6 Exchange of Chemicals Between the Atmosphere and Lakes

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1 Introduction

The exchange of chemical substances between the atmosphere and lakes can play an important role in determining abiotic and biotic conditions and levels of contamination. Natural substances such as carbon dioxide, oxygen, hydrogen sulfide, and methane migrate between air and water in pristine conditions, whereas contaminants such as polychlorinated biphenyls (PCBs), polycylic aromatic hydrocarbons (PAHs), and lead may enter lakes primarily from the atmosphere. For other contaminants, such as volatile organic chemicals, evaporation is the dominant route of loss from lakes. There is often appreciable cycling of chemicals between air and water with the magnitude and direction of net movement changing with season. It is now recognized that concentrations of chemicals prevailing in even large lakes, such as Lake Superior, can be influenced or even controlled by the presence of these chemicals in the atmosphere (Eisenreich 1987).

Perhaps the most convincing demonstration of the role of the atmosphere is the case of the remote Siskiwit Lake in Isle Royale in Lake Superior (Swain 1978). The water, sediment, and fish of this pristine lake have been observed to contain appreciable quantities of organochlorine compounds, which can only have reached the lake by atmospheric transport. Remote Arctic lakes have shown similar behavior.

In this chapter we describe the phenomena involved in air–water exchange and suggest approaches to quantifying rates of transfer. Whereas experimental measurements can determine the concentrations in air and water, rates of transfer cannot be measured directly, but can only be inferred by calculations. The magnitude and even the direction of transfer may not be obvious. We first address this issue by quantifying chemical equilibrium between air and water in the form of partition coefficients or the Henry's Law Constant, because it is the departure from equilibrium that drives the processes of evaporation and absorption. The rates of these diffusive processes are then considered, first by briefly reviewing the fundamentals of diffusion, then describing the two-resistance approach for estimating air–water transfer rates. Key determinants of exchange rates are mass-transfer coefficients, which essentially control the velocity of diffusion. Methods of estimating values of these coefficients are described. The "availability" of chemicals in dissolved form in water, and gaseous form in air, is also an important consideration that is addressed, and is essentially an assessment of the extent of sorption. The mechanisms and rates of nondiffusive processes of wet and dry deposition are then described. It is by these processes that chemicals that are sorbed to aerosol particles are conveyed to the water by dustfall or rainfall. This is the dominant mechanism of transfer for involatile substances, such as lead, but it is also important for "semivolatile" substances such as PCBs.

The overall picture of these air–water exchange processes, as illustrated in Fig. 1, can thus be very complex with several complementary and competing processes in effect. To assist the reader to appreciate the nature of these processes a specimen calculation is provided for a PCB congener in which the rates of all processes are deduced from specified concentrations in air and water.

Finally, case studies are presented for specific lakes in which the role of air–water exchange has been quantified.

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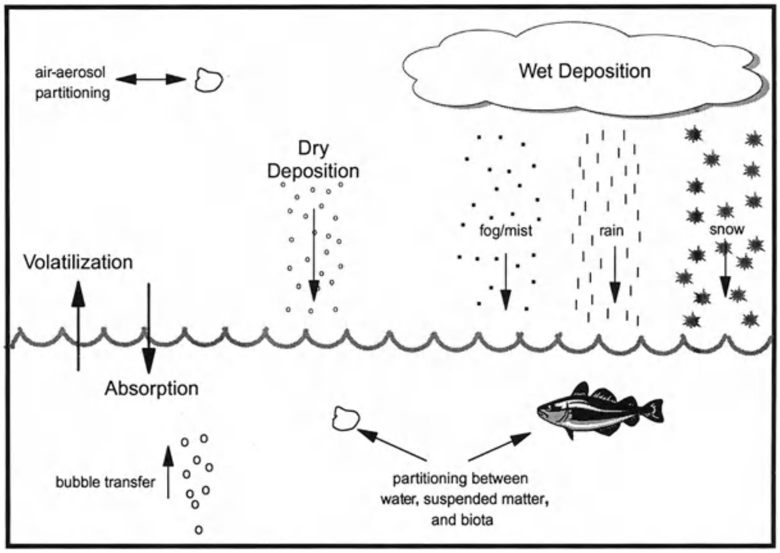

Fig. 1. Air–water exchange processes

2 Air–Water Partitioning Equilibria

Equilibrium between air and water is usually expressed as a dimensionless air–water partition coefficient (K_{AW}), or by a Henry's Law constant H (Pa m^3/mol), which relates equilibrium concentrations of a chemical in the two phases as follows:

$$K_{AW} = C_A/C_W \quad \text{or} \quad P_A = HC_W. \tag{1}$$

Here, C is concentration (mol/m^3), P is partial pressure (Pa), and subscripts A and W refer to air and water phases. Note that C is the concentration of the dissolved chemical and does not include any sorbed material. Other definitions of H are used, for example, to express concentration as a mole fraction.

The relationship between air-phase gaseous concentration and partial pressure can be determined using the ideal gas law ($C_A = n/V = P_A/RT$), where n is the number of moles, V is volume (m^3), R is the gas constant [8.314 Pam^3/(molK)], and T is temperature (K). The equilibrium partition coefficient K_{AW} can thus be shown to be H/RT. If these equations are applied to saturation conditions (designated superscript S) at which a pure chemical phase can coexist with air and water, then

$$K_{AW} = C_A^S/C_W^S = P_A^S/(RTC_W^S) \tag{2}$$

where P_A^S is the chemical's saturation vapor pressure (Pa) in air and C_W^S is its saturation solubility in water (mol/m^3). It follows that H can often be deduced from the vapor pressure and solubility in water as P_A^S/C_W^S. For some chemicals, such as ethanol, no solubility exists, and H or K_{AW} must be determined by direct experimental measurement of C_A and C_W.

It should be noted that when applying physical chemical data, such as H, P_A^S, or C_W^S from handbooks to real lakes, these properties are dependent on temperature, and appropriate corrections must be made. The dependence of H on temperature can be estimated from the expression

$$\ln(H) = A - \Delta h/RT$$
$$\text{or } \ln(H_1/H_2) = -(\Delta h/R)(1/T_1 - 1/T_2), \tag{3}$$

where A is a proportionality constant and Δh is the enthalpy of evaporation (kJ/mol) from solution, and subscripts 1 and 2 refer to two different temperatures. For example, for PCBs Δh is approximately 50 kJ/mol (Hulsher 1992). A general rule is that H doubles for every 10 °C increase in temperature (Mackay and Shiu 1981). For example, in the Great Lakes during the month of August, surface waters reach their highest temperatures; this elevates the Henry's Law constant, facilitating water-to-air exchange (McConnell et al. 1993).

Although lower H values are expected for less volatile chemicals, this is not always the case. For some substances, such as PCBs, although the

