation is consistent with the previous discussion that anaerobic degradation coefficients are larger than aerobic degradation coefficients for some chlorinated aliphatic compounds.

ESTIMATION OF THE IMPORTANCE OF MICROBIAL DEGRADATION

Analysis of the rate coefficients for microbial degradation presented and discussed previously indicates that the largest coefficient for any of the target analytes was the value of 1.39 day^{-1} for aerobic degradation of naphthalene (table 12). This analysis excludes from consideration the values of 3.6 day^{-1} for 1,2-dimethylbenzene and 6.7 day^{-1} for styrene (Bouwer, 1989) because the degradation characterized by these coefficients occurred only after amendment of the medium with nutrients. Also, these coefficients were for adapted bacteria and, therefore, apply only to specific conditions.

The change in concentration of a solute with distance due to the effects of multiple first-order processes in a stream can be approximated by

$$C/C_o \cong \exp\left[-(L/U)\sum_{i=1}^{n} K_i\right] \qquad (73)$$

where

C_o is the concentration at the source or zero distance,

C is the concentration at longitudinal distance L,

U is the water velocity, and

K_i is the first-order rate coefficient for process i (Falco and Mulkey, 1976; Rathbun and others, 1988).

If the active processes are volatilization and microbial degradation, equation 73 becomes

$$C/C_o \cong \exp[-(L/U)(K_v + K'_d)] \qquad (74)$$

where

K_v and K'_d are the first-order rate coefficients for volatilization and microbial degradation defined previously by equations 1 and 71, respectively.

Equations 73 and 74 are simplified in that they assume a one-dimensional stream system.

Equation 74 was used to compute the change in the concentration ratio with distance downstream for naphthalene. Computations were done for volatilization alone and for volatilization plus microbial degradation by using both the maximum and minimum coefficients for microbial degradation from table 12. Volatilization coefficients for naphthalene were computed using equations 53, 54, and 55 and procedures discussed previously. Three sets of hydraulic conditions were selected to obtain a large range of volatilization coefficients. These conditions correspond to the extremes of the three rectangles presented in figure 6. For the upper left-hand corner of the O'Connor-Dobbins rectangle, a water velocity of 0.07 m/s and a flow depth of 10 m were used as representative of a deep, low-velocity stream. For the lower right-hand corner of the Owens and others rectangle, a water velocity of 0.56 m/s and a flow depth of 0.12 m were used as representative of a shallow, medium-velocity stream. For the approximate middle of the right-hand edge of the Churchill and others rectangle, a water velocity of 1.52 m/s and a flow depth of 1.5 m were used as representative of an intermediate-depth, high-velocity stream. Distances were selected so as to have approximately 10 percent of the initial concentration remaining at the downstream end of the stream reach for the maximum loss process.

The results are presented in figure 11. For the deep, low-velocity stream, microbial degradation of naphthalene was significant, with even the minimum microbial degradation coefficient contributing substantially to the total loss relative to volatilization alone. The contribution of the minimum coefficient to the loss of naphthalene in the intermediate-depth, high-velocity stream was minimal; however, the maximum coefficient indicated that microbial degradation was still significant relative to volatilization. Finally, results for the shallow, medium-velocity stream indicate virtually little contribution from microbial degradation to the total loss of naphthalene from such a stream because of large losses as a result of volatilization.

The results in figure 11 indicate that microbial degradation of naphthalene is most likely to be important is streams where losses from volatilization are minimal. Volatilization coefficients are inversely proportional to the flow depth and directly proportional to the water velocity. Therefore, microbial degradation is most likely to be important in deep, low-velocity streams, as indicated by the results in the O'Connor-Dobbins section of figure 11. Other target analytes have rate coefficients for microbial degradation (tables 9–12) smaller than the coefficient for naphthalene; therefore, contributions of microbial degradation to the loss of these compounds in streams is expected to be less than for naphthalene. Coefficients in tables 9–12 indicate that microbial degradation is most likely to be important for the aromatic compounds, 2-propenal, and 2-propenenitrile, and less likely to be important for the halogenated alkanes and alkenes. These conclusions, however, must be considered highly qualitative because of the very system-specific and site-specific nature of the microbial degradation process. Each situation must be evaluated to determine if microbial degradation is important in the loss of VOCs from streams.

SORPTION

Streams as depicted schematically in figure 1 contain sediment. This sediment is present both as a suspended phase, which is transported along with the water, and as the materials composing the bottom and banks of the stream. The suspended and bottom sediment phases are not, however, independent of each other. There is a continual exchange of sediment between these phases, with the direction of net exchange dependent on flow conditions. With increasing flows, normally there will be degradation of the bottom and resuspension of sediments into the suspended phase of the stream. With decreasing flows, normally there will be aggradation and settling of sediments to the bottom. With a constant flow and equilibrium conditions, normally there will be a continuous exchange of sediment particles between the suspended and bottom phases; however, there will be no net change in the sediment concentration in the water.

Organic compounds such as VOCs sorb to sediment particles to varying degrees, depending on the characteristics of both the VOC and the sediment. Once sorbed, the transport and fate of the VOC in a water and sediment system (fig. 1) can be quite different from that of a VOC in the water phase alone because of the continuous exchange of sediments between the water and bottom phases. Also, the reactivity of a VOC in the sorbed state may differ substantially from the reactivity in aqueous solution, both in terms of extent of reaction and reaction pathway (Pionke and Chesters, 1973; Karickhoff, 1984). The transport in the downstream direction of the sorbed VOCs will be largely with the suspended sediment of the flow. However, there may be some downstream movement of the sorbed VOCs with the surface bed sediments, depending on the water velocity and the shear stresses at the water/streambed interface. Under conditions of aggradation, some sediment particles with sorbed VOCs may be buried for long periods of time, which could threaten human and ecosystem health long after the initial source of the VOCs has dissipated. Organic compounds buried

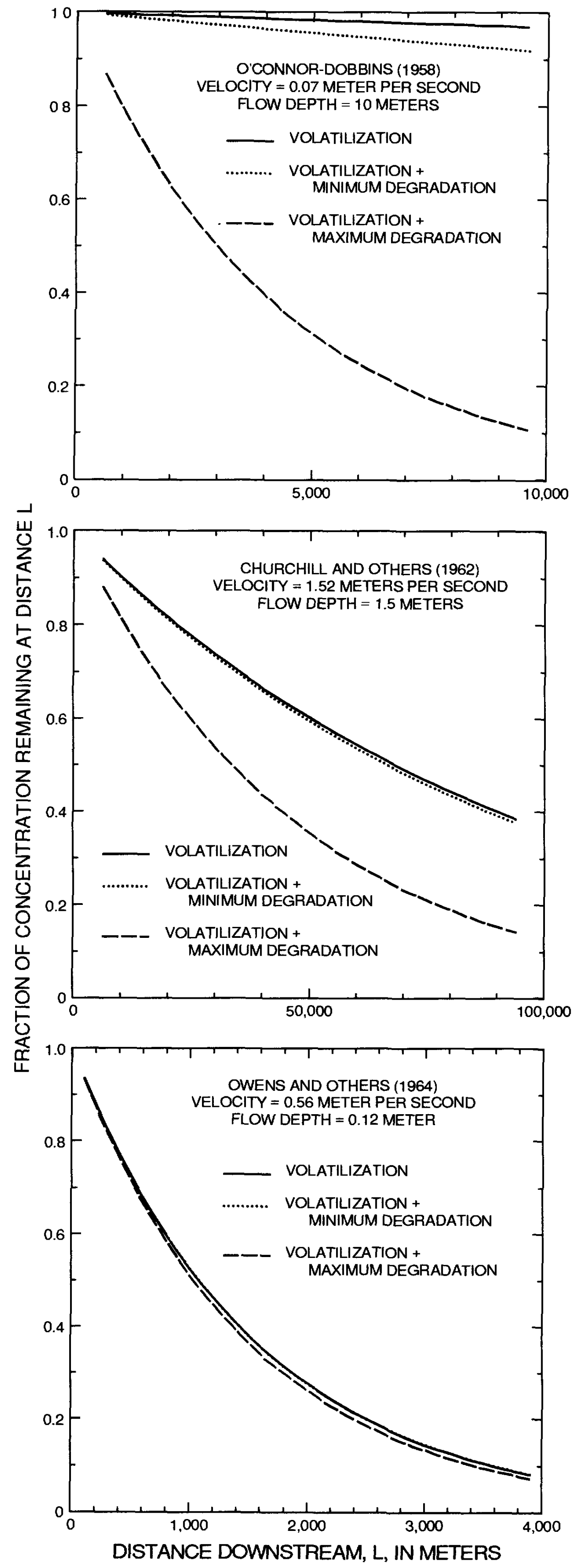

Figure 11. Fraction of the concentration of naphthalene remaining as a function of distance downstream for volatilization and for volatilization and microbial degradation combined at 20 degrees Celsius; Henry's law constant is 36.6 pascals cubic meter per gram mole.

with the sediment may appear in the stream water at a later time during periods of high flow when sediment is being resuspended, or they may gradually desorb from the sediment particles and subsequently move by molecular diffusion through the pore water into the stream water.

FUNDAMENTALS OF THE SORPTION PROCESS

Sorption has been defined as any accumulation of a dissolved organic compound by solid particles (Voice and Weber, 1983). Sorption is generally considered to involve the processes of adsorption and partitioning. Adsorption is the formation of a chemical or physical bond between the organic compound and the mineral surface of the solid particle. Partitioning involves the "dissolution" of the organic compound into the organic matter associated with the solid, much like the dissolution of an organic compound into an organic solvent.

Adsorption to the mineral surfaces of the solid particles can result from physical adsorption due to van der Waal's forces or chemisorption resulting from electronic interactions between the organic molecule and the solid surface (Voice and Weber, 1983). The adsorption process is characterized by high heats of sorption, nonlinear isotherms, and competition between the molecules of the organic compound for the adsorption sites on the solid surfaces (Chiou and others, 1979; Chiou and others, 1983). The partitioning process is characterized by low heats of sorption, linear isotherms, noncompetitive sorption, and a dependence of the sorption coefficient on the water solubility of the organic compound (Chiou and others, 1979; Chiou and others, 1983).

Some debate exists in the literature regarding the relative importance of the adsorption and partitioning processes. Mingelgrin and Gerstl (1983) indicated that there may be a continuum of possible combinations of these two processes, ranging from pure fixed-site adsorption to true partitioning, with the contribution of each depending on the characteristics of both the organic molecule and the solid. Similarly, Voice and Weber (1983) suggested that the actual sorption process may involve varying contributions from different types of reactions but with one type often predominating. Chiou and others (1983) noted for nonpolar molecules that solute partitioning predominates over adsorption because polar water molecules competitively suppress solute adsorption on polar mineral surfaces. Conversely, adsorption may contribute or dominate for highly polar molecules or for solids with low organic-matter contents, especially when the solids also have a high clay content (Karickhoff, 1984).

Studies of the sorption of nonpolar organic compounds, including several VOCs, on various soils and sediments indicated that the isotherms were linear over wide concentration ranges and that the sorption coefficients were dependent on the water solubilities of the compounds (Chiou and others, 1979; Chiou and others, 1983; Kile and others, 1995). Such behavior is consistent with the partitioning process being dominant for these compounds. Therefore, because the target analytes (table 1) are nonionic compounds, sorption to solids is expected to be largely a partitioning process.

SORPTION COEFFICIENTS

The defining equation for the sorption coefficient is

$$S = K_p C_s \qquad (75)$$

where

S is the mass of organic compound sorbed per unit mass of solid (g/kg),

C_s is the concentration of the compound in the water (g/L), and

K_p is the sorption coefficient (L/kg).

By convention, concentration units are selected such that the mass unit for the solution concentration is the same as the mass unit for the sorbed compound on the sediment (Karickhoff, 1984). Thus, typical units for K_p are L/kg or mL/g. Equation 75 indicates a linear isotherm with constant partitioning. Values of K_p are determined from laboratory measurements of the sorbed concentration as a function of the water concentration at constant temperature and constant solids concentration. Sorption isotherms determined in this way usually are linear if the organic-compound concentration is less than the smaller of 10^{-5} molar or about one-half the water solubility (Karickhoff, 1981).

The Freundlich isotherm also is used to describe sorption data. This isotherm has the form

$$S = K_f C_s^{1/n} \qquad (76)$$

where

K_f and n are the constants of the isotherm.

The Freundlich K_f has been used extensively to quantify the extent of sorption and to compare different solids, solutes, and experimental conditions (Voice and Weber, 1983). Values of n usually range from 0.7 to 1.1, although extremes of 0.3 and 1.7 have been observed (Lyman, 1990c). This parameter n indicates the degree of linearity of the isotherm. When n = 1.0, the isotherm is linear, and equation 76 reduces to equation 75 and $K_f = K_p$. Weber and others (1983) found that sorption of PCBs on various solids was best described by the linear model (eq. 75) over narrow ranges of concentrations and by the Freundlich model (eq. 76) over larger concentration ranges.

Sorption of nonpolar organic molecules is largely partitioning into the organic matter of the solids. This organic matter usually is indicated by the organic-carbon fraction of the solids. Consequently, sorption coefficients commonly are normalized with the organic-carbon fraction to give

$$K_{oc} = \frac{K_p}{f_{oc}} \qquad (77)$$

where

K_{oc} is the normalized sorption coefficient (L/kg oc), and

f_{oc} is the weight fraction of organic carbon in the solid.

The weight unit for K_{oc} is on a kg of organic carbon (oc) basis rather than a kg of solids basis. Such normalization reduced a twentyfold to thirtyfold variation in K_p for sorption of phenanthrene and pyrene on various soils and sediments to less than a twofold variation in K_{oc} values (Karickhoff, 1981). Similar behavior was noted for benzene, naphthalene, and anthracene. However, in another study (Weber and others, 1992), normalization of the Freundlich K_f values for three solutes on six soils did not reduce the data to a single isotherm. Kile and others (1995) determined that K_{oc} values for tetrachloromethane and 1,2-dichlorobenzene for large sets of soils and bed sediments were relatively constant for each type of solid, although the values for the bed sediments were about twice those for soils.

Several authors (Mingelgrin and Gerstl, 1983; Friesel and others, 1984; Chiou and others, 1985) used soil organic-matter fraction rather than soil organic-carbon fraction. The soil organic-matter fraction can be converted to the soil organic-carbon fraction by dividing by 1.724 (Kenaga and Goring, 1980). This procedure is approximate, however, in that it assumes the soil or sediment organic-matter consists of 58 percent carbon (Smith and others, 1988). If precise values are needed, the organic-carbon fraction should be measured.

Normalizing the sorption coefficient with the fraction of organic carbon removes much, but not all, of the variability observed for the sorption of the same organic compound on different soils and sediments. For example, Garbarini and Lion (1985) determined that the K_{oc} values for methylbenzene on a variety of sorbents varied by a factor of 2.5, and the sorbents that had the highest and lowest organic-carbon fractions had almost the same K_{oc} value. This K_{oc} value also was the largest for methylbenzene for all the sorbents considered. Sorption coefficients compiled from the literature by Mingelgrin and Gerstl (1983) and normalized with the organic-matter fraction also showed considerable variability. Factors contributing to this remaining variability include inherent differences in the sorption characteristics of the organic matter of the different soils, differences in experimental procedures, and contributions of other soil properties and constituents to the sorption process (Kenaga and Goring, 1980). Much of this remaining variability is eliminated by using a consistent experimental procedure, as was demonstrated for a large number of sediments and soils by Kile and others (1995).

FACTORS AFFECTING THE SORPTION PROCESS

In addition to the organic-carbon fraction of the solids, the sorption process also may depend on other factors such as temperature, pH, size distribution and surface area of the solids, salinity, clay mineral composition, and cation exchange capacity (Hamaker and Thompson, 1972; Karickhoff, 1984; Lyman, 1990c).

Experimental studies of the effect of temperature are limited and sometimes contradictory. Huang (1971) determined that temperature had no significant effect on the sorption and desorption of dieldrin on a montmorillonite clay. This result is contrary to expectations because sorption to a clay should be largely adsorption, which is characterized by a high heat of sorption. Chiou and others (1979) determined that the sorption of 1,1,1-trichloroethane on a soil was significantly higher at 20°C than at 3.5°C; conversely, data for 1,2-dichlorobenzene at these temperatures were virtually indistinguishable. This difference in behavior for these two compounds was attributed to the fact that the solubility of 1,2-dichlorobenzene varied little between these temperatures (133 mg/L at 3.5°C and 148 mg/L at 20°C), whereas the solubility of 1,1,1-trichloroethane decreased from 1,790 mg/L at 3.5°C to 1,360 mg/L at 20°C (Chiou and others, 1979). Weber and others (1983) determined that the sorption of a PCB to a river sediment at 12°C was significantly less than at 22°C. Oliver (1985) determined the temperature dependence of the desorption of 20 chlorinated nonionic organic compounds from three sediments from Lake Ontario. Desorption coefficients for 18 of the 20 compounds decreased as the temperature increased from 10°C to 30°C, with percentage decreases ranging from –3.0 to –63 percent and averaging –43 percent. The increases observed for 1,2-dichlorobenzene and one of the PCB compounds were apparently anomalous.

A review of the effect of temperature on the sorption process (ten Hulscher and Cornelissen, 1996) also indicated various and sometimes contradictory results. The extent of sorption decreased as the temperature increased for 1,4-dichlorobenzene and 1,2,4-trichlorobenzene, whereas three measurements for naphthalene indicated a decrease in sorption with increasing temperature for two of the isotherms and an increase for the third. These sometimes contradictory results probably occur because the overall process of sorption consists of a combination of adsorption to the mineral surface and partitioning into the organic matter of the solid, with a continuum of combinations of these two processes possible depending on the characteristics of the compound and the solid (Mingelgrin and Gerstl, 1983). The adsorption process has a high heat of sorption, the partitioning process has a low heat of sorption (Chiou and others, 1979), thus giving a range of possible temperature effects on the sorption process.

Sorption of nonionic organic compounds is affected little in the pH range of 5 to 9 considered normal for surface waters (Lyman, 1990c). Sorption and desorption of dieldrin on a montmorillonite clay (Huang, 1971) at pHs of 6.0, 8.0, and 10.0 indicated that pH had only a slight effect. Hamaker and Thompson (1972) indicated that sorption of neutral molecules would be expected to show virtually no effect as a result of pH changes unless the pH change resulted in significant change of some important property of the soil. They also noted that polar molecules, while not actually forming ionic species, could form hydrogen bonds and, therefore, pH could have some effect for these molecules.

The size distribution and surface area of the solids could affect the sorption coefficient. Richardson and Epstein (1971) observed that sorption of three insecticides on various size classes of particles from two soils was greatest for the <0.08-µm colloidal fraction and the 0.08–0.5-µm fraction. Karickhoff and others (1979) reported that sorption coefficients were very small for the sand sizes, largest for the medium and fine silt sizes, and somewhat smaller for the clay sizes. Karickhoff (1981) concluded that sorption occurred mostly on the fine material and that the sand acted primarily as a diluent. The dependence of the sorption coefficient on particle size can be determined if the organic-carbon fraction of each size fraction is known. However, such information normally is not available.

Voice and Weber (1983) cited three references suggesting an inverse relationship between particle size and sorption; however, the correlations were generally poor. Weber and others (1983) observed increased sorption capacity for sediment particles smaller than 75 µm, which was attributed to the greater organic-carbon fraction of the smaller particles. They concluded that the observed effect of particle size on sorption capacity of natural sediments probably was the result of the nonhomogeneous physicochemical nature of the sediment rather than the particle size itself. Weber and others (1983) also observed that surface area had some effect because the amount of a PCB compound sorbed on a pure montmorillonite clay was greater than on a pure kaolinite clay having a substantially smaller specific surface area. However, amounts sorbed on these pure clays were much smaller than the amount sorbed on a natural clay, presumably because of the partitioning of the PCB compound into the organic matter of the natural clay. This is an experimental example of the dominance of the partitioning process over the adsorption process for sorption on nonionic organic molecules by natural soils and sediments.

Salinity or ionic strength can have a significant effect on the sorption of ionic molecules but have little effect on the sorption of nonionic or nonpolar molecules. In a situation where adsorption was likely dominant, Huang (1971) determined little effect on the sorption of dieldrin on montmorillonite at concentrations of sodium chloride of 0.03, 0.3, and 3.0 percent by weight. In a situation where partitioning was likely to dominate, Karickhoff and others (1979) measured about a 15-percent increase in the sorption coefficient of pyrene on a pond sediment with an organic-carbon fraction of 0.0234 when the salt content was increased from zero to 20 mg/mL. Similarly, Garbarini and Lion (1985) determined no significant effect of 0.1 molar sodium chloride on the sorption of trichloroethene by a commercial humic acid compared with sorption in distilled water.

SOLIDS CONCENTRATION EFFECT

One of the important and controversial issues in the sorption of nonpolar compounds by solids is whether the sorption coefficient depends on the solids concentration. O'Connor and Connolly (1980) determined that the sorption coefficient for four pesticides decreased with increasing solids concentration. DDT showed the greatest effect, and this compound also had the greatest tendency to partition to the solids. Similarly, Voice and others (1983) determined that the sorption coefficients of chlorobenzene, naphthalene, and two PCBs on sediments from Lake Michigan decreased with increasing solids concentration. They observed about an order of magnitude increase in the partition coefficient for every two orders of magnitude decrease in the solids concentration. They concluded that this phenomenon was the result of the presence of microparticles from the sediments that were in solution and not removed by the conventional separation procedures such as centrifugation and filtration used to separate the solids from the water.

Other investigations also have attributed the observed concentration dependence to experimental artifacts. Karickhoff (1984) suggested the effect is the result of failure to achieve sorption equilibrium, which depends significantly on the solids concentration; failure to correct the aqueous phase sorbed concentration for the concentration associated with the colloid phase; and failure to account for sorption to other surfaces, such as the container walls, at low solids concentrations. Gschwend and Wu (1985) demonstrated that sorption coefficients for seven PCBs were constant over a wide range of solids concentrations if precautions were taken to account for sorption to nonsettling or colloidal particles. Standard laboratory procedures such as filtration or centrifugation do not remove such particles, and the compound sorbed to these particles would be incorrectly reported as dissolved rather than as sorbed. A three-phase model including these nonsettling or nonfilterable particles was applied to PCBs sorbed on sediments from Lake Superior, and the results indicated that the colloid-associated PCBs may be the dominant species in surface waters (Baker and others, 1986).

Other studies also have indicated that the observed dependence of the sorption coefficient on the solids concentration is an experimental artifact. McCarthy and others (1986) argued that even relatively small amounts of impurities in the radioactive tracers used for sorption studies could result in underestimates of sorption coefficients, the appearance of irreversible sorption, and sorption coefficients that appeared to decrease as the solids concentration increased. Jepson and others (1995) observed that the sorption coefficient for hexachlorobenzene on natural sediments decreased as the solids concentration increased. This observation was attributed to two factors. For experimental times longer than 10 to 20 days, significant amounts of hexachlorobenzene sorbed to the colloidal matter initially present in the tap water used for the experiments. For experimental times shorter than 10 to 20 days, the slow dissolution of the hexachlorobenzene in the water resulted in the persistence of undissolved hexachlorobenzene. Correction for these two factors resulted in sorption coefficients that were independent of the solids concentration. Thus, the presence of organic material of a molecular size such that the material is in the phase normally considered "dissolved" can significantly affect the results of some sorption experiments, with the effect dependent on the concentration and characteristics of the compound being sorbed.

Sorption of nonpolar organic compounds to colloidal or dissolved organic material can decrease sorption by solids (Hassett and Anderson, 1982), enhance the apparent water solubility (Chiou and others, 1986), or decrease the sorption coefficient as the solids concentration increases (Voice and others, 1983). The importance of these processes depends on the characteristics of both the organic compound and the organic matter. For example, Chiou and others (1986) indicated that solubility enhancement by moderate concentrations of dissolved organic matter is most likely to be important for highly water-insoluble compounds. For a more soluble compound such as 1,2,3-trichlorobenzene with a water solubility of 18.0 mg/L at 25°C, solubility enhancement will be small for dissolved organic-matter concentrations less than 100 mg/L (Chiou and others, (1986).

KINETICS OF THE SORPTION PROCESS

Equations 75 and 76 are equilibrium expressions; that is, K_p and K_f relate the sorbed concentrations to the water concentrations at equilibrium. Many investigators (for example, Schnoor and others, 1982; DiToro and others, 1982; Thomann and DiToro, 1983; Burns, 1983; Corwin, 1986; and Griffioen and van de Meent, 1988) assumed that this linear isotherm (eq. 75) applies in environmental systems. This assumption requires that equilibrium be rapid and reversible so that equilibrium conditions can be maintained on a time scale that is short relative to the water velocity of the stream.

Experimental evidence, however, indicates that the attainment of equilibrium may be slow. Hamaker and Thompson (1972) discussed several studies showing a slow approach to equilibrium. They also noted that the sorption process could contain a very slow step such as intraparticle diffusion, which is diffusion within the pores of the individual solid particles. In this case, an apparent steady-state condition would be reached very quickly, which would be mistaken for equilibrium. Thus, with short equilibration times, a slow drift in this apparent equilibrium concentration would be missed. Equilibration times in many experimental studies were relatively short because of complications that become more important as time increases. Such complications include microbial degradation, hydrolysis, or oxidation of the test compound. Kenaga and Goring (1980) noted that there appeared to be an initial rapid sorption, followed by slow sorption over a long time period. Karickhoff (1980) determined that the sorption of three polycyclic aromatic hydrocarbons could be divided into two stages, with the first stage completed in minutes and the second stage requiring days to weeks for complete equilibration, with the time dependent on the characteristics of the compound. Approximately one-half of the total sorption was completed in the first stage, with this result seemingly independent of the compound or the sediment. Desorption also showed two stages, with an initial fast desorption followed by much slower desorption. Desorption coefficients were consistently smaller than the sorption coefficients; however, the difference was at most a factor of two and, therefore, was not considered significant for these types of data. Pignatello and Xing (1996) summarized several examples in which the apparent sorption coefficient increased from 30 percent to tenfold when contact was increased from short times ranging from 1 to 7 days to long times ranging from 10 to 300 days.

The use of equation 75 and the assumption of equilibrium also assumes sorption is reversible; that is, desorption is described by the sorption isotherm. Such reversibility is usually assumed; however, there are experimental studies showing distinct differences between sorption and desorption isotherms (Horzempa and DiToro, 1983). Rao and Davidson (1982) rationalized that these nonsingular isotherms could be the result of experimental artifacts, failure to achieve complete equilibrium during the sorption process, and microbiological or chemical changes during the experiments. However, consideration of these factors (Horzempa and DiToro, 1983) did not explain the nonsingular isotherms observed for the sorption and desorption of a PCB compound on sediments. Desorption coefficients were substantially larger than sorption coefficients, and desorption appeared to involve two distinct isotherms, with the slower process controlled by strongly bound molecules. Pignatello and Xing (1996) noted that data showed greater and greater resistance to desorption with time, indicating a continuum of resistances. They attributed this to the intrinsic heterogeneity of solids as indicated by polydisperse primary and secondary particles, a wide range of pore sizes, and spatial variations of mineral and organic components on the microscale. Also, they noted that the slow desorption step often was markedly dependent on the initial concentration, resulting from increased intraparticle retardation as the pore concentration decreased.

The observation that some of the molecules appeared to be strongly bound is consistent with the observation (Karickhoff, 1984) that lengthy extraction periods of days, multiple solvents, and/or abrasive mixing techniques are necessary for quantitative chemical recovery in some studies. In other studies (Rutherford and others, 1992), a two-solvent system with an extraction time of 24–48 hours was sufficient to obtain greater than 95-percent recovery in most cases. Karickhoff (1984) noted that the ease of extraction of a sorbed compound decreased as the equilibration time of the experiment increased. The importance of equilibration time on both the magnitude of the measured sorption coefficient and the recovery of the compound during desorption is demonstrated by data for sorption of hexachlorobenzene (Karickhoff, 1984). For equilibration times of 5, 32, and 58 days, the measured sorption coefficients normalized for the organic-carbon fraction of the sediment (K_{oc}) were 7.6×10^4, 1.5×10^5, and 1.9×10^5 L/kg oc, respectively. Thus, the measured sorption coefficient increased as the equilibration time increased. When the desorption study was done using a purge technique, about 90 percent of the hexachlorobenzene was recovered from the 5-day equilibration time sample with 2 days of purging. Conversely, for the 32- and 58-day equilibration time samples, 20 days of purging was necessary to recover about 90 and 85 percent, respectively, of the hexachlorobenzene. These results clearly demonstrate that the sorption-desorption process is at some point controlled by diffusion of the organic molecules into or out of the particle aggregates and the associated organic-carbon matter.

The importance of equilibration time and the need for long times in laboratory sorption studies are indicated by two studies. Jepson and others (1995) studied the sorption of hexachlorobenzene to sediments from the Detroit River. They concluded that a steady-state equilibrium was always attained. However, equilibration times of from 2 to 5 months were necessary. Brannon and others (1995) measured the sorption of two PCB compounds and one polycyclic aromatic hydrocarbon compound to three sediments over a 6-month period. They observed that the value of the sorption coefficient normalized with the organic-carbon fraction increased slowly with time throughout the equilibration period. They attributed this slow increase to intraparticle diffusion of the organic compounds.

Kinetic models of the sorption-desorption process have been developed (Karickhoff and Morris, 1985; DiToro, 1985). On the basis of previous observations in the literature, Karickhoff and Morris (1985) developed a two-component model that considered a rapid or labile sorption requiring a few hours to complete and highly retarded or nonlabile sorption requiring days to weeks to complete. Application of this model to the sorption of pyrene, pentachlorobenzene, and hexachlorobenzene to various sediments and soils indicated that the fraction of the sorption that was labile ranged from 0.25 to 0.6. However, for highly hydrophobic compounds and high solids concentrations, the labile fraction was 0.1 or less. The more highly sorbed compounds sorbed at the slowest rates. Desorption studies using a purge technique indicated no irreversible bonding; however, in some cases, recovery of the final 10 percent of the compound required more purge time than the time used for the first 90 percent. DiToro (1985) developed a model that assumes the sorbed compound consists of a reversible component and a component that does not appreciably desorb under the conditions of the experiment. The key assumption of the model is that the linear isotherm applies both to the sorption and desorption of the reversible component. The resultant model contained three parameters that were determined from a data set of 128 partition coefficients by using a nonlinear least-squares procedure. The agreement between calculated and experimental partition coefficients was good. This analysis indicated that the reversible sorption coefficient normalized with the organic-carbon fraction was equal to the octanol-water partition coefficient, indicating that partitioning into the organic carbon was physically the same as partitioning into octanol.

The subject of reversibility was considered also by Gschwend and Wu (1985). They conducted sorption-desorption experiments by using a PCB compound and prewashed sediments from Lake Superior. Sorption and desorption isotherms were identical. The purpose of the prewashing was to remove nonsettling colloidal material. They also demonstrated through calculations that the nonsingular isotherms observed by DiToro and Horzempa (1982) could be explained by the presence of nonsettling microparticles or colloidal material. These particles and/or colloidal material served as sorbing media but were treated in the analytical technique as part of the dissolved phase.

SOLIDS, SOILS, AND SEDIMENTS

Most of the previous discussion referred to the sorbing media in sorption studies as the "solids" phase. "Solids" is a generic term used to define any solid particle to which organic molecules can sorb or adsorb. This particle may or may not contain organic matter. The terms "soils" and "sediments" also have been used in a few specific cases in the previous text. Soils and sediments are not the same, however.

Soils are units formed at the Earth's surface and have distinctive zones characterized by differences in mineralogy, organic content, texture, and structure (Leopold and others, 1964). The two fractions having the most effect on sorption are the mineral fraction and the organic fraction. The mineral fraction consists primarily of layer silicates (clays) and metal hydroxides (Tinsley, 1979). The organic fraction is tightly bound to the mineral fraction, and is generally considered to consist of humin, humic acids, and fulvic acids (Tinsley, 1979). Humin is operationally defined as the material that cannot be extracted by alkaline reagents; humic acids are the fraction extracted by the alkaline reagents that precipitate upon acidification; fulvic acids are the fraction remaining in solution.

Karickhoff and others (1979) defined a sediment as an eroded soil that has been subjected to continuous redispersion and particle-size fractionation. These processes begin with runoff from the soil surface and continue with subsequent transport in the stream system. Transport within the system in controlled primarily by grain size, which can range from gravel and boulders to colloids.

One classification of sediment according to grain size is given in table 13 (Chow, 1964). Particles generally have different organic-carbon fractions and different surface areas for the different size classes. Consequently, their capacity for sorption of organic compounds varies from size class to size class, mostly because the organic-matter fraction varies approximately inversely with the particle size. Sediments from different drainage basins are likely to have different distributions of these types of particles within the sediment and, consequently, different sorption characteristics. Normalization with the organic-carbon fraction of the sediment removes much, but not all, of this variation. Karickhoff and others (1979) cited an example of the effect of grain size where two hydrophobic compounds concentrated in the clay fraction and a more soluble compound concentrated on the larger particles.

The organic matter associated with soils and sediments also undergoes changes with time. These changes, referred to as diagenetic alteration (Young and Weber, 1995), involve conversion by biotic and abiotic processes of biopolymers such as carbohydrates, proteins, and lipids to humic substances such as fulvic acids, humic acids, and humin. Over longer time periods and under more extreme conditions, these humic substances are converted to materials such as kerogens, coals, or graphite. This diagenetic alteration usually results in removal of oxygen-containing functional groups, increases in molecular weight, and increases in the fraction of carbon present in condensed aromatic nuclei compared with the fraction present in the aliphatic linkages (Young and Weber, 1995). In qualitative terms, Young and Weber (1995) modeled soil organic matter as a macromolecule with a structure ranging from one that is completely amorphous (fulvic acids) in a relatively young soil to one that is increasingly condensed as diagenetic alteration occurs, eventually becoming highly crystalline in an old organic-carbon structure such as anthracite coal.

The fact that soils and sediments and the associated organic matter have different properties results in different sorption characteristics. Kile and others (1995) determined the sorption of tetrachloromethane and 1,2-dichlorobenzene on a number of soils and sediments from various parts of the United States and China. The mean sorption coefficients normalized with the organic-carbon fraction were 1.7 times larger for the sediments than for the soils. This difference indicates that the erosion process that converts soils into sediments results in a change in the characteristics of the organic matter. Kile and others (1995) hypothesized that the erosion process and subsequent water transport result in dissolution of the more polar and more water-soluble constituents of the organic matter, leaving the less polar organic constituents associated with the sediments. Analysis of 17 soil and 7 sediment samples by ^{13}C nuclear magnetic resonance (NMR) spectroscopy indicated median polar organic-carbon contents of 51.6 and 42.2 percent for the soils and sediments, respectively, supporting this hypothesis (Kile and others, 1996).

Table 13. Classification of sediments according to grain size (from Chow, 1964)

[mm, millimeter; µm, micrometer (10^{-6} meter); >, greater than; <, less than]

Class	Grain size
Gravel, boulders	>2 mm
Sand	<2 mm, >64 µm
Silt	<64 µm, >5 µm
Clay	<5 µm, >0.5 µm
Colloid	<0.5 µm

The dividing line between soils and sediments is not always definitive, however, because the exact time of erosion from the land surface is unknown. Kile and others (1995) determined a sorption coefficient for one sediment sample from a creek that was significantly lower than the values for other sediments but was similar to the coefficients for the soils. They attributed this result to the fact that this sediment may have been a recently eroded soil. Values for two other sediments were somewhat lower than expected, possibly indicating that the conversion from a soil to a sediment was incomplete. Sorption coefficients for sediments from large rivers and lakes were comparable, presumably because the sediments were aged and had little contribution from recently eroded soils.

Kile and others (1995) limited their soils and sediments to those with organic-carbon contents greater than 0.1 percent, and they used relatively nonpolar solutes to emphasize the partitioning part of the adsorption process. For solutes with higher polarities and sorbents with lower organic-carbon contents, adsorption to the mineral surfaces may be important. Such adsorption will result in higher overall sorption coefficients.

Karickhoff (1984) presented some general guidelines for estimating the contribution of mineral adsorption to total sorption. These are listed in table 14. The target analytes (table 1) are largely nonpolar, and all have less than 10 carbon atoms. Therefore, the results in table 14 indicate that the sorption coefficient normalized with the organic-carbon fraction, K_{oc}, will be from 50 to 100 times the coefficient for sorption to the mineral surfaces, K_m. Also, the threshold ratio indicates that mineral adsorption will become important only for soils and sediments with a mineral fraction greater than 60 times the organic-carbon fraction. These results indicate that partitioning of the target analytes into the organic matter of sediments is likely to be much more important than adsorption to the mineral surfaces for most environmental situations.

Other natural sorbents that may contribute to the behavior of VOCs in a stream system (fig. 1) are colloids, microorganisms, and algae. Colloids are of such a size (table 13) that they will not be separated from the water phase by common filtration and centrifugation techniques. Consequently, colloids and any organic compounds sorbed to the colloids will be treated as dissolved by normal laboratory separation techniques. This effect has been proposed as an explanation for both the solids concentration dependence of the sorption coefficient and nonsingularities in the sorption-desorption isotherms. Also, Hassett and Anderson (1982) noted decreased sorption of two hydrophobic organic compounds from concentrated solutions of dissolved organic matter when compared with sorption from distilled water or an unconcentrated solution of the organic matter. This effect was attributed to sorption of the compounds by the dissolved organic matter. Thus, sorption to the colloid phase can be a very important process in understanding the sorption of organic compounds in a stream system. Sorption to microorganisms and algae is discussed in the next section.

