

HANDBOOK OF CHEMICAL PROPERTY ESTIMATION METHODS

Environmental Behavior of Organic Compounds

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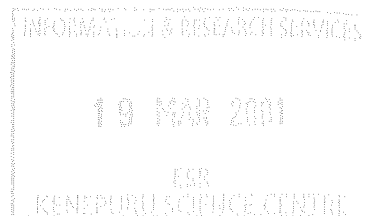
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VOLATILIZATION FROM WATER

Richard G. Thomas

15-1 INTRODUCTION

The vaporization of organic chemicals from water bodies is an important mass-transfer pathway from water to air. Knowledge of volatilization rates is necessary to determine the amount of chemical that enters the atmosphere and the change of pollutant concentrations in water bodies. The transfer process from the water to the atmosphere is dependent on the chemical and physical properties of the pollutant in question, the presence of other pollutants, and the physical properties (e.g., flow velocity, depth, and turbulence) of the water body and atmosphere above it. The factors that control volatilization are the solubility, molecular weight, and vapor pressure of the chemical and the nature of the air-water interface through which it must pass.

The mathematical modeling of volatilization involves the use of interphase exchange coefficients that depend on the properties mentioned above, some of which are difficult to measure or estimate in the actual environment. They can be measured under controlled laboratory conditions, but the results often cannot be extended with confidence to the varied and changeable conditions encountered in the environment. Part of this difficulty is due to the lack of environmental volatilization data against which laboratory-based hypotheses can be tested.

Thus, estimates of volatilization rates from surface waters on the basis of mathematical data and laboratory measurements are necessarily

of unknown precision. No attempt is made here to give a quantitative estimate of the error implicit in the methods to be described; however, comparisons of experimental results with theoretical predictions indicate that these predictive techniques are generally in agreement with actual processes within about a factor of ten at the most and probably within a factor of two or three in most cases.

Volatilization rates from water vary over a large range. Some chemicals volatilize from well-mixed surface waters quite rapidly, with a half-life on the order of hours; others may remain in the water almost indefinitely unless they degrade or are removed by a different transfer mechanism. For example, trichloroethylene has a computed half-life of three to five hours for volatilization from a river; the pesticide dieldrin, on the other hand, volatilizes more slowly than water and its concentration would actually increase, at least in the short term, so that its half-life due to volatilization is on the order of a year or more.

This chapter describes the volatilization process, discusses some of the theoretical methods that have been developed to model the volatilization of chemicals from surface waters, and presents a method for estimating the rate at which this process takes place. Various organic chemicals are listed together with their properties related to volatilization, and basic steps and examples are presented to show how to compute the mass transfer coefficients and half-lives in water for organic chemicals.

15-2 MODELING VOLATILIZATION IN THE ENVIRONMENT

Many factors affect the volatilization process. Although these factors are known, they can change rapidly and over a wide range in a natural environment. This complicates the task of providing average or mean values for use in an analytical model. The processes are often nonlinearly interdependent and do not behave in simple, deterministic ways.

Specifically, the volatilization process depends on the thermodynamic or physical properties of a chemical, particularly its aqueous solubility, vapor pressure, Henry's law constant and diffusivity coefficient, and the presence of modifying materials such as adsorbents, organic films, electrolytes, and emulsions [10,11]. The true "dissolved" and "total" concentrations are highly dependent on the presence of these modifying materials [3]. The values of the rate-controlling factors also depend on the physical and chemical properties of the water body, such as its depth, flow rate, the presence of waves, sediment content, and the

other pollutants present. Atmospheric conditions, particularly wind speed and stability, also affect the rate-controlling factors. Volatilization is, in general, relatively temperature-insensitive, since the principal effect of temperature is on the vapor pressure. The latter has little influence on volatility except for the few classes of chemicals whose volatilization is controlled by processes that occur in the vapor phase. (These are addressed later.)

The transport and transfer of a chemical may involve several sequential stages depending on the type of water body involved. Each of these stages has a characteristic rate, diffusion velocity, or resistance [12], and the slowest stage controls the overall volatilization rate. For a stratified lake, the stages may be: (1) release from the sorbed state on sediments; (2) diffusion through the hypolimnion; (3) diffusion through the thermocline; (4) diffusion through the epilimnion to the near surface (approximately one millimeter below the surface); (5) diffusion through the liquid surface "stagnant film"; (6) transfer across the water/air interface; and (7) diffusion through the atmospheric film to the bulk of the atmosphere. Transfer through the different layers in the water can occur only by bulk movement (as in the case of turbulent eddy motion) or by molecular diffusion [9,14]. If the water body is well mixed, as in a flowing river, most of the resistance to transport lies in the gas- and liquid-phase interfacial layers a few millimeters or centimeters above or below the surface [10,11,13]. The interface between the gas- and liquid-phase interfacial layers is believed to offer little or no resistance. Hence, a concentration gradient develops in the surface layers. For most substances and most water bodies, resistance in one phase tends to dominate [9].

Under given conditions of turbulence, layer thicknesses vary both spatially and temporally [9]. High turbulence in the liquid causes the liquid film or boundary layer to be thin; similarly, high turbulence in the gas causes the gas layer to be thin [18]. Wind also modifies surface hydrodynamics, affecting chemical mass-transfer coefficients.

Vertical transport to the surface of rivers and large lakes is controlled by currents, both direct and wind-induced. In rivers, diffusion from the bottom to the surface is accelerated by eddies caused by the interaction of the current with the bottom [12]. Since turbulence is generated mainly at the river bottom, the deeper rivers have more quiescent surfaces, and the transfer resistance tends to be higher [10]. In lakes, wind speed and fetch (the length of water over which the wind blows) are the controlling factors: turbulence is normally present in the atmosphere, but there is usually little in the water unless it is induced by wind-generated waves on the surface, subsurface springs, or thermally driven convective

action. Regardless of the cause, turbulence can greatly increase the liquid-phase exchange coefficient.

Horizontal and vertical turbulent diffusion affect the rate and extent of mixing [10]. In water, horizontal turbulent diffusion is usually an order of magnitude faster than vertical turbulent diffusion; as a result, pollutants spread faster laterally than they do vertically. In the atmosphere, vertical diffusion is usually more rapid than in the water, and chemicals are transported from the interface quickly. During the stable conditions of temperature inversions (when temperature increases with height), however, vertical atmospheric diffusion decreases, the water surface is calmer, resistance to chemical transfer through the air and water boundary films increases, and volatilization rates decrease.

Sediments are important because they can act as permanent or temporary sinks for chemicals in the water [10,12]. The exchange between the water column and the sediment has a significant effect on the rate of removal from the water proper. The sediment/water partition (sorption) coefficient is affected by the characteristics of the sediment, e.g., type, spatial distribution, particle size and density, and organic matter. Chapter 4 of this handbook describes the adsorption phenomenon and methods for estimating adsorption coefficients.

15-3 APPROACHES TO ESTIMATION OF THE VOLATILIZATION RATE

The two-layer film or resistance concept of the interface — i.e., the theory that resistance to mass transport exists in both the gas- and liquid-phase interfacial layers — was first discussed in 1923 [23]. However, most of the analytical work has been done only in the last several years. Four basic approaches have been used; these are described below.

Method of Mackay and Wolkoff. These authors [14] analyzed the volatilization of chemicals from bodies of water on the basis of thermodynamic equilibrium considerations. This theory expresses the flux from a solution in water to the air above in terms of the ratio of contaminant mass in the vapor phase to the total vapor mass of the water plus chemical, expressed as a function of the chemical vapor pressure. The following assumptions are made:

- (1) The contaminant concentration used is that which is truly in solution; there are no colloidal, suspended, ionic, complexed, or adsorbed forms of the contaminant.

- (2) The concentration of the diffusing substance in the vapor adjacent to the interface is that which is in equilibrium with the concentration in the liquid at the interface.
- (3) Diffusion or mixing in the liquid is sufficiently rapid that concentrations at the liquid side of the interface are equal to concentrations in the bulk of the liquid (which implies thorough mixing).
- (4) The water evaporation rate is negligibly affected by the presence of the contaminant.

Ancillary to these assumptions are two others that affect the utility of the theory: (a) evaporation is the limiting process in the total volatilization process, and (b) there are no concentration gradients in the upper layers due to the evaporation. The latter follows from assumption (3) above, namely, that there is perfect mixing in the water phase and equilibration between the water and air. Because of these assumptions, this method will overestimate the volatilization rate if mixing or diffusion in the water body is slow, thus retarding the overall process.

This method is applicable only to a restricted class of compounds and is thus not recommended for general use. The significant conclusion reached by Mackay and Wolkoff was that volatilization may be significant, i.e., half-lives short, for compounds which have vapor pressures much lower than that of water, provided that the compound is sparingly soluble.

In a subsequent study, Mackay and Leinonen [11] extended the method to include consideration of the resistance due to diffusion in the liquid phase and estimated volatilization half-lives for all classes of compounds. Their work was an extension of methods previously developed by Liss and Slater [9].

Method of Liss and Slater. The volatilization process was analyzed on the basis of a two-layer film by Liss and Slater [9]. This has been shown [16] to be a more realistic approach than that originally developed by Mackay and Wolkoff [14]. The main water body is assumed to be well mixed, with a thin layer on the surface in which there is a concentration gradient. The air above is assumed to be well mixed (i.e., the background concentration is low), and a thin layer in contact with the surface contains another concentration gradient. (Thus, diffusion in the water body is not assumed to be a rate-limiting process.) At the interface between these two layers is a concentration discontinuity, and the ratio of con-

centrations across it (air to water) is assumed to equal the Henry's law constant.