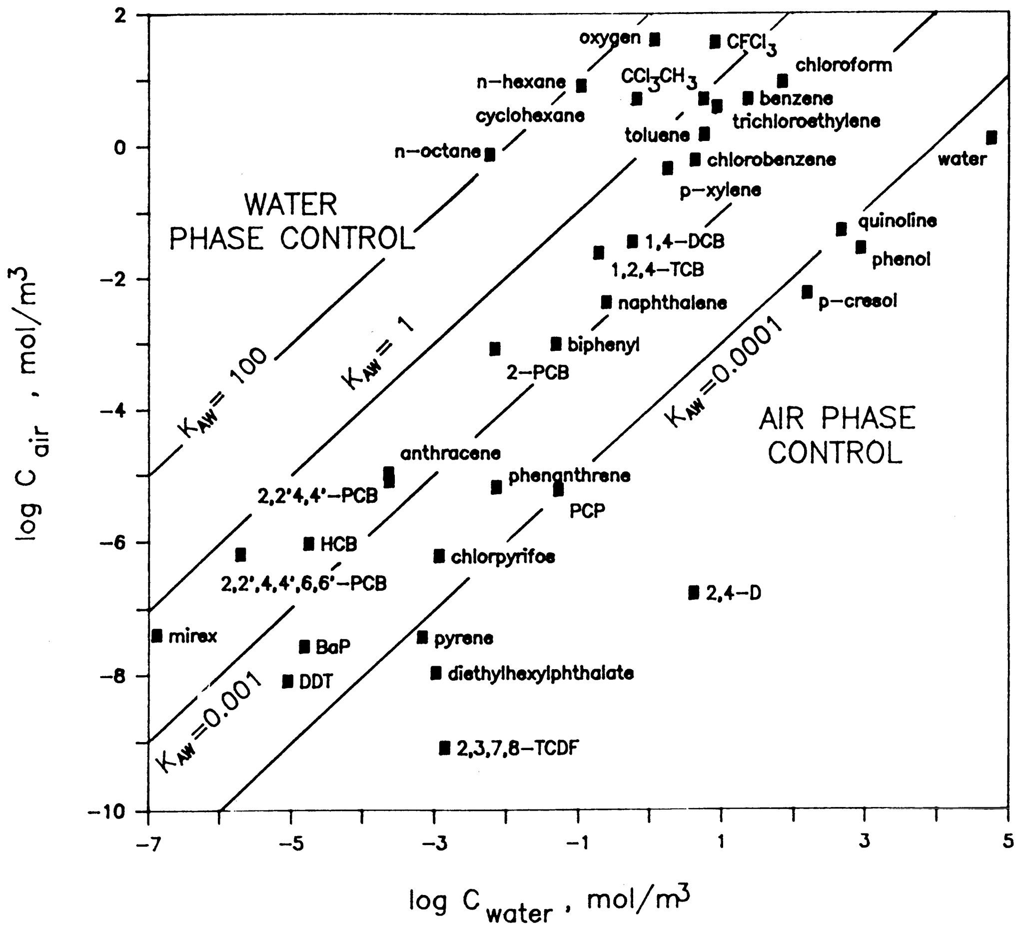

Fig. 2. Plot of log solubility in air (i.e., vapor pressure/RT) vs log solubility in water for selected chemicals. Chemicals of equal H or K_{AW} lie on the same 45° angle. (Reproduced from Mackay 1991, with permission)

vapor pressure is low, the solubility in water is also low (i.e., they are hydrophobic), and the ratio of these quantities can be large, implying significant potential for volatilization (appreciable values of H). Homologous series of chemicals tend to exhibit similar values of K_{AW} and H, even when P^S and C^S vary by orders of magnitude as shown in Fig. 2. For more detailed accounts of air–water partition coefficients, as well as their measurement and correlation, the reader is referred to reports by Shiu and Mackay (1986), Meylan and Howard (1991), Suntio et al. (1988), and Mackay (1991).

3 Diffusion Between Water and Air

Diffusion is a passive process that occurs within and between the air and water phases. Unlike unidirectional atmospheric deposition, diffusion is reversible and contributes to cycling between these phases. As shown in Fig. 3, a molecule moving from water to air must diffuse to the air/water interfacial region through the bulk water, and then through a near-stagnant water film, the thickness of which depends on environmental factors such as turbulence and wind speed. It must then cross the interface and pass through an air-boundary layer into the bulk air region. These boundary layers present the greatest resistance to chemical passage and involve the slowest or rate-limiting steps to transfer.

The rate of transfer, or *flux*, by diffusion in air or water is described by Fick's First Law, which, in its integrated form states that the flux N (mol/h) is inversely proportional to the distance or path length y (m), through which it must diffuse, directly proportional to the area through which it is diffusing, A (m^2), and proportional to the difference in the dissolved concentration (C_1 − C_2)

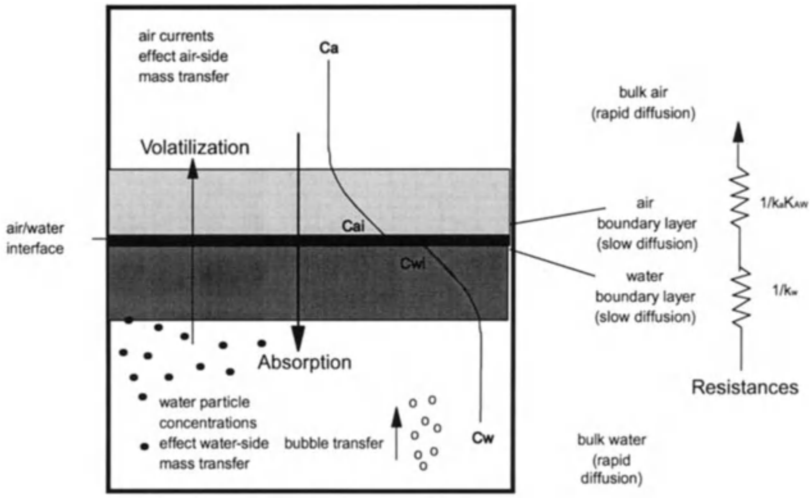

Fig. 3. Mass transfer between water and air illustrating the two-resistance concept

(mol/m^3) applying over the path length. The constant of proportionality is the diffusion coefficient or diffusivity D (m^2/h):

$$N = AD(C_1 - C_2)/y. \tag{4}$$

It should be emphasized here that the diffusing molecules are merely undergoing random motion in all directions, but in the presence of a concentration gradient there will be net transfer in one direction, namely, from high to low concentration. The diffusion coefficients in air and water can be determined from correlations. They depend on the properties of the diffusing species, the phases through which it is diffusing, temperature, and pressure. Detailed derivations and correlations are available in texts on the properties of fluids (e.g., Reid et al. 1987).

Because there may be doubt about the magnitude of D and y, it is convenient to define the group D/y as a single parameter, the mass-transfer coefficient k (m/h), which can be determined experimentally by measuring N, A, and ($C_1 - C_2$) under controlled conditions. The mass-transfer coefficient has units of velocity, and is therefore an actual velocity of transport or a diffusion velocity. Equation (4) now becomes

$$N = k_iA(C_1 - C_2). \tag{5}$$

4 Volatilization and Absorption: Two-Resistance Approach

As shown in Fig. 3, the chemical diffuses across two boundary layers in series, and thus experiences two diffusive resistances. The flux of chemicals during evaporation through the water-boundary layer to the interface can be expressed as

$$N = k_W A(C_W - C_{Wi}), \tag{6}$$

where C_W is the bulk air concentration, C_{Wi} is the water side interfacial concentration, and k_W is the water-side mass-transfer coefficient. For air the flux is similarly

$$N = k_A A(C_{Ai} - C_A). \tag{7}$$

At steady state both fluxes must be equal, because there is no accumulation of chemicals at the interface. We further assume that C_{Ai} and C_{Wi} are in such intimate contact that they are related by the air–water partition coefficient:

$$C_{Ai}/C_{Wi} = K_{AW} \tag{8}$$

Substitution of this expression into Eqs. (6) and (7) and elimination of C_{Ai} and C_{Wi} gives, after some rearrangement,

$$\begin{aligned} N &= k_{OW}\,A(C_W - C_A/K_{AW}) \\ &= k_{OA}A(C_WK_{AW} - C_A), \end{aligned} \tag{9}$$

where

$$\begin{aligned} 1/k_{OW} &= 1/k_W + 1/(k_AK_{AW}) \\ \text{and } 1/k_{OA} &= 1/k_A + K_{AW}/k_W \\ &= K_{AW}/k_{OW}. \end{aligned} \tag{10}$$

Here, k_{OW} is the *overall water-side mass-transfer coefficient*. Similarly, k_{OA} is the *overall air-side mass-transfer coefficient*. The equations in k_{OW} and k_{OA} are ultimately identical algebraically.