Table 14. Threshold values of the ratio of the mineral fraction to the organic-carbon fraction at which mineral adsorption becomes important for three types of organic compounds (from Karickhoff, 1984)

[K_{oc}, sorption coefficient normalized with the organic-carbon fraction by weight; K_m, mineral sorption coefficient; cm, fraction by weight of mineral in the sediment; oc, fraction by weight of organic carbon in the sediment; <, less than; >, greater than; C_{10} denotes molecule with 10 carbon atoms]

Type of compound	$\frac{K_{oc}}{K_m}$	Threshold
		$\frac{cm}{oc}$
Neutral organics with polar functional groups	10–50	25–60
Small nonpolar organics ($<C_{10}$)	50–100	>60
Large nonpolar organics ($>C_{10}$)	>100	insignificant at any value

SORPTION TO OTHER SORBENTS

The widespread occurrence of VOCs has resulted in the need for information on the sorption of VOCs to surfaces in addition to the soils and sediments of the environment. Dobbs and others (1989) measured the sorption of six VOCs and seven high-molecular-weight compounds on primary, mixed-liquor, and digested solids from municipal wastewater-treatment plants. These solids had organic-matter contents ranging from 65 to 85 percent, which are much higher that the organic-matter contents of natural soils and sediments. When the sorption coefficients were normalized with the organic-matter content, the coefficients were equivalent for all the solids.

Steen and Karickhoff (1981) studied the sorption of two polycyclic aromatic hydrocarbon compounds to bacterial populations isolated from 14 soils and sediments. The results indicated that sorption coefficients normalized with the bacterial mass were nearly independent of the source of the bacteria. When the sorption coefficients were normalized with the carbon content of the bacteria, the resultant sorption coefficients approximated the values of the coefficients for sorption of the two compounds to soils and sediments.

A study (Whitman and others, 1995) of the sorption of naphthalene in a system containing both soil and bacteria indicated that sorption to the bacteria was negligible when the soil had an organic-carbon content of 5.1 percent. However, when a clean sand containing no organic carbon was used, as much as 10 percent of the initial naphthalene was sorbed to the bacteria.

Weber and others (1983) measured the sorption of a PCB compound to samples of live and dead bacteria and algae. The sorption coefficient for the live bacteria was about 10 percent larger than the coefficient for the dead bacteria. The sorption coefficient for the live algae was more than twice the coefficient for dead algae. This result indicates movement of the molecules into the viable cells of the algae, allowing for more surface sorption. The sorption coefficient for the live algae was the largest measured for any of the sorbents and was about 11 times larger than the largest measured coefficient for natural stream sediments and suspended solids.

VOCs in snow also may involve sorption processes. Czuczwa and others (1988) noted that snow contained the highest concentrations of alkylbenzenes in all types of precipitation. They also determined that concentrations of all the compounds considered in the study were the highest in winter precipitation, possibly indicating the contribution of a sorption process. This possibility has resulted in fundamental studies of the processes involved in the sorption of VOCs by ice and snow (Goss, 1993; Hoff and others, 1995). Preliminary results indicated that sorption of nonpolar organic molecules to ice surfaces is similar in magnitude to that for a water surface, although some data indicated ice sorption may be as much as a factor of two greater than for sorption to water surfaces.

A combined soil-sorption and snow-sorption event was observed in the central Canadian Arctic when brown snow occurred (Welch and others, 1991). Various organic compounds were detected in the brown snow, melted snow, and sorbed to the soil particles in the snow. Most of these were high-molecular-weight trichlorobenzenes, pesticides, and polycyclic aromatic hydrocarbon compounds. Naphthalene, one of the target analytes (table 1), was one of the dominant polycyclic aromatic hydrocarbons. Air-mass trajectories, clay-mineral composition of the soil particles, and visible organic detritus such as straw indicated an Asian source of these materials. The source of the organic compounds could not be estimated with the same certainty because of unknown sources and source strengths and also possible atmospheric transformations.

EXPERIMENTAL SORPTION COEFFICIENTS

Much of the experimental work on aqueous sorption to sediments and soils has been directed toward pesticides and PCB compounds because these compounds have low water solubilities and, therefore, are most likely to be involved in sorption processes. Sorption coefficients have been measured, however, for a number of VOCs on the target analyte list (table 1). These experimental sorption coefficients are presented in table 15 as K_{oc} values, that is, sorption coefficients normalized with the organic-carbon fraction, along with information on the type of sorbents used in the studies and the organic-carbon fractions of these sorbents. Average coefficients for each VOC were not computed because of expected differences in the sorption characteristics of the various sorbents. Although normalization of the sorption coefficient with the organic-carbon fraction removes much of the variation among sorbents, normalization does not remove all the variation.

Aqueous sorption coefficients in table 15 ranged from 0.05 L/kg oc for methylbenzene on cellulose (Garbarini and Lion, 1986) to 14,800 L/kg oc for 1,2,3-trichlorobenzene on plant cuticle (Boyd and others, 1990). Cellulose was chosen for study because of its abundance in plants and its use in many industrial applications (Rutherford and others, 1992).

Table 15. Experimental sorption coefficients for 27 target analytes

[USGS, U.S. Geological Survey; f_{oc}, fraction of organic carbon by weight; K_{oc}, sorption coefficient normalized with the fraction by weight of organic carbon; L/kg oc, liter per kilogram of organic carbon; ns, not specified; mg/L, milligram per liter; <, less than; >, greater than]

USGS parameter code	Compound	Sorbent	f_{oc}	K_{oc} (L/kg oc)	Reference
34423	dichloromethane	3 sewage solids	0.38–0.49	198	Dobbs and others (1989)
32106	trichloromethane	3 sewage solids	0.38–0.49	243	Dobbs and others (1989)
32102	tetrachloromethane	3 sewage solids	0.38–0.49	771	Dobbs and others (1989)
		Extracted peat	0.640	115	Rutherford and others (1992)
		Peat	0.571	78	Rutherford and others (1992)
		Muck	0.531	52	Rutherford and others (1992)
		Cellulose	0.444	4	Rutherford and others (1992)
		32 soils	0.0016–0.0609	60	Kile and others (1995)
		36 sediments	0.0011–0.0473	102	Kile and others (1995)
32103	1,2-dichloroethane	Soil	0.0093	33	Chiou and others (1979)
34506	1,1,1-trichloroethane	Soil	0.0093	179	Chiou and others (1979)
		32 soils	0.0012–0.31	107	Friesel and others (1984)
34511	1,1,2-trichloroethane	3 soils	0.002	60	Seip and others (1986)
			0.022	64	Seip and others (1986)
			0.037	108	Seip and others (1986)
77651	1,2-dibromoethane	Soils	<0.087	32	Hamaker and Thompson (1972)
		Soils	>0.087	14	Hamaker and Thompson (1972)
		Soil	0.0093	62	Chiou and others (1979)
		Soils	ns	44	Kenaga and Goring (1980)
		Soils	0.00290–0.126	36–160	Mingelgrin and Gerstl (1983)
		3 soils	0.011	135	Steinberg and others (1987)
			0.0161	129	Steinberg and others (1987)
			0.0165	103	Steinberg and others (1987)
34541	1,2-dichloropropane	Soil	0.0093	47	Chiou and others (1979)
82625	1,2-dibromo-3-chloropropane	Soil	0.0093	129	Chiou and others (1979)
		Soils	ns	129	Kenaga and Goring (1980)
34501	1,1-dichloroethene	3 sewage solids	0.38–0.49	293	Dobbs and others (1989)
39180	trichloroethene	32 soils	0.0012–0.31	101	Friesel and others (1984)
		3 soils	0.002	72	Seip and others (1986)
			0.022	96	Seip and others (1986)
			0.037	142	Seip and others (1986)
		7 organic compounds	0.12–0.65	2.0–120	Garbarini and Lion (1986)
		5 soil fractions	0.0014–0.833	106–460	Garbarini and Lion (1986)
		Peat	0.571	58	Rutherford and Chiou (1992)
34475	tetrachloroethene	Soil	0.0093	362	Chiou and others (1979)
		Aquifer material	0.0015	373	Schwarzenbach and Westall (1981)
		32 soils	0.0012–0.31	237	Friesel and others (1984)
		3 soils	0.002	177	Seip and others (1986)
			0.022	205	Seip and others (1986)
			0.037	348	Seip and others (1986)
		3 sewage solids	0.38–0.49	1,720	Dobbs and others (1989)
34704	*cis*-1,3-dichloropropene	Soils	<0.087	26	Hamaker and Thompson (1972)
			>0.087	27	Hamaker and Thompson (1972)
34699	*trans*-1,3-dichloropropene	Soils	<0.087	28	Hamaker and Thompson (1972)
			>0.087	27	Hamaker and Thompson (1972)

Table 15. Experimental sorption coefficients for 27 target analytes—Continued

[USGS, U.S. Geological Survey; f_{oc}, fraction of organic carbon by weight; K_{oc}, sorption coefficient normalized with the fraction by weight of organic carbon; L/kg oc, liter per kilogram of organic carbon; ns, not specified; mg/L, milligram per liter; <, less than; >, greater than]

USGS parameter code	Compound	Sorbent	f_{oc}	K_{oc} (L/kg oc)	Reference
34030	benzene	3 sediments	0.00086–0.0329	83	Karickhoff and others (1979)
		2 soils	0.026	100	Rogers and others (1980)
			0.018	92	Rogers and others (1980)
		17 sediments and soils	0.0011–0.0238	60	Karickhoff (1981)
		Soil	0.0093	31	Chiou and others (1983)
		3 soils	0.002	38	Seip and others (1986)
			0.022	44	Seip and others (1986)
			0.037	54	Seip and others (1986)
		2 soils	0.0094	31	Boyd and others (1990)
			0.0184	38	Boyd and others (1990)
		Corn residues	0.427	40	Boyd and others (1990)
		Plant cuticle	0.99	155	Boyd and others (1990)
		Extracted peat	0.640	32	Rutherford and others (1992)
		Peat	0.571	22	Rutherford and others (1992)
		Muck	0.531	14	Rutherford and others (1992)
		Cellulose	0.444	1	Rutherford and others (1992)
34696	naphthalene	3 sediments	0.00086–0.0329	1,300	Karickhoff and others (1979)
		17 sediments and soils	0.0011–0.0238	870	Karickhoff (1981)
		2 sediments	0.029		Voice and others (1983)
		(10 mg/L)		14,400	
		(100 mg/L)		3,860	
		(300 mg/L)		2,070	
			0.038		Voice and others (1983)
		(10 mg/L)		12,900	
		(100 mg/L)		4,260	
		(300 mg/L)		2,530	
		Soil	0.051	804	Whitman and others (1995)
34010	methylbenzene	Aquifer material	0.0015	247	Schwarzenbach and Westall (1981)
		2 soils	0.0023	77	Garbarini and Lion (1985)
			0.0041	191	Garbarini and Lion (1985)
		7 organic compounds	0.12–0.65	0.05–151	Garbarini and Lion (1986)
		4 soil fractions	0.0014–0.0751	151–348	Garbarini and Lion (1986)
		3 soils	0.002	56	Seip and others (1986)
			0.022	94	Seip and others (1986)
			0.037	134	Seip and others (1986)
34371	ethylbenzene	Soil	0.0093	165	Chiou and others (1983)
		2 soils	0.0094	112	Boyd and others (1990)
			0.0184	187	Boyd and others (1990)
		Corn residues	0.427	132	Boyd and others (1990)
		Plant cuticle	0.99	1,630	Boyd and others (1990)
77342	n-butylbenzene	Aquifer material	0.0015	2,460	Schwarzenbach and Westall (1981)
85795	1,3-dimethylbenzene	3 soils	0.002	129	Seip and others (1986)
			0.022	158	Seip and others (1986)
			0.037	289	Seip and others (1986)
85795	1,4-dimethylbenzene	Aquifer material	0.0015	333	Schwarzenbach and Westall (1981)

Table 15. Experimental sorption coefficients for 27 target analytes—Continued

[USGS, U.S. Geological Survey; f_{oc}, fraction of organic carbon by weight; K_{oc}, sorption coefficient normalized with the fraction by weight of organic carbon; L/kg oc, liter per kilogram of organic carbon; ns, not specified; mg/L, milligram per liter; <, less than; >, greater than]

USGS parameter code	Compound	Sorbent	f_{oc}	K_{oc} (L/kg oc)	Reference
34301	chlorobenzene	Aquifer material	0.0015	260	Schwarzenbach and Westall (1981)
		Soil	0.0093	83	Chiou and others (1983)
		2 sediments	0.029		Voice and others (1983)
		(10 mg/L)		5,000	
		(100 mg/L)		690	
		(300 mg/L)		269	
			0.038		Voice and others (1983)
		(10 mg/L)		6,200	
		(100 mg/L)		1,240	
		(300 mg/L)		579	
		3 sewage solids	0.38–0.49	753	Dobbs and others (1989)
34536	1,2-dichlorobenzene	Soil	0.0093	310	Chiou and others (1979)
		Soil	0.0093	321	Chiou and others (1983)
		Peaty soil	0.17	529	Friesel and others (1984)
		32 soils	0.0016–0.0609	290	Kile and others (1995)
		36 sediments	0.0011–0.0473	502	Kile and others (1995)
34556	1,3-dichlorobenzene	Soil	0.0093	293	Chiou and others (1983)
		Peaty soil	0.17	478	Friesel and others (1984)
34571	1,4-dichlorobenzene	Aquifer material	0.0015	733	Schwarzenbach and Westall (1981)
		Soil	0.0093	273	Chiou and others (1983)
		Peaty soil	0.17	429	Friesel and others (1984)
		Sediment	0.0816	1,070	Wu and Gschwend (1986)
77613	1,2,3-trichlorobenzene	Aquifer material	0.0015	2,650	Schwarzenbach and Westall (1981)
		2 soils	0.0094	1,380	Boyd and others (1990)
			0.0184	1,630	Boyd and others (1990)
		Corn residues	0.427	1,050	Boyd and others (1990)
		Plant cuticle	0.99	14,800	Boyd and others (1990)
34551	1,2,4-trichlorobenzene	Aquifer material	0.0015	2,350	Schwarzenbach and Westall (1981)
		Soil	0.0093	864	Chiou and others (1983)
		Peaty soil	0.17	1,440	Friesel and others (1984)
		Sediment	0.0816	3,250	Wu and Gschwend (1986)

However, despite the high organic-carbon fraction of cellulose (table 15), sorption of VOCs on this sorbent was minimal (Garbarini and Lion, 1986; Rutherford and others, 1992). Plant cuticle is virtually all organic matter, and sorption on this sorbent was about 10 times greater than on soils for ethylbenzene and 1,2,3-trichlorobenzene and about 5 times greater for benzene (table 15). The lesser effect for benzene is presumably because benzene is more soluble than the two substituted benzenes. Sorption of VOCs on the sewage solids with organic-carbon fractions from 0.38 to 0.49 was variable, with the sorption coefficients for some VOCs such as tetrachloroethene being larger than for the other sorbents. This brief discussion of the sorption coefficients for VOCs indicates that normalization with the organic-carbon fraction of the sorbent is not sufficient to remove all the variability of the sorption coefficients.

However, the sorption coefficients presented in table 15 are for sorbents with a much wider range of organic-carbon fractions than will normally be present in streams. Hamaker and Thompson (1972) arbitrarily used an organic-carbon fraction of 0.087 as the dividing line between “real world” or normal soils and sediments and sorbents with high organic-carbon fractions. Many of the sorption coefficients in table 15 are for “real world” soils and sediments. Sorbents with organic-carbon fractions larger than 0.087 are atypical but are included in table 15 because of the possibility that they could be important in some situations. The variability in the sorption coefficients in table 15 indicates that composition of the sorbent also is important because the effect of the organic-carbon fraction has theoretically been removed through the normalization process.

Voice and others (1983) observed that the sorption coefficients for naphthalene and chlorobenzene decreased as the sediment concentration increased as a result of the “solids concentration” effect discussed previously. Consequently, coefficients for these two VOCs are presented in table 15 at three sediment concentrations interpolated from the sorption coefficient-concentration relationships presented by Voice and others (1983). These coefficients are included as an indication of the possible effect of concentration on the sorption coefficient.

PREDICTION EQUATIONS FOR SORPTION COEFFICIENTS

The sorption of nonionic organic compounds by soils and sediments containing organic matter is dominated by the process of partitioning of the organic molecules into the organic matter. Partitioning of the molecules between the water and organic-matter phases is analogous to partitioning between water and an organic solvent. Consequently, sorption coefficients frequently are correlated with the octanol-water partition coefficient. Water solubility also is important because the less soluble a compound, the greater the tendency to partition into the octanol and, by inference, the greater the tendency to sorb to soils and sediments. Thus, sorption coefficients also are correlated with the water solubility of the compound.

Most of the equations resulting from correlation of sorption coefficients with the octanol-water partition coefficient or the water solubility were developed for sorption of pesticides by soils. A few were based on data bases that included chlorinated aliphatic compounds, aromatic and chlorinated aromatic compounds, and polycyclic aromatic hydrocarbon compounds. Equations considered most appropriate for estimating the sorption coefficients for three general classes of VOC compounds are given in table 16. Independent variables were either the water solubility or the octanol-water partition coefficient. Original equations that were normalized with the organic-matter content were converted to organic-carbon content by assuming the organic matter was 58 percent carbon by weight (Smith and others, 1988). Also, original equations having solubilities in millimoles or micromoles per liter were converted to moles per liter, and base e logarithms were converted to base 10.

The data base for equation 78 in table 16 consisted of the target analytes 1,2-dichloroethane, 1,2-dichloropropane, 1,2-dibromo-3-chloropropane, 1,1,1-trichloroethane, 1,2-dichlorobenzene, tetrachloroethene, 1,2-dibromoethane plus one additional VOC, four pesticides, and three PCB compounds. The data base for equation 79 consisted of the target analytes 1,1,1-trichloroethane, trichloroethene, and tetrachloroethene. The data base for equations 80 and 81 consisted of the target analytes benzene and naphthalene plus six other polycyclic aromatic hydrocarbons, one pesticide, and one PCB compound. Equation 82 was based on data for benzene, naphthalene, and three other polycyclic aromatic hydrocarbons. Equation 83 was based on data for the target analytes methylbenzene, 1,4-dimethylbenzene, n-butylbenzene, tetrachloroethene, chlorobenzene, 1,4-dichlorobenzene, 1,2,4-trichlorobenzene, and 1,2,3-trichlorobenzene plus three other alkyl benzenes and two other chlorinated benzenes. The data base for equations 84 and 85 consisted of the target analytes benzene, chlorobenzene, ethylbenzene, 1,2-dichlorobenzene, 1,3-dichlorobenzene, 1,4-dichlorobenzene, and 1,2,4-trichlorobenzene plus one other substituted benzene and four PCB compounds.

Each of the equations in table 16 was developed from data for a somewhat limited range of types of compounds. Kenaga and Goring (1980) developed equations using all the data available at that time as one group. The resultant equations were

Table 16. Equations for predicting sorption coefficients of volatile organic compounds

[VOC, volatile organic compound; log, logarithm to the base 10; K_{oc}, sorption coefficient normalized with the organic carbon content, in liters per kilogram of organic carbon; S, water solubility, in moles per liter; K_{ow}, octanol-water partition coefficient]

VOC class	Equation number	Equation	Reference
Halogenated aliphatics	(78)	$\log K_{oc} = 0.935 - 0.557 \log S$	Chiou and others (1979)[1]
	(79)	$\log K_{oc} = 1.35 - 0.337 \log S$	Friesel and others (1984)[2]
Aromatic	(80)	$\log K_{oc} = 1.38 - 0.54 \log S$	Karickhoff and others (1979)[3]
	(81)	$\log K_{oc} = -0.21 + \log K_{ow}$	Karickhoff and others (1979)
	(82)	$\log K_{oc} = -0.346 + 0.989 \log K_{ow}$	Karickhoff (1981)
Mixed aromatics and chlorinated aromatics	(83)	$\log K_{oc} = 0.49 + 0.72 \log K_{ow}$	Schwarzenbach and Westall (1981)
	(84)	$\log K_{oc} = 0.238 - 0.729 \log S$	Chiou and others (1983)[4]
	(85)	$\log K_{oc} = -0.542 + 0.904 \log K_{ow}$	Chiou and others (1983)

[1] Equation converted from organic-matter normalization to organic-carbon normalization assuming organic matter is 58 percent by weight organic carbon; solubility changed from micromoles per liter to moles per liter.

[2] Equation converted from organic-matter normalization to organic-carbon normalization assuming organic matter is 58 percent by weight organic carbon; solubility changed from millimoles per liter to moles per liter; converted from base e logarithms to base 10 logarithms.

[3] Solubility changed from mole fraction solubility to moles per liter.

[4] Equation converted from organic-matter normalization to organic-carbon normalization assuming organic matter is 58 percent by weight organic carbon.

$$\log_{10} K_{oc} = 3.64 - 0.55 \log_{10} WS \qquad (86)$$

and

$$\log_{10} K_{oc} = 1.377 + 0.544 \log_{10} K_{ow} \qquad (87)$$

where

WS is the water solubility (mg/L).

Equations 86 and 87 were based on 106 and 45 pairs of data points, respectively, and the correlation coefficients were −0.84 and +0.86. The correlation coefficients for the equations in table 16 ranged from 0.970 to 1.00. These coefficients were larger than the coefficients for equations 86 and 87, presumably because of the smaller data bases and the greater uniformity of the characteristics of the compounds within each of the data bases. However, all of these equations are based on log-log correlations; therefore, considerable variation about the line of agreement should be expected, even when the correlation coefficients are large.

Molecular topology theory also has been applied to the prediction of sorption coefficients (Sabljic, 1987; Sabljic and others, 1995). This procedure correlated the first-order molecular connectivity index, ${}^1\chi$, with the sorption coefficient. This index was computed from

$$ {}^1\chi = \sum_{k=1}^{n} (\delta_i \delta_j)^{0.5} \qquad (88)$$

where each nonhydrogen atom in the molecule was described by its atomic δ value. This δ value was equal to the number of adjacent nonhydrogen atoms, and the i and j subscripts corresponded to the pairs of adjacent nonhydrogen atoms. Summation was over all bonds between nonhydrogen atoms, where n was the number of these bonds. The resultant equation for predominantly hydrophobic organic compounds was

$$\log_{10} K_{oc} = (0.52)\,{}^1\chi + 0.70 \qquad (89)$$

The correlation coefficient for equation 89 was 0.980 for a sample size of 81 compounds, of which 33 were target analytes. Equation 89 requires only a knowledge of molecular structure to predict the sorption coefficient.

Sorption coefficients for the 28 target analytes for which experimental coefficients were not available were predicted from the equations in table 16 and equations 86, 87, and 89. The water solubilities and octanol-water partition coefficients were mostly from the compilations of Mackay and others (1992a; 1993). Exceptions were as follows. Solubilities for trichlorofluoromethane and dichlorodifluoromethane were from Warner and Weiss (1985). The solubility for 1,1,2-trichloro-1,2,2-trifluoroethane was from Bu and Warner (1995). The solubility and the octanol-water partition coefficient for bromoethene were estimated as discussed previously for the calculation of the Henry's law constant for this compound. The solubility for ethyl tertiary-butyl ether was from Evan and Edlund (1936), and the solubility for tertiary-amyl methyl ether was from Stephenson (1992). The octanol-water partition coefficients for these two compounds were assumed to be the same as the measured value of Funasaki and others (1985) for diisopropyl ether because these authors showed that the log K_{ow} is related to the molar volume, and all three of these ethers have the same computed molar volume. The solubility for 2-propenenitrile was from Lyman (1990b, Table 2–14), and the octanol-water partition coefficient was from Verschueren (1983). Finally, the solubility for 2-propenal was from Verschueren (1983), and the octanol-water partition coefficient was from Callahan and others (1979).

The results presented in table 17 indicate considerable variation among the coefficients predicted with the different equations, as was expected considering the log-log nature of the equations. For the halogenated alkanes and alkenes, the results indicate that the overall equation (eq. 87) based on the octanol-water partition coefficient always predicted the highest sorption coefficient, whereas equation 89 based on molecular structure (Sabljic, 1987; Sabljic and others, 1995) generally predicted the lowest coefficients. The results for the alkyl benzene target analytes indicate that the overall equation (eq. 87) gave the highest predicted coefficients and equation 84 (Chiou and others, 1983) gave the lowest coefficients, although equation 86 (Kenaga and Goring, 1980) gave values comparable to equation 84 for most compounds. The predicted coefficients for the ether compounds, 2-propenenitrile, and 2-propenal were generally small, presumably because these compounds are the most soluble of any of the target analytes. The coefficients predicted from equation 89 on the basis of molecular structure were at or near the lower limit of the range of coefficients predicted by the other equations for the halogenated alkanes and alkenes, and within the range of predicted coefficients for the one aromatic hydrocarbon and the alkylbenzenes. For the ethers, 2-propenenitrile, and 2-propenal, the coefficients predicted with equation 89 were the highest of the predicted values.

ESTIMATION OF THE IMPORTANCE OF SORPTION

The fraction of a target analyte that will be sorbed to sediment at equilibrium can be estimated following a procedure used by Voice and Weber (1983). Combining a mass balance for the analyte-water-sediment system at equilibrium with equations 75 and 77 gives

$$fs = \frac{f_{oc}\,K_{oc}\,C_{sd}}{1 + f_{oc}\,K_{oc}\,C_{sd}} \qquad (90)$$

where

fs is the fraction by weight of the analyte that is sorbed to the sediment,

f_{oc} is the weight fraction of organic carbon in the sediment, and

C_{sd} is the sediment concentration (kg/L).

Equation 90 indicates that the fraction sorbed is dependent on the sorption coefficient as expected, the organic-carbon fraction of the sediment, and the sediment concentration.

Equation 90 was applied to the sorption of hexachlorobutadiene, 1,2,3-trichlorobenzene, and naphthalene for sediments with organic-carbon fractions of 0.01, 0.04, and 0.087, where 0.087 is the arbitrarily assumed dividing line between "real-world" soils and sediments and sorbents with high organic-carbon fractions (Hamaker and Thompson, 1972). Hexachlorobutadiene was selected because it had the highest predicted sorption coefficient of any of the analytes (table 17). The analyte 1,2,3-trichlorobenzene was selected because it had the highest experimental sorption coefficient of any of the analytes (table 15), exclusive of the plant cuticle values and the values of Voice and others (1983), which will be discussed in more detail below. Naphthalene was selected because it is a solid at normal environmental temperatures, with a melting point of 80.5°C (Mackay and others, 1992b).

Table 17. Predicted sorption coefficients for 28 target analytes

[USGS, U.S. Geological Survey; K_{oc}, sorption coefficient normalized with the fraction by weight of organic carbon; eq., equation]

USGS parameter code	Compound	K_{oc} (liter per kilogram of organic carbon)								
	Halogenated alkanes	**eq. 78**	**eq. 79**				**eq. 86**	**eq. 87**	**eq. 89**	
34418	chloromethane	30.0	47.6				38.8	74.5	16.6	
34413	bromomethane	23.6	41.2				21.7	106	16.6	
32104	tribromomethane	99.4	98.3				52.2	447	39.9	
32101	bromodichloromethane	80.4	86.5				53.7	331	39.9	
32105	chlorodibromomethane	101	99.2				59.0	394	39.9	
34311	chloroethane	33.1	50.6				37.4	143	27.2	
34496	1,1-dichloroethane	43.9	60.0				39.0	224	39.9	
34396	hexachloroethane	1,350	476				710	3,270	245	
77443	1,2,3-trichloropropane	97.2	97.0				68.7	430	145	
34488	trichlorofluoromethane	109	104				80.3	567	55.0	
34668	dichlorodifluoromethane	223	160				174	356	55.0	
77652	1,1,2-trichloro-1,2,2-trifluoroethane	220	159				135	1,250	245	
	Halogenated alkenes	**eq. 78**	**eq. 79**				**eq. 86**	**eq. 87**	**eq. 89**	
39175	chloroethene	49.5	64.5				56.6	134	27.2	
77093	*cis*-1,2-dichloroethene	54.8	68.6				49.1	245	49.6	
34546	*trans*-1,2-dichloroethene	39.5	56.2				35.5	315	49.6	
50002	bromoethene	30.7	48.3				26.3	160	27.2	
39702	hexachlorobutadiene	4,660	1,010				2,290	9,490	1050	
	Aromatic hydrocarbon	**eq. 80**	**eq. 81**	**eq. 82**	**eq. 84**	**eq. 85**	**eq. 86**	**eq. 87**	**eq. 89**	
77128	styrene	605	537	364	135	131	203	947	555	
	Alkyl benzenes				**eq. 83**	**eq. 84**	**eq. 85**	**eq. 86**	**eq. 87**	**eq. 89**
77224	n-propylbenzene				1,360	497	597	502	2,360	1,010
77223	iso-propylbenzene				1,170	440	495	459	2,110	1,300
77135	1,2-dimethylbenzene				502	156	171	224	1,110	477
77222	1,2,4-trimethylbenzene				1,630	464	750	477	2,710	764
	Ethers and other compounds							**eq. 86**	**eq. 87**	**eq. 89**
78032	methyl tertiary-butyl ether							13.6	77.3	108
50004	ethyl tertiary-butyl ether							24.9	160	196
50005	tertiary-amyl methyl ether							27.8	160	210
81577	diisopropyl ether							34.2	160	212
34210	2-propenal							5.2	21.3	38.7
34215	2-propenenitrile							8.8	7.5	49.6

It also has relatively low water solubility and, therefore, is likely to sorb to sediments. For reference purposes, the average of six naphthalene water solubilities at 25°C determined by the generator column technique was 31.5 mg/L (Mackay and others, 1992b). The solubility of hexachlorobutadiene was 3.23 mg/L at 25°C (Banerjee and others, 1980), and the solubility of 1,2,3-trichlorobenzene was 12.3 mg/L at 25°C (Miller and others, 1985).

The results presented in figure 12 indicate that very little of these three compounds will be sorbed to sediments for sediment concentrations less than 100 mg/L. For higher concentrations, the fraction of the organic compound sorbed increases rapidly. Hexachlorobutadiene is sorbed to the greatest extent, and naphthalene is sorbed the least, in agreement with the previous indication that the extent of sorption is inversely proportional to the water solubility. The results in figure 12 also indicate that the extent of sorption increases as the organic-carbon fraction of the sediment increases.

Suspended-sediment concentrations in streams vary, depending on flow conditions, characteristics of the stream, and the drainage-basin characteristics. As one point of reference, suspended-sediment concentrations in two urban stormwater-runoff studies ranged from 101 to 1,400 mg/L (von Guerard and Weiss, 1995) and from 0.5 to 750 mg/L (Pitt and others, 1995). Consequently, sorption of the target analytes to sediments could be a significant process, particularly for the less soluble analytes. Each situation should be evaluated individually to determine if sorption to sediments is a significant process in determining the fate of VOCs in streams.

The results of Voice and others (1983) indicated an apparent dependence of the sorption coefficient on the sediment concentration (table 15). The organic-carbon fractions of the two sediments used in this study were 0.029 and 0.038. Combining these fractions with the sorption coefficients appropriate for the corresponding sediment concentrations gives sorbed fractions ranging from 0.0042 to 0.028 for naphthalene. These fractions are in qualitative agreement with the low fractions for the concentration range from 10 to 300 mg/L indicated in figure 12. Corresponding

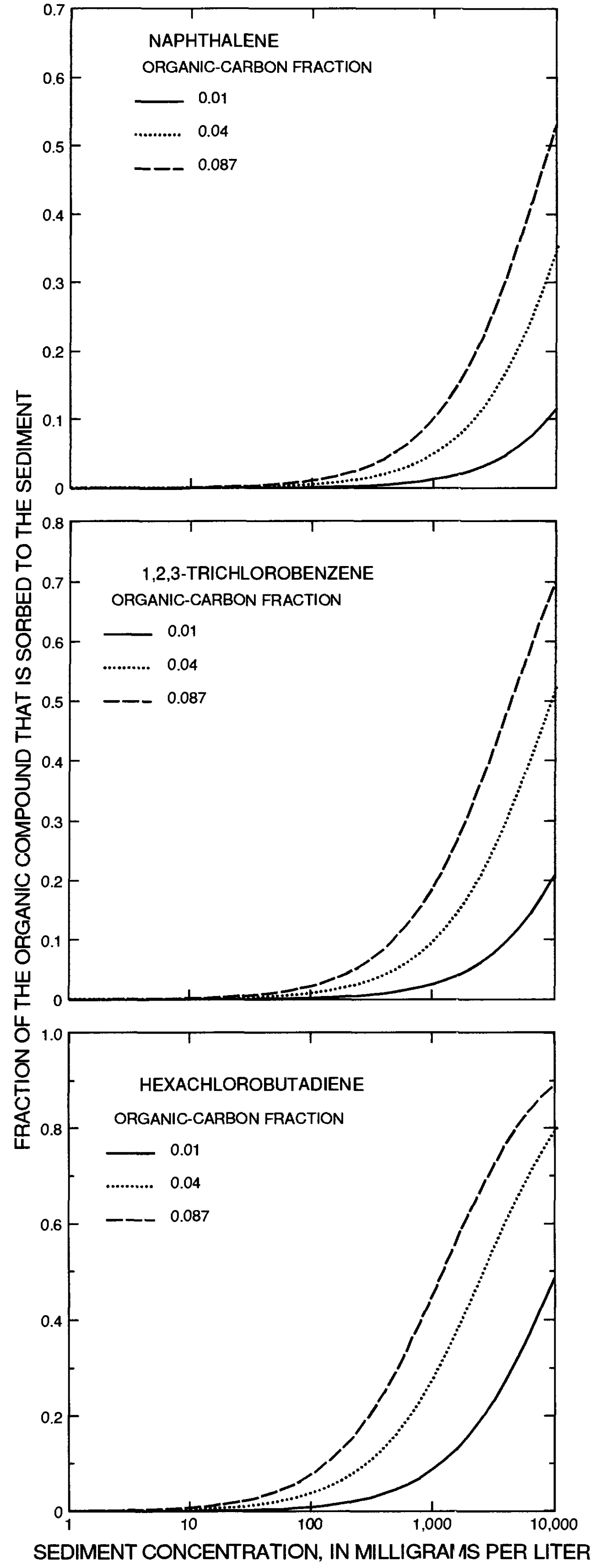

Figure 12. Fraction of the organic compound sorbed to sediment as a function of the sediment concentration for three target analytes.

fractions for chlorobenzene ranged from 0.0014 to 0.0067, indicating little sorption of this compound for sediment concentrations between 10 and 300 mg/L.

The development of equation 90 assumes that the water and sediment phases are in equilibrium, and a rapid and reversible equilibrium frequently is assumed in sorption studies. However, the review of the kinetics of the sorption process presented previously indicated that the assumption of a rapid and reversible equilibrium may not be completely valid because of strongly bound molecules. As an example of the effect of strongly bound molecules, Steinberg and others (1987) determined in desorption experiments that 1,2-dibromoethane applied to soils as long as 19 years earlier was far from equilibrium with the water phase. This lack of equilibrium was attributed to the fact that the 1,2-dibromoethane had diffused into the soil micropores where it was inaccessible to soil bacteria and not readily available for equilibration with the air and water phases of the system. This fraction of the 1,2-dibromoethane was estimated to have half-equilibration times for a 1:2 soil-water mixture of two to three decades at 25°C.

Another example of the importance of intraparticle diffusion is that of Wu and Gschwend (1986), who studied the sorption of four chlorobenzene compounds on three soils and sediments. They reported a slower approach to equilibrium for large particles; however, when the particles were disaggregated by sonication, the approach to equilibrium was faster. Wu and Gschwend also observed that the more hydrophobic (less water soluble) compounds had slower sorption rates; consequently, the greater the tendency to sorb, the slower the approach to equilibrium. They suggested on the basis of their work that the assumption of equilibrium may be valid for contact times of days and months. However, for situations where the water is continually being replaced with "new" water and contact times are much shorter, the assumption of equilibrium probably is not valid. This suggestion is supported by the work of Rostad (1996) who concluded that concentrations of several pesticides, herbicides, and PCB compounds in the water, colloid, and suspended-sediment phases of the Mississippi River were not in equilibrium. Similarly, Cheng and others (1995) used calculations to predict that the mass of organic compound desorbed from sediments in the Buffalo River, New York, during a resuspension event would be overpredicted with the assumption of equilibrium conditions.

The effect of failing to achieve equilibrium will be to overpredict the mass sorbed during a sorption process and to underpredict the mass desorbed during a desorption process. Consequently, the fractions shown in figure 12 are likely to be maximum predictions.

RECENT DEVELOPMENTS

The partition model (eq. 75) for the sorption of nonionic compounds to solids containing organic matter has been used extensively. This model has the advantage that sorption isotherms are linear, and the equilibrium expressed by equation 75 normally is assumed to be established rapidly. Consequently, incorporating into a numerical model the effect of sorption on the transport and behavior of organic compounds in streams is relatively easy. Recent developments, however, indicate that some of the assumptions of the partition model may not be valid in some situations. Specifically, nonlinear isotherms and competitive sorption have been determined. These results are inconsistent with the partition model, and several models have been proposed in attempts to explain these phenomena.

