Sediment—Water Distribution of Organic Contaminants in Aquatic Ecosystems: The Role of Organic Carbon Mineralization

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The distribution between sediments and water plays a key role in the food-chain transfer of hydrophobic organic chemicals. Current models and assessment methods of sediment-water distribution predominantly rely on chemical equilibrium partitioning despite several observations reporting an "enrichment" of chemical concentrations in suspended sediments. In this study we propose and derive a fugacity based model of chemical magnification due to organic carbon decomposition throughout the process of sediment diagenesis. We compare the behavior of the model to observations of bottom sediment-water, suspended sediments-water, and plankton-water distribution coefficients of a range of hydrophobic organic chemicals in five Great Lakes. We observe that (i) sedimentwater distribution coefficients of organic chemicals between bottom sediments and water and between suspended sediments and water are considerably greater than expected from chemical partitioning and that the degree sedimentwater disequilibrium appears to follow a relationship with the depth of the lake; (ii) concentrations increase from plankton to suspended sediments to bottom sediments and follow an inverse rather than a proportional relationship with the organic carbon content; and (iii) the degree of disequilibrium between bottom sediment and water, suspended sediments and water, and plankton and water increases when the octanol-water partition coefficient K_{OW} drops. We demonstrate that these observations can be explained by a proposed organic carbon mineralization model. Our findings imply that sediment-water distribution is not solely a chemical partitioning process but is to a large degree controlled by lake specific organic carbon mineralization processes.

Introduction

The exchange and/or partitioning between sediment and water plays an important role in the uptake and accumulation of organic chemicals in organisms of aquatic food-chains (1). High sediment concentrations relative to those in the water can result in predominant transfer of chemical from the sediments through the benthic food-chain into organisms of higher trophic levels, whereas relatively low concentrations in sediments favors uptake directly from the water (via the

10.1021/es020925+ CCC: \$25.00 © 2003 American Chemical Society Published on Web 01/11/2003

respiratory surface of organisms, e.g. gills) or indirectly through dietary transfer via the pelagic food-chain. The degree of sediment-water partitioning of a substance therefore plays a key role in the development of sediment quality criteria [e.g. ref 2], the application of Biota Sediment Accumulation Factors (BSAFs) in risk assessments [e.g. ref 3], modeling the environmental fate (4-7) and food-chain bioaccumulation [e.g. refs 1 and 8] of pollutants. Current descriptions of the sediment-water exchange of organic chemicals include equilibrium based partitioning in organic carbon (9-11) and soot carbon (12) and particle-interaction models (13) as well as compartmental kinetic models (4, 6, 7) accounting for deposition and resuspension. The equilibrium models assume that the fugacity of organic substances in sediments (f_S) equals that in the water (f_W) . However, a number of authors have reported an enrichment of aromatic hydrocarbons on settling particles (5, 14-17), indicating that $f_{\rm S}$ may exceed $f_{\rm W}$. A similar enrichment has been observed in intestines of fish, where digestion of organic matter is associated with an elevation of chemical fugacities (18, 19). Organic carbon breakdown during the sediment diagenesis (20) may cause a similar increase in fugacity and create disequilibria between sediment and water. It can therefore be hypothesized that as a result of organic carbon decomposition, chemical concentrations on suspended and bottom sediments are being elevated to levels that are beyond their chemical equilibrium levels with the water. The degree of elevation may depend on the carbon-cycling and budget in the system, which varies between lakes, rivers, and estuaries. To test this hypothesis, we propose a mechanistic model to describe the role of organic carbon utilization on the distribution of organic chemicals between sediments and water and test the model against reported field data from five lakes in Canada and the United States.

Theory

General. Our hypothesis is that the sediment-water distribution of hydrophobic organic substances in lakes is closely linked to the degree of organic carbon decomposition. Phytoplankton and algae absorb organic substances as a result of organic carbon-water partitioning (21, 22). These primary producers undergo organic carbon decomposition as they settle through the lake's water column and reside in surface sediments. The organic carbon decomposition changes the amount and character of the organic carbon in a way that enriches the concentration of hydrophobic organic chemicals beyond their equilibrium partition concentrations. This process acts like a "pump" of chemical activity increasing concentrations above their chemical equilibrium concentrations. To explain and formalize this hypothesis we will first present a model and test it against six independent data sets for five large lakes.

Fugacity Approach. Our model and analysis follows the fugacity approach (*23*). The merit of the fugacity analysis is that the concentrations in the various media are expressed on a common or "normalized" basis. This allows us to compare observed concentrations to their chemical equilibrium values. The fugacity *f* is viewed as the escaping tendency of the chemical substance. It is the pressure that the chemical potential of a chemical substance in a medium. It is related to the concentration *C* (mol/m³) as *C/Z* (*23*). *Z* is the fugacity capacity (mol/m³·Pa), which can be viewed as the ability of the medium to solubilize the chemical substance. If a substance in media 1 and 2 is at a chemical equilibrium, then (i) $f_1 = f_2$, (ii) the fugacity ratio $F_{12} =$

VOL. 37, NO. 4, 2003 / ENVIRONMENTAL SCIENCE & TECHNOLOGY = 735

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FIGURE 1. Conceptual model of the fate of organic chemicals throughout the process of sediment diagenesis.

