ASSESSING SEDIMENT QUALITY: A METHOD TO MEASURE THE FUGACITY OF HYDROPHOBIC ORGANIC CONTAMINANTS IN SEDIMENT

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Abstract

Fugacity is a useful tool for measuring the partitioning behaviour and dynamics of sediment-associated chemicals, and may provide a better indication of contaminant bioavailability than concentration. We present a method, based on thin film solid phase extraction techniques, to measure the fugacity of hydrophobic organic contaminants in sediment. The method involves placing sediment in vials coated with the solid phase extracting medium, ethylene vinyl acetate (EVA). When equilibrium is reached, the fugacity in the sediment (f_s) is equal to that in the EVA, and f_{EVA} can be determined using the EVA concentrations (C_{EVA}) and fugacity capacities (Z_{EVA}). Equilibrium EVA concentrations were determined using a two-compartment uptake model fitted to the measured EVA concentrations over time. Z_{EVA} was estimated using the test chemicals' octanol-air partition coefficients (Koa). We applied thin-film solid-phase extraction to measure the fugacities of chlorobenzenes and polychlorinated biphenyls (PCBs) in two different sediments that were spiked in the laboratory and in field sediment collected from Sydney Harbour, Nova Scotia. Results indicate that the method is reproducible, with coefficients of variation for triplicate extractions averaging 6.6% for the spiked sediment experiments and 7.8% for the field sediment experiment. Time to reach 95% equilibrium (t_{95}) was determined using the uptake model, and ranged from 3.4 to 492 hours. Uptake rate constants were negatively correlated to the octanol-water partition coefficient for congeners in the field collected sediment, and for chemicals in the spiked

sediment experiments. The effect of ageing was examined by comparing the equilibrium EVA concentrations from spiked sediments aged for different periods. A significant decrease in available concentration was observed for the chlorobenzenes and two PCB congeners (PCB 26 and PCB 52) in the spiked Robert's Bank sediment. We believe that this method provides a simple and relatively rapid means to approximate chemical bioavailability in sediment.

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1 Introduction

1.1 Assessing sediment quality

Hydrophobic organic contaminants (HOCs), such as polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs), tend to accumulate in sediments. As a result, sediments present an important exposure route for HOCs to biota. Benthic organisms, in particular, are exposed to contaminants through contact with pore water and through ingestion of sediment particles (Power and Chapman 1992). Consequently, accumulation of these contaminants may lead to tissue concentrations that exceed the organism's toxic threshold. For example, adverse biological responses, ranging from impaired growth to death, have been observed in organisms exposed to sediments contaminated with PCBs (Cleveland et al 1997, Bettinetti et al 2003, Zeng et al 2003, Savage et al, 2002). When predators (e.g. fish) consume benthic organisms, the potential exists for sediment-associated contaminants to adversely affect biota in the local food web. This is particularly worrisome for hydrophobic chemicals that are known to

biomagnify. Biomagnification is the process by which organisms achieve a lipid-normalized concentration greater than their diet resulting in a greater accumulation and potential for toxic effects in organisms at higher trophic levels (Gobas et al 1999)).

Efforts have been made internationally to understand the complex interactions between sediments, chemicals and organisms, with an emphasis on developing tools to quantify the risk posed to aquatic organisms (e.g. Chapman 1990, Borgmann et al 2001, Ingersoll et al 2001). A common strategy has been to measure the total concentration of contaminants in sediment (expressed as mass of chemical per total volume of sediment) and use this value to determine whether or not adverse biological responses are likely. For this purpose, sediment quality guidelines (SQGs) have been derived for a number of chemicals and adopted by numerous governing agencies (CCME, NOAA, ANZECC). SQGs are, in general, concentrations of contaminants in sediment above which adverse effects are likely to occur. The SQGs adopted in the U.S. and Canada are based on matching sediment chemistry and biological effects data from field and laboratory studies conducted throughout North America (Long et al 1990, and 1995). Guidelines are derived by plotting the distribution of sediment concentrations associated with adverse effects, and selecting specific percentiles to represent the desired level of protection (e.g. 10^{th} percentile for low effects range,(US EPA 1997)). Some uses of the guidelines include screening sites for further investigation, setting clean-up targets, and characterizing environmental risk (Long and MacDonald, 1998, Birch 2002, Hunt et al 2001, Kemble et al, 2000). The empirically derived sediment quality guidelines are limited, however, by their reliance on total sediment concentrations, which are not necessarily representative of bioavailable concentrations. The bioavailable concentration

is the concentration of chemical in the environment that is available for uptake by an organism.

The bioavailability of a chemical in sediment is often related to the chemical potential of the contaminant in the sediment environment (DiToro et al 1991). A convenient way to express the chemical potential is by use of fugacity. Fugacity is the "escaping" tendency of a chemical in an environment and is measured in units of pressure (Mackay 1991). The bioavailability of sediment-associated chemicals is complex, as it is a function of sediment properties (amount and type of organic carbon), chemical properties (speciation, size, hydrophobicity), environmental factors (temperature, pH), organism behaviour (feeding habits etc), and time (sediment-contaminant contact time, uptake kinetics). Despite this complexity, determining the bioavailable concentration is extremely desirable, because it is this concentration that results in observed toxic effects. Consequently, bulk sediment concentrations alone cannot be used to predict adverse effects in benthic organisms, and SQGs derived using one particular type of sediment might not be appropriate when applied to a site characterized by different environmental and sediment properties. Thus, to effectively assess the toxic relevance of sediment contamination, it is key to know the bioavailable chemical concentration, or the fugacity.

1.2 Predicting bioavailability

DiToro and others (1991) have shown that as a first approximation, the bioavailable chemical concentration can be predicted with the use of equilibrium partitioning theory. In essence, chemicals partition between pore water and sediment particles to build up a chemical concentration in the pore water that can diffuse into the

organism. When a system is at thermodynamic equilibrium, chemicals will distribute themselves between water, sediments and organisms in proportions predicted by their respective partitioning coefficients (see Figure 1-1). Assuming that neutral organic chemicals accumulate solely in the organic fraction of sediment, we can predict pore water concentration with the following equation:

$$C_w = C_{sed} / (\phi_{oc} \cdot K_{oc}) \quad (1)$$

where K_{oc} is the organic carbon–water partition coefficient (l/kg), C_w (mg/l) and C_{sed} (mg/kg dry weight sediment) are the concentrations in pore water and sediment, and ϕ_{oc} is the fraction of organic carbon (g organic carbon /g dry weight sediment) in the sediment. The above relationship indicates that as the organic carbon fraction (ϕ_{oc}) increases, lower concentrations of chemicals will be present in the pore water (C_w decreases), decreasing the availability of the chemical to organisms. Assuming that these neutral organic chemicals accumulate in the lipid fraction of organisms, concentrations in biota can be predicted using equation 1.2:

$$C_{org} = C_w \cdot Kow \cdot \phi_{lipid} \quad (2)$$

where K_{ow} is the chemical's octanol-water partition coefficient (octanol is used as a surrogate for lipid), C_{org} (mg/l) and C_w (mg/l)are concentrations in the organism and water, and ϕ_{lipid} is the fraction of lipid in the organism. Biota-sediment accumulation factors (BSAFs) are often used to express the ratio of an organism's concentration (lipid normalized) to that of the sediment organic carbon. The BSAF is calculated using the following equation:

$$BSAF = (C_{org}/\phi_{lipid}) / (C_{sed}/\phi_{oc}) \quad (3)$$

Theoretically, once equilibrium is reached, the BSAF is equal to the ratio between Kow and Koc, which should be constant across sediments and organisms (DiToro et al 1991). The above relationships present a straightforward means of transforming total sediment concentration into biologically relevant concentrations (i.e., concentrations in pore water or biota tissue). The U.S. EPA (1997) has applied these principles to develop draft sediment quality criteria that are normalized for organic carbon content, making them applicable to a wider range of sediments than the total concentration-based SQGs.

Unfortunately, the distribution of chemicals in the field is more difficult to predict. For example, BSAFs measured in the field have been found to vary considerably, suggesting that equilibrium partitioning alone cannot predict bioavailability (Wong et al 2001, Kraaij et al 2002a). The discrepancies between theoretical bioavailability and observed bioavailability are likely due to the over-simplified system considered by equilibrium partitioning theory. Sediments cannot always be reduced to pools of organic carbon just as organisms cannot always be reduced to bags of lipid. In addition, the assumption of thermodynamic equilibrium is not always met in real ecosystems.

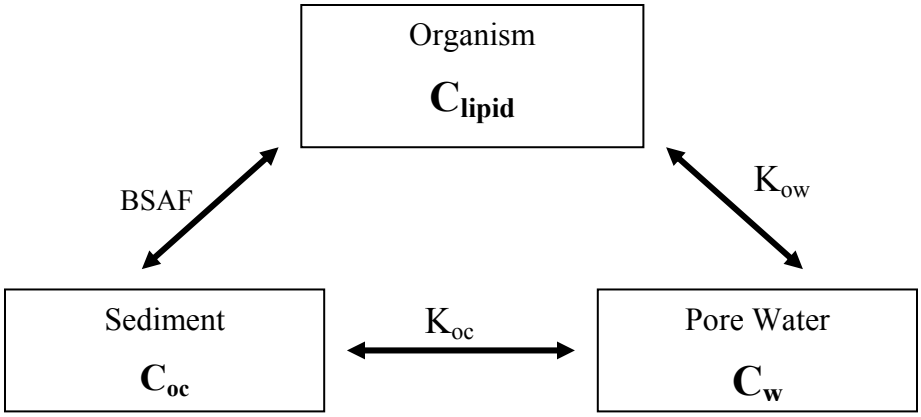

Figure 1-1 Equilibrium partitioning between an organism, pore water and sediment

Predicting bioavailability becomes increasingly difficult in situations of non-equilibrium, as is common in real sediment systems. For that reason, we must consider some of the factors that prevent the system from reaching equilibrium. In any given sediment-water-organism system, there are several competing kinetic processes occurring at any point in time influencing the distribution of contaminants in the environment, and the extent to which these contaminants are available to biota. Movement of HOCs from sediment to pore water is influenced by the rate that contaminants desorb from sediment organic matter. Thus, availability of sediment-associated chemicals is a function of both the length of the organism's exposure to the pore water and the rate of desorption from the sediment. To further complicate the issue, several studies have identified the presence of two organic carbon compartments: one associated with rapid chemical desorption, and the second associated with slow chemical desorption (Cornelissen et al 1997, Ghosh et al 2000). Rate constants associated with the slowly desorbing fraction are

generally quite small (on the order of 10^{-4} to 10^{-2} h^{-1}), and organisms are not likely to reach equilibrium with chemicals in these pools, making them essentially unavailable. Kraaij et al (2001b) found that BSAFs for selected PAHs correlated well with the fraction of chemical in the rapidly desorbing pool. This suggests that bioavailability is not only a function of the total amount of organic carbon, but rather the fraction of organic carbon from which chemicals can desorb rapidly.

The length of contact time between sediment and contaminants also plays a role in the bioavailability of sediment-associated contaminants. It has been observed that as sediment-contaminant contact time increases, bioavailability (measured as concentration in biota or occurrence of adverse effects) decreases, in what has been termed the 'ageing effect' or sequestration (Kraaij et al 2002b, Kelsy et al 1997). Sediment ageing has been described as the movement of contaminants from the rapidly desorbing compartment to the slowly desorbing compartment (Reid et al, 2000). Consequently, we might expect newly contaminated sediment (or laboratory spiked sediment) to have more bioavailable chemical, and lead to higher concentrations in organisms, than historically contaminated sediment.

In addition to contaminant kinetics, it may also be important to consider the nature and dynamics of the sediment organic matter when predicting bioavailability. The majority of sediment-contaminant models view the organic matter as a static, homogeneous and amorphous entity, with linear and reversible partitioning behaviour. However, recent studies suggest that all organic matter is not alike in its ability to sequester organic contaminants (Kukkonen et al 2003, Luthy et al, van Noort 2003, McGroddy et al 1996). Rather, organic matter should be considered heterogeneous, as it

is comprised of both 'young' materials (e.g. humic acids), which exhibit linear, reversible partitioning behaviour, and diagenetically aged materials (with high C/O ratios, e.g. soot carbon), which exhibit non-linear and apparently irreversible partitioning behaviour (Rockne et al 2002). For example, soot-carbon has been found to increase adsorption of some HOCs (e.g. PAHs and PCDDs), above levels predicted by equilibrium partitioning (Jonker and Koelmans 2002, Bucheli and Gustafsson 2000). This suggests that the presence of soot carbon has a strong influence on the bioavailability of some HOCs. Kukkonen et al (2003) also observed that desorption rates of contaminants from sediment for some HOCs are influenced by the composition of organic matter and the particle size distribution of sediments.