Weber and others (1992) and McGinley and others (1993) proposed a distributed reactivity model (DRM) to account for isotherm nonlinearities and competitive effects determined in their sorption studies. This model allows for the fact that soils which appear homogeneous on a macroscopic scale can be highly heterogeneous on a microscopic scale, with reactivities distributed among a variety of matrix components. To test this model, Weber and others (1992) measured isotherms for the sorption of tetrachloroethene, 1,4-dichlorobenzene, and 1,2,4-trichlorobenzene on six soils. The Freundlich n (eq. 76) was used as an indicator of nonlinear behavior, and n ranged from 0.68 to 1.20, with 16 of 18 values less than the 1.0-value corresponding to linear behavior. The degree of nonlinearity increased with increasing sorption capacity of the soils and increased as the solute hydrophobicity increased. The degree of nonlinearity varied only slightly among solutes for a specific soil and varied considerably among soils for a specific solute. McGinley and others (1993) determined the sorption of tetrachloroethene in the presence of a constant initial concentration of 1,2,4-trichlorobenzene. The 1,2,4-trichlorobenzene markedly reduced the sorption of trichloroethene on one soil, reduced the sorption to somewhat lesser extent on a second soil, and had little effect on a third soil. The results for the first two soils indicated competitive sorption, which was contrary to expectations based on the partition model.

The DRM is somewhat qualitative at this point in its development, and from a practical standpoint, only one or two nonlinear components can be differentiated in a specific situation. However, model calculations (McGinley and others, 1993) indicated for 0.1 weight percents of nonlinearly sorbing and linearly sorbing organic carbon that only about 10 percent of the sorption of tetrachloroethene was attributed to the linearly sorbing component at a solution concentration of 1 μg/L. On the other hand, about 50 percent was attributable to the linearly sorbing component at a solution concentration of 10,000 μg/L. This calculation indicates that the nonlinearly sorbing component will have a much greater effect at the low concentrations typical of environmental situations.

Young and Weber (1995) expanded the DRM concept by suggesting that sorption could lie at any point along a spectrum ranging from simple phase partitioning to pure surface adsorption. This spectrum can be either continuous or discontinuous, with different organic-matter fractions responsible for different degrees of reactivity. The degree of diagenetic alteration that each organic-matter fraction has undergone is the principal factor determining the reactivity of each fraction and where the overall sorption process lies along the spectrum. Consequently, they modeled soil organic matter as a macromolecule with a structure ranging from completely amorphous in a relatively young soil such as fulvic acids to a structure that is increasingly condensed as diagenesis occurs. The ultimate endpoint is a highly crystalline structure of extremely old organic carbon such as anthracite coal.

Young and Weber (1995) determined the effect of temperature on the sorption of phenanthrene to three soils. The changes in the Freundlich isotherm parameters with temperature were not statistically significant. However, trends were consistent with adsorption theory, with a weak trend toward increasing linearity and decreasing sorption capacity as the temperature increased. They concluded that the DRM provides a qualitative basis for explaining these temperature effects, as well as the isotherm nonlinearities and competitive sorption effects determined previously by Weber and others (1992) and McGinley and others (1993).

Spurlock and Biggar (1994a; 1994b) developed a thermodynamic partition model for linear and nonlinear organic-carbon-based sorption. The Freundlich partition coefficient, K_f, was related to the aqueous-phase activity coefficient and sorbate solubility in the humic phase. The Freundlich exponent, n, was related to the variation of the sorbate partial molar free energy with the sorbed-phase loading. Spurlock and Biggar (1994b) determined the sorption of five substituted phenylureas on three sorbents. The sorbate residual free energies decreased rapidly as the sorbed-phase concentrations decreased, indicating strong specific sorbate-sorbent interactions at low sorbed-phase loadings. Nonlinearity was related to the variations of the sorbate partial molar free energy in the sorbed phase.

Xing and others (1996) hypothesized that soil organic matter is a dual-mode sorbent, with sorption occurring by a combination of partition and hole-filling mechanisms. The holes are conceptualized as specific sites within the matrix where complexation follows the Langmuir isotherm. The holes are considered to discriminate on the basis of molecular structure, and it is likely that more than one type of hole exists because of the intrinsic physical/chemical heterogeneity of the soil organic matter. Xing and Pignatello (1996) determined 1-day, 30-day, and 180-day isotherms for the sorption of 1,3-dichlorobenzene, 2,4-dichlorophenol, and metolachlor on loam and peat soils. The Freundlich partition coefficient, K_f, increased by as much as 2.7 fold for the times greater than 1.0 day. The Freundlich exponent, n, was less than 1.0 in all cases, indicating nonlinear isotherms. The n values for the 30-day and 180-day isotherms were significantly smaller that the values for the 1-day isotherms, indicating that partitioning was much less ideal for the longer times. They concluded that the results were consistent with the dual-mode sorption model, with the adsorption process (hole-filling mechanism) being more important for the longer times. This indicates that the adsorption sites are internal to the soil organic-matter matrix and unevenly distributed with respect to access by the molecules being sorbed. Xing and Pignatello (1996) also noted that an important consequence of the nonlinear isotherm was that, as the concentration decreased, sorption became greater than would be expected for a linear isotherm.

Weber and Huang (1996) proposed a three-domain particle for modeling the sorption process. Domain I consists of exposed inorganic mineral surface where sorption is expected to be largely an adsorption process and, therefore, approximately linear. Domain II consists of amorphous soil organic matter where sorption is expected to be largely a partitioning process and, therefore, approximately linear. Domain III consists of condensed soil organic matter. They rationalized that the processes in domains I and II are relatively rapid. Consequently, once domains I and II have reached equilibrium, the overall sorption process is dominated by domain III. Weber and Huang (1996) hypothesized that sorption by the condensed soil organic matter of domain III will be energetically more favorable and more nonlinear than sorption by the amorphous soil organic matter in domain II because of the more heterogeneous composition and less polar nature of the condensed organic matter. Also, sorption by the condensed organic matter appears to be very slow, and this was attributed to slow intradomain diffusion.

Weber and Huang (1996) determined the sorption of phenanthrene on one soil and three sediments. Sorption isotherms were nonlinear, with Freundlich n values ranging from 0.726 to 0.890. The sorption capacity indicated by the Freundlich partition coefficient, K_f, increased rapidly with time, and n decreased rapidly with time. The changes in K_f and n appeared to occur in three stages: an initiation stage, a logarithmic stage, and an apparent equilibrium stage. Weber and Huang (1996) concluded that the logarithmic stage corresponded to domain III of the three-domain model.

Xing and Pignatello (1997) measured the sorption of chlorobenzene, 1,2-dichlorobenzene, and 1,3-dichlorobenzene on a peat soil, extracts of this soil, and two humic acids extracted from Canadian soils. The isotherms frequently were nonlinear, with Freundlich n values ranging from 0.777 to 0.956. The nonlinearity occurred over three orders of magnitude change in concentration and extended to very small concentrations. Competitive sorption also occurred between structurally similar molecules. The results were consistent with the dual-mode sorption model in which soil organic matter is conceptualized as an amalgam of rubbery and glassy phases. Each of these phases has a dissolution domain, and the glassy phase also contains holes that provide complexation sites. The holes are limited in size and number, and they cover a range of steric and electronic characteristics. These results conflict with the partition sorption model that assumes isotherms are linear and, consequently, that sorption coefficients are independent of concentration.

These recent developments have established that sorption isotherms frequently are nonlinear. The effect of this nonlinearity increases as the concentration decreases, with the result that sorption is most likely to be underpredicted in the low-concentration range of importance in environmental situations. The various versions of the DRM, dual-mode sorbent, and three-domain models can be used to explain qualitatively nonlinear isotherms, competitive sorption, and thermal effects inconsistent with the partition model of sorption. However, these models are not sufficiently developed to allow prediction of sorption coefficients and their concentration dependence in nonlinear systems. Consequently, the sorption coefficients presented in tables 15 and 17 must be used to estimate the effect of sorption on the concentrations of the target analytes in streams. This estimation should be done, however, with the understanding that sorption could be underestimated because of nonlinear effects.

HYDROLYSIS

Hydrolysis is the reaction of an organic compound with water. This reaction can involve the hydrogen ion or the hydroxyl ion of water, or the reaction can be neutral. An example of a neutral hydrolysis reaction is

$$RX + HOH = ROH + HX \tag{91}$$

where

RX is the organic compound with the functional group X that is capable of being hydrolyzed.

Examples of hydrolyzable functional groups include halogenated aliphatics, epoxides, organophosphorus esters, carboxylic acid esters, anhydrides, amides, carbamates, and ureas (Larson and Weber, 1994).

The rate of hydrolysis can be described by a general first-order expression of the form

$$-\frac{d[RX]}{dt} = K_h[RX] \tag{92}$$

where

$[RX]$ is the concentration of the organic compound,

t is time, and

K_h is the rate coefficient for hydrolysis.

However, because the hydrolysis process is known to be dependent on pH, this simplified equation must be modified to account for pH effects. This can be done by using the relationship (Washington, 1995)

$$-\frac{d[RX]}{dt} = K'_a[H^+][RX] + K_n[RX] + K'_b[OH^-][RX] \qquad (93)$$

where

K'_a and K'_b are the second-order rate coefficients for the acid and base hydrolysis reactions,

K_n is the first-order rate coefficient for the neutral hydrolysis reaction,

$[H^+]$ is the hydrogen-ion concentration, and

$[OH^-]$ is the hydroxyl-ion concentration.

Comparing equations 92 and 93 indicates that

$$K_h[RX] = K'_a[H^+][RX] + K_n[RX] + K'_b[OH^-][RX]. \qquad (94)$$

When the concentration of the organic compound is dilute, such as is common in environmental situations, concentration effects on the rate of hydrolysis are minimal, and the concentration can be canceled in equation 94. Also, the $[OH^-]$ ion concentration can be eliminated from equation 94 by substituting the kinetic expression for the dissociation of water. With these changes, equation 94 becomes

$$K_h = K'_a[H^+] + K_n + \frac{K'_b K_w}{[H^+]} \qquad (95)$$

where

K_w is the rate coefficient for the dissociation of water, which is defined as $K_w = [OH^-][H^+]$.

Equation 95 indicates that the hydrolysis rate coefficient depends on the relative magnitudes of the rate coefficients K'_a, K_n, and K'_b. In general, the first term on the right side of equation 95 will dominate for acidic conditions, the third term will dominate for basic conditions, and the middle term will dominate for neutral conditions. Washington (1995) indicated that neutral hydrolysis reactions are most likely to be important for VOCs in water.

Because of the assumptions involved in equations 92 and 93, the overall rate coefficient for hydrolysis is sometimes termed a pseudo first-order rate coefficient (Mabey and Mill, 1978; Washington, 1995). Consequently, integration of equation 92 gives

$$[RX]_t = [RX]_o \exp(-K_h t) \qquad (96)$$

where

$[RX]_t$ is the concentration at time t, and

$[RX]_o$ is the concentration at time zero.

The corresponding half-life for hydrolysis is

$$t_{0.5h} = \frac{0.693}{K_h} \qquad (97)$$

where

$t_{0.5h}$ is the time required for the concentration to be reduced to one-half by the process of hydrolysis.

Because rates of hydrolysis at environmental temperatures are slow for most compounds, laboratory hydrolysis experiments usually are done at high temperatures to increase reaction rates. These experiments are done in sealed glass ampules, with corrections applied for the amount of the compound that volatilizes into the head space. Results from these high-temperature conditions are extrapolated to lower temperatures characteristic of environmental conditions. Consequently, the temperature dependence of the rate coefficient for hydrolysis is important. This temperature dependence usually is expressed by the Arrhenius equation (Washington, 1995), which has the form

$$K_h = A_h \exp\left(-\frac{E_h}{RT}\right) \qquad (98)$$

where

A_h is a constant (day^{-1});

E_h is the activation energy for the hydrolysis process (kJ/g mol);

R is the ideal gas constant (kJ/g mol/K); and

T is the temperature, in kelvins.

The average activation energy for a number of VOCs was 110.1 kJ/g mol (Washington, 1995), which is larger than the value of 65 kJ/g mol used for a group of many different types of organic compounds (Mabey and Mill, 1978). This difference indicates that the hydrolysis rate coefficients for VOCs are more sensitive to temperature than the coefficients for other types of organic compounds.

The concentration also is important. Laboratory experiments usually are done at concentrations much higher than concentrations present in typical environmental situations. The extrapolation of results for high concentrations to low concentrations is rationalized on the basis that rate processes that are first order at high concentrations remain first order at low concentrations; that is, the rate coefficient is independent of concentration (Mabey and Mill, 1978). Of the VOCs, only tetrachloromethane has a rate coefficient for hydrolysis that is dependent on concentration (Mabey and Mill, 1978). More recent experimental work coupled with a reanalysis of the older tetrachloromethane data indicated that hydrolysis was first order with a half-life of about 40 years (Jeffers and others, 1996). Consequently, rate coefficients should be independent of concentration, and extrapolation of high concentration results to low concentrations should be valid for all the target analytes. Similarly, semilogarithmic Arrhenius plots based on equation 98 resulted in linear plots, thus supporting the procedure of extrapolating high temperature results to lower temperatures characteristic of environmental conditions.

The ionic strength of the solution also affects the rate of hydrolysis, but the effect is difficult to predict. Mabey and Mill (1978) determined that ionic-strength effects can either increase or decrease the hydrolysis rates, depending on the organic compound, the specific salts causing the change in ionic strength, and their concentrations. However, the ionic strength of most natural waters usually is less than 0.01 molar in total cation and anion concentrations (Mabey and Mill, 1978); consequently, they recommended that buffer concentrations of 0.01 molar be used in determinations of hydrolysis rate constants to minimize any possible effect of ionic strength.

The preceding paragraphs give only a brief summary of the principles of hydrolysis of organic compounds in water. A more thorough discussion is given by Larson and Weber (1994).

HYDROLYSIS HALF-LIVES FOR THE TARGET ANALYTES

Hydrolysis half-lives and estimates from the literature of the potential for hydrolysis for 49 target analytes are presented in table 18. Most of these values are from literature reviews such as Radding and others (1977), Mabey and Mill (1978), Callahan and others (1979), Mabey and others (1982), Howard and others (1991), Mackay and others (1992a; 1993), Kollig (1993; 1995), and Washington (1995). For some of the VOCs, values in the literature reviews differed slightly from values in the original references, presumably because of differences in the procedures used for extrapolation to environmental temperatures; in these cases, both values are presented in table 18. Most values are for a pH of 7 and a temperature of 25°C, although Washington (1995) gives values for a pH of 5.6 and a temperature of 10°C. The pH of 5.6 was chosen because this is the approximate pH of water in equilibrium with the atmospheric concentration of carbon dioxide. The temperature of 10°C was chosen as more representative of ground-water temperatures than the 25°C commonly used for environmental studies.

Numerical values of the hydrolysis half-lives were available for 30 target analytes, and hydrolysis was judged to be insignificant for 19 other target analytes, in many cases because the molecule contained no hydrolyzable groups. Information was not available for iso-propylbenzene, 1,2,3-trichlorobenzene, and the four ether compounds (table 1).

Estimation of the importance of hydrolysis for iso-propylbenzene and 1,2,3-trichlorobenzene can be made on the basis of available information for similar compounds. The alkyl benzene compounds methylbenzene, ethylbenzene, n-propylbenzene, and n-butylbenzene were judged to have no hydrolyzable groups (Mabey and others, 1982; Kollig, 1993; 1995), and methylbenzene and ethylbenzene were considered to be recalcitrant with respect to hydrolysis (Washington, 1995). A similar conclusion seems reasonable for iso-propylbenzene. Hydrolysis for 1,2,4-trichlorobenzene was judged to be not significant (Mabey and others, 1982; Kollig, 1993) or to have a half-life of 3.4 years at pH 7 and 25°C (Mackay and others, 1992a) as shown in table 18.

Table 18. Literature values of half-lives for hydrolysis of 30 target analytes and estimates of the potential for hydrolysis of 19 target analytes

[USGS, U.S. Geological Survey; °C, degrees Celsius; $t_{0.5h}$, half-life for hydrolysis, in years; A, acidic conditions, pH not specified; NS, not specified; NACM, no acid catalyzed mechanism known; B, basic conditions, pH not specified; HPHI, hydrolysis pH independent; HNES, hydrolysis not environmentally significant; RC, recalcitrant toward hydrolysis; PNS, probably not significant; N, neutral pH condition; NLFG, no labile functional group; iNS, isomer not specified; NHFG, no hydrolyzable functional group]

USGS parameter code	Compound	pH	Temperature (°C)	$t_{0.5h}$ (years)	Reference
34418	chloromethane	7	25	1.14×10^{0}	Radding and others (1977)
		7	25	9.3×10^{-1}	Mabey and Mill (1978)
		7	25	1.16×10^{0}	Mabey and others (1982)
		7	25	3.58×10^{4}	Washington (1995)
		7	10	3.16×10^{5}	Washington (1995)
		A	NS	NACM	Mabey and others (1982)
		5.6	25	9.00×10^{5}	Washington (1995)
		5.6	10	7.93×10^{5}	Washington (1995)
		B	NS	HPHI	Mabey and others (1982)
		NS	20	2.5×10^{0}	Callahan and others (1979)
34423	dichloromethane	7	25	7.04×10^{2}	Radding and others (1977)
		7	25	6.87×10^{2}	Mabey and Mill (1978)
		7	25	6.93×10^{2}	Kollig (1993)
		7	25	1.05×10^{7}	Washington (1995)
		A	NS	NACM	Mabey and others (1982)
		5.6	25	2.65×10^{8}	Washington (1995)
		5.6	10	2.77×10^{9}	Washington (1995)
		B	NS	HPHI	Mabey and others (1982)
		NS	20	$\cong1.5\times10^{0}$	Dilling and others (1975)
32106	trichloromethane	7	25	3.5×10^{3}	Radding and others (1977)
		7	25	3.16×10^{4}	Mabey and others (1982)
		7	25	1.85×10^{3}	Jeffers and others (1989)
		7	25	6.93×10^{3}	Kollig (1993)
		7	25	1.76×10^{3}	Washington (1995)
		7	10	1.80×10^{4}	Washington (1995)
		A	NS	NACM	Mabey and others (1982)
		5.6	25	5.93×10^{3}	Washington (1995)
		5.6	10	7.85×10^{4}	Washington (1995)
		NS	25	$\cong1.25\times10^{0}$	Dilling and others (1975)
32102	tetrachloromethane	7	25	7.0×10^{3} (1 mg/L)	Radding and others (1977)
		7	25	7.0×10^{0} (10^{3} mg/L)	Radding and others (1977)
		7	25	4.05×10^{1}	Jeffers and others (1989)
		7	25	4.08×10^{1}	Kollig (1993)
		7	25	3.81×10^{1}	Washington (1995)
		7	25	4.0×10^{1}	Jeffers and others (1996)
		7	10	4.41×10^{2}	Washington (1995)
		A	NS	NACM	Mabey and others (1982)
		5.6	25	3.81×10^{1}	Washington (1995)
		5.6	10	4.41×10^{2}	Washington (1995)
		B	NS	HPHI	Mabey and others (1982)

Table 18. Literature values of half-lives for hydrolysis of 30 target analytes and estimates of the potential for hydrolysis of 19 target analytes—Continued

[USGS, U.S. Geological Survey; °C, degrees Celsius; $t_{0.5h}$, half-life for hydrolysis, in years; A, acidic conditions, pH not specified; NS, not specified; NACM, no acid catalyzed mechanism known; B, basic conditions, pH not specified; HPHI, hydrolysis pH independent; HNES, hydrolysis not environmentally significant; RC, recalcitrant toward hydrolysis; PNS, probably not significant; N, neutral pH condition; NLFG, no labile functional group; iNS, isomer not specified; NHFG, no hydrolyzable functional group]

USGS parameter code	Compound	pH	Temperature (°C)	$t_{0.5h}$ (years)	Reference
34413	bromomethane	7	25	5.5×10^{-2}	Radding and others (1977)
		7	25	5.4×10^{-2}	Howard and others (1991)
		7	20	1.04×10^{-1}	Howard and others (1991)
		A	NS	NACM	Mabey and others (1982)
		B	NS	HPHI	Mabey and others (1982)
		NS	25	7.3×10^{-2}	Mackay and others (1993)
32104	tribromomethane	7	25	6.86×10^{2}	Radding and others (1977)
		7	25	6.90×10^{2}	Washington (1995)
		7	10	6.85×10^{3}	Washington (1995)
		A	NS	HNES	Mabey and others (1982)
		5.6	25	1.73×10^{4}	Washington (1995)
		5.6	10	1.72×10^{5}	Washington (1995)
32101	bromodichloromethane	7	25	1.37×10^{2}	Mabey and Mill (1978)
		7	25	1.28×10^{2}	Washington (1995)
		7	10	1.26×10^{3}	Washington (1995)
		A	NS	NACM	Mabey and others (1982)
		5.6	25	3.23×10^{3}	Washington (1995)
		5.6	10	3.18×10^{4}	Washington (1995)
32105	chlorodibromomethane	7	25	2.74×10^{2}	Mabey and Mill (1978)
		7	25	2.77×10^{2}	Washington (1995)
		7	10	2.97×10^{3}	Washington (1995)
		A	NS	NACM	Mabey and others (1982)
		5.6	25	6.96×10^{3}	Washington (1995)
		5.6	10	7.46×10^{4}	Washington (1995)
34311	chloroethane	7	25	1.10×10^{-1}	Radding and others (1977)
		7	25	1.04×10^{-1}	Mabey and Mill (1978)
		7	25	2.54×10^{0}	Washington (1995)
		7	25	2.6×10^{0}	Jeffers and Wolfe (1996)
		7	10	2.72×10^{1}	Washington (1995)
		A	NS	NACM	Mabey and others (1982)
		5.6	25	2.54×10^{0}	Washington (1995)
		5.6	10	2.72×10^{1}	Washington (1995)
		B	NS	HPHI	Mabey and others (1982)
34496	1,1-dichloroethane	7	25	6.88×10^{2}	Mabey and others (1982)
		7	25	6.13×10^{1}	Jeffers and others (1989)
		7	25	5.82×10^{1}	Washington (1995)
		7	10	6.06×10^{2}	Washington (1995)
		A	NS	NACM	Mabey and others (1982)
		5.6	25	5.82×10^{1}	Washington (1995)
		5.6	10	6.06×10^{2}	Washington (1995)

Table 18. Literature values of half-lives for hydrolysis of 30 target analytes and estimates of the potential for hydrolysis of 19 target analytes—Continued

[USGS, U.S. Geological Survey; °C, degrees Celsius; $t_{0.5h}$, half-life for hydrolysis, in years; A, acidic conditions, pH not specified; NS, not specified; NACM, no acid catalyzed mechanism known; B, basic conditions, pH not specified; HPHI, hydrolysis pH independent; HNES, hydrolysis not environmentally significant; RC, recalcitrant toward hydrolysis; PNS, probably not significant; N, neutral pH condition; NLFG, no labile functional group; iNS, isomer not specified; NHFG, no hydrolyzable functional group]

USGS parameter code	Compound	pH	Temperature (°C)	$t_{0.5h}$ (years)	Reference
32103	1,2-dichloroethane	7	25	5.0×10^{4}	Radding and others (1977)
		7	25	4.4×10^{4}	Mabey and others (1982)
		7	25	7.2×10^{1}	Jeffers and others (1989)
		7	25	7.00×10^{1}	Washington (1995)
		7	25	7.15×10^{1}	Jeffers and Wolfe (1996)
		7	10	6.44×10^{2}	Washington (1995)
		A	NS	NACM	Mabey and others (1982)
		5.6	25	7.01×10^{1}	Washington (1995)
		5.6	10	6.44×10^{2}	Washington (1995)
34506	1,1,1-trichloroethane	7	25	1.1×10^{0}	Jeffers and others (1989)
		7	25	7.3×10^{-1}	Mackay and others (1993)
		7	25	1.08×10^{0}	Kollig (1993)
		7	25	8.26×10^{-1}	Washington (1995)
		7	10	1.03×10^{1}	Washington (1995)
		A	NS	NACM	Mabey and others (1982)
		5.6	25	8.26×10^{-1}	Washington (1995)
		5.6	10	1.03×10^{1}	Washington (1995)
		NS	25	5.0×10^{-1}	Dilling and others (1975)
		NS	25	9.6×10^{-1}	Haag and Mill (1988)
34511	1,1,2-trichloroethane	7	25	1.39×10^{2}	Jeffers and others (1989)
		7	25	2.54×10^{4}	Kollig (1993)
		7	25	3.7×10^{1}	Mackay and others (1993)
		7	25	1.37×10^{2}	Washington (1995)
		7	10	9.04×10^{2}	Washington (1995)
		A	NS	NACM	Mabey and others (1982)
		5.6	25	3.02×10^{3}	Washington (1995)
		5.6	10	2.13×10^{4}	Washington (1995)
		9	25	8.94×10^{0}	Mackay and others (1993)
34396	hexachloroethane	7	NS	HNES	Mabey and others (1982)
		7	25	RC	Jeffers and Wolfe (1996)
		A	NS	NACM	Mabey and others (1982)
		B	NS	HNES	Mabey and others (1982)
77651	1,2-dibromoethane	7	25	5.0×10^{3}	Radding and others (1977)
		7	25	1.1×10^{0}	Kollig (1993)
		7	25	1.4 to 2.7×10^{-2}	Mackay and others (1993)
		7	25	8.0×10^{0}	Mackay and others (1993)
		7	25	6.4×10^{0}	Jeffers and Wolfe (1996)
		7	25	2.2×10^{0}	Mackay and others (1993)
		7.5	25	2.5×10^{0}	Vogel and Reinhard (1986)
		NS	25	4.1×10^{0}	Haag and Mill (1988)

Table 18. Literature values of half-lives for hydrolysis of 30 target analytes and estimates of the potential for hydrolysis of 19 target analytes—Continued

[USGS, U.S. Geological Survey; °C, degrees Celsius; $t_{0.5h}$, half-life for hydrolysis, in years; A, acidic conditions, pH not specified; NS, not specified; NACM, no acid catalyzed mechanism known; B, basic conditions, pH not specified; HPHI, hydrolysis pH independent; HNES, hydrolysis not environmentally significant; RC, recalcitrant toward hydrolysis; PNS, probably not significant; N, neutral pH condition; NLFG, no labile functional group; iNS, isomer not specified; NHFG, no hydrolyzable functional group]

USGS parameter code	Compound	pH	Temperature (°C)	$t_{0.5h}$ (years)	Reference
34541	1,2-dichloropropane	7	25	1.51×10^{1}	Kollig (1993)
		7	25	1.66×10^{1}	Washington (1995)
		7-9	25	1.58×10^{1}	Mackay and others (1993)
		7	10	1.75×10^{2}	Washington (1995)
		A	NS	NACM	Mabey and others (1982)
		5.6	25	1.66×10^{1}	Washington (1995)
		5.6	10	1.75×10^{2}	Washington (1995)
77443	1,2,3-trichloropropane	7	25	4.1×10^{1}	Kollig (1993)
		7–9	25	4.4×10^{1}	Mackay and others (1993)
82625	1,2-dibromo-3-chloropropane	7	25	3.8×10^{1}	Burlinson and others (1982)
		7	25	3.84×10^{1}	Howard and others (1991)
		7	25	1.73×10^{2}	Kollig (1993)
		7	15	1.41×10^{2}	Burlinson and others (1982)
		9	25	3.8×10^{-1}	Howard and others (1991)
34488	trichlorofluoromethane	7	25, 10	RC	Washington (1995)
		5.6	25, 10	RC	Washington (1995)
34668	dichlorodifluoromethane	NS	NS	PNS	Callahan and others (1979)
77652	1,1,2-trichloro-1,2,2-trifluoroethane	N, A, B	25	NLFG	Kollig (1993)
39175	chloroethene	7	25	$>9.91\times10^{0}$	Washington (1995)
		7	10	$>1.07\times10^{2}$	Washington (1995)
		N, A, B	NS	HNES	Mabey and others (1982)
		NS	25	$<1.0\times10^{1}$	Hill and others (1976)
		5.6	25	$>9.91\times10^{0}$	Washington (1995)
		5.6	10	$>1.07\times10^{2}$	Washington (1995)
		4.3–9.4	NS	PNS	Callahan and others (1979)
34501	1,1-dichloroethene	7	25	1.2×10^{8}	Jeffers and others (1989)
		7	25	1.19×10^{8}	Washington (1995)
		7	10	1.93×10^{9}	Washington (1995)
		N, A, B	NS	HNES	Mabey and others (1982)
		5.6	25	2.99×10^{9}	Washington (1995)
		5.6	10	4.85×10^{10}	Washington (1995)
77093	*cis*-1,2-dichloroethene	7	25	2.1×10^{10}	Jeffers and others (1989)
		7	25	2.06×10^{10}	Washington (1995)
		7	10	3.34×10^{11}	Washington (1995)
		5.6	25	2.06×10^{12}	Washington (1995)
		5.6	10	8.40×10^{12}	Washington (1995)
		N, A, B	25	NLFG	Kollig (1993)
34546	*trans*-1,2-dichloroethene	7	25	2.06×10^{10}	Washington (1995)
		7	10	3.34×10^{11}	Washington (1995)
		N, A, B	NS	HNES	Mabey and others (1982)
		5.6	25	5.18×10^{11}	Washington (1995)
		5.6	10	8.40×10^{12}	Washington (1995)
		N, A, B	25	NLFG	Kollig (1993)

Table 18. Literature values of half-lives for hydrolysis of 30 target analytes and estimates of the potential for hydrolysis of 19 target analytes—Continued

[USGS, U.S. Geological Survey; °C, degrees Celsius; $t_{0.5h}$, half-life for hydrolysis, in years; A, acidic conditions, pH not specified; NS, not specified; NACM, no acid catalyzed mechanism known; B, basic conditions, pH not specified; HPHI, hydrolysis pH independent; HNES, hydrolysis not environmentally significant; RC, recalcitrant toward hydrolysis; PNS, probably not significant; N, neutral pH condition; NLFG, no labile functional group; iNS, isomer not specified; NHFG, no hydrolyzable functional group]

USGS parameter code	Compound	pH	Temperature (°C)	$t_{0.5h}$ (years)	Reference
39180	trichloroethene	7	25	1.3×10^{6}	Jeffers and others (1989)
		7	25	1.66×10^{5}	Washington (1995)
		7	25	$\cong1\times10^{5}$	Jeffers and Wolfe (1996)
		7	10	2.08×10^{6}	Washington (1995)
		N, A, B	NS	HNES	Mabey and others (1982)
		5.6	25	2.78×10^{5}	Washington (1995)
		5.6	10	3.61×10^{6}	Washington (1995)
		NS	25	8.9×10^{-1}	Dilling and others (1975)
		N, A, B	25	NLFG	Kollig (1993)
34475	tetrachloroethene	7	25	9.9×10^{8}	Jeffers and others (1989)
		7	25	9.56×10^{8}	Washington (1995)
		7	10	1.33×10^{10}	Washington (1995)
		N, A, B	NS	HNES	Mabey and others (1982)
		5.6	25	2.40×10^{10}	Washington (1995)
		5.6	10	3.34×10^{11}	Washington (1995)
		NS	25	7.3×10^{-1}	Dilling and others (1975)
		N, A, B	25	NLFG	Kollig (1993)
50002	bromoethene	NS	NS	NHFG	Howard and others (1991)
iNS	1,3-dichloropropene	7	25	1.88×10^{-1}	Mabey and others (1982)
		7	25	1.5 to 3.1×10^{-1}	Mackay and others (1993)
		7	25	1.62×10^{-2}	Washington (1995)
		7	10	1.38×10^{-1}	Washington (1995)
		A	NS	NACM	Mabey and others (1982)
		5.6	25	1.62×10^{-2}	Washington (1995)
		5.6	10	1.38×10^{-1}	Washington (1995)
		B	NS	HPHI	Mabey and others (1982)
34704	*cis*-1,3-dichloropropene	7	25	1.73×10^{-2}	Kollig (1993)
34699	*trans*-1,3-dichloropropene	7	25	1.73×10^{-2}	Kollig (1993)
39702	hexachlorobutadiene	N, A, B	NS	HNES	Mabey and others (1982)
		N, A, B	25	NLFG	Kollig (1993)
34030	benzene	7	25, 10	RC	Washington (1995)
		5.6	25, 10	RC	Washington (1995)
		N, A, B	25	NHFG	Kollig (1993)
77128	styrene	N, A, B	25	NHFG	Kollig (1993)
34696	naphthalene	N, A, B	NS	NHFG	Mabey and others (1982)
		N, A, B	25	NHFG	Kollig (1993)
34010	methylbenzene	7	25, 10	RC	Washington (1995)
		N, A, B	NS	NHFG	Mabey and others (1982)
		5.6	25, 10	RC	Washington (1995)
		N, A, B	25	NHFG	Kollig (1993)

Table 18. Literature values of half-lives for hydrolysis of 30 target analytes and estimates of the potential for hydrolysis of 19 target analytes—Continued

[USGS, U.S. Geological Survey; °C, degrees Celsius; $t_{0.5h}$, half-life for hydrolysis, in years; A, acidic conditions, pH not specified; NS, not specified; NACM, no acid catalyzed mechanism known; B, basic conditions, pH not specified; HPHI, hydrolysis pH independent; HNES, hydrolysis not environmentally significant; RC, recalcitrant toward hydrolysis; PNS, probably not significant; N, neutral pH condition; NLFG, no labile functional group; iNS, isomer not specified; NHFG, no hydrolyzable functional group]

USGS parameter code	Compound	pH	Temperature (°C)	$t_{0.5h}$ (years)	Reference
34371	ethylbenzene	7	25, 10	RC	Washington (1995)
		N, A, B	NS	NHFG	Mabey and others (1982)
		5.6	25, 10	RC	Washington (1995)
		N, A, B	25	NHFG	Kollig (1993)
77224	n-propylbenzene	NS	25	NHFG	Kollig (1995)
77342	n-butylbenzene	NS	25	NHFG	Kollig (1995)
77135	1,2-dimethylbenzene	7	25, 10	RC	Washington (1995)
		5.6	25, 10	RC	Washington (1995)
		N, A, B	25	NHFG	Kollig (1993)
85795	1,3-dimethylbenzene	7	25, 10	RC	Washington (1995)
		5.6	25, 10	RC	Washington (1995)
		N, A, B	25	NHFG	Kollig (1993)
85795	1,4-dimethylbenzene	7	25, 10	RC	Washington (1995)
		5.6	25, 10	RC	Washington (1995)
		N, A, B	25	NHFG	Kollig (1993)
34301	chlorobenzene	7	25, 10	RC	Washington (1995)
		N, A, B	25	HNES	Mabey and others (1982)
		5.6	25, 10	RC	Washington (1995)
		N, A, B	25	NLFG	Kollig (1993)
34536	1,2-dichlorobenzene	7	25, 10	RC	Washington (1995)
		N, A, B	25	HNES	Mabey and others (1982)
		5.6	25, 10	RC	Washington (1995)
		N, A, B	25	NLFG	Kollig (1993)
34566	1,3-dichlorobenzene	7	25	$>8.79\times10^{2}$	Mackay and others (1992a)
		7	25, 10	RC	Washington (1995)
		N, A, B	25	HNES	Mabey and others (1982)
		5.6	25, 10	RC	Washington (1995)
34571	1,4-dichlorobenzene	7	25	$>8.79\times10^{2}$	Mackay and others (1992a)
		7	25, 10	RC	Washington (1995)
		N, A, B	25	HNES	Mabey and others (1982)
		5.6	25, 10	RC	Washington (1995)
		N, A, B	25	NLFG	Kollig (1993)
34551	1,2,4-trichlorobenzene	7	25	3.4×10^{0}	Mackay and others (1992a)
		N, A, B	NS	HNES	Mabey and others (1982)
		N, A, B	25	NLFG	Kollig (1993)
34210	2-propenal	NS	NS	NHFG	Callahan and others (1979)
		N, A, B	NS	NHFG	Mabey and others (1982)
34215	2-propenenitrile	7	NS	1.21×10^{3}	Howard and others (1991)
		5	NS	1.88×10^{2}	Howard and others (1991)
		9	NS	1.3×10^{1}	Howard and others (1991)
		N, A, B	NS	HNES	Mabey and others (1982)

A similar conclusion seems reasonable for 1,2,3-trichlorobenzene. Finally, a literature review (Mackay and others, 1993) has a number of aliphatic ethers listed in its compilations but no specific information on the hydrolysis characteristics of any of these ether compounds. Consequently, it seems reasonable to assume that hydrolysis will not be important for the four ether target analytes. The fact that hydrolysis of ether compounds has not been studied also indicates that hydrolysis probably is not significant.

Most of the hydrolysis half-lives in table 18 are large. However, nine target analytes have half-lives of 548 days or less, and hydrolysis of these compounds could be important in determining the fate of these compounds in some streams. Half-lives for some of these compounds vary by orders of magnitude from study to study (for example, chloromethane, dichloromethane, 1,2-dichloroethane, 1,1-dichloroethene, and tetrachloroethene). Therefore, values for these compounds should be used with caution.

Hydrolysis half-lives in table 18 increased as expected as the temperature increased for every compound for which temperature data were available. Half-lives increased as the pH decreased for about 60 percent of the compounds for which data were available; half-lives did not change for the other 40 percent.

Table 18 indicates that 2-propenal is not subject to hydrolysis. However, opinions differ about this compound. Kollig (1993) stated that 2-propenal undergoes rapid hydrolysis through the addition of water across the double bond. Half-life for this neutral hydrolysis reaction was 1.0×10^{-9} years. Callahan and others (1979) stated, however, that this water addition reaction is not a hydrolysis process because the reaction is reversible, and they suggested that 2-propenal contains no hydrolyzable groups suitable for environmental transformations, as indicated in table 18. Nordone and others (1996) determined overall half-lives of 1.16×10^{-3} and 2.83×10^{-3} years for the disappearance of 2-propenal from weedy and nonweedy canals by all processes. These results indicate that 2-propenal is not undergoing the rapid hydrolysis indicated by the short half-life reported by Kollig (1993).