Transfer through these films is by straightforward molecular diffusion. The molecules are assumed to diffuse through the layers at a rate dependent on the phase exchange coefficients found in the equations rather than to vaporize directly from solution along with the water vapor.

Environmental conditions leading to turbulence in either phase influence the thickness, diffusivity, resistance, and geometry of the layers. Since resistance to diffusion is dependent on layer geometry and composition, the molecular phase exchange coefficients used in the determination of the overall mass transfer are affected by environmental conditions. These coefficients are somewhat empirical, in that they cannot yet be readily computed using basic physical principles, but values for the gas-phase and liquid-phase exchange constants have been determined for the transfer of certain gases across the air/sea interface. These can be adjusted to apply to certain other classes of chemicals; however, the best method for doing this is not clear [10,15]. Schwarzenbach *et al.* [17] indicate that the coefficients based on open-ocean data may overestimate the transfer in lakes.

Method of Chiou and Freed. Chiou and Freed [1,2] present another method for estimating the volatilization of chemicals. It appears to be based on gas dynamic and thermodynamic considerations involving the mean free path of molecules and the vapor pressures of the chemical. A Langmuir-type equation is used to describe observed rates of volatilization from both single-component and multicomponent systems. No data have been offered to support the validity of this method, and its efficacy is not known. Little notice has been taken of it in recent studies of volatilization of chemicals from water.

Method of Smith *et al.* This approach is based on reaeration studies by Tsivoglou [21], who demonstrated that inert gases could be used as tracers for oxygen reaeration measurement. Since the transfer rates of oxygen and the inert gases are controlled by diffusion in the near surface film, these rates are similar; a correction is necessary only for the differing diffusivities, which are related primarily to molecular diameter. Smith *et al.* [18,19] applied this approach to other compounds and verified that the magnitude of the diffusivity correction term was as expected for compounds that experience the same liquid-phase resistance as oxygen. Compounds with lower Henry's law constants which also experience a gas-phase resistance volatilize more slowly, so this method of approximation is not applicable to such compounds.

For the class of compounds to which it is applicable, the advantage of this approach is that the volatilization rate can be related to the rate of oxygen reaeration. The latter is known for natural systems such as rivers and lakes. If one can obtain a laboratory-measured ratio of the reaeration rate of a chemical to that of oxygen, it can simply be multiplied by the environmental value of oxygen reaeration to yield an environmental value of the volatilization rate constant for the chemical. These investigators have also developed procedures for deriving the ratio when an experimental value cannot be found.

Smith *et al.* have demonstrated that their method is valid for the class of chemicals which have high volatility, high molecular weight, and low solubility (i.e., high Henry's law constants).

15-4 METHOD ERRORS

The environmental, physical, and chemical processes that control the volatilization rate have been described above. Their number and variety indicate the difficulties involved in devising an adequate model of the process. The fundamental mechanisms are reasonably well understood, however, and can be described by relatively simple mathematical expressions [10]; the results are often practically the same as those from more sophisticated models. The present inadequacies are primarily due to a lack of data for some of the parameters in the equations [10].

At the most basic level, some properties of chemicals may not be accurately known; these are needed to determine the Henry's law constant, which indicates the propensity of a chemical to volatilize. The gas- and liquid-phase exchange coefficients, on which the predictive techniques ultimately depend, are not known with certainty for diverse environmental conditions and a wide range of chemicals. Environmental and hydrodynamic factors that affect the movement of a chemical in water and its transfer into the air are difficult to quantify and relate to the volatilization rate; these factors may include wind speed, stratification, sediment content, and the presence of other pollutants. The range of values for these factors over a period of time, their variable nature, and their nonlinear interdependencies indicate the problems inherent in using time-averaged or mean values and reduce the validity of the calculations.

The overall environmental mass transfer coefficient for a particular chemical leaving a given water body, which is dependent on gas- and liquid-phase transfer coefficients and chemical properties, is difficult to

predict on the basis of laboratory studies. This is especially true if average values are desired, since the phase exchange coefficients are sensitive to variable environmental and hydrodynamic factors [17]. The methods used for estimating the exchange coefficients have been verified for only a few chemicals in a few laboratory experiments using stirrers and fans to simulate environmental conditions [3-5,8,14,16,18,19]. The overall volatilization rates measured in these experiments are often quite similar to those computed by theoretical methods [20]. This agreement may be fortuitous, however, since the basic factors are so dissimilar: the computations use phase exchange coefficients based loosely on environmental data, while the experiments use measured rates of stirring, air speed, etc. Nevertheless, the differences between experiment and computation are well within an order of magnitude, lending credibility to the predictive techniques.

Schwarzenbach *et al.* [17], in a study of dichlorobenzene (DCB) and tetrachloroethylene in Lake Zurich, Switzerland, suggested that the average mass transfer coefficient computed from an overall mass balance is about a factor of ten larger than that derived from mass balance computations based on other measurements of DCB in the lake. However, they note that their observed value of the overall mass transfer coefficient for the lake compares well with those found in a similar study of small Canadian lakes by different investigators.

The laboratory-based volatilization rates (computed) are comparable to those found for the open ocean; this is not surprising, as the phase exchange coefficients used in the calculations are based on open-ocean data. It may be incorrect to apply open-ocean data to lakes and other smaller bodies of water, but this question has not been discussed in the literature.

In view of these observations and the difficulty of performing in-situ volatilization experiments, it is not possible to quantify the error in the calculated values of the volatilization rate constants. The lake example indicates that the error may be as large as a factor of ten, although laboratory data suggest that it could be much less. When one is applying the results of calculations to actual environmental situations, it would probably be advisable to assume that the values of volatilization rate may be high by a factor of ten at most and low by a smaller factor of possibly three.

15-5 METHODS OF ESTIMATION

Recommended General Method. The methods of estimation recommended in this chapter follow the two-film concept for estimating the flux of volatiles across the air-water interface. This was described by Liss and Slater [9] and extended by Mackay and others [3,10-15]. Additional refinements suggested by other investigators are introduced where useful. Figure 15-1 shows the basics of this concept.

The method is based on a finite difference approximation to Fick's law of diffusion, which can be written as

$$N = k \Delta C \quad (15-1)$$

where

- N = flux ($\text{g}/\text{cm}^2 \cdot \text{s}$)
- k = D/z , a first-order exchange constant (cm/s)
- D = coefficient of molecular diffusion of chemical in the film (cm^2/s)
- z = film thickness (cm)
- ΔC = concentration difference across the film (g/cm^3)

In a steady-state process, Eq. 15-1 becomes

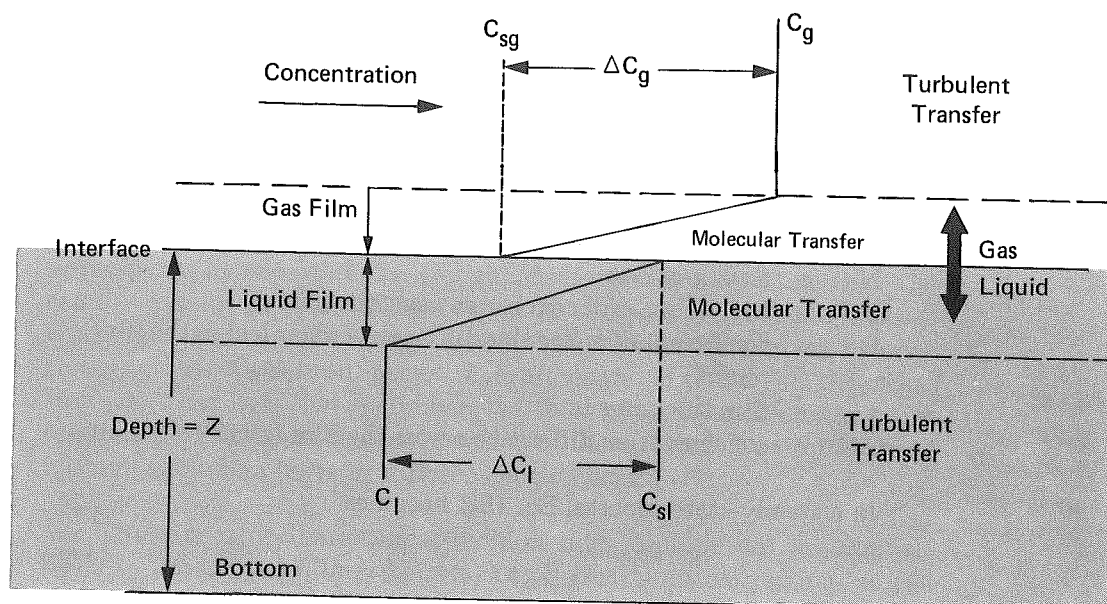
$$N = k_g (C_g - C_{sg}) = k_l (C_{sl} - C_l) \quad (15-2)$$

where

- k_g = gas-phase exchange coefficient (cm/s)
- C_g = concentration in gas phase at the outer edge of the film (g/cm^3)
- C_{sg} = concentration in gas phase at interface (g/cm^3)
- k_l = liquid-phase exchange coefficient (cm/s)
- C_{sl} = concentration in liquid phase at interface (g/cm^3)
- C_l = concentration in liquid phase at the outer edge of the film (g/cm^3)

The nondimensional Henry's law constant (H') relates the concentration of a compound in the gas phase to its concentration in the liquid phase:

$$H' = C_{sg}/C_{sl} \quad (15-3)$$



Source: Liss and Slater [9]. (Reprinted with permission from Macmillan Journals Ltd.)