 $f_1/f_2 = 1$, and (iii) the ratio of the chemical concentrations in the media (i.e. the distribution coefficient K_{12}) is equal to the chemical's equilibrium partition coefficient K_{12}^* , which by definition is the ratio of the chemical's fugacity capacities Z_1/Z_2 :

$$K_{12} = C_1 / C_2 = f_1 \cdot Z_1 / f_2 \cdot Z_2 = (f_1 / f_2) \cdot (Z_1 / Z_2) = F_{12} \cdot K_{12}^* \quad (1)$$

Equation 1 illustrates that one can express the equilibrium status in water, plankton, and suspended and bottom sediments, by comparing the distribution coefficients from reported concentration data for bottom sediments and water ($K_{BSW} = C_{BS}/C_W$), suspended sediments and water ($K_{SSW} = C_{SS}/C_W$), and plankton and water ($K_{FW} = C_P/C_W$) to the equilibrium partition coefficients between bottom sediments and water (K_{SSW}^*), and plankton and water (K_{FW}^*) with the goal to determine the corresponding fugacity ratios F_{BSW} , F_{SSW} , and F_{PW} .

Model. Figure 1 presents a conceptual diagram of the hypothesized fate of organic chemicals as a result of organic carbon decomposition during sediment diagenesis. The model distinguishes between phytoplankton or algae in surficial water, suspended sediments in bottom water, and bottom sediments in interstitial or pore water. Uptake in phytoplankton and algae is expressed by the following fugacity based differential equation

$$dX_{\rm P}/dt = D_{\rm PW} \cdot f_{\rm SW} - (D_{\rm PW} + D_{\rm G} + D_{\rm P}) \cdot f_{\rm P}$$
(2)

where X_P is the chemical mass (mol) in the phytoplankton biomass, D_{PW} , D_G , and D_P are the transport parameters (mol/ Pa·d) for plankton–water exchange, growth, and phytoplankton sedimentation, respectively, and f_{SW} and f_P are the fugacities (Pa) in surficial water and phytoplankton respectively, *t* is time (d). dX_P/dt represents the net change in the chemical mass (mol/day) in the phytoplankton/algae biomass; D_{PW} . f_{WS} is the uptake of chemical from the water (mol/ day) via passive diffusion; D_{PW} . f_P is the chemical elimination (mol/day) from the organism to the water through passive diffusion; D_G . f_P represents the quasi-elimination of chemical (mol/day) through "growth dilution" (e.g. during blooms) when the growth rate exceeds the rate of chemical uptake (24); and $D_{P} \cdot f_{P}$ is the chemical mass that is removed (mol/day) from the phytoplankton biomass through deposition. Under steady-state conditions ($dX_{P}/dt = 0$), the chemical fugacity in the phytoplankton and algae can then be expected to follow the following relationship with the surficial water fugacity f_{SW} :

$$F_{\rm PW} = f_{\rm P}/f_{\rm SW} = D_{\rm PW}/(D_{\rm PW} + D_{\rm G} + D_{\rm P})$$
 (3)

Equation 3 illustrates that when the chemical exchange rate (D_{PW}) between the organism and water is large relative to the rates of growth dilution (D_G) and sedimentation (D_{PW}) , the chemical substance can be expected to achieve a chemical equilibrium, where $F_{PW} = 1$. This is likely the case for lower \vec{K}_{OW} substances, which appear to achieve equilibria quickly in laboratory tests (21, 24). However, when K_{OW} increases, chemicals typically require longer times to achieve chemical equilibria, indicating that the organism-to-water exchange rate D_{PW} falls with increasing K_{OW} compared to D_G and D_P which are not a function of K_{OW} (22, 24). For those substances, sedimentation and growth become increasingly more important causing F_{PW} to fall below 1.0. The latter is consistent with observation that plankton-water distribution coefficients fail to increase with increasing K_{OW} for high K_{OW} substances (22)

When phytoplankton and macrophytes decompose or are consumed by higher organisms, their remains (i.e. dead and degrading cells and fecal pellets) become part of what we will refer to (for simplicity) as the suspended sediments mass. The mass balance for the chemical concentration in the suspended solids can be described as

$$dX_{SS}/dt = D_{P} \cdot f_{P} + D_{SSW} \cdot f_{BW} + D_{RES} \cdot f_{BS} - (D_{SSW} + D_{S}) \cdot f_{SS}$$
(4)

where X_{SS} is the mass (mol) of chemical in the suspended sediment mass, D_{SSW}, D_{RES}, and D_S are the transport parameters (mol/Pa·d) for suspended sediment-water exchange (i.e. for suspended sediment-to-water and water-to-suspended sediment), bottom sediment resuspension, and suspended solid sedimentation, respectively, and f_{BW} , f_{BS} , and f_{SS} are the fugacities (Pa) in bottom water, bottom sediments, and suspended sediments, respectively. $D_{\rm P}.f_{\rm P}$ is the flux of chemicals associated with plankton entering the decomposition process. $D_{SSW} \cdot f_{BW}$ is the flux of chemical partitioning from the bottom water to the suspended solids. $D_{\text{RES}} \cdot f_{\text{BS}}$ is the chemical flux associated with bottom sediments entering the suspended sediments pool. $D_{SSW} \cdot f_{SS}$ is the flux of chemical desorbing from the suspended sediments into the bottom water, and $D_{\rm S}$ f_{SS} is the flux of suspended solids settling into the bottom sediments. Under steady-state conditions $(dX_{ss}/dt = 0)$, this equation becomes

$$F_{\text{SSW}} = f_{\text{SS}}/f_{\text{BW}} = \{D_{\text{P}} \cdot (f_{\text{P}}/f_{\text{BW}}) + D_{\text{SSW}} + D_{\text{RES}} \cdot (f_{\text{BS}}/f_{\text{BW}})\}/(D_{\text{SSW}} + D_{\text{s}})\}$$
(5)

