A METHOD TO MEASURE THE SORPTIVE CAPACITY OF SEDIMENT AND PLANKTON FOR SELECTED ORGANOCHLORINES

by

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ABSTRACT

Most environmental fate models and assessment methods of sediment-water distribution of hydrophobic organic chemicals rely on equilibrium partitioning theory. In many cases, this theory incorrectly predicts chemical concentrations in real aquatic systems, leading to the conclusion that the system is in chemical disequilibrium. There are no methods to test whether sediment–water systems are at equilibrium or in disequilibrium. As a result, it is also unclear what the sorptive capacities of sediment are, and whether the recommended relationship between Koc and Kow is correct. This study presents an empirical approach to examine equilibrium partitioning and to measure the sorptive capacities of sediment for a series of test organochlorines. The method measures the diffusive partitioning between a thin film of ethylene vinyl acetate (EVA) that is spiked with selected organochlorines and an adjacent volume of sediment. By monitoring the depletion of chemicals from the EVA phase, values of the sorptive capacities of sediment (Zs) for the test chemicals can be derived. The measured Zs values were approximately 10-fold less than values predicted using the conventional formula. Part of reason for over-estimation may be that the recommended relationship between Koc and Kow was not correct for this sediment, as demonstrated by comparing of the measured sorptive capacities of sediment and 1-octanol. The thin film method was also applied to measure the sorptive capacity of living phytoplankton. The results were approximately 10 times less than values predicted using the conventional formula, but consistent with values predicted using the formula based on the observed relationship between the sorptive capacities of organic carbon and octanol. It is concluded that this thin film EVA method provides a reliable means to assess chemical sorption and associated sediment-water equilibrium partition coefficients. With this method, it should be possible to improve our understanding of why discrepancies occur between predicted and measured Koc values, which in turn can be used to improve models of the fate of chemicals in real ecosystems. The method to measure Z values will also allow us to translate measured concentrations to fugacities, and to test for thermodynamic equilibrium.

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LIST OF ABBREVIATIONS AND ACRONYMS

BSAF – biota-sediment accumulation factor

DCM – dichloromethane

EVA – ethylene vinyl acetate

GC – gas chromatograph

GIT – gastrointestinal tract

Kea **–** EVA-air partition coefficient

Koa **–** octanol-air partition coefficient

Kow **–** octanol-water partition coefficient

Ksw **–** sediment-water partition coefficient

OC – organic carbon

PAHs – polycyclic aromatic hydrocarbons

PCBs – polychlorinated biphenyls

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1 PREAMBLE

Nearly all environmental fate models and assessment methods of sediment-water distribution of hydrophobic organic chemicals rely on equilibrium partitioning theory. In many cases, this theory is inadequate to predict chemical concentrations in real aquatic systems and it is often concluded that the system is in a state of chemical disequilibrium. One reason for disequilibrium occurring is that other processes can affect chemical distribution and these are not described by equilibrium partitioning theory (e.g., the amplification of chemical concentrations in sediment that is postulated to occur during carbon mineralization). Another limitation of the equilibrium partitioning model is that the “true” equilibrium partition coefficients between sediment and water are experimentally difficult to measure. This is because the fraction of hydrophobic chemical that actually participates in equilibrium partitioning is seldom, if ever, known.

There are currently no direct experimental methods to test whether sediment–water systems are at equilibrium or disequilibrium. As a result, it is also unclear what the sorptive capacities of sediment are, and whether the widely-used relationship to predict sorptive capacity is correct.

The study described here is a purely empirical approach to examine equilibrium partitioning and, in so doing, measure the sorptive capacities (Z) of natural sediment and plankton for a series of environmentally relevant organochlorines. Measures of Z are critical to understanding partitioning processes between environmental media, and

Z is a fundamental input parameter in all fugacity-based fate models. If the Z of adjacent media were known, it would allow us to translate measured chemical concentrations to fugacities and to test for thermodynamic equilibrium.

The objective of this research is to develop a laboratory method to measure the sorptive capacity of environmental media for hydrophobic organic chemicals. The method is used to measure the Z value of samples of sediment (Zs) and plankton (Zp) and of 1-octanol (Zo) for a series of environmentally relevant organochlorines. Empirical measures of Zs and Zo allow a key question to be addressed: how well do equilibrium-based regressions describe partitioning of hydrophobic chemicals between sediment and water? This is addressed in Chapter 2. Secondly, deviations from equilibrium -based regressions are interpreted as disequilibria, and several mechanisms have been proposed to account for this. One of these, the "early diagenesis" theory, could be tested if measures of Zs and Zp were available. The question put forth by this theory is: are the progressive losses of organic carbon observed in settling planktonic particles associated with declining Z values during sedimentation? This question is not directly addressed here, but Chapter 3 establishes the methodology to do so.

2 DETERMINATION OF THE FUGACITY CAPACITIES OF SEDIMENT (Zs) AND 1-OCTANOL (Zo) FOR SELECTED HYDROPHOBIC ORGANIC CHEMICALS

2.1 Introduction

In the environment, equilibrium partitioning to the organic carbon (OC) phase of sediment is generally assumed to be the primary process controlling the distribution of hydrophobic organic chemicals between water and sediment. The process is viewed as identical to chemical partitioning observed in the laboratory between water and octanol, with some correction made for the quantitative difference in sorptive capacities of OC and octanol. Support for this view comes from two widely cited studies showing that the partition coefficients between sediment OC and water (Koc) are linearly related to the octanol-water partition coefficients (Kow) for a range of hydrophobic organic chemicals. Koc (expressed in units of L/kg of OC) is the OC-normalized sediment-water distribution coefficient, Ksw/ϕ_{OC}, where Ksw is the ratio of concentrations in sediment (Cs, in mg/kg sediment) and water (Cw, in mg/L) at equilibrium, and ϕ_{OC} is the mass fraction of OC in the sediment sample (kg/kg). The first study by Karickhoff (1981) suggested that $Koc = 0.41 * Kow$ for five aromatic hydrocarbons. More recently, a second and more comprehensive study by Seth et al. (1999) found a similar linear relationship from reported data sets of Koc and Kow for 121 hydrophobic chemicals. They reported that $Koc = 0.35 * Kow$ with 95% confidence boundaries of a factor of 2.5 in both directions.

The constant 0.35 (or 0.41) can be interpreted as an expression of the degree to which OC mimics 1-octanol in its ability to solubilize or sorb organic chemicals.

The equation Koc = 0.35$*$ Kow (or Koc = 0.41$*$ Kow) was initially suggested as a rough and generalizable way to predict a chemical's Koc value, using Kow as a single and readily available descriptor. It has become widely used in the development and application of BSAFs (biota-sediment accumulation factors) in risk assessments (e.g., Morrison et al., 1996; and sediment quality criteria (DiToro et al, 1991). It is also relied on in modelling the environmental fate and food-chain bioaccumulation of chemical pollutants (Mackay, 1989; Gobas et al., 1995; Mackintosh, 2003). Among the underlying assumptions in the use of this equation are

i) that OC contributes all of the sorptive capacity of sediments, and

ii) that all chemicals equilibrate between aqueous and OC phases by simple passive diffusion and with time, achieve a chemical equilibrium.

Both of these assumptions have been questioned because Ksw values measured in field-collected samples have repeatedly been shown (McGroddy & Farrington, 1995; Morrison et al, 1996; Koelmans et al, 1997; Gobas & Maclean, 2003) to be much greater than the equilibrium values which have been defined in terms of OC partitioning according to the formula Koc = 0.35* Kow. A number of hypotheses have been proposed to explain the apparent chemical disequilibria. One proposal is "enrichment" of the concentrations of hydrophobic pollutants on settling particles (Baker et al., 1991). Contaminants dissolved in water could be scavenged by large, rapidly settling particles such as zooplankton fecal pellets, depleting surface water relative to bottom sediments. Sorption to soot carbon (Gustafsson et al., 1997; Jonker and Koelmans, 2002; Accardi-Dey & Gschwend, 2002; 2003) has also been suggested to explain the discrepancy. According to this hypothesis, a portion of a hydrophobic chemical is sorbed onto a non-OC, combustion-derived “black carbon” fraction of sediment and is unavailable for equilibrium partitioning. Gschwend (Accardi-Dey & Gschwend, 2002, 2003) re-evaluated literature Koc’s for PAHs by considering sorption to both OC and to soot carbon, and showed that chemical sequestered in soot carbon can account for the apparent disequilibrium between field measured and predicted Koc for PAHs. There has been some question whether the association with soot carbon is unique to PAHs that are produced during combustion processes, but avid binding of both native and added PAHs, as well as several co-planar PCBs, to soot carbon was recently demonstrated (Jonker and Koelmans, 2002). More recently, Gobas and Maclean (2003) proposed that the observed disequilibrium between PCB concentrations in water and bottom sediments could be created if the rate of decomposition of particles as they pass down through the water column exceeds the rate of desorption of PCBs from the settling particles. This has been termed a “persistent state of partitioning disequilibrium" (deBruyn & Gobas, 2004). It would result in elevated OC-normalized chemical concentrations of hydrophobic chemicals in sediments, and could explain observed reciprocal relationships between OC content and contaminant concentration.

One problem with all of the hypotheses proposed is that the disequilibria are assessed by comparing observed distribution coefficients with predicted equilibrium partition coefficients which were derived using the relationship between the sorptive capacities of sediment OC and octanol (i.e., the equation Koc = 0.35* Kow), not values measured empirically at equilibrium. There are currently no direct experimental methods to test whether sediment–water systems are at equilibrium or in disequilibrium. As a result, it is also unclear what the sorptive capacities of sediment are, and whether the recommended relationship between Koc and Kow is correct. The aim of this study is to develop a laboratory method to measure the sorptive capacity of natural sediment and 1-octanol for a series of environmentally relevant organochlorines. A reliable method to assess chemical sorption and associated sediment-water equilibrium partition coefficients would improve our understanding of why discrepancies occur between deduced and observed Koc values, which in turn can be used to improve models of the fate of chemicals in real ecosystems. It would also allow us to translate measured concentrations to fugacities and test for thermodynamic equilibrium.

2.2 THEORY

Equilibrium partitioning is more clearly expressed in terms of chemical fugacity (f) than as concentration ratios because fugacity analysis expresses concentrations in terms that are common to all phases. A chemical's fugacity is related to its chemical potential in a medium, and can be viewed as the "escaping tendency" of the chemical from that medium. Fugacity is defined as the pressure (in Pa) that a chemical exerts when dissolved in a medium (Mackay, 1979; 1991) and is of ecotoxicological importance because it reflects the fraction of chemical available for partitioning into surrounding organisms. Mathematically, fugacity is defined as

$$f = \frac{C}{Z} \qquad \text{(Equation 2.1)}$$

where C is the concentration of freely available (i.e. dissolved) chemical in an environmental medium (in mol·m^{-3}) and Z is the fugacity capacity or "absorbing capacity" of that medium for the chemical (in units of mol·m^{-3}·Pa^{-1}).

Our approach is to determine the fugacity capacity (Z) of environmental media for hydrophobic pollutants, and to express the (unitless) partition coefficients in terms of

Z ratios, rather than concentration ratios. For example, using Equation 2.1 to express concentrations in fugacity format, Ksw becomes

$$Ksw = \frac{Cs}{Cw} = \frac{fs * Zs}{fw * Zw} \qquad \text{(Equation 2.2)}$$

At equilibrium, the fugacity of the chemical in sediment (fs) and water (fw) are equal by definition, and Equation 2.2 simplifies to the ratio of the fugacity capacity of sediment (Zs) and water (Zw),

$$Ksw = \frac{Zs}{Zw} \qquad \text{(Equation 2.3)}$$

The advantage of expressing equilibrium partition coefficients in terms of fugacity capacities (Z ratios) instead of concentration ratios is that the Z -value of a particular chemical in a medium is a characteristic property of that medium (under specified experimental conditions). If determined correctly, Z is independent of changes in the total mass of chemical in the system.

The fugacity capacity of water (Zw) and air (Za) can be determined through fundamental thermodynamic relationships: Zw is calculated as 1/H, where H is the Henry's Law constant (Pa m^3/mol) for the chemical of interest, and Za is calculated as 1/RT, where R is the gas constant (Pa.m^3/mol.K) and T is absolute temperature (K). For other media, Z has conventionally been estimated by exploiting partition coefficients with air or water. For example, Zs = $Zw * Ksw$, where Ksw is predicted from 0.35* Kow *ϕ_{OC}*d_s (Mackay, 1991), where d_s is density (kg/L of bulk sediment) and the factor 0.35 has units of L/kg. As described earlier, such predictions rely on the assumptions of equilibrium partitioning between aqueous and sorbed phases, and on a fixed relationship between Koc and Kow for all chemicals (i.e., Koc = 0.35*Kow). In the method described here, Zs is measured at equilibrium empirically using a simple two-phase system comprised of field-collected sediment and a thin film of ethylene vinyl acetate (EVA) copolymer. Zs is derived using the equation

$$Zs = Ze * \frac{Cs}{Ce} \qquad \text{(Equation 2.4)}$$

where Ze is the fugacity capacity of the chemical in the EVA phase, and the ratio Cs/Ce is the sediment-EVA distribution coefficient measured at near-equilibrium. Ze is determined using a modification of the method published earlier by our group (Wilcockson and Gobas, 2001). The fugacity capacity of octanol (Zo) is also measured empirically here. Zo is derived from $Ze * Co/Ce$, where Co/Ce is the ratio of concentrations in octanol and EVA phases at near-equilibrium. The value Zo for hydrophobic chemicals is of interest because of octanol's universal use as a surrogate for OC (and for lipid) in environmental calculations.

2.3 EXPERIMENTAL DESIGN

2.3.1 Measurement of Ze

The value of Ze is determined from experiments in which EVA spiked with selected organochlorines is coated as a thin film (<0.25 μm) on the interior surface of a glass autosampler vial, the vial is sealed and time is permitted for the chemical to equilibrate between the EVA film and headspace air. At equilibrium, Ze of each chemical is determined according to Equation 2.1 as the ratio Ce/fe, where Ce is the chemical concentration (mol m^{-3}) in the EVA film (measured by solvent extraction of the film and quantification by gas chromatography, GC), and fe is the fugacity of the chemical in EVA. By definition, at equilibrium the fugacity of the chemical is the same in EVA (fe) and in headspace air (fa). The value of fa is derived through rearrangement of the Ideal Gas Law as the product of the concentration measured by GC in headspace air (Ca, expressed in mol m^3), the gas constant (R) and absolute temperature (T). Mathematically, Ze is calculated by the equation

$$Ze = \frac{Ce}{fe} = \frac{Ce}{Ca.RT} = \frac{Kea}{RT} \qquad \text{(Equation 2.5)}$$

where Kea is the equilibrium partition coefficient of the chemical between headspace air and EVA, Ce/Ca.