FIGURE 15-1 Two-Layer Model of Gas-Liquid Interface

Equation 15-2 can then be written as

$$N = \frac{C_g - H'C_l}{1/k_g + H'/k_l} = \frac{C_g/H' - C_l}{1/k_l + 1/H'k_g} \quad (15-4)$$

The overall mass transfer coefficients for the gas phase (K_G) and liquid phase (K_L) can be defined as follows:

$$1/K_G = 1/k_g + H'/k_l \quad (15-5)$$

and

$$1/K_L = 1/k_l + 1/H'k_g \quad (15-6)$$

By substitution in Eq. 15-4,

$$N = K_G (C_g - H'C_l) = K_L (C_g/H' - C_l) \quad (15-7)$$

The Henry's law constant can also be written in the form:

$$H = P_{vp}/S \quad (15-8)$$

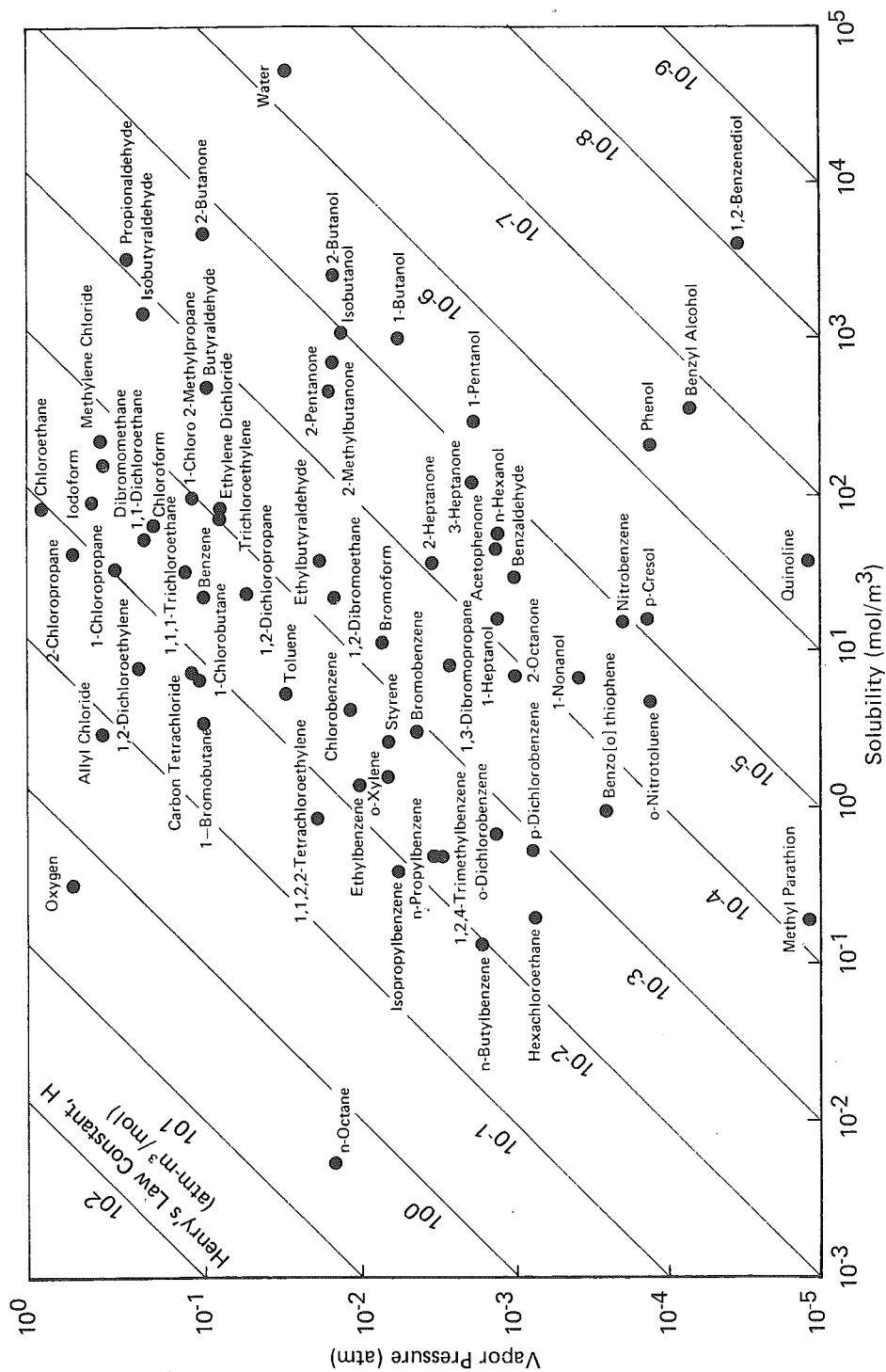
where P_{vp} is in atm, S is in mol/m³, and H is in atm-m³/mol. Figure 15-2, a graphical representation of Eq. 15-8, shows values of H for water, air, and numerous organic compounds.

When H is calculated by Eq. 15-8, the data must be for the same temperature and applicable to the same physical state of the compound. For example, P_{vp} for a liquid should not be divided by S for the solid state. (This error can occur if P_{vp} is estimated by extrapolating data from higher pressures.) Furthermore, only data for the pure compound should be used, as the vapor pressures and solubilities of mixtures — e.g., polychlorinated biphenyl isomers — may be suspect.

Note that Eq. 15-8 is only approximate. If measured values of P_{vp} and S are not available, they can be estimated by methods given in Chapters 14 and 2, respectively. An alternate method of estimating S , via estimated activity coefficients, is provided in Chapters 3 and 11.

Mackay and Leinonen [11] give a slightly different but equivalent expression for $1/K_L$ to be used when H is computed according to Eq. 15-8:

$$1/K_L = 1/k_l + 1/(Hk_g/RT) \quad (15-9)$$



Source: Mackay and Yuen [15]. (Reprinted with permission from the authors.)

FIGURE 15-2 Solubility, Vapor Pressure and Henry's Law Constant for Selected Chemicals

where T is the absolute temperature (K) and R is the gas constant, 8.2×10^{-5} atm-m³/mol-K. (At 20°C, $RT = 2.4 \times 10^{-2}$ atm-m³/mol.) Equations 15-6 and 15-9 give identical values of $1/K_L$, since H/RT equals H' .

The same authors give the following equation for the flux:

$$N = K_L \left(C - \frac{P}{H} \right) \quad (15-10)$$

P/H must be expressed in g/cm³. If we assume the background atmospheric level to be negligible and integrate Eq. 15-10, the concentration at any time t can be expressed as

$$C = C_0 e^{-k_v t} = C_0 e^{-K_L t/Z} \quad (15-11)$$

where

$$\begin{aligned} C_0 &= \text{initial concentration (g/cm}^3\text{)} \\ k_v &= K_L/Z = \text{volatilization rate constant} \\ Z &= \text{mean depth of the water body (cm)} \end{aligned}$$

The half-life can be written as

$$\tau_{1/2} = 0.69 Z/K_L = 0.69/k_v \quad (15-12)$$

The term $1/K_L (=R_L)$ can be thought of as the total resistance to flux [2]. It depends on the exchange constants of the individual phases and the value of the Henry's law constant. Similarly, the individual terms $1/k_l$ and RT/Hk_g (or $1/H'k_g$) can be thought of as liquid-phase resistance r_l and gas-phase resistance r_g respectively. The values of these resistances indicate the relative importance of the gas and liquid phases in the exchange of a compound.

In addition to the resistances offered by the gas and liquid phases, another resistance can be analyzed [15] — namely, the resistance r_w to transfer from the bulk of the water body to the interface. (This resistance can be added to r_l and r_g to give the total resistance, R_L .) The bulk water resistance can be expressed as

$$r_w = \tau_D/Z \quad (15-13)$$

where τ_D is a characteristic time for the eddying motion of a turbulent water body to transport the volatile material to the surface. The value of τ_D indicates whether volatilization is limited by turbulent diffusion to the surface.

Associated with this transport is a turbulent diffusivity coefficient, which is a measure of the efficiency of macroscopic eddy motion in mixing the water. Because of stream geometry, the turbulent diffusivity takes on different values associated with different directions. Generally the value in the longitudinal direction, which is usually reported in the literature, is much larger than the values for the other directions because of larger eddy scale and intensity. Elder [6] relates the perpendicular turbulent diffusivity, D_z , to the longitudinal value, D_L , by

$$D_z \approx 0.039 D_L \quad (15-14)$$

The time τ_D associated with movement a mean distance Z , which in this case is the mean depth of the water body, is

$$\tau_D = Z^2 / 1.3 D_z \quad (15-15)$$

If this time is assumed to be equivalent to the half-life for the turbulent transfer process from depth Z to the surface, it can be compared with the volatilization half-life given in Eq. 15-12.

Typical values of the aquatic turbulent diffusivity are shown in Table 15-1. Values for streams, rivers, and estuaries were given as longitudinal diffusivities and converted to perpendicular values by Eq. 15-14.