To illustrate the mechanism of interest, eq 5 can be simplified by assuming that the water column is well mixed (i.e. $f_{SW} = f_{BW} = f_W$) and that the introduction of bottom sediments to the suspended sediment mass through resuspension is insignificant (i.e. $D_{RES} = 0$). This gives

$$F_{\rm SSW} = (D_{\rm P} \cdot (f_{\rm P}/f_{\rm W}) + D_{\rm SSW})/(D_{\rm SSW} + D_{\rm S}) \tag{6}$$

and illustrates that if suspended sediment-to-water exchange (i.e. desorption) is fast compared to sediment diagenesis (i.e. $D_{SSW} \gg D_P$ and D_S), F_{SSW} can be expected to reach 1, i.e., a chemical equilibrium. However, if the desorption kinetics (D_{SSW}) are slow compared to the rate of deposition (D_P) and sedimentation (D_S), i.e., $D_{SSW} \ll D_P$ and D_S , then F_{SSW} will approach $(D_P/D_S) \cdot (f_P/f_W)$. D_P is $Q_P \cdot Z_P$ where Q_P is the flow of phytoplankton and/or macrophytes (e.g. in units of m³/day) that is being digested and Z_P is the fugacity capacity (mol/ m³·Pa) of phytoplankton. Assuming that organic carbon (including lipids) is the main site for storage of organic chemicals in plankton, $Q_{\rm P} \cdot Z_{\rm P}$ is approximately equal to $Q_{\rm POC} \cdot$ Z_{POC} , i.e., the product of the flux of planktonic organic carbon $Q_{\rm POC}$ (m³/day) and the fugacity capacity (mol/m³·Pa) of the planktonic organic carbon $Z_{POC} \cdot D_S$ is $Q_{SS} \cdot Z_{SS}$ where Q_{SS} is the flow of suspended sediments settling into the bottom sediments (m^3/day) and Z_{SS} is the fugacity capacity (mol/ m³·Pa) of the suspended solids. Assuming that organic carbon is also the main site for storage of organic chemicals in suspended sediments, Q_{SS} , Z_{SS} is approximately equal to Q_{SSOC} . Z_{SSOC} , i.e., the product of the flux of suspended sediment associated organic carbon Q_{SSOC} (m³/day) and the fugacity capacity (mol/m³·Pa) of the organic carbon in suspended sediments Z_{SSOC}.

$$F_{\text{SSW}} = (D_{\text{P}}/D_{\text{S}}) \cdot (f_{\text{P}}/f_{\text{W}}) = (Q_{\text{P}}/Q_{\text{SS}}) \cdot (Z_{\text{P}}/Z_{\text{SS}}) \cdot (f_{\text{P}}/f_{\text{W}}) \approx (Q_{\text{POC}}/Q_{\text{SSOC}}) \cdot (Z_{\text{POC}}/Z_{\text{SSOC}}) \cdot (f_{\text{P}}/f_{\text{W}})$$
(7)

Equation 7 illustrates that the decomposition of planktonic organic carbon will cause $Q_{\rm SSOC} < Q_{\rm POC}$ and $(Q_{\rm POC}/Q_{\rm SSOC}) >$ 1.0. In essence, the organic carbon decomposition of the plankton causes an enrichment of the chemical concentration because the organic carbon content falls, while the amount of chemical contaminant in the organic carbon does not fall accordingly. The latter occurs because the predating organism(s) will approach an equilibrium with the digested organic carbon, which reduces net chemical transfer from the digested organic carbon to zero (at equilibrium) as long as diffusion is the main mechanism of transport.

A further enrichment occurs as a result of the change in composition of organic matter due to the decomposition process. Because more easily digestible lipids and oils are more efficiently extracted and digested by predating organisms than less digestible organic matter, the organic matter content of the suspended solids is likely transforming from a more "liquid" to a more "crystalline" state. The "crystalline" organic carbon is expected to have a lower solubility and fugacity capacity for hydrophobic organic substances than the "liquid" organic carbon. Hence Z_{SSOC} is likely less than Z_{POC} , and the ratio $Z_{\text{POC}}/Z_{\text{SSOC}} > 1.0$ and $F_{\text{SSW}} > F_{\text{PW}}$.

