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The Role of Volatilization in Removing Polycyclic Aromatic Hydrocarbons from Aquatic Environments[1,2]

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The movement of organic contaminants from water to the atmosphere can be important in reducing concentrations of foreign substances in aquatic ecosystems (HILL et al. 1976, DILLING 1977, MACKAY and LEINONEN 1975). Polycyclic aromatic hydrocarbons (PAH), a class of chemical produced in the combustion and pyrolysis of organic fuels, possess properties which suggest that their volatility in solution may be significant (MACKAY and WOLKOFF 1973). Since many PAH are potent carcinogens, a knowledge of their persistence, transport, and fate in aquatic environments is critical. The objective of this paper is to determine the relative volatility of two to five ring PAH structures in water, and estimate the importance of the volatilization process in removing PAH from aquatic environments.

The theoretical basis for describing the transfer of volatile substances across an air-water interface has been succinctly detailed (LISS 1973, LISS and SLATER 1974). The rate of the process under a given set of conditions is described as a simple first order exponential decay with rate constant K_L/depth. K_L, the overall mass transfer coefficient, has units of distance time (such as cm/hr) and three components: k_g, k_l and H, related by the expression

$$K_L = \frac{Hk_g k_l}{Hk_g + k_l} \quad , \qquad (1)$$

where: H = the Henry's Law constant, a distribution coefficient representing the equilibrium distribution of a material between gaseous and liquid phases. Units used for H in this paper are molar concentration PAH_{air}/molar concentration PAH_{water}.

k_g = the gas phase exchange constant, a measure of the rate of transport of the material away from the interface in the air. Units are cm/hr.

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k_l = the liquid phase exchange constant, a measure of the rate of transport of the material to the interface in the water. Units are cm/hr.

Both k_g and k_l are influenced by mixing within their respective phases, and to a lesser extent by mixing within the adjoining phase (LISS 1973). The rate of volatilization of a substance from a given water body will be determined by properties of the substance (H) and the environment (wind, water turbulence, and temperature). Temperature acts to influence H (SCHWARZ and WASIK 1977), while k_l and k_g are primarily functions of wind and water turbulence, which vary to a lesser degree with temperature.

MATERIALS AND METHODS

Henry's Law constants at 25°C were estimated for napthalene, anthracene, phenanthrene, pyrene, benz(a)anthracene and benz(a) pyrene, using the method of MACKAY (1976), which consists of sparging a column of water containing PAH with a measured flow of nitrogen. Preliminary experiments indicated that the PAH concentration within the nitrogen attained 95% of the equilibrium value in passing through a 38-cm column, 6 cm in diameter. PAH concentration was analyzed using fluorescence spectrophotometry. Henry's Law constant was calculated directly as the rate constant for the exponential decay of aqueous PAH concentration vs volume of nitrogen. A second estimation of H was obtained using literature values to calculate the ratio of equilibrium vapor pressure to aqueous solubility limit (MACKAY and WOLKOFF 1973).

The gas phase mass transfer coefficients (k_g) were calculated at various wind velocities by multiplying the data of LISS (1973) for H_2O by $\left(\frac{\text{Mol.wt } H_2O}{\text{Mol.wt PAH}}\right)^{1/2}$. Liquid phase mass transfer coefficients were calculated for various current velocities from stream reaeration coefficients (k_2) using the expression of CHURCHILL et al. converted to metric units - (NEMEROW 1974)

$$k_2 \text{ (25 C)} = 0.2351 \, \frac{V^{0.969}}{R^{1.673}} \, \text{hr}^{-1} \quad , \qquad (2)$$

where V is current velocity (m/sec), and R is mean depth (m).

The reaeration coefficient (a first order rate constant) was converted to the mass transfer coefficient by multiplying it by the depth. While the most direct effect of varying wind velocity is upon k_g and current velocity upon k_l, each also affects the mass transfer coefficient of the adjoining phase. In order to take this interaction into account, wind and water velocities were summed before determining k_g, and the observed relationship between wind and k_l was incorporated into the estimation of k_l by fitting an exponential curve to the data of LISS (1973) (for values outside the range of LISS (1973), i.e. wind velocity 1.9 m/sec; k_l was assumed to be unaffected by wind). The equations used to generate k_g and k_l as functions of wind and current velocity were

$$k_g = 1137.5\ (V_{wind} + V_{current}) \left(\frac{18}{Mol.wt\ PAH}\right)^{1/2} ; \qquad (3)$$

for V_{wind} 1.9 m/sec,

$$k_l = 23.51\ \frac{V_{current}^{0.969}}{R^{0.673}} \left(\frac{32}{Mol.wt\ PAH}\right)^{1/2} ; \qquad (4)$$

and for V_{wind} 1.9 m/sec,

$$k_l = 23.51\ \frac{V_{current}^{0.969}}{R^{0.673}} \left(\frac{32}{Mol.wt\ PAH}\right)^{1/2} (e^{0.526\ (V_{wind}-1.9)}) \qquad (5)$$

