DOI: 10.1016/0045-6535(87)90009-9

Chemosphere, Vol.16, No.4, pp 745-757, 1987
Printed in Great Britain

0045-6535/87 $3.00 + .00
Pergamon Journals Ltd.

Sorption of Hydrophobic Chemicals From Water: A Hypothesis for the Mechanism of the Particle Concentration Effect

Donald Mackay and Bruce Powers

Department of Chemical Engineering and Applied Chemistry,
University of Toronto, Toronto, Ontario, Canada M5S 1A4

ABSTRACT

The phenomena of hydrophobic organic chemical sorption to particulate organic matter in aqueous systems are reviewed. It is speculated that the primary process is "loose sorption" in which an organic chemical reduces the total organic-water interfacial area and hence free energy by associating loosely with the natural organic surface, displacing the water from the surface and from part of the chemical. This process is easily reversible as a result of particle collisions, thus the apparent sorption partition coefficient decreases as the particle concentration and collision rate rise. Quantifying this speculated phenomenon using a mass transfer approach yields an expression for a variable partition coefficient which is in agreement with observations that a maximum of approximately half the sorbate present can be sorbed to particles. Some implications are discussed.

INTRODUCTION

The environmental fate and effects of organic chemicals are profoundly affected by the extent to which the chemicals sorb to substrates such as soils, bottom sediments and suspended sediments. The sorbed chemical may be less "available" for, or susceptible to, processes such as volatilization, bio-uptake and reaction. It is thus essential to quantify the extent of sorption, usually in terms of a partition coefficient K_p or ratio of sorbed concentration C_s and dissolved concentration C_w. Conventionally C_s has units such as mg/kg (or g/Mg) and C_w mg/L (or g/m^3) and K_p has thus units of reciprocal density of L/kg or m^3/Mg or cm^3/g.

Environmental sorption science has relied heavily on the concepts developed by Langmuir and others who described the process as attachment of the sorbate molecule to the sorbent surface by a relatively weak bond. As the surface becomes covered or "saturated" by sorbate, the equilibrium K_p may change. Equations such as the Langmuir or Freundlich isotherms may be applied. In recent years it has become apparent that for hydrophobic organic environmental contaminants this conceptual model is inadequate. Certain general principles of behavior have been observed to apply environmentally.

(1) The chemical is usually present at concentrations which are so low that sorptive sites are not "saturated" and behavior is thus linear, i.e. K_p is constant. This appears to apply as long as the chemical concentration is less than 30% of its solubility (Karickhoff[1,2]).

(2) The primary site of sorption for non-polar organic chemicals is organic matter which may be attached to the mineral substrate. The mineral sites only contribute a substantial sorptive capacity at low organic matter contents. It is thus convenient to characterize sorption in terms of an organic carbon partition coefficient (Lambert[3], Briggs[4]).

(3) The organic carbon partition coefficient of a chemical correlates well with its octanol-water partition coefficient (Karickhoff[2]).

(4) The sorbed chemical experiences differing degrees of accessibility to the surrounding solution. Labile, non-labile or less labile fractions, or reversible and resistant fractions may be observed. Care must thus be taken when measuring sorption isotherms to define the time of exposure for sorption and desorption (Karickhoff[5], DiToro and co-authors[6,7,8]).

(5) Finally, and most perplexing, is the particle concentration phenomenon first described by O'Connor and Connolly[9] and more recently reviewed by DiToro[10] and others. It is observed that K_p for suspended sediment varies with suspended sediment concentration in apparent contradiction to conventional thermodynamic principles.

Two principal schools of thought have emerged to explain this latter phenomenon. First is the "third phase" explanation, that the dissolved concentrations are in error because part of the chemical allegedly in solution i.e. C_w, is actually sorbed to colloidal or non-filterable matter. Variations in the concentration of such colloids explain the apparent variation in K_p[(11-13)]. The second explanation is of "particle interactions" primarily promulgated by DiToro[10], in which it is proposed that at higher particle concentrations there is enhanced desorption as a result of increased frequency of particle collisions.

Other explanations have been advanced which seem less likely. Increased coagulation or aggregation of particles at higher concentrations could result in less net area, but it is difficult to conceive that the area would be as sensitive to particle concentration as the data indicate. Addition of sorbent in the regime of variable K_p would have to result in no net area increase. The water structure may be affected by the proximity of a solid surface leading to changes in mean water solubility or activity coefficient of the chemical. The distance of any such effect is however, unlikely to be sufficient to influence an appreciable fraction of the water.

The most convincing experiments in favor of the particle interaction theory are the elegant resuspension and dilution experiments described by DiToro[8]. Further, the magnitude of the effect is so large that it is difficult to accept that the entire effect is attributable to a third phase. As illustrated in Figure 1 (modified from DiToro[10]), the slope of the log K_p versus log particle concentration curve approaches -1 thus the extent of sorption is essentially independent of particle concentration, i.e. adding more particles reduces K_p proportionately and there is no net increase in extent of sorption. DiToro[10] has devised an ingenious model in which, in addition to the conventional sorption-desorption process, there is a second particle-induced desorption step in which collisions between particles induce desorption. This leads to an expression for K_p which is consistent with the experimental data. One puzzling feature is that the inferred ratio of the rate constants for adsorption and particle-induced desorption is constant (i.e., independent of the sorbent and the chemical) with a value of close to unity. As DiToro has noted of his model, "The most significant shortcoming of the model - is the lack of a mechanistic explanation for the particle induced desorption reaction - ."