There also is some disagreement regarding the effect of the hydrolysis process on 2-propenenitrile. Mabey and Mill (1978) indicated that nitriles should be considered hydrolytically inert under ordinary conditions, whereas Schnoor and others (1987) indicated that nitriles are generally susceptible to hydrolysis. Half-lives in table 18 range from 13 years for basic hydrolysis to 1,210 years for neutral hydrolysis, indicating some hydrolysis but not complete recalcitrance.

ESTIMATION OF THE IMPORTANCE OF HYDROLYSIS

The importance of hydrolysis of the target analytes with respect to volatilization was estimated using a procedure similar to that used for estimating the importance of microbial degradation, with one difference. Equation 74 used for microbial degradation gives the fraction of the concentration remaining at distance L downstream. To demonstrate an alternative procedure, the fraction of the compound removed at distance L downstream was used for comparing the relative effects of hydrolysis and volatilization. The fraction-removed procedure is likely to be of most use to those interested in estimating the contributions of various processes determining the fate of VOCs in streams. The fraction-remaining procedure is likely to be of most use to individuals such as water managers who are interested in estimating the concentrations of VOCs remaining at various points downstream. In either case, the fractions are easily converted from one to the other.

Substituting the hydrolysis rate coefficient for the microbial degradation coefficient in equation 74, it can be shown that the fraction of the total concentration, Tf, removed by hydrolysis and volatilization at distance L, is given by.

$$\mathrm{Tf} = 1-\exp\left[-\frac{\mathrm{L}}{\mathrm{U}}(\mathrm{K_h}+\mathrm{K_v})\right]. \tag{99}$$

Similarly, the fractions removed by hydrolysis, Hf, and volatilization, Vf, are given by

$$\mathrm{Hf} = 1-\exp\left[-\frac{\mathrm{L}}{\mathrm{U}}(\mathrm{K_h})\right] \tag{100}$$

and

$$\mathrm{Vf} = 1-\exp\left[-\frac{\mathrm{L}}{\mathrm{U}}(\mathrm{K_v})\right]. \tag{101}$$

These fractions are not additive, however, because of the exponential nature of equation 99. It can be shown that

$$Tf = Hf + Vf - (Hf)(Vf) \; . \qquad (102)$$

The importance of hydrolysis relative to volatilization was estimated for the nine target analytes with hydrolysis half-lives of 548 days or less for a temperature of 25°C and a pH of 7. First-order rate coefficients for hydrolysis were computed from the half-lives in table 18 and equation 97. The compound 1,2-dibromo-3-chloropropane has a half-life of 0.38 year at pH 9; however, this compound was not included because the half-lives at neutral pH were much longer than 548 days. The same three sets of hydraulic conditions used previously for estimating the importance of microbial degradation were used to obtain a range of volatilization coefficients.

Distances downstream of 100,000, 20,000, and 170 m were used for the hydraulic conditions corresponding to the O'Connor-Dobbins (1958), Churchill and others (1962), and Owens and others (1964) equations. This distance was varied so as to obtain approximately the same fractional loss by volatilization for each of the three sets of hydraulic conditions. The short distance required for the Owens and others equation and the long distance required for the O'Connor-Dobbins equation again indicates the importance of flow depth in determining the volatilization coefficient. Minimum hydrolysis half-lives were used for those compounds with the widely varying experimental coefficients discussed previously so as to maximize the effect of hydrolysis.

The results are presented in table 19. These results indicate that hydrolysis was significant for the deep, low-velocity stream for several of the target analytes. The fraction removed by hydrolysis exceeded the fraction removed by volatilization for bromomethane, 1,2-dibromoethane, and 1,3-dichloropropene. Hydrolysis also was significant for chloroethane. For the other compounds, fractions removed by hydrolysis were much smaller, ranging from 0.0207 for dichloromethane to 0.0610 for 1,1,1-trichlorethane and 1,1-dichloroethene, with the corresponding fractions removed by volatilization ranging from 0.346 for dichloromethane to 0.310 for 1,1,1-trichloroethane. Consequently, hydrolysis has a measurable effect in a deep, low-velocity stream, even for a hydrolysis half-life as long as 548 days.

The results in table 19 indicate that hydrolysis was not significant for the shallow, medium-velocity stream. Similarly, hydrolysis was not important for the intermediate-depth, high-velocity stream, with the possible exception of 1,2-dibromoethane and 1,3-dichloropropene, for which hydrolysis has some significance relative to volatilization.

This analysis indicates that hydrolysis of VOCs is most likely to be important in deep, low-velocity streams, where the first-order rate coefficient for hydrolysis is comparable to or larger than the volatilization coefficient. As the water velocity increases and/or the flow depth decreases, the volatilization coefficient increases, resulting in less effect of hydrolysis in the determination of the overall fate of VOCs in streams.

This analysis of the importance of hydrolysis of the target analytes should be considered with the following qualifications. Experimental values for the half-lives for most of the analytes for which hydrolysis was important vary considerably, in some cases, by orders of magnitude (table 18). Minimum half-lives were used in the analysis to maximize the contribution of hydrolysis. Consequently, these estimates should be considered as qualitative only, and each situation should be evaluated specifically to determine if hydrolysis is contributing to the determination of the fate of VOCs in streams.

AQUATIC PHOTOLYSIS

Photolysis of organic compounds in streams is the reaction of the molecules of the compounds with sunlight. The molecules absorb light and are raised to an excited state. These excited molecules return to their ground states by photochemical degradation (photolysis) or by photophysical transitions such as fluorescence, quenching, radiationless transfer, and phosphorescence (Harris, 1990). The photolysis process must be rapid to compete favorably with photophysical processes, and it is estimated that more than 95 percent of the light absorbed results in photophysical deactivation rather than photolysis (Harris, 1990). Photolysis generally results in conversion to simpler compounds rather than complete conversion to inorganic products such as carbon dioxide, water, salts, and oxides (Bedding and others, 1983). In many cases, products of photolysis are the same as metabolites resulting from microbial degradation.

Table 19. Fractions removed by volatilization and hydrolysis and total fraction removed for nine target analytes with hydrolysis half-lives of 548 days or less

[USGS, U.S. Geological Survey; Hyd, hydrolysis; V fract, fraction of the concentration removed by volatilization; H fract, fraction of the concentration removed by hydrolysis; T fract, total fraction of the concentration removed by both processes; U, water velocity; m/s, meters per second; Y, flow depth; m, meters; L, distance downstream; iNS, isomer not specified]

USGS parameter code	Compound	Hyd half-life (days)	V fract	H fract	T fract
O'Connor-Dobbins (1958); U = 0.070 m/s; Y = 10 m; L = 100,000 m					
34418	chloromethane	339	0.377	0.0332	0.398
34423	dichloromethane	548	.346	.0207	.360
34413	bromomethane	20	.373	.436	.646
34311	chloroethane	38	.346	.260	.516
34506	1,1,1-trichloroethane	182	.310	.0610	.352
77651	1,2-dibromoethane	5.1	.314	.894	.928
34501	1,1-dichloroethene	182	.332	.0610	.373
34475	tetrachloroethene	266	.301	.0422	.330
iNS	1,3-dichloropropene	5.5	.311	.876	.914
Churchill and others (1962); U = 1.52 m/s; Y = 1.5 m; L = 20,000 m					
34418	chloromethane	339	.390	.0003	.391
34423	dichloromethane	548	.343	.0002	.343
34413	bromomethane	20	.380	.0053	.383
34311	chloroethane	38	.360	.0028	.362
34506	1,1,1-trichloroethane	182	.323	.0006	.323
77651	1,2-dibromoethane	5.1	.243	.0205	.259
34501	1,1-dichloroethene	182	.348	.0006	.348
34475	tetrachloroethene	266	.314	.0004	.314
iNS	1,3-dichloropropene	5.5	.282	.0190	.296
Owens and others (1964); U = 0.56 m/s; Y = 0.12 m; L = 170 m					
34418	chloromethane	339	.405	.0000	.405
34423	dichloromethane	548	.318	.0000	.318
34413	bromomethane	20	.379	.0001	.379
34311	chloroethane	38	.378	.0001	.378
34506	1,1,1-trichloroethane	182	.342	.0000	.342
77651	1,2-dibromoethane	5.1	.148	.0005	.148
34501	1,1-dichloroethene	182	.373	.0000	.373
34475	tetrachloroethene	266	.332	.0000	.332
iNS	1,3-dichloropropene	5.5	.219	.0004	.219

Two types of photolysis can occur. Direct photolysis involves absorption of light by the molecules of the compound followed by chemical reaction (Zepp and Cline, 1977). Indirect photolysis or sensitized photolysis occurs when energy is transferred from energized molecules of one chemical species in the aquatic system to molecules of another species, followed by chemical reaction (Harris, 1990). This first species is called a photosensitizer (Bedding and others, 1983); compounds such as humic substances, transition-metal ions, free radicals of organic molecules, peroxides, singlet oxygen, and ozone can serve as photosensitizers (Smith and others, 1988). Chlorophyll also has been considered a photosensitizer (Bedding and others, 1983). Indirect photolysis has not been defined as completely as direct photolysis (Callahan and others, 1979; Baughman and Burns, 1980; Smith and others, 1988); consequently, it is difficult to separate the effect of these two processes in natural aquatic systems.

Photolysis depends on the properties of the organic molecule of interest, the characteristics of the stream, and the input of sunlight (Smith and others, 1988). Molecules most likely to undergo photolysis are those with an extended conjugated hydrocarbon system, such as a polycyclic aromatic hydrocarbon, and those with a carbonyl, azo, or nitro group (Harris, 1990). Characteristics of the stream that are important include the presence of the photosensitizers, and the presence of quenching agents such as dissolved molecular oxygen and inorganic ions, which could change the yields of the photolysis reaction. Suspended-sediment concentrations and water depth are important considerations in determining light input to the water column, and these characteristics are discussed further below. The sunlight input is complex because it varies diurnally, seasonally, and with geographic location. This variation is discussed in more detail in the next section.

KINETICS OF THE AQUATIC PHOTOLYSIS PROCESS

The average rate of photolysis, $\left\{\frac{d[C_{ph}]}{dt}\right\}_\lambda$ at wavelength λ in a completely mixed body of water, is directly proportional to the rate of absorption of light by the molecules of the compound of interest (Zepp and Cline, 1977). The amount of light of wavelength λ absorbed per unit time, I_λ, by the water alone can be computed from the Beer-Lambert law in the form

$$I_\lambda = I_{o\lambda}(1 - 10^{-\alpha_\lambda z}) \tag{103}$$

where

$I_{o\lambda}$ is the incident light intensity (photon/cm^2/s) on the water surface,
α_λ is the absorption coefficient of the water (cm^{-1}), and
z is the pathlength of the light (cm).

Light incident on the water surface consists of direct radiation and sky radiation, where sky radiation is that resulting from molecular and aerosol scattering of direct radiation (Smith and others, 1988). Consequently, the average rate of absorption of light of wavelength λ per unit volume of water, $I_{a\lambda}$ (photon/cm^2/s), is given by (Zepp and Cline, 1977)

$$I_{a\lambda} = \frac{[I_{d\lambda}(1 - 10^{-\alpha_\lambda z_d}) + I_{s\lambda}(1 - 10^{-\alpha_\lambda z_s})]}{Y_{ph}} \tag{104}$$

where

$I_{d\lambda}$ and $I_{s\lambda}$ are the incident light intensities (photon/cm^2/s) at the water surface resulting from direct and scattered radiation,
z_d and z_s are the corresponding pathlengths (cm), and
Y_{ph} is the water depth (cm).

Zepp and Cline (1977) determined that the pathlength for direct radiation, z_d, is Y_{ph}secant θ where θ is the angle of refraction of the light in the water. The angle of refraction is dependent on the angle of incidence, which for sunlight is the solar zenith angle. As this angle increases during the solar day, the degree of refraction increases. Thus, for light coming from the horizon where the solar zenith angle is greater than 85°, the light is strongly refracted to an angle of 48° (Zepp and Cline, 1977). Because the secant of 48° is 1.49, the pathlength for direct radiation, z_d, will be less than or equal to 1.49 Y_{ph} during the solar day. The pathlength for scattered radiation, z_s, was shown to be equal to 1.20 Y_{ph}, assuming the index of refraction of water is 1.34 (Zepp and Cline, 1977).

The presence of the molecules of the organic compound of interest in the water changes the absorption coefficient from α_λ for the water alone to $\alpha_\lambda + \varepsilon_\lambda [C_{ph}]$ where ε_λ is the molar extinction coefficient of the organic compound (L/g mol/cm) and $[C_{ph}]$ is the molar concentration (g mol/L). The fraction of the light absorbed by the molecules of the organic compound of interest is $\varepsilon_\lambda [C_{ph}]/(\alpha_\lambda + \varepsilon_\lambda [C_{ph}])$. Because concentrations in environmental situations are generally low, it follows that the $\varepsilon_\lambda[C_{ph}]$ term is negligible with respect to α_λ, and the fraction can be approximated by $\varepsilon_\lambda [C_{ph}]/\alpha_\lambda$. Consequently, the average rate of light absorption of wavelength λ by the organic compound, $I_{a\lambda}'$ (photon/cm^2/s), is

$$I_{a\lambda}' = \frac{I_{a\lambda}\varepsilon_\lambda[C_{ph}]}{j\,\alpha_\lambda} \tag{105}$$

where

j is a conversion factor equaling 6.02×10^{20} when the intensities are expressed in photon/cm^2/s and concentration is in g mol/L.

Equation 105 can be written in the form

$$I_{a\lambda}' = k_{ph\lambda}[C_{ph}] \qquad (106)$$

where

$k_{ph\lambda}$ is a pseudo first-order rate coefficient for photolysis given by

$$k_{ph\lambda} = \frac{I_{a\lambda}\, \varepsilon_\lambda}{j\, \alpha_\lambda} \ . \qquad (107)$$

Equation 104 simplifies for two limiting cases.

1. For deep flows where essentially all the incident light is absorbed and $\alpha_\lambda z_d$ and $\alpha_\lambda z_s$ are both greater than 2, equation 104 reduces to (Zepp and Cline, 1977)

$$I_{a\lambda} = \frac{(I_{d\lambda} + I_{s\lambda})}{Y_{ph}} \qquad (108)$$

and equation 107 becomes

$$k_{ph\lambda} = \frac{[\varepsilon_\lambda (I_{d\lambda} + I_{s\lambda})]}{(j\, Y_{ph} \alpha_\lambda)} \ . \qquad (109)$$

Equation 109 indicates that the photolysis rate coefficient is inversely proportional to the water depth for depths greater than the photic zone, where the photic zone is the depth to which the light penetrates.

2. For shallow flows where $\alpha_\lambda z_d$ and $\alpha_\lambda z_s$ are both less than 0.02, the terms (1 minus 10) approximate as $2.303\alpha_\lambda z$, and equation 104 simplifies to

$$I_{a\lambda} = \frac{2.303\ \alpha_\lambda\ (I_{d\lambda} z_d + I_{s\lambda} z_s)}{Y_{ph}} \qquad (110)$$

and equation 107 becomes

$$k_{ph\lambda} = \frac{2.303\ \varepsilon_\lambda\ (I_{d\lambda} z_d + I_{s\lambda} z_s)}{j\, Y_{ph}} \ . \qquad (111)$$

The efficiency with which the absorbed light is used to produce products by the photolysis reaction is the reaction quantum yield, ϕ_λ (Mill and others, 1982), where the quantum yield is in gram moles reacted per photon of light absorbed. Consequently,

$$-\left\{\frac{d[C_{ph}]}{dt}\right\}_\lambda = \phi_\lambda\, k_{ph\lambda}\, [C_{ph}] \ . \qquad (112)$$

Equation 112 applies to a specific wavelength of light, λ. Sunlight, however, is not of a constant wavelength but has contributions from the ultraviolet, visible, and infrared parts of the spectrum. About 10 percent of the incident light energy is in the ultraviolet range and 45 percent is in each of the visible and infrared ranges (Harris, 1990). A comparison of energy, wavelength, and frequency ranges with typical chemical bond dissociation energies indicates that only the electronic transitions corresponding to ultraviolet/visible absorption are energetic enough to result in chemical reactions (Harris, 1990). Consequently, the wavelength range of importance for photolysis reactions is from 110 to 750 nm. Within this range, wavelengths less than 300 nm are filtered out by the ozone layer, leaving an effective wavelength range from about 300 to 750 nm.

Because of this variation in wavelength, equation 112 must be integrated to obtain the overall photolysis rate, $-\left\{\frac{d[C_{ph}]}{dt}\right\}_T$. Thus,

$$-\left\{\frac{d[C_{ph}]}{dt}\right\}_T = \int_{\lambda_o}^{\lambda_m} \phi_\lambda\, k_{ph}\, [C_{ph}]\, d\lambda \qquad (113)$$

where integration usually is over the wavelength range from about 300 to 750 nm. Zepp and Cline (1977) indicated that the quantum yield, ϕ_λ, is independent of wavelength, and Harris (1990) argued that the solar spectrum is sufficiently constant in its wavelength distribution so that the assumption of a constant quantum yield is reasonable for comparison of similar solar irradiation situations. However, Harris (1990) also noted that quantum yields determined in the laboratory at 254 nm are not equal to quantum yields at 300 nm, and in some cases, processes and products at these two wavelengths are different. Thus, there are arguments both for and against assuming that the quantum yield is independent of wavelength.

For the purpose of this discussion, the quantum yield was assumed independent of wavelength as was done by Zepp and Cline (1977). With this assumption and approximating the integral as a sum, equation 113 becomes

$$-\left\{\frac{d[C_{ph}]}{dt}\right\}_T \cong \phi[C_{ph}]\sum_{\lambda_o}^{\lambda_m} k_{ph\lambda} \quad . \qquad (114)$$

Equation 114 requires $k_{ph\lambda}$, and application of equations 109 and 111 for $k_{ph\lambda}$ is complicated by the fact that the sunlight intensity at a specific wavelength, I_λ, is a function of the time of day, the day of the year, and the geographic location as specified by the latitude. The sunlight decreases from midday to sunset, from summer to winter, and from points on the equator to higher and lower latitudes. To simplify calculations, Zepp and Cline (1977) provided tabular values of the light-intensity functions in equations 109 and 111.

The rate coefficients for the two limiting cases (eqs. 109 and 111) discussed previously are written (Zepp and Cline, 1977)

$$k_{ph\lambda} = \frac{W_\lambda \varepsilon_\lambda}{j\, Y_{ph} \alpha_\lambda} \qquad (115)$$

where

$$W_\lambda = I_{d\lambda} + I_{s\lambda}$$

and

$$k_{ph\lambda} = \frac{2.303\, \varepsilon_\lambda Z_\lambda}{j} \qquad (116)$$

where

$Z_\lambda = I_{d\lambda}$ secant $\theta + 1.2\, I_{s\lambda}$.

Values of W_λ and Z_λ are presented by Zepp and Cline (1977) as a function of wavelength at 40° north latitude for midday and midseason of each of the four seasons. Equation 115 applies for deep depths where essentially all the incident light is absorbed and equation 116 applies to shallow depths in natural waters and up to 0.5 m in distilled water (Zepp and Cline, 1977). The actual depth to which equation 116 applies depends on the absorption coefficient of the natural water and the degree of error that can be tolerated.

An analysis (Harris, 1990) of the W_λ and the Z_λ factors indicated that the summer and winter values differed by no more than a factor of four for wavelengths longer than 320 nm. Conversely, for wavelengths in the 295- to 320-nm range where organic molecules are most likely to absorb light, the summer value was as much as 36 times larger than the winter value. This variation indicates that the assumption that the quantum yield is independent of wavelength used in deriving equation 114 may be less valid for seasonal comparisons.

Values of W_λ and Z_λ presented by Zepp and Cline (1977) are for clear-sky conditions and average ozone concentrations. Ozone concentrations, however, increase with latitude in the northern hemisphere and from fall to spring. Cloud cover can decrease the sunlight intensity in the 280- to 320-nm range by as much as 50 percent, and intensity increases 15 to 20 percent for each kilometer increase in elevation above sea level (Zepp and Cline, 1977). In the case of streams, shielding by the banks and vegetation could result in an additional restriction of the light reaching the water surface.

Absorption of the incident sunlight within the water column, indicated by the absorption coefficient α_λ, can occur as a result of the water itself or constituents within the water such as phytoplankton and organic degradation products. The transmission and attenuation of the light also depends on the sediment concentration. Suspended sediments in the water column increase the degree to which the incident light is attenuated and, therefore, decreases the depth to which the light penetrates. This effect is likely to be one of the most important factors in determining rates of photolysis of organic compounds in streams (Bedding and others, 1983). Reported results of the effect of suspended sediment are contradictory, however. One study reported that photolysis rates generally were more rapid in turbid water than in clear water, the explanation being that the diffusiveness of the light caused by the scattering increased the rates (Bedding and others, 1983). Conversely, a second study resulted in decreased photolysis rates, the explanation being that the sediment particles shielded the organic molecules from the light. Suspended sediments also directly affected photolysis in that higher rates of photolysis were determined for pesticides and polycyclic aromatic hydrocarbons sorbed on sediments compared with rates for the dissolved compounds (Bedding and others, 1983). In streams, a dynamic equilibrium will exist as sediments containing these sorbed compounds move into and out of the photic zone by the processes of deposition and resuspension.

The overall photolysis process can be described by

$$-\left\{\frac{d[C_{ph}]}{dt}\right\}_T = K_{ph}[C_{ph}] \qquad (117)$$

where

K_{ph} is the first-order rate coefficient (day^{-1}) for photolysis.

Comparing equations 117 and 114 indicates that

$$K_{ph} = \phi\sum_{\lambda_o}^{\lambda_m} k_{ph\lambda} \qquad (118)$$

where

$k_{ph\lambda}$ is given by equation 116 for shallow flows and by equation 115 for deep flows.

The corresponding half-life for photolysis, $t_{0.5ph}$, is given by

$$t_{0.5ph} = 0.693/K_{ph}\ . \qquad (119)$$

PHOTOLYSIS HALF-LIVES FOR THE TARGET ANALYTES

Very little information was found on the half-lives for photolysis of the target analytes in aquatic systems. References such as Callahan and others (1979), Mabey and others (1982), Harris (1990), Howard and others (1991), and Mackay and others (1992a; 1992b; 1993) contained numerical values of the half-life for only four target analytes. This lack of information is consistent with the previously discussed statement (Harris, 1990) that organic molecules having moderate-to-strong absorption in the greater than 290-nm wavelength range characteristic of sunlight generally have either an extended conjugated hydrocarbon structure such as the fused ring of polycyclic aromatic hydrocarbons or a functional group having an unsaturated bond such as a carbonyl, azo, or nitro group. Because few of the 55 target analytes (table 1) have such structures, photolysis in the water phase of the environment likely will not be important for most.

Values of experimental half-lives for aquatic photolysis of benzene, naphthalene, chlorobenzene, and 1,2,4-trichlorobenzene are presented in table 20. Also presented in table 20 are negative results from photolysis studies of four target analytes. These results are presented as time periods for which concentration changes as a result of photolysis were not observed; consequently, if photolysis of these compounds occurred, the half-lives must be longer than the specified times. Hill and others (1976) observed no direct photolysis of chloroethene, but they did observe rapid photolysis in the presence of photosensitizers such as acetone and hydrogen peroxide. They noted that only high-energy sensitizers such as acetone are

Table 20. Photolysis half-lives for nine target analytes; all values for the surface layer of water except the 5-meter value for naphthalene

[USGS, U.S. Geological Survey; $t_{0.5ph}$, half-life for photolysis; ∞, infinite half-life; >, greater than; m, meters]

USGS parameter code	Compound	$t_{0.5ph}$ (days)	Reference
34423	dichloromethane	>365	Dilling and others (1975)
32106	trichloromethane	>365	Dilling and others (1975)
34506	1,1,1-trichloroethane	>365	Dilling and others (1975)
77652	1,1,2-trichloro-1,2,2-trifluoroethane	∞	Howard and others (1991)
39175	chloroethene	>3.8	Hill and others (1976)
34030	benzene	117–673	Mackay and others (1992a)
34696	naphthalene	3* (surface) 550* (5 m)	Mackay and others (1992a)
34301	chlorobenzene	6.2×10^{4}**	Dullin and others (1986)
34551	1,2,4-trichlorobenzene	1.6×10^{5}**	Dullin and others (1986)

*Midday summer values at 40 degrees north latitude.

**Twenty-four-hour summer values at 40 degrees north latitude.

effective with chloroethene because of the high triplet-state energy of this compound. Because little is known about the concentration and distribution of high-energy sensitizers in the environment, the importance of this indirect photolysis process can not be estimated. Another complicating factor is the presence in the environment of competing energy acceptors such as dissolved oxygen. Photolysis of 1,1,2-trichloro-1,2,2-trifluoroethane was not observed; thus, the half-life is considered to be infinite for this compound (Howard and others, 1991).

Finite values of the half-lives for benzene and chlorobenzene (table 20) contrast somewhat with the conclusion (Mabey and others, 1982) that aquatic photolysis was not significant for these compounds. One might argue, however, that a half-life of 6.2×10^4 days for chlorobenzene is insignificant for practical purposes. Half-lives for benzene were much shorter, and photolysis might be important for this compound. Photolysis of benzene is considered in more detail in the discussion of the relevant importance of photolysis and volatilization of naphthalene and benzene.

Photolysis was considered to be unimportant for 32 target analytes and an unspecified isomer of 1,3-dichloropropene. This assessment was based on the chemical structure and comparisons with similar types of molecular structures and the fact that some of the molecules contained no chromophores absorbing in the spectral range of sunlight (Callahan and others, 1979; Mabey and others, 1982; Howard and others, 1991). These target analytes are listed in table 21. Three of these are compounds listed in table 20 as having no observable change in concentration as a result of photolysis over a 365-day period (dichloromethane, trichloromethane, and 1,1,1-trichloroethane) and one (chloroethene) over a period of 3.8 days. Hexachlorobutadiene has an absorption spectrum that extends into the sunlight spectrum; however, the absorption coefficient may not be large enough for direct photolysis to be important (Callahan and others, 1979).

No information was available on the photolysis characteristics in aquatic systems of 18 target analytes. These analytes are listed in table 22. Two ether compounds (ethyl tertiary-butyl ether and tertiary-amyl methyl ether) were not listed in any of the references cited previously. However, Harris (1990) pointed out that ethers do not absorb

Table 21. Thirty-three target analytes for which aquatic photolysis was not considered significant

[USGS, U.S. Geological Survey; iNS, isomer not specified]

USGS parameter code	Compound	Reference
34418	chloromethane	Mabey and others (1982)
34423	dichloromethane	Callahan and others (1979) Mabey and others (1982)
32106	trichloromethane	Callahan and others (1979) Mabey and others (1982)
32102	tetrachloromethane	Mabey and others (1982) Howard and others (1991)
34413	bromomethane	Mabey and others (1982)
32104	tribromomethane	Mabey and others (1982)
32101	bromodichloromethane	Mabey and others (1982)
32105	chlorodibromomethane	Mabey and others (1982)
34311	chloroethane	Mabey and others (1982)
34496	1,1-dichloroethane	Mabey and others (1982)
32103	1,2-dichloroethane	Mabey and others (1982)
34506	1,1,1-trichloroethane	Callahan and others (1979) Mabey and others (1982)
34511	1,1,2-trichloroethane	Callahan and others (1979) Mabey and others (1982)
34396	hexachloroethane	Mabey and others (1982)
34541	1,2-dichloropropane	Callahan and others (1979) Mabey and others (1982)
34488	trichlorofluoromethane	Mabey and others (1982)
34668	dichlorofluoromethane	Mabey and others (1982)
39175	chloroethene	Callahan and others (1979)
34501	1,1-dichloroethene	Callahan and others (1979) Mabey and others (1982)
34546	*trans*-1,2-dichloroethene	Callahan and others (1979) Mabey and others (1982)
39180	trichloroethene	Callahan and others (1979) Mabey and others (1982)
34475	tetrachloroethene	Callahan and others (1979) Mabey and others (1982)
iNS	1,3-dichloropropene	Mabey and others (1982)
39702	hexachlorobutadiene	Callahan and others (1979) Mabey and others (1982)
34030	benzene	Mabey and others (1982)
34010	methylbenzene	Mabey and others (1982)
34371	ethylbenzene	Mabey and others (1982)
34301	chlorobenzene	Mabey and others (1982)
34536	1,2-dichlorobenzene	Mabey and others (1982)
34566	1,3-dichlorobenzene	Mabey and others (1982)
34571	1,4-dichlorobenzene	Mabey and others (1982)
34210	2-propenal	Mabey and others (1982)
34215	2-propenenitrile	Mabey and others (1982)

light in the sunlight spectral range; therefore, photolysis in aquatic systems is not likely to be important for these compounds. It also seems reasonable to assume on the basis of information in tables 20 and 21 that photolysis in aquatic systems will not be important for the halogenated alkanes and alkenes in table 22. Conversely, photolysis could be significant for the aromatic hydrocarbons, the alkyl benzenes, and the halogenated aromatics because these are the types of compounds for which photolysis occurs to some extent (table 20). Finally, Callahan and others (1979) noted that 2-propenenitrile does not absorb significantly in the sunlight spectral range. However, because of the conjugate double bonds of this molecule, they rationalized that indirect photolysis might be important in polluted streams where the appropriate photosensitizers are present.

Table 22. Eighteen target analytes for which no information was available on aquatic photolysis

[USGS, U.S. Geological Survey]

USGS parameter code	Compound	Reference
77651	1,2-dibromoethane	Howard and others (1991)
77443	1,2,3-trichloropropane	Howard and others (1991)
82625	1,2-dibromo-3-chloropropane	Howard and others (1991)
77093	*cis*-1,2-dichloroethene	Howard and others (1991)
50002	bromoethene	Howard and others (1991)
34704	*cis*-1,3-dichloropropene	Callahan and others (1979)
34699	*trans*-1,3-dichloropropene	Callahan and others (1979)
77128	styrene	Howard and others (1991)
77224	n-propylbenzene	Mackay and others (1992a)
77223	iso-propylbenzene	Howard and others (1991)
77342	n-butylbenzene	Mackay and others (1992a)
77135	1,2-dimethylbenzene	Howard and others (1991)
85795	1,3-dimethylbenzene	Howard and others (1991)
85795	1,4-dimethylbenzene	Howard and others (1991)
77222	1,2,4-trimethylbenzene	Howard and others (1991)
77613	1,2,3-trichlorobenzene	Mackay and others (1992a)
78032	methyl tertiary-butyl ether	Howard and others (1991)
81577	diisopropyl ether	Mackay and others (1993)

ESTIMATION OF THE IMPORTANCE OF AQUATIC PHOTOLYSIS

The results in table 20 indicate that photolysis in the aquatic phase is most likely to be important for naphthalene. The results in table 20 also indicate water depth has a strong influence on the importance of photolysis of naphthalene, with the effect of photolysis decreasing rapidly as the depth increases. The photolysis half-life for a 5-m depth was 183 times longer than the half-life for photolysis in the surface layer of the water. This increase in the half-life was the result of light attenuation with increasing depth.

The comparison of the relative effects of photolysis and volatilization on the concentrations of naphthalene in streams must be done over a 24-hour period, or a multiple thereof, because photolysis ceases during the nighttime. Volatilization, however, continues at virtually the same rate, except possibly for a small decrease as a result of lower water temperatures during the nighttime. The half-lives in table 20 for naphthalene are midday summer values; hence, they correspond to the maximum photolysis rate. These values are not, however, applicable over a 24-hour period because of the diurnal variation of the sunlight intensity.

To obtain a mean rate coefficient for photolysis over a 24-hour period, the half cycle sine wave approximation of the production of oxygen by photosynthesis (O'Connor and DiToro, 1970) was used to indicate the variation of the sunlight intensity with time over 24 hours. Adapted for photolysis, this equation has the form

$$k_{ph}(t) = k_{phm} \sin\left[\left(\frac{\pi}{p}\right)(t-t_s)\right] \qquad (120)$$

where

$k_{ph}(t)$ is the rate coefficient for photolysis (day^{-1}) at time t (fractional day),

k_{phm} is the maximum photolysis rate coefficient (day^{-1}),

p is the fraction of the 24-hour time period over which sunlight reaches the water surface, and

t_s is the time (fractional day) at which the sunlight first reaches the water surface.

A solar day from 0500 to 2100 hours was assumed, resulting in values of 0.208 for t_s, 0.667 for p, and 0.875 for the end of the solar day. The deep-flow half-life for naphthalene in table 20 (550 days) corresponds to a photolysis rate coefficient of 0.00126 day^{-1}, and this was used for k_{phm} in equation 120. This maximum rate according to equation 120 occurred just past midday at 0.542 fractional days.

Photolysis rate coefficients were computed from equation 120 as a function of time over the solar day, and an integral mean coefficient was computed from these values. The result for a depth of 500 cm was 0.000798 day^{-1}, which is 37 percent of the midday value. For deep flows, equation 115 indicates that the photolysis rate coefficient is inversely proportional to the water depth, Y_{ph}. Consequently, it follows that

$$k_{ph} = \frac{0.399}{Y_{ph}} \qquad (121)$$

which gives a rate coefficient of 0.000798 day^{-1} for a depth of 500 cm.

Equations 99 and 100 were modified by replacing the first-order rate coefficient for hydrolysis with the first-order rate coefficient for aquatic photolysis. These modified equations were then used with equation 101 and the O'Connor and Dobbins equation (eq. 55) to estimate the relative contributions of photolysis and volatilization to the fate of naphthalene in streams. Volatilization coefficients were computed as a function of depth from equations 55, 27, 28, 16, and 13 by using procedures discussed previously. An average air-film mass-transfer coefficient at 20°C of 756 m/day and depths covering the range (0.27 to 11.3 m) appropriate for the O'Connor-Dobbins equation (fig. 6) were used. The results indicated that the fraction of naphthalene removed by photolysis for all depths between 0.27 and 11.3 m was less than 2 percent of the total removed by both processes.

The shallow approximation (eq. 110) requires that the factors $\alpha_\lambda z_d$ and $\alpha_\lambda z_s$ be less than 0.02. Zepp and Cline (1977) indicated that an α value of the order of 0.11 cm^{-1} at a wavelength of 313 nm is appropriate as an average value for 10 streams in the southeastern United States, and a value for pure water at this wavelength is 0.0020 cm^{-1}. The corresponding maximum water depths for the z_d and z_s parameters meeting the criterion are 0.15 and 0.12 cm for natural waters and 8.3 and 6.7 cm for pure water. Gas-transfer coefficients for such shallow flows in natural streams have not been measured, but large coefficients would be expected.

For comparison, the minimum flow depth of 11.9 cm from the work of Owens and others (1964) was used as an example of a shallow flow. Again, the minimum water velocity of their data set (0.04 m/s) was used to minimize the contribution of volatilization. Estimating the volatilization coefficient for naphthalene for these conditions by using equation 53 and procedures discussed previously resulted in a coefficient of 11.4 day^{-1}. The integral mean coefficient for photolysis for the solar day corresponding to the midday shallow-flow half-life of 3 days (table 20) was 0.146 day^{-1}. Using a 24-hour time period for volatilization and a 16-hour time period for photolysis results in estimated fractions removed of 0.999999 for volatilization and 0.0928 for photolysis, assuming each process acting alone. The contribution of photolysis is minimal relative to volatilization, and it is expected that the volatilization coefficient would be even larger for the shallower flows for which the shallow approximation applies.

The previous analysis of the importance of photolysis of naphthalene was based on deep-flow and shallow-flow estimates of the photolysis half-lives. The deep value is for a 5-m quiescent water column. Water in streams, however, is not quiescent but is subject to continual mixing as a result of shear forces at the bottom and banks of the stream. It was previously noted that concentration gradients of dissolved constituents over the vertical dimension (depth) in streams generally are not observed because of this mixing process. Consequently, water parcels are moving continuously to the surface where photolysis can occur in the surface layers. It can be argued then that a more appropriate evaluation of the relative contributions of photolysis and volatilization would be to compare the shallow-flow photolysis process with the deep-flow volatilization process.

The results of this comparison are presented in figure 13 for naphthalene and benzene. A flow-depth range of 0.27 to 11.3 m appropriate for the O'Connor-Dobbins equation was used as in the previous example. The results are for a downstream distance of 5,010 m, which is the distance traveled in 24 hours at a water velocity of 0.058 m/s. Figure 13 indicates that the fraction removed by volatilization decreases rapidly as the depth increases. Conversely, with the assumption that photolysis occurs only in surface layers continually replaced with water from below, the fraction removed by photolysis is constant. Figure 13 indicates that the fractions removed by the two processes are approximately equal for a flow depth of about 3 m for naphthalene and 5.7 m for benzene. For deeper flows, the fractions removed by photolysis exceed the fractions removed by volatilization, indicating that photolysis is significant for these two compounds for deep, low-velocity streams.

This analysis is based on the assumption that photolysis in the surface layers is not rate-limited by the movement of water parcels to the surface from the lower parts of the water depth and, thus, the results should be considered as an upper bound on the effect of photolysis. The fact that vertical concentration gradients of dissolved constituents do not occur in streams would seem to argue in favor of no rate limitation. On the other hand, volatilization decreases as the flow depth increases, presumably because the thickness of the water film increases as the depth increases. However, the effect of this increased film thickness on photolysis in the surface layer and the rate of replacement of the photolyzed compound with compound from the deeper parts of the flow is unknown. Experimental verification of the effect of vertical mixing on photolysis is needed.