2.3.2 Measurement of Equilibrium Distribution Coefficients (Cs/Ce and Co/Ce)

The method for determining Cs/Ce at equilibrium is shown schematically in FIGURE 2-1. Two glass vials are prepared identically by coating the interior surface with a thin film of EVA spiked with selected organochlorines. Vial 1 is filled with water and Vial 2 is filled with sediment collected freshly from the field. The number of moles of chemical is the same in both vials, and the volumes (in m^3) of the EVA, water and sediment phases are known.

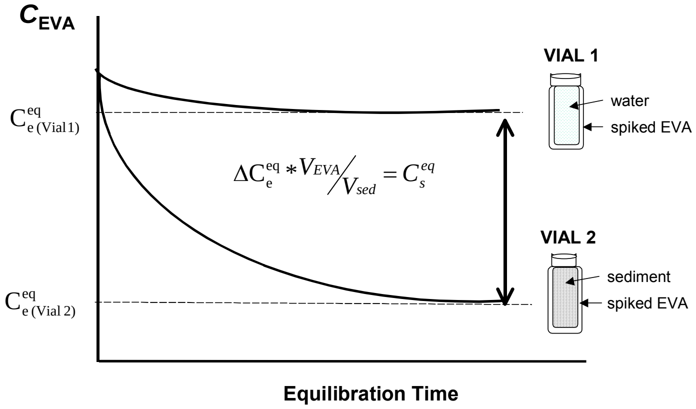

Figure 2-1: Diagram of the method for determining Cs/Ce ratio at equilibrium. Vials 1 and 2 are identical except that in addition to a film of spiked EVA, Vial 1 contains water, and Vial 2 contains the sediment sample. Ce is the chemical concentration in the EVA film in Vial 2 at equilibrium ($Ce^{eq}_{e(Vial\,2)}$). The value of Cs at equilibrium in Vial 2 is calculated as the difference between the mass of chemical in the EVA films in Vial 1 and Vial 2 at equilibrium, corrected for the volume differences between EVA film (V_{EVA}) and sediment (V_{sed}).

Depletion of chemical from the EVA film occurs as the chemical partitions from the EVA film into the contents of the vial. The extent of this depletion at equilibrium is an expression of the sorptive capacity of the water (in Vial 1) and sediment (in Vial 2), and can be used to derive Cs/Ce equilibrium partition coefficients. Ce is determined from the mass (in moles) of chemical remaining in the EVA film in Vial 2 (measured in solvent extracts of EVA, performed after removing the sediment from the vial) and the volume of the EVA film (in m^3, calculated from the reported density of EVA). Cs is determined not through exhaustive solvent extraction of the sediment, but rather from the difference in the mass of chemical remaining in the EVA films in Vials 1 and 2 at equilibrium.

Because the vials are identical in all respects except that Vial 1 contains water and Vial 2 contains sediment and associated water, any loss of chemical from the spiked EVA film in Vial 2 *beyond* that seen in Vial 1 must be the mass of chemical that has partitioned into the sediment phase. Cs can be calculated from this difference in mass (in moles), divided by the known volume of the sediment (in m^3). Co/Ce is measured similarly, except the volume of EVA is increased to compensate for the greater loss of chemical into octanol compared to sediment.

2.4 Materials and Methods

2.4.1 Chemicals

Seven organochlorines were examined here: a series of five chlorobenzenes (Aldrich Chemical Co, Milwaukee, WI, USA 1,4-dichlorobenzene (diCBz), 1,3,5-trichlorobenzene (triCBz), 1,2,4,5-tetrachlorobenzene (tetraCBz), pentachlorobenzene (pentaCBz), hexachlorobenzene (hexaCBz) and two PCBs (Accustandard, New Haven CT, USA), 2,2',5,5'-tetrachlorobiphenyl " IUPAC PCB #52" (tetraCBP) and 2,2',4,4',6,'6-hexchlorobiphenyl "IUPAC PCB #155" (hexaCBP). These chemicals were selected to cover a range of Kow ($10^{3.4}$ – 10^7) and for their ease of assay by GC.

2.4.2 Sediment Sample

Intertidal sediment was collected on two occasions from the mudflats of Port Moody Arm of Burrard Inlet, BC. During low tide, the top 0.5 to 1.0 cm of sediment was skimmed off and transferred to a clean glass jar. Samples were used immediately upon returning to the lab. Organic carbon content (ϕ_{OC}) was determined to be 0.035 (± 0.0038, n=3).μg OC/μg dry sediment using the method of Van Iperen and Helder (1985) by Linda White at the Institute of Ocean Sciences, Sidney, BC. The average ϕ_{OC} of the same data expressed on a wet weight basis was 0.017 (± 0.005, n=3).μg OC/μg wet sediment.

2.4.3 Thin Film Preparation

A solution of ethylene vinyl acetate copolymer, EVA (Elvax 40W®, Dupont Chemical Co., Wilmington, DE, USA) was prepared by dissolving the EVA beads in DCM (Analar, HPLC grade) to a concentration of 6.68 g/L. This solution was spiked with the seven test organochlorines to the following final concentrations: diCBz (0.35 mg/ml), triCBz (0.25 mg/ml), tetraCBz (0.26 mg/ml), pentaCBz (0.42 mg/ml), hexaCBz (0.32 mg/ml), tetraCBP (0.10 mg/ml), hexaCBP (0.14 mg/ml). A small volume (25 μl) of this solution was used to coat the interior surface of 2 ml glass autosampler vials (silanized, pre-rinsed with a volume of DCM, purchased from Agilent). The vial was slowly rolled for 1 minute so that the EVA solution passed over the walls of the vial until liquid was no longer visible. The vial was left uncapped for an additional 3 mins to allow any remaining DCM to evaporate. The vial was then capped using a screw cap with a teflon/rubber/teflon septum (Agilent), and kept at room temperature. The EVA film thickness was calculated to be 0.24 μm, based on the volume of the EVA coating and the interior surface area of the vial, which was directly estimated. The volume of the EVA film was 0.000173 cm^3, which was determined from the mass of EVA (167 μg) added to the vial and the density of EVA (965 mg/cm^3, Dupont Chemical Co information). The EVA film appeared to be uniformly applied, based on the even distribution of Sudan IV dye added to a separate EVA solution and coated in an identical manner.

2.4.4 Ze Determination from Observed Kea

Capped vials coated with a thin film of spiked EVA were stored at room temperature for up to 168 hr. After 24, 48 and 168 hr, headspace air was sampled by puncturing the septum with a gas-tight Hamilton syringe and withdrawing a1 µl volume of air from the vial. This was immediately injected onto the GC column for analysis. The chemicals in the EVA film were extracted (by mixing for 10 sec on a vortex mixer) into six 1 ml volumes of hexane, which were pooled, and 1 µl of the pooled extract analyzed by GC. Peak heights and areas on the chromatograms were within the range of the standard curves, and the standard curves were linear over the range of chemical concentrations in hexane examined. Kea ($= Ce/Ca$) values for each of the organochlorines were determined from the ratio of chemical mass in the samples of hexane extract and headspace air, corrected for volumes of air and EVA phases. For most experiments, absolute concentrations were not determined using standard curves, and the ratios of peak sizes obtained from the chromatograms were used instead. It is not possible to construct standard curves for the chemicals in air, and Ca values were calculated using standards in hexane. Ze values (in mol m^{-3} Pa^{-1}) of each chemical were determined according to Equation 2.5.

2.4.5 Sediment Experiments

Sealed vials coated with a thin film of spiked EVA and filled with sediment or water were gently rotated at $33^1/_3$ rpm at room temperature. At various time points (over the course of 265 hr in one experiment, and 861 hr in the second experiment), water or sediment was removed from the vials in duplicate, and the films were rinsed 3 times with water. Hexane (1.5 ml) was added to extract the remaining chemicals from the EVA film, and 1 µl hexane extract was injected onto the GC column for quantifying Ce. The concentration of chemical in sediment (Cs) was measured from the difference in Ce values of the vials containing water and sediment, corrected for the volume difference between EVA and sediment. The data were expressed in terms of uptake by sediment from the EVA film, not as depletion from the EVA. An example of the calculations is given in Appendix A.

The time profile of uptake into sediment was examined by comparing the fit of one- and two-compartment models (SYSTAT 11.0, SPSS Inc., 2001) to the data. The equation for the one-compartment model was

$$Cs = Cs_{\text{plateau}}(1-e^{-kt}) \qquad \text{(Equation 2.6)}$$

where Cs is the mass of chemical measured in a known volume of bulk sediment (μg/ml sediment) at time t (hr), Cs_{plateau} is the theoretical concentration in the sediment at equilibrium, and k is the desorption rate constant from sediment (hr^{-1}). The equation for the two-compartment model was

$$Cs = Cs_{\text{plateau1}}(1-e^{-k_1 t}) + Cs_{\text{plateau2}}(1-e^{-k_2 \cdot t}) \qquad \text{(Equation 2.7)}$$

where Cs is the mass of chemical measured in a known volume of bulk sediment (μg/ml sediment) at time t (hr), Cs_{plateau1} and Cs_{plateau2} are the plateau concentrations in compartments one and two, respectively, and k_1 and k_2 are the desorption rate constants (hr^{-1}) from compartments one and two, respectively. Goodness of fit to the two models was compared using F tests. The ratios Cs/Ce measured at near-equilibrium were multiplied by Z_E to give observed Z_S values for each chemical. Predicted values of Zs were calculated using the equation $Zs = 0.35 * Kow * \phi_{OC} * d_s / H$, where ϕ_{OC} on a wet weight basis was 0.017 (kg/kg), density of sediment, d_s = 1.5 L/kg (Mackay, 1991), and H and Kow for these chemicals were selected by Mackay (1992). The time to reach

95% of the theoretical Cs_{plateau} (t_{95}, hr) for the one-compartment model was determined as -ln(0.05)/k, where k is the desorption rate constant from sediment (hr^{-1}) determined from the fit of Equation 2.6.

2.4.6 Octanol Experiments

Because of the very high absorptive capacity of 1-octanol for the test chemicals, the relative volumes of EVA and octanol had to be altered so that at equilibrium, measurable chemical remained in the EVA phase. EVA pellets (0.1 g) were weighed into a 2 ml autosampler vial, and melted by placing the vial on its side on a hotplate (setting = 4). In these experiments, the EVA was manipulated into the form of a flat, elongated mound, not a thin film. The weight of the EVA mound (0.100 $\pm$ 0.004 g, n = 15) was converted to a volume (0.105 cm^3) using the known density of EVA. The interior walls of the vials and the EVA mound were coated with spiked EVA solution in DCM as described in Section 2.4.3. The vials were then filled with 1-octanol, sealed and gently rotated at $33^1/_3$ rpm at room temperature. Control vials contained an identical mass of spiked EVA, but received no octanol. They were sealed and equilibrated alongside the vials containing octanol. Instead of using hexane as the extraction solvent, the EVA was soaked in a 2 ml volume of DCM for 30 min. This was repeated 6 times with fresh volumes of DCM, and the DCM was pooled in a tapered glass tube. Toluene (100 µl) was added to the pooled DCM as a “keeper”. The volume of DCM was then reduced under a gentle stream of nitrogen until only the toluene remained, after which 5 ml of methanol was added to precipitate the EVA. The tubes were spun at 3000 rpm for 5 min and an aliquot of the supernatant was transferred to a GC autosampler vial and 1 µl of this was injected onto the GC column. Standard curves were constructed for each test chemical, and used to determine the mass and concentration of chemical in EVA and octanol phases at equilibrium. Calculated recoveries were determined by comparing the mass of chemical in the two phases relative to the known mass of chemical added to the study vial. The recoveries were 86% for the most volatile chemical (diCBz), and ranged between 91-101% for the six other test chemicals. An example of the calculations to derive Zo is given in Appendix B.

2.4.7 Gas Chromatography

A Hewlett-Packard 5890 gas chromatograph (GC) equipped with a ^{63}Ni electron-capture detector, a cool on-column injection port and a 30 m x 0.25 mm x 2.65 (film thickness μm) HP-5 column (Agilent Technologies, Mississauga, ON) was used for the analysis. The oven temperature program was 35º C for 0.2 min, 20º C/min to 270º C, which was held for 4 min. The injection port temperature and detector temperatures were 38º C and 350º C, respectively, and the carrier gas was helium (1 ml/min). Injections were done manually, using a gas-tight syringe with a Teflon-tipped plunger (Agilent). Peaks were integrated using Chemstation (Hewlett Packard, Mississauga, ON) software.

2.4.8 Uncertainty

Unless stated otherwise, uncertainty was expressed as mean ± 1 standard deviation. For Z values, the error in Cs/Ce or Co/Ce ratios measured at near-equilibrium (i.e.> t_{95} hr) was propagated with the error in Ze. The error in Ze was the error observed in the Kea measurements (Ze = Kea / RT).

2.5 RESULTS and DISCUSSION

2.5.1 Relationship between Kea and Koa

The chemicals reached equilibrium between the EVA and air phases within 24 hr, as shown by the similarity in log Kea values measured after 24, 48 and 168 hr equilibration times (FIGURE 2-2). The difference between log Kea of hexaCBP measured after 24 hr and 168 hr equilibration time reached statistical significance ($p<0.05$), but the mean Kea value was higher at 168 hr, not lower as would be expected if equilibrium were still being approached. Rapid exchange kinetics between spiked EVA films and ambient air were observed earlier by Wilcockson (Figure 18, M.Sc. thesis, SFU, 1997) for two of these test chemicals. He observed desorption half-lives of 1.2 hr and 2.5 hr for tetraCBP and hexaCBP, respectively. Although these rates may not be achieved in the closed system with no convection examined here, they indicate that diffusion of these chemicals through the soft EVA film to air can occur rapidly.

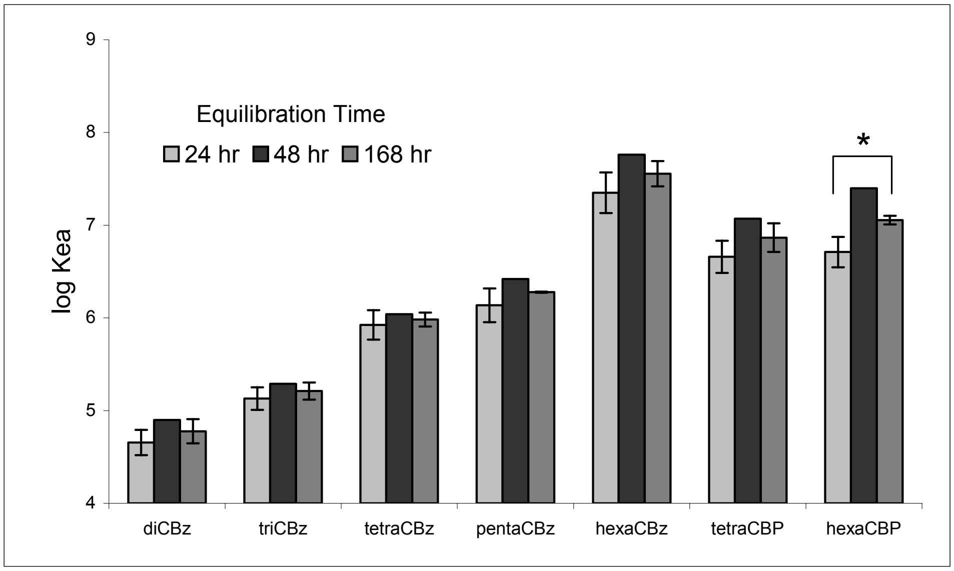

Figure 2-2: Effect of equilibration time on log Kea for the seven test chemicals. The difference between the log Kea of hexaCBP measured after 24 hr and 168 hr equilibration time was statistically significant ($p<0.05$). No replicates were performed at 48 hr.