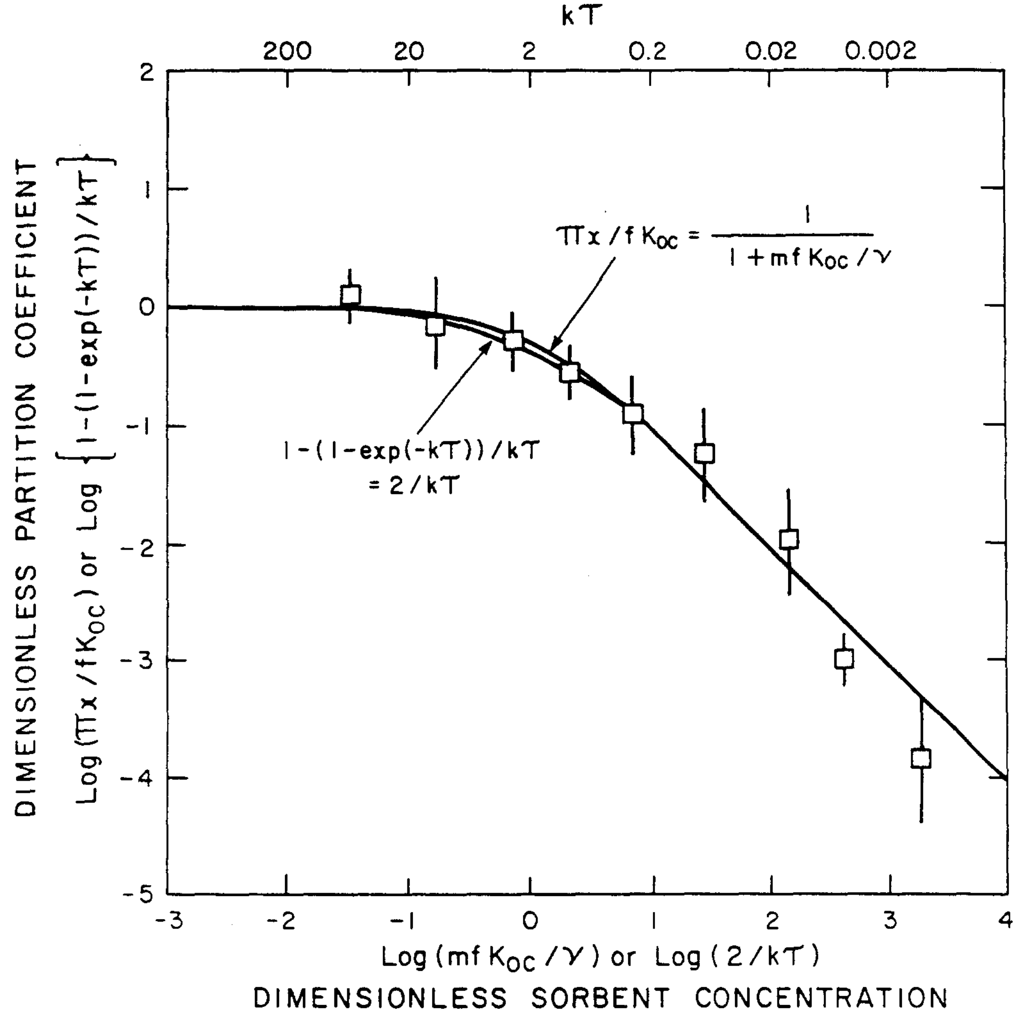

Figure 1: Plot of dimensionless partition coefficient as a function of particle concentration (modified by DiToro[10]). Also shown is the "exponential" plot of the kT function.

We first discuss several aspects of the fundamental mechanism of sorption of organic chemicals to natural substrates. From this basis a model is proposed which is conceptually different from the traditional sorption models and leads to a speculative physical explanation and model of the phenomena discussed above.

Magnitude of K_{oc}

Choiu et al.[14,15] have suggested that the chemical is "dissolved" in the organic carbon matrix, rather than adsorbed to the surface. The most compelling evidence for this is that the organic carbon sorption phenomenon is consistent with dissolution of the chemical in a phase in which the chemical has a solubility approximately 40% of the chemical's solubility in octanol. K_{oc} is then approximately 40% of K_{ow} as shown for bottom sediments by Karickhoff[1]. Miller et al.[16] have calculated the solubilities or pseudo-solubilities of chemicals in octanol and have shown that they range from 100 to 2000 mol/m^3 (organic carbon solubilities are thus 40 to 800 mol/m^3) for chemicals of molar volume 300 to 100 cm^3/mol. The volume fractions corresponding to such solubilities in organic carbon are thus 0.012 to 0.08. The mole fractions (which can not be determined exactly because of the indeterminate molecular weight of the organic matter) are probably a factor of approximately ten higher, and thus lie in the range 0.1 to 0.8. These mole fractions correspond to activity coefficients on a Raoult's Law basis of approximately 10 to 1.2 which is fairly close to ideality and is the range of values expected when a chemical dissolves in a "like" solvent. This may be a coincidence but it supports the idea that the chemical is "dissolving" in a solid matrix of chemically similar material.