Changes in sediment organic matter volume and structure occur over time due to microbial degradation. Several authors have proposed that the resulting carbon mineralization (and decrease of organic matter volume) could explain observed magnifications in contaminant availability (or fugacity) for decomposing sediment (Gobas and MacLean 2003, Koelmans et al, 1997, Baker et al, 1993). In this situation, the rate of mineralization exceeds the rate of desorption of the contaminants into overlying water, resulting in steady state organic carbon concentrations greater than equilibrium predictions.

To summarize, the bioavailability of sediment-associated contaminants is dependent on, among other factors, the amount and nature of organic carbon, the physical composition of sediment particles and the kinetics that drive (or hinder) the movement of contaminants into the pore water and/or sediment. Rarely are all of these factors known or explicitly considered when assessing sediment quality, especially the extent of ageing

and kinetic effects. Even if we could obtain measurements for all of the sediment properties, the complexity of interaction between them is still poorly understood, and predictions of uptake are not so straightforward. Therefore, in many cases it is more practical to measure contaminant bioavailability in sediment than attempting to predict it with models.

1.3 Measuring bioavailability

1.3.1 Passive samplers

Obtaining direct measurements of chemical bioavailability is the most straightforward means to determine the toxic relevance of sediment contamination. Unfortunately, no universally accepted measurement technique exists to date. The most common approach has been to extract contaminants from sediments using materials that "mimic" biological tissue. Some authors have attempted to approximate bioavailable contaminant fractions in soil and sediments by extracting with solvents (e.g. methanol, hexane) (Kelsey et al 1997) and Tenax beads (an organic polymer) (ten Hulscher et al 2003). Most notable, perhaps, has been the development of techniques using passive samplers (e.g. semi-permeable membrane devices (SPMD), solid phase micro-extraction (SPME)). These techniques involve bringing small volumes of a lipid-surrogate (i.e. bags of octanol (SPMD) or polymer-coated fibers (SPME)) to equilibrium with a contaminated environment, and using the resulting sampler concentrations to approximate uptake by biota. Passive samplers have been applied in various environmental media including water (e.g. Leslie et al 2002, Verbruggen et al 2000), air

(e.g. Ockenden et al 2001, Harner et al 2003), soil (e.g. Krauss and Wilcke 2001, van der Wal 2003), and sediment porewater (e.g. Mayer 2000, Kraaij et al 2003). Little work has been done using whole sediments, however.

In a recent publication, Mayer et al (2003) discussed some of the desirable characteristics of passive samplers. They suggest that equilibrium should be reached within a practical time frame. Samplers with low surface area to volume ratios (e.g. SPMD) are generally associated with low uptake rate constants, and very long times to reach equilibrium. Thus, it is advantageous to use an organic phase with high surface area to volume ratio in order to minimize delays caused by diffusion within the sampler. Also, Mayer et al (2003) recommend that the passive sampler not deplete the concentration in the sample. Instead, the sampler is meant to 'sense' the available chemical without affecting the test matrix, just as an organism would take up chemical without changing the distribution of contaminants in the surrounding environment. The development of a passive sampling technique that possesses these properties, and is practical to apply in the field, would be an ideal method to obtain simple, biologically relevant measures of sediment-associated contamination.

1.3.2 Measuring fugacity

When investigating chemical bioavailability in sediment, it may be more meaningful to measure fugacity rather than concentration. Fugacity is the partial pressure exerted by a chemical in a specific medium, often described as the "escaping" tendency of a chemical in that medium. Since fugacity is related to chemical potential, it is an especially relevant measure of bioavailability. Working with fugacity is particularly valuable when studying multi-compartment environments (such as the sediment/pore

water/biota system of interest), because movement of chemicals is driven by differences in fugacity rather than differences in concentration, and equilibrium is most usefully defined as equal fugacity in all compartments (Mackay 1991). Fugacity is related to concentration by the following equation:

$$f = C/Z, \quad (4)$$

where f is fugacity, measured in units of Pascals, C is concentration, measured in mol/m^3 and Z is the fugacity capacity, measured in units of mol/m^3Pa. The fugacity capacity is a measure of a medium's ability to hold a chemical. In materials with a high Z for the chemical substance, more chemical (higher concentration) needs to be added to achieve a one unit increase in fugacity compared to a material with a low Z. For example, when two different types of sediment contain the same concentration of a contaminant, the sediment with the lowest Z value can be expected to have the highest fugacity. For sediments, Z can be approximated (for an individual chemical) using the following equation (Mackay 1991):

$$Z_{sed} = (\phi_{oc} \cdot K_{oc} \cdot d_s)/ H , \quad (5)$$

where ϕ_{oc} is the fraction of organic carbon, K_{oc} is the chemical's organic carbon partitioning coefficient (in l/kg), d_s is the sediment density (kg/l) and H is the chemical's Henry's Law constant (in $Pa \cdot m^3/mol$). Equation 4 indicates that as the organic fraction of sediment increases, its capacity to hold hydrophobic organic chemicals (chemicals with a high K_{oc}) increases, reducing the fugacity or bioavailability of the chemical. This phenomenon is analogous to equilibrium partitioning theory predictions. However, as discussed in the previous section, organic carbon varies considerably in its ability sorb contaminants. Therefore, we can expect the fugacity capacity of sediment to vary

according to both quantity and quality of organic matter, which is not considered in equation 5. Thus, as with the concentration approach, it is more valuable to obtain measurements of chemical fugacity than attempting to predict it.

Few methods exist to obtain fugacity measurements in environmental media. Direct measurements have been attempted using gas-purging techniques (e.g. Yin and Hassett 1986, Horstmann and McLachlan 1992), however these methods are not practical when applied in the field. Wilcockson and Gobas (2001) successfully applied a passive sampler technique (thin-film solid-phase extraction), to measure the fugacities of several semi-volatile organic contaminants in biological tissues. The technique involves equilibrating contaminated tissue with a thin film of ethylene vinyl acetate (EVA), and calculating the chemical fugacities in the EVA based on the measured concentrations and fugacity capacities. At equilibrium, the fugacity of the sample is equal to the fugacity in the EVA. The advantage of using this technique is that it is simple to conduct and requires fairly quick equilibration times due to the high surface area to volume ratio of the EVA. This method has not yet been applied to measure the fugacity of chemicals in sediments.

1.4 Objectives of this research

The aim of this research project was to develop a method to measure the bioavailable fraction of contaminants in sediment. To address this goal, we applied a passive sampler technique (thin-film solid-phase extraction in this case) to measure the fugacities of hydrophobic organic chemicals in sediment samples. The method involves coating vials with a thin film of ethylene vinyl acetate (EVA), and measuring the uptake

of contaminants from sediment. Once equilibrium is reached, the fugacity in the sediment is equal to that in the EVA, which can be determined from concentration when the fugacity capacity of the EVA is known. In this manner, we applied thin-film solid-phase extraction to measure the fugacities of PCBs and chlorobenzenes (CBs) in spiked sediment samples, and to measure the fugacities of several PCB congeners in field contaminated sediment samples. Ultimately, we hope to apply this method to obtain biologically relevant measures of contaminant exposure. There are currently over 10,000 contaminated sites in Canada alone that require assessment and possibly remediation. Thus, the development of an assessment tool that explicitly considers chemical bioavailability would be extremely valuable in this effort.

2 Materials and Methods

2.1 Overview

We applied thin-film solid phase extraction to two sediments spiked with chlorobenzenes and polychlorinated biphenyls, and to field contaminated sediment collected from Sydney Harbour, Nova Scotia. Figure 2.1 summarizes the methodology. Briefly, we coated vials with a thin film of EVA, exposed the EVA to contaminated sediment, and removed the sediment at specific times to track the migration of chemicals into the films. We then extracted the EVA films using hexane and analyzed the extract using gas chromatography. In the following sections additional methodology details are provided, including film preparation (section 2.2), spiking procedures (section 2.3), uptake experiments (sections 2.3-2.4), and thin film analysis (section 2.5). Data analysis (section 2.6) involved fitting models to the data and calculating fugacity and fugacity capacity for the individual contaminants.

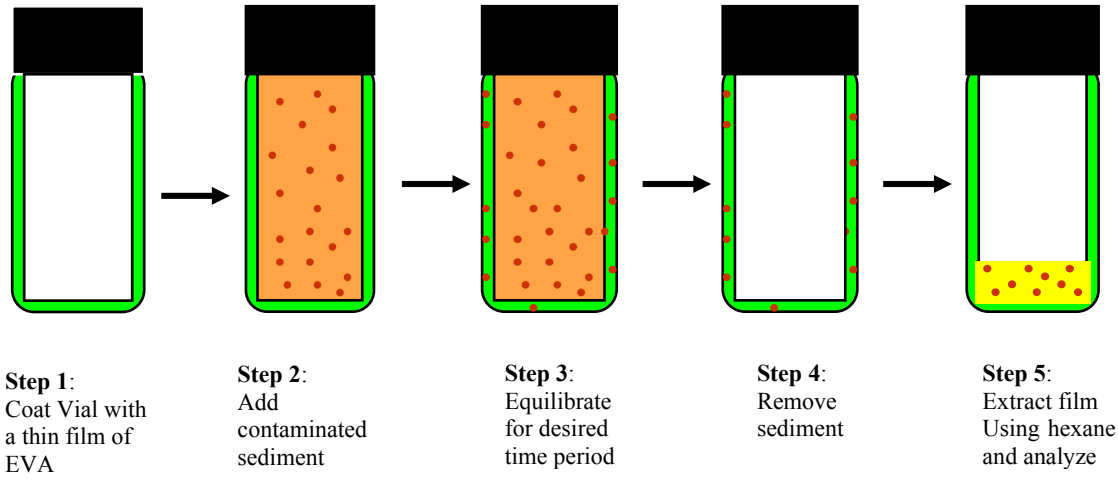

Figure 2-1 Overview of thin-film solid-phase extraction methodology

2.2 Thin-film preparation

A 6.21 ppm ethylene vinyl acetate (EVA) solution was prepared by dissolving 0.621 g of EVA (Elvax 40W, Dupont, Wilmington, DE) in 100ml of dichloromethane (DCM). Scintillation vials (20 ml) were cleaned with lab grade detergent followed by solvent rinses using acetone and hexane. To coat the vials, 150 µl of the EVA/DCM solution was added to each scintillation vial. The uncapped scintillation vials were then rolled to allow the DCM to evaporate, forming a thin film on the vial interior. Initial trials were conducted with an EVA solution containing the red dye Sudan IV to ensure that the vials were evenly coated. Upon visual inspection, films appeared reasonably uniform. Thin film specifications are presented in table 2.1. The resulting thin film volume (1µL) was chosen to maximize the volume of the sampling phase (EVA), improving detection of low quantities of chemicals expected in the field sediment, while

maintaining a minimal EVA to organic carbon ratio (mass of EVA / mass of OC) to ensure that film uptake did not affect sediment concentration. EVA to organic carbon ratios were estimated for the three sediments and are presented in table 2.2.

Table 2-1 Thin film specifications

Mass of EVA	0.00092 g
Volume of EVA	1 μL
Surface Area to Volume ratio	3770 mm^{-1}
Average film thickness	0.27 μm

2.3 Spiked sediment experiments

2.3.1 Port Moody Arm sediment

Marine sediments were collected from the top centimeter during low tide at Port Moody Arm, British Columbia and stored at 4°C in pre-cleaned glass jars. Chemicals used for spiking included: 1,2,4,5-tetrachlorobenzene, pentachlorobenzene, hexachlorobenzene, 2,2',5,5'-tetrachlorobiphenyl (PCB 52), and 2,2',4,4',6,6'-hexachlorobenzene (PCB 155). A 5 g sample of the unspiked sediment was sent to the Institute of Ocean Sciences (IOS) in Sidney, British Columbia, for organic carbon analysis. Table 2.2 outlines the sediment characteristics, and Table 2.3 lists the properties and concentrations of the spiked chemicals.

