

INTER-PHASE MASS TRANSPORT: MODELLING OF AIR-WATER MOVEMENT OF  
ORGANIC CHEMICALS

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### Abstract

Air-water inter-phase mass transport of organic contaminants is often an important factor in their environmental fate and behaviour. The equilibrium situation is given by the Henry's Law Constant of the compound, but is rarely attained under environmental conditions. Approach to equilibrium is commonly described by the two-film theory involving molecular (Fickian) diffusion through thin stagnant films adjacent to the air-water interface. This theory is formulated in terms of mass transfer coefficients and fugacity transport parameters. Penetration and Surface Renewal Theories of mass transfer are also discussed. The importance of the Henry's Law Constant ( $H$ ) is shown. Compounds such as phenol with relatively low values of  $H$  encounter most of their resistance to transport in the air and are said to be under air film control. Compounds such as methane with relatively large values of  $H$  encounter most of their resistance to transport in the water and are said to be under water film control. Estimation methods for mass transfer coefficients and fugacity transport parameters to enable modelling are shown.

**Keywords:** inter-phase mass transfer, Henry's Law Constant, two-film theory, fugacity

### บทคัดย่อ

บ่อยครั้งที่การเคลื่อนที่มวลมลพิษอินทรีย์ระหว่างสถานะอากาศ-น้ำเป็นปัจจัยสำคัญของพฤติกรรมเป็นไปในสิ่งแวดล้อม สถานการณ์สมดุลของสารประกอบอธิบายด้วยค่าคงที่ของกฎเฮนรี ( $H$ ) นั้น ยกที่จะไปถึงภายใต้เงื่อนไขสิ่งแวดล้อม ปกติการเข้าสู่สมดุลอธิบายด้วยทฤษฎีสองฟิล์มเกี่ยวกับการแพร่กระจายโมเลกุล (ฟิกคียน) ผ่านฟิล์มนิ่งบางๆซึ่งติดกับผิวหน้าระหว่างอากาศ-น้ำ ทฤษฎีนี้ประกอบขึ้นด้วยพารามิเตอร์สัมประสิทธิ์เคลื่อนย้ายมวลและเคลื่อนที่ฟุ้งแก๊สซิติทฤษฎีการลอดผ่านและกลับมาใหม่ของพื้นผิวของมวลเคลื่อนย้ายได้อธิบายไว้และแสดงความสำคัญของ  $H$  สารประกอบ เช่น ฟีนอลซึ่งมีค่า  $H$  ค่อนข้างต่ำจะต้องประสบกับความต้านทานส่วนใหญ่ในการเคลื่อนที่ในน้ำและอย่างทีกล่าวกันว่าอยู่ภายใต้การควบคุมของฟิล์มบางๆของอากาศ วิธีประเมินสัมประสิทธิ์เคลื่อนย้ายมวลและพารามิเตอร์เคลื่อนที่ฟุ้งแก๊สซิติทได้แสดงไว้เพื่อให้สามารถทำโมเดลได้

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## Introduction

Air and water are fundamental components of the environment, and exchange of organic chemicals between them can be important in the fate and behaviour of such chemicals. The process of movement from water to air is commonly known as volatilisation, while the reverse (air to water) process is defined as absorption<sup>(1)</sup>. Chemicals can also move from the air phase to water via the processes of wet and dry deposition. In the former, the chemical is typically sorbed to an atmospheric particle that falls to the surface of the water, often under the influence of gravity. In the latter, such particles are scavenged by precipitation (rain or snow), and carried to the water's surface entrained in the precipitation. For the purposes of this work the only air to water process considered is absorption, where individual gas phase molecules move to the water.

Given sufficient time in a closed air-water system, a chemical will reach equilibrium. In this circumstance, there is no thermodynamic tendency for net movement either from air to water or water to air, and the concentrations remain steady with time. In an open system such as the environment, the tendency is still to try to attain equilibrium, though this is unlikely

to ever be achieved in practice.

The ratio of the chemical concentration in air and water at equilibrium, is given by the Henry's Law Constant ( $H$ ). Whereas Raoult's Law relates equilibrium concentrations in the overlying air to concentrations in solution for ideal solutions (e.g. benzene and toluene or  $\text{SiCl}_4$  and  $\text{CCl}_4$ ), Henry's Law is relevant to non-ideal solutions. Classically, Raoult's Law is given by

$$P = P^oX \quad (1)$$

where  $P$  is the partial pressure or concentration of the organic chemical in air,  $P^o$  is the vapour pressure of the compound, and  $X$  the mole fraction in solution. Mole fraction is related to concentration in solution and can vary from zero to a maximum value of one. A solution of an organic contaminant in water is anything but ideal, even solutions of methanol in water. In such situations, Henry's Law is applicable.

$$P = \gamma P^oX = HX \quad (2)$$

The activity coefficient  $\gamma$  is a measure of the non-ideality of the solution and also a measure of the deviation from Raoult's Law. For organic contaminants in water, it is usually found that  $\gamma > 1$ , meaning a positive deviation from Raoult's Law. This is illustrated below in Figure 1. The Henry's Law Constant can be seen as the slope of the plot of Henry's Law.