Freeman and Cheung[17] have described the solution as a "gel" which can be induced to swell and compress by addition of other solvents.

DiToro[10] has noted that in the dilute suspended sediment range the "reversible" K_{oc} is indistinguishable from K_{ow} suggesting that for these particles the "solubility" in organic carbon is identical to that in octanol and thus even closer to ideality than occurs in bottom sediments.

Accessibility of Sorbing Sites

DiToro[6-8] and Karickhoff[5] have shown that part of the sorbing sites is rapidly accessible in minutes or hours, or "reversible" or "labile", but part is less accessible with sorption or desorption times being of the order of days. The desorption rate correlates inversely with K_{oc}, i.e. more strongly sorbing chemicals desorb more slowly and the rate is proportional to the square root of time.

As has been pointed out by both authors it is likely that slow diffusion within an organic carbon matrix is responsible for the delay. The square-root-of-time relationship suggests unsteady state diffusion in pores. Further evidence of pore diffusion is the observation that when a chemical is sorbed into a soil which is subsequently dried, the chemical becomes difficult to desorb. Presumably the matrix shrinks, or water is unavailable to act as a diffusion medium.

These observations are consistent with the model that the chemical can sorb to the outer organic carbon surface, or it can enter pores and become attached to internal surfaces. The surface chemical is "labile" or "reversible" whereas the pore chemical is "non-labile" or "resistant". But surface sorption is not a true solution, so why is the activity coefficient so close to that for ideality? The answer may be that, as illustrated in Fig. 2 when the chemical molecule attaches to the surface there is a reduction in the total organic-water interfacial area of approximately half the chemical molecular area (if the molecule is flat like anthracene), plus a corresponding area reduction of organic carbon, totalling the net area of the molecule. Thus the net free energy change on sorption is equivalent to the molecule entering a organic phase and the activity coefficent is approximately unity. One would expect that molecules which are not flat will not sorb as strongly.

Perhaps in the pores, there is less surface area available per unit mass of organic carbon than occurs at the surface thus the average area corresponds to K_{oc} being 40% of K_{ow}. It

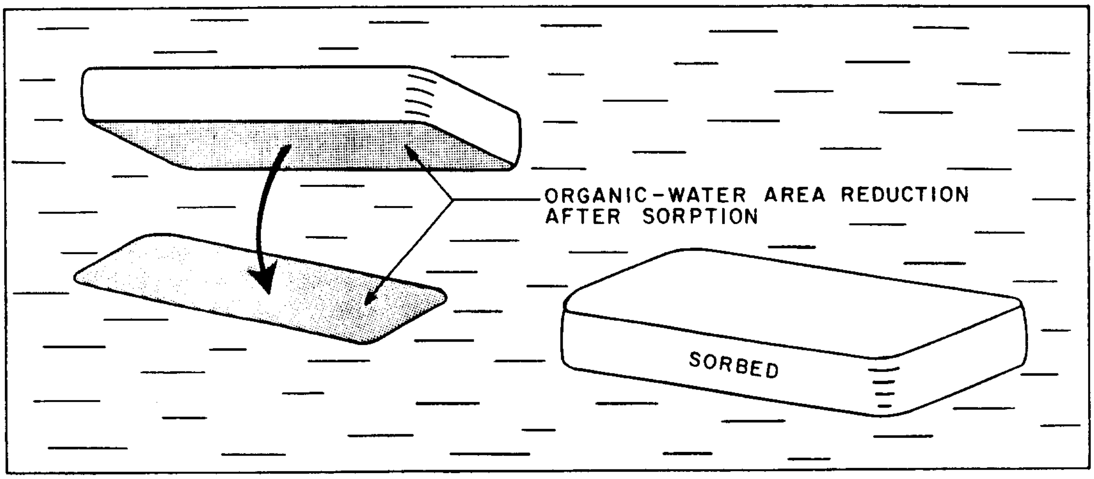

Figure 2: Illustration of the organic-water area reduction resulting from sorption of a molecule at an organic surface. The reduction approximates the molecule surface area.

is also likely that humic and fulvic acids and other "loose" organic matter sorb to the attached organic matter thus competing to some extent for available area. The organic carbon of all origins may seek to minimize its area exposed to water.

We thus hypothesize that the primary interaction between non-polar organic chemicals and natural organic matter is simply rapidly reversible surface sorption without any specific bonding or interaction other than that which normally occurs when non polar organic molecules are in close proximity We term this phenomenon "loose sorption".