When the suspended sediments settle into the bottom sediment, additional organic carbon decomposition takes place as microorganisms, deposit feeding invertebrates, fish, and other organisms further digest the sediments. The removal of organic carbon from settled suspended solids can be expected to decrease the fugacity capacity and volume of the particulate matter in a similar fashion as described above for suspended sediments. This can be expected to cause an increase in fugacity if chemical desorption to interstitial water or by uptake of sediment ingesting organisms is low. This can be described by

$$\mathrm{d}X_{\mathrm{BS}}/\mathrm{d}t = D_{\mathrm{S}} \cdot f_{\mathrm{SS}} + D_{\mathrm{BSW}} \cdot f_{\mathrm{IW}} - (D_{\mathrm{BSW}} + D_{\mathrm{RES}} + D_{\mathrm{BUR}}) \cdot f_{\mathrm{BS}}$$
(8)

where X_{BS} is the mass (mol) of chemical in the bottom sediments, D_{BSW} and D_{BUR} are the transport parameters (mol/ Pa·d) for bottom sediment–water exchange (i.e. for bottom sediment-to-water and water-to-bottom sediment) and sediment burial, respectively, and f_{IW} is the fugacity (Pa) in interstitial water. D_{S} · f_{SS} is the chemical flux through settling of suspended sediments into bottom sediment. D_{BSW} · f_{IW} is the flux of chemical diffusion from the interstitial water into the bottom sediment solids. D_{BSW} · f_{SS} is the flux of chemical desorbing from the bottom sediment solids into interstitial water. D_{RES} · f_{ES} is the flux of chemical leaving the bottom sediments through resuspension, and D_{BUR} is the chemical flux leaving the active sediment layer through accretion. Under steady-state conditions, eq 8 becomes

$$F_{\rm BSW} = f_{\rm BS}/f_{\rm W} = \{D_{\rm S} \cdot (f_{\rm SS}/f_{\rm W}) + D_{\rm BSW} \cdot (f_{\rm IW}/f_{\rm W})\} / (D_{\rm BSW} + D_{\rm RES} + D_{\rm BUR})\}$$
(9)

If the exchange of chemical between the interstitial water and bottom sediments is small relative to respectively suspended sediment settling and burial, eq 9 simplifies to

$$F_{\rm BSW} = (D_{\rm S}/(D_{\rm RES} + D_{\rm BUR})) \cdot (f_{\rm SS}/f_{\rm W}) \tag{10}$$

The ratio $D_{\rm S}/(D_{\rm RES} + D_{\rm BUR})$ represents the ecosystem's natural capacity for chemical magnification in bottom sediments. As explained earlier, $D_{\rm S}$ (which is $Q_{\rm S} \cdot Z_{\rm SS}$) can be approximated by $Q_{\rm SSOC} \cdot Z_{\rm SSOC}$. In a similar fashion, $D_{\rm RES}$ and $D_{\rm BUR}$ represent $Q_{\rm RES} \cdot Z_{\rm BS}$ and $Q_{\rm BUR} \cdot Z_{\rm BS}$, respectively, where $Q_{\rm RES}$ is the rate of bottom sediment resuspension (in m³/day), and $Z_{\rm BS}$ is the fugacity capacity of the bottom sediments. Because of the association of hydrophobic organic contaminants with organic carbon, $Q_{\rm RES} \cdot Z_{\rm BS}$ and $Q_{\rm BUR} \cdot Z_{\rm BS}$ approximate $Q_{\rm ROC} \cdot Z_{\rm BSOC}$ and $Q_{\rm BOC} \cdot Z_{\rm BSOC}$, respectively, where $Q_{\rm ROC}$ is the rate of organic carbon resuspension (in m³/day), $Q_{\rm BUR}$ is the rate of organic carbon burial (in m³/day), and $Z_{\rm BSOC}$ is the fugacity capacity (mol/m³·Pa) of the organic carbon in bottom sediments. This transforms eq 10 into

$$F_{\text{BSW}} = f_{\text{BS}}/f_{\text{W}} = (Q_{\text{S}}/(Q_{\text{RES}} + Q_{\text{BUR}})) \cdot (Z_{\text{SS}}/Z_{\text{BS}}) \cdot (f_{\text{SS}}/f_{\text{W}}) \approx (Q_{\text{SSOC}}/(Q_{\text{ROC}} + Q_{\text{BSOC}})) \cdot (Z_{\text{SSOC}}/Z_{\text{BSOC}}) \cdot (f_{\text{SS}}/f_{\text{W}}) \quad (11)$$

Since digestion of settled suspended sediments deprives the sediments of organic carbon and given that organic carbon is the predominant site for chemical accumulation in bottom and suspended sediments, Z_{BS} can be expected to be lower than Z_{SS} , elevating F_{BSW} over F_{SSW} and f_{BS} over f_{SS} . In terms of organic carbon fluxes, $Q_{ROC} + Q_{BSOC}$ can be expected to be less than $Q_{\rm SSOC}$ due to organic carbon utilization by benthic organisms. Since resuspension essentially reintroduces particulate matter in the pool of suspended sediments, the ratio $(Q_{\rm SSOC}/Q_{\rm BSOC}) \cdot (Z_{\rm SSOC}/Z_{\rm BSOC})$ represents the maximum magnification of the chemical fugacity in the suspended sediments that can be achieved in the bottom sediments. This maximum magnification is not always achieved with chemical loss rates from the bottom sediments to the water column and uptake (possibly followed by metabolic transformation) in sediment ingesting organisms reducing the degree of magnification.