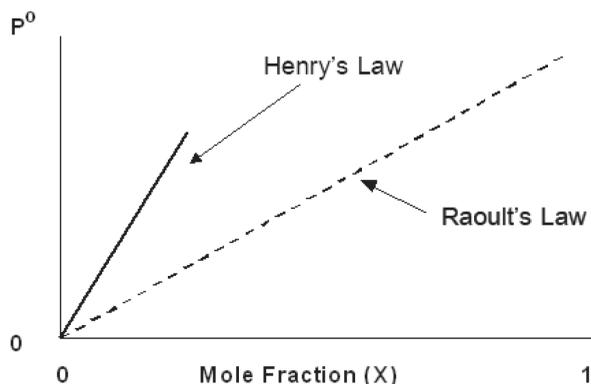


Figure 1 A graphical representation of Henry's Law and Raoult's Law

It is important to consider the units of  $H$ . Since mole fraction is strictly unitless, from Equation 2, the units of  $H$  will simply be pressure. However, there are other ways of expressing Henry's Law, such as

$$P = HC_w \quad (3)$$

in which case the units are pressure/concentration (e.g. Pa m<sup>3</sup>/mol), or

$$C_A = HC_w \quad (4)$$

where Henry's Law Constant is dimensionless. No matter what the form of expression is, it is also important to remember that  $H$  is also an equilibrium constant, and as such temperature dependent. The temperature dependence of  $H$  is therefore adequately described over a modest temperature range (such as experienced environmentally) by a van't Hoff expression of the following form<sup>(2)</sup>.

$$\ln H = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{R} \left( \frac{1}{T} \right) \quad (5)$$

In equation 5, it is emphasised that  $H$  is the dimensionless form. Further,  $\Delta S^o$  is the entropy of volatilisation,  $\Delta H^o$  the enthalpy of volatilisation,  $R$  the Universal Gas Constant and  $T$  the Kelvin temperature.

Rather than equilibrium conditions, the focus of this manuscript is on non-equilibrium conditions as mentioned previously, this is the typical situation in the environment.

### Diffusive Processes

#### Intra-phase Processes

Before considering inter-phase chemical movement, it is instructive to consider how chemicals move within a single phase i.e. intra-phase movement. With quiescent or stagnant fluid phases e.g. air and water, chemical movement occurs down concentration gradients by molecular diffusion according to Fick's First Law of Diffusion<sup>(3)</sup>.

$$J = -DA \frac{dC}{dx} \quad (6)$$

In this expression,  $J$  is the flux, with units of mol/s for example and  $A$  the area through which the flux occurs. The differential term  $\frac{dC}{dx}$  represents the concentration gradient  $D$  and is a proportionality constant called the (molecular) diffusion coefficient, with units of  $m^2/s$  for example. The negative sign is necessary because a flux occurs due to a negative concentration gradient i.e. from areas of high concentration in a fluid to areas of relatively low concentration. When there is no concentration gradient, there is no net flux. Molecular diffusion occurs because of the random motion of molecules in a fluid and is actually a relatively slow process.

In environmental situations, a bulk fluid is rarely completely stagnant. Fluids, by definition flow, and chemical movement simply by being in a fluid current is termed advection. Turbulent fluids also result in mixing of chemicals and processes such as turbulent diffusion and dispersion are recognised<sup>(4)</sup>. A chemical flux still occurs down a concentration gradient however, and as such may be described by an expression of the form of Fick's First Law. For example, mixing due to eddies and swirling fluid is described by

$$J = -EA \frac{dC}{dx} \quad (7)$$

where  $E$  is termed a turbulent diffusion coefficient and is typically orders of magnitude larger than the molecular diffusion coefficient  $D$ . Turbulent diffusion is likely to be anisotropic

i.e. different in different directions in the fluid, so turbulent diffusion coefficients along the x, y and z axes are usually defined ( $E_x$ ,  $E_y$  and  $E_z$ )<sup>(5)</sup>.

Turbulent diffusion coefficients are relatively unpredictable, depending on the variable characteristics of fluid motion. The molecular diffusion coefficient  $D$  is however more predictable. There are various semi-empirical estimation techniques available<sup>(6)</sup>, while a more theoretical treatment based on spherical molecules is given by the Stokes-Einstein Equation.

$$D = \frac{k_B T}{6\pi\eta r} \quad (8)$$

In this expression,  $k_B$  is Boltzmann's Constant,  $T$  Kelvin temperature,  $\eta$  the fluid viscosity and  $r$  the radius of the molecule. From this, it can be seen that any flux due to molecular diffusion should be smaller for larger molecules and more viscous fluids.