Further support for this concept comes from three areas. Platford et al.[18,19] have observed anomalously high K_{ow} values when hydrophobic organic chemicals partition into thin films of octanol. Perhaps the observed partitioning is the sum of bulk dissolution and loose sorption. Only when the octanol area/volume ratio is large (film thickness is small) does this effect become detectable. Several studies[20-23] have shown that hydrophobic organic chemicals gather at the air-water interface; indeed this phenomenon is the basis of the process of bubble sublation for removal of organic chemicals from water. The process is rapidly reversible. Presumably the chemical can reduce its area exposed to water, and hence its free energy, by locating at the interface. Third, the remarkable constancy of the K_{oc}-K_{ow} relationship over a range of temperatures suggests that the enthalpies of phase transfer in both cases are equal. If stronger sorption existed, a higher enthalpy of desorption would be expected and a different temperature dependence would result.

The non-labile or resistant sorption may be the same phenomenon but taking place in pores, or in locations in which the chemical is sandwiched between layers of organic matter which have aggregated. The solid solution model is another way of depicting this process but it is suggested that the physical situation is loose sorption of the chemical on the internal surfaces of organic carbon which is like a sponge saturated with water.

Mineral surfaces may be strongly hydrated thus less free energy reduction can be accomplished when an organic chemical sorbs to them. Further in the environment they may

Particle Interactions

If the sorption is loose and rapidly reversible it is conceivable that particle-particle collisions will be sufficiently energetic to dislodge the accumulated chemical. At higher particle concentrations, collisions are more frequent thus desorption is more frequent. DiToro[10] expressed this in terms of rate constants. We reproduce his model below using his nomenclature.

$$\text{adsorption/desorption} \qquad c + m \underset{k_{s-d}}{\overset{k_{ads}}{\rightleftarrows}} c{=}m \tag{1}$$

$$\text{particle induced desorption} \qquad c{=}m + m \xrightarrow{k_{p-d}} c + 2m \tag{2}$$

where c is chemical concentration in water (mg/L), m is particle concentration (kg/L), c=m is concentration of chemical in sorbed form (mg/L of water). Writing the steady state equation for c=m gives

$$k_{ads}c.m - k_{s-d}c{=}m - k_{p-d}.c{=}m.m = 0, \tag{3}$$

$$\text{thus } c{=}m = k_{ads}c.m/(k_{s-d} + mk_{p-d}) \tag{4}$$

But the partition coefficient Π_x L/kg is given by

$$\Pi_x = \frac{c{=}m}{c.m} = \frac{k_{ads}}{k_{s-d} + mk_{p-d}} = \frac{\Pi_{xc}}{1 + m\Pi_{xc}/\nu_x} \tag{5}$$

where Π_{xc} is k_{ads}/k_{s-d} and ν_x is k_{ads}/k_{p-d}. At low particle concentrations (small m), Π_x approaches Π_{xc} the classical partition coefficient, but at high concentration Π_x approaches ν_x/m and falls linearly with increasing m. This model is consistent with the experimental observations. It is observed that ν_x is relatively constant with a value of approximately unity. Why this is so is not clear.

Since Π_{xc} is apparently equal to the product of f the mass fraction organic carbon and K_{oc}^x, the reversible organic carbon partition coefficient, it is convenient to rewrite the equation in terms of organic carbon as

$$\Pi_x = \frac{f\,K_{oc}^x}{1 + m\,fK_{oc}^x/\nu_x} \tag{6}$$

the limits of Π_x are then fK_{oc}^x at low m and ν_x/m at high m. The effective K_{oc}^x at high m is then $\nu_x/(fm)$. DiToro uses K_{oc}^x to designate the reversible sorption coefficient which like Π_x has dimensions of L/kg.

We rewrite this model in mass transfer rather than reaction terms recognizing that the fundamental driving force is fugacity or chemical potential. It is convenient to use different nomenclature and units.

A volume of water V_w m^3 is considered containing N particles of diameter D m. The total particle volume V_p is thus $N\,\pi\,D^3/6$ m^3 and the volume fraction concentration is $N\pi D^3/6V_w$. The particles contain a mass fraction f of organic matter thus the mass and volume of organic matter are respectively $f\rho_p N\pi D^3/6$ kg and $f\rho_p N\pi D^3/(6\rho_o)$ or V_o m^3 where ρ_p and ρ_o are the particle and organic matter densities (kg/m^3). The particle moves through the liquid by diffusion and eddies at a velocity U m/s thus it encounters or sweeps through $U\pi D^2/4$ m^3 of water per second where $\pi D^2/4$ is the particle cross sectional area. Alternatively this could be expressed as a diffusive mass transfer coefficient k_L and the volume encountered would be $k_L\pi D^2$, the area in this case being the surface area of the sphere instead of the cross sectional area. We thus postulate that the uptake of chemical by the particle follows the differential equation

$$(V_o/N)\ dC_o/dt = (U\pi D^2/4)\ (C_w - C_o/K_{oc}) \qquad (7)$$

where C_o is the concentration of chemical sorbed to the organic carbon of the particle (mol/m^3), C_w is the water concentration (mol/m^3), and K_{oc} is the dimensionless organic carbon-water partition coefficient $(mol/m^3)/(mol/m^3)$ and differs from the K_{ow} used by DiToro by a factor of the density of organic carbon. Integrating from C_o of zero at zero time t gives

$$C_o = K_{oc}C_w\{1-\exp(-NU\pi D^2t/4V_oK_{oc})\} = K_{oc}C_w\ \{1-\exp(-kt)\} \qquad (8)$$

C_o thus rises from zero to $K_{oc}C_w$ at long times with a rate constant k equal to $(NU\pi D^2/4V_oK_{oc})$.