The results of the headspace air injections were variable, with coefficients of variation ranging between 20-25%, but when the relatively low chemical concentrations in air were expressed relative to the much greater concentrations in EVA and these ratios expressed in logarithmic form, there was less than 5% error in log Kea values measured within-day. The variability between time points in FIGURE 2-2 reflects between-day replicate variation (<7%), and the data from the three time points (n = 14 independent determinations) were pooled to derive the log Kea values given in FIGURE 2-3.

FIGURE 2-3 shows the relationship between observed log Kea values and the log Koa values reported for the CBz series and tetraCBP (Wania et al., 2002) and for hexaCBP (Harner and Mackay, 1995). There was a strong linear relationship between log *Kea* and log *Koa* for the CBz series, but the two PCB congeners fell off this regression line.

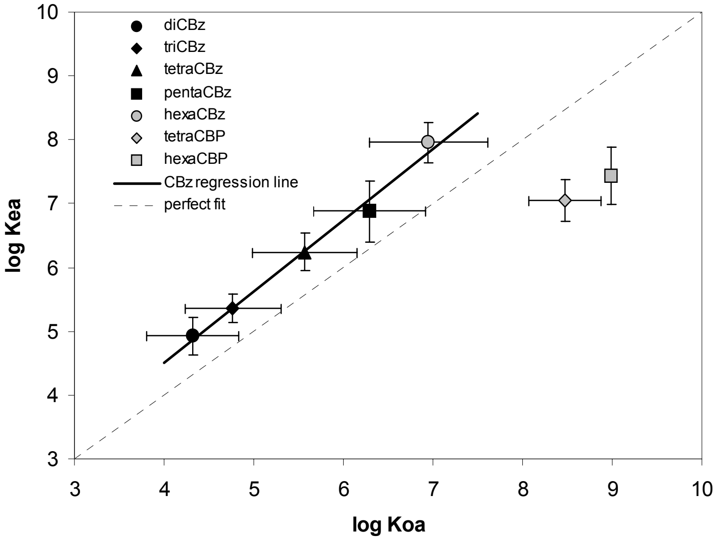

Figure 2-3: Relationship between log *Kea* and reported log *Koa*. The partition coefficients of the seven test organochlorines between EVA films and headspace air, log *Kea*, are the mean ± SD of n=14 determinations. Error bars for the reported log *Koa* values represent ±1 SD, as reported by Wania et al., 2002.

Omitting the two PCBs from the calculation, the regression equation describing the relationship between log *Koa* and log *Kea* of the CBz series is:

log Kea = (1.12 ±0.07) log K_{OA} + (0.03 ±0..38), $r^2 = 0.99$, n = 5 (Equation 2.8)

Almost identical relationships between *Kea* and *Koa* were reported previously for a similar combination of CBz and PCBs (Wilcockson & Gobas, 2001) and for five

PCB congeners (Harner et al., 2003). Both studies examined the equilibrium partitioning of air-phase chemicals into EVA films. The reason for the discrepancy between these PCB results and results obtained previously is not clear. The extraction efficiency of the PCBs from the EVA films into hexane was essentially 100%. Similar PCB concentrations in the EVA phase were obtained if the EVA films were dissolved in dichloromethane and precipitated with methanol. The discrepancy is most likely related to the problems we encountered with the manual injections of headspace air for these two chemicals. We observed considerable variability in peak size that depended on the injection technique (e.g., speed of injection, number of pumps of the plunger, and the length of time that the sample was held in the glass barrel of the syringe). It may be that the PCBs partitioned into residual solvent remaining after the needle washes or they were sorbed by the Teflon™ tip of the syringe plunger, and were unavailable for analysis. Yang et al. (1998) found that 21 PCBs examined sorbed to a Teflon™ stir bar.

As suggested by Wilcockson and Gobas (2001) and by Harner et al. (2003), the regression equation of log Kea on log Koa can be used to predict the Kea of structurally similar chemicals from their reported Koa values. Because we do not consider our PCB results to be reliable, we obtained estimates of log Kea values for tetraCBP and hexaCBP by substituting their reported log Koa values into Equation 2.8. TABLE 2-1 lists the observed values of log Kea for the CBz series, and the log Kea values of the two PCBs estimated in this way.

Table 2-1: **Logarithms of reported octanol-water (Kow) and octanol-air (Koa) partition coefficients at 20°C, EVA-air (Kea) partition coefficients (± SD, n = 14) observed at 20°C or estimated using Equation 2.8, fugacity capacity (mol m^{-3} Pa^{-1}) of EVA (Ze), octanol (Zo) and sediment (Zs) and reported Henry's Law constant (H) for the seven test chemicals.**

Chemical	log Kow[1]	log Koa ±SD	log Kea ±SD	log Ze (mol m^{-3} Pa^{-1})	log Zo (mol m^{-3} Pa^{-1})	H[1] (Pa.m^{3} mol^{-1})	log Zs ± SD (mol m^{-3} Pa^{-1})
diCBz	3.4	4.32 ± 0.52[2]	4.93 ± 0.29	1.54	1.00	376	-1.74 ± 0.06
triCBz	4.1	4.77 ± 0.54[2]	5.36 ± 0.22	1.97	1.45	1096	-1.40 ± 0.26
tetraCBz	4.5	5.57 ± 0.58[2]	6.24 ± 0.30	2.86 (2.57[5])	2.29	122	-0.64 ± 0.34
pentaCBz	5	6.29 ± 0.62[2]	6.88 ± 0.48	3.50 (3.38[5])	2.90	85	0.48 ± 0.26
hexaCBz	5.5	6.95 ± 0.66[2]	7.96 ± 0.31	4.57 (3.95[5])	4.00	131	0.19 ± 0.19
tetraCBP	6.1	8.47 ± 0.40[2]	9.51[4]	6.12 (5.22[5])	5.47	47	1.82 ± 0.13
hexaCBP	7	8.99[3]	10.09[4]	6.70 (5.44[5])	6.10	87	1.97 ± 0.13

[1] Mackay et al., 1992

[2] Wania et al., 2002

[3] Harner and Mackay, 1995

[4] value estimated using Equation 2.8

[5] Value of log Ze determined by Wilcockson and Gobas, 2001

2.5.2 The Measured Fugacity Capacity of EVA (Ze)

The logarithm of the fugacity capacity of EVA, log Ze, in mol m^{-3} Pa^{-1} for each test chemical (calculated as Kea/RT) is given in TABLE 2-1. Also included in this table are the values of log Ze determined using different methodology by Wilcockson & Gobas (2001). The earlier results are 0.12 –1.3 log units lower than the Ze values determined here.

2.5.3 Kinetics of Chemical Partitioning into Sediment

The results of statistical analyses using F-tests (Table 2-2) indicated that the one-compartment model provided a good fit to the data. As shown in Table 2-2, uptake of all test chemicals into sediment followed a one-compartment model in the time course study conducted for 265 hr ($p>0.05$). In the 851 hr time course study, the kinetics of uptake were also best described by a one-compartment model for all chemicals except hexaCBz and tetraCBP. For these, the fit of a two-compartment model was significantly better, but the statistical difference was small and just reached significance in both cases (the F ratios were 5.21 and 4.55, respectively, *versus* the critical F statistic = 3.74 at $p=0.05$ (one tailed). Furthermore, if the largest of the duplicate data points measured at 861 hr is eliminated from the analysis, the uptake curves for hexaCBz and tetraCBP are also best fit by the one-compartment model. It was concluded that these data were fit better by the one-compartment model, and the kinetic parameters estimated by the one-compartment fit are given in Table 2-3. Coefficients of determination (r^2) of the fit of a one-compartment model to the observed Cs uptake curves for all chemicals ranged between 0.81 and 0.95 (Table 2-3).

Table 2-2: **Results of F-tests used to determine if chemical uptake into sediment is described by a one-compartment model better than a two-compartment model. In Experiment 1 (where samples were analyzed over the course of 265 hr), the degrees of freedom for one– and two-compartment analyses were 8 and 6, respectively, and the critical F-statistic was 4.15. In Experiment 2 (where samples were analyzed over the course of 861 hr), the degrees of freedom were 9 and 7, respectively, and the critical F-statistic was 3.74. A statistically better fit of the data to a two-compartment model was obtained when p (one-tailed) < 0.05.**

	Chemical	Sum of Squares		F Statistic	p value
		One compartment	Two compartments		
Expt.1 (265 hr)	diCBz	0.003	0.390	2.98	0.10
	triCBz	0.056	0.184	2.07	0.20
	tetraCBz	0.240	0.580	1.76	0.25
	pentaCBz	0.996	1.697	1.24	0.41
	hexaCBz	0.288	1.584	2.45	0.15
	tetraCBP	0.006	0.060	2.70	0.12
	hexaCBP	0.011	0.105	2.67	0.12
Expt. 2 (861 hr)	diCBz	0.016	0.950	-3.44	0.06
	triCBz	0.212	0.189	0.42	0.87
	tetraCBz	0.837	0.632	1.14	0.44
	pentaCBz	7.831	4.841	2.16	0.16
	hexaCBz	5.370	2.157	5.21*	0.02
	tetraCBP	0.144	0.063	4.55*	0.03
	hexaCBP	0.197	0.138	1.50	0.30

Table 2-3: **Kinetic parameters derived by fitting a one-compartment model to the chemical uptake into sediment data. Cplateau is the theoretical concentration of chemical in the sediment at equilibrium. Uptake data was collected for 265 hr in Experiment 1 and for 861 hr in Experiment 2.**

Chemical	Cplateau ± SE (μg cm^{-3})		Desorption rate constant (k) ± SE (hr^{-1})		r^2	
	Expt 1	Expt 2	Expt 1	Expt 2	Expt 1	Expt 2
diCBz	0.186 ± 0.006	0.268 ± 0.007	0.156 ± 0.009	0.0.045 ± 0.009	0.88	0.94
triCBz	0.766 ± 0.029	0.937 ± 0.027	0.044 ± 0.008	0.033 ± 0.005	0.90	0.94
tetraCBz	1.56 ± 0.062	1.873 ± 0.055	0.039 ± 0.007	0.030 ± 0.004	0.90	0.93
pentaCBz	3.05 ± 1.151	3.672 ± 0.184	0.026 ± 0.005	0.021 ± 0.004	0.90	0.87
hexaCBz	1.52 ± 0.070	2.549 ± 0.147	0.036 ± 0.007	0.024 ± 0.006	0.88	0.81
tetraCBP	0.35 ± 0.017	0.537 ± 0.028	0.017 ± 0.002	0.013 ± 0.002	0.95	0.89
hexaCBP	0.378 ± 0.052	0.468 ± 0.043	0.008 ± 0.002	0.006 ± 0.001	0.93	0.82

FIGURE 2-4 shows the observed data and the one-compartment fitted functions for the time course experiment that ran 861 hr.

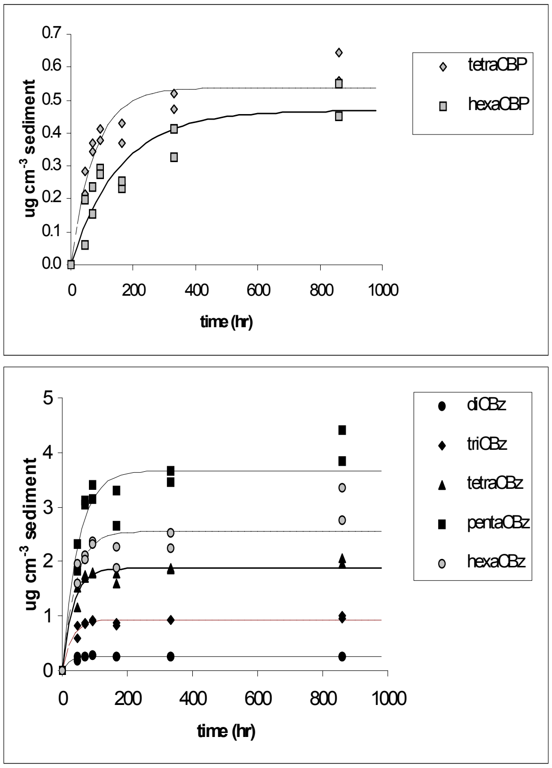

Figure 2-4: **Uptake curves of test chemicals into sediment. The lines are the fits to a one-compartment model.**

Although the data plotted in FIGURE 2-4 are consistent with a first-order one-compartment model, the existence of more than one sorption site in this sediment sample cannot be ruled out. It is possible that slower site(s) contributed negligibly to the uptake during the time frame of this experiment, and so were not captured in the kinetic analysis. Evidence of this possibility may be the statistically better fit of a two-compartment model to hexaCBz and tetraCBP data. The toxicological relevance of such slow site(s) to organisms dwelling in contaminated sediment is not known, but it seems likely that the extremely slow desorption rates mean that this pool of chemical is not bioavailable. This is supported by the experiments by Kraaij et al (2003) who demonstrated that accumulation of hydrophobic chemicals in a benthic organism (*Tubificidae*) were predicted accurately from measurements of the rapidly-desorbing fraction of chemical in sediment only.

To determine Zs , it is crucial that the concentrations of chemicals in sediment be measured at or very near equilibrium. From the present uptake data, it appears that near-equilibrium was reached at the end of the experiment. Using the average desorption rate constants (k) calculated by the one-compartment fitted equation, the time to reach 95% of the theoretical plateau (t_{95}, expressed in hr) for each chemical were less than the experimental exposure times (TABLE 2-4), with one exception: hexaCBP in the experiment that was conducted for 265 hr.

Table 2-4: The time to reach 95% of the predicted equilibrium concentration in sediment (t_{95} in hr) for the seven test chemicals determined by kinetic analyses of two experiments conducted over 265 hr (Experiment 1) and 861 hr (Experiment 2).

Chemical	t_{95} (hr) Expt 1 (265 hr)	 Expt 2 (861 hr)
diCBz	19	67
triCBz	68	90
tetraCBz	77	99
pentaCBz	115	145
hexaCBz	83	123
tetraCBP	176	230
hexaCBP	374	466

In both experiments, there was a clear trend of decreasing desorption rate constants (k) with increasing Kow, as illustrated in FIGURE 2-5.