The term $1/k_{OW}$ can be viewed as the total resistance to transfer, which is the sum of the water resistance ($1/k_W$) and air resistance ($1/k_A K_{AW}$). The analogy to Ohm's Law is obvious. The air resistance is adjusted by the air–water partition coefficient, which dictates the absolute concentration in each phase at equilibrium. When K_{AW} is large, the concentration of the diffusing species in the air is large relative to the concentration in water. Diffusion in the air is thus facilitated; the air-resistance term is small; thus, the water resistance dominates k_{OW}. Such systems are said to be *water-phase-resistance controlled*. When the K_{AW} term is small, the concentration in the water is greater, the resistance in air becomes the limiting factor, and the system is *air-phase-resistance controlled*. Typically, k_A is approximately 100 times larger than k_W, because of the greater diffusivity in air; thus, when K_{AW} is approximately 0.01, or H is approximately 25 Pa m^3/mol, the resistances are approximately equal. A consequence of this two-resistance-in-series behavior is that one resistance is often insignificant and there is little need to know the corresponding mass-transfer coefficient accurately. Although the mass-transfer coefficient k can be regarded as a ratio of diffusivity D to diffusion path length, the reality is more complex. The dependence of k on D is rarely linear, k usually being proportional to D raised to a power ranging from 0.5 to 0.8. The reason for this is that diffusive conditions are partly nonsteady state is nature as eddies of water are exposed to transfer at the interface for periods of seconds giving rise to penetration transfer in which Fick's Second Law, rather than Fick's First Law, applies. It is somewhat misleading to report values of y deduced as D/k, because these path lengths are hypothetical, rather than real.

5 Factors Affecting Mass-Transfer Coefficients

Air-water mass-transfer coefficients depend on a number of factors including molecular properties, temperature, and boundary-layer conditions, which vary with wind conditions and the turbulence of the water surface as induced by current. Several studies of transfer dependence on wind speed have been conducted in tanks with a more limited number in lakes. Wind speeds over bodies of water up to 3 m/s result in near-laminar conditions, in transitional conditions between 3 and 6 m/s, and in turbulent conditions above 6 m/s. Under near-laminar conditions a near-stagnant layer of air exists over the air–water interface, which is on the order of 1 mm in thickness, through which diffusing molecules must pass. The mass-transfer coefficients k_A and k_W are then on the order of 3 and 0.01 m/h, respectively. As wind speeds increase the boundary layer thins and conditions become turbulent. The result is a nonuniform air–water interface that exhibits waves and greater drag forces caused by the friction of the moving wind over the water. The drag force can be related to the air-side friction velocity, which, in turn, determines the magnitude of both mass-transfer coefficients (Mackay and Yeun 1983). Typical ranges at higher wind speeds are 10–30 m/h for k_A and 0.02–0.2 m/h for k_W.

Several correlations describing mass-transfer dependence on wind velocity (U, m/s) have been proposed. Mackay and Yeun (1983) have quantified this dependence for both air and water:

$$k_W(\mathrm{m/s}) = 1.0 \times 10^{-6} + 3.41 \times 10^{-3} U^* Sc_W^{-0.5} \quad (U > 9\,\mathrm{m/s}) \tag{11a}$$

$$= 1.0 \times 10^{-6} + 1.44 \times 10^{-2} U^{*2.2} Sc_W^{-0.5} \quad (U < 9\,\mathrm{m/s}) \tag{11b}$$

$$k_A(\mathrm{m/s}) = 1.0 \times 10^{-3} + 4.62 \times 10^{-2} U^* Sc_A^{-0.67}, \tag{12}$$

where Sc is the dimensionless Schmidt number, which is the ratio of viscosity/(density × diffusivity) and is commonly in the range of 0.5–2.0 for gases (Sc_A) and 500–2000 for water (Sc_W); U^* is the friction velocity caused by the wind and can be related to the 10-m wind speed U by

$$U^* = 0.01U(6.1 + 0.63U)^{0.5}. \tag{13}$$

Schwarzenbach et al. (1993) suggest the following simpler correlations for air and water mass-transfer coefficients as a function of wind speed U (m/s):

$$k_A\,(\mathrm{cm/s}) = 0.3 + 0.2U \tag{14}$$

$$k_W\,(\mathrm{cm/s}) = 4 \times 10^{-4} + 4 \times 10^{-5} U^2. \tag{15}$$

Under very turbulent conditions, such as breaking waves, waterfalls, or cascades when air bubbles are propelled into the water column, or when water spray is generated, the area of transfer becomes much larger and uncertain, and Eq. (9) can no longer be applied.

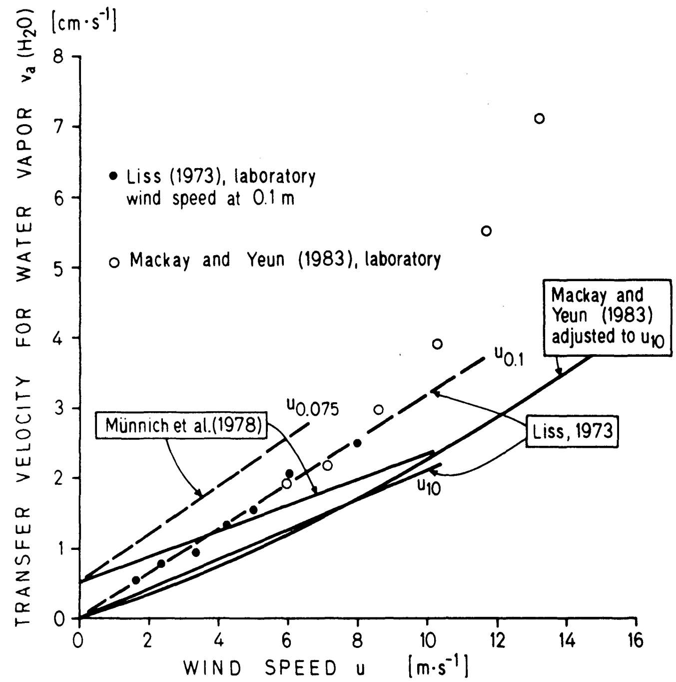

Fig. 4. Correlations showing the dependence of air-phase mass-transfer coefficients k_A on wind speed. (Reproduced from Schwarzenbach et al. 1993, with permission)

Figures 4 and 5 illustrate the dependence of k_A and k_W on wind speed as expressed by several correlations. Temperatures and pressures also affect the magnitude of k_A and k_W. The relationship between these variables can be expressed by extrapolation of the effects of temperature and pressure on the diffusion coefficient:

$$k_{A2} \propto k_{A1}(P_1/P_2)(T_2/T_1)^{3/2}. \qquad (16)$$

6 Partitioning of Chemical to Particulate Matter in Air and Water

Not all the chemical in the air and water phases is available to diffuse, adsorb, or evaporate, because some may be sorbed to particles. Essentially, such sorbed chemical does not contribute to the concentrations employed in the Fick's Law equations. It is thus essential to measure or calculate this extent of sorption.

6.1 Air

The extent of sorption onto airborne particulate matter or aerosols can be calculated from measured concentrations of chemicals in the air in vapor form C_V and in the particulate phases C_P both in ng/(m^3 air). It is common to combine these quantities with the total suspended particulate concentration TSP ng/m^3 as the group $C_V TSP/C_P$. This group is essentially a partition coefficient between gaseous phase and particles. As illustrated later, Mackay et al. (1986) have correlated the partition coefficient directly with the chemical's liquid or subcooled liquid vapor pressure. The extent of sorption, and thus the relative quantities of chemicals associated with particles and in the vapor phase, depends on several properties such as vapor pressure, temperature, relative humidity, and the nature of the particles (Yamasaki et al. 1982; Bildeman and Foreman 1986; Pankow et al. 1993). Metals (with the exception of Hg) in the atmosphere are completely sorbed to particulate matter. As temperature decreases and molecular weight increases the chemical becomes increasingly sorbed.