We further postulate that after a period of time τ the particle collides with another particle and complete desorption of the loosely sorbed chemical occurs from both. This time τ occurs when the volume swept out $U\pi D^2t/4$ equals the volume of water occupied by one particle V_w/N thus τ is $4V_w/(NU\pi D^2)$. The sorbed concentration thus tends to follow a saw-tooth history as shown in Figure 3. Now the mean concentration during one sorption-desorption cycle is C_{mo} which is given by

$$C_{mo} = (1/\tau)\int_o^{\tau} C_o dt = C_wK_{oc}\ [1 - (1-\exp(-k\tau))/k\tau] \qquad (9)$$

when $k\tau$ is large, C_{mo} approaches C_wK_{oc}, thus the effective mean K_{oc} or ratio C_{mo}/C_w approaches K_{oc}. When $k\tau$ is small C_{mo} approaches $C_wK_{oc}k\tau/2$ by expanding the series in $\exp(-k\tau)$). Now the critical variable $k\tau$ is given by

$$k\tau = (NU\pi D^2/4V_oK_{oc})(4V_w/NU\pi D^2)) = V_w/(V_oK_{oc}) \qquad (10)$$

thus for small $k\tau$, C_{mo} approaches $C_wV_w/(2V_o)$ and the mean effective K_{oc} is $V_w/(2V_o)$ which, remarkably, is independent of the chemical and of the particle diameter and its velocity. The reason for this independence is that the extent of sorption is controlled only by the encounter rate between particle and solution. Equilibrium is never reached. Faster particles sorb faster but they also collide faster.