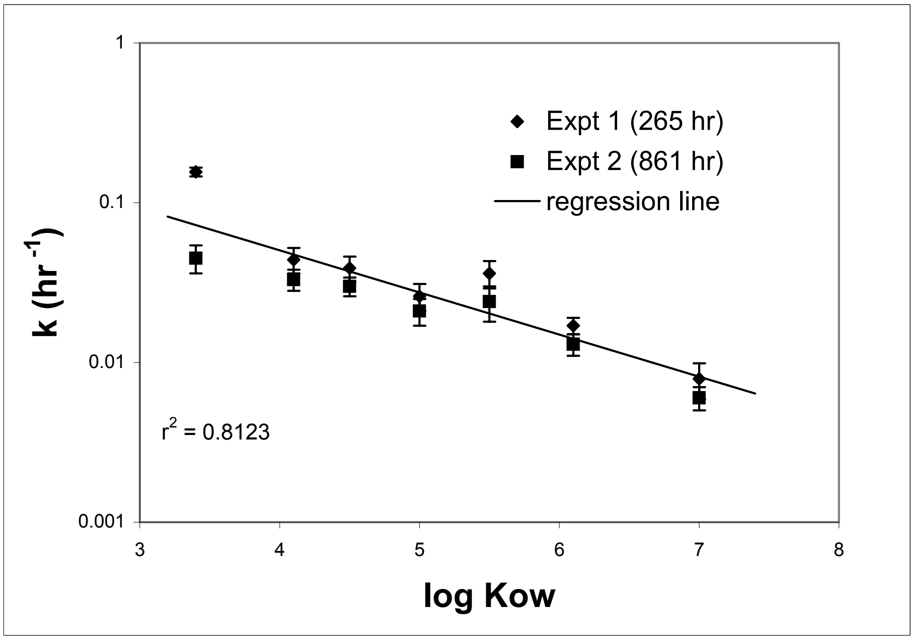

Figure 2-5: Relationship between the logarithms of the desorption rate constants determined using a one-compartment fit, k (hr^{-1}), and Kow. The regression line was obtained using the average values determined in the two experiments. Error bars for k are the SE estimated from nonlinear regression analysis.

This means that equilibration times of the chemicals increased with increasing log Kow. Similar observations have been made by others (Wilcockson & Gobas, 2001; Leslie et al., 2002), and presumably reflect Stoke's Law, which states that diffusion rate is inversely proportional to the cube root of the molecular weight. Chemicals with higher Kow tend to have larger molecular size, and so diffuse more slowly.

2.5.4 The Measured Fugacity Capacity of Sediment (Zs)

The logarithm of Cs/Ce ratios measured at near-equilibrium (i.e. at equilibrations times > t_{95}) were linearly related to log Kow (FIGURE 2-6). This suggests that the equilibrium partitioning of chemicals between sediment and EVA is similar to the process of diffusive partitioning between octanol and water.

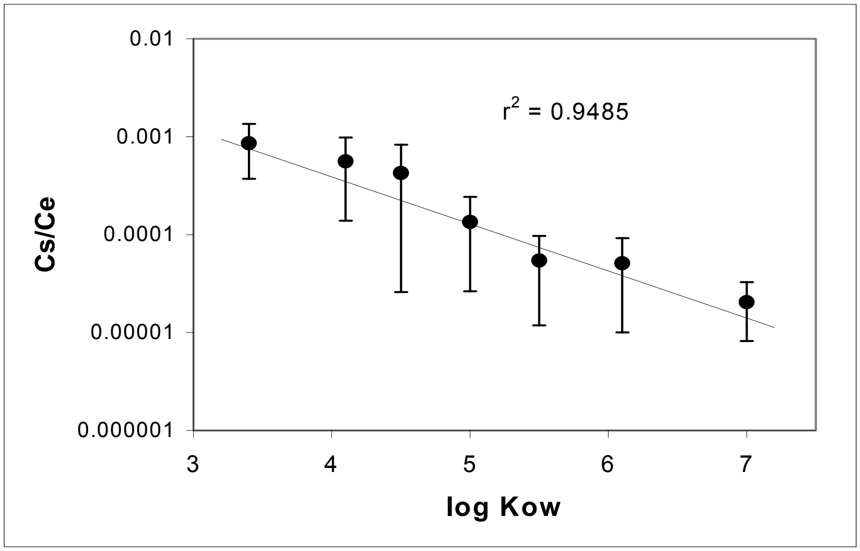

Figure 2-6: **Relationship between the observed log sediment-EVA partition coefficient at equilibrium and the log Kow of the test chemicals. Each point is the average ±SD of the log Cs/Ce determined at near-equilibrium (i.e., after t_{95} hr) for the 861 hr equilibration experiment. The n of each point varied from n = 7 for diCBz to n = 3 for hexaCBP.**

The measured log Z_S values for each chemical are given in TABLE 2-1. These are the mean ±SD of pooled values from two independent experiments performed using two samples of sediment from Port Moody mudflats. For each chemical, Zs was determined from Cs/Ce ratios measured at near-equilibrium (i.e., after t_{95} hr) multiplied by the value of Ze. The number of data points after t_{95} hr varied among the test chemicals (there were more data points for chemicals with lower Kow), and n varied between 7 for diCBz and 3 for hexaCBP.

The relationship between measured log Zs values and log Zs values predicted using the equation $Zs = 0.35 * Kow * \phi_{OC} * ds/H$ is given in FIGURE 2-7.

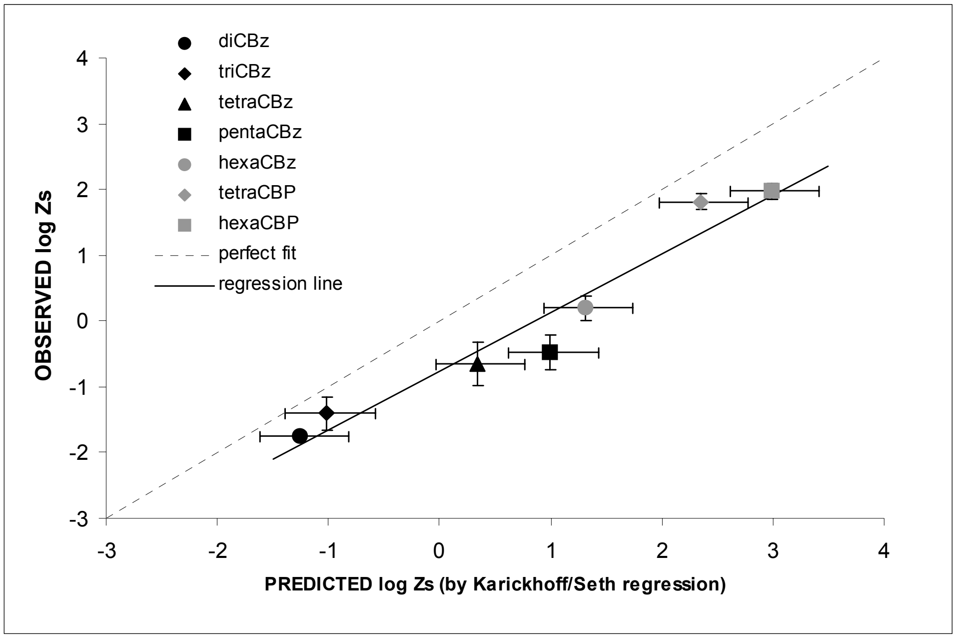

Figure 2-7: **Comparison of the measured values of log Zs with values predicted using the equation $Zs = 0.35 * Kow * \phi_{OC} * ds/H$. Error in the predicted Zs values is given by the 95% confidence interval determined by Seth et al. (1999) for the constant 0.35 in the equation $Koc = 0.35 * Koc$. The error bars for the measured Zs values are ± SD, with the n of each point ranging between n = 7 for diCBz and n = 3 for hexaCBP.**

The measured log Zs values were closely correlated with the predicted values ($r^2 = 0.94$). The vertical distance between the regression line and the line of perfect agreement was between 0.5 and 1.5 log units, indicating that the log Zs values predicted by the equation of Seth el al (1999) were 3 – 30 times higher than those measured for the same chemical. The regression equation for the seven test chemicals is

observed log Z_S = predicted log Z_S (0.89±0.10) – (0.77±0.11), $r^2 = 0.94$ (Equation 2.9)

For each chemical, the predicted value of Zs is based on the quantity of OC determined in the sediment sample (ϕ_{OC}) and on the assumption that the sorptive capacity of that measured OC is approximately 35% of the sorptive capacity of octanol for the test chemical. The measured value of Zs expresses both the quantity of OC that the chemicals are partitioning into and the sorptive quality of that OC. One reason for the higher predicted Zs values may be related to the possible existence of two kinetically-distinct pools of OC in sediment. Kraaij et al (2003) suggested that one form of OC, termed “fast OC”, is characterized by relatively rapid exchange with chemicals in pore water, whereas chemical associated with the “slow OC” fraction exchanges so slowly that it is considered to be sequestered, and not available for partitioning. In their model, hydrophobic chemicals partition between pore water and the “fast”, non-sequestered OC fraction of the sediment. Measures of total OC however cannot distinguish these two putative OC types, and may overestimate the amount of OC that is relevant to partitioning. This would lead to the predicted Zs values being higher than measured values.

Another possible explanation for the discrepancy between predicted and measured Zs is that the relative sorptive capacities of OC and octanol which were obtained through the regression analyses of Seth et al (1999) is not correct for the test chemicals in the test sediment. This possibility is testable using the current method. If the fugacity capacity measured for a sample of sediment is not related by a factor of approximately 0.35*ϕ_{OC} to the measured fugacity capacity of octanol (Zo) for the test chemicals, then the Koc = 0.35* Kow 'rule of thumb' may need to be re-examined. The factor 0.35*ϕ_{OC} was derived by re-writing Koc = 0.35* Kow as (Zs / Zw)/ϕ_{OC} = 0.35* Zo / Zw , which simplifies to Zs = 0.35*ϕ_{OC}* Zo .

2.5.5 The Measured Fugacity Capacity of Octanol (Zo)

Equilibration between EVA and octanol phases appeared to be rapid, and Co / Ce ratios were stable between 24 hr and 10 days (data provided in Appendix D). The pooled values of Co and Ce measured after 1 to 10 days equilibration time are provided in Table 2-5. Relative error for these values varied between 5-10% for Co measurements, and between 11-14% for Ce .

Table 2-5: Mean concentrations of test chemicals measured in EVA, Ce, expressed in μg cm^{-3} (n = 12 determinations) and in octanol, Co, expressed in μg cm^{-3}. The values of Co were calculated as the difference in the average mass of chemical in the EVA phase in the study and control vials at equilibrium, expressed relative to the volume of octanol. The SD of Co was determined by propagating the errors in the mass of chemical in EVA in the control (n = 6) and study (n = 8) vials.

Test Chemical	**Concentration in EVA ± SD (μg cm^{-3})**	**Concentration in Octanol ± SD (μg cm^{-3})**
diCBz	11.57 ± 1.14	3.29 ± 0.39
triCBz	8.46 ± 0.63	2.53 ± 0.33
tetraCBz	10.15 ± 0.54	2.73 ± 0.37
pentaCBz	17.33 ± 1.27	4.33 ± 0.50
hexaCBz	11.56 ± 0.94	3.10 ± 0.35
tetraCBP	4.24 ± 0.40	0.95 ± 0.13
hexaCBP	5.99 ± 0.44	1.50 ± 0.19

FIGURE 2-8 compares the concentrations (in μg/cm^3) of the test chemicals in EVA (Ce) and 1-octanol (Co) after at least 24 hours equilibration time (the first time point examined).

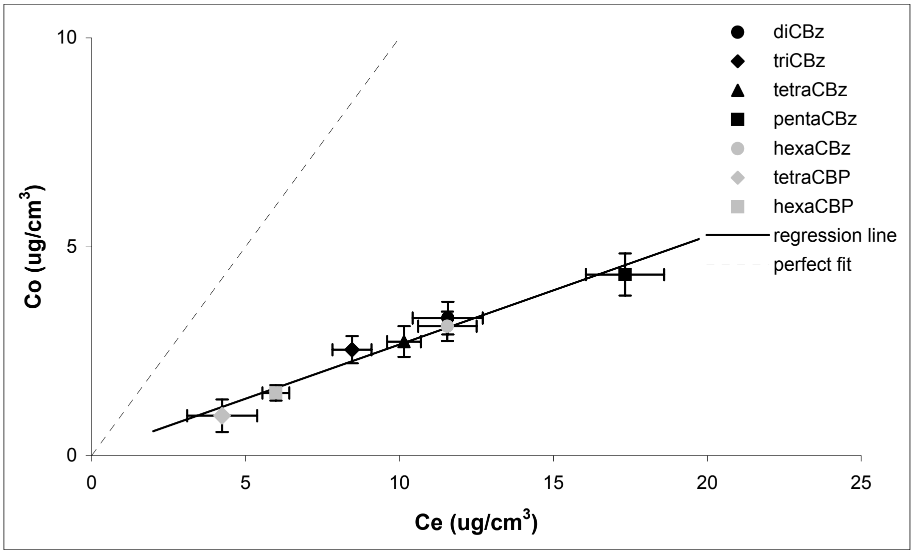

Figure 2-8: **Chemical distribution (expressed in μg/cm^3) between EVA and 1-octanol at equilibrium.**

FIGURE 2-8 compares the concentrations (in μg/cm^3) of the test chemicals in EVA (Ce) and 1-octanol (Co) after at least 24 hours equilibration time (the first time point examined). FIGURE 2-8 indicates that the relationship between the sorptive capacity of 1-octanol and EVA is constant for all of the test chemicals, i.e., Co/Ce is not related to Kow. The equation of the regression line is

$$Co = 0.260 \pm 0.021\ Ce + 0.063 \pm 0.222,\ r^2 = 0.97,\ n = 7 \quad \text{(Equation 2.10)}$$

The ratios Co/Ce were multiplied by the value of Ze determined earlier to derive the fugacity capacity of octanol, Zo (in units of mol m^{-3} Pa^{-1}) for each chemical. These are given in logarithmic form in TABLE 2-1. FIGURE 2-9 compares the log Zo values with values predicted using the formulae Kow/H and Koa/RT.