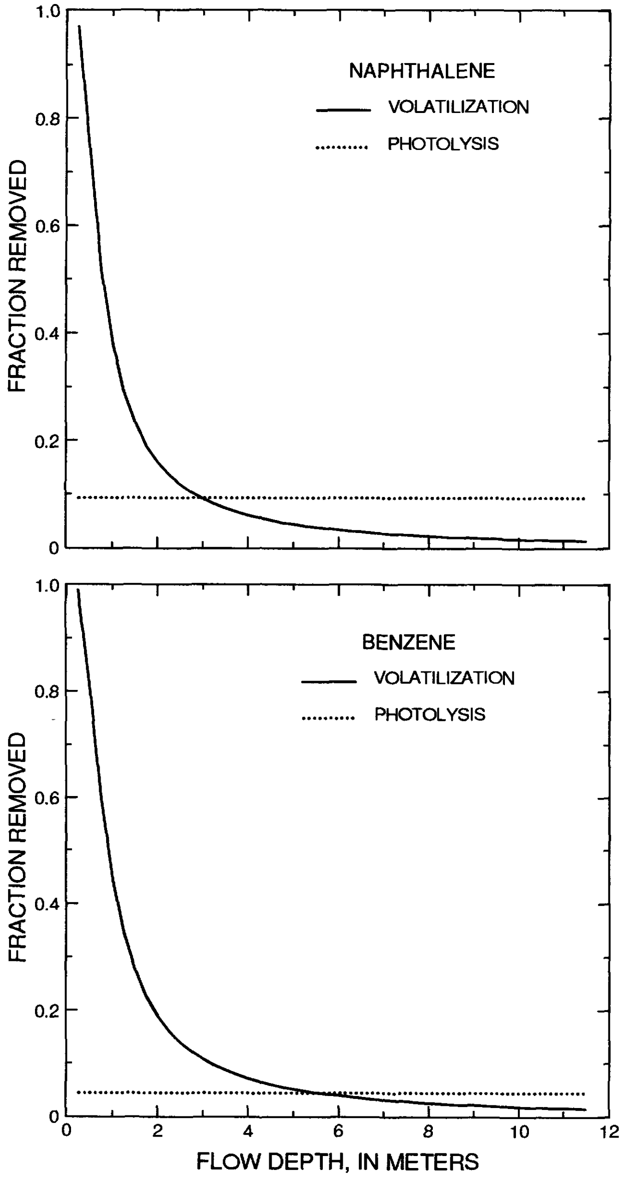

Figure 13. Fraction of naphthalene and benzene removed by volatilization and photolysis as a function of flow depth at 20 degrees Celsius; Henry's law constants are 36.6 and 507 pascals cubic meter per gram mole for naphthalene and benzene, respectively.

Bedding and others (1983) discussed the possibility that organic compounds might accumulate in the surface films of natural waters where they would be subject to the maximum sunlight intensity. No experimental data were available to support this hypothesis, and they concluded that the mass of compounds present in these thin films is insignificant relative to the mass in the water column, thus resulting in an insignificant effect on the overall rate of photolysis. This conclusion, however, neglects the continual replacement in streams of the surface concentrations with concentrations of the compound from below.

The analysis of the photolysis characteristics of naphthalene was limited to a wavelength of 313 nm because this is the wavelength at which naphthalene molecules most strongly absorb (Harris, 1990). Actually, the contributions of the various sunlight wavelengths should be summed as indicated by equation 114, and such summation would probably result in lower rate coefficients because of lower contributions at the longer wavelengths. Also, the photolysis half-lives were for summer conditions, and the half-lives for the other three seasons of the year are likely to be longer. Consequently, the importance of photolysis relative to volatilization would be less than that indicated by the previous analyses. Finally, the summation indicated by equations 114, 115, and 116 requires molar absorption coefficients as a function of wavelength, and such information is available for only a few polycyclic aromatic hydrocarbons and pesticides (Harris, 1990).

These estimates of the importance of photolysis in streams were based on a consideration of direct photolysis only. Zepp and others (1975), however, noted that the overall photolysis rate of an ester in a stream water was twice the rate observed in distilled water, presumably because of the presence of photosensitizers in the natural water. Therefore, this possibility should always be evaluated when considering the transport and fate of the target analytes in streams, especially those analytes with an aromatic ring structure.

OXIDATION AND CHEMICAL REACTION

Oxidation is the reaction of an organic molecule with an oxidant that is a reactive electron-deficient species. The most common oxidants that might be significant in oxidation processes in environmental waters are the peroxy radical ($RO_2\bullet$), photoexcited diradicals ($RO\bullet$), the hydroxy radical ($HO\bullet$), singlet oxygen ($^1O_2$), and ozone (O_3) (Mill, 1980). These oxidants apparently result from photolysis of natural humic materials present in the water (Mill, 1980). Molecular oxygen (O_2) is rarely involved directly in reactions but is the ultimate electron sink in most environmental oxidation reactions (Mill and others, 1982).

Oxidation can be described by

$$-\frac{d[C]}{dt} = k_{ox}[C][OX] \qquad (122)$$

where

$[C]$ is the molar concentration of the organic compound of interest,

t is time,

k_{ox} is the second-order rate coefficient for oxidation, and

$[OX]$ is the molar concentration of the oxidant (Mill and others, 1982).

The units of k_{ox} are usually $M^{-1}\ s^{-1}$, where M is the molar concentration. The total rate of oxidation is the sum of the rates of reaction for each of the oxidants, or

$$-\frac{d[C]}{dt} = [C]\sum_{i=1}^{n} k_{oxi}[OX]_i\,. \qquad (123)$$

If some type of average effective oxidant concentration can be determined for the time of interest, then $[OX]_i$ can be considered constant and equation 123 can be integrated to give

$$[C]_t = [C]_o \exp\left(-\sum_{i=1}^{n} k'_{oxi}\, t\right) \qquad (124)$$

where

$[C]_t$ is the molar concentration at time t,

$[C]_o$ is the molar concentration at time zero, and

k'_{oxi} is the pseudo first-order rate coefficient for oxidation equivalent to $k_{oxi}\,[OX]_i$.

The corresponding half-life for oxidation is

$$t_{0.5oxi} = \frac{0.693}{\sum_{i=1}^{n} k'_{oxi}}\,. \qquad (125)$$

Use of an average oxidant concentration might be questioned because the oxidants apparently result from photolysis of natural humic materials (Mill, 1980), and the sunlight intensity that drives photolysis varies diurnally. However, little is known about the variation of the concentrations of these oxidants with time. Mabey and others (1984) indicated that concentrations of these oxidants in water averaged over several diurnal cycles for the spring and summer seasons are known only within a factor of 10.

Mabey and others (1984) estimated that the peroxy radical ($RO_2\bullet$) has a concentration of 10^{-9} to 10^{-10} M in natural waters. Consequently, only compounds with second-order rate coefficients larger than about $10^3\ M^{-1}\ s^{-1}$ will oxidize in water at significant rates. Combining this rate coefficient with a peroxy radical concentration of 10^{-9} M gives a half-life of 8 days, and a pseudo first-order oxidation rate-coefficient of $10^{-6}\ s^{-1}$. Mabey and others (1984) concluded that aromatic amines and phenols are the two major classes of organic compounds reactive enough toward the peroxy radical for oxidation to be significant in natural waters. None of the target analytes (table 1), however, are these types of compounds. Similarly, Mill (1980), using rate coefficients from the literature for reaction with the peroxy radical, computed oxidation half-lives of 9×10^4 days for olefins and 8 days for polycyclic aromatic hydrocarbons. Because naphthalene (table 1) is a polycyclic aromatic hydrocarbon, oxidation of this target analyte might be important in some types of streams.

Estimated half-lives for oxidation by the photoexcited diradical ($RO\bullet$) using a radical concentration of 10^{-14} M were 73 years and 334 days for alkanes and olefins, respectively (Mill, 1980). Oxidation by the hydroxy radical (HO•) generally is assumed to be negligible because the concentration of this radical is so low in natural waters (Mill, 1980). Conversely, in the atmosphere, the hydroxy radical is the only radical oxidant of importance. However, discussion of atmospheric processes is beyond the scope of this report.

Singlet oxygen ($^1O_2$) is an electronically excited form of oxygen that undergoes a wide variety of reactions with organic molecules; most of these reactions are not observed with triplet oxygen. Using a reported aquatic concentration of about 10^{-12} M and rate coefficients from the literature, estimated half-lives for oxidation by singlet oxygen are 7.3 years, 8 days, and 19 hours for olefins, substituted olefins, and dienes, respectively (Mill, 1980). Consequently, oxidation by singlet oxygen may be significant for target analytes (table 1) within these classifications, such as the halogenated alkenes and hexachlorobutadiene.

Significant concentrations of ozone have not been observed in natural waters. However, ozone is used to disinfect drinking water and wastewaters before discharge, and such use could result in direct oxidation of some organic compounds. Also, because ozone in water can form the hydroxy radical, oxidation of compounds resistant to ozone itself may occur (Mill, 1980) through oxidation by the hydroxy radical.

OXIDATION HALF-LIVES FOR THE TARGET ANALYTES

Experimental values of the half-lives for oxidation of 12 target analytes are presented in table 23 for low (5×10^{-19} M) and high (2×10^{-17} M) concentrations of the hydroxy radical likely to be present in relatively oligotrophic and eutrophic natural waters. Half-lives from Haag and Yao (1992) were calculated from their experimental second-order rate coefficients for oxidation by the hydroxy radical and these expected low and high concentrations of the hydroxy radical by using equation 125.

It was previously suggested (Mill, 1980) that oxidation by the hydroxy radical is generally assumed to be negligible in natural waters because the concentration of the hydroxy radical is so low. The results listed in table 23 indicate that this is a valid assumption for the halogenated alkanes but that this assumption may not be valid for the aromatic hydrocarbons, the alkyl benzenes, and the halogenated aromatics where many of the half-lives were less than 1 year for the possible high concentrations of hydroxy radical in natural waters.

Calculated values of half-lives for the oxidation of 39 target analytes by the peroxy radical, singlet oxygen, and the hydroxy radical are presented in table 24. Concentrations of 10^{-9} M for the peroxy radical and 10^{-12} M for singlet oxygen were used as appropriate for surface waters under natural sunlight conditions (Mabey and others, 1982). Exceptions were the Howard and others (1991) results for 1,2-, 1,3-, and 1,4-dimethylbenzene for which peroxy radical concentrations of 5×10^{-10} and 10^{-11} M were used. The lower and higher concentrations of the hydroxy radical presented previously were used for this oxidant. Half-lives were computed from these concentrations, equation 125, and calculated values of the second-order rate coefficients for oxidation by the different oxidants.

Mabey and others (1982) used two procedures to calculate second-order rate coefficients for oxidation by the peroxy radical. The first consisted of using a measured rate coefficient available from the literature for a similar chemical structure. The second was based on structure-activity relationships for hydrogen-atom transfer and addition to double bonds. The latter procedure was used most frequently. Only a few target analytes are reactive toward singlet oxygen. When no reactive centers were noted, the compounds were assigned a rate coefficient of less than 360 M^{-1} $hour^{-1}$, which corresponds to a half-life of greater than 2.2×10^5 years. Reactive compounds were given rate coefficients on the basis of similar structures with known rate coefficients for reaction with singlet oxygen (Mabey and others, 1982).

Values for the three dimethylbenzenes (table 24) were from scientific judgment based on estimated rate coefficients for alkyl peroxy radicals in aqueous solution (Howard and others, 1991). The calculated values of Haag and Yao (1992) were obtained using two procedures. Values for the halogenated alkanes were estimated from a correlation of experimental rate coefficients for oxidation by hydroxy radical in water as a function of the experimental rate coefficient for oxidation in the atmosphere. Chlorinated aromatics did not fit the same correlation; consequently, half-lives for these compounds were estimated using the Hammett σ constant (Haag and Yao, 1992).

Table 23. Experimental values of the half-lives for oxidation of 12 target analytes in water by the hydroxy radical

[USGS, U.S. Geological Survey; $t_{0.5ox}$, half-life for the oxidation process]

USGS parameter code	Compound	Oxidant concentration (moles per liter)	$t_{0.5ox}$ (years)	Reference
34423	dichloromethane	2×10^{-17}	5.0×10^{1}	Haag and Yao (1992)
		5×10^{-19}	2.0×10^{3}	
		2×10^{-17}	1.9×10^{1}	Haag and Yao (1992)
		5×10^{-19}	7.6×10^{2}	
		2×10^{-17}	1.2×10^{1}	Haag and Yao (1992)
		5×10^{-19}	4.9×10^{2}	
32106	trichloromethane	2×10^{-17}	7.8×10^{1}	Howard and others (1991)
		5×10^{-19}	3.1×10^{3}	
		2×10^{-17}	1.0×10^{2}	Haag and Yao (1992)
		5×10^{-19}	4.0×10^{3}	
		2×10^{-17}	2.0×10^{1}	Haag and Yao (1992)
		5×10^{-19}	8.1×10^{2}	
32104	tribromomethane	2×10^{-17}	8.4×10^{0}	Haag and Yao (1992)
		5×10^{-19}	3.4×10^{2}	
34511	1,1,2-trichloroethane	2×10^{-17}	1.0×10^{1}	Haag and Yao (1992)
		5×10^{-19}	4.0×10^{2}	
		2×10^{-17}	8.4×10^{0}	Haag and Yao (1992)
		5×10^{-19}	3.4×10^{2}	
34541	1,2-dichloropropane	2×10^{-17}	2.9×10^{0}	Haag and Yao (1992)
		5×10^{-19}	1.2×10^{2}	
82625	1,2-dibromo-3-chloropropane	2×10^{-17}	3.4×10^{0}	Haag and Yao (1992)
		5×10^{-19}	1.4×10^{2}	
		2×10^{-17}	2.6×10^{0}	Haag and Yao (1992)
		5×10^{-19}	1.0×10^{2}	
34030	benzene	2×10^{-17}	9.2×10^{-1}	Howard and others (1991)
		5×10^{-19}	3.7×10^{1}	
34010	methylbenzene	2×10^{-17}	3.6×10^{-2}	Howard and others (1991)
		5×10^{-19}	1.5×10^{-1}	
77223	iso-propylbenzene	2×10^{-17}	3.7×10^{-1}	Howard and others (1991)
		5×10^{-19}	1.5×10^{1}	
77222	1,2,4-trimethylbenzene	2×10^{-17}	1.2×10^{-1}	Howard and others (1991)
		5×10^{-19}	4.9×10^{0}	
34301	chlorobenzene	2×10^{-17}	1.8×10^{-1}	Howard and others (1991)
		5×10^{-19}	7.1×10^{0}	
34566	1,3-dichlorobenzene	2×10^{-17}	2.2×10^{-1}	Haag and Yao (1992)
		5×10^{-19}	8.8×10^{0}	

The calculated values of the half-lives in table 24 are greater than 2 years, with the following exceptions. The half-lives for oxidation by singlet oxygen of chloroethene, 1,1-dichloroethene, 1,3-dichloropropene (isomer not specified), and 2-propenenitrile were estimated as greater than 0.79 year. The "greater than" value results from the fact that the estimated rate coefficients were listed as less than 10^{8} M^{-1} $hour^{-1}$ by Mabey and others (1982). The half-lives for oxidation by the hydroxy radical at the maximum concentration (2×10^{-17} M) likely to be present in natural waters were 0.28 year for 1,2- and 1,4-dichlorobenzene and 1,2,3- and 1,2,4-trichlorobenzene. Calculated half-lives for naphthalene were greater than 10^{4} years, in contrast to the 8 days estimated previously (Mill, 1980) for polycyclic aromatic hydrocarbons.

Table 24. Calculated values of the half-lives for oxidation of 39 target analytes in water

[USGS, U.S. Geological Survey; $t_{0.5ox}$, half-life for the oxidation process; $^1O_2$, singlet oxygen at a concentration of 10^{-12} moles per liter; RO_2•, peroxy radical at a concentration of 10^{-9} moles per liter, except for the data of Howard and others (1991), which used high and low concentrations of 5×10^{-10} and 10^{-11} moles per liter; OH•, hydroxy radical at concentrations of 2×10^{-17} and 5×10^{-19} moles per liter; >, greater than; ∞, infinite half-life; ≅, approximately equal to]

USGS parameter code	Compound	Oxidant	$t_{0.5ox}$ (years)	Reference
34418	chloromethane	$^1O_2$	$>2.2\times10^5$	Mabey and others (1982)
		RO_2•	1.6×10^6	
34423	dichloromethane	$^1O_2$	$>2.2\times10^5$	Mabey and others (1982)
		RO_2•	4.0×10^5	
		OH•	9.2×10^0	Haag and Yao (1992)
		OH•	3.7×10^2	
32106	trichloromethane	$^1O_2$	$>2.2\times10^5$	Mabey and others (1982)
		RO_2•	1.1×10^5	
32102	tetrachloromethane	$^1O_2$	$>2.2\times10^5$	Mabey and others (1982)
		RO_2•	$>7.9\times10^4$	
		OH•	$>5.5\times10^2$	Haag and Yao (1992)
		OH•	$>2.2\times10^4$	
34413	bromomethane	$^1O_2$	$>2.2\times10^5$	Mabey and others (1982)
		RO_2•	7.9×10^5	
32104	tribromomethane	$^1O_2$	$>2.2\times10^5$	Mabey and others (1982)
		RO_2•	1.6×10^5	
32101	bromodichloromethane	$^1O_2$	$>2.2\times10^5$	Mabey and others (1982)
		RO_2•	4.0×10^5	
32105	chlorodibromomethane	$^1O_2$	$>2.2\times10^5$	Mabey and others (1982)
		RO_2•	1.6×10^5	
34311	chloroethane	$^1O_2$	$>2.2\times10^5$	Mabey and others (1982)
		RO_2•	$>7.9\times10^4$	
34496	1,1-dichloroethane	$^1O2$	$>2.2\times10^5$	Mabey and others (1982)
		RO_2•	7.9×10^4	
32103	1,2-dichloroethane	$^1O_2$	$>2.2\times10^5$	Mabey and others (1982)
		RO_2•	$>7.9\times10^4$	
34506	1,1,1-trichloroethane	$^1O_2$	$>2.2\times10^5$	Mabey and others (1982)
		RO_2•	7.9×10^4	
34511	1,1,2-trichloroethane	$^1O_2$	$>2.2\times10^5$	Mabey and others (1982)
		RO_2•	2.6×10^4	
		OH•	5.5×10^0	Haag and Yao (1992)
		OH•	2.2×10^2	
34396	hexachloroethane	$^1O_2$	∞	Mabey and others (1982)
		RO_2•	∞	
34541	1,2-dichloropropane	$^1O_2$	$>2.2\times10^5$	Mabey and others (1982)
		RO_2•	$\cong7.9\times10^4$	
82625	1,2-dibromo-3-chloropropane	OH•	3.8×10^0	Haag and Yao (1992)
		OH•	1.5×10^2	
34488	trichlorofluoromethane	$^1O_2$	∞	Mabey and others (1982)
		RO_2•	∞	

Table 24. Calculated values of the half-lives for oxidation of 39 target analytes in water—Continued

[USGS, U.S. Geological Survey; $t_{0.5ox}$, half-life for the oxidation process; $^1O_2$, singlet oxygen at a concentration of 10^{-12} moles per liter; RO_2•, peroxy radical at a concentration of 10^{-9} moles per liter, except for the data of Howard and others (1991), which used high and low concentrations of 5×10^{-10} and 10^{-11} moles per liter; OH•, hydroxy radical at concentrations of 2×10^{-17} and 5×10^{-19} moles per liter; >, greater than; ∞, infinite half-life; ≅, approximately equal to]

USGS parameter code	Compound	Oxidant	$t_{0.5ox}$ (years)	Reference
34668	dichlorodifluoromethane	$^1O_2$	∞	Mabey and others (1982)
		RO_2•	∞	
39175	chloroethene	$^1O_2$	$>7.9\times10^{-1}$	Mabey and others (1982)
		RO_2•	2.6×10^{4}	
34501	1,1-dichloroethene	$^1O_2$	$>7.9\times10^{-1}$	Mabey and others (1982)
		RO_2•	2.6×10^{4}	
34546	*trans*-1,2-dichloroethene	$^1O_2$	$>7.9\times10^{2}$	Mabey and others (1982)
		RO_2•	1.3×10^{4}	
39180	trichloroethene	$^1O_2$	$>7.9\times10^{4}$	Mabey and others (1982)
		RO_2•	1.3×10^{4}	
34475	tetrachloroethene	$^1O_2$	$>7.9\times10^{5}$	Mabey and others (1982)
		RO_2•	1.3×10^{4}	
iNS	1,3-dichloropropene	$^1O_2$	$>7.9\times10^{-1}$	Mabey and others (1982)
		RO_2•	1.8×10^{3}	
34030	benzene	$^1O_2$	$>2.2\times10^{5}$	Mabey and others (1982)
		RO_2•	$>7.9\times10^{4}$	
34696	naphthalene	$^1O_2$	$>2.2\times10^{5}$	Mabey and others (1982)
		RO_2•	$>7.9\times10^{4}$	
34010	methylbenzene	$^1O_2$	$>2.2\times10^{5}$	Mabey and others (1982)
		RO_2•	5.5×10^{2}	
34371	ethylbenzene	$^1O_2$	$>2.2\times10^{5}$	Mabey and others (1982)
		RO_2•	1.1×10^{2}	
77135	1,2-dimethylbenzene	RO_2•	4.3×10^{1}	Howard and others (1991)
		RO_2•	3.1×10^{4}	
85795	1,3-dimethylbenzene	RO_2•	5.5×10^{2}	Howard and others (1991)
		RO_2•	2.7×10^{4}	
85795	1,4-dimethylbenzene	RO_2•	3.1×10^{2}	Howard and others (1991)
		RO_2•	1.6×10^{4}	
34301	chlorobenzene	$^1O_2$	$>2.2\times10^{5}$	Mabey and others (1982)
		RO_2•	$>7.9\times10^{4}$	
34536	1,2-dichlorobenzene	$^1O_2$	$>2.2\times10^{5}$	Mabey and others (1982)
		RO_2•	$>7.9\times10^{4}$	
		OH•	2.8×10^{-1}	Haag and Yao (1992)
		OH•	1.1×10^{1}	
34566	1,3-dichlorobenzene	$^1O_2$	$>2.2\times10^{5}$	Mabey and others (1982)
		RO_2•	$>7.9\times10^{4}$	
34571	1,4-dichlorobenzene	$^1O_2$	$>2.2\times10^{5}$	Mabey and others (1982)
		RO_2•	$>7.9\times10^{4}$	
		OH•	2.8×10^{-1}	Haag and Yao (1992)
		OH•	1.1×10^{1}	

Table 24. Calculated values of the half-lives for oxidation of 39 target analytes in water—Continued

[USGS, U.S. Geological Survey; $t_{0.5ox}$, half-life for the oxidation process; $^1O_2$, singlet oxygen at a concentration of 10^{-12} moles per liter; RO_2•, peroxy radical at a concentration of 10^{-9} moles per liter, except for the data of Howard and others (1991), which used high and low concentrations of 5×10^{-10} and 10^{-11} moles per liter; OH•, hydroxy radical at concentrations of 2×10^{-17} and 5×10^{-19} moles per liter; >, greater than; ∞, infinite half-life; ≅, approximately equal to]

USGS parameter code	Compound	Oxidant	$t_{0.5ox}$ (years)	Reference
77613	1,2,3-trichlorobenzene	OH•	2.8×10^{-1}	Haag and Yao (1992)
		OH•	1.1×10^{1}	
34551	1,2,4-trichlorobenzene	$^1O_2$	$>2.2\times10^{5}$	Mabey and others (1992)
		RO_2•	$>7.9\times10^{4}$	
		OH•	2.8×10^{-1}	Haag and Yao (1992)
		OH•	1.1×10^{1}	
34210	2-propenal	$^1O_2$	7.9×10^{0}	Mabey and others (1982)
		RO_2•	2.3×10^{1}	
34215	2-propenenitrile	$^1O_2$	$>7.9\times10^{-1}$	Mabey and others (1982)
		RO_2•	2.2×10^{3}	

ESTIMATION OF THE IMPORTANCE OF OXIDATION

Fourteen target analytes have experimental or calculated half-lives for oxidation of less than 1 year (tables 23 and 24). Four of these are calculated values of greater than 0.79 year for reaction with singlet oxygen (table 24). These values are included because present knowledge does not indicate how much larger than 0.79 year these half-lives might be. The half-lives for these 14 analytes range from 0.036 year for methylbenzene to 0.92 year for benzene, both for the hydroxy radical.

The oxidants causing oxidation of the target analytes presumably result from photolysis of natural humic materials in the water. Consequently, the concentrations of the oxidants are dependent on the diurnal variation of the sunlight intensity. Also, it has been estimated (Mill, 1980) that these oxidants persist in natural waters for only a few milliseconds.

Estimation of the importance of oxidation of the target analytes in streams is similar to estimation of the importance of aquatic photolysis. The question is one of deep flows compared to shallow flows and whether or not vertical mixing in streams is rapid enough that the shallow-flow approximation applies to deep flows. For the purpose of this report, it was assumed that vertical mixing is rapid enough that penetration of the sunlight to the deeper depths is not limiting the extent of oxidation, with oxidation occurring primarily in the surface layers that are continually replaced with water from the deeper flows by the vertical mixing processes. This approach will maximize the contribution of oxidation relative to volatilization.

The fraction of the concentration removed by oxidation was compared with the total fraction removed by volatilization and oxidation combined, using the same procedure as was used for estimating the importance of aquatic photolysis. Figure 14 shows the ratio of the fraction removed by oxidation to the total removed by both processes for four target analytes. The flow depth was varied from 0.27 to 11.3 m for a downstream distance of 5,010 m. This is the distance traveled by a water parcel in 24 hours at a water velocity of 0.058 m/s. Integral mean first-order rate coefficients for oxidation were computed from equation 125, using the half-lives from tables 23 and 24.

Figure 14 indicates that the importance of oxidation relative to volatilization increases as the flow depth increases because of reduced volatilization at the increased depths, as was observed for other comparisons. The effect was greatest for methylbenzene, least for benzene, with intermediate effects for 1,2,4-trimethylbenzene and 1,3-dichlorobenzene. These four compounds were selected as representative of the 14 target analytes with oxidation half-lives of less than 1 year, and the results for the other

10 analytes fall within the range of results shown in figure 14. The other 10 analytes were isopropylbenzene, chlorobenzene, 1,2- and 1,4-dichlorobenzene, 1,2,3- and 1,2,4-trichlorobenzene, chloroethene, 1,1-dichloroethene, 1,3-dichloropropene (isomer not specified), and 2-propenenitrile. The latter four analytes had fractions removed comparable to those for benzene shown in figure 14. The other six analytes had fractions removed comparable to those for 1,3-dichlorobenzene shown in figure 14, as would be expected.

These results should be considered as upper bounds on the extent of oxidation because no depth effect on the rate of replacement of the surface layer of water in which oxidation occurs was assumed. The fact that vertical concentration gradients of dissolved constituents do not occur in streams would seem to argue in favor of no rate limitation. On the other hand, volatilization decreases as the flow depth increases, presumably because the thickness of the water film increases as the depth increases. However, the effect of this increased film thickness on oxidation in the surface layer and the rate of replacement of the oxidized compound with compound from the deeper parts of the flow is unknown. Experimental verification of the effect of vertical mixing on oxidation is needed.

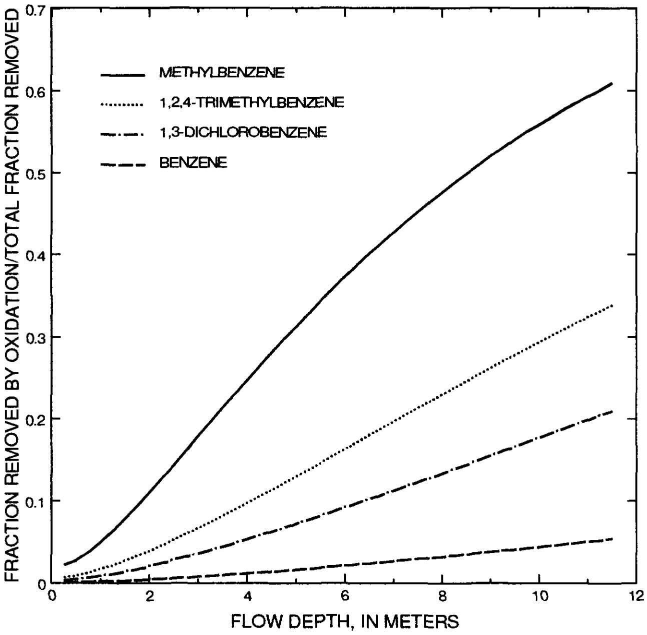

Figure 14. Ratio of the fraction of four target analytes removed by oxidation to the fraction removed by oxidation and volatilization as a function of flow depth.

The results shown in figure 14 indicate that oxidation is significant relative to volatilization for methylbenzene, particularly for the deeper flows, whereas the effect of oxidation on benzene is minimal. The fractions removed for the other alkyl benzenes and halogenated aromatics are intermediate between these extremes. Thus, oxidation is negligible for most of the target analytes. However, in any assessment of the processes contributing to the determination of the fate of VOCs in streams, all processes should be considered as possible during the initial stages of the evaluation, with processes being eliminated only as it is determined that they are not significant for the VOC of interest.

CHEMICAL REACTION

The possibility of chemical reaction of the target analytes with other chemical compounds in streams is remote, other than the hydrolysis, aquatic photolysis, and oxidation reactions previously discussed. The target analytes may undergo various chemical reactions, but these most likely would occur at temperatures, pressures, and in the presence of catalysts not normally observed in natural water bodies. There also is the possibility of chemical reaction occurring in the sorbed phase. As indicated in the sorption section, however, most of the target analytes have little tendency to sorb to sediments. Hence, contributions of chemical reactions other than those previously discussed are considered negligible in determining the fate of VOCs in streams.

BIOCONCENTRATION AND AQUATIC TOXICOLOGY

Bioconcentration is the uptake of organic compounds from water by organisms within an aquatic system. The tendency of an organic compound to accumulate in an aquatic organism is indicated by the bioconcentration factor, BCF. This factor is defined (Bysshe, 1990) as follows:

$$BCF = \frac{\text{concentration in organism}}{\text{concentration in water}} . \qquad (126)$$

Units for the concentration in the organism are usually ng/kg wet weight, and water concentrations are usually in ng/L. BCFs are usually for fish, and with the assumption that 1 gram of fish is equivalent to 1 mL of water (Oliver and Niimi, 1985), the BCF is dimensionless. Values of the BCF can range from about 1 to 10^6 (Bysshe, 1990). BCFs commonly are expressed on a logarithm base 10 basis. Consequently, log BCF varies from about 0 to 6.

Absorption of an organic compound from water by an organism involves a number of steps. These include movement of the chemical to the absorbing membrane (for example, the gill or stomach wall of a fish), diffusion through these membranes into the bloodstream, and transport by the blood to the lipid reservoir (Barron, 1990). Each of the steps can be rate-limiting and, thus, can control the uptake rate and the extent of accumulation.

The BCF depends on the species of organism, the body size, environmental factors, and the chemical properties of the organic compound (Barron, 1990). The most important chemical property is the lipophilicity of the compound because bioconcentration is a thermodynamically driven partitioning between the lipid phase of the organism and the surrounding water, with the final state that of equilibrium between the two phases.

Equation 126 is an equilibrium expression describing this partitioning of the organic compound between the lipid reservoir of the organism and the water of the aquatic system. However, unlike a water-solvent system where equilibrium is reached rapidly, equilibrium may be approached slowly because of the necessity for molecular diffusion of the compound into the lipid phase of the organism (Smith and others, 1988). The time to reach equilibrium generally increases as the water solubility of the compound decreases and as the size of the organism increases. Failure to achieve equilibrium results in underestimated values of the BCFs for organisms initially exposed to high water concentrations of organic compounds. Conversely, failure to achieve equilibrium results in overestimated values of the BCFs for organisms previously exposed to high water concentrations and then moved to uncontaminated water.

Concentrations of the organic compound in the fish (eq. 126) are usually on a wet-weight basis of the total fish. Chiou (1985) and Thomann (1989) argued that a lipid-based concentration would eliminate a potential major source of variability in the whole-body concentrations because whole-body concentrations may vary with lipid content. Thomann (1989) noted, however, that not all the variability is eliminated by using lipid-based concentrations. Chiou (1985) concluded that lipid-based BCFs for guppies and rainbow trout were basically identical when the uncertainties associated with the measurement of the BCFs were considered. Conversely, Sijm and van der Linde (1995) determined that lipid-normalized BCFs for six size classes of fathead minnow varied much more than the BCFs based on total fish weight. Also, Barron (1990) cited several models showing only a weak relationship between organic-compound accumulation and lipid content of the organisms, and he concluded that the lipid content may not be as important as previously thought. C.T. Chiou (U.S. Geological Survey, written commun., 1996) indicated that the accumulation of relatively nonpolar organic compounds would be more closely related to the lipid content of the organism than the accumulation of more polar compounds. On the other hand, the more polar organic compounds would tend to accumulate in the more polar nonlipid materials of the organism such as the proteins (C.T. Chiou, U.S. Geological Survey, written commun., 1996). Both lipid-based and weight-based BCFs have been reported in the literature, with the lipid-based factors larger because the lipid content is only a small fraction of the total weight.

There are numerous factors that contribute to variability in measured values of BCFs. In laboratory studies, these factors include the time to reach equilibrium, which can vary substantially for different compounds and different species of organisms. Lipid content not only varies between species but can vary within a specific species, depending on growth stage and position in the reproductive cycle (Bysshe, 1990). Lipid content varies with the particular fish taken for analysis. A PCB concentration in fish was largest in the liver, with decreasing concentrations in the gills, whole fish, heart, brain, and muscle (Chiou, 1981). Water temperature and dissolved-oxygen concentration could affect the time required to reach equilibrium (Bysshe, 1990). The water concentration also may contribute to variability. Oliver and Niimi (1983) found that the BCFs at a high-concentration level were about 2.2 times larger than BCFs at a low-concentration level. Conversely, Smith and others (1988) cited two studies that observed no dependence on the water concentration. Barron (1990) indicated that the observation of Oliver and Niimi (1983) may have been the result of saturation of the processes controlling uptake, distribution, and excretion, causing deviations at the high concentrations from the first-order processes usually observed at low concentrations.

Three experimental procedures have been used to measure BCFs in the laboratory (Kenaga and Goring, 1980): (1) a flow-through system in which fish are exposed to a continuous flow of water containing the organic compound of interest, (2) a model ecosystem containing various organisms in quiescent water that contains the organic compound of interest, and (3) a terrestrial/aquatic model ecosystem containing various organisms in a quiescent soil/water combination. Data from flow-through systems are preferred because model ecosystem tests do not always represent the maximum bioconcentration potential (Bysshe, 1990). The concentration of the organic compound is likely to be much more variable in ecosystems than in flow-through systems because of losses from other processes such as volatilization, sorption to surfaces, biotransformation, or microbial degradation. Thus, while ecosystems were designed to mimic the real environment, results from flow-through systems are probably more reliable.

Many of the parameters causing variability in laboratory BCFs also result in variability in field BCFs, with the variability in the field values likely to be greater because of greater ranges in ambient conditions (Bysshe, 1990). Other factors, however, are of importance in the environment. Fish may avoid areas of contamination by moving to other parts of the aquatic system, while such avoidance is not possible in laboratory systems. Exposure depends also on whether the fish are surface or bottom dwelling, migratory, or remaining in a relatively small volume of the system (Bysshe, 1990).

Seasonal as well as daily variations in factors such as temperature, ionic strength, pH, dissolved oxygen, and other water-quality parameters could affect the bioconcentration process. Temperature effects have not been studied extensively. However, temperature affects the physiology and the biochemistry of aquatic organisms (Barron, 1990). Generally, increasing temperature increases the rates of uptake and excretion, with the effect on bioconcentration dependent on the relative effects of temperature on each of these two processes. Ionic strength also has not been studied extensively, and limited data are conflicting. One study reported no differences in bioconcentration between marine and freshwater fish, whereas a second study reported much higher BCFs for freshwater fish (Barron, 1990). The pH of the water appears to be important for ionizable compounds because it affects the concentration of the nonionized form, which is absorbed faster that the ionized form (Barron, 1990). Sorption to dissolved organic matter may reduce the bioavailability of some compounds; the effect is most likely to be important for the very hydrophobic compounds. Barron (1990) concluded that the effects of environmental conditions on bioconcentration are largely unpredictable.

Finally, the type of source of the organic compound is important. The BCF (eq. 126) is an equilibrium parameter, and accurate determination of the parameter requires long-term exposure of the organism to a constant water concentration of the organic compound. With present-day controls on waste discharges, long-term constant concentrations of organic compounds in streams may be the exception rather than the general rule. Connolly and Pedersen (1988) noted that it may be invalid to compute a BCF on the basis of the present water concentration and present body burden of an organism when the organism has been exposed to a fluctuating concentration of the organic compound.

KINETICS OF THE BIOCONCENTRATION PROCESS

The uptake and excretion of an organic compound by a fish can be described by the equation (Oliver and Niimi, 1985)

$$\frac{dC_f}{dt} = k_u C_w - k_e C_f \qquad (127)$$

where

C_f and C_w are the concentrations of the organic compound in the fish and in the water,

k_u is the rate coefficient for the uptake of the compound by the fish,

k_e is the rate coefficient for excretion of the compound by the fish, and

t is time.

At equilibrium, $dC_f/dt = 0$, and it follows that

$$\mathrm{BCF} = \frac{C_f}{C_w} = \frac{k_u}{k_e}. \qquad (128)$$

Equation 128 can be used to compute the BCF from a measurement of the concentration of the organic compound in the fish after exposure to water containing a concentration of C_w of the target compound. The exposure time must be long enough to ensure equilibrium between the fish and the water.