The equation for the mean or observed K_{oc} is thus

$$\overline{K_{oc}} = K_{oc}\ [1-(1-\exp(-k\tau))/k\tau] \qquad (11)$$

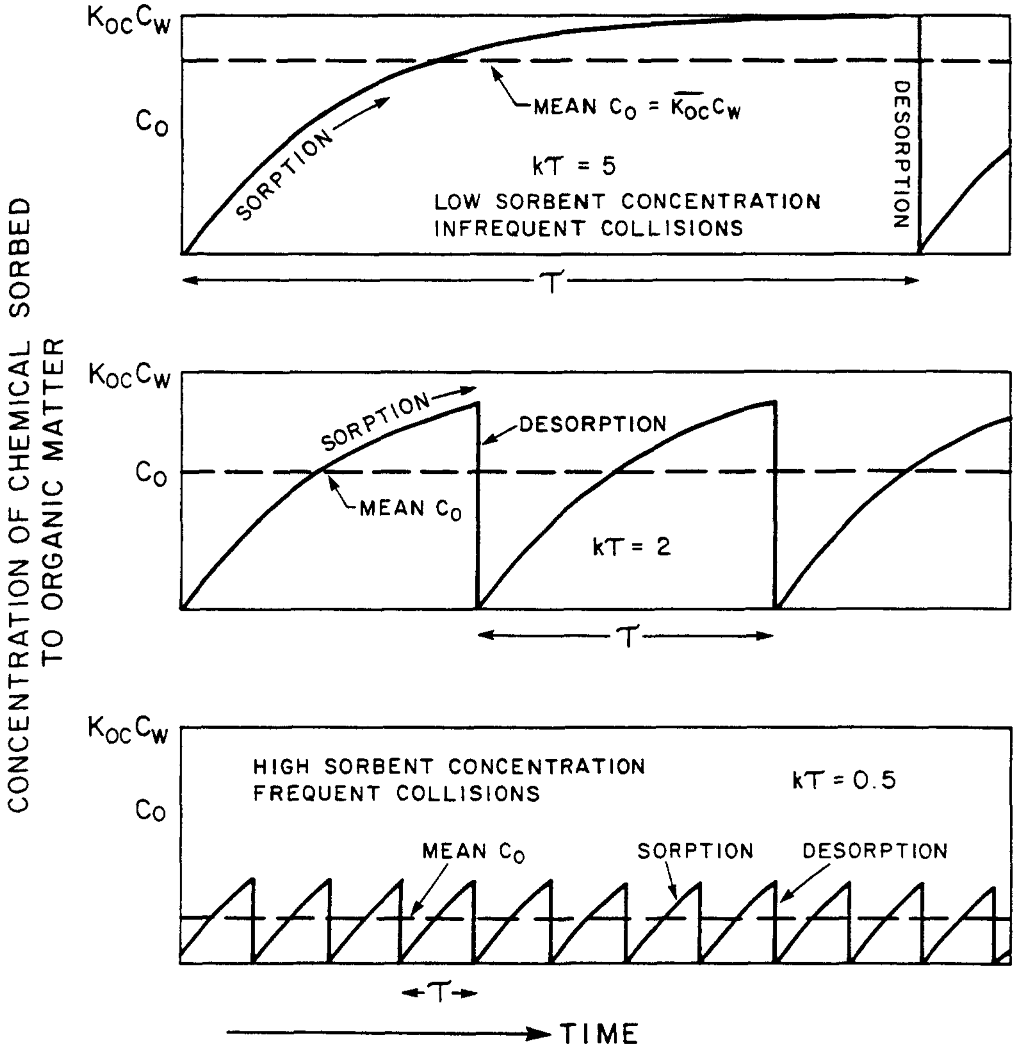

Figure 3: Plot of sorbed concentration variation with time for three values of $k\tau$ illustrating how the "sawtooth" effect at high particle concentrations or short collision intervals τ results in a low mean sorbed concentration.

DISCUSSION

There are significant, but not immediately obvious similarities between equation 11 and equation 6 which was developed by DiToro. It is useful first to establish the relationship between the unit systems. The subscripts refer to water (w), particles (p) and organic matter (o), volumes are in m^3 and densities in kg/m^3.p

$m = V_p\rho_p/1000\ V_w$ kg/L

$f = V_o\rho_o/V_p\rho_p$ mass fraction

$$\Pi_x = 1000\ \overline{K_{oc}}\ f/\rho_o \quad \text{kg/L}$$

$$K_{oc} = 1000\ K_{oc}/\rho_o \quad \text{kg/L}$$

At low particle concentrations (i.e. m is small or kτ large) and particle interactions are unimportant, equations 6 and 11 reduce to the equivalent forms.

$$\Pi_x = fK_{oc}^{x} \text{ and } \overline{K_{oc}} = K_{oc} \tag{12}$$

At high particle concentrations (i.e. m is large or kτ small) and particle interactions dominate, the equations reduce to

$$\Pi_x = \nu_x/m \text{ and } \overline{K_{oc}} = k\tau/2 = V_w/2V_o \tag{13}$$

Thus rearranging and substituting gives

$$\nu_x = m\Pi_x = \overline{K_{oc}}\ V_o/V_w = 1/2 \tag{14}$$

Thus the model developed here predicts that ν_x should be constant, which is observed experimentally. The original definition of ν_x is the ratio of the sorption and particle-induced desorption rates constants. But in this region the rates of sorption and particle induced desorption must be equal, thus from equation 3

$$k_{ads}.c.m = k_{p-d}.\ c{=}m.m \tag{15}$$

$$\text{and} \quad k_{ads}/k_{p-d} = c{=}m/c = 1/2 \tag{16}$$

The implication is that one third of the chemical should be sorbed and two thirds in solution regardless of the nature of the chemical, the particle and the concentration (within limits). In practice ν_x is observed to be larger, approximately 1.0 to 1.5, thus approximately 50 to 70% of the chemical is sorbed, regardless of conditions. This is equivalent to stating that K_{oc} adopts a value of V_w/V_o, thus the product $K_{oc}V_w/V_o$ is always approximately unity. The model predicts a lower extent of sorption than is observed, perhaps because collisions are less than 100% efficient. Incorporating a collision efficiency E into the equations would give a value of ν_x of approximately 0.5/E, thus E appears to be 35 to 50%.

It follows that DiToro's dimensionless partition coefficient and particle concentrations as plotted in Figure 1 are:

$$\Pi_x/fK_{oc}^{x} = \overline{K_{oc}}/K_{oc} = 1 - (1-\exp(-k\tau)/k\tau) \tag{17}$$

$$mfK_{oc}^{x}/\nu = 2\ K_{oc}V_o/V_w = 2/k\tau \tag{18}$$

This is actually a plot of two functions of the variable kτ and a good correlation is not surprising!

The break point in the curve occurs approximately when mfK_{oc}^{x}/ν_x or kτ or V_w/V_oK_{oc} equals unity, i.e. when there is a sufficient concentration of sorbent to sorb half the chemical. At higher sorbent concentrations it is impossible to sorb more than half because the collision induced desorption rate is rapid.

To calculate the extent of sorption in a given situation the easiest procedure is to use DiToro's equation with the mean value of $1/\nu_x$ of 0.7, recognizing that it may be inherently a collision efficiency term. The exponential and DiToro equations are drawn on Figure 1 for comparison and show little difference. The working equation is

$$K_p(\mathrm{kg/L}) = fK_{oc}^{x}/(1 + 0.7\ fK_{oc}^{x}.m) \qquad (19)$$

where the term 0.7 is $1/\nu_x$ or 2E where E is the collision efficiency.

Alternatively, the quantity $k\tau$ can be estimated as $V_w/V_o\ K_{oc}$ using an assumed density for organic matter (which cancels in the product V_oK_{oc}). The low particle concentration organic carbon partition coefficient K_{oc} can then be "corrected to give the mean value using equation 11.