Chemicals were purchased from AccuStandard, Inc. (New Haven, CT). A spiking solution was prepared by dissolving the test chemicals in hexane at concentrations ranging from 50 to 65 ppm. 10 ml of the spiking solution was added to 847g of wet

sediment (51% moisture content) and stirred for 8 hours, allowing the hexane to evaporate. Assuming that no chemical was lost during the spiking procedure, resulting total sediment concentrations ranged from 1.18 to 1.53 μg/g dry weight (see table 1 for specific concentrations). Once spiked, sediments were stored at 4°C until needed for the two uptake experiments (21 and 102 days after spiking). Prior to each experiment, sediments were manually stirred once again.

To investigate the effects of contaminant-sediment contact time (or ageing), uptake experiments using the thin-film method were conducted at two different ageing periods. The first experiment was conducted 21 days after spiking, and the second on day 102. On both experiment days, 20 ml of the spiked sediment was added to each of 18 EVA lined scintillation vials. Sediments were removed at specific times in order track the uptake of the chemicals into the EVA over time. After 21 days of ageing, sediments were incubated with EVA thin films (in triplicate) for 0.25, 1, 3, 7, 70 and 288 hours. The first 4 extraction times were used to obtain measurements of initial uptake rates, while the 70 and 288 hour extractions were conducted to determine whether equilibrium had been reached (i.e., whether chemical concentrations in the EVA were unchanging over time). For the second ageing period (102 days), sediments were incubated with EVA thin film for 0.167, 0.33, 0.67, 1, 2, 4, 6, 8, 18, 28, 53, 104, and 194 hours. Extractions for times 6 h and 28 h were conducted in triplicate (sediment from 3 vials was removed at both times) to test for reproducibility. We chose to forgo triplicate extractions at each incubation period with the aim of obtaining more time steps in total to improve the model fitting (see section 2.6.1 for data analysis). Three additional vials

were filled with unspiked sediment to ensure that no measurable background contamination was present.

2.3.2 Robert's Bank sediment

Sediments were collected from Robert's Bank (RB), British Columbia, for use as reference sediment by Environment Canada's Pacific Environmental Science Center (PESC), at which time they were dried, sieved, and analyzed for particle size distribution and organic carbon content. Total organic carbon was measured as 0.35%, and particle size was mainly in the sandy range (80% sand). Prior to spiking, the sediments were reconstituted in water to obtain approximately 50% moisture by weight.

Nine test chemicals were used to spike the Robert's Bank sediment, including three chlorobenzenes (1,2,4,5-tetra-, penta-, and hexa- chlorobenzene), and 6 PCB congeners (#26, 52, 101, 155, 180, 194), purchased from AccuStandard Inc. The additional congeners (26, 101, 180, and 194), not present in the Port Moody spiking mixture, were added to obtain a greater range of physical-chemical properties, (for example log Kows ranging from 4.5 to 7.8). Spiking was carried out as described in section 2.3.1, with resulting sediment concentrations ranging from 0.86 to 1.66 ug/g sediment (dry weight) (see Table 2.1 for specific concentrations).

Uptake experiments were conducted at two ageing periods, i.e. 17 days and 52 days. The ageing periods differed from those for the Port Moody sediment due to scheduling difficulties (the Robert's Bank sediment was obtained and spiked at a later date than the PM sediment). Similar to the Port Moody experiment, vials were incubated for specific periods to track the uptake of the chemicals into the EVA films. Sediments

aged for 17 days were added to 18 EVA lined scintillation vials. One vial was emptied at each of the following times: 0.167, 0.333, 0.667, 1, 2, 4, 6, 8, 14, 28, 50, 98, 174, and 336 hours. Triplicate vials were extracted at times 2, 6 and 28 h to test for reproducibility. Sediments aged for 52 days were added to 18 scintillation vials which were incubated with EVA thin films for 0.167, 0.33, 0.67, 1, 2, 4, 6, 18, 28, 53, 104, and 194 hours. Triplicate vials were extracted for 6 and 28 h to test for reproducibility. In addition, 3 vials were filled with the unspiked sediment and incubated for 24 h to control for any background contamination present in the sediment and during the extraction procedure.

Table 2-2 Characteristics of the three test sediments, including percent organic carbon, EVA to organic carbon ratios, dominant particle size and ageing periods

	Port Moody	**Robert's Bank**	**Sydney Harbour**
% TOC	3.77	0.35	16.49
EVA/OC ratio	0.00199	0.0175	0.000372
dominant particle size	silty	sandy (80%)	silty (66.4% <0.063mm)
ageing periods	21 and 102 days	17 and 52 days	N/A

Table 2-3 Spiking mixtures, chemical properties (log Koa and log Kow) and spiking concentrations (μg/g dry weight) for the Port Moody and Robert's Bank sediment experiments

Chemical name	**abbreviation**	**log k_{ow} [a]**	**log k_{oa} [b]**	**Csed[c] (μg/g dw)**	
				Port Moody	*Robert's Bank*
1,2,4,5-tetrachlorobenzene	4CB	4.50	5.81	0.70	1.66
pentachlorobenzene	5CB	5.00	6.46	0.60	1.24
hexachlorobenzene	6CB	5.50	6.78	0.67	1.38
2,3',5-trichlorobiphenyl	PCB26	5.66	8.27		0.97
2,2',5,5'-tetrachlorobiphenyl	PCB52	5.84	8.49	0.55	1.15
2,2',4,5,5'-pentachlorobiphenyl	PCB101	6.38	9.28		0.95
2,2',4,4',6,6'-hexachlorobiphenyl	PCB155	6.41	9.13	0.67	1.15
2,2',3,4,4',6,6'-heptachlorobiphenyl	PCB180	7.36	10.70		0.86
2,2',3,3',4,4',5,5'-octachlorobiphenyl	PCB194	7.80	11.59		1.27

a –Hawker and Connell 1988, Mackay et al 1992,
b- Harner and Bidleman 1996 , Wania et al 2002
c- Spiking concentration in μg of chemical per g dry weight sediment

2.4 Field contaminated sediment experiment

Environment Canada staff collected sediment from Sydney Harbour, Nova Scotia in September of 2002, using a 0.1 m^2 Van Veen grab. A portion of the sediment, stored in 4 litre buckets and kept cool on ice in picnic coolers, was shipped to Environment Canada's Pacific Environmental Science Centre (PESC), in North Vancouver, British Columbia. We obtained a subsample from PESC (approximately 1 litre of wet sediment) for EVA uptake experiments. Sediment was stored in a sterilized glass jar and refrigerated at 4°C until further use. A 5 g sample of the sediment was sent to Institute of Ocean Sciences (IOS) for measurement of total organic carbon (see Table 2.3). Sediment chemistry was analyzed by Axis Environmental (Sidney, British Columbia) using GC-LRMS. Total sediment concentrations for individual PCB congeners are summarized in Appendix A. Prior to filling the vials, sediments were manually stirred to decrease the heterogeneity between sample units. Sediment (at approximately 50% moisture) was added to twelve 20mL scintillation vials, and incubated with EVA thin films (in duplicate) for 0.25, 1, 4, 8, 24, and 75 hours. Extraction of the thin films was carried out similarly to the spiked experiment thin films (described in section 2.5.1). Three empty EVA coated vials were also extracted and analyzed to control for any background contamination present during the extraction procedure.

2.5 Thin film analysis

2.5.1 Solvent Extraction

Immediately following sediment removal, scintillation vials were rinsed with water until the EVA film appeared clean. In most cases, 2 gentle rinses with approximately 10 ml of water each sufficed to remove all remaining sediment particles. Control vials were rinsed in the same manner. To remove any residual water, the vials were centrifuged for 2 minutes at 3500 rpm, and the pooled water was extracted with a Hamilton syringe. Due to the hydrophobic nature of the test chemicals (with Kow's exceeding 30,000), water rinsing was not expected to remove any significant fraction of contaminants from the EVA.

Hexane was used to extract the chemicals from the EVA thin films. Once the films were cleaned and free of water, 0.5 ml of hexane was added to each vial, and the vials were vortexed for 30 seconds. Each scintillation vial was rinsed twice with 0.5 ml of the solvent to ensure that all chemicals were removed from the film. The hexane extract was removed from the scintillation vials using a Hamilton syringe and stored in pre-weighed 2 ml GC vials prior to chemical analysis. The final weights of the GC vials were recorded to obtain the total mass of hexane used for each extraction.

2.5.2 Chemical Analysis

Extracts from the spiked sediment experiments were analyzed using a Hewlett Packard 5890 series gas chromatograph, equipped with an electron capture detector and a 30 m x 0.53 mm x 2.65 μm (film thickness) HP-5 column. Helium (ultra-high purity 5.0) was used as a carrier gas at a flow rate of 1 ml/min. Injections of 1 μl were made

manually, with a temperature program of 40°C to 270°C at 20°C/min. The temperature increase rate was altered to 15°C/min for the Robert's Bank extract in order to separate the co-eluting peaks for PCB congeners 155 and 101. Samples were quantified using external standards (AccuStandard, Inc).

Once the concentrations in the hexane extract (C_{Hexane}, in μg/ml) were determined, the chemical concentrations in the EVA films (C_{EVA}, in μg/ml), were calculated using the following equation:

$$C_{EVA} = \frac{C_{Hexane} \cdot m_{Hexane}}{V_{EVA} \cdot \delta_{Hexane}} \quad (6)$$

where m_{Hexane} is the mass of hexane used to extract the EVA film (g), δ_{Hexane} is the density of hexane (g/ml), and V_{EVA} is the volume of the thin-film (ml).

Analysis of the Sydney Harbour samples was conducted at the Institute for Ocean Sciences, in Sidney, British Columbia. High resolution GC-MS was used to identify and quantify individual PCB congeners present in the hexane extracts. Prior to analysis, the extracts were spiked with 50⊠l of BIG - PCB internal standard ($^{13}C_{12}$ labeled congeners # 15, 18, 52, 118, 136, 181 and 209), blown down to near dryness under nitrogen, and transferred to micro-vials using small amounts of toluene, at which time a $^{13}C_{12}$ PCB-111 recovery standard was added. Specific GC-MS methods have been described in more detail elsewhere (Ikonomu and Fraser 2001). Because the entire volume of hexane was analyzed, PCB congener concentrations were calculated as:

$$C_{EVA} = X_{congener} / V_{EVA} \quad (7)$$

where C_{EVA} (in μg/ml) is the chemical concentration in the EVA film, $Xc_{ongener}$ is the mass of the PCB congener (in μg), and V_{EVA} is the volume of EVA (0.001 ml).

2.6 Data Analysis

2.6.1 Non-linear regression

To obtain estimates of equilibrium EVA concentrations, first-order uptake models were fit to the observed EVA data using non-linear regression (SPSS 11.0). Following a very basic uptake model, migration of test chemicals from the sediment into the EVA can be described using the following equation:

$$C_{EVA}(t) = C_{EVA(eq)}(1- \exp(-k \cdot t)), \quad (8)$$

where t is time (hours), $C_{EVA(eq)}$ (μg/ml) is the concentration in the EVA at equilibrium (μg/ml), and k is the apparent uptake rate constant (h^{-1}). It has been observed, however, that desorption of hydrophobic organic chemicals from sediment occurs from more than one compartment (Cornelissen et al, 1997, Gong et al, 1998). Unfortunately, desorption is complex, and the mechanisms of multi-compartmental contaminant behaviour are not well understood (Pignatello and Xing 1996). Thus, several authors have opted for simplified empirical models based on discrete sediment fractions, each subject to its own rate constant (Kukkonen et al 2003, Cornelissen et al 1997, Ghosh et al 2000). It was expected that uptake into the EVA films would reflect desorption from the multiple compartments, therefore the following empirical two-compartment model was also fitted to the observed EVA concentration data:

$$C_{EVA}(t) = C_{EVA(f)}(1-\exp(-k_{fast}t)) + C_{EVA(s)}(1-\exp(-k_{slow}t)) \quad (9)$$

where $C_{EVA(f)}$ and $C_{EVA(s)}$ are the concentrations in the EVA film reflecting equilibrium with the fast and slowly desorbing compartments, and k_{fast} and k_{slow} are the apparent rate constants describing uptake from these compartments. In order to determine which of the two models was most suitable for the observed data, we compared R^2s and plotted the residuals. To investigate relationships between the apparent uptake rate constants and chemical properties (e.g. Kow), linear regression was performed using SPSS 11.0.