Often, the diffusion distance, represented by  $dx$  (or as an approximation  $\Delta x$ ) in Fick's Law describing molecular diffusion is unknown. This diffusion distance can be combined with  $D$  to form a new parameter known as a mass transfer coefficient ( $k$ ) with units of velocity. Mass transfer coefficients are widely used in environmental transport equations for chemicals<sup>(1)</sup> and Fick's First Law in terms of mass transfer coefficients is

$$J = -kA dC \approx -kA \Delta C \quad (9)$$

An alternative expression involves the parameter of fugacity ( $f$ ), which has units of

pressure and is related to chemical potential and concentration in a phase<sup>(1,7)</sup>. In this format,  $C = f/Z$  where  $Z$  (e.g.  $\text{m}^3/\text{mol}\cdot\text{Pa}$ ) is the fugacity capacity constant of the phase, a measure of its capacity to accumulate chemical.

$$J = D \Delta f = kAZ \Delta f = \frac{D}{\Delta x} AZ \Delta f \quad (10)$$

Equation 10 represents Fick's First Law in terms of molecular diffusion coefficients, mass transfer coefficients and fugacity. In this equation,  $D$  (e.g.  $\text{mol}/\text{Pa}\cdot\text{h}$ ) is known as a transport parameter, and relates fugacity difference to flux just as a mass transfer coefficient relates concentration difference to flux.

### Inter-Phase Processes

The movement of a chemical contaminant

within a phase is relatively simple compared to movement between phases. With inter-phase processes, movement can actually occur from a phase where it has a low concentration to another where it has a higher concentration. An approach that has proved useful with the air-water system is the two-film approach developed by Whitman<sup>(8)</sup> and first applied to water-air transfer of gases by Liss and Slater<sup>(9)</sup>. It is depicted in Figure 2 and considers that the bulk air and water phases are well mixed and chemical transport occurs via processes such as turbulent diffusion. Friction at the air-water interface dampens turbulence however<sup>(10)</sup>. Therefore, there exists adjacent to the interface a stagnant air layer or film and a stagnant water layer or film. Movement through these films is by molecular diffusion.

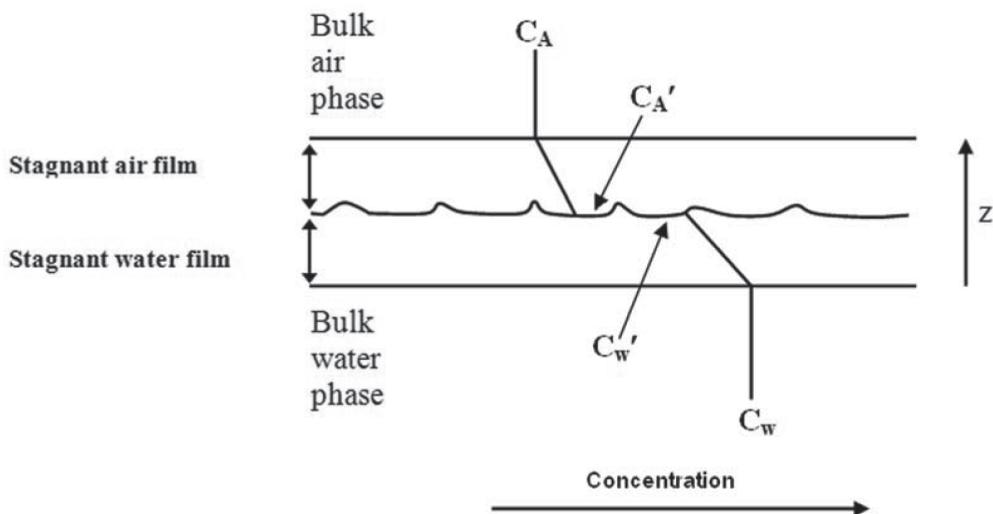


Figure 2 Diagram depicted the concentration profile of a chemical moving from water to air through stagnant water and air films in series.

Figure 2 as drawn shows water to air movement of an organic chemical. The bulk air and water phases are well mixed with no change in concentration with depth, but there exists a concentration gradient in each of the thin stagnant films. The concentration in the water at the air-water interface is denoted by  $C_w'$  and the concentration in the air at the interface by  $C_A'$ . Equilibrium is assumed to exist at the interface and so  $C_A' / C_w' = H$ .