TABLE 15-1

Typical Values of Aquatic Turbulent Diffusivities

Water Body	D_z (m^2/sec)	Source
Flumes and Small Streams	10^{-4} to 10^{-2}	} Gloyne [7]
Large Rivers	10^{-2} to 1	
Estuaries	1 – 20	
Lakes		
Hypolimnion	10	} Mackay [10]
Thermocline	1	
Epilimnion	3×10^5	

Surface active agents (surfactants) can reduce or inhibit volatilization. These agents form a layer one or more molecules thick on the surface of the water. The resistance of this layer is given by Smith *et al.* [19] as

$$r_s = 1/H'k_s = RT/Hk_s \quad (15-16)$$

k_s is the mass transfer coefficient at the interface and is defined as

$$k_s = \alpha \sqrt{RT/2\pi M} \quad (15-17)$$

where

- α = the accommodation coefficient, or the fraction of molecules striking the surface that condense on the surface
- R = gas constant = 8.3×10^7 ergs/mol-K
- T = temperature (K)
- M = molecular weight (g/mol)

These authors give no values for α and no method for estimating it.

The values of H for different chemicals give some insight into the controlling rate processes. Figure 15-3 postulates certain ranges of H [10,15] and presents some generalizations regarding the volatility of chemicals that fall in these ranges. (As in Figure 15-2, H is computed by Eq. 15-8 with P_{vp} in atm and S in mol/m³.)

- If H is less than about 3×10^{-7} atm-m³/mol, the substance is less volatile than water and its concentration will increase as the water evaporates. Humidity in the air reduces the volatilization rate of water somewhat, so the lower limit can be set at about 10^{-7} . The substance could be considered essentially nonvolatile.
- In the range $10^{-7} < H < 10^{-5}$ atm-m³/mol, the substance volatilizes slowly at a rate dependent on H . The gas-phase resistance dominates the liquid-phase resistance by a factor of ten at least. The rate is controlled by slow molecular diffusion through air.
- For H below about 2×10^{-5} atm-m³/mol, the pollutant tends to partition into the liquid (i.e., it is quite soluble) and the transfer is gas-phase-controlled.

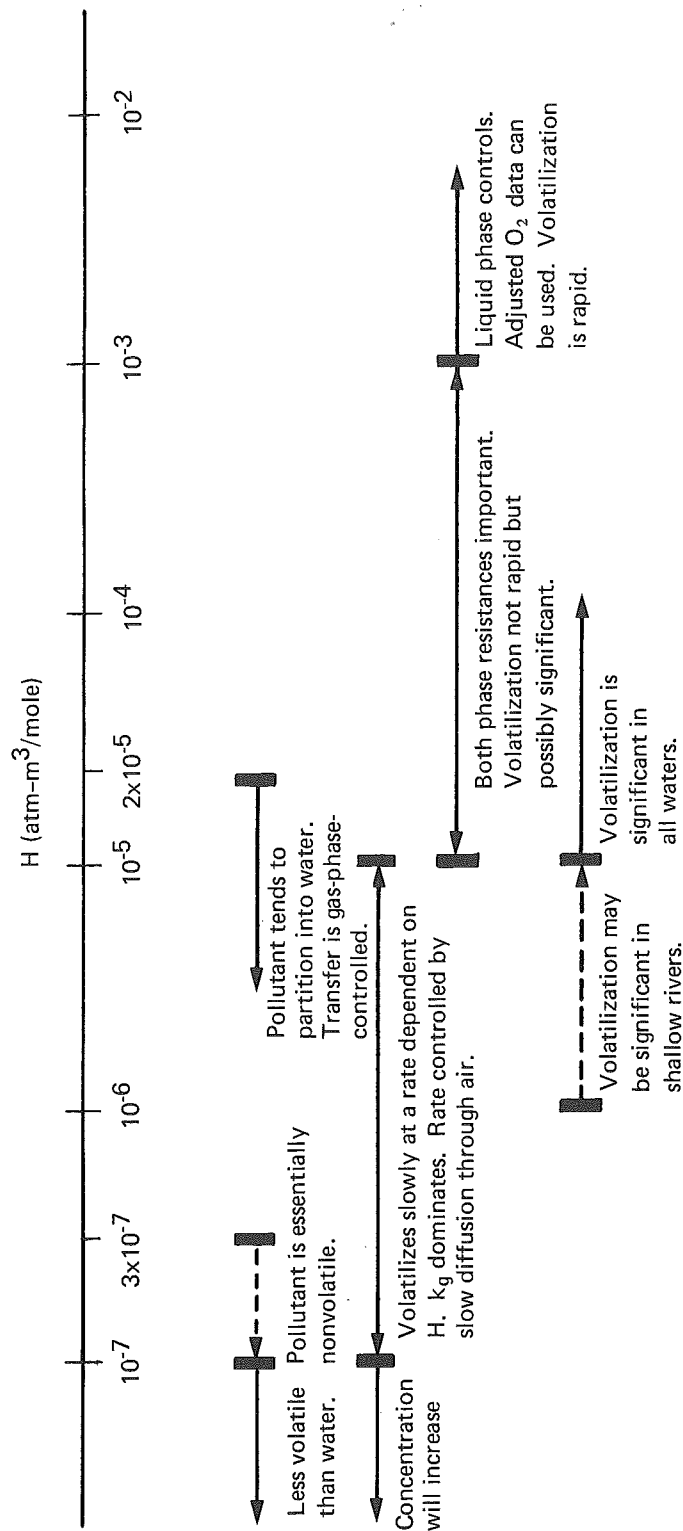


FIGURE 15-3 Volatility Characteristics Associated with Various Ranges of Henry's Law Constant

- In the range of $10^{-5} < H < 10^{-3}$ atm-m³/mol, liquid-phase and gas-phase resistances are both important. Volatilization for compounds in this range is less rapid than for compounds in a higher range of H but is still a significant transfer mechanism. Polycyclic aromatic hydrocarbons and halogenated aromatics lie in this range.
- Where H is high ($> 10^{-3}$ atm-m³/mol), the resistance of the water film dominates by a factor of at least ten. The transfer is liquid-phase-controlled. In this region $k_1 \ll Hk_g/RT$ (or $r_1 \gg r_g$), and Eq. 15-10 becomes

$$N = k_1 \left(C - \frac{P}{H} \right) \quad (15-18)$$

where the flux N is in g/cm².s and P/H is g/cm³. For most hydrocarbons that are only sparingly water-soluble (hydrophobic) and have relatively high values of the Henry's law constant, the resistance lies in the liquid phase.

If the atmospheric concentration (and thus P/H) is negligible, the transfer coefficient is independent of the value of the Henry's law constant, so the latter can be disregarded in the overall mass transfer rate equation (15-10).

Temperature affects volatilization mainly through its effect on H via its effect on vapor pressure, but it also influences k_1 through its effect on diffusivity. Since in this case the volatilization rate is independent of H , the temperature effect is slight.

Method of Smith et al. For high-volatility compounds with $H > 10^{-3}$, Smith *et al.* [18,19] have developed a method for using the oxygen reaeration rate constant to determine the first-order volatilization rate constant. They show that¹

$$k_v^c/k_v^0 = K_L^c/K_L^0 = d^0/d^c \approx D^c/D^0 \quad (15-19)$$

where

k_v^c = overall liquid-phase exchange coefficient or first-order volatilization rate constant — chemical (hr⁻¹)

1. The relation to D^c/D^0 , while not exact, is useful for estimation purposes.

- k_v^o = oxygen overall liquid-phase exchange coefficient or oxygen reaeration rate constant (hr^{-1})
 K_L^c = overall liquid-film mass transfer coefficient — chemical (hr^{-1})
 K_L^o = overall liquid-film mass transfer coefficient — oxygen (hr^{-1})
 D^c = diffusion coefficient in solution — chemical (cm^2/s)
 D^o = diffusion coefficient in solution — oxygen (cm^2/s)
 d^o = molecular diameter — oxygen (cm)
 d^c = molecular diameter — chemical (cm)

If the oxygen reaeration rate constant is known for a given water body or type of water body, it is clear from Eq. 15-19 that the volatilization rate constant can be estimated from either the ratio of diffusivities or the ratio of molecular diameters:

$$k_v^c = k_v^o (d^o/d^c) \approx k_v^o (D^c/D^o) \quad (15-20)$$

Table 15-2 compares measured and predicted values of these ratios.

TABLE 15-2

Measured Reaeration Coefficient Ratios for High-Volatility Compounds

Compound	H ($\frac{\text{atm-m}^3}{\text{mole}}$)	Measured k_v^c/k_v^o	Predicted d^o/d^c	Diffusion Coeff. Ratio D^c/D^o	Molecular Wt. Ratio (M^o/M^c) ^{0.5}
Chloroform	3.8×10^{-3}	$\left\{ \begin{array}{l} .57 \pm .02 \\ .66 \pm .11 \end{array} \right\}$.40	.47	.52
1,1-Dichloroethane	5.8×10^{-3}	$.71 \pm .11$.44	.47	.57
Oxygen	7.2×10^{-2}	1.0	1.0		
Benzo[b] thiophene	2.7×10^{-4}	$.38 \pm .08$.38		
Dibenzothiophene	4.4×10^{-4}	.14	.33		
Benzene	5.5×10^{-3}	$.57 \pm .02$.45	.64
Carbon dioxide		$.89 \pm .03$.84	.85
Carbon tetrachloride	2.3×10^{-2}	$.63 \pm .07$.43	.47
Dicyclopentadiene		$.54 \pm .02$.31	.49
Ethylene	8.6	$.87 \pm .02$.70	1.06
Krypton		$.82 \pm .08$.78	.62
Propane		$.72 \pm .01$.53	.85
Radon		$.70 \pm .08$.66	.38
Tetrachloroethylene	8.3×10^{-3}	$.52 \pm .09$.40	.44
Trichloroethylene	1×10^{-2}	$.57 \pm .15$.44	.49

Source: Smith et al. [18,19]. (Reprinted with permission from the American Institute of Chemical Engineers.)