2.6.2 Fugacity calculations

To determine the fugacity of the chemical in the EVA film, the following equation was used:

$$f_{EVA} = C_{EVA} / Z_{EVA} \quad (10)$$

where C_{EVA} is the chemical concentration in the EVA (converted to mol/m^3), and Z_{EVA} is the fugacity capacity ($mol/m^3 \cdot Pa$) of the EVA for the chemical. The fugacity capacity of EVA (Z_{EVA}) can be determined once the EVA-air partition coefficients (K_{EA}) for the individual chemicals are known. At equilibrium, the fugacity of the air is equal to that in the EVA, therefore:

$$\frac{C_{EVA}}{Z_{EVA}} = \frac{C_{AIR}}{Z_{AIR}} \quad (11)$$

Since $Z_{AIR} = 1/RT$, and $C_{EVA}/C_{AIR} = K_{EA}$, Z_{EVA} can be derived as:

$$Z_{EVA} = K_{EA}/RT \, , \quad (12)$$

where Z_{EVA} is in units of $mol/m^3 \cdot Pa$, R is the gas constant (8.31 J/mol·K), and T is the temperature (298 K). K_{EA} can be measured directly by coating vials with spiked EVA and measuring the concentration in the air phase when equilibration has been reached.

Detection of air concentration is difficult, however, for non-volatile chemicals with very high octanol-air partition coefficient (K_{OA}), such as the PCB congeners used in the present study. A linear relationship has been observed between K_{EA} and K_{OA} (Wilcockson and Gobas 2001, Otton 2004) for a series of PCB congeners and chlorobenzenes. Otton (2004) observed the following relationship between EVA and octanol concentrations (at equilibrium) for a selection of chlorobenzenes:

$$C_{oct} = 0.260\ (\pm\ 0.021)\cdot C_{EVA} + 0.063\ (\pm\ 0.222), \qquad (13)$$

where C_{oct} (μg/ml)is the concentration in octonol, and C_{EVA} (μg/ml) is the concentration in EVA. Therefore, to obtain estimates of Z_{EVA} for the large number of non-volatile chemicals in the present study, a conversion factor of 4 (from the above relationship) was applied to transform K_{OA} (obtained from the literature) to $K_{EA,}$ and Z_{EVA} was calculated as:

$$Z_{EVA} = 4\cdot K_{OA}/RT \qquad (14)$$

When a system has reached thermodynamic equilibrium, the chemical fugacities are equal in all compartments. Therefore, once equilibrium has been reached between the EVA film and the sediment, the fugacity in the sediment is equal to that in the EVA. Equilibrium EVA concentrations were determined using the model results from the previous section.

3 Results and Discussion

3.1 Uptake curves and model fitting

3.1.1 Spiked sediment experiments

The concentration of test chemicals was below detection limit in the control (unspiked) sediments. The EVA film was disrupted during the sediment removal and water rinsing for three samples: the 173 hour extraction, and one of the 6 hour extractions of the Robert's Bank sediment (aged 17days) and the 1 hour extraction of the Robert's Bank sediment (aged 52 days). Therefore, the results from these samples were omitted from the analysis. Thin film disruption was not observed in the Port Moody sediment. Table 3.1 summarizes the coefficients of variations (COVs) among replicate EVA concentrations (for the 6 hour and 28 hours extractions) in the aged Port Moody and Robert's Bank sediments. COVs (calculated as standard deviation divided by average EVA concentration) for triplicate EVA extractions averaged 6.23% in the Port Moody

sediment aged for 102 days, and 6.93% for the Robert's Bank sediment aged for 52 days. These results suggest that variation among replicate samples is relatively low, making the method reproducible.

Table 3-1 Coefficients of variation (%) among replicate EVA extracts (at times 6 hours and 28 hours) for the Port Moody sediment (aged 102 days) and Robert's Bank sediment (aged 52 days) experiments

Chemical	*Port Moody sediment Aged 102 days*		*Robert'sBank Aged 52 days*	
	6 hours	28 hours	6 hours	28 hours
4CB	3.14	4.33	7.67	3.38
5CB	6.28	4.88	6.35	0.420
6CB	5.92	15.4	9.15	0.252
PCB 26			9.10	1.38
PCB 52	3.23	1.30	6.66	1.56
PCB 101			4.34	2.48
PCB 155	7.24	10.62	18.6	2.09
PCB 180			32.5	3.77
PCB 194			10.9	4.09
Average	**6.23**		**6.93**	

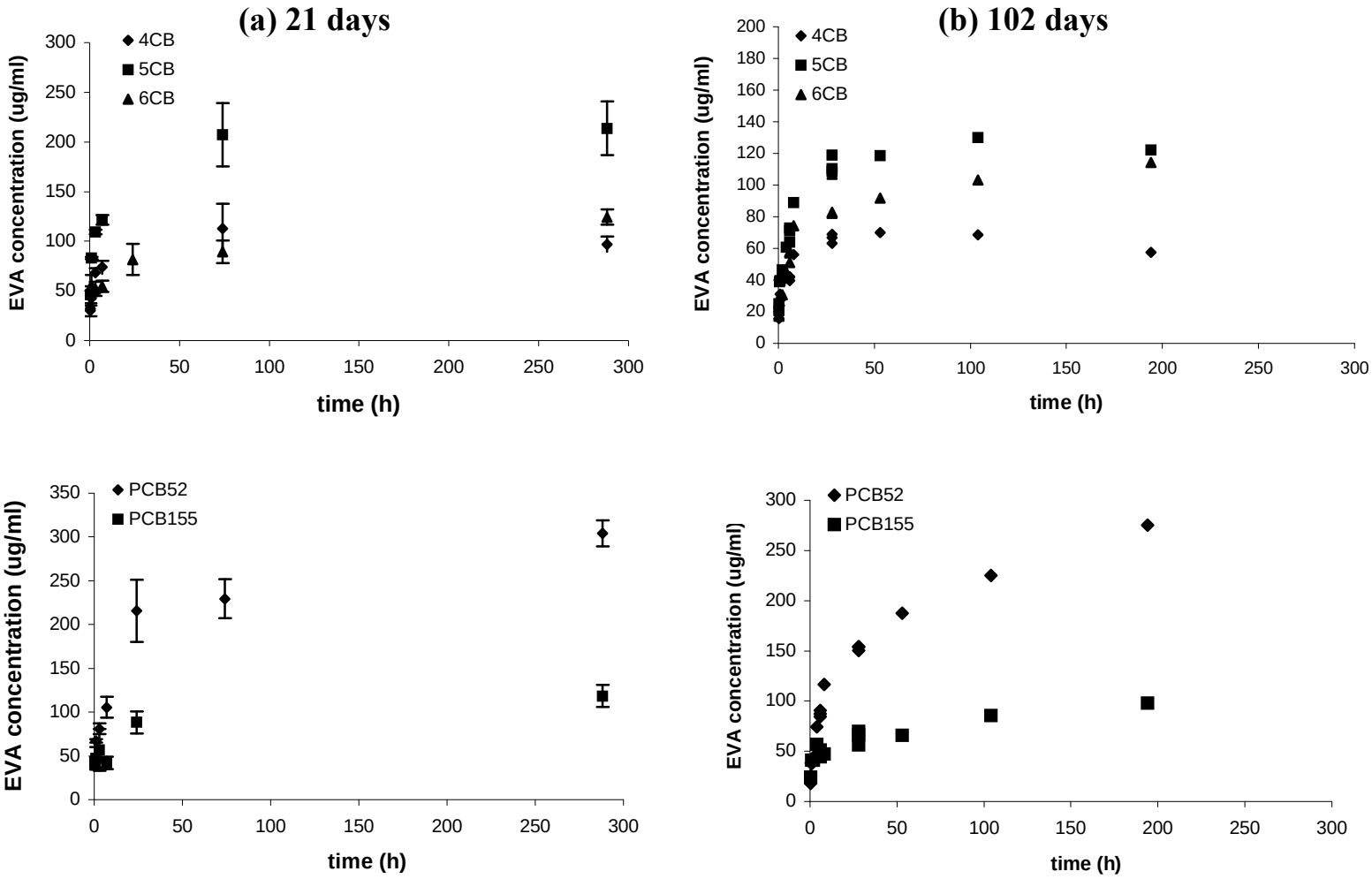

Figure 3-1 EVA thin-film extraction of chlorobenzenes and PCB congeners from spiked Port Moody sediment, aged for (a) 21 days (b) and 102 days

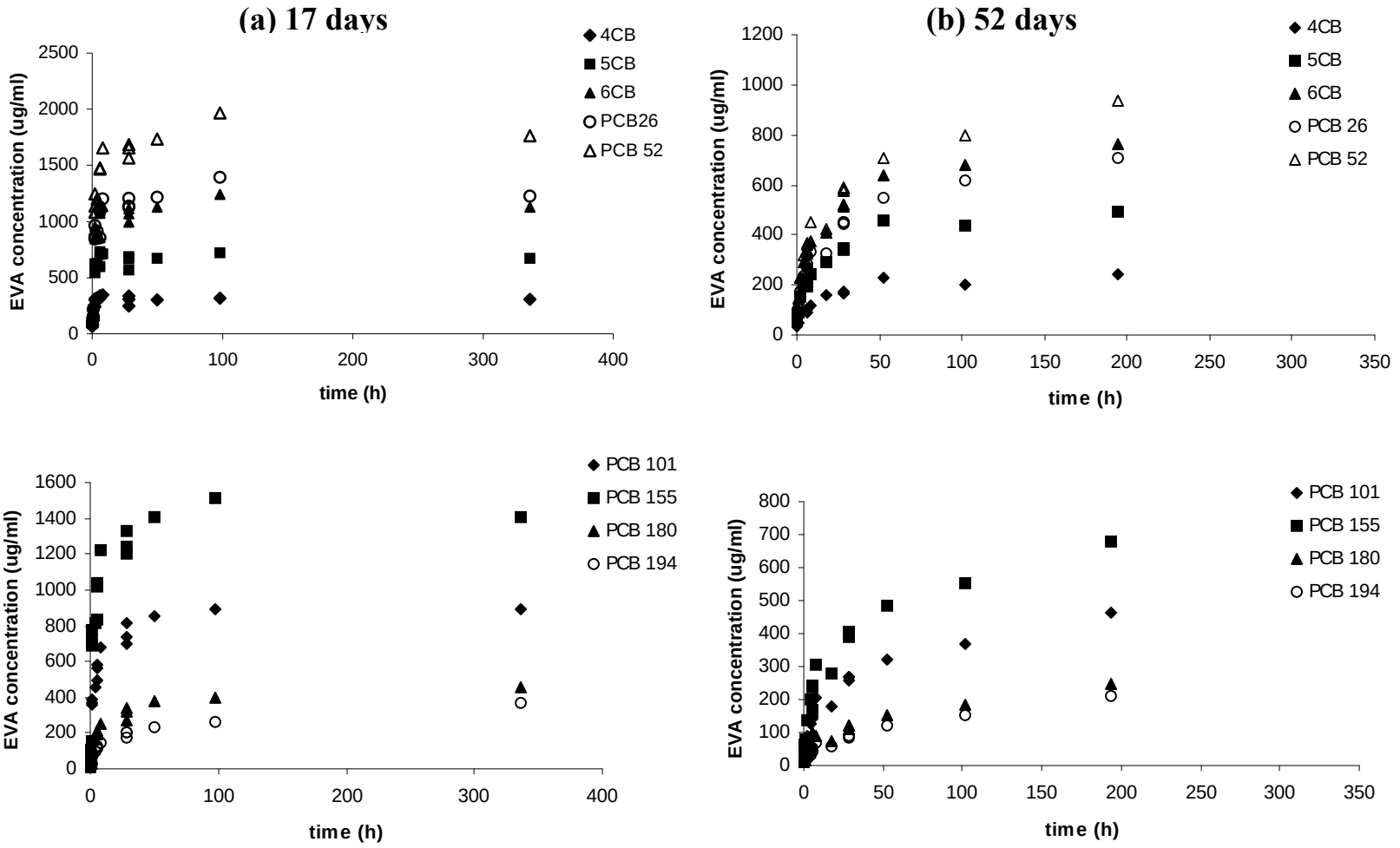

Figure 3-2 EVA thin-film extraction of chlorobenzenes and PCB congeners from spiked Robert's Bank sediment, aged for (a) 17 days and (b) 52 days

Measured EVA concentrations from the spiked sediment experiments are summarized in Appendix B. EVA concentrations over time for the Port Moody spiked sediment experiments are plotted in figure 3.1. For both of the Port Moody experiments, equilibrium between the sediment and EVA film appears to have been reached for tetra- and pentachlorobenzene within the uptake experiment. Hexachlorobenzene (5CB) and the two PCB congeners (52 and 155) did not appear to reach equilibrium within the time frame of the experiments (288 hours and 194 hours). Uptake curves for the Robert's Bank spiked sediment experiments are presented in figure 3.2. Similar to the Port Moody results, the lowest Kow compounds (4CB and 5CB) appeared to reach equilibrium within the time frame of the experiment (for both ageing periods), whereas the highest Kow compounds (PCB congeners 180 and 194) did not. Hexachlorobenzene and PCB congeners 26, 52, 101 and 155 seem to have reached equilibrium within 300 hours in the sediment aged for 17 days. However, the EVA film did not appear to reach equilibrium with these same chemicals in the sediment aged for 52 days.