Assuming also a steady-state situation, the chemical flux across air and water films (where the main resistance to water/air inter-phase transport occurs) must be equal. Therefore,

$$J = k_A A (C_A' - C_A) = k_w A (C_w - C_w') \quad (11)$$

$$= k_A A (H C_w' - C_A) = k_w A (C_w - C_w') \quad (12)$$

where  $k_A$  and  $k_w$  are the mass transfer coefficients in the air and water films respectively. Air and water concentrations have the same units so that  $H$  here is dimensionless. It is relatively easy to measure the concentrations in the bulk, well-mixed air and water, but very difficult to measure to the concentrations at the air-water interface. Isolating  $C_w'$  in order to eliminate it,

$$C_w' = \frac{k_A C_A + k_w C_w}{k_w + k_A H} \quad (13)$$

Therefore

$$\begin{aligned} J &= k_A A \left( H \left[ \frac{k_A C_A + k_w C_w}{k_w + k_A H} \right] - C_A \right) \\ &= k_w A \left( C_w - \frac{k_A C_A + k_w C_w}{k_w + k_A H} \right) \end{aligned} \quad (14)$$

Evaluating either expression,

$$\begin{aligned} J &= \frac{k_A k_w A}{k_w + k_A H} (H C_w - C_A) \\ &= K_A A (H C_w - C_A) = K_A A (C_A^* - C_A) \end{aligned} \quad (15)$$

where  $C_A^*$  is the hypothetical air concentration that would be in equilibrium with  $C_w$ , and  $K_A$  (with units of velocity) is called the overall air phase mass transfer coefficient. For water to air chemical movement,  $C_A^*$  has to be greater than  $C_A$ .

Alternatively, one could isolate  $C_A'$  in order to eliminate it from flux expressions. Thus,

$$C_A' = \frac{k_w C_w + k_A C_A}{k_A + k_w / H} \quad (16)$$

Going back to either initial flux expression in Equation 11,

$$\begin{aligned} J &= \frac{k_A k_w A (C_w - C_A / H)}{k_A + k_w / H} \\ &= K_w A (C_w - C_A / H) = K_w A (C_w - C_w^*) \end{aligned} \quad (17)$$

Here,  $C_w^*$  is the hypothetical water concentration that would be in equilibrium with  $C_A$ . For water to air movement of a chemical to occur,  $C_w$  has to be greater than  $C_w^*$ .

When these quantities are equal, there is no net flux, and the system has reached equilibrium, although as mentioned previously, this is very unlikely in an open system.

From Equation 17 it can be seen that

$$K_w = \frac{k_A k_w A}{k_A + k_w / H} \quad (18)$$

It follows that

$$\frac{1}{K_w} = \frac{1}{k_w} + \frac{1}{Hk_A} \quad (19)$$

Mass transfer coefficients have units of velocity, and therefore their reciprocal can be interpreted as a resistance. Equation 19 then says that the overall resistance is equal to the sum of the individual phase resistances. Some authors place an extra term in equations such as this to represent resistance at the interface itself<sup>(6)</sup>. This modification is usually not necessary, except when there is an extra film (e.g. a hydrocarbon slick) between air and water.

By analogy to Equation 19,

$$\frac{1}{K_A} = \frac{1}{k_A} + \frac{H}{k_w} \quad (20)$$

and it can be seen that  $K_w$  and  $K_A$  are related by the dimensionless form of  $H$  ( $K_w = HK_A$ ). With this information, it is now possible to express Equation 15 or Equation 17 as

$$J = K_w AC_w - K_A AC_A \quad (21)$$

that highlights that the net flux is the difference between two individual phase based fluxes. Whether Equation 15 or 17 is actually used to determine air-water flux of a chemical depends on whether which phase concentration-time data is available for.

Flux within a phase is simply the product of a mass transfer coefficient and a concentration difference. The chemical flux between different phases however one could either use Equation 15, involving an overall mass transfer coefficient and the difference between a hypothetical and a real air concentration, or Equation 17 involving a separate overall mass transfer coefficient and the difference between a real and a hypothetical water concentration.

A simplification of this approach often undertaken is to assume the concentration in one of the phases is effectively zero, and remains zero due to dissipation. Considering water to air movement for example, if  $C_A$  is taken as zero, from Equation 17,

$$J = K_w AC_w \quad (22)$$

and since flux is the rate divided by volume, rate is given by the following expression.

$$Rate = -\frac{dC_w}{dt} = \frac{J}{z} = \frac{K_w}{zA} AC_w = \frac{K_w}{z} \quad (23)$$

Equation 23 can easily seen as a simple first order loss expression. In this example,

the rate constant for volatilisation would be given by  $\frac{K_w}{z}$ <sup>(11)</sup>.