To extend the utility of this method, Smith *et al.* [19] have measured the ratio k_v^c/k_v^o in the laboratory for several chemicals. The volatilization coefficient $(k_v^c)_{env}$ can be estimated from

$$(k_v^c)_{env} = (k_v^c/k_v^o)_{lab} (k_v^o)_{env} \quad (15-21)$$

In principle, k_v^c is the same as K_L/Z , but since k_v^c has the depth and other water-body characteristics embedded within it due to the use of k_v^o , no adjustment is required to use it directly in Eq. 15-11 or 15-12.

The ratio $(k_v^c/k_v^o)_{lab}$ was found to be independent of turbulence conditions for high-volatility compounds with $H > 6.5 \times 10^{-3}$ atm-m³/mol. It was also found to be independent of k_v^o over the range $0.05 < k_v^o < 15$ hr⁻¹ and independent of temperature from 4°C to 50°C.

Equation 15-21 applies particularly to rivers. For lakes and ponds, the following equation may be more accurate:

$$(k_v^c)_{env} = (k_v^c/k_v^o)_{lab}^{1.6} (k_v^o)_{env} \quad (15-22)$$

Alternatively, $(k_v^c)_{env}$ can be estimated for lakes and ponds by

$$(k_v^c)_{env} \approx (D^c/D^o) (k_v^o)_{lake} \quad (15-23)$$

and for rivers by

$$(k_v^c)_{env} \approx (D^c/D^o) (k_v^o)_{river} \quad (15-24)$$

Diffusion coefficients for compounds in water can be estimated by the following equation:²

$$D^c = \frac{14 \times 10^{-5}}{\mu_w^{1.1} / V_b^{0.6}} \quad (15-25)$$

where μ_w is the viscosity of water (cp) and V_b is the molar volume of the chemical at its normal boiling point (cm³/mol). The value of μ_w is about 1.0 cp at 20°C.

Typical values of k_v^o in the environment are given in Table 15-3 or can be computed from the equations below. If a $(k_v^c/k_v^o)_{lab}$ value is not known, one for a similar high-volatility chemical should be a reasonable

2. Additional estimation methods are given in Chapter 17.

TABLE 15-3

Oxygen Reaeration Coefficients, $(k_v^0)_{env}$, for Water Bodies

Water Body	Literature Values (hr ⁻¹)	Calculated Values ^a (hr ⁻¹)
Pond	0.0046 – 0.0096	0.008
River	0.008, 0.04 – 0.39	0.04
Lake	0.004 – 0.013	0.01

a. From Tsivoglou [21]

Source: Smith *et al.* [19]. (Reprinted with permission from the American Chemical Society.)

substitute. The values of k_v^0 for ponds and lakes are speculative and depend on depth.

For predicting reaeration rates in rivers, Mackay and Yuen [15] present the equations listed below; these correlate k_v^0 with river flow velocity, depth, and slope.

$$\text{Tsivoglou-Wallace: } k_v^0 = 638 V_{curr} s \text{ hr}^{-1} \quad (15-26)$$

$$\text{Parkhurst-Pomeroy: } k_v^0 = 1.08 (1 + 0.17 F^2) (V_{curr} s)^{0.0375} \text{ hr}^{-1} \quad (15-27)$$

$$\text{Churchill } et al.: k_v^0 = 0.00102 V_{curr}^{2.695} Z^{-3.085} s^{-0.823} \text{ hr}^{-1} \quad (15-28)$$

If no slope data are available:

$$\text{Isaacs-Gundy: } k_v^0 = 0.223 V_{curr} Z^{-1.5} \text{ hr}^{-1} \quad (15-29)$$

$$\text{Langbein-Durum: } k_v^0 = 0.241 V_{curr} Z^{-1.33} \text{ hr}^{-1} \quad (15-30)$$

where

- V_{curr} = river flow velocity (m/s)
- s = river bed slope = m drop/m run (nondimensional)
- Z = river depth (m)
- F = Froude number = V_{curr} / \sqrt{gZ} (dimensionless)
- g = acceleration of gravity = 9.8 m/s²

Since none of the foregoing is clearly superior to the others, the best approach is probably to use all that are applicable and then average the

results.³ The values of k_v^o , D^o and D^o are then used in Eq. 15-19 to determine k_v^c .

For the range $10^{-5} < H < 10^{-3}$ atm-m³/mol, Southworth [20] developed a method for estimating the volatilization rates of polycyclic aromatic hydrocarbons (PAHs). He derived equations for estimating the phase exchange coefficients k_g and k_l from laboratory data, which are used in computing the overall liquid-phase mass transfer coefficient,

$$K_L = \frac{H'k_g k_l}{H'k_g + k_l} \text{ cm/hr} \quad (15-31)$$

For the gas-phase exchange coefficient, Southworth's equation is

$$k_g = 1137.5 (V_{\text{wind}} + V_{\text{curr}}) \sqrt{18/M} \text{ cm/hr} \quad (15-32)$$

where V_{wind} and V_{curr} are in m/s. The equation used for the liquid-phase exchange coefficient depends on the wind speed. For $V_{\text{wind}} < 1.9$ m/s,

$$k_l = 23.51 \left(\frac{V_{\text{curr}}^{0.969}}{Z^{0.673}} \right) \sqrt{32/M} \text{ cm/hr} \quad (15-33)$$

where Z is in meters. For $1.9 < V_{\text{wind}} < 5$ m/s,

$$k_l = 23.51 \left(\frac{V_{\text{curr}}^{0.969}}{Z^{0.673}} \right) \sqrt{32/M} e^{0.526(V_{\text{wind}}^{-1.9})} \text{ cm/hr} \quad (15-34)$$

Estimated values of k_l and k_g from these equations are plotted in Figures 15-4 and 15-5, respectively, for a range of molecular weights and environmental parameters. They are also listed in Table 15-4 for a variety of organic compounds.

If values for the phase exchange coefficients are not available, they can be roughly estimated. For k_l , Cohen *et al.* [3] have defined three regions:

- (1) $V_{\text{wind}} < 3$ m/s
 - Water surface is relatively calm.
 - Flow is aerodynamically smooth.

3. The reaeration rate for a river 2 m deep and flowing at 1 m/s is about 0.042/hr.

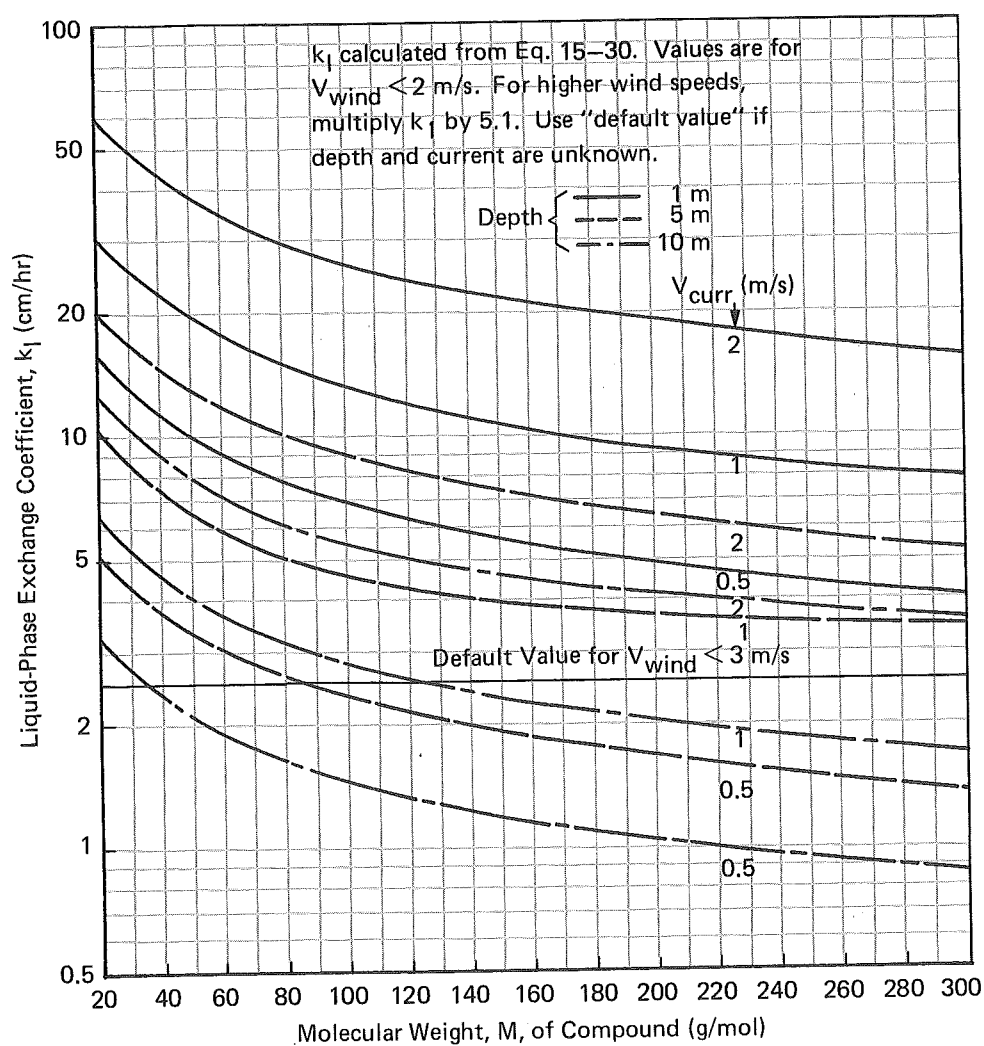


FIGURE 15-4 Effect of Molecular Weight and Environmental Characteristics on Liquid-Phase Exchange Coefficient