An important consideration is thus the frequency of particle collisions. This is well quantified as a result of coalescence studies as reviewed by Stumm and Morgan[24]. The total collision frequency between like particles is approximately $2^{-18}\ N^2$ collisions/m^3.s where N is the number of particles per m^3. The constant is usually expressed as 2×10^{-12} cm^3/s. If the particle diameter is D and the concentration is m kg/L or $(1000\ m/\rho_p)$ m^3/m^3 then the number of particles is $(1000m/\rho_p)/(\Pi D^3/6)$ or approximately $1.3\ m/D^3$ for ρ_p of 1500 kg/m^3. For example if D is 1 µm and m is 100 mg/L or 10^{-4}kg/L, N will be 1.3×10^{14}. The collision frequency per particle is 2×10^{-18} N collisions/s thus in this case the frequency is 2.6×10^{-4}collisions/s or the interval between collisions τ is approximately one hour. It seems likely that to reach equilibrium would take a time period of several τ, thus short term (1 hour) experiments may not reach equilibrium.

If the particle diameter is 0.1 µm, N increases by a factor of 1000 and τ decreases to 4 seconds. It can thus be argued that the collision theory is valid only for particles less than 1 µm. Larger particles collide too infrequently, except at high concentrations. There is thus a domain of values of m and D in which long equilibration times are expected. In practice it is likely that there will be a spectrum of particle diameters with the smaller particle collisions dominating.

For soils and bottom sediments conditions are static, the particle interaction effect is absent thus the Karickhoff equation should be followed. It is possible that the K_{oc} - K_{ow} relationship is sensitive to the condition of the organic carbon, i.e. its degree of consolidation or density. The mechanism presented here implies that the more open and "fluffy" the organic carbon the closer K_{oc} will approach K_{ow}.

There are several implications that are worthy of note. Organic solutes may seek interfaces other than organic carbon which offer the possibility of a free energy reduction, including the air-water interface, as occurs in sublation. The volatilization process may thus be retarded for hydrophobic organic chemicals because when an eddy of water reaches the surface it may first adjust to a condition in which an appreciable fraction of the solute is "loosely sorbed" at the surface, thus reducing the fugacity driving force. This would be observed as a lower-than-expected mass transfer coefficient. DiToro and Thomann[25] and Richardson[26] have questioned whether the mass transfer coefficients estimated by conventional correlations (eg.

Mackay and Yeun[27]) are of the correct magnitude since their lake mass balances can not be reconciled unless the coefficients are much lower. Sorption phenomena on suspended matter and on the air-water interface may be the cause of this discrepancy. All experimental mass transfer coefficients have been obtained under conditions in which little sorption is expected. How this phenomenon influences bioavailability of dissolved and sorbed chemicals to fish is not known.

There is obviously a need to conduct careful experiments to test the validity of this proposed mechanism, especially to examine the energetics of the sorption, the rate of equilibration, behaviour at low and high sorbent concentrations and the effects of the nature of other surfaces and sorbents.

CONCLUSIONS

A novel conceptual model of the sorption process has been presented which is consistent with DiToro's particle induced desorption hypothesis and yields predictions which are in agreement with experimental observations. The sorption process considered here is viewed as being a loose surface accumulation which can be disrupted by collisions between particles. A mass transfer analysis predicts that when a significant fraction (eg. half) of the sorbate is sorbed, collision-induced desorption becomes important and limits the sorbed concentrations to approximately an equal amount to that in solution. This constaint applies regardless of nature of the particles and the sorbate. The implications regarding the fate of hydrophobic organic chemicals in aquatic systems could be significant because it seems unlikely that a large fraction of organic material can be sorbed from the water column. The effects on volatilization, bioavailability, and sediment deposition are not known. Clearly there is a continuing need to study the fundamental nature of the sorption phenomena which occur when hydrophobic chemicals are exposed to suspended particles in the water column.

ACKNOWLEDGEMENTS

The authors are grateful to NSERC and the Ontario Ministry of Environment for financial support. Dr. D.M. DiToro contributed greatly through many stimulating discussions and by making several perceptive criticisms.

REFERENCES

(1) Karickhoff, S.W. "Semi-Empirical Estimation Estimation of Sorption of Hydrophobic Pollutants on Natural Sediments and Soils". Chemosphere. **1981**, 10(8), 833.

(2) Karickhoff, S.W.; Brown, D.S.; Scott, T.A. "Sorption of Hydrophobic Pollutants on Natural Sediments". Wat. Res. Res.b1979, 13, 241-248.

(3) Lambert, S.M. "Fundamental Relationship Between Sorption in Soil and and Chemical Structure". J. Agric. and Food Chem. **1967**, 15, 572-576.

(4) Briggs, G.C. "A Simple Relationship Between Soils Adsorption of Organic Chemicals and their Octanol-Water Partition Coefficients". Proc. 7th British Insecticide and Fungacide

Conf. **1973**, 83-86.

(5) Karkickhoff, S.W. "Sorption Kinetcs of Hydrophobic Pollutants in Natural Sediments". Contaminants and Sediments, Vol. 2, (ed. R.A. Baker), Ann Arbor Sci. Publ. **1980**, 193-205.