Non-linear regression was performed to fit one- and two-compartment uptake models (i.e. equations 8 and 9) to the observed EVA concentrations. Results from the model fitting were used to obtain estimates of equilibrium EVA concentrations. To determine which model better represented the observed data, we compared coefficients of determination and model residuals. Coefficients of determination (R^2 values) are summarized in Table 3.2. R^2 values for the one- and two- compartment model fit were equal on two occasions: for tetra- and penta-chlorobenzene in the Robert's Bank sediment, aged for 17 days. All remaining coefficients of determination were greater for the two-compartment model fit than for the 1-compartment model fit. Residuals from

both models are plotted in Appendix C. Plotted residuals from the one-compartment model demonstrated a substantial bias, while no bias was observed in residuals from the two-compartment model fit. The higher coefficients of determination and unbiased residuals obtained from the two-compartment model fit suggest that this model is more representative of the measured EVA concentrations than the one-compartment model. Figure 3.3 illustrates the one-compartment and two-compartment model fit to the uptake data for PCB 52 in the (a) Port Moody sediment (aged 102 days) and (b) Robert's bank sediment (aged 52 days). For these two cases, is evident that the two-compartment model is more appropriate than the one-compartment model. For consistency, EVA concentrations for all chemicals were fitted using the two-compartment equation.

Table 3-2 Coefficients of determination (R^2) for 1- and 2-compartment model fit

	Port Moody sediment				Robert's Bank sediment			
	aged 21 days		aged 102 days		aged 17 days		aged 52 days	
Model compartments:	1	2	1	2	1	2	1	2
4CB	0.771	0.890	0.781	0.958	0.926	0.926	0.874	0.978
5CB	0.793	0.956	0.91	0.988	0.933	0.933	0.897	0.989
6CB	0.447	0.947	0.858	0.942	0.926	0.931	0.891	0.991
PCB 26					0.915	0.926	0.901	0.989
PCB 52	0.878	0.941	0.879	0.987	0.920	0.935	0.896	0.987
PCB 101					0.955	0.974	0.911	0.990
PCB 155	0.324	0.844	0.696	0.969	0.942	0.957	0.908	0.981
PCB 180					0.940	0.985	0.868	0.979
PCB 194					0.872	0.990	0.906	0.991

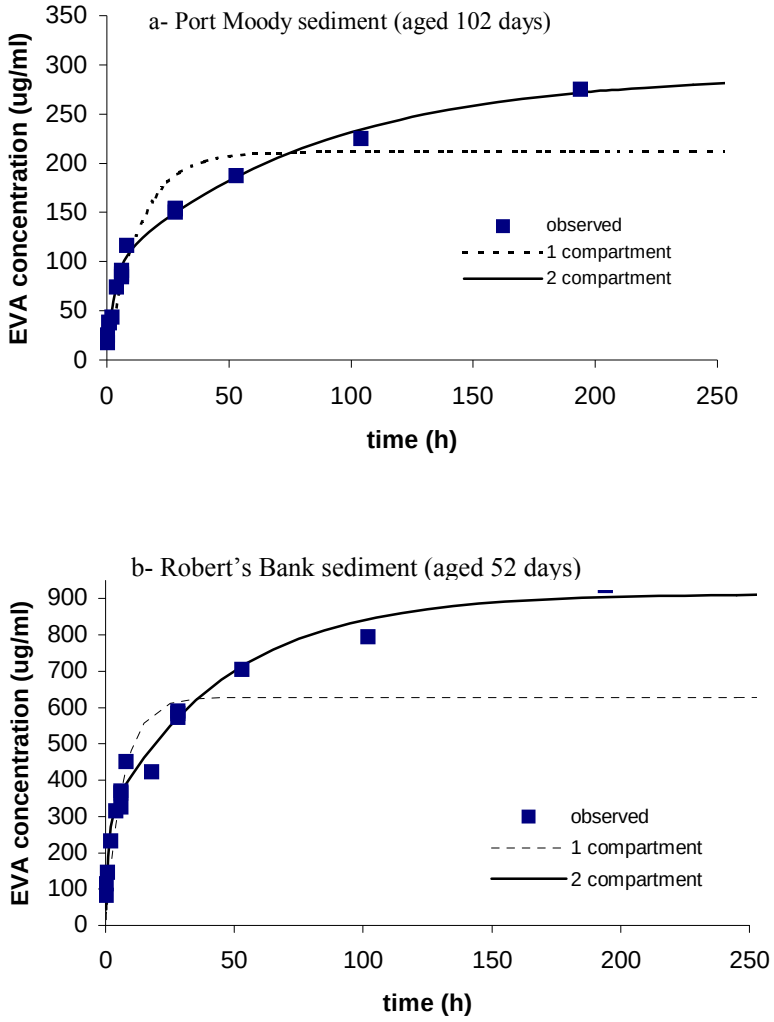

Figure 3-3 One-compartment and two-compartment uptake models fit to observed PCB 52 concentrations in EVA for the Port Moody and Robert's Bank spiked sediment experiments

By using a two-compartment model, we are assuming that uptake into EVA occurs from two different compartments. The model is empirical, however, and does not necessarily offer a mechanistic explanation for the observed EVA uptake behaviour. Non-linear regression using the two-compartment model resulted in the estimation of four parameters: $C_{EVA(f)}$ and $C_{EVA(s)}$ - the concentrations in EVA reflecting equilibrium

with the fast and slow compartments, k_{fast} and k_{slow}, the fast and slow apparent uptake rate constants. Based on uptake kinetics, the time required for a chemical to reach 95% of equilibrium concentration (t_{95}) can be estimated as 3/k, where k is the uptake rate constant (Wilcockson and Gobas 2001). Therefore, t_{95} for the fast and slow compartment is equal to:

$$t_{95(f)} = 3/k_{fast,} \quad (15)$$

and

$$t_{95(s)} = 3/k_{slow} \quad (16)$$

Because uptake from the slow compartment is the rate-limiting step, t_{95} for the total uptake ($t_{95(total)}$) is also equal to $3/k_{slow}$.

Results from the two-compartment model fitting for the Port Moody and Robert's Bank spiked sediment experiments are summarized in Tables 3.3 and 3.4. In the Port Moody sediment, aged for 21 days, equilibrium with the rapid compartment had nearly been reached before the completion of the 15 minute extraction period for tetrachlorobenzene, hexachlorobenzene, PCB 52 and PCB 155. As a result, k_{fast} could not be determined. This intial very rapid uptake was not observed in the in the Robert's Bank sediment, making estimates of k_{fast} possible. When k_{fast} could not be estimated, the uptake model was simplified to:

$$C_{EVA}(t) = C_{EVA(f)} + C_{EVA(s)}\,(1-\exp(-k_{slow}t)) \quad (17)$$

The above equation assumes that the uptake of chemical from the fast compartment was rapid enough (i.e., $\exp(-k_{fast}t) \approx 0$) to achieve equilibrium with the EVA film almost immediately. In table 3.3, k_{fast} is expressed as >3 when this very rapid initial uptake occurred, meaning that $t_{95(fast)}$ was assumed to be less than 1 hour.

Table 3-3 Uptake rate constants (h^{-1}) and equilibrium EVA concentrations (μg/ml) for the rapidly and slowly desorbing compartments in the Port Moody sediment, aged 21 and 102 days (1 standard error in parentheses)

Chemical	k_{fast} (h^{-1})	k_{slow} (h^{-1})	$C_{EVA(f)}$ (μg/ml)	$C_{EVA(s)}$ (μg/ml)	t_{95} (h)
			21 days		
4CB	> 3	0.127 (0.053)	39.9 (10.6)	64.7 (11.5)	23.6
5CB	2.69 (1.02)	0.0446 (0.013)	89.2 (13.1)	124 (13)	67.3
6CB	> 3	0.0143 (0.003)	48.1 (3.9)	75.5 (8.5)	210
PCB52	> 3	0.0412 (0.0096)	57.1 (13.2)	221 (16)	72.8
PCB155	> 3	0.031 (0.011)	41.9 (6.8)	77.2 (10.6)	96.8
			102 days		
4CB	3.81 (1.89)	0.104 (0.033)	27.1 (5.1)	39.6 (4.96)	28.9
5CB	4.33 (1.76)	0.0914 (0.013)	33.4 (5.6)	88.9 (4.55)	32.8
6CB	4.42 (3.66)	0.0732 (0.023)	28.8 (7.4)	73.9 (7.61)	41.0
PCB52	0.34 (0.11)	0.0121 (0.0036)	92.6 (13.9)	198 (17)	248
PCB155	3.26 (0.86)	0.0130 (0.0042)	42.6 (2.6)	59.1 (7.6)	231

Table 3-4 Uptake rate constants (h^{-1}) and equilibrium EVA concentrations (μg/ml) for the rapidly and slowly desorbing compartments in the Robert's Bank sediment, aged 17 and 52 days (1 standard error in parentheses)

Chemical	k_{fast} (h^{-1})	k_{slow} (h^{-1})	$C_{EVA(f)}$ (μg/ml)	$C_{EVA(s)}$ (μg/ml)	t_{95} (h)
			17 days		
4CB	0.882 (0.140)	-	317 (10)	-	3.4
5CB	0.698 (0.098)	-	680 (23)	-	4.3
6CB	0.644 (0.142)	0.0193 (0.049)	1040 (96)	131 (131)	155
PCB26	0.577 (0.156)	0.0255 (0.042)	1060 (140)	236 (157)	118
PCB52	0.537 (0.152)	0.0287 (0.034)	1410 (200)	441 (221)	105
PCB101	0.373 (0.104)	0.0306 (0.034)	568 (100)	335 (98)	98
PCB155	0.421 (0.129)	0.0330 (0.027)	1010 (200)	451 (186)	91
PCB180	0.265 (0.059)	0.0158 (0.0058)	236 (35)	217 (34)	190
PCB194	0.225 (0.034)	0.0061 (0.0021)	156 (14)	246 (21)	492
			52 days		
4CB	2.28 (0.84)	0.036 (0.0068)	71.4 (8.3)	159 (10.6)	83
5CB	1.75 (0.46)	0.035 (0.0046)	145 (12.4)	333 (15.8)	86
6CB	1.56 (0.34)	0.029 (0.0035)	238 (16.1)	503 (22.2)	103
PCB26	1.00 (0.27)	0.024 (0.0033)	204 (17.1)	483 (24.0)	125
PCB52	0.929 (0.26)	0.022 (0.0034)	291 (24.1)	623 (35.8)	136
PCB101	0.220 (0.045)	0.0073 (0.0041)	201 (25.2)	340 (7.52)	411
PCB155	0.218 (0.063)	0.0087 (0.0060)	300 (54.7)	457 (96.7)	500
PCB180	0.319 (0.159)	0.0073 (0.0045)	69.8 (15.8)	230 (60.2)	411
PCB194	0.206 (0.055)	0.005 (0.0027)	59.0 (9.6)	246 (72.9)	600