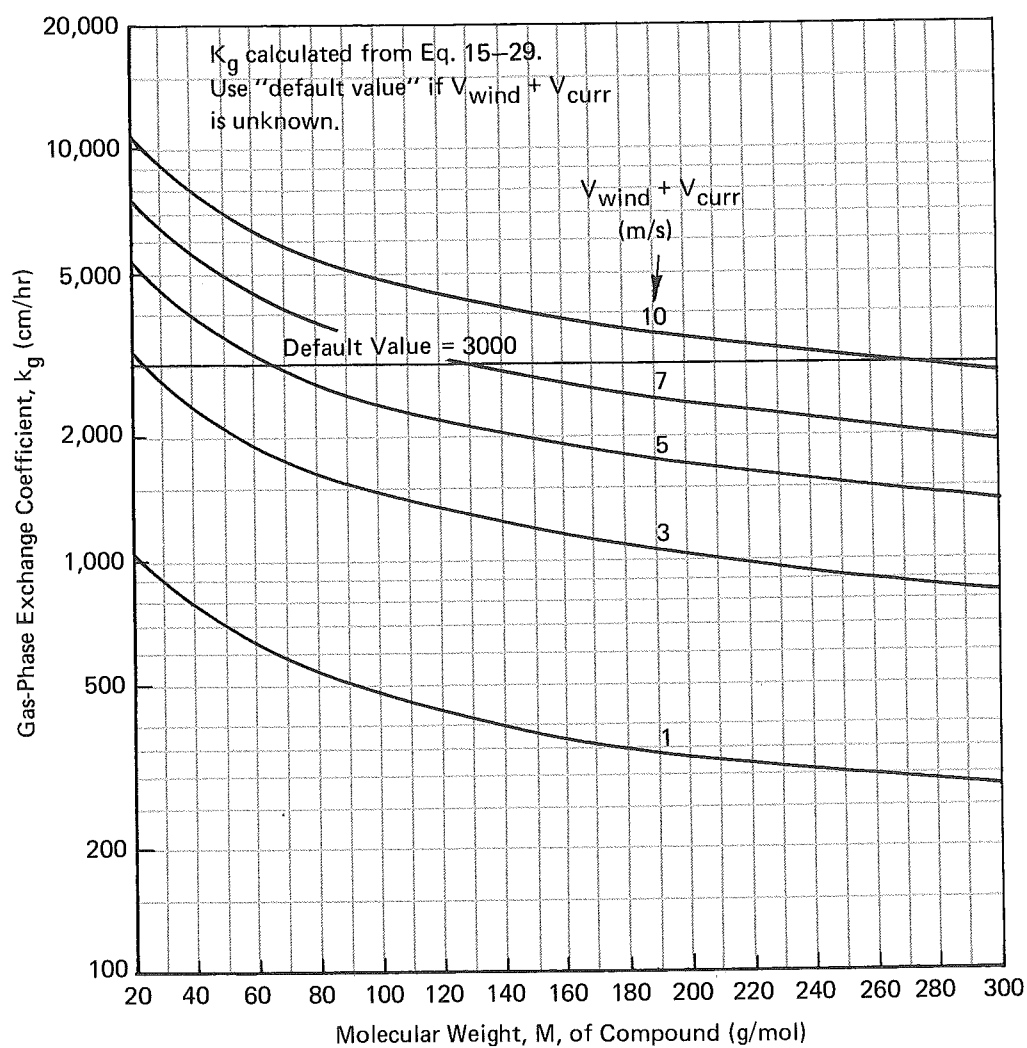


FIGURE 15-5 Effect of Molecular Weight, Wind Speed and Current on Gas-Phase Exchange Coefficient

TABLE 15-4

Volatilization Parameters for Selected Chemicals

Chemical	M (g/mol)	Solubility ^a mg/L	Solubility ^a mol/m ³	Vapor Pressure at 20°C mm Hg atm	Henry's Law Const. $\frac{H}{H'}$ (atm-m ³ /mol) (Non-dim.)	Phase Exchange Coeff. $\frac{b}{b'}$ (cm/hr) Liquid k_l Gas k_g	Mass Transfer Coeff. K_L (cm/hr)	Half-life, ^c $\tau_{1/2}$ (hr)
Low Volatility ($H < 3 \times 10^{-7}$)								
3-Bromo-1-propanol	139	1.7×10^{-5}	1223	0.1 1.3×10^{-4}	1.1×10^{-7} 4.6×10^{-6}	16 1600	7.4×10^{-3}	9400
Dieldrin	381	0.25	6.6×10^{-4}	1×10^{-7} 1.3×10^{-10}	2×10^{-7} 8.9×10^{-6}	12 990	8.8×10^{-3}	7840
Middle Range ($3 \times 10^{-7} < H < 10^{-3}$)								
Lindane	290.9	7.3	2.5×10^{-2}	9.4×10^{-6} 1.2×10^{-8}	4.8×10^{-7} 2.2×10^{-5}	14 1130	0.025	2760
m-Bromonitrobenzene	170	10^4	58.8	0.07 9.2×10^{-5}	1.6×10^{-6} 7.4×10^{-5}	16 1500	0.11	626
Pentachlorophenol	266	14	5.3×10^{-2}	1.4×10^{-4} 1.8×10^{-7}	3.4×10^{-6} 1.5×10^{-4}	12 1150	0.17	406
4-t-Butylphenol	150	10^3	6.7	0.046 6.1×10^{-5}	9.1×10^{-6} 3.8×10^{-4}	17 1600	0.59	117
Triethylamine	101	7.3×10^4	723	7.0 9.2×10^{-3}	1.3×10^{-5} 5.4×10^{-4}	22 1900	0.98	7
Aldrin	365	0.2	5.5×10^{-4}	6×10^{-6} 7.9×10^{-9}	1.4×10^{-5} 6.1×10^{-4}	12 1810	1.0	68
Nitrobenzene	123	2×10^3	16.3	0.27 3.5×10^{-4}	2.2×10^{-5} 9.3×10^{-4}	20 1700	1.5	45
Epichlorohydrin	92.5	6.6×10^4	711	17.3 2.3×10^{-2}	3.2×10^{-5} 1.3×10^{-3}	24 2000	2.3	29
DDT	354.5	1.2×10^{-3}	3.4×10^{-6}	1×10^{-7} 1.3×10^{-10}	3.8×10^{-5} 1.7×10^{-3}	13 1025	1.5	45
Phenanthrene	178	1.29	7×10^{-3}	2.1×10^{-4} 2.8×10^{-7}	3.9×10^{-5} 1.7×10^{-3}	18 1450	2.2	31
Acenaphthene	154	3.9	2.5×10^{-2}	2.8×10^{-3} 3.7×10^{-6}	1.5×10^{-4} 6.2×10^{-3}	19 1560	6.4	11
Acetylene tetrabromide	344	650	1.9	0.3 3.9×10^{-4}	2.1×10^{-4} 8.9×10^{-3}	13 1000	5.3	13.1
Aroclor 1242	254	0.24	9.5×10^{-4}	4.1×10^{-4} 5.3×10^{-7}	5.6×10^{-4} 2.4×10^{-2}	15 1210	9.9	7
Ethylene dibromide	188	4.3×10^3	22.9	11.6 1.5×10^{-2}	6.6×10^{-4} 2.8×10^{-2}	16 1400	11.4	6.1

TABLE 15-4 (Continued)