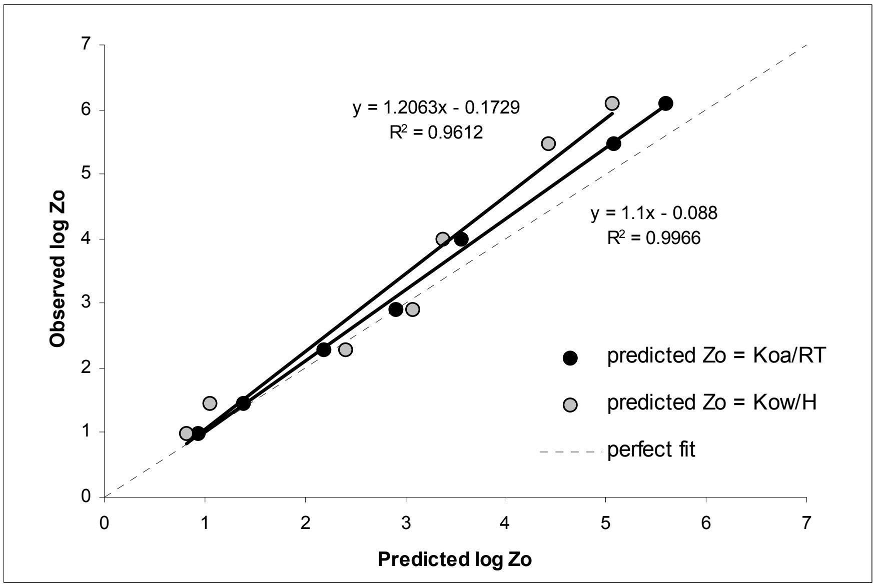

Figure 2-9: Relationship between observed log Zo and log Zo predicted using two different formulae involving reported Kow or Koa data.

The agreement between observed Zo and independently-derived values of Zo predicted from Kow or Koa data was excellent, although values predicted from Koa /RT gave a slightly closer fit to the observed data. Deviations from perfect fit were greater for the more hydrophobic chemicals (log $Kow \geq 5.5$). This was especially the case when Zo is predicted from Kow/H, and may be related to uncertainties in both H and Kow for these chemicals. Precise values of H and Kow for very hydrophobic chemicals are experimentally difficult to obtain. Measurement of H may be limited by lack of reliable water solubility data or because the vapor pressure of the water-saturated organic substance – which is what should properly be used in the estimation of H – differs significantly from the value of the vapor pressure of the pure substance, which is the value usually used to estimate H (Gossett, 1987). Kow values for highly hydrophobic chemicals are also difficult to obtain as their concentrations of in the water phase are low, and small errors in estimates of chemical concentration in the water phase will result in large differences in measured values of Kow. By contrast, Koa values can be determined with small measurement error using relative GC retention times (Wania et al., 2002). We are not aware of any data indicating that EVA is soluble in n-octanol.

FIGURE 2-9 indicates that the Zo values measured using this method are in close agreement with values predicted using physical properties, especially values predicted using Koa/RT. This largely reflects the close relationship between Koa and Kea (observed Zo is derived from $Ze * Co/Ce$, where $Ze = Kea$/RT). Kea and Koa are thus directly related to each other through Co/Ce. The sorptive capacity of octanol is approximately 25% that of EVA ($C_O/C_E = 0.26 \pm 0.02$), and Kea can be predicted by correcting tabulated values of Koa by this amount.

2.5.6 Relationship between Zs, Zo and Kow

FIGURE 2-10 compares the log Z values measured for EVA, sediment and octanol with log Kow. Also included in this plot are estimates of the log Z of air and water for the test chemicals, predicted from Zw = 1/RT and Za = 1/H. For each test chemical, the Z value of the five media decreases, in order, from EVA to octanol to sediment to water to air and the extent of the decreases are related to the Kow of the chemical.

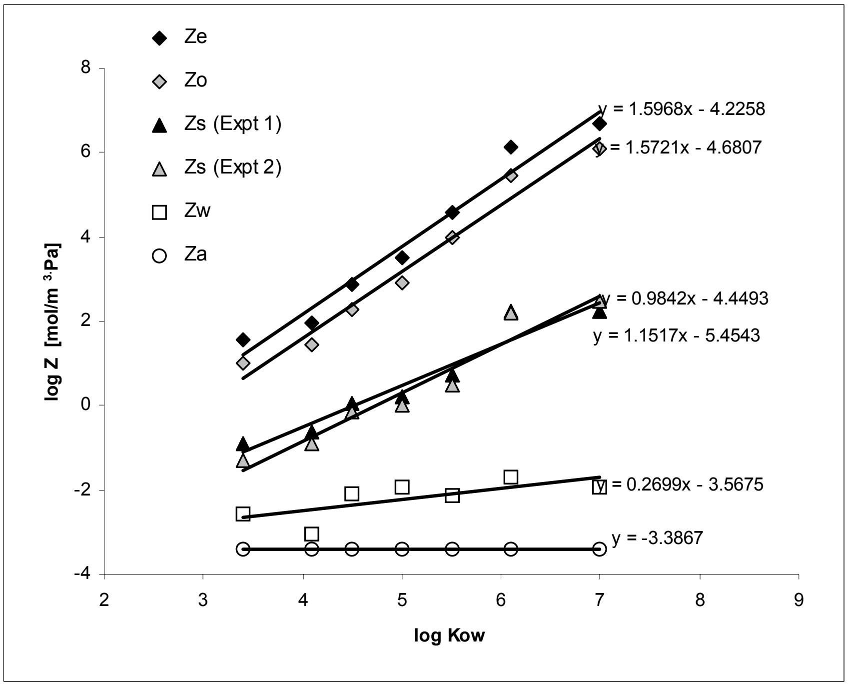

Figure 2-10: **Relationship to log Kow of measured log Z for EVA (Ze), octanol (Zo) and the sediment sample (Zs), and predicted values of Z for water (Zw) and air (Za).**

Unlike the environmental phases in FIGURE 2-10, the relationship between the measured fugacity capacities of octanol (Zo) and EVA (Ze) increase in parallel with Kow. The slopes of the regression lines for EVA and octanol are 1.60 ± 0.13 and 1.58 ± 0.13, respectively. As shown in the section above, measured Zo and Ze differ by a constant factor of 0.26 for the seven test chemicals examined.

The values of log Zs also increase with log Kow, but the slopes of the regression lines of log Zs vs. log Kow are lower (1.15 ± 0.13 and 0.98 ± 0.13). This indicates that (at least within this congener series) the relationship between Zo and Zs is not constant for all chemicals, but varies with the chemical's Kow. The measured values of Zs and Zo diverge as log Kow increases. For example, the Zo and Zs measured for diCBz (log Kow = 3.4) given in TABLE 2.1 differ by about 2 orders of magnitude. In contrast, the Zo and Zs values of hexaCBP (log Kow = 7) differ by over 4 orders of magnitude. Because OC is assumed to be the dominant sorbing component of sediment and determines sediment's sorptive capacity (i.e., Zs), this observation is not consistent with the formula $Koc = 0.35 Kow$ (Karickhoff, 1981; Seth et al., 1999). That is, the relationship between the sorptive capacities of octanol and OC cannot be represented as 35% alike for chemicals of all Kow.

In FIGURE 2-11, the observed Zs data are expressed in terms of Koc by rearranging the equation $Koc = Ksw/\phi_{OC}$ to $Koc = Zs/Zw * \phi_{OC}^{-1}$, where $Zw = 1/H$, and ϕ_{OC} for this sediment sample is 0.017 g ϕ_{OC}/g sediment.

Included in FIGURE 2-11 are the log Koc values for each test chemical determined using the conventional formula suggested by Karickhoff (1981) and Seth et al (1999). The conventional prediction method consistently gives higher values of Koc.

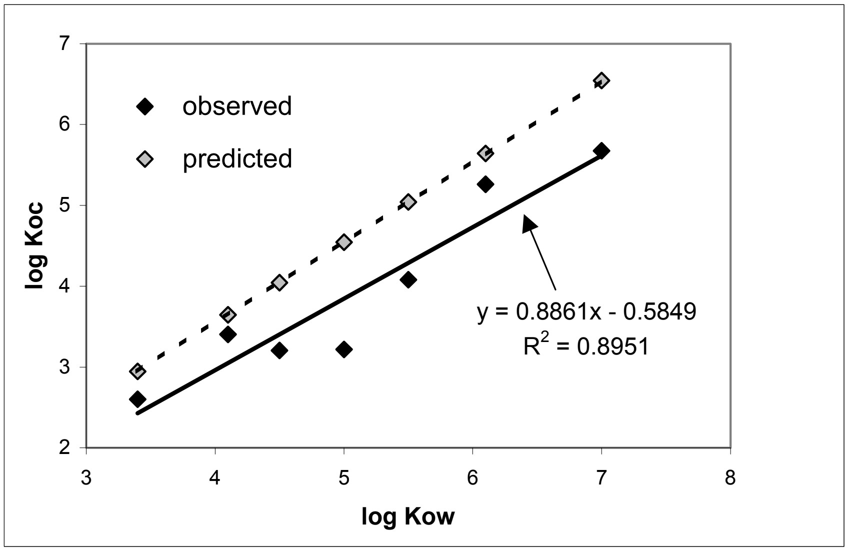

Figure 2-11: Comparison of log *Koc* calculated using measured *Zs* and log *Kow* predicted from 0.35* *Kow* against log *Kow*.

Employing an entirely different approach, Kraaij et al. (2003) made a similar observation when they compared the Karickhoff/Seth log *Koc* - log *Kow* regression and what they termed the log Koc_{rap} – log *Kow* regression for several PCBs and chlorobenzenes. Koc_{rap} was defined as the partition coefficient between chemical freely dissolved in pore water (measured using non-depleting SPME) and the estimated fraction of sediment-associated chemical which is readily available for partitioning. (In their studies, Kraaij et al. (2002, 2003) obtained experimental evidence for the concept that hydrophobic chemicals in sediments are distributed as rapidly and slowly desorbing fractions, and that the slowly desorbing fraction is functionally sequestered and not available for uptake into benthic organisms). Kraaij et al (2003) reported that their measured data for the PCBs and chlorobenzenes conformed to a single log Koc_{rap} -log *Kow* relationship over a log Kow range of 4.5 to 7, and that the Karickhoff/Seth regression over-estimated their log Koc_{rap} values by up to one order of magnitude. They did not report the regression equation for their data.

In FIGURE 2-12, the regression equation for measured values of log Koc on log Kow is given for this sediment sample. In non-logarithmic form, it is

$$Koc = 0.26 * Kow^{0.89} \qquad \text{(Equation 2.11)}$$

This is a nonlinear relationship between Koc and Kow, not a direct linear relationship as suggested by Karickhoff (1981) and Seth et al. (1999).

In order to understand the discrepancy between equations, we must examine the derivation of the Karickhoff/Seth regression (Koc = 0.35*Kow). Karickhoff's constant of 0.41 was obtained from Koc values of 5 PAHs, which were selected from a set of 50 Koc - Kow data pairs for chemicals such as PAHs, carbamates, organophosphates and phenyl ureas. Seth et al. (1999) obtained Koc data for 175 hydrophobic organic chemicals from six published data sets, and plotted 118 of these in Figure 1 of their report. No reason was provided for selecting these particular 118 points. The log Koc – log Kow regression equation they observed for these pooled 118 data points was log Koc = 0.81log Kow + 0.09, n = 118, r^2 = 0.89. Examination of their Figure 1 scatter plot led the authors to suspect that the low Koc values reported for the very hydrophobic chemicals (log > 5.5) were "erroneous" because they may have been measured under non-equilibrium conditions. They concluded that these Koc values were "distorting" the correlation, and they eliminated all but 2 of them from their analysis, leaving n = 98 data points. In place of these data, they inserted n = 23 Koc values calculated from Ksa (soil-air) partition coefficients that had been measured after approximately 3 months equilibration time (Cousins et al., 1998; Hippelein and

MacLachlan, 1998). (Each Koc value was derived from the measured Ksa value and estimates of Kaw (air-water) partition coefficient). The formula $Koc = 0.35\ Kow$ and the 95% confidence interval derived by Seth et al. (1999) is therefore based on these 23 Ksa data and on 98 of the 175 Koc values available from the six data sets originally selected (n = 1 21 points).

In FIGURE 2-12, the 175 Koc data points obtained from the six original publications are plotted versus Kow. The open symbols are the Koc data of chemicals not included in the Seth analyses, either because they had log Kow > 5.5 and were possibly measured under non-equilibrium conditions, or for unspecified reasons. This plot shows that if no data are eliminated from the analysis, the relationship between Koc and Kow is not linear across a wide range of log Kow (1.4 to 7.3). The Seth et al (1999) regression equation under-estimates Koc values for lower Kow chemicals, and over-estimates it for chemicals with higher Kow. Furthermore, there appears to be more scatter in this Koc - Kow relationship than reported by Seth et al (1999).

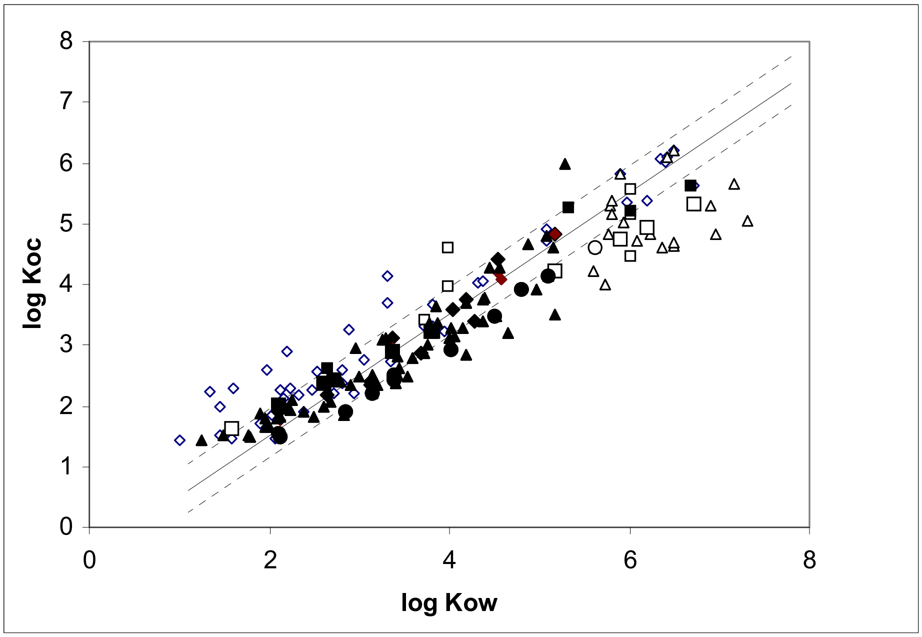

Figure 2-12: Plot of the 174 Koc - Kow pairs collected by Seth et al (1999) from six published data sets. Filled symbols are the data selected by Seth et al. (1999) to derive the linear relationship between Koc and Kow. Empty symbols are data points eliminated from their analysis. Data sets were: ◇◆ Karickhoff (1981), △▲ Sablijic et al, 1985, □■ Schwarzenbach and Westall, 1981, ●○ Chiou et al, 1983, □■ Chin et al, 1988, ▲ Pussemier et al, 1990. The solid line is the regression Koc = 0.35* Kow and the dotted lines are the 95% confidence interval for this, according to Seth et al., 1999.