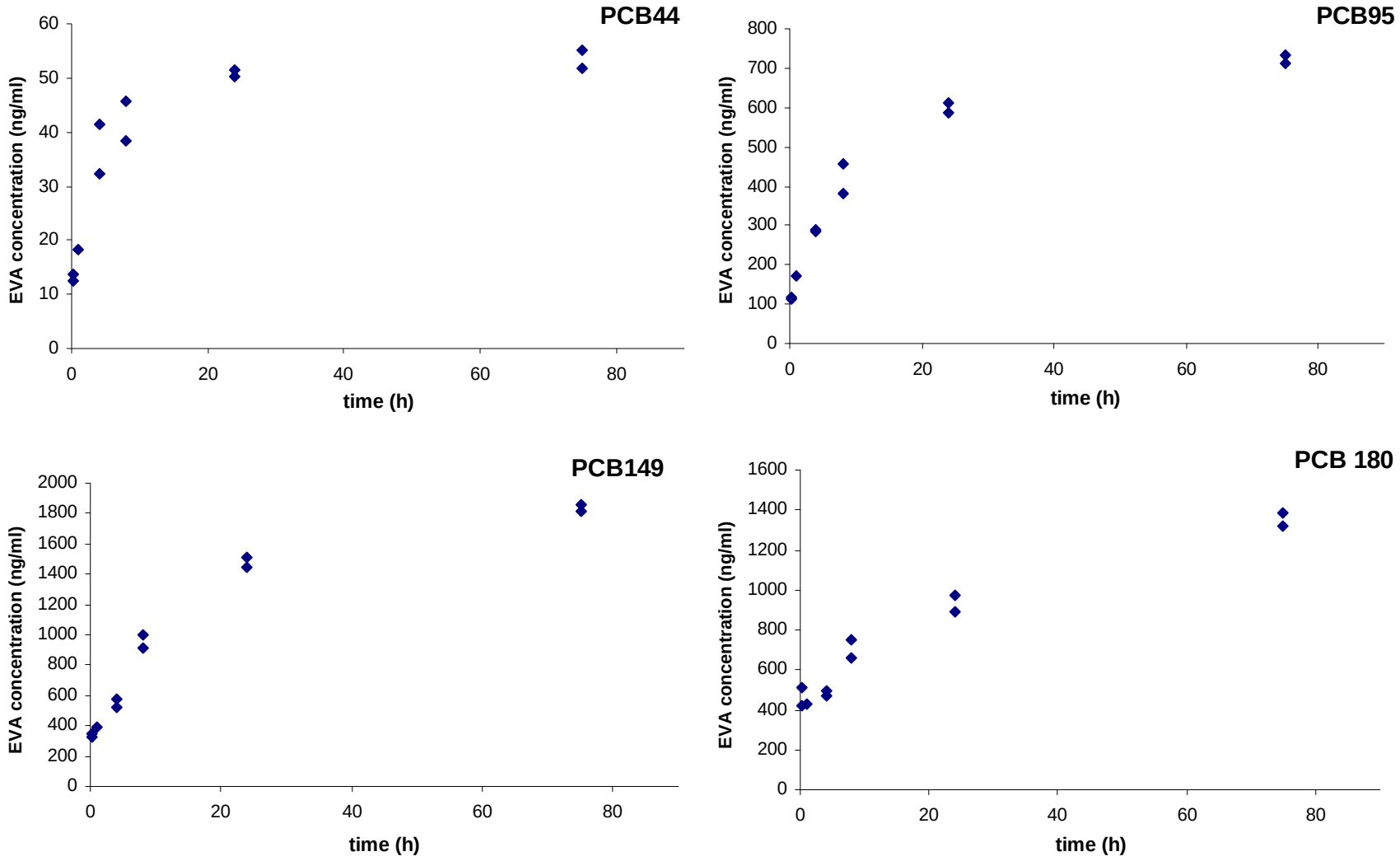

Figure 3-4 EVA thin-film extraction of four PCB congeners from the Sydney Harbour sediment

3.1.2 Field sediment experiment

Over 50 PCB congeners were detected in the thin-film extraction experiment using the field-contaminated sediment from Sydney Harbour. Observed EVA concentrations are reported in Appendix B. Detection limits ranged from 1.0 to 2.1 pg/sample, and recovery of ^{13}C-labelled standards averaged 90%. Congeners for which EVA concentrations were non-detectable in the early extractions (0.25 – 4 h) were omitted from the analysis. Some congeners could not be distinguished due to co-elution with one or more congener (e.g. PCB 59 and PCB 42). For the purpose of analysis, co-eluting congeners were identified as one chemical and the sum of the concentrations was reported. Where chemical properties were required (e.g. Koa for Z_{EVA} calculation), the average value for the co-eluting congeners was used. Coefficients of variation for duplicate samples were on average 7.8 %.

Uptake curves for four PCB congeners (44, 95, 149, 180) are illustrated in Figure 3.4. Higher congeners numbers are generally associated with higher Kow. The higher Kow chemical (i.e. PCB 180) appears to take longer to reach equilibrium with the EVA film than the lower Kow chemical (e.g. PCB 44). One- and two-compartment uptake models were fitted to the data and the resulting R^2 values are plotted versus log Kow in Figure 3.5. Similar to the spiked sediment experiments, the two-compartment model resulted in higher R^2 (average value of 0.97) than the one compartment model (average value of 0.78). Differences in fit between the two models were greatest for the higher Kow congeners. Results from the non-linear regression of observed EVA concentrations using the two-compartment model are summarized in Table 3.5. The majority of PCB congeners exhibited a very rapid initial uptake, and estimates for k_{fast} were not possible.

Thus, the simplified uptake equation (17) was used to obtain estimates of $C_{EVA(f)}$, $C_{EVA(s)}$, and k_{slow}; k_{fast} was assumed to be greater than 3, and is not presented in the table.

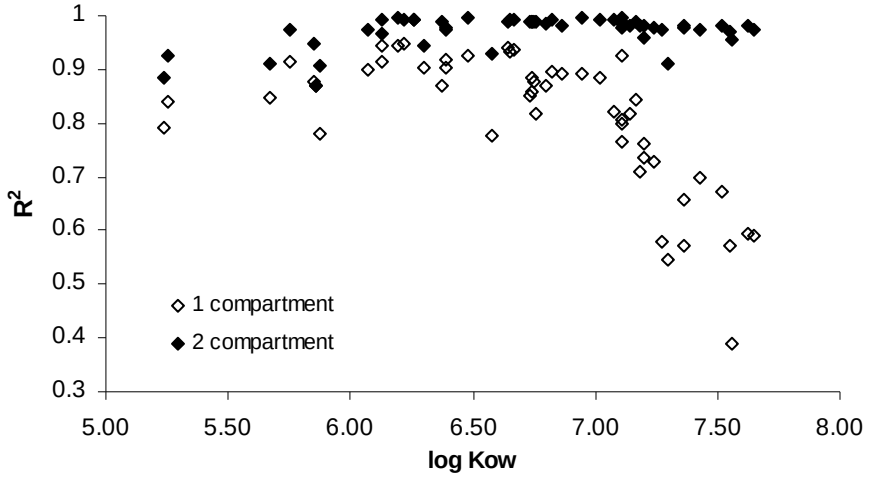

Figure 3-5 One-compartment (◊) and two-compartment(♦) model fit (R^2) for PCB congeners in Sydney Harbour sediment

Table 3-5 Uptake rate constants (h^{-1}) and equilibrium EVA concentrations (μg/ml) for the rapidly and slowly desorbing compartments in the Sydney Harbour sediment (1 standard error in parentheses)

Congener number	log Kow[a]	k_{slow} (h^{-1})	$C_{EVA(f)}$ (μg/ml)	$C_{EVA(s)}$ (μg/ml)	t_{95} (h)
17	5.25	0.31 (0.11)	4.95 (1.44)	11.6 (1.56)	9.6
18	5.24	0.31 (0.15)	11.9 (4.19)	25.7 (4.59)	9.5
31	5.67	0.44 (0.29)	9.34 (3.19)	20.1 (3.29)	6.8
44	5.75	0.21 (0.039)	11.3 (2.58)	40.5 (3.00)	14
49	5.85	0.21 (0.057)	9.11 (2.62)	28.2 (3.07)	14
59/42	5.86	0.19 (0.057)	3.23 (1.21)	11.9 (1.43)	16
71/41/64	5.87	0.035 (0.029)	39.1 (6.39)	34.5 (8.50)	86
85	6.30	0.077 (0.028)	4.93 (0.94)	12.5 (1.31)	39
89	6.07	0.072 (0.019)	14.7 (3.68)	38.2 (3.82)	42
91	6.13	0.076 (0.032)	7.06 (2.11)	11.4 (2.00)	40
92/84	6.20	0.064 (0.006)	16.1 (2.28)	74.5 (2.56)	47
95	6.13	0.073 (0.009)	147 (26.0)	571 (27.7)	41
97/86	6.26	0.081 (0.010)	9.19 (1.50)	35.1 (1.59)	37
99	6.39	0.098 (0.018)	11.6 (2.53)	50.2 (3.30)	31

Congener number	log Kow[a]	k_{slow} (h^{-1})	$C_{EVA(f)}$ (μg/ml)	$C_{EVA(s)}$ (μg/ml)	t_{95} (h)
101/90	6.37	0.060 (0.009)	178 (25.8)	574 (29.4)	50
110	6.48	0.056 (0.006)	73.4 (7.87)	253 (8.94)	54
115/87	6.39	0.054 (0.012)	24.0 (5.34)	85.8 (6.28)	56
118	6.74	0.052 (0.007)	40.5 (4.76)	122 (5.68)	58
119	6.58	0.032 (0.023)	2.90 (1.17)	6.83 (1.34)	94
128	6.74	0.053 (0.007)	16.9 (1.73)	56.7 (2.81)	57
130	6.80	0.044 (0.007)	15.4 (1.81)	59.6 (3.25)	68
132/153	6.75	0.046 (0.006)	388 (39.9)	1520 (70.3)	65
133	6.86	0.052 (0.008)	45.8 (6.64)	196 (10.9)	58
135/144	6.66	0.059 (0.005)	63.3 (6.62)	321 (10.2)	51
136	6.22	0.068 (0.009)	42.4 (6.75)	253 (9.85)	44
141	6.82	0.051 (0.005)	81.7 (6.99)	336 (11.5)	59
149	6.67	0.061 (0.006)	291 (34.4)	1560 (52.3)	49
151	6.64	0.065 (0.008)	117 (18.1)	653 (26.9)	46
158	7.02	0.046 (0.005)	25.0 (1.97)	99.9 (3.45)	65
160/163/164/138	6.94	0.051 (0.004)	299 (20.5)	1190 (34.0)	59
168	7.11	0.059 (0.005)	54.0 (5.02)	256 (7.73)	51
170/190	7.37	0.032 (0.007)	195 (15.9)	494 (39.8)	94
171	7.11	0.037 (0.008)	44.6 (4.59)	129 (9.66)	81
174/181	7.11	0.039 (0.006)	188 (16.5)	582 (33.0)	77
175	7.17	0.040 (0.007)	7.99 (0.95)	25.2 (1.32)	75
176	6.76	0.047 (0.007)	38.1 (3.42)	116 (5.90)	63
177	7.08	0.042 (0.005)	96.6 (7.15)	307 (13.4)	71
178	7.14	0.042 (0.008)	36.9 (4.01)	118 (7.55)	71
179	6.73	0.042 (0.006)	89.1 (7.68)	315 (14.5)	71
180	7.36	0.029 (0.007)	430 (32.1)	1040 (94.7)	110
183	7.20	0.038 (0.007)	113 (10.3)	310 (21.3)	79
185	7.11	0.043 (0.007)	25.1 (2.34)	74.9 (4.35)	70
187/182	7.19	0.039 (0.007)	246 (21.7)	714 (43.4)	77
191	7.55	0.019 (0.009)	8.25 (0.67)	18.8 (3.99)	160
192/172	7.43	0.033 (0.008)	30.4 (2.93)	78.0 (7.12)	92
193	7.52	0.036 (0.007)	19.0 (1.43)	43.6 (3.14)	84
195	7.56	0.019 (0.011)	43.8 (3.77)	87.0 (25.2)	160
197	7.30	0.017 (0.012)	3.86 (0.63)	13.6 (4.95)	170
199	7.20	0.033 (0.011)	12.1 (1.66)	34.0 (3.99)	91
200	7.27	0.021 (0.008)	28.1 (2.21)	69.4 (11.7)	140
201	7.62	0.014 (0.006)	72.0 (5.02)	235 (58.6)	210
202	7.24	0.015 (0.007)	20.5 (2.00)	86.4 (22.8)	210
203/196	7.65	0.016 (0.008)	106 (8.72)	320 (82.6)	190

a- Hawker and Connell, 1988

3.2 Uptake kinetics

3.2.1 Spiked sediment experiments

Apparent uptake rate constants for the Port Moody spiked sediment experiments are summarized in Table 3.3. Estimates of k_{fast} were quite high for both the day 21 and day 102 uptake experiments. Most chemicals in the 21day experiment had reached equilibrium within the first few extractions (< 1 hour), and k_{fast} could not be calculated. Estimates of k_{fast} for the 102-day sediment were also variable. The slowest k_{fast} in this sediment was observed for PCB 52, at 0.34 h^{-1}, corresponding to a $t_{95(fast)}$ of 8.8 hours. Rate constants associated with the slowly desorbing compartment (k_{slow}) ranged from 0.014 to 0.127 h^{-1} in the sediment aged for 21 days and 0.012 to 0.104 h^{-1} in the sediment aged for 102 days. The time required for 95% equilibration, approximated as $t_{95(slow)}$, ranged from 23.6 h for tetra-chlorobenzene in the sediment aged for 21 days to 231 h for PCB155 in the sediment aged for 102 days. A paired t-test (SPSS 11.0) was used to compare the estimates of k_{slow} for individual chemicals between the two ageing periods. Differences in k_{slow} among the two ageing periods were not significant (μ=-0.0074, p = 0.715).