This model illustrates that the association of hydrophobic organic contaminants with organic carbon in aquatic ecosystems results in a tendency for hydrophobic organic chemicals to be magnified as a result of organic carbon mineralization: Hydrophobic organic chemicals associate with primary producers (phytoplankton, algae, macrophytes) by simple physicochemical partitioning and then are magnified each time the organic matrix in which they reside is broken down. The maximum chemical magnification potential in bottom sediments may therefore depend on the degree of primary production and organic mineralization in the system and may be approximated as the ratio of the rates of organic carbon production and burial $\Phi = (Q_{POC}/Q_{BSOC})$ and the planktonic organic carbon/bottom sediment organic carbon partition coefficient $K_{PBOC} = (Z_{POC}/Z_{BSOC})$.

$$F_{\text{BSW}} = (Q_{\text{POC}}/Q_{\text{BSOC}}) \cdot (Z_{\text{POC}}/Z_{\text{BSOC}}) \cdot (f_{\text{P}}/f_{\text{W}}) = \Phi \cdot K_{\text{PBOC}} \cdot (f_{\text{P}}/f_{\text{W}}) \quad (12)$$

This ratio is likely to vary between various aquatic ecosystems with higher values for systems with a greater degree of organic carbon decomposition. To test the model, we compare the distribution coefficients K_{PW} , K_{SSW} , and K_{BSW} to their corresponding equilibrium partition coefficients K_{PW} , K_{SSW} , and K_{BSW} and determined the fugacity ratios for a range of organic pollutants in five large Lakes.

Empirical Observations

Lake Ontario. Two independent data sets from Lake Ontario were analyzed. The first data set (A) was collected between 1981 and 1986 at several sampling locations throughout the lake (25). Concentrations of 40 individual PCB congeners and 18 organochlorine pesticides were reported in water, plankton, suspended sediments, and bottom sediments and used in the analysis. Since water samples were centrifuged prior to chemical analysis, reported water concentrations reflect operationally defined freely dissolved water concentrations. The mean lipid content of plankton was reported as 0.5% (n = 3). The organic carbon content of suspended sediment was not reported and was assumed to be 10.0%. Mean organic carbon content of bottom sediment was $2.7 \pm 1.4\%$ (n = 38). Error terms represent 1 standard deviation. A second data set (B) of PCB concentrations in Lake Ontario (26) was used. Data were collected between 1992 and 1993, at several sampling locations in the central portion of the lake. Twenty-six individual PCB congeners ranging in log K_{ow} from 5.6 to 8.3 were reported in water, plankton, and bottom sediment and were used in the analysis. Mean lipid content of plankton was reported as $0.90 \pm 0.30\%$ (n=4). Organic carbon content of bottom sediment was not reported and was assumed to be equal to that in ref 25.

Lake Superior. Concentrations of 28 PCB congeners ranging in log K_{ow} from 4.9 to 7.6 in water and suspended sediment for Lake Superior were obtained from ref 27. PCB concentrations were measured throughout Lake Superior in 1980 and in western Lake Superior in 1983. Suspended sediment exhibited a mean organic carbon content of 15.98 \pm 11.42% (n = 18). Individual means for the 2 years were not reported, so the same value for organic carbon content was used for both years.

Lake Erie. PCB concentration data for water, plankton, and bottom sediment from western Lake Erie were obtained from refs 28 and 29. Twenty-five individual PCB congeners (log K_{ow} from 5.6 to 7.6) in water, plankton, and bottom sediment were used. The mean lipid content of Lake Erie plankton was $1.2 \pm 0.24\%$ (n = 5). Mean organic carbon content of Lake Erie bottom sediment was $7.4 \pm 1.78\%$ (n = 9).

Green Bay of Lake Michigan. Concentrations of 64 individual PCB congeners in water (n = 183), plankton (n = 114), and bottom sediments (i.e. top 1 cm, n = 85) collected in 1989 and 1990 were gathered from the USEPA Great Lakes National Program Office (*30*). Dissolved water concentrations were used for the calculation of the distribution coefficients. The mean organic carbon content of plankton was 2.0 ± 1.1 kg organic carbon/kg wet weight sample, and the mean organic carbon content of dry sediments was $5.68 \pm 2.70\%$.

Lake St. Clair. Water and bottom sediment chemical concentration data were obtained for Lake St. Clair from ref *31.* Pentachlorobenzene, hexachlorobenzene, octachlorostyrene, and PCB congeners 52, 101, and 153 were reported in water (n = 3) and bottom sediment (n = 6). Water concentrations were collected using a sparging apparatus (*32*) and are therefore expected to reflect freely dissolved chemical concentrations. Mean organic carbon content of the bottom sediment was $3.96 \pm 2.21\%$ (n = 6).