A kinetic approach (Oliver and Niimi, 1985) also can be used. If a flow-through system is used such that the concentration of the organic compound in the water is constant, equation 127 can be integrated to give

$$C_f = (k_u)\left(\frac{C_w}{k_e}\right)[1 - \exp(-k_e t)] \ . \qquad (129)$$

The rate coefficient k_e is determined by exposing the fish to contaminated water, transferring the fish to clean water, and measuring the excretion rate of the organic compound from the fish. The excretion rate coefficient is given by

$$k_e = \frac{0.693}{t_{0.5e}} \qquad (130)$$

where

$t_{0.5e}$ is the half-life for excretion of the organic compound from the fish.

In a separate experiment, the uptake of the organic compound by the fish from the water is determined. According to equation 129, a plot of the fish concentration as a function of [1 minus $\exp(-k_e t)$] should be linear with a slope of $k_u C_w / k_e$. Because C_w and k_e are known, k_u can be computed and the BCF can be determined from equation 129 (Oliver and Niimi, 1985).

The one compartment model defined by equation 127 is based on several assumptions (Barron, 1990). First, it is assumed that the uptake and excretion processes are first order such that the BCF is independent of the concentration of the organic compound. Second, it is assumed that uptake is limited only by diffusion processes in the various membranes and fluids, and the BCF is determined only by the lipophilicity of the organic compound and the lipid content of the organism. Finally, the model assumes the metabolism of the compound by the organism is negligible.

This latter assumption has been questioned by some who believe that organisms higher in the food chain could consume organisms from the bottom of the food chain that have bioconcentrated some organic compound. This higher organism could then be consumed by another organism still higher in the food chain, resulting in movement of the organic compound up the food chain. This process is called biomagnification. However, there has been considerable debate over whether or not biomagnification actually occurs and is significant. Smith and others (1988) cited several examples that indicated that biomagnification is not well substantiated by existing data. Similarly, Bysshe (1990) cited several laboratory studies that indicated that absorption of organic compounds from water is far more significant than food ingestion for bioconcentration by fish. However, in natural systems, this observation may not necessarily be true because the ambient water concentrations are so low. Also, Connolly and Pedersen (1988) concluded that food-chain transfer can result in an increase in concentration with trophic level, with this effect significant for compounds with log K_{ow} values greater than about 4. Thomann (1989) cited other examples supporting the contribution of food to the overall accumulation of organic compounds and presented a model to account for this contribution.

The Thomann (1989) model is based on a four-level food chain involving phytoplankton, zooplankton, small fish, and the top predator. Food-chain accumulation is defined as the increase in the concentration of an organic compound in an organism compared with the concentration that would be expected from exposure to the water only. Primary parameters in the model are the rate coefficients for uptake and excretion and the assimilation efficiency factor for the organic compound. The model also incorporates a growth factor that accounts for the dilution of the concentration of the compound in the lipid reservoir as a result of organism growth.

The rate coefficient for uptake indicates how fast the organic compound is taken up by the fish, and this information is important for short-term exposures such as might occur during a spill when equilibrium is not attained (Sijm and van der Linde, 1995). The uptake coefficient also is important for long-term exposures to organic compounds with low water solubilities that approach equilibrium slowly. The uptake coefficient depends on properties of the organic compound such as the lipid partition coefficient, steric properties, and molecular weight (Thomann, 1989). For compounds with low octanol-water partition coefficients, transfer across the gill membranes of a fish is rapid through the aqueous diffusion layer but is much slower through the lipid membrane because of low solubility in the lipid. For compounds with larger octanol-water partition coefficients, the compound is more soluble in the lipid, resistance is reduced, and rate of movement is directly proportional to the octanol-water partition coefficient. For compounds with very large octanol-water partition coefficients, the water solubility of the compound limits rate of movement in the water, and chemical uptake is reduced. Thomann (1989) presented a plot of the efficiency of uptake as a function of the logarithm of the octanol-water partition coefficient (log K_{ow}) for three fish weights. The efficiency increases with increasing log K_{ow} up to a plateau, is constant for a range of log K_{ow} values, and then decreases for log K_{ow} values larger than about 6. The range of the plateaus varied, depending on fish weight. Also, the efficiency appears to be larger for the smaller fish with log K_{ow} between 4 and 6.

The excretion coefficient indicates how fast the organic compound is depurated from the fish and, thus, is a measure of the biological half-life of the compound in the fish (Sijm and van der Linde, 1995). This half-life is defined by equation 130. Thomann (1989) assumed that the lipid-normalized BCF is equal to the octanol-water partition coefficient for equilibrium conditions with zero growth, where the lipid-normalized BCF is computed from equation 126 by using the weight of the lipid tissue rather than the total weight of the organism. With these assumptions, it follows from equation 127 that

$$k_e = \frac{k_u}{K_{ow}} . \qquad (131)$$

A log-log plot of literature data for laboratory results shows reasonable agreement with equation 131, with an increase in slope occurring at a log K_{ow} value of about 6. Thomann (1989) attributed this change in slope to a varying efficiency of release across the membranes of the organisms. Lower release rates were observed for the larger fish because of decreased respiration and a generally larger ratio of volume-to-membrane area. This difference was expected to cause about an order of magnitude decrease in the excretion coefficient for compounds with log K_{ow} values in the 4 to 6 range. Under field conditions, the relationship is different because of the effect of growth. A plateau is reached for compounds with log K_{ow} values larger than about 6 because of the additional apparent loss resulting from growth and dilution of the lipid reservoir. Weight of the fish was important for both the laboratory and field results.

Assimilation of the organic compound through ingestion of food involves transport across the membrane between the gastrointestinal tract and the bloodstream. Thomann (1989) evaluated data from laboratory experiments and found an approximately constant assimilation efficiency for some compounds. For other compounds with log K_{ow} values greater than about 6, the assimilation capacity decreased as log K_{ow} increased.

Calibration of the model (Thomann, 1989) and application to various organic compounds with fish and squid as the organisms resulted in several general conclusions. A maximum field log BCF (lipid-based) of about 5.5 is expected for a compound with a log K_{ow} of about 6. Larger values of the log K_{ow} do not result in proportional increases in the log BCF because of growth and transfer efficiency effects. Measured concentrations in the upper trophic levels were significantly higher than those calculated using field BCF values for compounds with log K_{ow} values in the range of 5 to 7. These higher concentrations were attributed to food chain magnification. Such magnification does not occur for compounds with log K_{ow} values less than 5 because of decreased uptake and increased excretion.

The model of Thomann (1989) was discussed in some detail as an example of one type of model available for bioconcentration and biomagnification of organic compounds in organisms. Other models have been developed that consider different effects. Clark and others (1990) included size- and species-dependent parameters in their model and also considered bioavailability. The presence of large concentrations of sorbents such as suspended sediments and humic materials reduces the bioavailability of the organic compounds. For organic compounds with log K_{ow} values between 4 and 5, Clark and others (1990) estimated that most of the compound will be in the water. For a log K_{ow} of 6, about one-half of the compound will be sorbed, and for a log K_{ow} of 8, most of the compound will be sorbed. The concentration of the sorbent material is also important, as previously discussed in the sorption section of this report. The model of Sijm and others (1992) included biotransformation of the organic molecules as well as life stage, sex, reproduction, and growth characteristics of the fish. Main parameters in the model of Sijm and van der Linde (1995) were gill exchange surface area and lipid content of the fish and the molecular weight and log K_{ow} of the organic compound.

OCTANOL-WATER PARTITION COEFFICIENTS FOR THE TARGET ANALYTES

The previous discussion pointed out that the logarithm of the octanol-water partition coefficient is a good indicator in determining the possibility of bioconcentration. For this reason, the logarithms of the octanol-water partition coefficients of the target analytes are presented in tables 25 and 26. Table 25 contains experimental values for 40 analytes from the compilations of Mackay and others (1992a; 1992b; 1993). For those analytes for which more than one experimental value was available, an arithmetic average log K_{ow} value was computed. This is equivalent to computing a geometric mean of the K_{ow} values, as suggested by Lyman (1990b). Calculated values of the octanol-water partition coefficients for the remaining 15 target analytes are presented in table 26. These coefficients were calculated using structure-activity relationships and equations relating water solubility and the octanol-water partition coefficient. The octanol-water partition coefficient for bromoethene was estimated from its structure, as discussed previously in the section on the Henry's law constant. The coefficients for ethyl tertiary-butyl ether and tertiary-amyl methyl ether were estimated from a molar volume-log K_{ow} relationship, as discussed previously in the section on sorption.

The logarithms of the octanol-water partition coefficients of the target analytes range from −0.92 for 2-propenenitrile to 4.78 for hexachlorobutadiene, with a median of 2.34 for tribromomethane. The frequency distribution of the log K_{ow} values is presented in figure 15.

The results in tables 25 and 26 and figure 15 indicate that the log K_{ow} values for the target analytes are generally small in comparison with values noted in the previous discussion of bioconcentration models. Only four analytes have values larger than 4. As indicated previously, Clark and others (1990) estimated that compounds with log K_{ow} values between 4 and 5 will be mostly in the water, with little bioconcentration. However, while the bulk of the organic compound may remain in the water phase, organisms may still take up small amounts of organic compounds, and BCFs have been measured for a number of target analytes.

Table 25. Experimental values of the octanol-water partition coefficient for 40 target analytes (from Mackay and others, 1992a; 1992b; 1993)

[USGS, U.S. Geological Survey; log K_{ow}, logarithm base 10 of the octanol-water partition coefficient]

USGS parameter code	Compound	log K_{ow}
34418	chloromethane	0.91
34423	dichloromethane	1.25
32106	trichloromethane	2.00
32102	tetrachloromethane	2.71
34413	bromomethane	1.19
32101	bromodichloromethane	2.10
32105	chlorodibromomethane	2.24
34311	chloroethane	1.45
34496	1,1-dichloroethane	1.86
32103	1,2-dichloroethane	1.47
34506	1,1,1-trichloroethane	2.48
34511	1,1,2-trichloroethane	2.38
34396	hexachloroethane	3.93
34541	1,2-dichloropropane	2.00
34488	trichlorofluoromethane	2.53
34668	dichlorodifluoromethane	2.16
77652	1,1,2-trichloro-1,2,2-trifluoroethane	3.16
39180	trichloroethene	2.43
34475	tetrachloroethene	2.64
39702	hexachlorobutadiene	4.78
34030	benzene	2.17
77128	styrene	2.94
34696	naphthalene	3.35
34010	methylbenzene	2.71
34371	ethylbenzene	3.14
77224	n-propylbenzene	3.66
77223	iso-propylbenzene	3.58
77342	n-butylbenzene	4.29
77135	1,2-dimethylbenzene	3.15
85795	1,3-dimethylbenzene	3.23
85795	1,4-dimethylbenzene	3.20
77222	1,2,4-trimethylbenzene	3.78
34301	chlorobenzene	2.84
34536	1,2-dichlorobenzene	3.46
34566	1,3-dichlorobenzene	3.55
34571	1,4-dichlorobenzene	3.46
77613	1,2,3-trichlorobenzene	4.07
34551	1,2,4-trichlorobenzene	4.04
78032	methyl tertiary-butyl ether	.94
81577	diisopropyl ether	1.52

Table 26. Calculated values of the octanol-water partition coefficient for 15 target analytes

[USGS, U.S. Geological Survey; log K_{ow}, logarithm base 10 of the octanol-water partition coefficient]

USGS parameter code	Compound	log K_{ow}	Reference
32104	tribromomethane	2.34	Mackay and others (1993)
77651	1,2-dibromoethane	1.60	Radding and others (1977)
77443	1,2,3-trichloropropane	2.36	Mackay and others (1993)
82625	1,2-dibromo-3-chloropropane	2.26	Howard (1991)
39175	chloroethene	1.33	Mackay and others (1993)
34501	1,1-dichloroethene	2.00	Mackay and others (1993)
77093	*cis*-1,2-dichloroethene	1.68	Mackay and others (1993)
34546	*trans*-1,2-dichloroethene	1.84	Mackay and others (1993)
50002	bromoethene	1.52	This study
34704	*cis*-1,3-dichloropropene	2.20	Kollig (1993)
34699	*trans*-1,3-dichloropropene	2.20	Kollig (1993)
50004	ethyl tertiary-butyl ether	1.52	This study
50005	tertiary-amyl methyl ether	1.52	This study
34210	2-propenal	–0.09	Callahan and others (1979)
34215	2-propenenitrile	–0.92	Verschueren (1983)

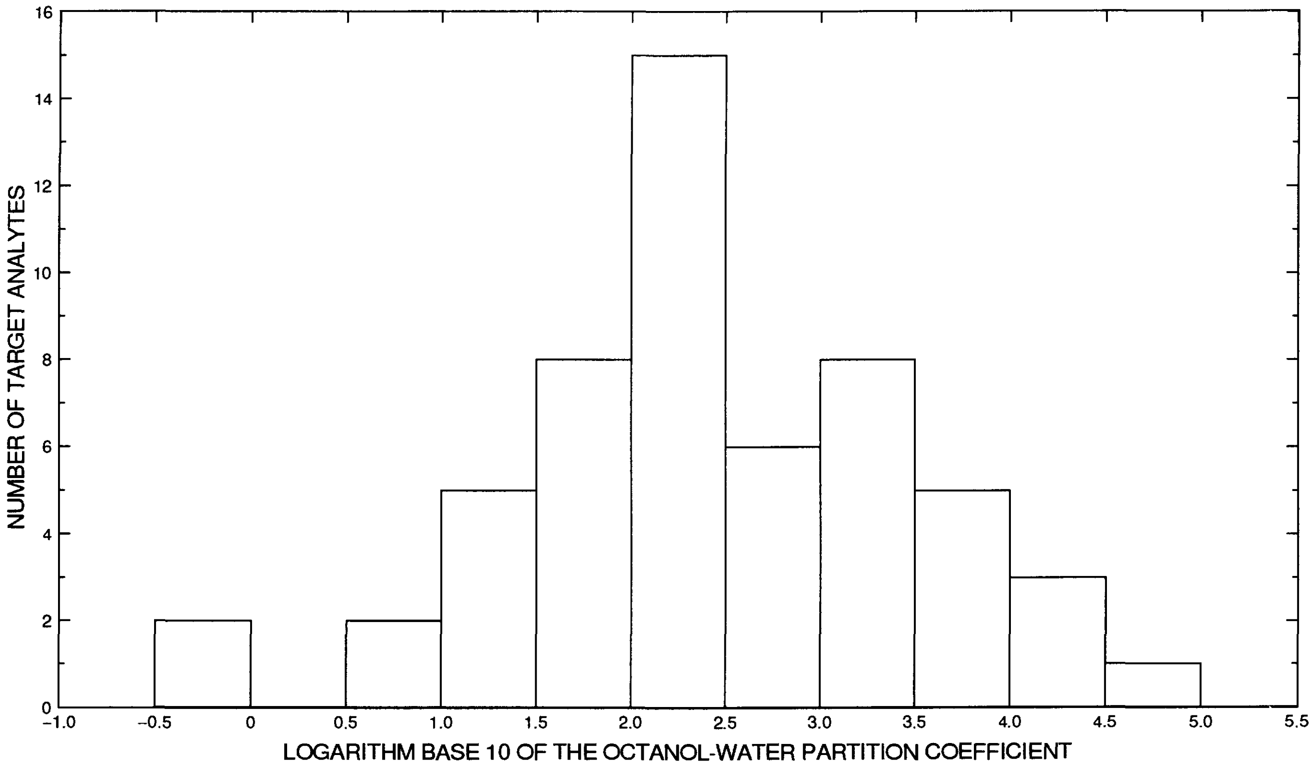

Figure 15. Frequency distribution of the logarithm base 10 of the octanol-water partition coefficient for the target analytes.

BIOCONCENTRATION FACTORS FOR THE TARGET ANALYTES

Experimental values of the bioconcentration factor on a whole body basis are presented in table 27 for 26 target analytes for several types of organisms. Log BCF values ranged from 0.20 for trichloromethane in bluegill sunfish to 4.23 for hexachlorobutadiene in rainbow trout. The large value for hexachlorobutadiene is consistent with this compound having the largest log K_{ow} of any of the target analytes (tables 25 and 26).

Most of the BCFs are for fish. However, several pure strains of alga and mixtures of algae were included, and these organisms generally had high BCFs. Algae have high BCFs because of the large surface-to-volume ratio relative to other organisms (Kenaga and Goring, 1980), which facilitates absorption of the organic compounds. Many algae also have high lipid contents which contribute to the high BCFs. This high lipid content may be more important than the surface-to-volume ratio at equilibrium conditions (C.T. Chiou, U.S. Geological Survey, written commun., 1996).

Table 27. Experimental values of the bioconcentration factor based on the whole body weight for various organisms for 26 target analytes

[USGS, U.S. Geological Survey; log BCF, logarithm base 10 of the bioconcentration factor]

USGS parameter code	Compound	Common name of organism	log BCF	Reference
32106	trichloromethane	bluegill sunfish	0.78	Veith and others (1980)
		bluegill sunfish	0.20–0.40	Howard (1990)
		rainbow trout	0.52–1.01	Howard (1990)
		largemouth bass	0.46–0.49	Howard (1990)
		catfish	0.52–0.57	Howard (1990)
		bluegill sunfish	0.78	Mackay and others (1993)
		green alga	2.84	Mackay and others (1993)
32102	tetrachloromethane	bluegill sunfish	1.48	Veith and others (1980)
		rainbow trout	1.24	Howard (1990)
		bluegill sunfish	1.48	Mackay and others (1993)
		rainbow trout	1.72	Mackay and others (1993)
		green algae	2.48	Mackay and others (1993)
		fish	1.24	Mackay and others (1993)
32103	1,2-dichloroethane	bluegill sunfish	0.30	Veith and others (1980)
		bluegill sunfish	0.30	Howard (1990)
34506	1,1,1-trichloroethane	bluegill sunfish	0.95	Veith and others (1980)
		bluegill sunfish	0.95	Howard (1990)
34396	hexachloroethane	bluegill sunfish	2.14	Veith and others (1980)
		rainbow trout	2.71, 3.08	Oliver and Niimi (1983)
		bluegill sunfish	2.14	Mackay and others (1993)
		fathead minnow	2.85	Mackay and others (1993)
39175	chloroethene	green alga	1.6	Mackay and others (1993)
39180	trichloroethene	bluegill sunfish	1.23	Veith and others (1980)
		rainbow trout	1.59	Mackay and others (1993)
		green alga	3.06	Mackay and others (1993)
34475	tetrachloroethene	bluegill sunfish	1.69	Veith and others (1980)
		rainbow trout	1.59	Mackay and others (1993)
		rainbow trout	2.06	Mackay and others (1993)
		rainbow trout	1.79	Mackay and others (1993)

Table 27. Experimental values of the bioconcentration factor based on the whole body weight for various organisms for 26 target analytes—Continued

[USGS, U.S. Geological Survey; log BCF, logarithm base 10 of the bioconcentration factor]

USGS parameter code	Compound	Common name of organism	log BCF	Reference
39702	hexachlorobutadiene	rainbow trout	3.76, 4.23	Oliver and Niimi (1983)
		Atlantic croaker	2.84	Pereira and others (1988)
		blue crab	1.66	Pereira and others (1988)
		spotted sea trout	2.42	Pereira and others (1988)
		blue catfish	3.07	Pereira and others (1988)
34030	benzene	Pacific herring	0.64	Mackay and others (1992a)
		eels	0.54	Mackay and others (1992a)
		green algae	1.48	Mackay and others (1992a)
		goldfish	0.63	Mackay and others (1992a)
		green alga	1.63	Mackay and others (1992a)
77128	styrene	goldfish	1.13	Mackay and others (1993)
34696	naphthalene	mussel	1.64	Mackay and others (1992b)
		mussel	1.49	Mackay and others (1992b)
		water flea	2.12	Mackay and others (1992b)
		green alga	2.11	Mackay and others (1992b)
		bluegill sunfish	2.50	Mackay and others (1992b)
34010	methylbenzene	eels	1.12	Mackay and others (1992a)
		Manila clam	0.22	Mackay and others (1992a)
		mussel	0.62	Mackay and others (1992a)
		goldfish	0.92	Mackay and others (1992a)
		green alga	1.99	Mackay and others (1992a)
34371	ethylbenzene	clams	0.67	Mackay and others (1992a)
		goldfish	1.19	Mackay and others (1992a)
		green alga	2.31	Mackay and others (1992a)
77223	iso-propylbenzene	goldfish	1.55	Mackay and others (1992a)
77135	1,2-dimethylbenzene	eels	1.33	Mackay and others (1992a)
		clams	0.79	Mackay and others (1992a)
		goldfish	1.15	Mackay and others (1992a)
		green alga	2.34	Mackay and others (1992a)
85795	1,3-dimethylbenzene	eels	1.37	Mackay and others (1992a)
		clams	0.78	Mackay and others (1992a)
		goldfish	1.17	Mackay and others (1992a)
		green alga	2.40	Mackay and others (1992a)
85795	1,4-dimethylbenzene	eels	1.37	Mackay and others (1992a)
		goldfish	1.17	Mackay and others (1992a)
		green alga	2.41	Mackay and others (1992a)
34301	chlorobenzene	Atlantic croaker	2.09	Pereira and others (1988)
		blue crab	2.06	Pereira and others (1988)
		spotted sea trout	2.36	Pereira and others (1988)
		blue catfish	1.96	Pereira and others (1988)
		fathead minnow	2.65	Mackay and others (1992a)
		green algae	1.70	Mackay and others (1992a)
		fish	1.88	Mackay and others (1992a)
34536	1,2-dichlorobenzene	bluegill sunfish	1.95	Veith and others (1980)
		rainbow trout	2.43, 2.75	Oliver and Niimi (1983)

Table 27. Experimental values of the bioconcentration factor based on the whole body weight for various organisms for 26 target analytes—Continued

[USGS, U.S. Geological Survey; log BCF, logarithm base 10 of the bioconcentration factor]

USGS parameter code	Compound	Common name of organism	log BCF	Reference
34536	1,2-dichlorobenzene (Continued)	Atlantic croaker	2.29	Pereira and others (1988)
		blue crab	2.16	Pereira and others (1988)
		spotted sea trout	2.19	Pereira and others (1988)
		blue catfish	2.34	Pereira and others (1988)
34566	1,3-dichlorobenzene	bluegill sunfish	1.82	Veith and others (1980)
		rainbow trout	2.62, 2.87	Oliver and Niimi (1983)
		Atlantic croaker	1.94	Pereira and others (1988)
		blue crab	1.56	Pereira and others (1988)
		spotted sea trout	1.63	Pereira and others (1988)
		blue catfish	1.92	Pereira and others (1988)
		fathead minnow	1.99	Mackay and others (1992a)
34571	1,4-dichlorobenzene	bluegill sunfish	1.78	Veith and others (1980)
		rainbow trout	2.57, 2.86	Oliver and Niimi (1983)
		rainbow trout	2.71, 2.95	Oliver and Niimi (1985)
		Atlantic croaker	2.25	Pereira and others (1988)
		blue crab	2.23	Pereira and others (1988)
		spotted sea trout	2.45	Pereira and others (1988)
		blue catfish	2.03	Pereira and others (1988)
		green algae	2.00	Mackay and others (1992a)
		rainbow trout	2.33	Mackay and others (1992a)
		fathead minnow	2.04	Mackay and others (1992a)
		flagfish	2.47	Mackay and others (1992a)
77613	1,2,3-trichlorobenzene	rainbow trout	3.08, 3.42	Oliver and Niimi (1983)
		Atlantic croaker	2.89	Pereira and others (1988)
		blue crab	2.47	Pereira and others (1988)
		spotted sea trout	1.58	Pereira and others (1988)
		blue catfish	3.01	Pereira and others (1988)
		guppy	3.28	Mackay and others (1992a)
		fathead minnow	3.00–3.75	Sijm and van der Linde (1995)
34551	1,2,4-trichlorobenzene	rainbow trout	3.11, 3.51	Oliver and Niimi (1983)
		rainbow trout	3.36, 3.57	Oliver and Niimi (1985)
		Atlantic croaker	3.10	Pereira and others (1988)
		blue crab	2.60	Pereira and others (1988)
		spotted sea trout	1.91	Pereira and others (1988)
		blue catfish	3.19	Pereira and others (1988)
		fathead minnow	3.32, 3.45	Mackay and others (1992a)
		green sunfish	3.37	Mackay and others (1992a)
		rainbow trout	2.95	Mackay and others (1992a)
		bluegill sunfish	2.26	Mackay and others (1992a)
		green algae	2.40	Mackay and others (1992a)
		fish	2.69	Mackay and others (1992a)
		fathead minnow	2.61	Mackay and others (1992a)
		flagfish	3.31	Mackay and others (1992a)
34210	2-propenal	bluegill sunfish	2.54	Veith and others (1980)
34215	2-propenenitrile	bluegill sunfish	1.68	Veith and others (1980)

Experimental values of the bioconcentration factor on a lipid basis are presented in table 28 for seven target analytes for several types of organisms. Values in table 28 are higher than the corresponding values in table 27 because the lipid weight is only a small fraction of the whole body weight. Lipid fractions were from 0.071 to 0.112 for the rainbow trout used in the study of Oliver and Niimi (1983), 0.050 to 0.080 for the rainbow trout used in the study of Oliver and Niimi (1985), 0.005 for the blue crab to 0.033 for the blue catfish used in the study of Pereira and others (1988), and from 0.0147 to 0.238 for the six sizes of fathead minnows used in the study of Sijm and van der Linde (1995).

Table 28. Experimental values of the bioconcentration factor based on the lipid weight for various organisms for seven target analytes

[USGS, U.S. Geological Survey; log BCF, logarithm base 10 of the bioconcentration factor]

USGS parameter code	Compound	Common name of organism	log BCF	Reference
34396	hexachloroethane	rainbow trout	3.77, 4.09	Oliver and Niimi (1983)
39702	hexachlorobutadiene	rainbow trout	4.84, 5.30	Oliver and Niimi (1983)
34536	1,2-dichlorobenzene	rainbow trout	3.50, 3.81	Oliver and Niimi (1983)
		Atlantic croaker	3.74	Pereira and others (1988)
		blue crab	4.36	Pereira and others (1988)
		spotted sea trout	4.00	Pereira and others (1988)
		blue catfish	3.44	Pereira and others (1988)
34566	1,3-dichlorobenzene	rainbow trout	3.70, 3.93	Oliver and Niimi (1983)
		Atlantic croaker	3.60	Pereira and others (1988)
		blue crab	3.86	Pereira and others (1988)
		spotted sea trout	3.27	Pereira and others (1988)
		blue catfish	3.40	Pereira and others (1988)
34571	1,4-dichlorobenzene	rainbow trout	3.65, 3.92	Oliver and Niimi (1983)
		rainbow trout	3.88, 4.11	Oliver and Niimi (1985)
		Atlantic croaker	3.91	Pereira and others (1988)
		blue crab	4.53	Pereira and others (1988)
		spotted sea trout	4.08	Pereira and others (1988)
		blue catfish	3.51	Pereira and others (1988)
		guppy	3.26	Mackay and others (1992a)
		flagfish	3.56	Mackay and others (1992a)
77613	1,2,3-trichlorobenzene	rainbow trout	4.17, 4.48	Oliver and Niimi (1983)
		Atlantic croaker	4.54	Pereira and others (1988)
		blue crab	4.77	Pereira and others (1988)
		spotted sea trout	3.22	Pereira and others (1988)
		blue catfish	4.49	Pereira and others (1988)
		guppy	4.11	Mackay and others (1992a)
		fathead minnow	3.94–5.39	Sijm and van der Linde (1995)
34551	1,2,4-trichlorobenzene	rainbow trout	4.20, 4.57	Oliver and Niimi (1983)
		rainbow trout	4.54, 4.71	Oliver and Niimi (1985)
		Atlantic croaker	4.76	Pereira and others (1988)
		blue crab	4.90	Pereira and others (1988)
		spotted sea trout	3.54	Pereira and others (1988)
		blue catfish	4.68	Pereira and others (1988)
		flagfish	4.25	Mackay and others (1992a)

The objective of using the lipid weight rather than the whole body weight to compute BCFs is to reduce the variability in the computed BCFs. Results of a comparison of the data from the four studies cited above are presented in table 29. In three of the four studies, the relative standard deviation used as an indicator of variability was lower for the lipid-based BCFs, whereas in the fourth study, it was higher.

Table 29. Comparison of whole-weight and lipid-weight bioconcentration factors

[n, number of values; C_v, relative standard deviation, in percent]

Basis	n	C_v (percent)	Reference
Whole	14	±16.0	Oliver and Niimi (1983)
Lipid	14	±11.7	Oliver and Niimi (1983)
Whole	4	±11.0	Oliver and Niimi (1985)
Lipid	4	±7.73	Oliver and Niimi (1985)
Whole	28	±20.2	Pereira and others (1988)
Lipid	28	±12.0	Pereira and others (1988)
Whole	6	±7.26	Sijm and van der Linde (1995)
Lipid	6	±12.2	Sijm and van der Linde (1995)

Comparisons in table 29 were for different types of studies. The studies of Oliver and Niimi (1983; 1985) were for seven target analytes and two target analytes, respectively, at two levels of water concentration (tables 27 and 28). Results for the two concentrations were comparable. The study of Pereira and others (1988) was for seven target analytes and four organisms (tables 27 and 28). The average relative standard deviation across the organisms was larger than the average across the analytes for the weight-based BCFs (±17.8 percent compared to ±12.8 percent) and was approximately the same for the lipid-based BCFs (±10.1 percent compared to ±9.02 percent). The study of Sijm and van der Linde (1995) involved one target analyte and six size classes of fathead minnow (tables 27 and 28), with the lipid content generally decreasing as the age and size of the minnows increased. Results in table 29 indicate that the variability of the BCFs for the target analytes is reduced somewhat when based on the lipid content; however, considerable variability remained.

PREDICTION EQUATIONS FOR THE BIOCONCENTRATION FACTOR

Various equations are available in the literature for predicting BCFs for those target analytes for which experimental values are not available. BCFs have been related to the water solubility, the soil sorption coefficient, and the octanol-water partition coefficient (Kenaga and Goring, 1980). The octanol-water partition coefficient is the most logical choice for a correlating parameter because it describes the partitioning of an organic compound between the octanol and water phases, which closely mimics the partitioning of the same organic compound between the water and lipid phase of an aquatic organism. Relationships between the BCF and water solubility and the soil sorption coefficient follow indirectly because of the relationships of these two parameters to the octanol-water partition coefficient.

Bysshe (1990) summarized nine equations for estimating the BCF on a wet-weight basis. Six of these equations have the octanol-water partition coefficient as the independent variable, two have the water solubility, and one has the soil-sorption coefficient. The equation best suited for the target analytes is

$$\log \mathrm{BCF} = 0.76 \log K_{ow} - 0.23 \qquad (132)$$

which was based on 84 organic compounds, of which 15 were target analytes. Equation 132 was based on data for four species of fish and had a correlation coefficient of 0.823. Some of the other equations had larger correlation coefficients (Bysshe, 1990). However, these equations were based on much smaller numbers of compounds than the 84 compounds on which equation 132 was based. The numbers of target analytes also were much smaller than the 15 target analytes included in the data base used for equation 132. Equation 132 can be used with the octanol-water partition coefficients from tables 25 and 26 to predict the BCF for any of the target analytes. If other VOCs are important in some situations, then BCFs can be estimated from equation 132 and octanol-water partition coefficients from the literature.

ESTIMATION OF THE IMPORTANCE OF BIOCONCENTRATION

The previous discussion of bioconcentration models illustrated the complexity of the process. This discussion also indicated that bioconcentration is most likely to be important for high-molecular-weight, low-solubility compounds that persist for long time periods in surface waters. Because of the volatile nature of the target analytes of the present study, bioconcentration is less likely to be significant for these compounds.

The importance of bioconcentration in determining the fate of the target analytes in streams was estimated by combining a mass balance of an organic compound in a compartment of water with the defining equation (eq. 126) for the BCF. Assuming that bioconcentration is the only process affecting the concentration of the organic compound in the compartment, and also assuming that the water and organism phases are in equilibrium, it follows that

$$f_o = \frac{(BCF)(W_f)}{[1 + (BCF)(W_f)]} \qquad (133)$$

where

BCF is on a wet-weight basis,

f_o is the fraction by weight of the organic compound in the organism, and

W_f is the fraction by weight (gram of organism/gram of water) of the organism in the water.

Most BCF studies have been for fish (tables 27 and 28); consequently, estimation of the importance of bioconcentration will be for fish.

Application of equation 133 requires a value of W_f, which is basically the density of fish in the water. This density can vary widely, depending on conditions for productivity in the water. Neely and Mackay (1982) reported an areal density of fish ranging from 5.6 to 17 g/m^2 for natural lakes of glacial origin. Using a value of 10, which is near the middle of this range, gives

$$W_f = \frac{10^{-5}}{Y} \qquad (134)$$

where

Y is the water depth (m).

For a water depth of 10 m as used by Neely and Mackay (1982), equation 134 indicates a fish density of 10^{-6}, and the same value was used later (Mackay and others, 1992a; 1992b; 1993) in their hypothetical terrestrial/aquatic ecosystem model. A value of 10^{-6} also was used by McCall and others (1983). Because it is customary to assume that 1 g of fish is equal to 1 mL of fish (Oliver and Niimi, 1985), this weight fraction is identical to the volume fraction for the fish in the water. Fractions of the order of 10^{-6} also have been used in experimental studies. Boyle and others (1985) used fractions of 1.4×10^{-6} and 1.1×10^{-5} for bass and bluegill in a pond study of bioconcentration of a polycyclic aromatic compound.

The fish densities cited previously were areal densities and, thus, were per unit of surface area. Consequently, it is not known how the fish density varies with depth. An areal definition implies that the factor varies inversely with depth, as indicated by equation 134, although it also could imply a density independent of depth. To encompass a range of conditions, the importance of bioconcentration was estimated for both a fish density that decreased with depth, as indicated by equation 134, and a fish density independent of depth. Several values of the base fish density also were evaluated.

Hexachlorobutadiene was chosen as the target analyte for evaluation because it has the largest octanol-water partition coefficient (log $K_{ow} = 4.78$) of any of the analytes (tables 25 and 26) and, therefore, should exhibit the greatest tendency to bioconcentrate. The fraction removed by bioconcentration was computed from equation 133 for constant fish fractions (W_f) of 10^{-5}, 10^{-6}, and 10^{-7} and for fish fractions varying from these nominal values with the flow depth as indicated by equation 134. Flow depths ranged from 0.27 to 11 m and were for a constant water velocity of 0.058 m/s. Volatilization coefficients were computed from the O'Connor and Dobbins equation (eq. 55) and equations 27, 28, 16, and 13 using procedures described in the volatilization section of this report. An average air-film mass-transfer coefficient at 20°C of 756 m/day and a downstream distance of 5,010 m were used. This is the distance traveled during a 1.0-day period at a velocity of 0.058 m/s.

The results in figure 16 indicate for a fish density decreasing with depth that the fraction of hexachlorobutadiene removed by bioconcentration is comparable to that removed by volatilization for the fish fraction of 10^{-5}. For the 10^{-6} and 10^{-7} fish fractions, the fractions removed by bioconcentration are much smaller than the fraction removed by volatilization for shallow flows. For deep flows, all the fractions removed approach zero. The results in figure 16 indicate for a constant fish fraction of 10^{-5} that a constant 37.6 percent of the hexachlorobutadiene is removed by bioconcentration, which exceeds the fraction removed by volatilization over most of the flow-depth range. For a constant fish fraction of 10^{-6}, the fraction removed by volatilization exceeds the fraction removed by bioconcentration to a flow depth of about 4 m. For deeper flows, the fraction removed by bioconcentration exceeded that removed by volatilization. For a constant fish fraction of 10^{-7}, the fraction removed by bioconcentration is negligible for all depths. The fraction removed by volatilization shows the characteristic rapid decrease with increasing depth, which was discussed previously in the volatilization section of this report.

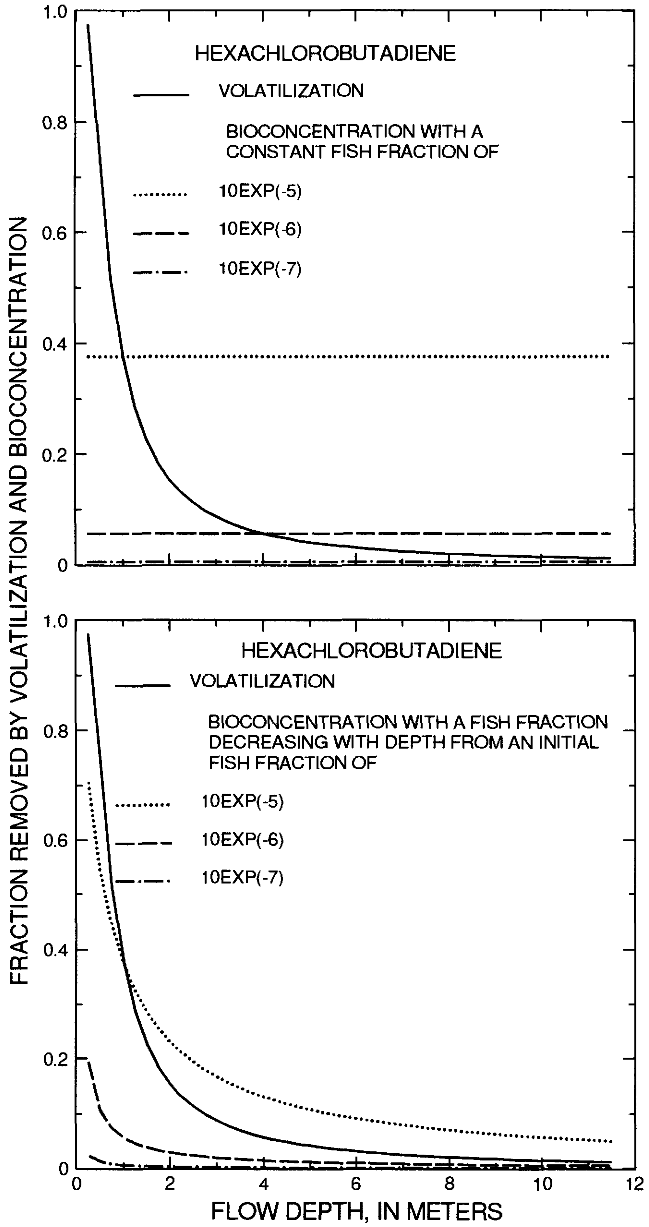

Figure 16. Fraction of hexachlorobutadiene removed by volatilization and bioconcentration as a function of flow depth.