Description of inter-phase mass transport in terms of fugacity is particularly useful. This is because the net flux is simply proportional to the difference in fugacity of a chemical on the two phases, in this instance, ambient air and water. There is no need for recourse to partition coefficients and real and hypothetical concentrations, as is the case with mass transfer coefficients above.

If looking at the water to air movement of a chemical, fugacity is initially higher in the water than in air. With time this fugacity decreases while that in the air increases until at equilibrium, net flux and fugacity difference is zero. The expression for net flux in terms of fugacity is,

$$J = D_{Aw} (f_w - f_A) \quad (24)$$

where  $D_{Aw}$  is now an inter-phase transport parameter (e.g. mol/d·Pa), and  $f_w$  and  $f_A$  are the fugacities of the chemical of interest in water and air respectively. As mentioned when considering intra-phase diffusive processes, the fugacity of a chemical in a phase can be related to concentration through a fugacity capacity constant ( $Z$  e.g. mol/m<sup>3</sup>·Pa) that is generally a function of the phase and chemical. For diffusive processes, individual phase transport parameters are related to individual phase mass transfer coefficients ( $k$ ) by<sup>(12)</sup>,

$$D = kAZ \quad (25)$$

The fugacity difference term in Equation 24 gives immediate information on the direction of chemical or mass transport. As written, if the term is positive, chemical moves from water to air. Alternatively, if the term is negative, movement is from air to water. This approach has been used with practical effect to determine movement of the organochlorine insecticide  $\alpha$ -hexachlorocyclohexane or lindane<sup>(1)</sup>. From initial observations in the northern Pacific Ocean in the 1980's, absorption was occurring. A decade later, decreased terrestrial use resulted in decreased atmospheric concentrations, and the situation was reversed. Volatilisation was occurring with net water to air movement<sup>(13)</sup>.

With inter-phase transport parameters as with mass transfer coefficients, the reciprocal of the overall transport parameter is simply equal to the sum of the reciprocals of the individual phase transport parameters.

Therefore from,

$$\frac{1}{D_{Aw}} = \frac{1}{D_A} + \frac{1}{D_w} = \frac{1}{k_A AZ_A} + \frac{1}{k_w AZ_w} \quad (26)$$

and

$$D_{Aw} = K_w AZ_w = K_A AZ_A \quad (27)$$

The one single inter-phase transport parameter can be related to both inter-phase mass transfer coefficients.

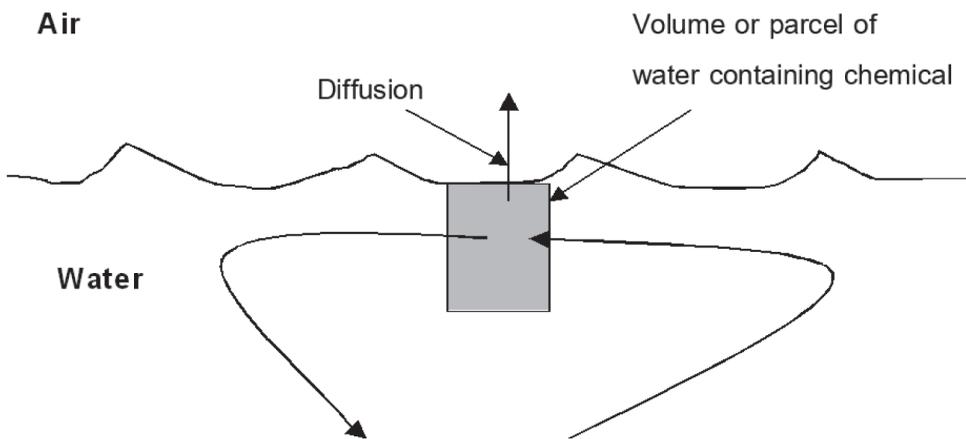
**Other approaches to inter-phase mass transport**

While the two-film approach is widely used in modelling the air-water movement of chemicals, there are others that will briefly be considered. Rather than a thin stagnant water film at the interface, Higbie<sup>(14)</sup> proposed that small volumes or parcels of water containing the chemical of interest at the concentration in the bulk phase ( $C_w$ ) are brought to the surface by eddies and turbulence. While a volume is at the interface, chemical diffuses across the air-water interface. This has come to be known as Penetration Theory since the chemical must penetrate from the parcel of water into the air. Starting from Fick's Second Law of Diffusion, the flux through the water is given by

$$J = k_w(C_w - C_w') = 2\sqrt{\frac{D}{\pi t}}(C_w - C_w') \quad (28)$$

Here,  $k_w$  is the mass transfer coefficient in water and  $D$  the molecular diffusion coefficient as before. The parameter  $t$  is the time a volume spends at the interface before being displaced by another. The original volume or parcel then simply merges or “dissolves” back into the bulk solution. It should be remembered that in considering air-water transfer, a molecule would still have to traverse the thin air film though.