Uptake rate constants for chemicals in the Robert's Bank spiked sediment experiments are presented in Table 3.4. Estimates of k_{fast} were possible in the sediment due to a slower initial uptake, with $t_{95(fast)}$ ranging from 1.32 to 14.3 hours. Rapid uptake rate constants for Robert's Bank sediment ranged from 0.225 to 0.882 h^{-1} after 17 days of ageing, and from 0.206 to 2.28 h^{-1} after 52 days of ageing. Estimates of k_{slow} ranged from 0.0033 to 0.061 h^{-1} in the sediment aged for 17 days and from 0.005 to 0.036 h^{-1} for the sediment aged for 52 days. For both ageing periods, the longest equilibration times were

observed for PCB 194, with t_{95}s of 491 h in the sediment aged for 17 days and 600 h in the sediment aged for 52 days. After 17 days of ageing, tetra- and pentachlorobenzene exhibited one-compartmental uptake, that is, the two-compartment model fit resulted in 100% of the EVA concentration originating from the rapidly desorbing compartment. Consequently, estimates of k_{slow} were not obtained for these chemicals. Estimates of k_{slow} in the day 17 experiment were associated with high standard errors. This is likely due to a missing data point at 176 hours, making the estimation of a precise equilibration time difficult. A two-sample paired t-test was used to test for differences in rate constant estimates between the two ageing periods. Differences in k_{slow} were not significant between the two ageing periods (μ=0.0088, p=0.119). Estimates of k_{fast} were slightly greater in the sediment aged for 52 days than they were in the sediment aged for 17 days, however the difference was not significant at the α=0.05 level (μ=-0.418, p=0.064).

Initial uptake of chemicals into the EVA thin film occurred much more rapidly from the Port Moody sediment than from the Robert's Bank sediment. These differences were not tested statistically however, due to inability to estimate k_{fast} in the Port Moody sediment. Estimates of k_{slow} for matching chemicals from the Port Moody sediment (aged 102 days) and the Robert's Bank sediment (aged 52 days) were compared using a paired t-test. The slow rate constants were generally higher in the Port Moody sediment, however the average difference was not significant (μ = -0.0327), p=0.095). One explanation for the difference in uptake rate constants may be the differences in particle size between the two sediments. Port Moody sediment has smaller particles (in the silty range) and a higher sediment surface area to facilitate desorption, while Robert's Bank sediment is primarily sandy, with a lower surface area. In addition, differences in the

nature organic matter composition may potentially influence the ability of the chemicals to desorb from the sediment. Analysis of the nature of organic matter was beyond the scope of this experiment, however the presence of older organic materials has been associated with slower desorption (Jonker and Koelmans 2002).

Estimates of k_{fast} and k_{slow} for the spiked sediment experiments are plotted versus log Kow in figures 3.6 and 3.7. Linear regression was perfomed (SPSS 11.0) to determine whether any significant relationship exists between the rate constant estimates and log Kow. Significant negative relationships were observed between log k_{slow} and log Kow for the Port Moody sediment, aged 102 days ($p = 0.037$) and the Robert's Bank sediment aged 52 days ($p = 0.000057$). Significant negative relationships were also observed between k_{fast} and log Kow in Robert's Bank sediment aged for 17 days ($p = 0.000017$) and 52 days ($p = 0.000018$). Relationships between k_{fast} and log Kow were difficult to distinguish in the Port Moody sediment due to estimation difficulties for the rapid uptake fraction. Other investigators (Gong et al 1998, Cornelissen et al 1997) have also observed a negative relationship between Kow and desorption rates for PCBs. The observed negative relationships can be explained when considering the chemicals' uptake path. Chemicals must pass through the pore water in order to travel from the sediment organic carbon to the EVA thin film. Therefore, chemicals with high log Kow would be expected to experience more resistance in the aqueous phase, slowing their travel and lowering the observed uptake rate constant.

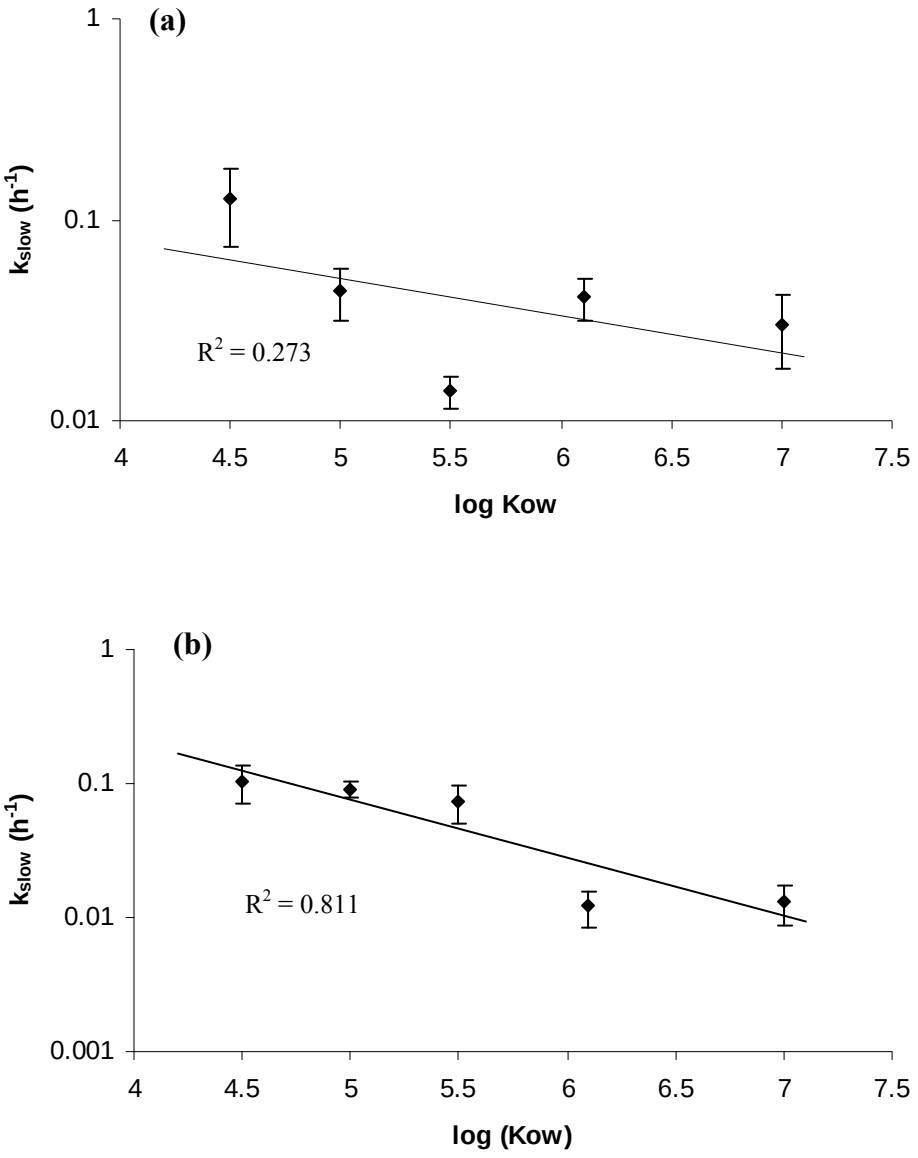

Figure 3-6 Estimated slow uptake rate constants (h^{-1}), +/- 1 standard error, versus log Kow for chemicals in the Port Moody sediment aged for (a) 21 days and for (b) 102 days

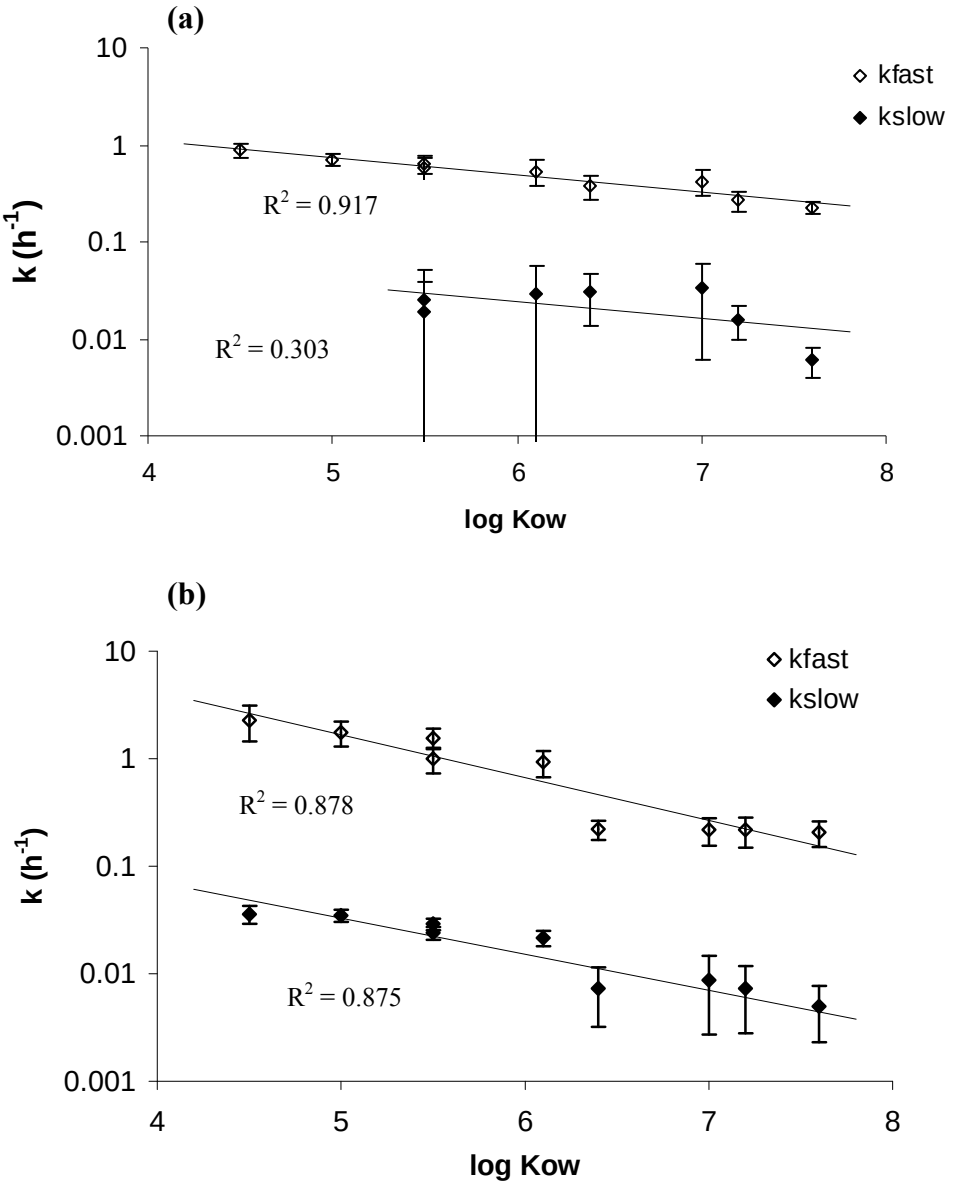

Figure 3-7 Estimated fast (◊)and slow (♦) uptake rate constants (h^{-1}), +/- 1 standard error, versus log Kow for chemicals in the Robert's Bank sediment aged for (a) 17 days and for (b) 52 days