Deep flows and a low water velocity were used in estimating the importance of bioconcentration so as to minimize the contribution of volatilization. With these conditions and a fish fraction of 10^{-5}, bioconcentration was significant for hexachlorobutadiene. However, a fish fraction of 10^{-5} is an order of magnitude larger than the value of 10^{-6} commonly used, and predicted bioconcentration fractions for this fraction were less than 0.06 for all except the very shallow flows. This analysis also assumes that equilibrium is established between the water and lipid phases, and such an equilibrium is slow to be established. Failure to achieve equilibrium results in lower fractions than those predicted in figure 16. Finally, Kenaga and Goring (1980) noted that when a hydrophobic compound is easily metabolized, the tendency to bioconcentrate is offset by the rapid rate of metabolism, and significant levels of the compound will not develop in the organism. The target analytes of the present study are all volatile organic compounds, and significant concentrations are not likely to persist for long times in streams because of volatilization losses. Consequently, it would seem that the same conclusion would be appropriate for these volatile organic compounds, with bioconcentration not being a significant mechanism for loss from streams relative to volatilization.

As with every process that might affect the concentration of VOCs in streams, each situation must be specifically evaluated because exceptions to these generalizations may occur. For example, previous discussion indicated that algae have higher BCFs than fish. If a stream has a reach containing a high concentration of algae or aquatic vegetation, significant bioconcentration may occur in this section. Such a section would be analogous to the use of wetlands to treat wastewaters. In general, however, densities of aquatic organisms in streams will be small enough that the effect of bioconcentration on the concentrations of VOCs will be negligible. This does not, however, necessarily mean that the small amounts removed will have negligible effect on the organism in which the VOC is concentrated.

AQUATIC TOXICOLOGY

Measuring the effects of organic compounds on aquatic organisms is difficult. The general procedure is to do a laboratory toxicity bioassay to determine a toxicity endpoint for a specific organic compound, determine the concentration of this compound in the aquatic system, and compare the concentration to the endpoint using the quotient method (Bascietto and others, 1990). The quotient method is the ratio of the concentration to the toxicity endpoint. An example is the water concentration divided by the LC_{50} value, where the LC_{50} value is the concentration resulting in death to 50 percent of the organisms. The closer the quotient is to unity or larger, the higher the probability that an adverse effect will occur. The greatest uncertainty in this procedure is interpreting the adverse effect because results in the natural system are not likely to be the same as in the laboratory. This uncertainty is compensated for by adding a safety factor to the no-observed-effect level to give a concentration below which exposures are assumed to be safe (Bascietto and others, 1990).

The U.S. Environmental Protection Agency (1996) assembled from the literature in a computer file designated AQUIRE all LC_{50} and EC_{50} values for organic compounds for six categories of organisms. These categories were amphibian, crustacean, fish, insect, invertebrate, and plant. The EC_{50} value is the concentration at which 50 percent of the organisms are affected, with an endpoint other than death. The U.S. Geological Survey (Rowe and others, 1997) abstracted from the AQUIRE file entries for the target analytes that were for freshwater studies and were of documentation codes C and M. A documentation code C is a study using published or well-documented procedures. A documentation code M is a study where procedures were generally satisfactory but some information was lacking. When more than two concentrations were reported for a specific target analyte for a specific organism with comparable experimental conditions, only the two lowest concentrations were abstracted from the data base.

Selected LC_{50} and EC_{50} values from this abstraction are presented in tables 30 and 31 for the target analytes. When several values were available for a category, maximum and minimum values were presented. Consequently, these maximum and minimum concentrations of the target analytes represent the range of minimum concentrations that might result in the indicated effect for the specific organism. Concentrations were not available for all six categories of organisms for most target analytes. For example, there were no LC_{50} values for the plant category for any of the target analytes listed in table 30.

LC_{50} values varied widely, ranging from 0.8 μg/L for bromomethane and guppies to four values of 10^6 μg/L or larger. These values were 1.1×10^6 μg/L for 1,2-dichloroethane and medaka; greater than 1.0×10^6 μg/L for 1,1,1-trichloroethane and medaka; greater than 1.0×10^6 μg/L for benzene and rotifers; and 1.3×10^6 μg/L for methylbenzene and mosquito fish. However, values in general are large. Of the 170 values in table 30, only 19 are less than 10^3 μg/L, only 5 are less than 10^2 μg/L, and only 2 are less than 10 μg/L. EC_{50} values varied widely also, ranging from 0.6 μg/L for bromomethane and guppies to 2.0×10^6 μg/L for dichloromethane and duckweed. Of the 120 values in table 31, only 23 are less than 10^3 μg/L, only 3 are less than 10^2 μg/L, and one is less than 10 μg/L. The small LC_{50} and EC_{50} values are concentrated in several compounds, with bromomethane, hexachlorobutadiene, 1,2,3-trichlorobenzene, and 2-propenal each having three or more values less than 10^3 μg/L. The large number of small values and the small concentrations for 2-propenal were not surprising because this compound has been used in dilute solutions to kill undesirable vegetation in irrigation canals (National Academy of Sciences, 1977).

Most of the LC_{50} and EC_{50} values in tables 30 and 31 are larger than 10^3 μg/L, and such large concentrations of VOCs are not likely to exist and/or to persist in streams for long periods of time because of the volatile nature of these compounds. On the other hand, streams in some parts of the Nation freeze during the winter, resulting in ice cover that prevents VOCs from volatilizing to the atmosphere. As an example, concentrations of VOCs in the upper Mississippi River were higher under ice cover than during ice-free conditions, although concentrations generally were in the low microgram-per-liter range (Barber and others, 1995). In the event of a spill, concentrations might be large for a short period, but exposure should be of short duration, minimizing acute exposure of the organisms to the VOCs. This variety of conditions requires that each situation be evaluated individually to determine possible adverse effects of acute exposure of organisms to VOCs.

The effect of long-term chronic exposure of aquatic organisms to low concentrations of VOCs has not been studied extensively, and results are likely to be different from short-term acute exposures. However, long-term exposures to low concentrations of VOCs in streams are unlikely because of the volatile, transient nature of VOCs and also because of the continuing effort to reduce and eliminate waste discharges to the streams of the nation. An exception might be those streams discussed above that are covered with ice for several months; a fairly long-term exposure could occur under these conditions.

Table 30. Minimum concentrations of 40 target analytes resulting in 50-percent mortality of various aquatic organisms (from Rowe and others, 1997); when two or more concentrations were available for an organism category, maximum and minimum values are presented; when two concentrations for an organism category were approximately the same, the minimum concentration is presented

[USGS, U.S. Geological Survey; LC_{50}, lethal concentration at 50-percent mortality; µg/L, microgram per liter; >, greater than]

USGS parameter code	Compound	Category of organism	Common name of organism	LC50 (µg/L)
34418	chloromethane	fish	bluegill	5.5×10^{5}
34423	dichloromethane	fish	medaka	8.4×10^{5}
			fathead minnow	1.9×10^{5}
		insect	water flea	3.1×10^{5}
			water flea	2.2×10^{5}
32106	trichloromethane	fish	medaka	5.0×10^{5}
			rainbow trout	1.2×10^{3}
		insect	water flea	2.9×10^{5}
			water flea	2.9×10^{4}
		invertebrate	rotifer	2.0×10^{3}
32102	tetrachloromethane	fish	medaka	6.7×10^{5}
			medaka	2.0×10^{3}
		insect	water flea	3.5×10^{4}
			water flea	2.3×10^{3}
		invertebrate	flatworm	2.0×10^{2}
34413	bromomethane	fish	carp	1.4×10^{4}
			guppy	8.0×10^{-1}
		insect	water flea	2.2×10^{3}
32104	tribromomethane	fish	carp	8.0×10^{4}
			bluegill	2.9×10^{4}
		insect	water flea	5.6×10^{4}
			water flea	4.4×10^{4}
32105	chlorodibromomethane	fish	carp	5.2×10^{4}
			carp	3.4×10^{4}
32103	1,2-dichloroethane	amphibian	salamander	6.5×10^{3}
			salamander	2.5×10^{3}
		crustacean	scud	$>1.0\times10^{5}$
		fish	medaka	1.1×10^{6}
			rainbow trout	3.4×10^{1}
		insect	water flea	2.5×10^{5}
			stonefly	$>1.0\times10^{5}$
34506	1,1,1-trichloroethane	fish	medaka	$>1.0\times10^{6}$
			bluegill	4.0×10^{4}
		insect	water flea	$>5.3\times10^{5}$
			water flea	5.4×10^{3}
34511	1,1,2-trichloroethane	fish	fathead minnow	8.2×10^{4}
			guppy	4.0×10^{4}
		insect	midge	1.5×10^{5}
			water flea	1.8×10^{4}
		invertebrate	zebra mussel	1.9×10^{5}
			snail	5.8×10^{4}
34396	hexachloroethane	amphibian	bullfrog	2.8×10^{3}
			bullfrog	2.4×10^{3}
		crustacean	crayfish	2.7×10^{3}

Table 30. Minimum concentrations of 40 target analytes resulting in 50-percent mortality of various aquatic organisms (from Rowe and others, 1997); when two or more concentrations were available for an organism category, maximum and minimum values are presented; when two concentrations for an organism category were approximately the same, the minimum concentration is presented—Continued

[USGS, U.S. Geological Survey; LC_{50}, lethal concentration at 50-percent mortality; µg/L, microgram per liter; >, greater than]

USGS parameter code	Compound	Category of organism	Common name of organism	LC50 (µg/L)
34396	hexachloroethane (Continued)		crayfish	$>2.1\times10^3$
		fish	catfish	1.6×10^3
			rainbow trout	7.7×10^2
		insect	water flea	$>1.0\times10^4$
			midge	1.2×10^3
		invertebrate	snail	$>2.1\times10^3$
77651	1,2-dibromoethane	fish	bluegill	1.8×10^4
			bass	1.5×10^4
34541	1,2-dichloropropane	fish	bluegill	3.2×10^5
			fathead minnow	1.3×10^5
		insect	water flea	9.9×10^4
			water flea	5.2×10^4
77443	1,2,3-trichloropropane	fish	fathead minnow	6.6×10^4
82625	1,2-dibromo-3-chloropropane	fish	bluegill	5.0×10^4
			bass	2.0×10^4
		invertebrate	snail	5.7×10^4
			bladder snail	2.4×10^4
34501	1,1-dichoroethene	fish	bluegill	7.4×10^4
			fathead minnow	2.9×10^4
		insect	water flea	1.2×10^4
34546	*trans*-1,2-dichloroethene	insect	water flea	2.3×10^5
			water flea	2.2×10^5
39180	trichloroethene	amphibian	axolotl	4.8×10^4
			toad	4.5×10^4
		crustacean	scud	2.4×10^4
		fish	medaka	2.7×10^5
			medaka	1.9×10^3
		insect	water boatman	1.1×10^5
			water flea	2.3×10^3
		invertebrate	tubificidae family	1.3×10^5
			flatworm	1.7×10^3
34475	tetrachloroethene	fish	bluegill	4.6×10^4
			rainbow trout	1.4×10^3
		insect	midge	5.5×10^4
			water flea	1.8×10^3
		invertebrate	flatworm	1.4×10^3
39702	hexachlorobutadiene	fish	bluegill	3.2×10^2
			fathead minnow	9.0×10^1
		insect	sowbug	1.6×10^2
			sowbug	1.3×10^2
		invertebrate	snail	2.1×10^2

Table 30. Minimum concentrations of 40 target analytes resulting in 50-percent mortality of various aquatic organisms (from Rowe and others, 1997); when two or more concentrations were available for an organism category, maximum and minimum values are presented; when two concentrations for an organism category were approximately the same, the minimum concentration is presented—Continued

[USGS, U.S. Geological Survey; LC_{50}, lethal concentration at 50-percent mortality; µg/L, microgram per liter; >, greater than]

USGS parameter code	Compound	Category of organism	Common name of organism	LC50 (µg/L)
34030	benzene	amphibian	axolotl	3.7×10^5
			toad	1.9×10^5
		crustacean	copepod	7.1×10^5
			scud	4.2×10^4
		fish	channel catfish	4.2×10^5
			pink salmon	4.6×10^3
		insect	water flea	3.9×10^5
			dragonfly	1.0×10^4
		invertebrate	rotifer	$>1.0\times10^6$
			rotifer	$>1.0\times10^3$
77128	styrene	crustacean	scud	6.2×10^4
		fish	guppy	7.5×10^4
			rainbow trout	2.5×10^3
		insect	sowbug	6.5×10^4
			water flea	2.3×10^4
		invertebrate	snail	5.6×10^5
			snail	1.1×10^5
34696	naphthalene	crustacean	copepod	6.8×10^4
			scud	3.9×10^3
		fish	mosquito fish	1.6×10^5
			rainbow trout	1.1×10^2
		insect	midge	1.3×10^4
			water flea	1.0×10^3
		invertebrate	snail	5.0×10^3
34010	methylbenzene	crustacean	copepod	4.5×10^5
		fish	mosquito fish	1.3×10^6
			coho and silver salmon	5.5×10^3
		insect	water flea	3.1×10^5
			midge	4.7×10^4
		invertebrate	rotifer	1.1×10^5
34371	ethylbenzene	fish	catfish	2.1×10^5
			rainbow trout	4.2×10^3
		insect	water flea	7.5×10^4
77224	n-propylbenzene	fish	rainbow trout	1.6×10^3
77223	iso-propylbenzene	fish	fathead minnow	6.3×10^3
			rainbow trout	2.7×10^3
		insect	water flea	9.5×10^4
77135	1,2-dimethylbenzene	amphibian	toad	7.3×10^4
		fish	fathead minnow	1.6×10^4
			rainbow trout	7.6×10^3
		invertebrate	snail	$>2.2\times10^4$

Table 30. Minimum concentrations of 40 target analytes resulting in 50-percent mortality of various aquatic organisms (from Rowe and others, 1997); when two or more concentrations were available for an organism category, maximum and minimum values are presented; when two concentrations for an organism category were approximately the same, the minimum concentration is presented—Continued

[USGS, U.S. Geological Survey; LC_{50}, lethal concentration at 50-percent mortality; µg/L, microgram per liter; >, greater than]

USGS parameter code	Compound	Category of organism	Common name of organism	LC50 (µg/L)
85795	1,3-dimethylbenzene	fish	goldfish	1.6×10^4
			rainbow trout	8.4×10^3
85795	1,4-dimethylbenzene	fish	goldfish	1.8×10^4
			rainbow trout	2.6×10^3
77222	1,2,4-trimethylbenzene	fish	fathead minnow	7.7×10^3
34301	chlorobenzene	fish	guppy	4.6×10^4
			bass	5.0×10^1
		insect	water flea	1.1×10^4
			water flea	7.9×10^3
34536	1,2-dichlorobenzene	fish	fathead minnow	9.5×10^3
			rainbow trout	1.5×10^3
		insect	midge	2.0×10^4
			water flea	2.4×10^3
34566	1,3-dichlorobenzene	fish	bluegill	2.2×10^4
			bluegill	5.0×10^3
		insect	water flea	7.2×10^3
			water flea	1.7×10^3
34571	1,4-dichlorobenzene	fish	bluegill	4.5×10^3
			rainbow trout	8.0×10^2
		insect	water flea	4.2×10^4
			water flea	1.1×10^4
77613	1,2,3-trichlorobenzene	fish	zebrafish	3.1×10^3
			guppy	3.5×10^2
		insect	midge	1.7×10^3
34551	1,2,4-trichlorobenzene	crustacean	crayfish	3.0×10^3
		fish	zebrafish	6.3×10^3
			medaka	1.1×10^3
		insect	water flea	2.1×10^3
			midge	9.3×10^2
		invertebrate	snail	3.2×10^3
			flatworm	1.1×10^3
78032	methyl tertiary-butyl ether	fish	fathead minnow	6.7×10^5
34210	2-propenal	amphibian	toad	7.0×10^0
		fish	brown trout	1.5×10^3
			fathead minnow	1.4×10^1
		insect	midge	$>1.5\times10^2$
			water flea	5.7×10^1
		invertebrate	snail	$>1.5\times10^2$
34215	2-propenenitrile	fish	medaka	5.0×10^4
			fathead minnow	2.6×10^3
		insect	water flea	1.3×10^4
			water flea	7.6×10^3

Table 31. Minimum concentrations of 31 target analytes that affected at the 50-percent level various functions of aquatic organisms (from Rowe and others, 1997); when two or more concentrations were available for an organism category, maximum and minimum values are presented; when two concentrations for an organism category were approximately the same, the minimum concentration is presented

[USGS, U.S. Geological Survey; EC$_{50}$, effective concentration at 50 percent affected; µg/L, microgram per liter; >, greater than; ter, quantifiable occurrence of birth defects; imm, immobilization; gro, measurable change in growth characteristics; clr, chlorophyll; rep, change in the reproductive ability; bms, biomass productivity affected; rgn, change in ability to regenerate a body part; beh, quantifiable change in behavior; hat, change in hatchability; equ, equilibrium, change in ability to maintain balance; pgr, population growth; loc, locomotor behavior; avo, avoidance or attraction to a chemical; enz, change in enzyme activity; ptr, photoactic response, attraction to or avoidance of light; pse, photosynthesis; mor, mortality; cyt, change in the genetic processes of the cell]

USGS parameter code	Compound	Category of organism	Common name of organism	End point	EC50 (µg/L)
34423	dichloromethane	amphibian	toad	ter	$>3.2\times10^4$
			bullfrog	ter	1.8×10^4
		fish	fathead minnow	imm	9.9×10^4
		insect	water flea	imm	1.7×10^6
			water flea	imm	1.4×10^5
		plant	duckweed	gro	2.0×10^6
			green algae	clr	$>5.0\times10^5$
32106	trichloromethane	amphibian	toad	ter	$>4.0\times10^4$
			peeper	ter	2.7×10^2
		insect	water flea	rep	3.4×10^5
			water flea	imm	5.2×10^4
		plant	green algae	gro	9.5×10^5
			green algae	bms	5.6×10^5
32102	tetrachloromethane	amphibian	toad	ter	$>9.2\times10^4$
			frog	ter	9.0×10^2
		insect	water flea	imm	9.7×10^4
		invertebrate	flatworm	rgn	1.5×10^3
34413	bromomethane	fish	medaka	beh	5.0×10^2
			guppy	imm	6.0×10^{-1}
		insect	water flea	imm	2.0×10^3
			water flea	beh	1.7×10^3
		plant	green algae	gro	6.7×10^3
			green algae	gro	2.1×10^3
32104	tribromomethane	plant	green algae	pgr	4.0×10^4
			green algae	clr	3.9×10^4
32103	1,2-dichloroethane	insect	water flea	imm	1.8×10^5
			water flea	imm	1.6×10^5
34506	1,1,1-trichloroethane	fish	fathead minnow	imm	1.1×10^4
		plant	green algae	clr	$>5.0\times10^5$
34511	1,1,2-trichloroethane	insect	water flea	imm	7.8×10^4
			water flea	rep	3.2×10^4
		invertebrate	snail	hat	3.6×10^4
34396	hexachloroethane	fish	rainbow trout	equ	8.4×10^2
		insect	water flea	imm	1.3×10^4
			water flea	imm	1.8×10^3
		plant	green algae	clr	8.7×10^4
			green algae	clr	6.7×10^4
34501	1,1-dichloroethene	plant	green algae	clr	$>5.6\times10^5$
			green algae	gro	4.1×10^5

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USGS parameter code	Compound	Category of organism	Common name of organism	End point	EC50 (µg/L)
39180	trichloroethene	fish	fathead minnow	imm	2.2×10^4
		insect	water flea	imm	7.6×10^4
			water flea	imm	7.8×10^3
		invertebrate	flatworm	rgn	1.7×10^3
		plant	green algae	gro	4.5×10^5
34475	tetrachloroethene	fish	fathead minnow	imm	1.4×10^4
		insect	water flea	imm	7.5×10^3
			water flea	imm	3.2×10^3
		invertebrate	flatworm	rgn	9.0×10^2
		plant	green algae	clr	$>5.0\times10^5$
39702	hexachlorobutadiene	fish	rainbow trout	loc	1.4×10^2
34030	benzene	fish	coho and silver salmon	avo	1.8×10^3
			fathead minnow	bms	1.7×10^2
		insect	midge	imm	1.4×10^6
			water flea	enz	6.3×10^3
		invertebrate	snail	imm	9.7×10^5
		plant	green algae	gro	$>1.4\times10^6$
			green algae	gro	2.9×10^4
34696	naphthalene	insect	water flea	imm	4.7×10^3
			water flea	ptr	6.9×10^2
		plant	green algae	gro	3.3×10^4
			diatom	pse	2.8×10^3
34010	methylbenzene	fish	coho and silver salmon	avo	2.3×10^3
			fathead minnow	bms	8.3×10^1
		insect	mosquito	imm	2.2×10^4
			water flea	enz	3.6×10^3
		plant	green algae	gro	2.4×10^5
			green algae	gro	9.4×10^3
34371	ethylbenzene	insect	water flea	imm	1.8×10^3
		plant	green algae	gro	4.6×10^3
77224	n-propylbenzene	insect	water flea	imm	2.0×10^3
		plant	green algae	gro	1.8×10^3
77223	iso-propylbenzene	insect	water flea	imm	1.4×10^3
			water flea	imm	6.0×10^2
		plant	green algae	gro	2.6×10^3
77342	n-butylbenzene	insect	water flea	imm	3.4×10^2
77135	1,2-dimethylbenzene	fish	coho and silver salmon	avo	7.6×10^2
			coho and silver salmon	avo	6.0×10^2

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[USGS, U.S. Geological Survey; EC_{50}, effective concentration at 50 percent affected; µg/L, microgram per liter; >, greater than; ter, quantifiable occurrence of birth defects; imm, immobilization; gro, measurable change in growth characteristics; clr, chlorophyll; rep, change in the reproductive ability; bms, biomass productivity affected; rgn, change in ability to regenerate a body part; beh, quantifiable change in behavior; hat, change in hatchability; equ, equilibrium, change in ability to maintain balance; pgr, population growth; loc, locomotor behavior; avo, avoidance or attraction to a chemical; enz, change in enzyme activity; ptr, photoactic response, attraction to or avoidance of light; pse, photosynthesis; mor, mortality; cyt, change in the genetic processes of the cell]

USGS parameter code	Compound	Category of organism	Common name of organism	End point	EC50 (µg/L)
77135	1,2-dimethylbenzene (Continued)	insect	water flea	imm	3.2×10^3
			water flea	imm	1.0×10^3
		plant	green algae	gro	5.5×10^4
			green algae	gro	4.2×10^3
85795	1,3-dimethylbenzene	insect	water flea	imm	9.6×10^3
			water flea	imm	4.7×10^3
		plant	green algae	gro	4.9×10^3
			green algae	gro	3.9×10^3
85795	1,4-dimethylbenzene	insect	water flea	imm	8.5×10^3
			water flea	imm	3.6×10^3
		plant	green algae	gro	4.4×10^3
			green algae	gro	3.2×10^3
77222	1,2,4-trimethylbenzene	insect	water flea	imm	3.6×10^3
34301	chlorobenzene	insect	water flea	mor	2.2×10^4
			water flea	imm	5.8×10^2
		plant	diatom	cyt	2.4×10^5
			green algae	pgr	2.0×10^5
34536	1,2-dichlorobenzene	fish	rainbow trout	loc	1.6×10^3
		insect	water flea	imm	7.8×10^2
			water flea	rep	5.5×10^2
		plant	green algae	clr	7.1×10^4
			green algae	gro	1.4×10^4
34566	1,3-dichlorobenzene	insect	water flea	imm	4.2×10^3
			water flea	rep	1.4×10^3
		plant	green algae	clr	1.2×10^5
			green algae	bms	1.9×10^4
34571	1,4-dichlorobenzene	fish	rainbow trout	equ	1.1×10^3
		insect	water flea	imm	1.6×10^3
			water flea	rep	9.3×10^2
		plant	green algae	gro	3.8×10^4
			green algae	gro	1.6×10^3
77613	1,2,3-trichlorobenzene	insect	water flea	imm	3.5×10^2
			water flea	rep	2.0×10^2
		plant	diatom	cyt	6.4×10^3
34551	1,2,4-trichlorobenzene	fish	rainbow trout	equ	1.3×10^3
		insect	water flea	imm	1.2×10^3
			water flea	rep	4.5×10^2
		invertebrate	flatworm	rgn	1.1×10^3
		plant	green algae	clr	2.2×10^4
			diatom	cyt	2.8×10^3
34210	2-propenal	insect	water flea	imm	9.3×10^1
			water flea	imm	5.1×10^1

The quotient method used for defining the effect of organic compounds on organisms has several weaknesses (Bascietto and others, 1990). It does not account for the effects of incremental dosages of the organic compound, nor can it be used to estimate indirect effects of toxic compounds such as food chain interactions. It does not account for other ecosystem effects such as predator-prey relationships, community metabolism, and structural shifts. Finally, the quotient method does not consider the differences between organisms used in the laboratory bioassay studies and the actual aquatic systems. Also, laboratory studies are usually done with single organic compounds, whereas organic compounds seldom, if ever, occur singularly in natural stream systems.

Mixtures of organic compounds are being emphasized in current efforts to improve methods for determining the effects of organic compounds on aquatic organisms. The toxicity of a mixture may be more or less than the sum of the toxicities of the individual compounds making up the mixture. Present efforts (Renner, 1996) are directed toward classifying chemical structures into five or six mode-of-action groups. The toxicity of a mixture is often dominated by narcotic chemicals because the mixture includes many industrial chemicals such as chlorinated benzenes, methylbenzenes, and alkanes not designed to be biologically active (Renner, 1996). Laboratory tests of such chemicals indicate that the effects of mixtures are additive for endpoints such as mortality and inhibition of reproduction and growth. However, attempts to transfer this information to natural systems are hindered because the mixture composition begins to change, once it enters the environment, as a result of processes such as volatilization. Consequently, there is no factor that can be used to transfer laboratory results to the natural system.

ADVECTION AND DISPERSION

A VOC dissolved in stream water is subject to the same advective and dispersive forces that act upon the mass of water in which the VOC is dissolved. The VOC is advected downstream with the flow of the stream. This advective flow usually is characterized by the water velocity, which is essential in estimating the effects of many processes on the VOC concentration as the water mass moves downstream.

The water velocity is not constant over the cross section of a stream but varies over the water depth and from bank to bank as a result of shear forces at the interface between the water and the banks and bottom of the stream and, to a much lesser extent, between the water and the atmosphere. The water velocity used in previous examples accounted for these variations by using a velocity averaged over the cross section of flow. These velocity variations also result in dispersive mixing in the vertical, lateral, and longitudinal directions of the stream.

VERTICAL MIXING

Vertical mixing or mixing over the flow depth is rapid in streams. Sayre (1973) indicated that the distance downstream from a source of contaminant necessary to obtain an approximately uniform concentration over the flow depth can be estimated from

$$L_y = \frac{0.5\ U\ Y^2}{\varepsilon_y} \tag{135}$$

where

L_y is the downstream distance (m) required for vertical mixing,
U is the mean water velocity (m/s),
Y is the flow depth (m), and
ε_y is the vertical eddy diffusivity (m^2/s) averaged over the depth.

Various experimental results (Fischer, 1973) indicated that the vertical eddy diffusivity can be approximated by

$$\varepsilon_y = 0.067\ Y\ u^* \tag{136}$$

where

u* is the shear velocity (m/s) given by

$$u^* = (g\ Y\ S)^{0.5} \tag{137}$$

where

g is the acceleration of gravity (m/s/s), and
S is the slope of the stream channel (m/m).

The shear velocity is related to the roughness of the stream channel by (Fischer and others, 1979)

$$u^* = U\left[\frac{f}{8}\right]^{0.5} \tag{138}$$

where

f is the Darcy-Weisbach friction factor.

Using 1/15 as a typical value of $(f/8)^{0.5}$ (Fischer and others, 1979) and combining equations 135, 136, and 138 gives

$$L_y = 112\,Y\,. \tag{139}$$

Equation 139 indicates that the distance downstream from a contaminant source necessary to obtain an approximately uniform concentration over the flow depth is 112 times the depth. Thus, for a stream with a depth of 0.5 m, vertical mixing is achieved in about 56 m, whereas for a stream with a depth of 10 m, about 1,120 m would be necessary. Equation 139 is generally consistent with the common estimate (Yotsukura and Sayre, 1976) that a reach length of 50 to 100 flow depths is necessary for an approximately uniform vertical concentration profile of a neutrally buoyant, water-soluble contaminant discharged at the surface of a stream.

LATERAL MIXING

Mixing over the lateral dimension of a stream commonly is called transverse mixing. Estimation of the downstream distance required for completion of transverse mixing depends on the location of the contaminant source in the stream cross section and the desired degree of mixing. The degree of mixing, P_m, in percent, can be computed from (Kilpatrick and Cobb, 1985)

$$P_m = 100 - \frac{50}{C_m Q}\sum_{i=1}^{n} |C_i - C_m|\,Q_i \tag{140}$$

where

C_m is the mean cross-sectional concentration,

C_i and Q_i are the concentration and the water discharge at point i in the cross section, and

n is the number of points in the cross section.

As the desired degree of mixing increases, the distance required to achieve such mixing increases rapidly. Yotsukura and Cobb (1972) estimated that the distance required to improve the degree of mixing from 95 to 99.5 percent may be as long as the distance required to achieve the initial 95-percent mixing. For this reason, 95-percent mixing commonly is used as a degree of mixing that can be attained with reasonable mixing distances (Kilpatrick and Wilson, 1989).

The mixing distance required for 95-percent mixing of a point source at the center of the cross section can be estimated (Fischer and others, 1979) from the following:

$$L_z = \frac{0.1\,U B^2}{\varepsilon_z} \tag{141}$$

where

L_z is the mixing distance (m),

B is the stream width (m), and

ε_z is the transverse eddy diffusivity (m^2/s).

The transverse eddy diffusivity is given by

$$\varepsilon_z = a_z\,Y\,u^* \tag{142}$$

where

a_z is a dimensionless parameter that varies widely, depending on the type of channel.

For straight, rectangular flumes, most experimental values are in the range of 0.1 to 0.2, with an irrigation canal having values of 0.24 and 0.25 (Fischer and others, 1979). In natural channels, bends and bank irregularities have a large effect on transverse mixing, and a_z values are usually in the range from 0.4 to 0.8. Fischer and others (1979) suggested a value of 0.6, with an error of ±50 percent. Such a value is appropriate for slowly meandering streams with moderate bank irregularities. For streams with sharp bends or rapid changes in cross-sectional geometry, a larger value should be used. However, there are no specific guidelines on how much larger the parameter should be. It is best to underestimate this parameter because such underestimation overestimates the distance required to achieve the commonly used 95-percent mixing.

Using a value 0.6 for a_z and combining equations 141, 142 and 137 gives

$$L_z = \frac{0.053\,U\,B^2}{Y^{1.5}\,S^{0.5}} \tag{143}$$

where

L_z is the distance (m) required for 95-percent transverse mixing of a contaminant source at the centerline of the stream.

For a contaminant source entering the stream at some point on one of the banks, such as a stormwater drain, the mixing distance is four times the distance computed from equation 143. This equation indicates that the mixing distance is strongly dependent on the stream width and increases with the square of the width. This equation also indicates that the mixing distance decreases as the depth and slope increase. Conversely, the mixing length increases as the velocity increases because the contaminant has less chance for transverse mixing at the higher velocity.

An alternative form of equation 143 can be obtained by combining it with the Manning equation. For metric units, the Manning equation has the form (Barnes, 1967)

$$U = \frac{Y^{0.67} S^{0.5}}{n} \qquad (144)$$

where

n is the roughness coefficient.

Equation 144 assumes a wide stream where the hydraulic radius is approximately equal to the flow depth. Combining equations 143 and 144 gives

$$L_z = 0.053 \left[\frac{B}{Y}\right]\left[\frac{B\,Y^{1/6}}{n}\right] \qquad (145)$$

which indicates for a constant width/depth ratio that the mixing distance is approximately proportional to the width. Equation 145 has the advantage that the water velocity and the stream slope do not need to be estimated; however, the roughness coefficient is needed. The roughness coefficients of streams has been discussed by Barnes (1967).

LONGITUDINAL MIXING

Longitudinal mixing or dispersion is the stretching out of the contaminant mass as the mass is advected downstream. Longitudinal dispersion occurs primarily as a result of velocity variations in the lateral direction of the stream cross section. That part of the contaminant mass in the center of the cross section is advected downstream at a velocity higher than the average velocity. Conversely, that part of the contaminant mass in the low-velocity regions near the streambanks moves downstream at a velocity lower than the average velocity, resulting in elongation or longitudinal mixing of the contaminant mass.

The effect of longitudinal dispersion is dependent upon the type of contaminant source. For a contaminant discharged continuously into a stream, constant plateau concentrations are eventually established in the stream and the effect of longitudinal dispersion is eliminated. The concentration may decrease with distance downstream as a result of other processes such as volatilization. However, longitudinal dispersion has no effect on the plateau concentrations because steady-state conditions are established.

Longitudinal dispersion is important, however, for an instantaneous slug injection of contaminant such as might occur with a spill. It has been shown (Fischer, 1966) that

$$C(L,t) = \frac{M}{A\sqrt{4\pi D_L t}} \exp\left[-\frac{(L-Ut)^2}{4D_L t}\right] \qquad (146)$$

where

C is the contaminant concentration ($\mu g/m^3$) at longitudinal position L (m) at time t (s),

M is the mass of contaminant released (μg),

A is the cross-sectional area (m^2),

D_L is the longitudinal dispersion coefficient (m^2/s), and

U is the mean water velocity (m/s).

Equation 146 applies to a one-dimensional system and it assumes that the contaminant is conservative.

If the contaminant is not conservative, then equation 146 becomes (Camp, 1963)

$$C(L,t) = \frac{M}{A\sqrt{4\pi D_L t}} \exp\left[-\frac{(L-Ut)^2}{4D_L t} - \sum_{i=1}^{n} K_i t\right] \qquad (147)$$

where

K_i is the first-order rate coefficient (s^{-1}) describing loss of the contaminant from the stream by process i.

Longitudinal dispersion in a stream continues indefinitely. For practical purposes, longitudinal dispersion ceases when the analytical procedure used for measuring the concentration of the contaminant is no longer able to detect changes in concentration with time as the contaminant mass passes a downstream point. Application of equations 146 and 147 indicates that these equations do not predict concentration-time distributions well near the contaminant source, nor do these equations predict the long tails commonly observed in contaminant distributions determined in natural stream systems.

Application of equations 146 and 147 requires the longitudinal dispersion coefficient, and this coefficient has been studied extensively. Despite this extensive study, estimation of the longitudinal dispersion coefficient is still subject to considerable error. Various approaches have been used to develop equations for predicting this coefficient.

A shear velocity analogy (Fischer and others, 1979) resulted in the equation

$$D_L = a_L Y u^* \qquad (148)$$

where

a_L is a dimensionless parameter.

Unfortunately, experimental values of a_L vary widely, ranging from 8.6 for a canal to 7,500 for the Missouri River (Fischer and others, 1979).

There have been numerous attempts to relate the longitudinal dispersion coefficient to the hydraulic and geometric properties of streams. Fischer and others (1979) proposed

$$D_L = \frac{0.011 U^2 B^2}{Y} \qquad (149)$$

where metric units are used with seconds as the time unit. Predictions using equation 149 are usually within a factor of about four of experimental dispersion coefficients. Fischer and others (1979) considered this agreement reasonable in view of the fact that the change of moment method and the routing procedure commonly used for analyzing experimental data may give dispersion coefficients differing by as much as a factor of two for the same set of data. Much of this difficulty results from the long tails on the concentration-time distributions and the effect of these tails on the computation of the variances of the distributions. However, it is these tails that define the dispersion being measured; consequently, it is difficult to decide at what point to truncate the calculations.

McQuivey and Keefer (1974) proposed

$$D_L = \frac{0.058\, Q}{S\, B} \qquad (150)$$

where

D_L is the longitudinal dispersion coefficient (m^2/s),

Q is the water discharge (m^3/s),

S is the slope of the channel (m/m), and

B is the channel width (m).

Equation 150 applies to a steady base-flow condition and was developed from 37 measurements on 18 streams. This equation has a standard error of estimate of about 30 percent. Measured longitudinal dispersion coefficients ranged from 5.4 m^2/s for the Monocacy River in Maryland to 1,030 m^2/s for the Missouri River in Nebraska and Iowa.

Estimates of the longitudinal dispersion coefficient from equations 148, 149, and 150 for a specific set of hydraulic and geometric properties for a stream could differ substantially. If this occurs, properties of the stream can be compared with those of streams for which longitudinal dispersion coefficients have been measured (McQuivey and Keefer, 1974; Fischer and others, 1979) to assist in determining what is the best estimate of the longitudinal dispersion coefficient for the stream of interest. Other equations have been presented in the literature. However, a complete review of the literature on longitudinal dispersion is beyond the scope of this report. Readers needing more information on any aspects of dispersion should consult Rutherford (1994).