Equilibrium Partition Coefficients. Plankton–water equilibrium partition coefficients K_{PW}^* were derived (i) for Lakes Ontario and Erie from (i) the reported lipid contents L_P (in kg lipid/kg plankton) of the plankton (i.e. no organic carbon content were reported) and the lipid–water partition coef-

ficient K_{LW} , which was assumed to be equal to the octanolwater partition coefficient K_{OW} and (ii) for Green Bay from reported organic carbon contents OC_P (in kg organic carbon/ kg plankton) of the plankton and the organic carbon-water partition coefficient K_{OC} , which was assumed to be equal to K_{OW} :

$$K_{\rm PW}^* = L_{\rm P} \cdot K_{\rm LW} = L_{\rm P} \cdot K_{\rm OW} \quad \text{and} \\ K_{\rm PW}^* = {\rm OC}_{\rm P} \cdot K_{\rm OC} = {\rm OC}_{\rm P} \cdot K_{\rm OW} \quad (13)$$

One of the difficulties characterizing K_{PW}^* is that the plankton samples collected in the field studies include a mixture of phyto- and zooplankton, diatoms, and suspended matter. While the equilibrium partition coefficient in zooplankton may be appropriately characterized by lipid-water partitioning, the equilibrium partition coefficient in phytoplankton is better characterized by an organic carbonwater partition coefficient (22). The plankton-water partition coefficient is probably best assessed by recognizing the sorptive capacities of both lipid and organic matter other than lipid. However, both lipid and organic carbon data are not available for any of the data sets. The application of eq 13 for Lakes Ontario and Erie therefore introduces an error in K_{PW}^* . This error is not expected to have a large effect on $F_{\rm PW}$, as $F_{\rm PW}$ is determined as $K_{\rm PW}/K_{\rm PW}^*$ and both $K_{\rm PW}$ and $K_{\rm PW}^*$ are normalized to either organic carbon or lipids in a similar manner and hence contain a similar error, which tends to cancel out. The density of plankton was assumed to be 1.1 kg/L.

Seth et al. (*33*) reviewed sediment–water partition coefficient at equilibrium and recommended that equilibrium sediment water partition coefficients for suspended (K_{SSW}^*) and bottom sediments (K_{BSW}^*) are related to K_{OW} according to

$$K_{\rm SSW}^* = \phi_{\rm SS} \cdot 0.35 \cdot K_{\rm OW} \cdot d_{\rm SS} \quad \text{and} \\ K_{\rm BSW}^* = \phi_{\rm BS} \cdot 0.35 \cdot K_{\rm OW} \cdot d_{\rm BS} \quad (14)$$

where ϕ_{SS} and ϕ_{BS} are the organic carbon contents of the suspended sediments and bottom sediments, respectively, and d_{SS} and d_{BS} are the densities (in kg/L) of the suspended or bottom sediments, respectively, and were assumed to be 1.5 kg/L. The constant 0.35 expresses the degree to which organic carbon mimics octanol. Seth et al. (*33*) suggested that there may be some variability in this value and suggested maximum and minimum values of 0.89 and 0.14, respectively. Equation 3 was used to determine K_{BSW}^* , and K_{SSW}^* . K_{ow} values were taken from ref *34* for PCB congeners, ref *35* for octachlorostyrene, and ref *36* for all other substances.

Results

Figure 2 shows distribution coefficients, equilibrium partition coefficients, and corresponding fugacity ratios in the lakes as a function of K_{OW}. For Lake Ontario (data set A), it shows that that without normalizing the data to organic carbon or lipid content, bottom sediment-water distribution coefficients are greater than those for suspended sediments, which in turn are greater than those for plankton. The fugacity ratios illustrate that normalizing the concentrations to organic carbon and lipid content increases the differences between the distribution coefficients. An analysis of variance shows that differences between fugacity ratios in bottom sediments, suspended sediments, and plankton are statistically significant (P < 0.05). Substances with low K_{OW} exhibit distribution coefficients that are orders of magnitude greater than their corresponding equilibrium partition coefficients. The discrepancy between the actual distribution coefficients and the equilibrium partition coefficients drops with increasing $K_{\rm OW}$. Only chemicals with the highest $K_{\rm OW}$ values exhibit distribution coefficients that are comparable to the equi-



FIGURE 2. Observed distribution coefficients, partition coefficients (marked with a *) in units of L/kg dry weight (for bottom and suspended sediments and L/kg wet weight for plankton), and corresponding fugacity ratios of organochlorines between bottom sediments—water (BS), suspended sediments—water (SS), and plankton—water (PW) in five lakes as a function of K_{0W} . Solid lines represent linear regression of the data. Dotted lines represent partition coefficients. Striped lines represent chemical equilibrium, i.e., a fugacity ratio of 1.0.

librium partition coefficients. This is reflected by the fugacity ratios, which drop with increasing $K_{\rm OW}$ from values as high as 10 000 to ratios close to 1.0 and less than 1.0 for plankton.

Data for Lake Ontario from ref 26 (data set B) show that bottom sediment—water distribution coefficients are greater than plankton—water distribution coefficients. Sediment water partition coefficients do not appear to show a statistically significant relationship with K_{OW} . They are greater than their corresponding equilibrium partition coefficients, and their fugacity ratios exceed 1.0. Plankton—water distribution coefficients also do not show a statistically significant correlation with K_{OW} . For the lower K_{OW} chemicals, they are greater than their corresponding partition coefficients, while for the higher K_{OW} substances, they tend to be lower than the equilibrium partition coefficients, giving fugacity ratios larger than 1.0 for the lower K_{OW} substances and values below 1.0 for the higher K_{OW} substances. Fugacity ratios in plankton and bottom sediment both fall with increasing K_{OW} .