Chemical	M (g/mol)	Solubility ^a mg/L mol/m ³	Vapor Pressure at 20°C mm Hg atm	Henry's Law Const. $\frac{H}{\text{atm}\cdot\text{m}^3}$ (Non-dim.)	Phase Exchange Coeff. $\frac{b}{\text{cm/hr}}$ Liquid k_l Gas k_g	Mass Transfer Coeff. K_L (cm/hr)	Half-life, ^c $\tau_{1/2}$ (hr)
High Volatility ($H > 10^{-3}$)							
Ethylene dichloride	99	8.0x10 ³	67 0.09	1.1x10 ⁻³ 4x10 ⁻²	22 1900	17.1	4
Naphthalene	128	33 0.26	0.23 3x10 ⁻⁴	1.15x10 ⁻³ 4.9x10 ⁻²	21 1765	16.9	4.1
Biphenyl	154	7.5 0.05	0.06 7.5x10 ⁻⁵	1.5x10 ⁻³ 6.8x10 ⁻²	19 1554	16.2	4.3
Aroclor 1254	326	1.2x10 ⁻² 3.7x10 ⁻⁵	7.7x10 ⁻⁵ 1x10 ⁻⁷	2.7x10 ⁻³ 1.2x10 ⁻¹	13 1070	11.9	5.8
Methylene chloride	85	1.3x10 ⁴ 155	349 0.46	3x10 ⁻³ 1.3x10 ⁻¹	25 2000	22.8	3
Aroclor 1248	292	0.054 1.85x10 ⁻⁴	4.9x10 ⁻⁴ 6.5x10 ⁻⁷	3.5x10 ⁻³ 1.6x10 ⁻¹	14 1130	12.9	5.3
Chlorobenzene	113	472 4.2	11.8 1.6x10 ⁻²	3.7x10 ⁻³ 1.65x10 ⁻¹	22 1820	15.1	4.6
Chloroform	119	8x10 ³ 67	246 0.32	4.8x10 ⁻³ 2.0x10 ⁻¹	20 1700	18.9	3.7
o-Xylene	106	175 1.7	6.6 8.7x10 ⁻³	5.1x10 ⁻³ 2.2x10 ⁻¹	23 1870	22	3.2
Benzene	78	1780 22.8	95.2 1.25x10 ⁻¹	5.5x10 ⁻³ 2.4x10 ⁻¹	27 2180	26	2.7
Toluene	92	515 5.6	28.4 3.7x10 ⁻²	6.6x10 ⁻³ 2.8x10 ⁻¹	25 2010	24	2.9
Aroclor 1260	361	2.7x10 ⁻³ 7.5x10 ⁻⁶	4.1x10 ⁻⁵ 5.3x10 ⁻⁸	7.1x10 ⁻³ 3.0x10 ⁻¹	13 1020	12.5	5.5
Perchloroethylene	166	400 2.4	14.3 2x10 ⁻²	8.3x10 ⁻³ 3.4x10 ⁻¹	17 1450	16.4	4.2
Ethyl benzene	106	152 1.43	9.5 1.25x10 ⁻²	8.7x10 ⁻³ 3.7x10 ⁻¹	23 1870	22.3	3.1
Trichloroethylene	131	1x10 ³ 7.6	60 8x10 ⁻²	1x10 ⁻² 4.2x10 ⁻¹	21 1700	20.4	3.4
Mercury	201	3x10 ⁻² 1.5x10 ⁻⁴	1.3x10 ⁻³ 1.7x10 ⁻⁶	1.1x10 ⁻² 4.8x10 ⁻¹	17 1360	16.6	4.2
Methyl bromide	95	1.3x10 ⁴ 137	1.4x10 ³	1.3x10 ⁻² 5.6x10 ⁻¹	23 2000	22.5	3.1
Cumene (isopropyl benzene)	120	50 0.416	4.6 6.1x10 ⁻³	1.5x10 ⁻² 6.2x10 ⁻¹	22 1760	21.6	3.2
1,1,1-Trichloroethane	133	950 7.1	100 0.13	1.8x10 ⁻² 7.7x10 ⁻¹	19 1650	18.7	3.7
Carbon tetrachloride	154	800 5.2	91 0.12	2.3x10 ⁻² 9.7x10 ⁻¹	19 1500	18.8	3.7
Methyl chloride	50.5	7.4x10 ³ 146	3.6x10 ³ 4.74	2.4x10 ⁻² 3.6x10 ⁻¹	30 2600	29	2.4
Ethyl bromide	109	900 8.3	460 6.1x10 ⁻¹	7.3x10 ⁻² 3.1	22 1800	22	3.1
Vinyl chloride	62.5	90 1.44	2580 3.4	2.4 99	28 2400	28	2.5
2,2,4-Trimethyl pentane	114	2.44 2.1x10 ⁻²	49.3 6.5x10 ⁻²	3.1 129	22 1810	22	3.1
n-Octane	114	0.66 5.8x10 ⁻³	14.1 1.85x10 ⁻²	3.2 136	22 1810	22	3.1
Fluorotrichloromethane	137			5.0	11.3 1090	11.3	6.1
Ethylene	28	131 4.7	> 40	> 8.6 ~ 360	40 3700	40	1.7

c. From Eq. 15-12, with $Z = 1$ mb. From Eqs. 15-32 to -34 and Figs. 15-4 and -5,
using $V_{\text{wind}} = 3\text{m/s}$ and $V_{\text{curr}} = 1\text{m/s}$

a. Source: Refs. 11, 13, 14, 22

- k_i values are typically 1-3 cm/hr and appear to be strongly influenced by mixing originating from within the water body.
 - Wind velocity in this range has no apparent effect on the value of k_i .
 - A suggested value for k_i is 2-3 cm/hr.
 - The mass transfer rate is dominated by the underlying hydrodynamics, which are very site-specific and dependent on recent environmental conditions.
- (2) $3 \text{ m/s} < V_{\text{wind}} < 10 \text{ m/s}$
- k_i increases from 3.5 to 30 cm/hr.
 - In the range of 3-6 m/s, the increase in k_i is attributable to the onset of ripples and an increase in surface roughness.
 - Above 6 m/s, wave growth is appreciable. Flow becomes completely rough, which increases the rate of mass transfer appreciably.
- (3) $10 \text{ m/s} < V_{\text{wind}}$
- Waves may begin to break.
 - k_i increases due to greater surface area, spray, bubble entrainment, and disintegration of wave crests.
 - k_i values can reach 70 cm/hr.

Liss and Slater [9] give values of k_i for several gases and suggest that 20 cm/hr is appropriate for the sea surface. This value should be applicable for gases of $15 < M < 65$; outside this range, k_i can be adjusted by multiplying by the square root of the ratio of the molecular weight of CO_2 to that of the other gas, i.e.,

$$k_i = 20 \sqrt{44/M} \text{ cm/hr} \quad (15-35)$$

The correction is not well established in extending data for low-molecular-weight gases to high-molecular-weight compounds such as PCBs.

The ratio k_g/k_i ranges from about 50 to 200 [10]. Liss and Slater [9] suggest a value of about 96 for oceans. For the transfer of water vapor from the ocean surface, they give a value of about 3000 cm/hr for k_g . The value of k_g for some other compound can be estimated by multiplying 3000 by the square root of the ratio of the molecular weights:

$$k_g = 3000 \sqrt{18/M} \text{ cm/hr} \quad (15-36)$$

There is evidence that the phase exchange coefficients for transfer across the air-sea interface may be too high for lakes and other smaller bodies of water [17].

Basic Steps of Calculation. The following data are the minimum required for calculating rates of vaporization:

- Chemical properties — vapor pressure, aqueous solubility, molecular weight.⁴
 - Environmental characteristics — wind speed, current speed, depth of water body.
- (1) Find Henry's law constant (H) from Eq. 15-8 and/or Figure 15-2.
 - (2) If $H < 3 \times 10^{-7}$, volatilization can be considered unimportant as an inter-media transfer mechanism, and no further calculations are necessary.
 - (3) If $H > 3 \times 10^{-7}$, the chemical can be considered volatile. Determine the nondimensional Henry's law constant, $H' = H/RT$ ($RT = 0.024$ at 20°C).
 - (4) Compute the liquid-phase exchange coefficient (k_l). For a compound of low molecular weight (<65), use Eq. 15-35. If $M > 65$, use Eq. 15-33 for $V_{\text{wind}} < 1.9$ m/s or Eq. 15-34 for $1.9 < V_{\text{wind}} < 5$ m/s. Alternatively, obtain the approximate value of k_l from Figure 15-4.
 - (5) Compute the gas-phase exchange coefficient (k_g). For a compound of low molecular weight (<65), use Eq. 15-36; if $M > 65$, use Eq. 15-32. Alternatively, read the approximate value of k_g from Figure 15-5.
 - (6) If the necessary data are available, compute the surfactant-resistance mass transfer coefficient (k_s), using Eq. 15-17.
 - (7) Compute overall liquid-phase mass transfer coefficient, K_L . If just the gas-phase and liquid-phase resistances are to be considered, use Eq. 15-31 or (if the dimensional Henry's law constant is used) the following equation, which is a rearrangement of Eq. 15-9:

$$K_L = \frac{(H/RT)k_g k_l}{(H/RT)k_g + k_l} \text{ cm/hr}$$

4. Estimation methods for aqueous solubility and vapor pressure are given in Chapters 2 and 14, respectively.

If resistances other than those of the gas and liquid phases must be considered, they can be included here (see Eqs. 15-13 and 15-16).

$$R_L = 1/K_L, r_1 = 1/k_1, r_g = 1/H'k_g = RT/Hk_g, r_w = \tau_D/Z = Z/1.3 D_z$$

$$r_s = 1/H'k_s = RT/Hk_s$$

and

$$R_L = r_1 + r_g + r_w + r_s$$

or

$$1/K_L = 1/k_1 + 1/H'k_g + Z/1.3 D_z + 1/H'k_s$$

- (8) Compute the half-life ($\tau_{1/2}$) from the above value of K_L and the depth of the water (Z), using Eq. 15-12.

Example 15-1: A High-Volatility Chemical Estimate the half-life of trichloroethylene at 20°C in a river 1 meter deep flowing at 1 m/s and with a wind velocity of 3 m/s. The vapor pressure of this compound is 0.08 atm, its molecular weight is 131 g/mol, and its solubility is 1.1 g/L (8.4 mol/m³).

- (1) Calculate the Henry's law constant from Eq. 15-8.

$$H = 0.08/8.4 = 0.01 \text{ atm-m}^3/\text{mol}$$

- (2) Since $H > 10^{-3}$ atm-m³/mol, trichloroethylene is highly volatile.