V_{wind} = wind velocity (m/sec), $V_{current}$ = current velocity (m/sec), R = stream depth (m), and units of k_l and k_g are cm/hr.

The estimations of $H_{25°C}$, k_g, and k_l were inserted into Equation (1) to calculate volatilization rates of naphthalene, anthracene, benz(a)anthracene, and benz(a)pyrene in a hypothetical river 1.0 m deep, at current velocities ranging from 0.1-1.0 m/sec and wind velocities ranging from 0.25-4.0 m/sec. Volatilization half lives and half distances (the distance traveled in the stream before 50% of a material volatilizes) were estimated.

Finally, laboratory estimates of k_g and k_l under varying conditions of mixing and wind velocity were carried out for benzene, naphthalene, and anthracene to assess the degree to which such conditions approximate environmental parameters.

Estimations of k_l and k_g in laboratory systems were carried out in 10 cm diameter culture dishes maintained in a 25°C water bath. Liquid depth was 2.7 cm, stirred by a 5.0 cm diameter stainless steel propeller. To estimate k_l for a given propeller depth and speed, the volatilization rate of benzene was measured experimentally. Initially, k_g was assumed to be 665 cm/hr (from LISS 1973), and k_l calculated from Equation (1). Benzene volatilization is primarily liquid phase controlled, hence estimates of k_l are relatively insensitive to k_g values. The volatilization rate of anthracene was then determined under the same conditions, and k_l obtained for benzene, adjusted for molecular weight, was inserted into Equation (1) to calculate k_g. The value of k_g thus obtained was used to recalculate k_l in the original benzene data, and that k_l used to recalculate k_g in the anthracene experiment. After two or three such iterations, k_l and k_g values no longer varied.

RESULTS AND DISCUSSION

Laboratory estimates of Henry's Law coefficients (H) and estimates based upon the ratio of equilibrium vapor pressure to aqueous solubility (MACKAY and WOLKOFF 1973) are presented in Table 1. The trend towards decreasing H with increasing molecular weight within the PAH group is clear for either group of estimations. The relationship between H and molecular weight for the laboratory data is given by:

Table 1. Estimations of Henry's Law constants for PAH in water at 25°C, S.E. of regression coefficient. Units of H are molar concentration of PAH in each phase. Exponent (10^{-n}) applies to both columns

	Experimental	Literature
Naphthalene	2.26 ± 0.03	1.9×10^{-2} (a)
Anthracene	2.66 ± 0.07	12×10^{-3} (b,d)
Phenanthrene	2.24 ± 0.05	2.0×10^{-3} (c,e)
Pyrene	7.64 ± 0.26	4.3×10^{-4} (b,f)
Benz(a)anthracene	3.28 ± 0.46	1.0×10^{-4} (c,f)
Benz(a)pyrene	$< 1 \times 10^{-4}$	2.1×10^{-5} (b,f)

[a] Schwarz and Wasik, 1977.

[b] Solubility from Schwarz and Wasik, 1976.

[c] Solubility from Davis, Krahl, and Clowes, 1942.

[d] Vapor pressure extrapolated from Handbook of Chemistry and Physics, 46th Edition.

[e] Vapor pressure extrapolated from Osborn and Douslin, 1975.

[f] Vapor pressure from Pupp and Lad, 1974.

$$\log H = -0.01910\ (\text{mol.wt}) + 0.78540,\ R^2 = 0.996\ . \qquad (6)$$

Except for anthracene, laboratory and literature values of H are in reasonable agreement, especially in view of the very low vapor pressures and solubilities which must be determined.