TABLE 2.6 gives the log-log regression equations for the 175 Koc - Kow data points. The slope obtained from pooling all six data sets is 0.80 ± 0.02 (SE), compared to the slope of 0.89 ± 0.14 (SE) obtained from the equilibrium partitioning experiments of our seven test chemicals into our sediment sample (FIGURE 2-11). Both slopes are less than one, indicating a nonlinear relationship between Koc and Kow. Only one of the six data sets (Pussemier et al, 1990, n = 11 points) exhibited a slope of 1.

Table 2-6: **Regression equations (log Koc = a log Kow + b) for the 175 Koc - Kow data points collected by Seth et al. (1999). These authors suggested the 'Rule of Thumb' Koc = 0.35* Kow based on their selection of 98 of these points, plus 23 data points obtained from elsewhere. Included is the regression equation obtained from the calculated log Koc from Zs *H/ϕ_{OC}, where the values of Zs were measured in the present study using sediment from Port Moody mudflats (ϕ_{OC} = 0.017).**

Reference	log Kow range	n	slope a	intercept b	n selected by Seth et al
Karickhoff, 1981	1 – 6.72	50	0.85	0.32	5
Chiou et al., 1983	2.13 – 5.62	12	0.90	-0.54	11
Sablijic et al., 1995	1.25 – 7.32	81	0.79	0.15	61
Schwarzenbach & Westall, 1981	1.59 – 6.72	11	0.72	0.49	6
Chin et al., 1988	2.64 – 6.67	10	0.66	1.25	4
Pussemier et al., 1990	2.11 – 5.18	11	1.01	-0.53	11
Seth et al., 1999 'Rule of Thumb'		121	1.00	0.46	
Present study	3.4 - 7	7	0.89	-0.58	

The laboratory-based data presented here of a non-linear relationship between Zs and Zo, and between calculated-Koc (= Zs / Zw *$\phi_{OC}{}^{-1}$, where Zw = 1/H) and Kow indicate that the relationships between Kow and field collected Koc data should be re-evaluated. As demonstrated above, re-evaluation may prove that the 'rule of thumb' proposed by Seth et al. (1999) should not be indiscriminately used to predict values of Koc for all chemicals, regardless of their Kow.

3 DETERMINATION OF THE FUGACITY CAPACITY OF LIVING PHYTOPLANKTON (Zp) FOR SELECTED HYDROPHOBIC ORGANIC CHEMICALS

3.1 Background and Significance

The hypothesis of “early diagenesis” to account for the higher-than-equilibrium chemical concentrations sometimes observed in bottom sediment was outlined earlier (see Section 1.3.1.2). Briefly, hydrophobic organic chemicals dissolved in water will partition into the organic matrix of phytoplankton suspended in surface water. The fate of such chemicals is then determined by two processes: vertical transport to bottom sediments by dead cells and entry into food webs by grazing zooplankton and filter feeders. Especially during periods of high productivity, such as during a bloom, the production of phytoplankton greatly exceeds the capacity of zooplankton to consume it, resulting eventually in large quantities of settling dead phytoplankton. During vertical transport, the organic portions of the dead phytoplankton are consumed by bacteria, and become depleted of organic carbon (OC). As the most labile OC (e.g., protein) is removed by microbial decomposition, the character of the remaining OC (e.g., carbohydrates) may become more “crystalline” and have less sorptive capacity for hydrophobic chemicals. The decrease in quantity and quality of OC is expected to result in a progressive decrease in the fugacity capacity of the particles for the chemical contaminants. The decrease in fugacity capacity of the particle is associated with increased chemical fugacity if the particle decomposes at a rate which is faster than the desorption rate of the chemical back into the water. In this case, equi-fugacity between the particle and water will never be achieved in the time it takes for the particle to descend down through the water column. Another way to express this is that as the OC is being decomposed, the concentration and fugacity of contaminating chemical associated with the remaining OC increases if the kinetics of chemical desorption are slower than the kinetics of OC loss. The end result is an increase in the fugacity of chemicals in the bottom sediment beyond what would be expected by simple equilibrium partitioning (Maclean, 1999; Gobas and Maclean, 2003). As noted by Maclean (1999), the microbial consumption of OC continues within the sediment until the particle has either undergone complete conversion to inorganic mineral matter or is buried at a depth where there is no microbial action. Benthic invertebrates may also increase the fugacity of chemicals in bottom sediment further through their digestive processes. Such organisms could magnify very hydrophobic chemicals in their food, which would result in elevated fugacity of their egested fecal material which becomes part of the bottom sediment layer. When the organism dies, it too becomes part of the bottom sediment, and adds its elevated body burden of chemical to this layer (Maclean, 1999).

To test the early diagenesis theory, Maclean (1999) conducted a field study to measure differences in OC content between plankton, suspended sediments and bottom sediments collected from Kitimat Arm, BC. The results indicated that the OC content of bottom sediment was less than that of suspended sediment, which in turn, was less than plankton. This is consistent with the hypothesis that $Z_{\text{plankton}} > Z_{\text{suspended sediment}} > Z_{\text{bottom sediment}}$ and that this is a mechanism that could account for the apparent disequilibrium observed between water and sediment. Maclean assumed that OC was the dominant matrix into which the PCB congeners partitioned, based on analyses indicating that the

Kitimat plankton was 24% OC (total organic carbon, determined by ASL Analytical Service Laboratories, Vancouver, BC) and only 1.5% lipid (determined gravimetrically). This was consistent with her samples containing primarily phytoplankton, which unlike zooplankton, do not have the digestive machinery to create and store lipids. Subsequently, Skoglund and Swackhamer (1999) compared PCB bioaccumulation in phytoplankton after normalizing to the OC and lipid pools with accumulation predicted using a kinetic-based model. They concluded that OC was the most appropriate sorptive medium for modelling PCB accumulation in phytoplankton, possibly because PCB sorption to membrane proteins is more important in plankton than in higher trophic level organisms.

Gobas and Maclean (2003) also presented an OC decomposition model to demonstrate how the apparent disequilibrium could arise. The model's findings were supported by re-analyses (using the fugacity format) of published field data of the concentrations of PCB congeners in plankton, suspended sediment and bottom sediment collected from the Great Lakes. The results demonstrated that the fugacity of any individual PCB congener calculated in plankton was less than the fugacity in suspended sediment, which in turn was less than the fugacity in sediment. More recently, deBruyn and Gobas (2004) developed models showing how competing organic matter decomposition and PCB desorption kinetics can produce a "state of persistent disequilibrium" between water and OC in organically-enriched sediments.

In the studies of PCB disequilibrium between water, plankton and sediment (Maclean, 1999; Gobas and Maclean, 2003), the magnitude of the disequilibrium depended on the Kow of the PCB congener. As log Kow increased, the extent of the disequilibrium decreased. The explanation suggested to account for this was that the time required for a chemical to equilibrate between water and plankton was related to

Kow. Low Kow chemicals are likely to achieve equilibrium more rapidly with plankton OC than high Kow chemicals. (The desorption rates of high Kow chemicals are slower than for low Kow chemicals; this means that the time required to equilibrate with plankton is slower too). High Kow chemicals may never attain an equilibrium between water and living plankton – especially if the plankton are growing rapidly -- meaning that their “initial” fugacity in phytoplankton is lower than in water. If the subsequent diagenesis process affects all particles and all chemicals equally, then the “final” fugacity of particles when they are deposited as bottom sediments will also be relatively lower for the more hydrophobic chemicals.

3.2 Objective

While clearly demonstrating the existence of disequilibria of hydrophobic organic chemicals between aquatic media, and proposing a mechanism by which this could occur, the experimental work by Maclean (1999) did not directly test the hypothesis of early diagenesis. Maclean observed decreasing OC content from plankton to suspended particles to bottom sediment, and inferred from this that there was a step-wise drop in fugacity capacity. Now that a method is available to empirically measure fugacity capacity of sediment (described in Chapter 2), that method is here applied to measure the fugacity capacity of living phytoplankton. The objective of this study is to measure $Zplankton$, the fugacity capacity of a sample of living plankton (Zp) for a range of hydrophobic test chemicals and to compare these values to Zp values predicted by equilibrium-based regressions.

If Zp can be reliably measured, the goal of subsequent research will be to apply the method to measure the fugacity capacity of particles collected during sedimentation in an aquatic ecosystem in disequilibrium. The early diagenesis hypothesis predicts that Zp will be greater than Zs for each chemical examined. The hypothesis would be disproved if $Zp = Zs$, or if $Zp < Zs$.

3.3 Methods

3.3.1 Chemicals

Seven organochlorines were examined here: a series of five chlorobenzenes (Aldrich Chemical Co, Milwaukee, WI, USA 1,4-dichlorobenzene (diCBz), 1,3,5-trichlorobenzene (triCBz), 1,2,4,5-tetrachlorobenzene (tetraCBz), pentachlorobenzene (pentaCBz), hexachlorobenzene (hexaCBz) and two PCBs (Accustandard, New Haven CT, USA), 2,2',5,5'-tetrachlorobiphenyl " IUPAC PCB #52" (tetraCBP) and 2,2',4,4',6,'6-hexchlorobiphenyl "IUPAC PCB #155" (hexaCBP). These chemicals were selected to cover a range of Kow ($10^{3.4} – 10^{7}$) and for their ease of assay by GC.

3.3.2 Thin Film Preparation

A solution of ethylene vinyl acetate copolymer, EVA (Elvax 40W®, Dupont Chemical Co., Wilmington, DE, USA) was prepared by dissolving the EVA beads in DCM (Analar, HPLC grade) to a concentration of 6.68 g/L. This solution was spiked with the 7 test organochlorines to the following final concentrations: diCBz (0.35 mg/ml), triCBz (0.25 mg/ml), tetraCBz (0.26 mg/ml), pentaCBz (0.42 mg/ml), hexaCBz (0.32 mg/ml), tetraCBP (0.10 mg/ml), hexaCBP (0.14 mg/ml). A small volume (25 μl) of this solution was used to coat the interior surface of 2 ml glass autosampler vials (silanized, pre-rinsed with a volume of DCM, purchased from Agilent). The vial was slowly rolled for 1 minute so that the EVA solution passed over the walls of the vial until liquid was no longer visible. The vial was left uncapped for an additional 3 mins to allow DCM to evaporate. The vial was then capped using a screw cap with a teflon/rubber/teflon septum (Agilent), and kept at room temperature. The EVA film thickness was calculated to be 0.24 μm, based on the volume of the EVA coating and the volume of the interior surface area of the vial, which was directly estimated. The volume of the EVA film was 0.000173 cm^3, which was determined from the mass of EVA (167 μg) added to the vial and the density of EVA (965 mg/cm^3, Dupont Chemical Co information). The EVA film appeared to be uniformly applied, based on the even distribution of Sudan IV dye added to a separate EVA solution and coated in an identical manner.

3.3.3 Plankton Collection

Phytoplankton were collected the day after a bloom in Port Moody Arm of Burrard Inlet, BC, on July 7, 2003 by towing a plankton net (mesh size 0.01 mm) at a depth of approximately 1 m from the surface. The contents of the net were poured into a clean glass jar and transported immediately to the laboratory. Light microscopy indicated the presence of motile phytoplankton, primarily diatoms and dinoflagellates (Rod MacVicar, personal communication).

3.3.4 Equilibrium Partitioning Experiment

The method used to determine equilibrium partition coefficient between the plankton and EVA was the same as described in Chapter 2 with sediment. Briefly, the suspension of sediment was placed in 2 ml autosampler vials that had previously been coated with a thin film of EVA containing seven test organochlorines. Control vials contained spiked EVA films and water. The sealed vials were gently rotated at 33 rpm at room temperature. After 22, 63 and 161 hr, water and plankton suspension were removed from two vials, the EVA films rinsed 3 times with water, and the chemicals remaining in the EVA film extracted into 1.5 ml hexane. A 1 μl sample of hexane was injected onto the GC column for quantitation of the amount of chemical in the EVA phase. The coefficients of variation in chemical concentrations in the EVA films ranged between 4% and 9%. Absolute chemical concentrations were not determined. Instead, peak heights on the chromatograms were used, and were corrected for the volume of the EVA film (0.000173 cm^3) or plankton (0.081 cm^3) in the vial. This allows us to avoid uncertainty introduced by constructing standard curves. The volume of plankton in the suspension was approximated through centrifugation (15 min at 3000 rpm) to be 4% (cm^3 plankton/cm^3 plankton suspension), and the EVA coated vial contained 2.032 cm^3 of suspension. The plankton/EVA partition coefficient was determined from the chemical concentration in the EVA film (Ce) and in plankton (Cp) in the vial that contained EVA and plankton. Ce was determined directly. Cp was calculated by subtracting the amount of chemical in the EVA film of the “plankton” vial from the amount in the film of the control (“water”) vial, and correcting for the volume of plankton. The ratio Cp/Ce at equilibrium was multiplied by the fugacity capacity of EVA (Ze) for each chemical (determined previously as described in Chapter 2) to derive a measured value of Zp. An example of the calculations is given in Appendix C.

3.3.5 Gas Chromatography

The assay method for the seven organochlorines was the same as described in Chapter Two. A Hewlett-Packard 5890 gas chromatograph (GC) equipped with a ^{63}Ni electron-capture detector, a cool on-column injection port and a 30 m x 0.25 mm x 2.65 (film thickness μm) HP-5 column (Agilent Technologies, Mississauga, ON) was used for the analysis. The oven temperature program was 35º C for 0.2 min, 20º C/min to 270º C, which was held for 4 min. The injection port temperature and detector temperatures were 38º C and 350º C, respectively, and the carrier gas was helium (1 ml/min).

Injections were done manually, using a gas-tight syringe with a Teflon-tipped plunger (Agilent). Peaks were integrated using Chemstation (Hewlett Packard, Mississauga, ON) software.

3.3.6 Predicted Values of Zp

The predicted fugacity capacity of the plankton sample (Zp) was OC-based, using the conventional equation

$$Zp = \frac{0.35 * Kow * \phi_{OC} * d_p}{H} \qquad \text{(Equation 3.1)}$$

where the fraction of OC, ϕ_{OC}, was assumed to be the same as that observed by Maclean (1999) for plankton collected in Kitimat Arm, 0.24 g OC/g wet weight plankton. The density of plankton, d_p, was assumed to be 1.1 L/kg (Gobas and Maclean, 2003), and H and Kow for the test chemicals were selected by Mackay (1992).

In Chapter 2, evidence was presented that the relationship between Koc and Kow is not best described by the factor 0.35, and that the more complex Equation 2.11 (Koc = 0.26* $Kow^{0.89}$) might be a better expression. The predicted Zp was also determined by altering the conventional equation accordingly to

$$Zp = \frac{0.26 * Kow^{0.89} * \phi_{OC} * d_p}{H} \qquad \text{(Equation 3.2)}$$

3.4 Results and Discussion

3.4.1 Time Course of Chemical Loss from EVA Films

The time course of chemical concentrations in plankton are given in FIGURE 3-1. There was no change over the three time points examined (22, 63 and 161 hr) that was consistent with chemical uptake into the plankton, and it is assumed that equilibrium was attained by the first time point (22 hr) for all test chemicals. The plankton were no longer motile after 22 hr equilibration time.