6.2 Water

Partitioning between chemicals and dissolved particulate matter in lakes is a more complex phenomenon, because of the variety of sorbents present in the water column. For hydrophobic chemicals partitioning depends primarily on the organic carbon content of the particulate matter. Chemicals tend to sorb to these particles to an extent inversely proportional to their solubility in

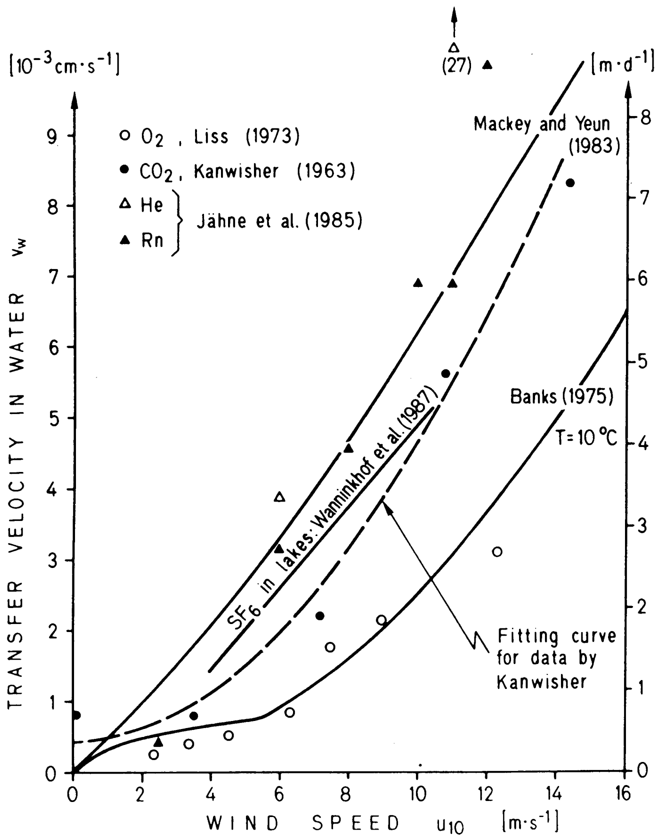

Fig. 5. Correlations showing the dependence of water-phase mass-transfer coefficients k_W on wind speed. (Reproduced from Schwarzenbach et al. 1993, with permission)

water. The most common approach for expressing the hydrophobic nature of a chemical, and thus its sorption to particles from solution, is its octanol–water partition coefficient K_{OW}. This quantity is inversely related to water solubility, and its use in this context implies that a chemical will partition to the organic carbon in particles to a similar extent to which it dissolves in octanol (DiToro 1985). For several chemicals the "equivalent" amount of octanol is obtained by correcting the organic carbon content by a factor of 0.2 to 0.8 (Karickhoff 1981), with 0.4 being a typical value. The value depends on the chemical in question and the nature of the organic matter.

Among the most abundant particulate matter in surface waters are photosynthetic algae, which exist within the first 20 m of the water column where there is sufficient light penetration. There is substantial sorption of hydrophobic contaminants onto this algal matter, which creates a distinct pathway for chemical transport by sedimentation when the algae die and settle. Chemical uptake occurs in a rapid initial adsorption followed by slower diffusion across the cell membrane. Correlations have been sought between the cell-water and the octanol-water partition coefficients, and with the organic carbon content of the algae, but these appear to be nonlinear, and the mechanism is not fully understood.

7 Atmospheric Deposition Processes

7.1 Dry Deposition

Particles or aerosols in the atmosphere result from naturally occuring dust and particulate matter from industrial and other emissions. These particles, and any chemicals sorbed to them, migrate, fall, or diffuse to the lake surface and are captured by water. This provides an important pathway for chemical transport from air to lake.

The amount of chemical delivered to a lake of area A (m^2) can be determined by the product of the dry particle settling rate U_D (m/h), the concentration of chemical on the particles C_P (ng/m^3air), and area A:

$$\text{dry deposition rate of chemical} = D_D\,(\text{ng/h}) = U_D C_P A. \tag{17}$$

Deposition velocities are on the order of 0.3 cm/s or 10 m/h, and particulate concentrations are usually in the range of 10–100 μg/m^3. The velocity of depositing particulate matter varies as a function of particulate sizes and shapes, the seasonal properties of the air (density, temperature, etc.), and the stability conditions of the atmosphere; thus, U_D represents an average value.

7.2 Wet Deposition

Wet deposition occurs in the form of rain, snow, and finer droplets of mist. As the droplet of water or the snowflake falls, it scavenges particulate matter and associated chemicals. It has been observed that during its fall a droplet can scavenge chemicals from as much as 200 000 times its volume of air. This quantity, called the scavenging ratio Q, varies depending on the nature of the water droplet, its exposure time in the atmosphere, and its ability to scavenge particles.

Contaminant delivery to a lake surface by wet deposition can be calculated from the rain rate R (m/h, but normally expressed in m/year) per unit area A (m^2), the concentration of the contaminant in the air in particulate form (C_P, ng/m^3), and the dimensionless scavenging ratio Q. The concentration in collected rainfall (C_R, ng/m^3) can also be measured directly by analyzing collected precipitation:

$$\text{chemical wet deposition} = D_W\,(\text{ng/h}) = QRAC_P = RAC_R. \tag{18}$$

A "wash-out ratio" is also defined as the ratio of total concentration of contaminant in rain (C_R) to that in air [(ng/m^3)/(ng/m^3)]. It may also be expressed in terms of mass ratios [(ng/kg)/(ng/kg)], which lowers the value by a factor of approximately 820, the density ratio of water to air. Snow is another form of wet deposition for which scavenging or washout ratios are less established.

In addition to the capture of particles, a falling water droplet may dissolve chemicals and approach equilibrium with the air. In such cases their chemical concentrations can be estimated from the air-water partition coefficient K_{AW} and the air concentration C_A as C_A/K_{AW}. This usually represents only a small fraction of the concentration in rainfall, most chemicals being particle-associated. The exceptions are chemicals of low K_{AW} or high water solubilities such as alcohols:

$$\text{chemical dissolution in rain} = D_R\,(\text{ng/h}) = RAC_A/K_{AW}. \tag{19}$$

8 Specimen Calculation

The nature and magnitudes of these processes are best appreciated by calculating the air–water exchange behavior of a chemical such as PCB congener 169, which is a coplanar hexachlorobiphenyl. It is considered one of the more toxic congeners and is highly bioaccumulative. Its estimated properties at 15 °C are given in Table 1.

We perform calculations for a fictitious lake with a surface area of 10 ha or 100 000 m^2 at a temperature of 15 °C (288 K). The total concentration of PCB in air is assumed to be 0.1 ng/m^3, whereas in water it is 0.5 ng/l. The data in Table 1 are used to deduce the rates of exchange by evaporation, absorption, and wet and dry deposition.

8.1 Step 1: Physicochemical Properties

The first step is to calculate H and K_{AW} using Eqs. (3) and (4). The water solubility is 500 × 10^{-6} g/m^3 or 1.39 × 10^{-6} mol/m^3.

$$H = 25 \times 10^{-6}/1.39 \times 10^{-6} = 18\,\text{Pa}\,\text{m}^3/\text{mol}$$

$$K_{AW} = H/RT = (18)/(8.314 \times 288) = 0.0075$$

At equilibrium the concentration of the chemical in water will be 133 times ($1/K_{AW}$) that in the air. Such values are characteristic of the PCB homologous series.

8.2 Step 2: Mass-Transfer Coefficients

From correlations for wind speed and chemical diffusivity it could be estimated that k_W is 0.05 m/h and k_A is 5 m/h. We then use Eq. (11) to determine the overall mass-transfer coefficient k_{OW}: $k_{OW} = (1/k_W + 1/(k_A K_{AW}))^{-1} = (20 + 26.7)^{-1} = 0.0215$ m/h.

The resistance in the water film is thus 20 h/m, whereas that in air is 26.7 h/m, a total of 46.7 h/m. The resistance in the air is 57% of the total; thus, both k_W and k_A must be known accurately.

Table 1. Estimated properties of PCB congener 169 at a temperature of 15 °C (Mackay et al. 1992)

Molecular weight (g/mol)	361
Melting point (°C)	202
Solid vapor pressure (Pa)	25×10^{-6}
Aqueous solubility of the solid (g/m^3)	5×10^{-4}
Log K_{ow}	7.0

8.3 Step 3: Sorption in Air and Water

8.3.1 Air

It is necessary to estimate the fraction of chemical that is dissolved in water or air (i.e., in gaseous form) as distinct from that associated with particles. This is best done experimentally by measuring the total concentration and the concentration after filtering. If only the total concentration is known, the partition coefficient may be estimated as described previously and the dissolved and sorbed concentrations deduced.