Difficulties with Equation 28 from Penetration Theory are that  $t$  and  $C_w'$  are hard to measure or quantify which means it is usually not of practical use in predicting mass transfer<sup>(3)</sup>. However, it does show that based on this theory, the mass transfer coefficient should be proportional to  $D^{\frac{1}{2}}$ , whereas the classical two-film theory predicts  $k_w$  to be directly proportional to  $D$ <sup>(5)</sup>.



**Figure 3** Conceptual basis of Penetration and Surface Renewal Theories of Water-Air Mass Transfer

One of the underlying assumptions in Penetration Theory is that the parcels of water all spend the same amount of time at the interface. This is probably unrealistic given that turbulence is largely a random or stochastic process. Danckwerts<sup>(15)</sup> therefore modified Penetration Theory by assuming that the volumes of water reach and leave the interface randomly. This approach is called Surface Renewal Theory. In this, the flux through the water is given by

$$J = k_w(C_w - C_w') = \sqrt{(D r_w)}(C_w - C_w') \quad (29)$$

where  $r_w$  (/time) is the rate of surface or interface renewal of the parcels. Various empirical relationships are available to estimate surface renewal rates<sup>(10)</sup>. The reciprocal of  $r_w$  can be interpreted as the average amount of time a parcel spends at the interface. Again, however the mass transfer coefficient is predicted to be proportional to  $D^{\frac{1}{2}}$ .

Surface Renewal Theory can also be extended to the air phase such that

$$k_w = \sqrt{(D_w r_w)} \text{ and } k_A = \sqrt{(D_A r_A)}$$

and from Equation 19

$$\frac{1}{K_w} = \frac{1}{k_w} + \frac{1}{Hk_A} = \frac{1}{\sqrt{(D_w r_w)}} + \frac{1}{H\sqrt{(D_A r_A)}} \quad (30)$$

for example. Careful measurement of volatilisation rates and mass transfer coefficients show that for standing water bodies such as lakes, often  $k_w \propto D$ , in line with two-film theory,

whereas for flowing, turbulent water results are closer to surface renewal theory<sup>(5)</sup>. In general, it is found  $k_w \propto D^n$  where  $0.5 \leq n \leq 1.0$ .

### Control of Mass Transport

Although the two-film theory or approach has limitations and is perhaps unrealistic in many environmental situations, it is widely used. One reason for this is it's relative simplicity and convenience. In this approach, the overall mass transfer coefficient is a function of the individual phase mass transfer coefficients and the dimensionless Henry's Law Constant ( $H$ ) as seen in Equations 19 and 20. The individual phase mass transfer coefficients are in turn function of the molecular diffusion coefficient  $D$ . The magnitude of these parameters varies with the chemical compound and also environmental factors such as temperature and wind speed. The greatest variance is with  $H$ . Schwarzenbach et al.<sup>(6)</sup> compiled relevant data on organic chemicals ranging from methane to polychlorinated biphenyl congeners. The molecular diffusion coefficient in air  $D_A$  varied by less than an order of magnitude as did  $D_w$  (although values of  $D_A$  for a given compound are typically a factor of  $10^4$  times greater than those in the denser, more viscous water). For these same compounds as compiled by Schwarzenbach et al.<sup>(6)</sup>,  $H$  varies by more than five orders of magnitude however. This means that two limiting situations present themselves. If  $H$  is relatively small,

$$\frac{1}{K_w} = \frac{1}{k_w} + \frac{1}{Hk_A} \approx \frac{1}{Hk_A} \Rightarrow K_w = Hk_A \quad (31)$$

and assuming  $k_A$  to be roughly constant,  $K_w$  is directly proportional to  $H$ . This situation is known as air film control, since all the resistance to inter-phase air-water movement effectively lies within the thin air film. Alternatively, if  $H$  is relatively large,  $K_w$  may be approximated by the following expression.

$$\frac{1}{K_w} = \frac{1}{k_w} + \frac{1}{Hk_A} \approx \frac{1}{k_w} \Rightarrow K_w = k_w \quad (32)$$

Here,  $K_w$  is seen to be independent of  $H$ . This situation is termed water film control, since transfer resistance is due to the water film. To attempt to quantify this, Mackay<sup>(1)</sup> noted

that under environmental conditions, typical values of  $k_A$  and  $k_w$  are of the order of 10 and 0.1 m/h respectively. Compounds with dimensionless  $H$  of  $> 0.1$  (or 250 Pa m<sup>3</sup>/mol at 298K) are volatile and water phase diffusion controlled. Examples would be methane, chlorofluorocarbons and even large alkanes. Compounds with dimensionless  $H$  of  $< 0.001$  (or 2.5 Pa m<sup>3</sup>/mol at 298K) are comparatively involatile and subject to air phase diffusion control. Examples would be phenol and relatively large polycyclic aromatic hydrocarbons (PAHs) such as benzo[a]pyrene<sup>(6)</sup>. For compounds with intermediate values of  $H$ , resistance in both air and water phases is important in inter-phase movement.