The k_g and k_l values determined for the laboratory system using benzene and anthracene are given in Table 2. When these were used to predict the volatilization rate of naphthalene in the same system, rate constants (K_L) of 0.43 and 3.07 cm/hr

Table 2. Estimated mass transfer coefficients for volatilization of a hypothetical substance (mol. wt = 100) from water in laboratory systems and natural water bodies (cm/hr)

	Conditions	k_l*	k_g*
PAH	quiescent	0.60	118
	100 rpm, prop. 0.5 cm,** no wind	5.79	377
	200 rpm, prop. 0.1 cm, no wind	15.9	539
	200 rpm, prop. 0.1 cm, 3-4 m/sec wind	17.0	3834
Chlorinated hydrocarbons	200 rpm, prop. 5 cm, no wind (Dilling 1977)***	11.8	896
River	1 m deep, current 0.1 m/sec, wind 0.25 m/sec	1.45	168
	current 1.0 m/sec, wind 1.0 m/sec	13.3	964
	current 1 m/sec, wind 4 m/sec	40.1	2410
Open ocean	"mean values" (Liss & Slater 1974)	13.3	1697

*Normalized to molecular weight = 100.

**Depth of propeller beneath interface.

***Calculated from volatilization rates of CCl_4 and $CH_2Cl\,CHCl\,CH_2Cl$.

were predicted for quiescent and 100 rpm, 0.5 cm propellor depth, no wind, respectively. Experimentally observed values for naphthalene under the same conditions (with 95% confidence intervals) were 0.47 ± 0.05 and 2.86 ± 0.35 cm/hr.

Laboratory measurements of volatilization rates from water have been conducted in rapidly stirred solutions maintained in quiescent air (DILLING et al. 1976). Observed rates in these studies are well predicted using estimates of k_g and k_l obtained from in situ studies of gas exchange in the open ocean (DILLING 1977). A comparison of mass transfer coefficients observed in their studies with those made for PAH in this study is shown in Table 2. It can be seen that large variations in volatilization rates can be observed in laboratory studies depending on water and air phase mixing, but that the rates observed are representative of the range likely to be encountered in natural environments. Mixing rates of 100-200 rpm produce k_l values typical of well mixed water bodies, but k_g values characteristic of a moderately windy system cannot be obtained without external mixing in the gaseous phase. A 3-4 m/sec air stream directed unto the surface produces a 7-fold increase in k_g, elevating it to levels representative of wind impacted water bodies. The effect of wind on k_l was less than observed by LISS (1973), suggesting that the action of wind in raising k_l is dependent upon the initial value of k_l (i.e., the effect of wind on k_l in an unmixed system is greater than in a turbulent system).

The variation in predicted volatilization rates with wind and current velocity for naphthalene, anthracene, benz(a)anthracene, and benz(a)pyrene are depicted in Fig. 1. The two high molecular weight carcinogens, benz(a)anthracene and benz(a) pyrene, can be seen to be persistent with respect to volatilization losses, with half lives greater than 100 hours. The distance of flow required to reduce these two compounds to 50% of their initial concentrations is generally well in excess of 100 km. The lower molecular weight PAH, naphthalene and anthracene, were more volatile, with predicted half lives of less than 100 hours under most of the conditions considered. Anthracene would thus be expected to require 14-240 km of stream flow to be reduced to 50% of its initial concentration, while for naphthalene the distance would be 7-40 km.

The relative importance of wind and water motion in determining volatilization half life can be seen in Fig. 1. Volatilization of compounds with relatively high Henry's Law coefficients, such as naphthalene, tends to be limited by aqueous phase processes (k_l) (DILLING 1977). Thus, factors directly affecting k_l, such as current velocity, dramatically affect volatilization. A 10-fold increase in current velocity (0.1 to 1.0 m/sec) increases the predicted volatilization rate of naphthalene about 7.5 times, while a 10-fold increase in wind velocity produces a 2-3 fold increase. For anthracene, 10-fold increases in wind and current each produce roughly four fold increases in volatilization, while for benz(a)anthracene and benz(a)pyrene a 10-fold increase in current velocity roughly doubles volatilization, while a 10-fold increase in wind velocity would produce a 5-fold increase.

The discontinuous model used to estimate k_l (equations 4 and 5) produces a disjointed curve for liquid phase controlled systems (naphthalene, Fig. 1). Coupled with the laboratory data previously discussed, it is likely that equation (5) overestimates the role of wind in influencing k_l.