Using the correlation suggested by Mackay et al. (1986), the dimensionless aerosol–air partition coefficient is deduced from the subcooled liquid vapor pressure P_L^S. In this case the fugacity ratio or ratio of solid (P_S^S) to liquid (P_L^S) vapor pressures is 0.0122 as estimated from the melting point using the expression

$$P_S^S/P_L^S = \exp[-6.79(T_M/T - 1)] = 0.0122,$$

where T_M is the melting point (475 K) and T is 288 K. The hypothetical liquid vapor pressure is thus 0.00205 Pa and the partition coefficient K_{QA} is

$$\begin{aligned} K_{QA} &= 6 \times 10^6/P_L^S \\ &= 6 \times 10^6/0.00205 = 2.93 \times 10^9. \end{aligned}$$

Assuming an aerosol concentration of $30\,\mu g/m^3$ and a density of $2.0\,g/cm^3$ gives a volume fraction of aerosol of 15×10^{-12}. The fraction in gaseous form is thus

$$\begin{aligned} &1/(1 + K_{QA} \times 15 \times 10^{-12}) \\ &\quad = 1/(1 + 0.044) = 0.958, \end{aligned}$$

and the remaining 4.2% is sorbed to aerosols. The gaseous concentration C_V is thus 95.8% of $0.1\,ng/m^3$ or $0.0958\,ng/m^3$. Alternatively, correlation of the group $C_V TSP/C_P$ could have yielded $684\,\mu g/m^3$, from which, inserting $30\,\mu g/m^3$ for TSP (total suspended particles) gives, a ratio of C_V/C_P of 22.8, i.e., 0.0958/0.0042. The concentration in aerosol particles is $K_{QA}C_V$ or $0.28\,g/m^3$ of particulate, which is very much larger than the concentration in air.

8.3.2 Water

Similarly, from the known total concentration in water we can deduce the fractions dissolved and associated with particles. The suspended particle concentration is taken to be $15\,g/m^3$. The sorbed contaminant concentration can be estimated using the organic carbon partition coefficient and an assumed 20% organic carbon in the particles

$$K_{OC} = 0.41K_{OW} = 0.41 \times 10^7;$$

thus,

$$K_P = 0.2K_{OC} = 0.82 \times 10^6 \text{ (L/kg)}.$$

The fraction in solution can then be deduced from K_P and the suspended particle concentration C_S (kg/L) as

$$\begin{aligned} 1/(1 + C_S K_P) &= 1/(1 + 15 \times 10^{-6} \times 0.82 \times 10^6) \\ &= 1/(1 + 12.3) = 0.075. \end{aligned}$$

The dissolved concentration is thus 7.5% of 0.5 ng/l, i.e., 0.0375 ng/l, whereas the sorbed concentration is 0.4625 ng/l.

The actual extent of sorption may differ from region to region within the lake and between lakes depending on the nature of the particles and their organic carbon content.

8.4 Step 4: Equilibrium Status

The concentration of PCB in air at equilibrium with the dissolved concentrations of 0.0375 ng/L is $K_{AW}C_W$ or 0.00028 ng/L or $0.28\,ng/m^3$. This exceeds the actual gaseous concentration of $0.0958\,ng/m^3$ by a factor of 2.9. The system is thus not at equilibrium, the water is *supersaturated* with regard to the air, and there is a net diffusive flux or evaporation from water to air.

8.5 Step 5: Volatilization and Deposition Rates

The rate of net volatilization, i.e., the rate of volatilization V_L minus the rate of absorption A_B, can be calculated using Eq. (10):

$$\begin{aligned} V_L - A_B &= k_{OW}A(C_W - C_A/K_{AW}) \\ &= 0.0215 \times 10^5 \times (0.0375 \times 10^{-6} \\ &\quad - 0.0958 \times 10^{-9}/0.0075) \\ &= 53.2 \times 10^{-6}\,g/h = 0.466\,g/year. \end{aligned}$$

This is actually the difference between the gross evaporation rate of $80.6\,\mu g/h$ or 0.706 g/year, and absorption of $27.4\,\mu g/h$ or 0.240 g/year. We also estimate the rates of deposition processes. Assuming a dry deposition velocity of 0.3 cm/s or 10.8 m/h, the rate of particle deposition using Eq. (11) is

$$10.8\,\mathrm{m/h} \times 10^5\,\mathrm{m}^2 \times 15 \times 10^{-12}\,\mathrm{m}^3\ \mathrm{particle/m}^3\ \mathrm{air} = 16.2 \times 10^{-6}\,\mathrm{m}^3/\mathrm{h}\ \mathrm{or}\ 0.142\,\mathrm{m}^3/\mathrm{year}.$$

Because the concentration on the particles is $0.28\,\mathrm{g/m}^3$ the dry deposition rate D_D is

$$D_D = 0.142 \times 0.28 = 0.0397\,\mathrm{g/year}.$$

Assuming a rain rate of 0.8 m/year and a scavenging coefficient of 200 000, the rate of wet deposition is

$$D_W = 200\,000 \times 0.8\,\mathrm{m/year} \times 10^5\,\mathrm{m}^2 \times 15 \times 10^{-12} \times 0.28\,\mathrm{g/m}^3 = 0.0672\,\mathrm{g/year}.$$

The total rate of transfer from air to water (dry and wet deposition and absorption) is thus 0.347 g/year, which is less than the gross evaporation rate of 0.706 g/year. We thus have a situation in which there is net water-to-air transfer or *net volatilization* of 0.359 g/year. The excess transfer from water to air is presumably accounted for by direct discharges of chemicals to the lake. A computer program that conducts a calculation such as the previous is included in the text by Mackay (1991).

9 Role of Air–Water Exchange in Lake Mass Balances

Having examined in detail the fluxes across the air–water interface, it is then possible to examine the larger picture of the mass balance over the entire lake. This places air–water exchange in perspective along with other processes such as reaction, sedimentation, and outflow, as well as with discharge rates from industrial, municipal, and other sources. In principle, the process rates can be combined to give the rate of change in mass of chemicals in the water of the lake (Mkg) as follows:

$$\begin{aligned} d(M)/dt &= \text{inputs} - \text{outputs} \\ &= (D_W + D_D + A_B + I + E) \\ &\quad - (V_L + R_X + O + S). \end{aligned} \tag{20}$$

Here, the inputs are rates of wet and dry deposition (D_W and D_D), absorption A, inflow to the lake I, and direct discharge E. The output processes include volatilization V_L and losses due to reaction R_X, outflow O, and the net sedimentation S.

The relative importance of all processes becomes clear. It is possible to solve this differential equation numerically or analytically to estimate the historical or future changes in mass of chemicals in the water, and hence concentrations in the water and its resident biota. A critically important quantity obtained from this analysis is the potential rate of recovery of the lake as a result of remedial measures to reduce inputs.

The remainder of this chapter is a series of case studies in which these principles are illustrated by considering whole-lake mass balances and specific cases of air–water exchange.

10 Case Studies

The role of air–water exchange of compounds such as the PCBs, PAHs, and HCHs (hexachlorocyclohexanes) in aquatic contaminant cycles has only recently been studied in a quantitative manner (e.g., Mackay 1979; McVeety and Hites 1988; Achman et al. 1993; McConnell et al. 1993). The strategies applied to air–water exchange include construction of chemical mass balances and calculation of fluxes based on simultaneously determined air and water concentrations and environmental parameters such as wind speed.

10.1 Mass Balance on Siskiwit Lake, Isle Royale

Hites and coworkers (McVeety and Hites 1988; Swackhamer et al. 1988) compiled mass balances for input and output of PAHs and PCBs in Siskiwit Lake, Isle Royale located in the central basin of remote Lake Superior. The location and uses of the lake ensure that chemical input is dominated by the atmosphere.