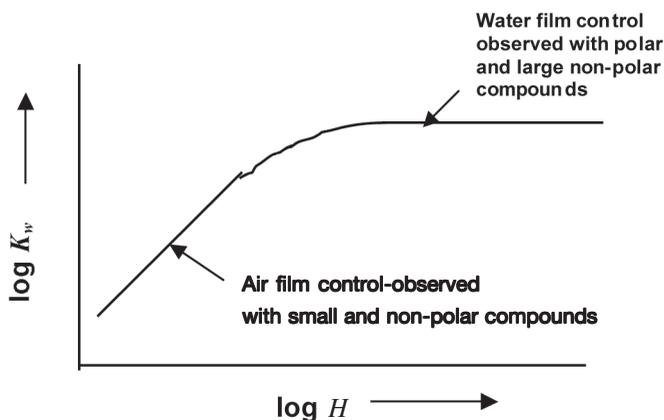


Figure 4 A plot of the overall mass transfer coefficient  $K_w$  as a function of  $H$  showing regions of water and air film control.

Wind speed alters turbulence which affects diffusion distances and in turn mass transfer coefficients. Therefore plots such as that shown in Figure 4 are relevant for a particular wind speed. For different wind speeds, the regions described as being under air and water film control will vary<sup>(6)</sup>.

In fugacity format, water film control is represented by

$$D_{Aw} = k_w AZ_w \quad (33)$$

and air film control by

$$D_{Aw} = Hk_A AZ_w = Hk_A Z_A \quad (34)$$

If working with air concentrations rather than water  $H$  concentrations, then for relatively large values of  $H$  and therefore water film control,

$$\frac{1}{K_A} = \frac{1}{k_A} + \frac{H}{k_w} \approx \frac{H}{k_w} \Rightarrow K_A = \frac{k_w}{H} \quad (35)$$

while for compounds with small Henry's Law Constants and therefore air film control,

$$\frac{1}{K_A} = \frac{1}{k_A} + \frac{H}{k_w} \approx \frac{1}{k_A} \Rightarrow K_A = k_A \quad (36)$$

This means that a plot of  $\log K_A$  versus  $\log H$  that is analogous to Figure 4 would be a mirror image about the y axis.

It is not often appreciated, but water itself has a Henry's Law Constant that can be determined from its vapour pressure and concentration (in itself) of  $5.5 \times 10^4 \text{ mol/m}^3$ <sup>(1)</sup>. At 298 K, it is  $1.6 \times 10^{-5}$  (in dimensionless

terms) or  $0.04 \text{ Pa m}^3/\text{mol}$ . If an organic contaminant has a smaller Henry's Law Constant than this, it will likely concentrate in water with time if there is little water vapour in the air, because the water will evaporate faster than the compound volatilises.

Earlier it was shown that under certain conditions, mass transfer from water to air could be treated as a simple first order loss process with a first order rate constant. Bartkow et al.<sup>(16)</sup> have summarised how rate constants can be related to mass transfer coefficients for inter-phase mass transfer. Rate constants are temperature dependent, shown by the well-known Arrhenius Equation.

$$k \propto e^{\left(\frac{-E_A}{RT}\right)} \quad (37)$$

Therefore so are the related mass transfer coefficients. Because fugacity transport parameters can also be related to mass transfer coefficients, they are also functions of temperature.

Considering inter-phase mass transfer coefficients to be functions of diffusion coefficients, diffusion distances and  $H$ , it is worth noting that all are temperature dependent. A molecular diffusion coefficient (Equation 8) has an explicit temperature term, but phase viscosity also changes with temperature. The relationship between air-water inter-phase mass transport and temperature is likely to be complex, however Rathbun and Tai<sup>(17)</sup> have

found mass transfer coefficients varied as the exponential of the reciprocal absolute temperature, just as in the Arrhenius Equation.

$$\frac{k_{w(x)}}{k_{w(O_2)}} = \left( \frac{D_{w(x)}}{D_{w(O_2)}} \right)^n = \left( \left( \frac{32}{MW} \right)^{\frac{1}{2}} \right)^n \quad (39)$$

Therefore,

### Modelling of Air-Water Mass Transfer

In order to predict the time course of inter-phase mass transfer, it is necessary to know or estimate the magnitude of mass transfer coefficients (or rate constants or fugacity transport parameters). These are conventionally estimated from comparison with the known behaviour of reference compounds<sup>(5)</sup>. For example, the water film mass transfer coefficient for an organic contaminant of interest is correlated to that for molecular oxygen ( $O_2$ ). The data for  $O_2$  are for overall air-water transfer, but all resistance is in the thin water film because  $O_2$  is already present in the air, and doesn't have to diffuse through the air layer. Thus, in practice, the  $O_2$  data relates to  $k_w$ .