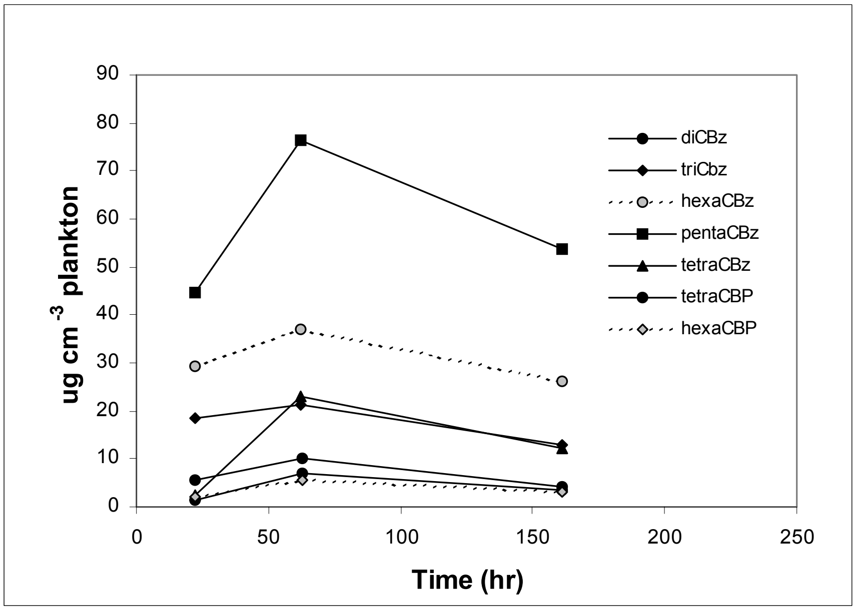

Figure 3-1: Time course of the uptake of chemicals into plankton.

3.4.2 Measured Fugacity Capacity of Plankton (Zp)

The logarithms of Zp calculated for each of the test chemicals are given in TABLE 3.1. The values are the mean log Zp ± SD of the three time points (22, 63 and 161 hr). The log Zp values ranged over 4 orders of magnitude and were closely correlated with log Kow ($r^2 = 0.97$). In part, this high degree of correlation arose due to the Ze variable used to derive Zp (i.e., $Zp = Ze * Cp / Ce$). The values of Ze for each chemical were determined in Chapter 2 from the equilibrium partition coefficient observed between EVA and air (i.e., $Ze = Kea$/RT, Equation 2.5). These independently determined Kea values were closely related to Kow ($r^2 = 0.97$ for regression of log Kea on log Kow).

The logarithms of the Cp / Ce ratios are plotted against log Kow in Figure 3-2. Included in this plot for comparison are the ratios observed between sediment and EVA (Cs / Ce) and between octanol and EVA (Co / Ce). The Cp / Ce values ranged only over approximately one order of magnitude. Their correlation with log Kow was weaker than that between Zp and Kow ($r^2 = 0.67$ for regression of log Cp / Ce on log Kow). (The Cp/Ce ratio for diCBz may be inaccurate because of the high volatility of this chemical. If this data point is eliminated from the regression analysis, the regression coefficient (r^2) becomes 0.75).

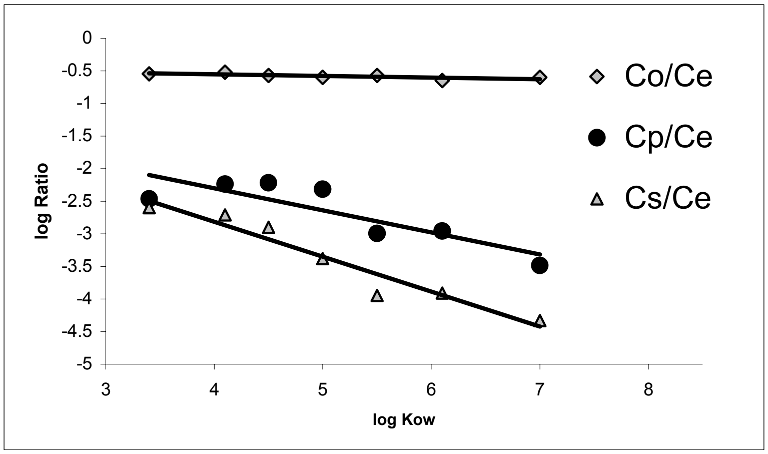

Figure 3-2: **Relationship between the logarithms of observed plankton-EVA (Cp/Ce) ratios and log Kow. The log-log relationships between Kow and sediment-EVA (Cs/Ce) and octanol-EVA (Co/Ce) are also shown.**

Table 3-1: **Logarithms of the reported Kow, observed EVA-plankton equilibrium partition coefficients and measured fugacity capacity of living phytoplankton (Zp) for the seven test organochlorines. Log Zp values are ± 1 SD, n = 3 determinations).**

Chemical	log Kow	log Cp/Ce	log Zp ± SD (mol $m^{-3}.Pa^{-1}$)
diCBz	3.4	-2.97	-1.55 ± 0.24
triCBz	4.1	-2.84	-0.87 ± 0.14
tetraCBz	4.5	-2.81	0.04 ± 0.09
pentaCBz	5	-2.92	0.58 ± 0.14
hexaCBz	5.5	-3.73	0.83 ± 0.52
tetraCBP	6.1	-3.62	2.50 ± 0.36
hexaCBP	7	-3.74	2.96 ± 0.17

3.4.3 Comparison between Measured and Predicted Fugacity Capacity of Plankton (Zp)

FIGURE 3-3 compares the values of Zp with values predicted using Equations 3.1 and 3.2 for each of the test chemicals.

The measured log Zp values were closely correlated with the values predicted using Equation 3.1 ($r^2 = 0.98$). However, the vertical distance between the regression line and the line of perfect agreement was between approximately 1.2 log units, indicating that the log Zp values predicted by this equation were approximately 15 times higher than the values measured for the same chemical.

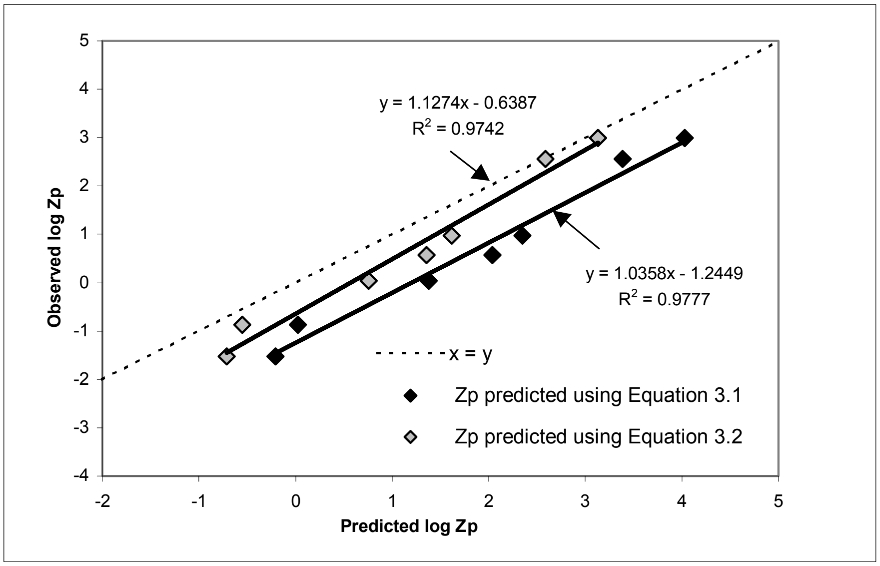

Figure 3-3: Relationship between measured values of Zp for the seven test chemicals and values predicted using two different equations to describe the similarity between OC and octanol.

In Chapter 2, the absorptive capacities of octanol and sediment OC for test hydrophobic chemicals were directly quantified, and the relationship between the two (expressed as equilibrium partition coefficients with water) was observed to be represented by Equation 2.11: $Koc = 0.26^* Kow^{0.89}$. Using this relationship as the basis for calculating the predicted Zp in Equation 3.2, the correspondence between observed and predicted values was close, and was identical for the two PCBs tested (FIGURE 3-3). The equation for the regression line between observed and these predicted log Zp values was

observed log Zp = 1.13 ($\pm$0.08)* predicted log Zp – 0.64 ($\pm$0.15), $r^2 = 0.97$, n = 7

(Equation 3.3)

This experiment illustrates that the methodology described in Chapter 2 to measure Zs can readily be applied to measure Zp, and that equilibration times between EVA and live plankton appear to be very fast (< 22 hr). There is approximately one order of magnitude deviation between the measured Zp values and values predicted by the conventional OC-based equation (Equation 3.1). These predicted Zp were calculated using an assumed, not measured, value for ϕ_{OC} of the Port Moody Arm plankton sample (0.24 g OC/g wet plankton). However, this appears to be a reasonable ϕ_{OC} value based on its similarity to the average ϕ_{OC} of 0.29 ± 0.09 observed by Skoglund and Swackhamer (1999) in 22 samples of phytoplankton collected from Green Bay, Lake Michigan. The observation of a close correspondence in Figure 3.2 between the measured Zp values and values predicted using Equation 3.2 is notable. This equation was derived based on the measured relationship between the sorptive capacities of OC and octanol (Chapter 2), not on the Karickhoff/Seth regression. The observed and predicted Zp values for each chemical were obtained independently and there is no reason to believe that the correspondence arose through autocorrelation.

This pilot experiment has demonstrated that the methodology is now available to test the hypothesis that higher-than-equilibrium chemical concentrations in sediment could arise through the process of "early diagenesis". The experiment to do this would be to collect plankton and bottom sediment from a aquatic system with high organic carbon cycling rates or from a lake where it is known that chemical pollutants are in disequilibrium. The present method using thin films of EVA can be employed to measure Zp and Zs of these samples for hydrophobic chemicals covering a range of Kow. Evidence that $Zp > Zs$ would support the early diagenesis hypothesis, whereas if $Zp < Zs$ or $Zp = Zs$, the hypothesis would be disproved.

4 CONCLUSIONS

The data obtained here are the first measured Z values of environmental phases (sediment and plankton) and of 1-octanol to be reported. The method relies on expressing the Z of these media relative to EVA, rather than to water as is conventionally done. One of the problems associated with using water as the reference phase for equilibrium partitioning is that hydrophobic chemicals can exist in water in many forms (e.g., freely dissolved, bound to dissolved OC and particulate bound), but it is only the freely dissolved form that participates in diffusive partitioning. This freely dissolved water fraction is not readily measured. In contrast, EVA is a homogeneous phase, and chemicals dissolved in EVA are expected to be uniformly distributed throughout the bulk of this phase. Additionally, EVA has a high Z for hydrophobic chemicals and the chemicals are concentrated in a small volume of plastic from which they can be reliably measured.

The goal of developing this method to assess chemical sorption and associated sediment-water equilibrium partition coefficients was to improve our understanding of why discrepancies occur between deduced and observed Koc values. This, in turn, could be used to improve models of the fate of chemicals in real ecosystems and thereby increase the accuracy of our assessments of risk to aquatic life. As outlined in this thesis, there are several potential reasons for the observed discrepancies:

i) One reason that was demonstrated here is that the generally accepted 'rule of thumb' relationship between Koc and Kow is not correct for all chemicals. The rule of thumb states that the sorptive capacity of sediment OC for all chemicals is approximately 35% that of octanol. However, when the measured sorptive capacities of sediment OC (here expressed as Zs) were compared with the measured sorptive capacities of octanol (Zo), it appears that this relationship is not constant. As the sorptive capacity of octanol increased with the Kow of the test chemical, there was not a corresponding increase in the sorptive capacity of sediment. The difference between Zs and Zo was approximately 2 orders of magnitude for the log Kow = 3.4 test chemical, and approximately 4 orders of magnitude for the test chemical with log Kow = 7. Whatever the intermolecular interactions are that control sorptive process in octanol, they are not the same as in sediment.

ii) A potential reason for discrepancies between observed and deduced Koc values is related to how the Koc is defined. The most current model of sediment-water partitioning (Kraaij et al., 2003) includes the possibility that not all of the mass of a sediment-bound hydrophobic chemical is available for partitioning. The model considers that a fraction of the chemical is essentially sequestered. Measures of solvent-extracted chemical in sediment include the mass of chemical that does not actually participate in diffusive partitioning, and may result in over-estimating actual Koc values. The advantage of the present method using EVA to examine partitioning is that it measures only that fraction of chemical that is actually partitioning into sediment OC.

iii) A third reason for discrepancies is that processes other than partitioning can occur which can affect chemical distribution and give rise to chemical disequilibria. Carbon mineralization during sedimentation is one such process and is a mechanism that has been postulated to account for the amplification of chemical concentrations in sediment. This theory can now be tested using the methodology described here to determine Zp and Zs in aquatic systems at disequilibrium. The measured values of Zp and Zs can be used to translate chemical concentrations to fugacities.

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APPENDIX A: CALCULATIONS TO DERIVE Z_S

MEASURED Zs VALUE –

The measured value of Zs is given by the formula

Zs = Ze*Cs/Ce,

where Ze is the fugacity capacity of EVA [mol m^{-3} Pa^{-1}], Cs is the equilibrium concentration of the chemical in sediment [mol m^{-3}], and Ce [mol m^{-3}] is the equilibrium concentration of the chemical in EVA. The values of Cs, Ce and Ze are determined as described below by using the size of chromatographic peaks.

1) Value of Ce in Film-Sediment Equilibrations:

Peak height (or peak area) recorded on the chromatogram from a 1 µl injection of the 1.5 ml hexane extract of the EVA film in Vial 2 (which is the vial where chemicals spiked in EVA equilibrated with sediment)

multiplied by 1500

= an expression of the mass of the chemical in the EVA film, assuming 100% extraction.

divided by 0.000173 cm^3 (the volume of EVA film)

= an expression of Ce, the concentration of the chemical in the EVA film per cm^3

2) Value of Cs in Film-Sediment Equilibrations:

Peak height (or peak area) recorded on the chromatogram from a 1 µl injection of the 1.5 ml hexane extract of the EVA film in Vial 1 (water control)

minus the peak height (or peak area) recorded on the chromatogram from a 1 µl injection of the 1.5 ml hexane extract of the EVA film in Vial 2 (which is the vial where chemicals spiked in EVA equilibrated with sediment)

multiplied by 1500

an expression of the mass of the chemical in the sediment, assuming 100% extraction.

divided by 2.023 cm^3 (the volume of sediment)

= an expression of Cs, the concentration of the chemical in the bulk sediment in cm^3

2) Value of Ze:

2a) Value of Ce in Film-Air Equilibrations

Peak height (or peak area) recorded on the chromatogram from a 1 µl injection of the 6 ml hexane extract of the EVA film

multiplied by 6000

= an expression of the mass of the chemical in the EVA film, assuming 100% extraction.

divided by 0.000173 cm^3 (the volume of EVA film)

= an expression of Ce, the concentration of the chemical in the EVA film per cm^3

2b) Value of Ca in Film-Air Equilibrations

Peak height (or peak area) recorded on the chromatogram from a 1 µl injection of the 2.032 ml of headspace air

multiplied by 2032

= an expression of the mass of the chemical in the headspace air

divided by 2.032 cm^3 (the volume of the headspace air)

= an expression of Ca, the concentration of the chemical in the headspace air per cm^3

2c) Value of Kea in Film-Air Equilibrations

= Ce (as determined in 2a above) divided by Ca (as determined in 2b above) which is unitless

2d) Value of Ze

= value of Kea (as determined in 2c above) divided by RT, where R = Avigadro's constant (8.314 Pa m^3 mol^{-1} K^{-1}) and T = temperature in degrees Kelvin (273 K). Ze has units of mol m^{-3} Pa^{-1}.