Measurement of rain and snow, atmospheric gas and aerosol, and water column and outflow concentrations on a seasonal basis, as well as surface-sediment concentrations, permit the calculation or assignment of all parameters of the mass balance Eq. (20), except for the dry deposition velocity U_D and the overall mass-transfer coefficient k_{OW}. Both parameters must be calculated from various correlations (e.g., Mackay and Yuen 1983; Schwarzenbach et al. 1993) or may be surmised from the previous mass-balance expression. By treating certain low molecular weight PAHs and PCBs that are known to exist only in the gas phase (i.e., C_P is negligible), the mass balance yields k_{OW} and air–water exchange fluxes. Considering those compounds known to exist primarily in the particle phase (high molecular weight species) yields U_D and dry particle deposition fluxes. The overall liquid phase mass-transfer coefficients were estimated to be 0.1 and 0.18 m/day for PCBs and PAHs, respectively. These values are consistent with the approach given previously, and resistance is dominated by transfer across the liquid phase. The estimated annual average dry-deposition velocities were estimated to be 0.16 and 0.99 cm/s for PCBs and PAHs, respectively. The latter differences cannot be easily explained, unless uncertainties in the mass balance and/or real differences in atmospheric chemistry and speciation between the compounds are invoked. At this remote location it is surmised that dry-particle-deposition velocities closer to 0.2 cm/s for submicron aerosols are more likely.

The inputs and outputs for several individual PCBs and PAHs are given in Figs. 6 and 7. The PCB inputs to Siskiwit Lake were dominated by wet deposition in rain and snow with a minor contribution from dry-particle deposition. Outputs from the remote lake were dominated by volatilization, especially for the lower molecular weight congeners. Total PCBs lost by volatilization amounted to 8.5 μg/m^2 per year in contrast to 5.6 μg/m^2 per year for sedimentation, the other major loss process. For PAHs inputs were dominated by dry-particle deposition, with rain and snow contributing little to the total loading. Losses of PAHs from Siskiwit Lake were dominated by volatilization for the low molecular weight compounds, especially phenanthrene, fluorene, and pyrene, but represented only minor losses for higher PAHs. In this case the role of volatilization decreased with decreasing vapor pressure, a feature common to most recent studies. This is attributed to the increased sorption of the chemicals to the atmospheric aerosol and water particulate phases.

10.2 Mass Balance on Lake Superior

Another strategy to demonstrate the importance of volatilization compared with other input and loss processes on a whole-lake scale was employed

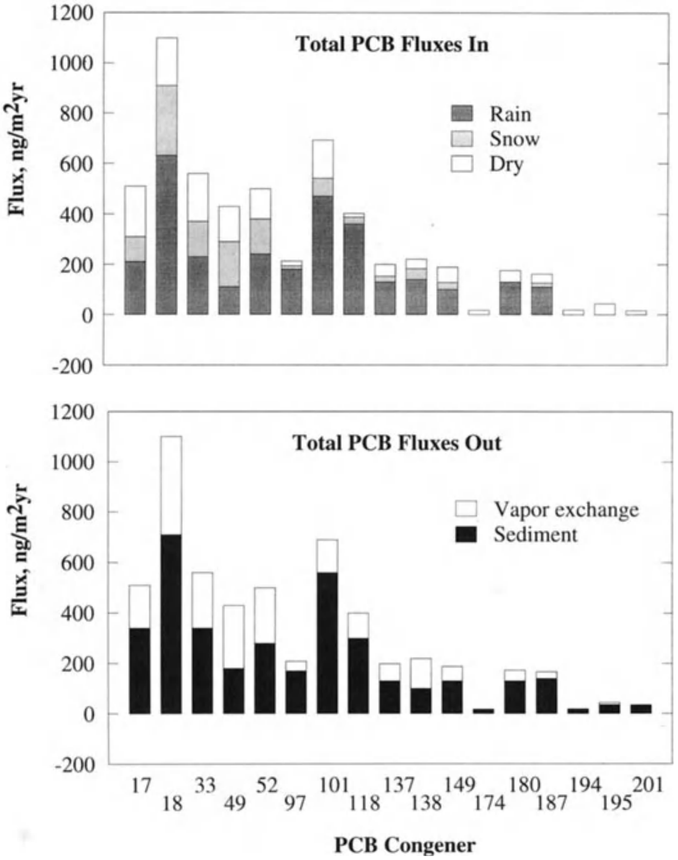

Fig. 6. Estimated fluxes of PCB congeners to and from Siskiwit Lake. Adapted from Swackhamer et al. (1988)

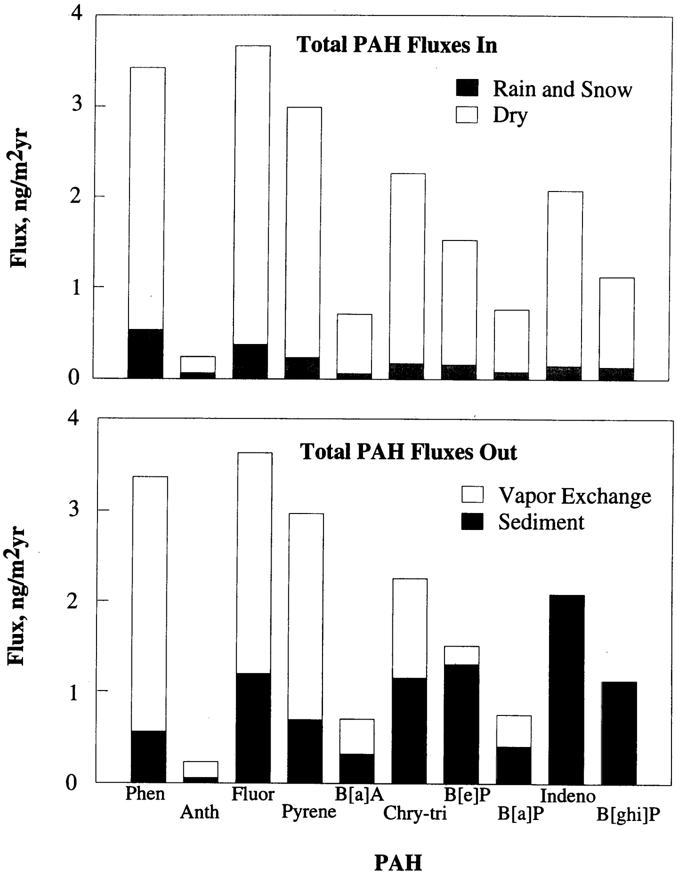

Fig. 7. Estimated fluxes of PAHs to Siskiwit Lake. Adapted from McVeety and Hites (1988)

by Jeremiason et al. (1994). They used the recorded decrease in PCB concentrations in the water column of Lake Superior from 1978–1992 to drive the mass balance of the system. Lake Superior is an atmospherically driven aquatic system, because this large lake has a relatively small basin area and receives more than 60% of its water input by direct precipitation on the lake surface. There are few sources of chemicals, other than atmospheric deposition and air–water exchange. The PCB concentrations in water decreased from ~2.4 ng/l in 1980 to 0.18 ng/l in 1992 corresponding to a loss of ~26 000 kg of PCBs with a first-order rate constant of 0.2/year. A mass balance of PCBs in Lake Superior was then constructed to determine the source of PCB loss in the system. In other words, Where did all the PCBs go? Table 2 shows the inputs and outputs of PCBs in Lake Superior for the comparison year of 1986, in which the net loss of PCB from the water column was calculated to be approximately 1800 kg, which must represent the excess of outputs over inputs.

Table 2. Estimated inputs and outputs of PCBs to Lake Superior in 1986. (Jeremiason et al. 1994)

Inputs	kg/year	Outputs	kg/year
Riverine	110	Outflow	60
Other[a]	41	Sedimentation	110
Dry deposition	32	Volatilization[b]	~1900
Wet deposition	125		
Total	308	Total	~2070

[a] Municipal and industrial discharges.
[b] Net volatilization = volatilization − absorbtion = inputs − outputs + mass lost.