Based on the Stokes-Einstein Equation as shown in Equation 8,  $D \propto 1/r$ . If molecular weight ( $MW$ ) is used as a surrogate for size and  $r$ , it is found empirically that  $D \propto 1/MW^{1/2}$ . For an organic contaminant of interest ( $x$ ) and  $O_2$  in a given environment

$$\frac{D_{w(x)}}{D_{w(O_2)}} = \left( \frac{32}{MW} \right)^{\frac{1}{2}} \quad (38)$$

As discussed previously in Section 2, it is found empirically that  $k_w \propto D^n$  where  $0.5 \leq n \leq 1.0$ . Assuming the same proportionality constant for organic contaminant and molecular oxygen, then

$$k_{w(x)} = \left( \frac{D_{w(x)}}{D_{w(O_2)}} \right)^n k_{w(O_2)} = \left( \left( \frac{32}{MW} \right)^{\frac{1}{2}} \right)^n k_{w(O_2)} \quad (40)$$

In rapidly flowing water, current velocity and depth of the water are the determinants of  $k_{w(O_2)}$ . Empirical relationships involving these factors may be used to estimate  $k_{w(O_2)}$  and hence  $k_{w(x)}$ <sup>(6)</sup>. Where water is relatively deep or current slow as in lakes and impoundments, wind friction on the air-water interface largely governs the magnitude of  $k_{w(O_2)}$ . In these situations, relationships between  $k_{w(O_2)}$  and wind speed may be used to estimate  $k_{w(O_2)}$  and hence  $k_{w(x)}$ <sup>(6)</sup>.

For the mass transfer coefficient in air, a commonly used reference substance is water vapour. Evaporation rate data are extensive and relate to  $k_{A(H_2O)}$ . Resistance is confined to the thin air film, since diffusion through water is unnecessary. By analogy with the approach outlined above for determining  $k_{w(x)}$ ,

$$k_{A(x)} = \left( \frac{D_{A(x)}}{D_{A(H_2O)}} \right)^m k_{A(H_2O)} = \left( \left( \frac{18}{MW} \right)^{\frac{1}{2}} \right)^m k_{A(H_2O)} \quad (41)$$

where  $0.5 \leq m \leq 1.0$ . Wind speed clearly governs the magnitude of  $k_{A(H_2O)}$ , and employing empirical relationships,  $k_{A(H_2O)}$  and hence  $k_{A(x)}$

may be determined.

Although little seen in the literature, fugacity transport parameters can also be estimated in this way.

$$D_{w(x)} = \left[ \left( \frac{32}{MW} \right)^{\frac{1}{2}} \right]^n D_{w(O_2)} = \left[ \left( \frac{32}{MW} \right)^{\frac{1}{2}} \right]^n k_{w(O_2)} AZ_w \quad (42)$$

$$D_{A(x)} = \left[ \left( \frac{18}{MW} \right)^{\frac{1}{2}} \right]^m D_{A(H_2O)} = \left[ \left( \frac{18}{MW} \right)^{\frac{1}{2}} \right]^m k_{A(H_2O)} AZ_A \quad (43)$$

With such data, and knowledge of  $H$  air-water mass transport behaviour can be predicted, either using a simple first order loss scenario, or by recognising the flux expressions are in fact differential equations in concentration or fugacity and can be integrated, albeit sometimes with difficulty.

## Conclusions

Air-water mass transport is an important factor in the fate and behaviour of many organic environmental contaminants. A commonly used approach is the two-film theory based on diffusion through stagnant films adjacent to the air-water interface. It is an extension of Fickian diffusion in single phases, but is more complex and necessarily involves the dimensionless form of Henry's Law Constant. There are two alternative flux expressions associated with two alternative overall mass transfer coefficients depending on whether air or water phase concentrations are employed. A parallel fugacity based approach does not encounter this

problem. The main determinant of inter-phase mass flux for a given concentration (or fugacity) difference is the Henry's Law constant of the compound. For compounds with relatively small values of  $H$ , air-water movement is said to be under air-film control, meaning that effectively all resistance is encountered in diffusing through the air. Conversely, compounds with relatively large values of  $H$  are said to be under water-film control. For compounds with intermediate values of  $H$ , there is resistance in both phases. There are various techniques for estimating the magnitude of mass transfer coefficients (or rate constants or fugacity transport parameters). These are conventionally estimated from comparison with the known behaviour of reference compounds. With this information, air-water inter-phase mass transport behaviour can be predicted.

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