The rate of volatilization of PAH from a relatively deep (> 1 m in depth), slow moving river (< 1 m/sec average current velocity) would be insufficient to prevent the persistence of such materials in the water for many kilometers downstream. Since H decreases with decreasing temperature, predicted volatilization rates at 25°C would be higher than those at lower temperatures, particularly for gas phase limited conditions. Under some

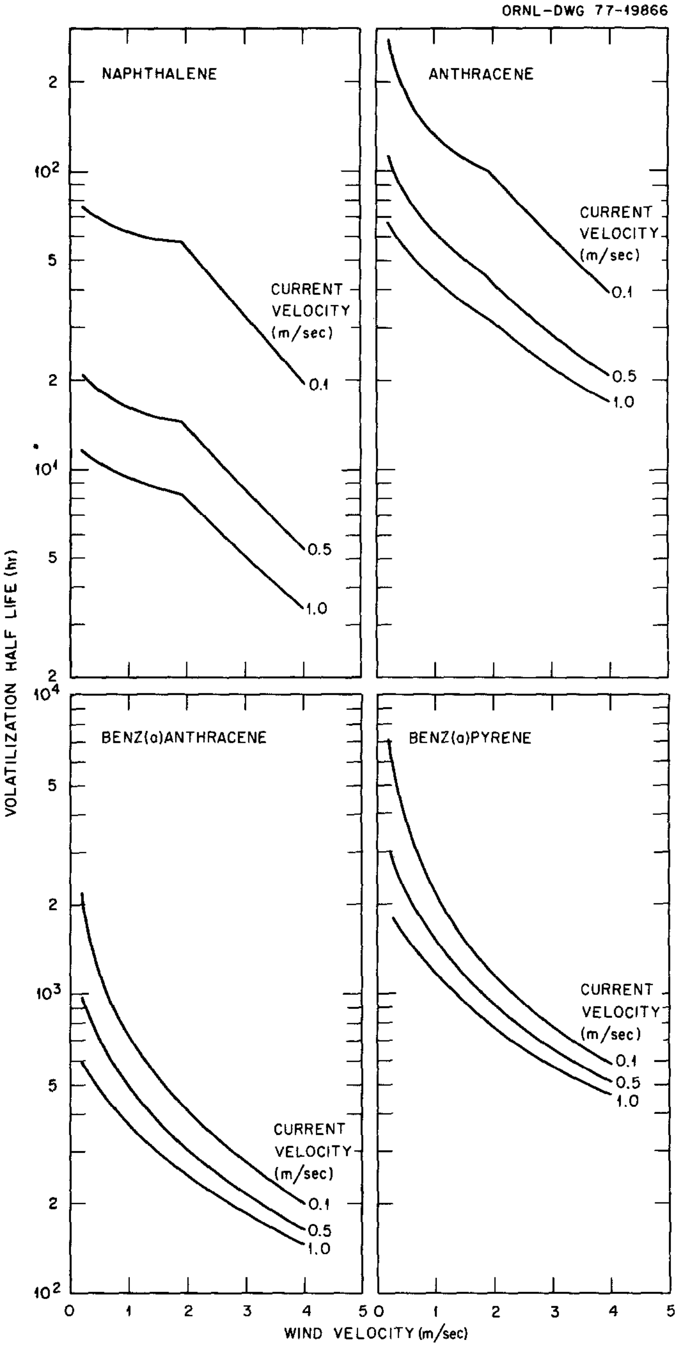

Figure 1. Variation in predicted volatilization rates of PAH at 25 C under varying conditions of wind and current velocity in a stream 1.0 m in depth.

conditions (high temperature, wind, and shallow depth) the rate of volatilization of low molecular weight materials such as naphthalene may be substantial. Volatilization of higher molecular weight PAH (4 or more aromatic rings) would be expected to be relatively insignificant in virtually any sizable water body, due to their low Henry's Law coefficients. While increased current velocity should act to increase volatilization rate (d PAH/dt) in a stream, the increased flow rate results in an extension of the distance traveled before 50% is volatilized.

It must be noted that in a given water body, bulk fluid mixing and phenomena such as stratification may play a large role in determining the overall impact of interface controlled processes in removing toxicants. Thus, the approach used in this paper yields theoretical maximum volatilization rates, which may be reduced by bulk fluid properties. Other factors which may affect volatilization are the presence of surface films (MACKAY and COHEN 1976), waves, and aerosol formation (LISS and SLATER 1974).

While volatilization cannot be anticipated to play an important role in reducing carcinogenic PAH concentrations in aquatic ecosystems, this does not mean that estimated half lives (Fig. 1) are measures of their overall persistence in such waters. Other removal processes, such as adsorption, photolysis, and microbial degradation may be critical in determining the persistence of PAH.

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