ESTIMATION OF THE IMPORTANCE OF LONGITUDINAL DISPERSION

The importance of longitudinal dispersion on the fate of the target analytes in streams was estimated for the deep, low-velocity stream, intermediate-depth, high-velocity stream, and shallow, medium-velocity stream examples used in previous calculations.

Dichloromethane and diisopropyl ether were selected as examples from the 55 target analytes (table 1). Temperature was assumed to be 20°C, and an average air-film mass-transfer coefficient of 756 m/day was used. Volatilization coefficients were calculated using equations 53, 54, 55, 27, 28, 16, and 13 and the same procedures used in previous examples. Longitudinal dispersion coefficients of 2 m^2/s (deep, low-velocity stream), 1,000 m^2/s (intermediate-depth, high-velocity stream), and 10 m^2/s (shallow, medium-velocity stream) were used.

Concentrations computed from equations 146 and 147 for various distances downstream are plotted in figures 17, 18, and 19 as a function of elapsed time from the release of the contaminants. The dispersant was assumed to be conservative, and the VOCs were assumed to be subject only to longitudinal dispersion and volatilization. The time unit in seconds used in equations 146 and 147 was converted to hours to facilitate plotting the results.

Figure 17 shows the results for the deep, low-velocity stream characteristic of the O'Connor-Dobbins (1958) equation. The peak concentration decreased substantially with distance downstream. There was, however, only a little difference between the curves for the conservative dispersant and the nonconservative VOCs. The ratio of the peak concentration of the conservative dispersant at 40,000 m to the concentration at 3,000 m was 0.273. Corresponding ratios for dichloromethane and diisopropyl ether were 0.238 and 0.244, respectively, indicating that 87 and 89 percent of the changes in the concentrations of dichloromethane and diisopropyl ether were the result of longitudinal dispersion.

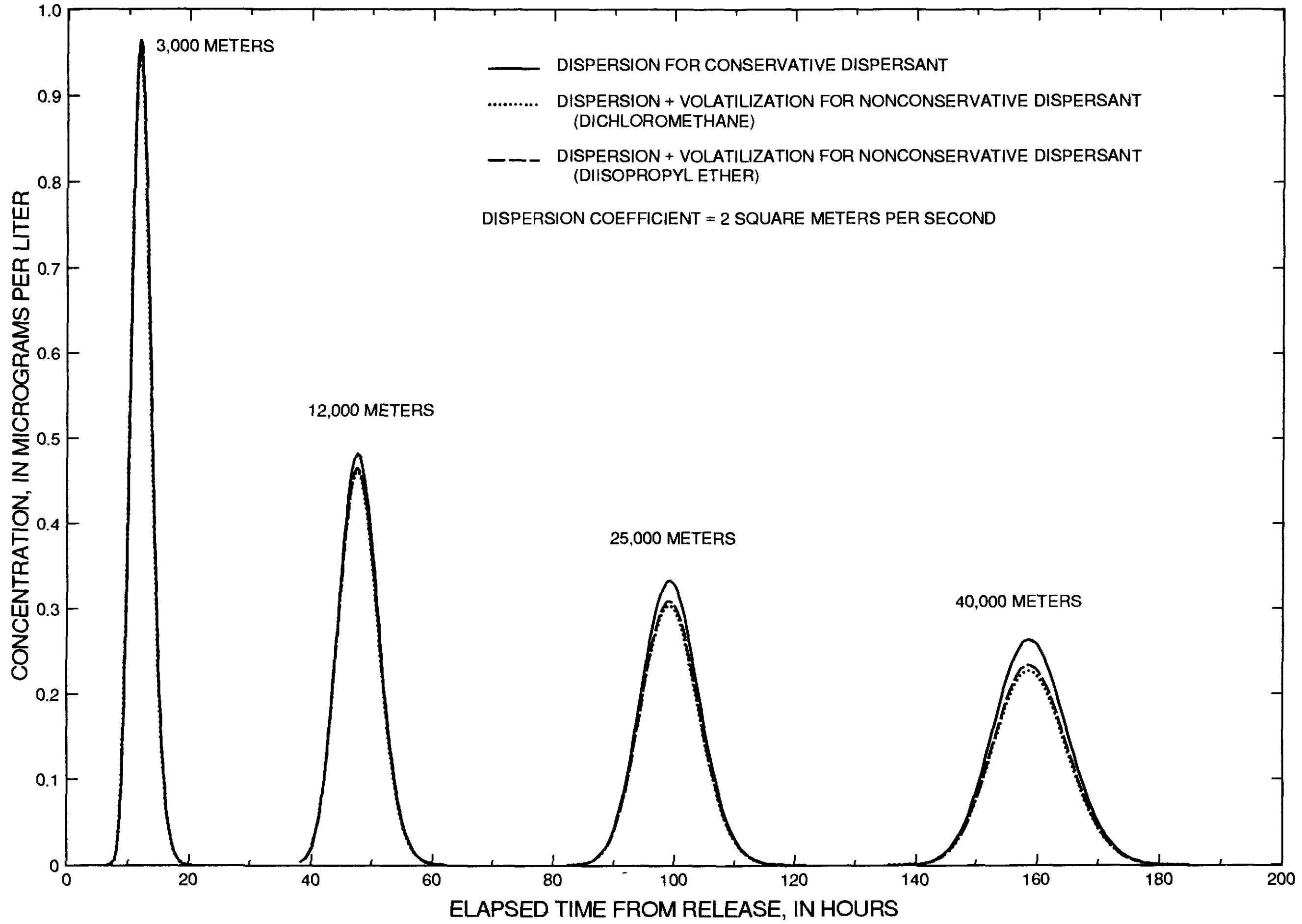

Figure 17. Concentration of a conservative dispersant and the nonconservative dispersants dichloromethane and diisopropyl ether as a function of time for a deep, low-velocity stream characteristic of the O'Connor-Dobbins (1958) equation; Henry's law constants are 229 and 167 pascals cubic meter per gram mole at 20 degrees Celsius for dichloromethane and diisopropyl ether, respectively.

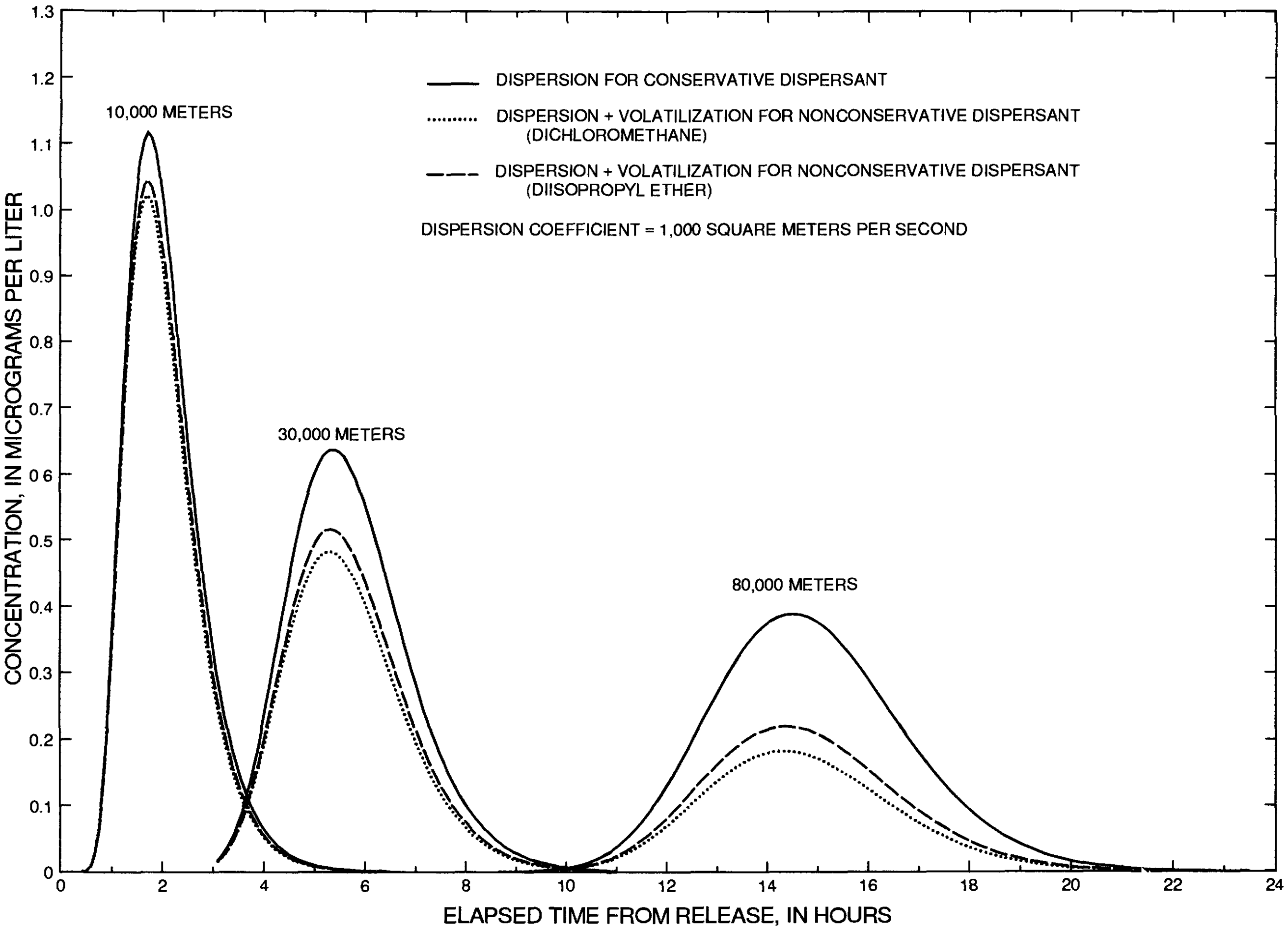

Figure 18. Concentration of a conservative dispersant and the nonconservative dispersants dichloromethane and diisopropyl ether as a function of time for an intermediate-depth, high-velocity stream characteristic of the Churchill and others (1962) equation; Henry's law constants are 229 and 167 pascals cubic meter per gram mole at 20 degrees Celsius for dichloromethane and diisopropyl ether, respectively.

Figure 18 shows the results for the intermediate-depth, high-velocity stream characteristic of the Churchill and others (1962) equation. The ratio of the peak concentration of the conservative dispersant at 80,000 m to the concentration at 10,000 m was 0.348. Corresponding ratios for dichloromethane and diisopropyl ether were 0.179 and 0.211, respectively, indicating that 51 and 61 percent of the changes in the concentrations of dichloromethane and diisopropyl ether were the result of longitudinal dispersion.

Figure 19 shows the results for the shallow, medium-velocity stream characteristic of the Owens and others (1964) equation. The ratio of the peak concentration of the conservative dispersant at 2,000 m to the concentration at 250 m was 0.350. Corresponding ratios for dichloromethane and diisopropyl ether were 0.0133 and 0.0289, respectively, indicating that 3.8 and 8.3 percent of the changes in the concentrations of dichloromethane and diisopropyl ether were the result of longitudinal dispersion.

The results in figure 19 and other examples described previously indicate that volatilization rates for shallow flows are rapid. The results in figure 17 indicate that substantial decreases in concentration can occur as a result of longitudinal dispersion, even when changes as a result of volatilization are minimal because of the deep flow. The results in figure 18 are for intermediate conditions, where both processes contribute to decreases in the concentration with distance downstream.

The results in figures 17, 18, and 19 are idealized somewhat because it is well known that concentration-time distributions in streams do

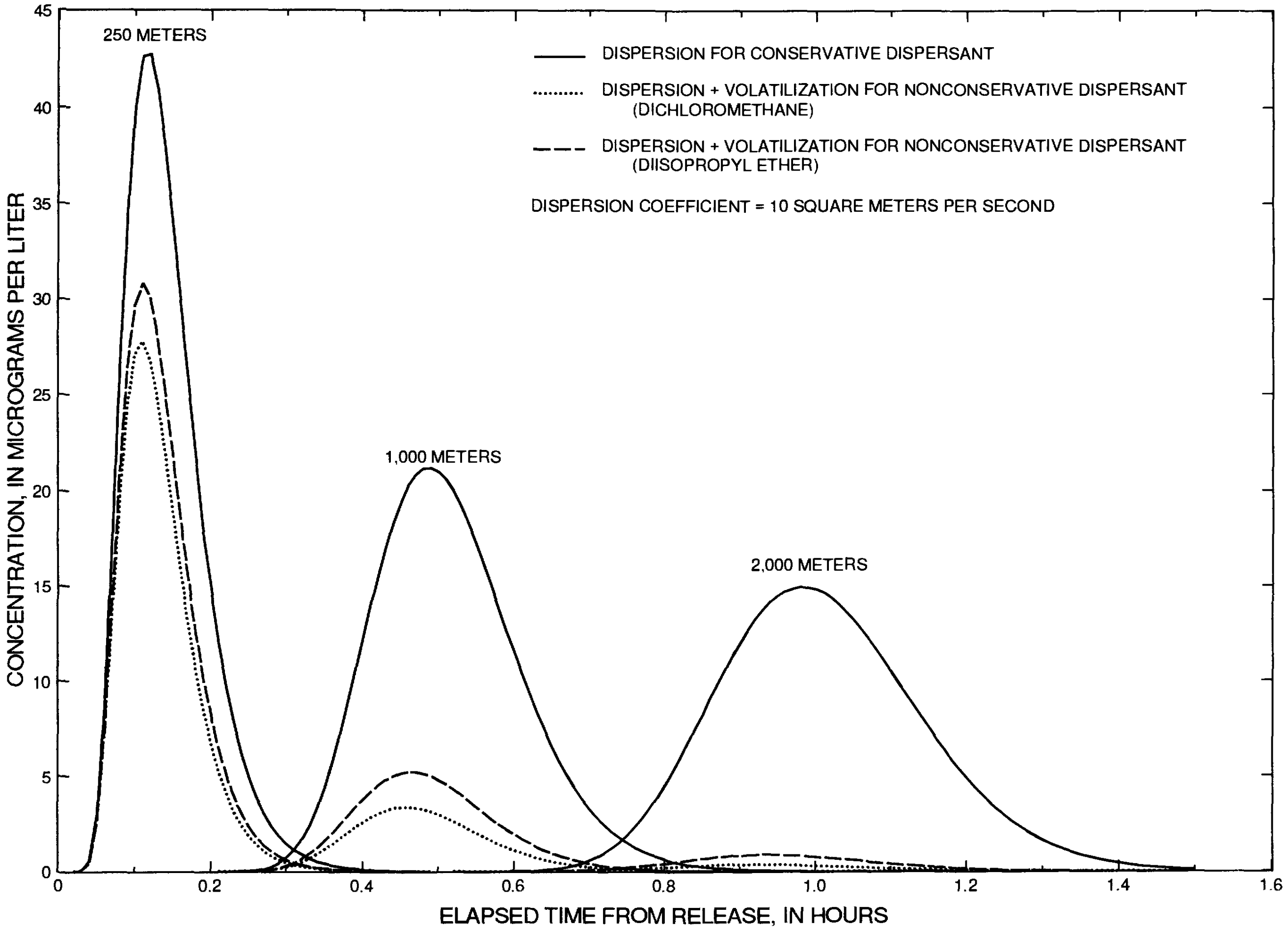

Figure 19. Concentration of a conservative dispersant and the nonconservative dispersants dichloromethane and diisopropyl ether as a function of time for a shallow, medium-velocity stream characteristic of the Owens and others (1964) equation; Henry's law constants are 229 and 167 pascals cubic meter per gram mole at 20 degrees Celsius for dichloromethane and diisopropyl ether, respectively.

not fit exactly the normal distributions predicted by equations 146 and 147. Specifically, the tails of the concentration-time distributions commonly are much longer than predicted by these equations. Equations 146 and 147 do provide, however, a useful first approximation of the effects of longitudinal dispersion on contaminant distributions in streams.

INFORMATION NEEDS

This review of the literature and application of the available information to predicting the fate of VOCs in streams in general, and specifically the target analytes, has identified several areas in which information was limited or was lacking. Specific areas where additional physical property data and process research are needed are discussed below.

VOLATILIZATION

The Henry's law constant is required to determine the tendency of a compound to partition between the water and air phases of the environment. For those compounds with Henry's law constants small enough that mixing processes in both the water and air phases are important, this constant also has a direct effect on the overall volatilization rate coefficient. Generally, good coverage of the temperature dependencies of the Henry's law constants for the target analytes was found (tables 2 and 4). However, Henry's law constants were not available for 12 of the target analytes. These analytes were bromoethene, 1,2-dibromo-3-chloropropane, *cis*-1,3-dichloropropene, *trans*-1,3-dichloropropene, iso-propylbenzene, n-butylbenzene, styrene, ethyl tertiary-butyl ether, tertiary-amyl methyl ether, diisopropyl ether, 2-propenal, and 2-propenenitrile. Constants for these analytes were predicted using vapor pressure and solubility data from the literature, although these data were limited, and, in many cases, of unknown quality. Specifically, there are currently no data for bromoethene. The solubility for this compound was calculated from an octanol-water partition coefficient estimated from the value for chloroethene. Also, there are few physical property data for the four ether compounds, a group of compounds that are important because of their use as automotive gasoline oxygenates. The Henry's law constant for methyl tertiary-butyl ether has been measured (Robbins and others, 1993) as a function of temperature. However, the temperature range was 25°C to 50°C, thus requiring extrapolation to the lower temperatures appropriate for most environmental conditions.

The reference-substance concept (eqs. 25 and 26) is fundamental to predicting the volatilization of VOCs from streams. The water-film reference-substance concept has been verified for a number of compounds. However, most of these compounds had Henry's law constants large enough that virtually all the resistance to volatilization was in the water film. There is little experimental data on the effect of an increasing air-film resistance on the volatilization process. Also, the air-film reference-substance concept has been verified for only one compound. The argument might be made that volatilization becomes less important and eventually negligible as the Henry's law constant decreases. However, if these solutes with low Henry's law constants are volatile enough to be considered as target analytes and if the Henry's law constant indicates an air-film resistance, then this resistance must be considered. Present knowledge is somewhat limited in this respect. A target analyte of current interest is methyl tertiary-butyl ether, and this compound has a Henry's law constant such that the air-film resistance can be important. More information is needed on the volatilization characteristics of this compound.

ABSORPTION

The volatilization model indicates that absorption should occur when the ambient air concentration exceeds the air concentration that would be in equilibrium with the ambient water concentration. Absorption is most likely to be important in geographic areas with high atmospheric concentrations of VOCs and low stream-water concentrations of the same VOCs. However, such absorption has not been explicitly demonstrated. Measurements are needed to determine if the atmosphere can be a significant source of VOCs in the streams of such areas.

WET DEPOSITION

Limited data exist on gas scavenging ratios for the target analytes, and there is considerable variability in the available data. For most analytes, ±1 standard deviation of the mean was a large percentage of the mean and, in some cases, approached the mean in value. This variability indicates the experimental difficulties involved in measuring small concentrations of VOCs in air and precipitation samples. With improved instrumentation and lower detection limits, more accurate determinations of these ratios should now be possible.

Henry's law constants at low temperatures are needed for some of the target analytes. These data would permit a more thorough evaluation of the relationship between the gas scavenging ratio and the Henry's law constant, as well as an accurate determination of the temperature dependence of the gas scavenging ratio.

The concentrations of VOCs in streams predicted to result from gas scavenging and wet deposition were very low, indicating that this process probably is not a significant source. However, a simplistic approach was used for these predictions, and experimental verification is necessary. The contributions from wet deposition onto surfaces and runoff into the stream are expected to be minimal because of rapid volatilization back into the atmosphere. VOCs have, however, been found in stormwater runoff, indicating that gas scavenging and wet deposition could be a source of VOCs in streams. Experimental determination of the possible magnitude of this source under a variety of conditions is needed.

MICROBIAL DEGRADATION

Considerable information exists in the literature on the microbial degradation of the target analytes. However, this is the one process for which it is probably the most difficult to predict effects on VOC concentrations in streams. Indeed, microbial degradation is a highly system-specific and site-specific process. For example, different microbial communities will need different periods of time to adapt to a VOC of interest. During this so-called lag period, the microbes develop the enzymes necessary to accomplish degradation of the VOCs. Information needs, therefore, include compound-dependent data on whether or not adaptation can occur during the time periods VOCs are expected to persist in streams. Adaptation is most likely to occur during long-term exposures such as would occur during continuous discharges of wastewaters. However, because such discharges are gradually being reduced or eliminated, a more important question is whether or not adaptation can occur during exposure to VOCs in transient events such as occur during stormwater runoff, surface-water runoff, and spills. The answer to this question is difficult because of the complex nature of the microbial degradation process and the transient nature of VOCs in streams.

SORPTION

The literature indicates that the extent of sorption of organic compounds can vary appreciably between soils and sediments, with the difference apparently dependent on the type and extent of diagenesis of the soil. A significant source of VOCs in urban streams may be those associated with sediment particles flushed from impervious surfaces into the streams during storm events. Information is needed on the organic-carbon contents and sorption characteristics of such particles, and how they compare with natural soils and sediments.

It has been hypothesized that VOCs sorbed to sediments in a stream under an aggrading condition could be buried and then pose a threat to humans or aquatic organisms at a later time long after the bulk of the VOC discharge has dissipated. VOCs have been found in bottom sediments, but there is no information as to when the VOCs were deposited in these sediments. Information is needed on the ability of VOCs to persist in bottom sediments.

Recent research has indicated that sorption isotherms may be nonlinear. Such behavior is in conflict with the linear isotherms commonly predicted by the partition model of sorption. A result of this apparent nonlinearity is a sorption coefficient that depends on concentration, and such dependence greatly complicates the prediction of the extent of sorption. Also, this nonlinearity appears to be most important for low concentrations of the compound being sorbed, and this is the concentration range most likely to be important in environmental situations. Research is needed to define the extent of this nonlinear effect and how it affects the prediction of the sorption of organic compounds in the low-concentration ranges prevailing in the environment.

HYDROLYSIS

Nine target analytes have reported hydrolysis half-lives of 548 days or less. These analytes are chloromethane, dichloromethane, bromomethane, chloroethene, 1,1,1-trichloroethane, 1,2-dibromoethane, 1,1-dichloroethene, tetrachloroethene, and 1,3-dichloropropene. For several of these analytes, the reported half-lives varied by orders of magnitude. Minimum half-lives, therefore, were used in the current evaluation to provide a conservative approach. However, if the true half-life for a specific compound is an order of magnitude longer than assumed, then in reality hydrolysis may not be significant relative to volatilization. A careful reevaluation of the hydrolysis half-lives is needed for those target analytes assumed to have short half-lives.

Controversy exists on the hydrolysis properties of 2-propenal and 2-propenenitrile, as discussed in detail in the hydrolysis section of this report. Because water is the medium of interest in this work, these questions must be answered to understand the behavior of these two compounds in streams.

Previous discussion in the sorption section of this report indicated that the target analytes with the higher molecular weights and lower water solubilities tended to sorb to sediments, with the extent of sorption depending on the concentration and organic-carbon content of the sediment. Larson and Weber (1994) used the hydrolysis of 1,2-dibromo-3-chloropropane to demonstrate that hydrolysis rates and pathways may be different for systems with and without sediments. They concluded that more information is needed on the effects of sediments on the hydrolysis of organic compounds. The presence of sediment also could affect the rates of other reactions such as microbial degradation, aquatic photolysis, and oxidation of the sorbed compounds.

AQUATIC PHOTOLYSIS

Very little information exists on the photolysis of the target analytes in the aquatic environment, in contrast to the atmosphere where photolysis is the major process for removal of many VOCs. Thus, there is a need for information on aquatic photolysis. The absorption spectrum of hexachlorobutadiene extends into the sunlight spectrum, but the belief (Callahan and others, 1979) is that the light absorption coefficient is not large enough for direct photolysis to be important. Experimental verification of this hypothesis is needed. The compound 2-propenenitrile does not absorb significantly in the wavelength range characteristic of sunlight, but this molecule may be subject to indirect photolysis in natural systems where the appropriate sensitizers are present (Callahan and others, 1979). The general topic of indirect photolysis has received little attention, and this process could be important for several of the target analytes. Indirect photolysis is a complex process, however, and information on the types, occurrences, and concentrations of the sensitizers necessary for this process is generally lacking.

The most important issue regarding photolysis is the question of the effect of water depth. It has been established that photolysis in a quiescent water column decreases as the depth increases because of reduced light penetration. In a flowing stream, however, the water is not quiescent, but there is a continual exchange and mixing of the water. Consequently, it may be reasonable to expect that photolysis is limited to the surface layers and can continue to occur in these layers as a result of replacement of surface water with water from below that contains the nonphotolyzed compound. If such a mechanism is operative, aquatic photolysis would be more significant than if the water column were quiescent and, therefore, could be significant relative to volatilization for deep flows. Experimental verification of this mechanism and the extent to which surface renewal facilitates aquatic photolysis in streams is needed.

OXIDATION

Much of the information available on the oxidation of VOCs in streams has been calculated or estimated based on results for molecules with similar structures. The available information indicates that oxidation can be significant for some target analytes in deep streams. However, the issue again is the question of the effect of depth, as was discussed for photolysis. It has been hypothesized that the oxidants causing oxidation of VOCs result from the photolysis of humic materials in the water, and verification of this hypothesis is necessary. Assuming that this mechanism for the formation of the oxidants is valid, it is important to know whether the production of these oxidants is limited by light penetration as the depth increases, or whether vertical mixing and replacement of the surface-water layers are rapid enough to preclude such depth limitations. If the formation of these oxidants is not limited as the depth increases, oxidation could be significant relative to volatilization for deep flows. Experimental verification of this hypothesis is needed.

BIOCONCENTRATION

The potential for bioconcentration correlates with the octanol-water partition coefficient. The octanol-water partition coefficients of the target analytes are such that the masses of VOCs removed from streams by this process are likely to be small. However, estimation of these masses depends directly on the organism density in the stream, and little information currently is available on this density. Using a fish density an order of magnitude larger than the commonly used density results in prediction of significant removal of hexachlorobutadiene by bioconcentration, relative to volatilization. More information is needed on the organism densities likely to exist in streams.

SUMMARY AND CONCLUSIONS

The transport, behavior, and fate of volatile organic compounds (VOCs) in streams are determined by combinations of various chemical, physical, and biological processes. These processes are volatilization, absorption, wet and dry deposition, microbial degradation, sorption, hydrolysis, aquatic photolysis, oxidation, chemical reaction, bioconcentration, advection, and dispersion. The literature on these processes was reviewed and used to estimate the effects these processes have in determining the fate in streams of 55 VOCs selected for emphasis by the U.S. Geological Survey National Water-Quality Assessment Program. These particular VOCs were selected because of their frequent occurrence in surface water and because they were known or suspected hazards to the health of humans and/or aquatic organisms. A few compounds were included because of special uses and/or environmental effects, such as those compounds used as oxygenates in reformulated automotive gasolines, those suspected of causing deterioration of the ozone layer, and those significantly bioconcentrated by aquatic organisms. While the focus of this report is on these 55 VOCs, the same principles and general conclusions based on these principles apply to other VOCs. Specific conclusions resulting from this study are presented in the following paragraphs.

1. Volatilization is the movement of a VOC from water across the water/air interface into the air. Volatilization of a VOC from a stream is dependent on the mixing conditions in both the water and air phases. The relative importance of mixing conditions in these two phases depends on the Henry's law constant of the VOC.
2. Average experimental Henry's law constants at 25°C for 43 target analytes range from 34.3 Pa m^3/g mol for 1,2,3-trichloropropane to 34,200 Pa m^3/g mol for dichlorodifluoromethane. Corresponding values at 20°C are 28.2 Pa m^3/g mol and 31,400 Pa m^3/g mol. Calculated Henry's law constants for 12 target analytes range from 7.92 Pa m^3/g mol for 2-propenal at 20°C to 1,520 Pa m^3/g mol for n-butylbenzene at 25°C. Of the 55 target analytes, 47 have Henry's law constants large enough that 90 percent or more of the resistance to volatilization is predicted to be in the water phase for average environmental conditions. Consequently, volatilization of these analytes is controlled by the mixing conditions within the water phase, and the Henry's law constant has little direct effect on the volatilization coefficient.
3. The two analytes with the lowest Henry's law constant are 2-propenenitrile and 2-propenal. The resistance to volatilization of these two analytes is predicted to be about equally divided between the water and air phases for average environmental conditions.
4. Estimates of the volatilization half-lives for tribromomethane, trichloromethane, and dichlorodifluoromethane for conditions approximating a deep, low-velocity stream, an intermediate-depth, high-velocity stream, and a shallow, medium-velocity stream indicate that the half-life decreases as the velocity increases for a constant depth. Conversely, the half-life increases as the flow depth increases for a constant velocity. The half-lives are longest for tribromomethane, which has the lowest Henry's law constant of these three compounds. The half-lives for trichloromethane and dichlorodifluoromethane are similar, despite the fact that the Henry's law constant for dichlorodifluoromethane is about one-hundred times larger than that for trichloromethane. This lack of dependence on the Henry's law constant is attributed to the fact that these two compounds have Henry's law constants large enough that volatilization is controlled almost completely by the mixing conditions in the water. The three compounds were selected for this comparison because they have Henry's law constants near the low, middle, and high end of the distribution of Henry's law constants for the target analytes.
5. Volatilization half-lives for tribromomethane, trichloromethane, and dichlorodifluoromethane decrease as the temperature increases for conditions characteristic of a deep, low-velocity stream, an intermediate-depth, high-velocity stream, and a shallow, medium-velocity stream. The decrease is largest for tribromomethane, which has a Henry's law constant low enough that the constant is important in contributing to the control of the volatilization process.
6. Absorption of VOCs from the atmosphere by a stream occurs when the ambient air concentration is greater than the concentration that would be in equilibrium with the ambient water

concentration. The importance of this process as a source of VOCs in streams has not been determined.

7. Dry deposition of VOCs with particles is not expected to be important for the target analytes. Vapor pressures of the analytes are high enough that little sorption of the analytes to particulates in the atmosphere is expected.
8. Wet deposition of VOCs can occur with particles and precipitation, although little sorption of the target analytes to atmospheric particulates is expected. Wet deposition with precipitation is characterized by the gas scavenging ratio, which is the ratio of the concentrations of the organic compound in the precipitation and in the ambient air. Equilibrium is established rapidly between the air and precipitation concentrations, resulting in the gas scavenging ratio being inversely proportional to the Henry's law constant.
9. The gas scavenging ratio is directly dependent on the temperature and inversely dependent on the Henry's law constant. The exponential dependence of the Henry's law constant on temperature has a much greater effect on the gas scavenging ratio than the explicit dependence on temperature, resulting in the gas scavenging ratio increasing as the temperature decreases. Consequently, VOCs exhibit a greater tendency to partition into the precipitation as the temperature decreases. Gas scavenging ratios appear to depend somewhat on the type of precipitation, with fog having higher values than other types of precipitation, presumably because of the greater interfacial area between the air and water phases.
10. Microbial degradation is the use of a VOC by microorganisms as a source of food and energy. Degradation is a series of processes that are highly system-specific and site-specific and requires that the microbial community develop enzymes suitable for degrading the VOCs of interest. VOCs in some situations may be degraded by the process of cometabolism, where some other organic compound is the source of food and energy for the microorganisms.
11. The target analytes most likely to be subject to microbial degradation in streams are the aromatic compounds, 2-propenal, and 2-propenenitrile.
12. Estimates of the importance of microbial degradation of naphthalene relative to volatilization indicate that microbial degradation could be important in deep, low-velocity streams, with lesser importance in intermediate-depth, high-velocity streams. Microbial degradation in shallow, medium-velocity streams is not expected to be important, relative to volatilization.
13. Sorption of VOCs to sediments in streams involves partitioning of the VOCs into the organic content of the sediment, with little physical adsorption to the mineral surfaces of the sediment.
14. Sorption to sediments is inversely proportional to the water solubility and directly proportional to the octanol-water partition coefficient of the VOC. The target analytes most likely to sorb to sediments are hexachlorobutadiene, n-butylbenzene, and 1,2,3-trichlorobenzene.
15. The fraction of VOCs sorbed to a sediment increases as the organic-carbon fraction of the sediment increases and as the sediment concentration increases. For sediment concentrations less than 100 milligrams per liter, estimates of the fractions sorbed are less than 0.1. The estimates of the fraction sorbed increases rapidly for higher sediment concentrations.
16. Hydrolysis is the reaction of a VOC with water, and nine target analytes have half-lives for hydrolysis of 548 days or less. The currently available experimental half-lives from the literature for several analytes vary by orders of magnitude, resulting in uncertainties in estimates of the importance of hydrolysis on concentrations of these VOCs in streams.
17. The estimates of the fractions of bromomethane, 1,2-dibromoethane, and 1,3-dichloropropene removed by hydrolysis exceed estimates of the fraction removed by volatilization for a deep, low-velocity stream. The effect of hydrolysis also is predicted to be important for chloroethane for this type of stream. Hydrolysis of the target analytes is not significant relative to volatilization for a shallow, medium-velocity

stream. Hydrolysis is not significant relative to volatilization for an intermediate-depth, high-velocity stream, with the possible exceptions of 1,2-dibromoethane and 1,3-dichloropropene, for which some effect is predicted.

18. Aquatic photolysis is the reaction of a VOC with the sunlight incident upon the surface of a stream. Little information was found in the literature on aquatic photolysis of the target analytes. The analytes considered most likely to undergo photolysis are those with ring structures.
19. Estimates of the importance of aquatic photolysis of naphthalene relative to volatilization indicate that photolysis is not significant. These estimates are based on the assumption that light penetration and the resultant photolysis are limited by the depth of the water column. However, in a stream, the water at the surface is continuously replaced with water from below as a result of vertical mixing, and the depth may not be rate-limiting. If surface photolysis with continual replacement is assumed, estimates of the losses as a result of photolysis exceed volatilization losses at a depth of about 3 m for naphthalene and at a depth of about 5.7 m for benzene. These estimates of the extent of photolysis should be considered as upper bounds because of the assumption of no effect of depth on the photolysis process. Experimental determination of the effect of depth on photolysis in a stream with continual replacement of the surface water with water from the lower parts of the stream is needed.
20. Oxidation is the reaction of a VOC with an oxidant. Oxidants most likely to be present in streams are the peroxy radical, photoexcited diradicals, hydroxy radical, singlet oxygen, and ozone. These oxidants are hypothesized to result from the photolysis of natural humic materials in the water.
21. Fourteen target analytes have experimental or calculated oxidation half-lives of less than 1 year. These analytes are benzene, three alkyl benzenes, six halogenated aromatics, three halogenated alkenes, and 2-propenenitrile. Oxidation relative to volatilization is predicted to be significant for deep flows for methylbenzene and is predicted to be minimally important for benzene. The predictions for the other 12 analytes are intermediate between these extremes. These estimates of the extent of oxidation should be considered as upper bounds because of the assumption of no effect of depth on the oxidation process. Experimental determination of the effect of depth on oxidation in a stream with continual replacement of the surface water with water from the lower parts of the stream is needed.
22. Bioconcentration is the uptake of a VOC from the water of a stream by an aquatic organism. This process is analogous to the partitioning of a VOC between water and an organic solvent such as octanol. Consequently, the bioconcentration factor is strongly dependent on the octanol-water partition coefficient. Logarithm base 10 octanol-water partition coefficients for the target analytes range from –0.92 for 2-propenenitrile to 4.78 for hexachlorobutadiene.
23. Estimates of the effect of bioconcentration on the concentration of hexachlorobutadiene in streams indicate that the fraction concentrated is generally less than 0.06 for a fish density typically used in the literature.
24. Analysis of aquatic toxicity values indicate that the concentrations of VOCs necessary to cause acute adverse effects on aquatic organisms are not likely to be routinely present in streams. Spills could result in short-term exposures to high concentrations. Target analytes most likely to cause adverse effects, should they occur, are bromomethane, hexachlorobutadiene, 1,2,3-trichlorobenzene, and 2-propenal. The effect of long-term chronic exposure to low concentrations of VOCs is largely unknown. However, persistence of VOCs in streams for long time periods is unlikely because of the volatile nature of these compounds. On the other hand, fairly long-term exposures could occur during winter under ice cover.
25. VOCs in streams are advected downstream with a mean velocity averaged over the cross section of the channel.
26. Vertical mixing of VOCs in streams is rapid, with mixing over the flow depth usually complete within a distance downstream of about 100 flow depths.
27. Lateral mixing of VOCs in streams requires long distances downstream, with the distance required proportional to the square of the channel width. A VOC source on the

streambank requires four times the downstream distance for lateral mixing that a centerline source requires.

28. Longitudinal dispersion affects the variation of the concentration of VOCs with distance downstream for an instantaneous source of VOCs but has no effect on a continuous source because steady-state concentrations are established. The predicted effect of longitudinal dispersion relative to volatilization on the concentrations of dichloromethane and diisopropyl ether is substantial for a deep, low-velocity stream. The predicted effect of longitudinal dispersion relative to volatilization is minimal for a shallow, medium-velocity stream. The predicted changes in the concentration as a result of longitudinal dispersion and volatilization for an intermediate-depth, high-velocity stream are approximately equal for dichloromethane and diisopropyl ether.
29. Volatilization is likely to be the dominant process affecting the concentrations of VOCs in streams. However, conclusions presented herein indicate that other physical as well as chemical and biological processes also could contribute to the determination of the behavior and fate of VOCs in streams. Consequently, each situation must be analyzed specifically to determine which processes are important and which processes can be neglected.

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