Table 2 indicates that 60 kg is lost to outflow from the lake, and ~100 kg is lost to sedimentation leaving a shortfall of ~1900 kg, which is attributed to volatilization. Given that inputs and outputs of PCBs are highly constrained by known levels of riverine, municipal, and atmospheric wet and dry deposition, as well as the decrease in water-column concentrations, the loss must be attributed to volatilization. It is a remarkable discovery that volatilization losses exceed sedimentation losses by a factor of 17. Hydrophobic organic chemicals, such as PCBs, have high values of K_{OW} and high affinities for particles rich in organic carbon. Although the delivery of PCBs to the benthic region is very efficient, their incorporation into the sediment is not. It is concluded that the importance of volatilization relative to other losses is attributable in large part to the inefficient burial of PCBs in the sediments of this lake, thereby increasing water-column residence times. In other large lakes in which sediment burial is more efficient as a result of higher sediment loads, a smaller proportion of total losses may be attributed to volatilization. Both examples strongly point to the absolute and relative importance of volatilization in whole-lake contaminant cycles.

10.3 Air–Water Exchange in Green Bay, Lake Michigan

As was outlined previously in the specimen calculation, it is possible to use information on physicochemical properties, concentrations, and environmental conditions to deduce the direction and rate of air–water exchange in specific situations. Achman et al. (1993) examined the air–water exchange of PCBs in Green Bay, Lake Michigan, a large freshwater estuary that is hypereutrophic, relatively shallow, and highly contaminated by historical PCB inputs from the Fox River. The PCB gradient from south (near the river mouth) to north (boundary with Lake Michigan) reveals water and sediment concentrations of PCBs decreasing by a factor of 200. Achman et al. (1993) collected air (gas phase) and water (dissolved phase) samples simultaneously from the bow of a 18-m boat in a south-to-north gradient during several cruises covering the ice-free period. A comparison of atmospheric gas phase and aqueous dissolved-phase concentration (Fig. 8) clearly shows their intimate linkage. Proceeding from the highly contaminated south to the less contaminated north, both air and water concentrations decreased in proportion. Hornbuckle et al. (1993) showed that water controlled the PCB concentrations in air throughout much of the Bay, and over-water concentrations exceeded over-land concentrations determined simultaneously nearby. Calculations showed that the direction of transfer was from water to air (i.e., volatilization) at all sites, during all seasons, and at all locations. In the framework of fugacity or PCB partial pressure differences, the fugacity of PCBs in the water column ranged from 5 to 100 times that of the overlying atmosphere. Volatilization was dominated by the di- through tetrachlorobiphenyls, and decreased with increasing molecular weight. A sensitivity analysis of the system demonstrated that dissolved-phase concentrations of PCBs, water temperature, and

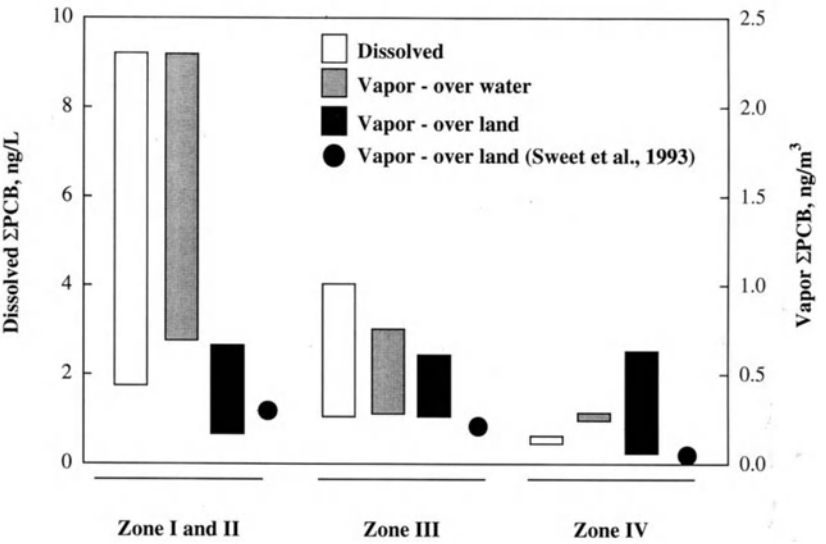

Fig. 8. Relationship between PCB concentrations dissolved in water and in the vapor phase from sample lakes over the water of Green Bay and over land

wind speed drove the fluxes. At low wind speeds of 1–3 m/s, PCB volatilization fluxes were 15–300 ng/m^2 per day. At higher wind speeds, PCB volatilization fluxes were 50–1300 ng/m^2 per day. The total net volatilization of PCBs from Green Bay, Lake Michigan is ~132 kg/year or an average of 314 ng/m^2 per year. This value was obtained by estimating instantaneous volatilization fluxes in several spatially distributed zones and summing over the seasons. This approach fails to recognize that temporally and spatially dependent variations in air and water concentrations add significant uncertainty to the whole-lake flux calculation on an annual basis, especially over the winter and in periods when no samples were taken. In addition, similar variations in wind speed and surface-water temperature over time and space make the estimation of an annual whole-lake calculation problematic. The final case study describes a scenario in which an attempt is made to include such variations.

10.4 Air–Water Exchange in Lake Superior

To determine the annual cycle of air–water exchange in Lake Superior, appropriate water temperature, wind speeds, and dissolved and vapor concentrations must be accurately known for all seasons. Hornbuckle et al. (1994) obtained normal water temperatures based on satellite and airborne surface-temperature imaging collected by government agencies, which provide the means for assessing water temperatures over space and time (seasonally) (Schneider et al. 1993). For calculating PCB air–water exchange, semimonthly average whole-lake values were used. Seasonal wind speeds were measured at Eagle Harbor, Michigan, on the south shore of the central basin of Lake Superior for 1992. Values of 1.34 m/s for December through February, 2.24 m/s for March through August, and 3.58 m/s for September through November were selected. No report of seasonal variations in dissolved total PCB have been reported for the open waters of Lake Superior or other large lake systems. Because so little information is available, a constant dissolved total PCB concentration of 0.173 ng/l, the 1993 value, was applied to the annual flux calculations.

Vapor-phase PCB concentrations vary significantly throughout the year, as shown in Fig. 9, with higher concentrations in the summer than in the winter (Hoff et al. 1992). These data describe a yearly maximum vapor PCB concentration in July/August, and were modeled as a Lorenzian function:

$$\chi(\tau) = \chi_{\mathrm{min}}\left(1 + \frac{A_{\mathrm{m}}\Gamma^2}{(\tau - \tau_{\mathrm{max}})^2 + \Gamma^2}\right),$$

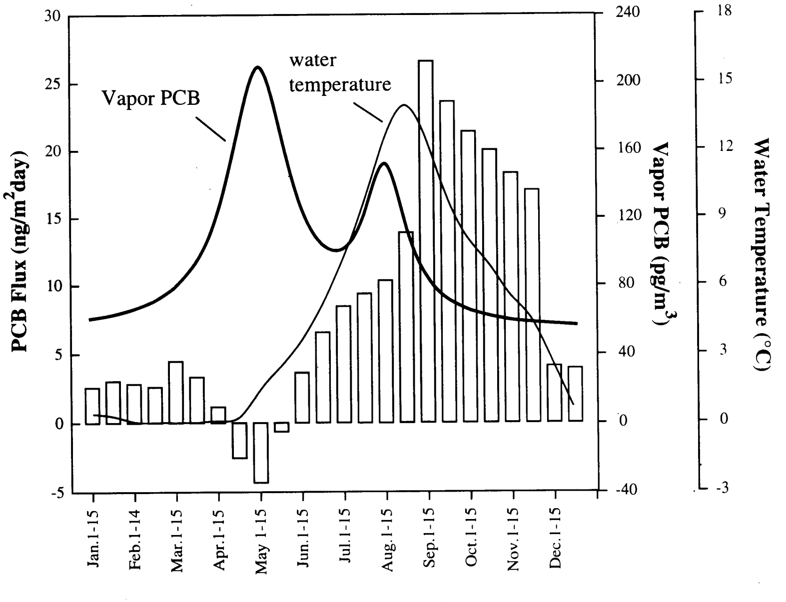

Fig. 9. Annual flux of total PCB (*bars*) plotted as the average daily flux (ng/m^2 per day) for 24 half-month periods. Negative fluxes indicate transport of PCB into Lake Superior. The *line* is the modeled vapor concentrations used for calculating PCB fluxes. The strong seasonal variation is evident. Reproduced from Hornbuckle et al. (1994) with permission