(6) DiToro, D.M.; Horzempa, L.M. "Reversible and Resistant Components of Components of Hexachlorobiphenyl Adsorption-Desorption: Isotherms. Environ. Sci. Technol. **1982**, 16, 594-602.

(7) DiToro, D.M.; Horzempa, L.M. "Reversible and Resistant Components of PCB Adsorption and Desorption: Adsorbent Concentration Effects. J. Great Lakes Res.b1982, 8(2), 336-349.

(8) DiToro, D.M.; Mahony, J.D.; Kirchgraber, P.R.; O'Byrne, A.L.; Pasquale, L.R.; Piccirilli, D.C. "Effects of Nonreversibility, Particle Concentration, and Ionic Strength on Heavy Metal Sorption. Submitted for publication, Envir. Sci. Technol. **1985**.

(9) O'Connor, D.J.; Connolly, J.P. "The Effect of Concentration of Adsorbing Solids on the Partition Coefficient". Water Res. **1980**, 14, 1517-1523.

(10) DiToro, D.M. "A Particle Interaction Model of Reversible Organic Chemical Sorption". Chemosphere. **1985**, 14, 1503-1538.

(11) Voice, T.C.; Rice, CP.; Weber, W.J. Jr. "Effect of Solids Concentration on the Sorptive Partitioning of Hydrophobic Pollutants in Aquatic Systems". Environ. Sci. Technol. **1983**, 17, 513-518.

(12) Gschwend, P.M.; Wu, S. "On the Constancy of Sediment-Water Partition Coefficients of Hydrophobic Organic Pollutants". Environ. Sci. Technol. **1985**, 19(1), 90.

(13) Voice, T.C.; Weber, W.J. "Sorbent Concentration Effects in Liquid/Solid Partitioning. Environ. Sci. Technol. **1985**, 19, 789-796.

(14) Chiou, C.T.; Schmedding, D.W. "Partitioning of Organic Compounds in Octanol-Water Systems". Environ. Sci. Technol. **1982**, 16, 4-10.

(15) Chiou, C.T.; Peters, L.J.; Freed, V.H. "A Physical Concept of Soil-Water Equilibria for Non Ionic Organic Compounds". Science. **1979**, 206, 831-832.

(16) Miller, M.M.; Wasik, S.P.; Huang, G.L.; Shiu, W.Y.; Mackay, D. "Relationships between Octanol Water Partition Coefficient and Aqueous Solubility. Environ. Sci. Technol. **1985**, 19, 522-529.

(17) Freeman, D.H.; Cheung, L.S. "A Gel Partition Model for Organic Desorption From a Pond Sediment. Science. **1981**, 214, 790-792.

(18) Platford, R.F.; Carey, R.F.; Hale, E.J. "The Environmental Significance of Surface Film: Part I Octanol-Water Partitioning Coefficient for DDT and Hexachlorobenzene. Environ. Pollut. Series B. **1982**, 125-128.

(19) Platford, R.F.; Carey, R.F.; Hale, E.J. "The Environmental Significance of Surface Film: Part II Enhanced Partitioning of Lindane in Thin Films of Octanol on the Surface of Water. Chemosphere. **1981**, 10, 719-722.

(20) Drazd, J.; Vejrosta, J.; Novak, J.; Jaensson, J.A. "Spurious Adsorption Effects in Headspace - Gas Determination of Hydrocarbons in Water". J. Chromatog. **1982**, 245, 185-192.

(21) Wilson D.J.; Valsaraj, K.T. "Removal of Refractory Organic by Aeration II A Fast Algorithms for Modelling Solvent Sublation Columns". Sep. Sci. Tech. **1982**, 17, 1387-1396. See also, 18, 941-966.

(22) Valsaraj, K.T.; Wilson, D.J. "Removal of Refractory Organics by Aeration IV Solvent Sublation of Chlorinated Organics and Nitrophenols. Colloids and Surfaces. **1983**, 8, 203-221.

(23) Sodergren, A.; Larsson, P. "Transport of PCBs in Aquatic Laboratory Model Ecosystem from Sediment to the Atmosphere via the Surface Microlayer". Ambio. **1981**, 10, 41-45.

(24) Stumm, W.; Morgan, J.J. "Aquatic Chemistry". 2nd Ed. Wiley, N.Y. **1981**.

(25) Thomann, R.V.; DiToro, D.M. "Physico-Chemical Model of Toxic Substances in the Great Lakes". J. Great Lakes Res. **1983**, 9, 474-496.

(26) Richardson, W.L.; Smith, V.E.; Wellington, R. "Dynamic Mass Balance of PCB and Suspended Solids in Saginaw Bay - A Case Study in Physical Behavior of PCBs in the Great Lakes". (D. Mackay, S. Paterson, S.J. Eisenreich and M.S. Simmons, Eds.) Ann Arbor Science. Ann Arbor, MI. **1983**, 329-366.

(27) Mackay, D.; Yeun, A.T.K. "Mass Transfer Coefficient Correlations for Volatilization of Organic Solutes from Water". Environ. Sci. Technol. **1983**, 17, 211-217.

(Received in Germany 3 July 1986; accepted 26 October 1986)