In Lake Superior, the logarithm of the suspended sediment—water partition coefficients collected in 1980 shows a slight but statically insignificant drop with increasing log K_{OW} . Similar data collected in 1983 illustrate a small and statistically significant increase of the logarithm of the suspended sediment—water partition coefficient with log K_{OW} . However, similar to the data for Lake Ontario, the suspended sediment—water distribution coefficients in lake Superior are in most cases considerably greater than their equilibrium partition coefficients. This is reflected by fugacity ratios greater than 1. The magnitude of the fugacity ratio differed substantially between 1980 and 1983 with greater fugacity ratios for 1980.

In Lake Erie, bottom sediment-water distribution coefficients exceed plankton-water distribution coefficients by approximately 10-fold, and all but one observation indicates that plankton—water and bottom sediment—water distribution coefficients are greater than their corresponding equilibrium partition coefficient, i.e., fugacity ratios > 1. Fugacity ratios for plankton and bottom sediments also fall with increasing K_{OW} .

In Green Bay, the bottom sediment—water distribution coefficient exceed their equilibrium partition coefficients for the lower K_{OW} PCBs. With increasing K_{OW} this discrepancy becomes smaller, and K_{BSW} starts to fall below K_{BSW}^* when log K_{OW} exceeds approximately 7.0. Plankton—water distribution coefficients are in reasonable agreement with their equilibrium partition coefficients up to a log K_{OW} of 7.0 and then drop below their equilibrium partition coefficients.

Bottom sediment—water distribution coefficients in Lake St. Clair also appear to be greater than their corresponding equilibrium partition coefficients. When freely dissolved instead of the total water concentrations are used to determine the sediment—water distribution, the distribution coefficients of the higher K_{OW} chemicals are slightly larger, while for the lower K_{OW} chemicals there is no difference in the distribution coefficients. Fugacity ratios dropped from approximately 10 for pentachlorobenzene to approximately 1.0 for PCB153.

Discussion

Three general observations can be made. First, distribution coefficients of organic chemicals between bottom sediments and water and also between suspended sediments and water are generally greater than would be expected from chemical partitioning. Similar observations have been reported for other locations (11, 12, 15-17). These findings are consistent

with the organic decomposition model shown earlier, which predicts sediment-water distribution ratios to exceed their equilibrium partitioning values because of organic carbon decomposition. For example, in Lake Ontario the autochthonous whole in-lake mean annual primary productivity between 1987 and 1992 was estimated at 173.6 \pm 26.6 g $carbon/m^2$ (37) and likely somewhat higher (i.e. approximately 200 g carbon/m² due to higher phosphorus inputs) between 1981 and 1986 when Lake Ontario data set A was collected. Other organic carbon inputs through inputs from rivers runoff and atmospheric deposition further contribute to the organic carbon flux into the lake. The annual organic carbon burial rate can be estimated at 9.8 g carbon/ m^2 (i.e. $1000 \times C_{SS} \times v_{bur} \times A_{BS} \times OC_{BS}$ where C_{SS} is the concentration of sediment solids in sediments [i.e 0.16 kg/L], v_{bur} is the mass transfer coefficient for sediment burial [i.e. 6.2×10^{-6} m/d], A_{BS} is the surface area of the bottom sediment $[1.17\times 10^{10}\mbox{ m}^2]$, and OC_{BS} is the organic carbon content of the bottom sediments i.e., 0.027 kg/kg), based on a sediment burial rate of 0.23 cm/year (4) and a bottom sediment organic carbon content of 2.7% (25). These values indicate a 94% ecosystem efficiency in organic carbon utilization and an approximate 18-20-fold reduction in organic carbon content (($\Phi = Q_{\text{POC}}/Q_{\text{BSOC}} \approx 18$) based on primary productivity rates. Based on the range of sorptive capacities of organic carbon reported in ref 33, it is not unreasonable to assume that the fugacity capacity of organic carbon in phytoplankton is 10fold greater than that in bottom sediment, suggesting that K_{PBOC} or $(Z_{\text{POC}}/Z_{\text{BSOC}})$ may be approximately 10. The two magnification processes combined result in a total sediment diagenesis generated chemical magnification factor $\Phi \cdot K_{PBOC}$ of approximately 180-200 and perhaps somewhat higher if other sources of organic carbon are considered.

The empirical data further suggest that the deeper lakes i.e., Lake Ontario (86 m) and Superior (147 m) exhibit larger sediment—water disequilibria than the shallower Lakes Erie (19 m), St. Clair (9 m), and Green Bay (15 m). This can be explained by the larger degree of organic decomposition that can take place during the larger surface-to-bottom deposition times in deeper lakes.

Distribution coefficients in plankton are not uniformly greater than their equilibrium partition coefficients but tend to show fugacity ratios F_{PW} exceeding 1 for lower K_{OW} substances, while substances of higher K_{OW} show smaller fugacity ratios which drop below 1 for substances with very high K_{OW} . The drop of the fugacity ratios F_{PW} can be explained by phytoplankton growth and deposition (22). The ratios exceeding 1.0 for the lower K_{OW} substances may be an artifact of the plankton sampling method which collects a mixture of phytoplankton alone. The fraction of zooplankton and suspended matter in the sample are likely to reflect a certain degree of chemical magnification.