PREDICTED Zs VALUE

Predicted values of Zs are based on the relationship of Karickhoff (1981) and Seth et al., (1999) that

$$Koc = 0.35.Kow$$

where Kow is the dimensionless octanol-water partition coefficient, and .

$$Koc = Ksw/\phi_{OC}$$

where Ksw = Cs/Cw and ϕ_{OC} is the fraction of OC of the sediment. In this case, the ϕ_{OC} of sediment from Port Moody mudflats was 0.017 μg OC/μg whole sediment. Cs has units of mol/kg whole sediment, and Cw has units of mol/L water. Ksw thus has units of L water/kg sediment. In order to express Ksw as a dimensionless partition coefficient, it is necessary to multiply Ksw (or Cs) by the sediment density (d_s), which is assumed here to be 1.5 kg sediment/L sediment.

By rearranging Ksw = Zs/Zw,

$$Zs = Ksw/Zw$$

Substituting, and using 1/H for Zw,

$$Zs = 0.35{*}Kow{*}\phi_{OC}{*}\ d_s/H$$

where predicted Zs has units of mol m^{-3} Pa^{-1}.

APPENDIX B: CALCULATIONS TO DERIVE Z_O

MEASURED Zo VALUE –

The measured value of Zo is given by the formula

Zo = Ze*Co/Ce,

where Ze is the fugacity capacity of EVA [mol m^{-3} Pa^{-1}], Co is the equilibrium concentration of the chemical in octanol [mol m^{-3}], and Ce [mol m^{-3}] is the equilibrium concentration of the chemical in EVA. The values of Co, Ce and Ze are determined as described below by using the size of chromatographic peaks.

1) Value of Ce in EVA-Octanol Equilibrations:

Peak height (or peak area) recorded on the chromatogram from a 1 μl injection of the 5 ml methanol used to precipitate the EVA from solution in dichloromethane in Vial 2 (which is the vial where chemicals spiked in EVA equilibrated with 1-octanol)

multiplied by 5000

= an expression of the mass of the chemical in the EVA, assuming 100% recovery.

divided by 0.10526 cm^3 (the volume of EVA mound)

= an expression of Ce, the concentration of the chemical in the EVA per cm^3

2) Value of Co in EVA-Octanol Equilibrations:

Peak height (or peak area) recorded on the chromatogram from a 1 μl injection of the 5 ml methanol used to precipitate the EVA from solution in dichloromethane in Vial 1 (air control)

minus the peak height (or peak area) recorded on the chromatogram from a 1 μl injection of the 5 ml methanol used to precipitate the EVA from solution in dichloromethane in Vial 2 (which is the vial where chemicals spiked in EVA equilibrated with octanol)

multiplied by 5000

= an expression of the mass of the chemical in the octanol, assuming 100% extraction.

divided by 1.92774 cm^3 (the volume of octanol)

= an expression of Co, the concentration of the chemical in the octanol in cm^3

2) Value of Ze:

2a) Value of Ce in Film-Air Equilibrations

Peak height (or peak area) recorded on the chromatogram from a 1 µl injection of the 6 ml hexane extract of the EVA film

multiplied by 6000

= an expression of the mass of the chemical in the EVA film, assuming 100% extraction.

divided by 0.000173 cm^3 (the volume of EVA film)

= an expression of Ce, the concentration of the chemical in the EVA film per cm^3

2b) Value of Ca in Film-Air Equilibrations

Peak height (or peak area) recorded on the chromatogram from a 1 µl injection of the 2.032 ml of headspace air

multiplied by 2032

= an expression of the mass of the chemical in the headspace air

divided by 2.032 cm^3 (the volume of the headspace air)

= an expression of Ca, the concentration of the chemical in the headspace air per cm^3

2c) Value of Kea in Film-Air Equilibrations

= Ce (as determined in 2a above) divided by Ca (as determined in 2b above) which is unitless

2d) Value of Ze

= value of Kea (as determined in 2c above) divided by RT, where R = Avigadro's constant (8.314 Pa m^3 mol^{-1} K^{-1}) and T = temperature in degrees Kelvin (273 K). Ze has units of mol m^{-3} Pa^{-1}.

PREDICTED Zo VALUE

Predicted values of Zs are derived by two methods.

a) Zo = Koa/RT

Rearranging Koa = Zo/Za,

$$Zo = Koa/RT$$

where Koa is the reported octanol-air partition coefficient (dimensionless), and R = Avigadro’s constant (8.314 Pa m^3 mol^{-1} K^{-1}) and T = temperature in degrees Kelvin (273 K). Predicted Zo has units of mol m^{-3} Pa^{-1}.

b) Zo = Kow/H

Rearranging Kow = Zo/Zw,

$$Zo = Kow/H$$

where Kow is the reported octanol-water partition coefficient (dimensionless), and H is the reported Henry’s Law Constant of the chemical, which has units of Pa m^3 mol^{-1}. Predicted Zo has units of mol m^{-3} Pa^{-1}.

APPENDIX C: CALCULATIONS TO DERIVE Z_P

MEASURED Zp VALUE –

The measured value of Zps is given by the formula

Zp = Ze*Cp/Ce,

where Ze is the fugacity capacity of EVA [mol m^{-3} Pa^{-1}], Cp is the equilibrium concentration of the chemical in plankton [mol m^{-3}], and Ce [mol m^{-3}] is the equilibrium concentration of the chemical in EVA. The values of Cp, Ce and Ze are determined as described below by using the size of chromatographic peaks.

1) Value of Ce in Film-Plankton Suspension Equilibrations:

Peak height (or peak area) recorded on the chromatogram from a 1 µl injection of the 1.5 ml hexane extract of the EVA film in Vial 2 (which is the vial where chemicals spiked in EVA equilibrated with plankton suspension)

multiplied by 1500

= an expression of the mass of the chemical in the EVA film, assuming 100% extraction.

divided by 0.000173 cm^3 (the volume of EVA film)

= an expression of Ce, the concentration of the chemical in the EVA film per cm^3

2) Value of Cp in Film- Plankton Suspension Equilibrations:

Peak height (or peak area) recorded on the chromatogram from a 1 µl injection of the 1.5 ml hexane extract of the EVA film in Vial 1 (water control)

minus the peak height (or peak area) recorded on the chromatogram from a 1 µl injection of the 1.5 ml hexane extract of the EVA film in Vial 2 (which is the vial where chemicals spiked in EVA equilibrated with plankton suspension)

multiplied by 1500

an expression of the mass of the chemical in the sediment, assuming 100% extraction.

divided by 2.023 cm^3 (the volume of the plankton suspension)

multiplied by 0.04 (to correct for plankton being approximately 4% of the volume of the plankton suspension)

= an expression of Cp, the concentration of the chemical in the plankton per cm^3 plankton

2) Value of Ze:

2a) Value of Ce in Film-Air Equilibrations

Peak height (or peak area) recorded on the chromatogram from a 1 µl injection of the 6 ml hexane extract of the EVA film

multiplied by 6000

= an expression of the mass of the chemical in the EVA film, assuming 100% extraction.

divided by 0.000173 cm^3 (the volume of EVA film)

= an expression of Ce, the concentration of the chemical in the EVA film per cm^3

2b) Value of Ca in Film-Air Equilibrations

Peak height (or peak area) recorded on the chromatogram from a 1 µl injection of the 2.032 ml of headspace air

multiplied by 2032

= an expression of the mass of the chemical in the headspace air

divided by 2.032 cm^3 (the volume of the headspace air)

= an expression of Ca, the concentration of the chemical in the headspace air per cm^3

2c) Value of Kea in Film-Air Equilibrations

= Ce (as determined in 2a above) divided by Ca (as determined in 2b above) which is unitless

2d) Value of Ze

= value of Kea (as determined in 2c above) divided by RT, where R = Avigadro's constant (8.314 Pa m^3 mol^{-1} K^{-1}) and T = temperature in degrees Kelvin (273 K). Ze has units of mol m^{-3} Pa^{-1}.

PREDICTED Zp VALUE

Predicted values of Zp were derived by the equation

$$Zp = 0.35*Kow*\phi_{OC}*\ d_p\ /H$$

where Kow is the reported octanol-water partition coefficient of the chemical (dimensionless), ϕ_{OC} is the fraction of organic carbon assumed in the plankton (0.24 μg/μg wet plankton, and d_p is the assumed density of the plankton (1.1 kg/L), and H is the reported Henry's Law constant for the chemical (with units of Pa m^3 mol^{-1}). Predicted Zp has units of mol m^{-3} Pa^{-1}.

APPENDIX D: TIME COURSE EXPERIMENT FOR CHEMICAL UPTAKE INTO 1-OCTANOL

Table D-1: Peak heights taken from chromatograms of hexane extracts of EVA exposed to 1-octanol or air for 47, 93 or 236 hr.

		PK HT						
		2CB	3CB	4CB	5CB	6CB	4CBP	6CBP
	Rt (min) =	6.318	7.21	8.565	9.76	10.842	11.93	12.716
TIME								
47 hr	Octanol	2,483	28,359	52,323	239,933	179,517	22,501	32,847
		2,524	29,745	52,163	239,530	179,090	22,631	32,747
		3,090	29,234	50,704	235,392	179,936	22,612	33,112
	mean	**2,699**	**29,113**	**51,730**	**238,285**	**179,514**	**22,581**	**32,902**
	SD	**339**	**701**	**892**	**2,514**	**423**	**70**	**189**
93 hr	Octanol	5,436	42,835	60,615	286,976	224,663	28,050	42,618
		5,470	39,099	56,491	257,203	198,143	24,908	37,138
		5,697	43,277	61,328	288,112	216,500	26,738	40,149
		5,534	**41,737**	**59,478**	**277,430**	**213,102**	**26,565**	**39,968**
		142	**2,295**	**2,611**	**17,527**	**13,583**	**1,578**	**2,744**
236 hr	Octanol	3,792	36,506	63,293	316,109	251,016	31,526	50,746
		6,616	45,308	69,927	387,907	307,035	36,794	60,902
		5,538	39,841	67,200	363,037	289,937	34,516	57,285
	mean	**5,315**	**40,552**	**66,807**	**355,684**	**282,663**	**34,279**	**56,311**
	SD	**1,425**	**4,444**	**3,334**	**36,459**	**28,709**	**2,642**	**5,148**
47 hr	Air	27,955	251,958	372,737	1,630,443	1,203,584	124,475	215,714
		31,220	269,218	399,212	1,768,636	1,319,173	132,030	231,289
		29,588	**260,588**	**385,975**	**1,699,540**	**1,261,379**	**128,253**	**223,502**
93 hr	Air	27,610	252,028	357,839	1,550,284	1,162,546	120,835	207,832
		28,786	263,231	359,661	1,542,393	1,160,313	121,437	207,293
		26,088	240,895	341,120	1,478,016	1,123,742	116,592	200,490
	mean	**27,495**	**252,051**	**352,873**	**1,523,564**	**1,148,867**	**119,621**	**205,205**
	SD	**1,353**	**11,168**	**10,219**	**39,643**	**21,788**	**2,641**	**4,092**

		PK HT						
		2CB	3CB	4CB	5CB	6CB	4CBP	6CBP
	Rt (min) =	6.318	7.21	8.565	9.76	10.842	11.93	12.716
236 hr	Air	25,439	249,394	367,593	1,627,353	1,225,639	133,621	224,902
		25,439	249,394	367,593	1,627,353	1,225,639	133,621	224,902
	mean	**25,439**	**249,394**	**367,593**	**1,627,353**	**1,225,639**	**133,621**	**224,902**

Table D-2: Ratios of Co/Ce at after 47, 93 and 236 hr equilibration between EVA and 1-octanol.

	2CB	3CB	4CB	5CB	6CB	4CBP	6CBP	
hours								
47	0.25016	0.307916	0.335568	0.31707	0.312358	0.245723	0.305082	
93	0.216225	0.265014	0.265859	0.239786	0.233174	0.18625	0.219618	
236	0.240615	0.303962	0.237028	0.186243	0.177948	0.256266	0.268371	
								Mean =
Mean =	0.235667	0.292297	0.279485	0.2477	0.24116	0.229413	0.264357	0.255726

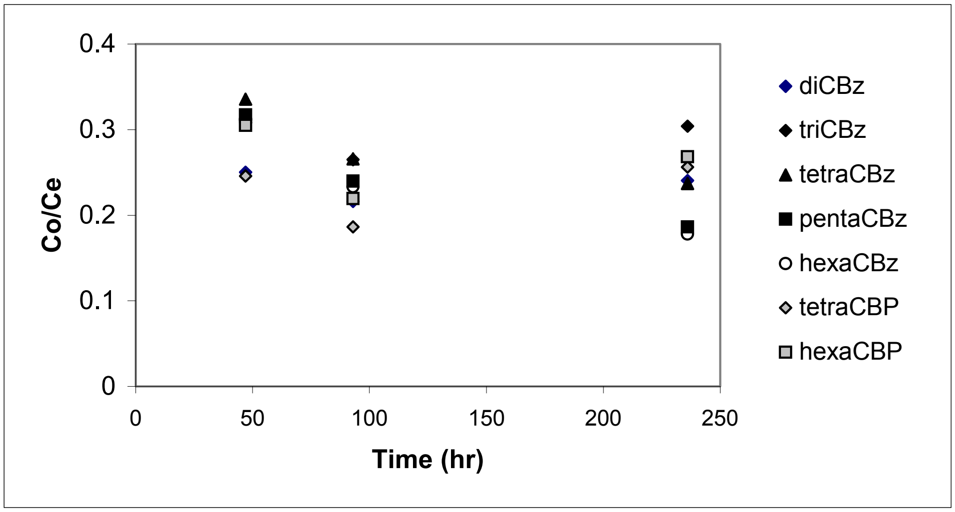

Figure D-1: Plot of the ratio of concentrations in octanol to EVA at 47, 93 and 236 hr.