where $\chi(\tau)$ is the compound vapor concentration (ng/m^3), χ_{min} is the minimum average monthly vapor concentration (ng/m^3), A_m is the ratio of highest-to-lowest monthly average vapor-phase concentration, Γ is the width of the peak at half height in months, and τ is the independent variable month. The months are defined from 0 to 12, where 0.5 is mid-January, 1 is the end of January, 1.5 is mid-February, 2 is the end of February, and so forth. For total PCBs χ_{min}, A_m, τ_{max}, and Γ were equal to 0.055 ng/m^3, 14, 6.7, (late July), and 0.67 months, respectively. Total PCB vapor concentrations from samples collected at Eagle Harbor averaged 0.095 ± 0.080 ng/m^3, ranged from 0.013 to 0.390 ng/m^3, and exhibited two maxima: The first and largest monthly average concentration was observed in April/May, whereas a second, smaller peak was observed in July/August.

The cause of the April/May peak in vapor-phase PCBs measured at Eagle Harbor is unclear, but may be related to the spring snow melt. The July/August peak is attributed to volatilization from terrestrial surfaces during periods of warm summer temperatures. A similar model, even if applied to the volatilization of chemicals from water surfaces, cannot explain the trend in the Eagle Harbor data. Melted snow may deliver PCBs to the air by direct volatilization from the melting snow, from the frozen terrestrial surface, or from runoff streams. Because the snow in this region rarely melts between November and April, atmospheric contaminants accumulate. More research into the annual cycle of dissolved PCBs, the impact of snow melt on PCB air and water cycles, and over-water vapor PCBs is clearly needed.

The annual vapor PCB cycle is modeled, therefore, using two Lorentzian functions, which, when summed, describe the annual cycle of atmospheric vapor total PCBs as shown in Fig. 9. The seasonal trend for PCB flux at the air–water interface is determined semimonthly using whole-lake mean water temperatures, 1992 seasonal wind speeds, and the May 1992 dissolved ΣPCB concentration 0.173 ng/L linked to the method outlined previously. All mass-transfer parameters, such as H, k_A, k_{OW}, and K_{OL}, were determined for all 85 PCB congeners in the same manner as for the instantaneous fluxes. The dimensionless Henry's Law Constant, H, the dissolved water concentration, and K_{OW} (m/day) were averaged by homolog group. The PCB homolog fluxes for each semimonthly period were then calculated using the Lorenzian function described previously for air concentrations. The average k_{OW} values for total PCBs is equal to 0.080 m/day, and the annual flux is approximately 250 kg/year. The more volatile (i.e., low molecular weight and chlorine number) congeners exhibited volatilization fluxes throughout the year, and the higher-chlorinated congeners show depositional fluxes at all times of the year, although they represent a very small proportion of the total.

The largest depositional flux of total PCBs was calculated for May, due to higher vapor concentrations. The highest volatilization flux was calculated for September (27 ng/m^2 per day), when water temperatures and seasonal wind speed (3.6 m/s) are highest (Fig. 8). The congeners with less than six chlorines constituted more than 90% of PCB volatilization (June–March) fluxes and ~50% of the deposition (April, May) fluxes. Instantaneous fluxes were frequently greater than the average values calculated by season, because daily wind speeds measured aboard ship were often higher than the 15-day average wind speed used in the annual calculations. (Vapor-phase PCB concentrations measured over water may exceed the modeled values from on-shore sampling, and surface-water temperatures on any given day may be different from semimonthly averages).

The annual flux of total PCB from Lake Superior in 1992 was calculated by multiplying daily average fluxes (ng/m^2 per day) by the appropriate time period. This resulted in average semi-monthly fluxes of −63 ng/m^2 to 404 ng/m^2 for the 24 periods. These fluxes were summed and applied to the surface area of the lake to yield an overall volatilization flux of 249 kg/year or ~8 ng/m^2 per day on an annual basis. Jeremiason et al. (1994) estimated that loss by volatilization was ~400 kg/year in 1992 or ~13 ng/m^2 per day based on decreasing PCB water concentrations and a highly constrained accounting of inputs and outputs. There is thus a satisfying reconciliation between the fluxes calculated by these independent methods.

Results of Hornbuckle et al. (1994) suggest that vapor deposition of PCBs to Lake Superior occurs only briefly in the spring, whereas volatilization occurs throughout the rest of the year. The large autumn volatilization fluxes result from moderate surface-water temperatures and low vapor concentrations. However, the effect of wind speed on air–water exchange may be

Table 3. Estimated air–water fluxes of total PCBs in natural waters (ng/m^2 per day) for a range of contaminated and less-contaminated sites

Location	Total PCB flux	Reference
	Freshwater	
Green Bay	+15 to +300 (1–3 m/s) +50 to +1300 (4–6 m/s)	Achman et al. (1993)
Green Bay	+35	Green Bay Mass Balance (1992)
Lake Superior	+19 (Still Air, 1992) +141 (5 m/s, 1992)	Baker and Eisenreich (1988)
Lake Superior	+63 (1986)	Strachan and Eisenreich (1988)
Lake Superior	+63 (1986) +13 (1992)	Jeremiason et al. (1994)
Lake Superior	+8.3 (1992)	Hornbuckle et al. (1994)
Siskiwit Lake, Lake Superior	+24 (1986)	Swackhamer et al. (1988)
Lake Michigan	0 to +13 000	Doskey and Andren (1981)
Lake Michigan	+240	Strachan and Eisenreich (1988)
Lake Michigan	+15	Swackhamer and Armstrong (1986)
Lake Ontario	+81	Mackay (1989)
River Elm, Sweden	+50	Larsson et al. (1990)
	Seawater	
Oceans	−160 to −450	GESAMP (1988)
Oceans	−4.5	Atlas and Giam (1986)
Oceans	−0.6 to −10	Atlas et al. (1986)
Oceans	−140 to +40	Iwata et al. (1993)

underestimated using this approach. Because k_W has a nonlinear dependence on wind speed, higher-than-average instantaneous winds will produce large fluxes that will not be balanced by wind speeds lower than average. Livingstone and Imboden (1993), using a Weibull probability function for the wind-speed input, suggested that the effect of large instantaneous wind speeds may double the fluxes calculated from average wind speeds.

As shown in Table 3, the magnitude of PCB flux across the air–water interface varies with the climatological and hydrological conditions of each specific location linked to the dynamics of chemical loading and cycling in the air and water. Even so, estimates of the air–water fluxes of PCB in natural waters nearly all show net volatilization with typical values of 10–60 ng/m^2 day in uncontaminated systems, and substantially more in contaminated systems. For chemicals in a homologous series, air–water exchange is likely to be greater for the lower molecular weight species. For chemicals that have lower K_{AW} values, the direction of transfer may be from air to water (i.e., absorption) and represent a net loading to the lake.

11 Conclusions

There is now a satisfactory understanding of the processes by which chemicals cross the air–water interface of lakes. The rates of these processes can be measured directly in some cases (such as wet deposition), but they can only be estimated from mathematical models in other cases, e.g., evaporation. For many chemicals there is active absorption, deposition, and volatilization, and the net direction of transfer may not be obvious. Often there will be strong seasonal variations in transfer rates and even in directions. Much remains to be done to better parameterize the various transfer coefficients and velocities, and to devise better averaging methods. It is hoped that the theoretical treatment and case studies presented in this chapter will encourage further work and a fuller appreciation of the rate of air–water exchange on the chemistry of lakes.

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