- (3) Calculate the nondimensional Henry's law constant:

$$H' = 0.01/0.024 = 0.42 \text{ (at 20°C)}$$

- (4) Compute the liquid-phase exchange coefficient, k_1 . Since $M > 65$ and $1.9 < V_{\text{wind}} < 5$, Eq. 15-34 is used.

$$k_1 = 23.51(1^{0.969}/1^{0.673}) \sqrt{32/131} e^{0.526(3-1.9)} \\ = 21 \text{ cm/hr}$$

- (5) Compute the gas-phase exchange coefficient, k_g , from Eq. 15-32.

$$k_g = 1137.5(3+1) \sqrt{18/131} = 1700 \text{ cm/hr}$$

- (6) Use Eq. 15-31 to find the overall liquid-phase mass transfer coefficient, K_L . (It is assumed that the gas and liquid phases account for the only important resistance.)

$$K_L = \frac{0.42 \times 1700 \times 21}{(0.42)(1700) + 21} = 20.4 \text{ cm/hr}$$

- (7) Use Eq. 15-12 to find the half-life.

$$\tau_{1/2} = 0.69(100/20.4) = 3.4 \text{ hr}$$

Alternatively, by the reaeration coefficient method:

- (1) Calculate the oxygen reaeration rate constant by Eqs. 15-29 and -30. (Eqs. 15-26, -27, and -28 are not usable, because the slope of the river bed is unknown in this example.)

$$(k_v^0)_{\text{env}} = 0.223(1)(1)^{-1.5} = 0.223 \text{ hr}^{-1}$$

and

$$(k_v^0)_{\text{env}} = 0.241(1)(1)^{-1.33} = 0.241 \text{ hr}^{-1}$$

The average of these values is about 0.23 hr^{-1} . This is within the range listed in Table 15-3 ($0.008 - 0.39 \text{ hr}^{-1}$).

- (2) The laboratory-measured value of k_v^c/k_v^0 (see Table 15-2) is 0.57 ± 0.15 . Therefore, by Eq. 15-21,

$$(k_v^c)_{\text{env}} = 0.57(0.23) = 0.13 \text{ hr}^{-1}$$

For comparison, the rate constant corresponding to the value of K_L found in the preceding method is $K_L/Z = 20/100 = 0.2 \text{ hr}^{-1}$.

- (3) Using Eq. 15-12,

$$\begin{aligned}\tau_{1/2} &= 0.69(Z/K_L) = 0.69(k_v^c)^{-1} \\ &= 5.8 \text{ hr}\end{aligned}$$

This agrees fairly well with the 3.4-hour half-life found by the preceding method.

Example 15-2: A Medium-Volatility Chemical Estimate the half-life of acenaphthene under the same environmental conditions as in Example 15-1. Given: $P_{vp} = 3.72 \times 10^{-6} \text{ atm}$, $M = 154 \text{ g/mol}$, $S = 3.9 \text{ mg/L} = 0.025 \text{ mol/m}^3$.

- (1) From Eq. 15-8,

$$H = 3.72 \times 10^{-6} / 0.025 = 1.5 \times 10^{-4} \text{ atm-m}^3/\text{mol}$$

- (2) Since $10^{-5} < H < 10^{-3} \text{ atm-m}^3/\text{mol}$, acenaphthene is of medium volatility.

- (3) Calculate the nondimensional Henry's law constant:

$$H' = H/RT = \frac{1.5 \times 10^{-4}}{0.024} = 6.2 \times 10^{-3} \text{ at } 20^\circ\text{C}$$

- (4) Compute the liquid-phase exchange coefficient, k_l . Since $M > 65$ and $1.9 < V_{\text{wind}} < 5$, Eq. 15-34 is used.

$$k_l = 23.51 (1^{0.969} / 1^{0.673}) \sqrt{32/154} e^{0.526 (3-1.9)} \\ = 19.1 \text{ cm/hr}$$

- (5) Compute the gas-phase exchange coefficient, k_g , from Eq. 15-32.

$$k_g = 1137.5 (3+1) \sqrt{18/154} = 1560 \text{ cm/hr}$$

- (6) Use Eq. 15-31 to find the overall liquid-phase mass transfer coefficient, K_L . (It is assumed that the gas and liquid phases account for the only important resistances.)

$$K_L = \frac{(6.2 \times 10^{-3}) (1560) (19.1)}{(6.2 \times 10^{-3}) (1560) + 19.1} = \frac{185}{28.8} = 6.4 \text{ cm/hr}$$

- (7) Use Eq. 15-12 to find the half-life.

$$\tau_{1/2} = 0.69 (100/6.4) = 11 \text{ hr}$$

Basic Steps of Calculation via Reaeration Coefficient. For a high-volatility chemical, the volatilization rate constant can be estimated by the reaeration coefficient method. The following data are required:

- $(k_v^c/k_v^o)_{\text{lab}}$ or the ratio of diffusion coefficients D^c/D^o or the ratio of molecular diameters d^o/d^c ;
 - $(k_v^o)_{\text{env}}$ or stream flow parameters (velocity, stream bed slope, depth).
- (1) Find the oxygen reaeration coefficient, $(k_v^o)_{\text{env}}$, from Table 15-3, or compute it from Eqs. 15-26 to 15-30. (It is recommended that k_v^o be computed from all the appropriate equations and an average be taken.)
 - (2) If $(k_v^c/k_v^o)_{\text{lab}}$ is known, calculate $(k_v^c)_{\text{env}}$ by Eq. 15-21 and use this value to find the half-life by Eq. 15-12.
 - (3) If molecular diameters or molecular diffusivities are known, calculate $(k_v^c)_{\text{env}}$ with Eq. 15-20 and then use Eq. 15-12 to find $\tau_{1/2}$.
 - (4) If neither (2) nor (3) is applicable, compute diffusivities for the chemical and oxygen via Eq. 15-25 and proceed as in step (3). (See Chapter 17 for other estimation methods.)

Example 15-3: A Low-Volatility Chemical Estimate the half-life of dieldrin in the same environment as in Example 15-1. Given: $P_{vp} = 1.3 \times 10^{-10}$ atm, $M = 381$ g/mol, $S = 0.25$ mg/L $= 6.6 \times 10^{-4}$ mol/m³.

(1) From Eq. 15-8,

$$H = 1.3 \times 10^{-10} / 6.6 \times 10^{-4} = 2.0 \times 10^{-7} \text{ atm-m}^3/\text{mol}$$

(2) Since the Henry's law constant is less than 3×10^{-7} , volatilization is unimportant as a transfer mechanism for dieldrin, and further calculations are unnecessary.

15-6 SYMBOLS USED⁵

C	=	concentration (M/L^3)
C_g	=	well-mixed concentration in gas phase (M/L^3)
C_l	=	well-mixed concentration in liquid phase (M/L^3)
C_o	=	initial concentration (M/L^3)
C_{sg}	=	concentration in gas phase at interface (M/L^3)
C_{sl}	=	concentration in liquid phase at interface (M/L^3)
ΔC	=	concentration difference (M/L^3)
D	=	diffusion coefficient (L^2/T)
D_L	=	longitudinal value of turbulent diffusivity in Eq. 15-14 (L^2/T)
D_z	=	perpendicular value of turbulent diffusivity in Eq. 15-14 (L^2/T)
d	=	molecular diameter (L)
F	=	Froude number
g	=	acceleration of gravity (L/T^2)
H	=	Henry's law constant (atm-m ³ /mol)
H'	=	nondimensional Henry's law constant = C_{sg}/C_{sl} or H/RT
K_G	=	overall gas-phase mass transfer coefficient (L/T)
K_L	=	overall liquid-phase mass transfer coefficient (L/T)
k	=	first-order rate constant (T^{-1})
k_g	=	gas-phase exchange coefficient (L/T)
k_l	=	liquid-phase exchange coefficient (L/T)
k_s	=	mass transfer coefficient at interface for surfactants (L/T)

5. M , L , and T indicate mass, length, and time units respectively.

k_v	= volatilization rate constant (T^{-1})
M	= molecular weight (g/mol)
N	= flux (M/L^2T)
P	= partial pressure (atm or mm Hg)
P_{vp}	= vapor pressure of compound (atm or mm Hg)
R	= gas constant = 8.2×10^{-5} atm-m ³ /mol-K or 8.3×10^7 ergs/mol-K
R_L	= overall liquid-phase resistance (T/L)
r_g	= gas-phase resistance (T/L)
r_l	= liquid-phase resistance (T/L)
r_s	= surfactant resistance (T/L)
r_w	= bulk water body resistance (T/L)
S	= aqueous solubility or saturation concentration (mol/m ³ or M/L^3)
s	= slope of river bed (L/L)
T	= temperature (K or °C)
t	= time (T)
V_b	= molar volume of chemical at normal boiling point (L^3/mol)
V_{curr}	= current speed (L/T)
V_{wind}	= wind speed (L/T)
Z	= average or mean water body depth (L)
z	= layer thickness (L)

Greek

α	= accommodation coefficient, or fraction of molecules striking the surface that condense on the surface
μ_w	= viscosity of water (centipoise) ≈ 1.0 cp at 20°C
$\tau_{1/2}$	= half-life (T)
τ_D	= half-life for turbulent diffusion (T)

Subscripts

env	= environmental value
lab	= laboratory value

Superscripts

c	= chemical
o	= oxygen

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