The second observation is that organic carbon normalized concentrations in bottom sediments appear to be greater than those in suspended sediments, which in turn are larger than those in plankton. If the concentrations are lipid and organic normalized or expressed in terms of fugacity ratios (relative to water), the differences become even larger. This is interesting because it shows that while the organic carbon content drops from plankton to suspended sediments to bottom sediments the distribution coefficients relative to water increase. Partitioning based models (e.g. eq 14) would predict distribution coefficients to fall proportional to the drop in organic carbon or lipid content. This indicates that sediment to water reequilibration of hydrophobic substances can be expected to occur at a slower rate than organic carbon degradation. Studies of the exchange kinetics of natural sediments confirms that desorption kinetics of hydrophobic organic chemicals from sediments are indeed small. For

example, desorption rate constants from natural sediments have been observed to fall from 0.095 yr⁻¹ for naphthalene (log $K_{\rm OW} = 3.37$) to 6.6×10^{-5} yr⁻¹ for benzo-a-pyrene (log $K_{\rm OW} = 6.5$) (*38*). In comparison, the rate constant for organic carbon breakdown, which is a function of time, varies between an initial rate of approximately 0.78 yr⁻¹ to 0.1 yr⁻¹ after 1 year (*39*). The observation that in phytoplankton, aging and mineralization increases organic carbon normalized plankton–water partition coefficients (*15*) further illustrates that desorption rates are too small to achieve chemical equilibration during decomposition.

The third observation is that the degree of disequilibrium, as represented by the fugacity ratios between bottom sediment and water, suspended sediments and water, and plankton and water, increases when *K*_{OW} drops, suggesting that the departure from chemical equilibrium is greater for low K_{OW} than for high K_{OW} substances. Similar observations were also made for PAHs in marine sediments (11, 12). This is surprising because low K_{OW} chemicals exhibit faster exchange kinetics with particulate matter than high K_{OW} substances, suggesting that chemical equilibria are quicker to establish (38, 40). Our model can explain this observation since low K_{OW} substances achieve a chemical equilibrium between water and phytoplankton and hence produce a $f_{\rm P}/f_{\rm W}$ ratio of 1, while high $K_{\rm OW}$ substances are unable to do this because of growth (22) and deposition causing $f_{\rm P}/f_{\rm W}$ to be less than 1. Subsequent magnification processes (due to plankton digestion and mineralization) will act to elevate the fugacity of the substance from f_P to a higher f_{BS} , but f_{BS}/f_W will always be lower for the higher K_{OW} substance than that for the lower K_{OW} substance because it started at a lower $f_{\rm P}/f_{\rm W}$.

Implications. We argue that in their interaction with hydrophobic organic chemicals bottom and suspended sediments should not be viewed as inanimate objects but as entities that are part of the larger organic carbon cycle. Sediment-water partition coefficients measured under laboratory conditions, where sediments are removed from the natural organic carbon cycle, are therefore substantially different from the distribution coefficients that have been observed in the field. The application of sediment-water partition coefficients in fate models and risk assessments should therefore be conducted with great caution as they may underestimate actual distribution coefficients. Distribution coefficients vary between lakes. Deep lakes with long sediment deposition times, which allow for a high degree of organic carbon decomposition, can be expected to see a high degree of chemical magnification in the sediments. In terms of assessing the degree of chemical biomagnification of organic chemicals in aquatic food-chains, it is important to recognize that a substantial degree of chemical magnification can take place before the chemical enters the higher trophic levels (e.g. fish). This degree of magnification may depend on the ecosystem. Ecosystems with larger organic carbon mineralization capacities may exhibit a greater degree of biomagnification, in essence reflecting longer food-chains.

It is especially interesting that the degree of sediment– water disequilibrium drops with increasing K_{OW} , indicating that lower K_{OW} substances are magnified in the sediments to a greater degree than higher K_{OW} substances. This implies that organisms feeding on sediment or sediment dwelling organisms may be exposed to lower K_{OW} chemicals via the diet to a much greater degree than currently expected. The apparent lack of biomagnification potential of lower K_{OW} substances in fish species may be counteracted by a large degree of magnification in the sediment. The latter may result in a K_{OW} dependence of the biomagnification factor that varies between ecosystems. The latter is indeed observed for PCBs in Lake Superior, where no K_{OW} dependence of the biomagnification factor was observed, while in a comparable food-chain in Lake Baikal the biomagnification factor of the same substances increased significantly with increasing K_{OW} (*41*). Depending on the degree of organic carbon mineralization in different ecosystems, hydrophobic organic chemicals may exhibit different bioaccumulation factors. Chemicals with low log K_{OW} less than 5.0, which are often considered to be "nonbioaccumulative" in POP protocols, may in certain ecosystems exhibit significant bioaccumulation factors due to exposure to chemicals in the sediments, that have been magnified throughout the process of sediment diagenesis.

Acknowledgments

We thank the Natural Sciences and Engineering Research Council of Canada for financial support.

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Received for review September 5, 2002. Revised manuscript received November 20, 2002. Accepted November 20, 2002.

ES020925+