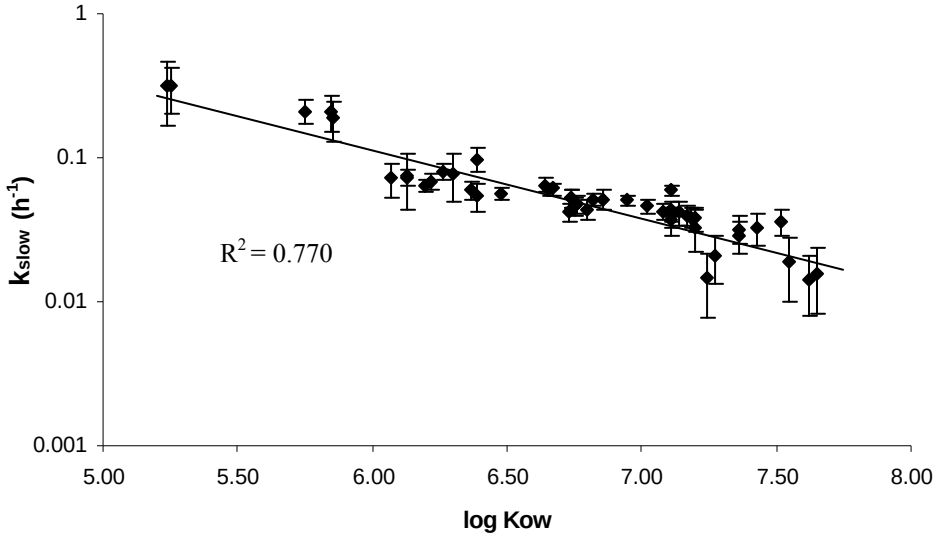

Figure 3-8 Slow uptake rate constants (h^{-1}) for PCB congeners in the Sydney Harbour sediment versus log Kow (error bars represent +/- 1 standard error)

3.2.2 Field sediment experiment

Uptake rate constants (k_{slow}) for PCB congeners in the Sydney Harbour experiment are shown versus log Kow in Figure 3.8. Estimates of k_{slow} ranged from 0.144 h^{-1} for PCB 201 to 0.441 h^{-1} for PCB 44. Linear regression resulted in a significant negative relationship between log k_{slow} and log Kow ($p= 6.4 \times 10^{-18}$). Therefore, the rate of extraction of chemicals by the EVA film decreased with increasing Kow. The initial very rapid uptake and range of k_{slow} for this sediment were similar to that of the Port Moody sediment, and somewhat greater than the Robert's Bank sediment. These higher rates could be attributed to the presence of a small particle fraction (66.4% of sediment by mass is less than 0.063 mm in diameter), increasing the surface area for desorption in comparison to the Robert's Bank sediment (with 80% of sediment by weight in the sandy

fraction). Also, an oily residue was observed in this sediment. This residue may have contributed a labile pool for rapidly desorbing contaminants.

3.2.3 Uptake rate constant

The apparent uptake rate constant is a result of chemicals leaving the sediment particle, traveling through the pore water and into the EVA film. Thus, the measured "apparent" rate constants are proportional to the sum of the resistances present in each of these three stages,

$$R_{total} = R_{sed} + R_w + R_{EVA} \quad (18)$$

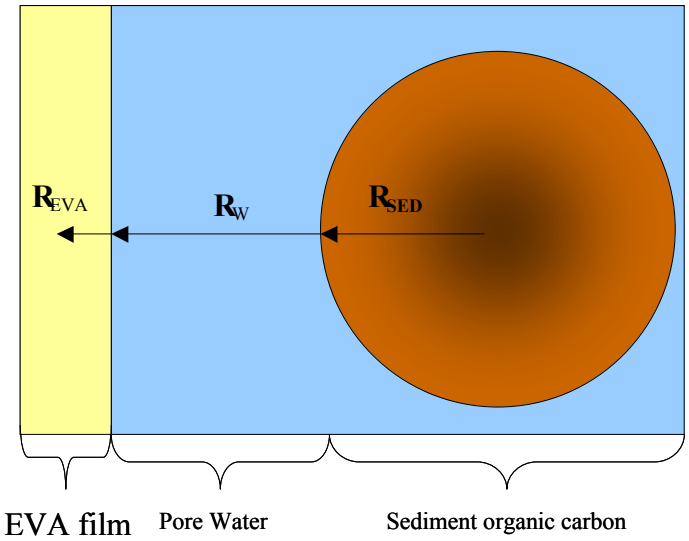

Figure 3-9 Resistance encountered for contaminants diffusing from sediment to EVA thin film

Figure 3.9 illustrates this process. The measured uptake rate constants would be representative of actual desorption from sediment particles if the resistances in the EVA and water phases were very small compared to that of the sediment organic carbon. Because movement of chemicals in this system is primarily through diffusion, we would

expect the kinetics to be influenced by surface area, distance of travel and fugacity gradients. The EVA film is not likely to contribute significantly to the total resistance because of its high surface area to volume ratio (3770 mm^{-1}) and small thickness (0.26 μm). To test this assumption, experiments would have to be run with films of varying thickness. Uptake rate constants measured with these films would theoretically increase as thickness decreased and would remain constant when the film was thin enough to provide negligible resistance. Resistance imposed by the water phase would likely be significant for chemicals that are very hydrophobic (high Kow), such as PCBs. Larger chemicals may also be expected to experience more resistance traveling through the organic matter matrix. The significant negative relationships resulting from linear regression between log Kow and the uptake rate constants confirm the increased resistance for hydrophobic chemicals. Therefore, the rate constants obtained from the model fit are likely representative of a combination of desorption from organic carbon and diffusion through the pore water.

Desorption of HOCs from sediment has been measured directly using techniques such as gas stripping (Gong et al) and extraction with Tenax beads (Cornelissen et al 1997, ten Hulscher et al 1999, Kukkonen et al 2003). Reported rate constants for fast desorption of PCBs and chlorobenzenes range from 0.03 to 0.3 h^{-1}, and from 0.0009 to 0.018 h^{-1} for slow desorption. Some authors have also identified the presence of a third contaminant fraction that is associated with "very" slow desorption. Measured desorption rate constants in the very slow compartment have been found to fall below 10^{-3} h^{-1} (ten Hulscher et al 1999, Kukkonen et al 2003). The rate constants observed in the present study are at the upper end of the fast and slow desorption ranges, suggesting

that desorption from the sediments may be the rate-limiting step in this system. None of the detected uptake rates constant are as low as those reported for very slowly desorbing fractions. This suggests that we are only detecting the contaminants that are desorbing relatively rapidly, and are not detecting the presence of chemicals associated with very slow desorption. Nevertheless, it is unlikely that contaminants desorbing very slowly contribute significantly to the bioavailable chemical fraction, because chemicals in this compartment are not likely to reach equilibrium with the pore water.

3.3 Ageing effects

Ageing effects were explored by comparing the equilibrium EVA thin-film concentrations (representative of chemical bioavailability) between the different ageing periods for both of the spiked sediments. EVA concentrations at equilibrium (C_{EVA} +/- two standard errors) from the Port Moody and Robert's Bank sediment experiments are plotted in Figure 3.10. EVA concentrations from the Port Moody spiked sediment are not significantly different (i.e., the 95% confidence intervals overlap) between the 21 day and 102 day ageing periods for all chemicals with the exception of pentachlorobenzene (5CB), which exhibits a higher concentration in sediments aged for 21 days. EVA concentrations from Robert's Bank sediment are significantly greater in the earlier ageing period (17 days) than in the longer ageing period (52 days) for the chlorobenzenes as well as for PCB 26 and PCB 52. The decrease in total EVA concentration suggests that some fraction of the chemical is no longer available for uptake by EVA (and biota, potentially) after an increase in sediment-contaminant contact time. It is possible that some of the contaminants have moved into a very slowly desorbing compartment where they are no

longer able to reach equilibrium with the pore water, making them essentially undetectable by the EVA film. Unfortunately, our observations of ageing effects are limited to the two ageing periods sampled in this study. It is possible that the higher Kow chemicals (i.e. most of the PCBs), for which ageing effects were not observed between the two periods, require longer contact times to become sequestered. Alternately, sequestration of chemicals may have occurred prior to the first experiment (17 days for Robert's Bank sediment and 21 days for Port Moody sediment). Further research is needed (using several ageing periods) to make more meaningful deductions with respect to ageing behaviour. Application of the thin-film solid-phase extraction method would be useful in this regard, as it takes into account contaminant sequestration, with only the readily available chemical fraction being sensed by the EVA film.

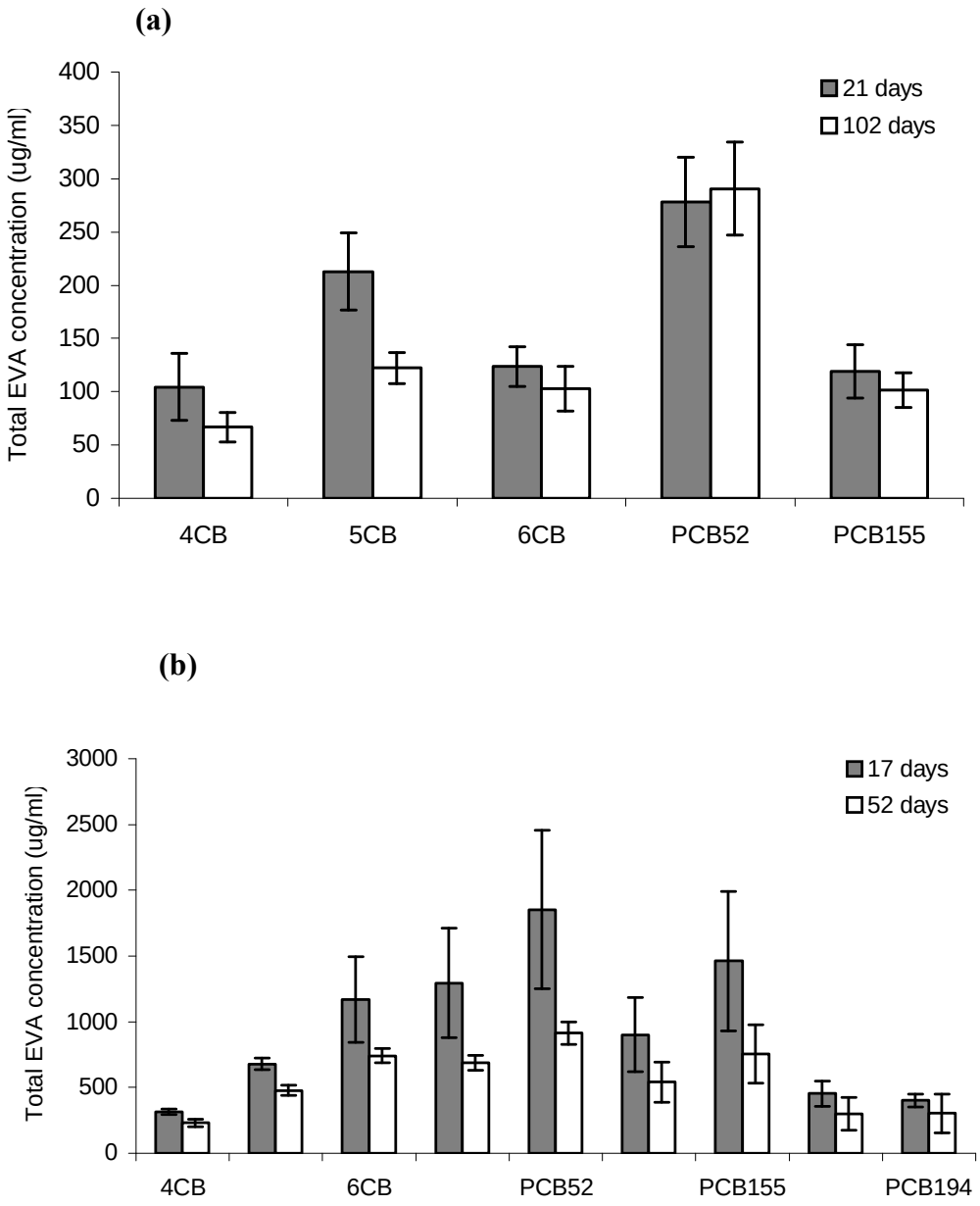

Figure 3-10 Equilibrium concentrations in EVA (μg/mL) for chemicals in (a) Port Moody sediment, aged 21 and 102 days, and (b) Robert's Bank sediment, aged 17 and 52 days (error bars represent 95% confidence intervals)

So far, our compartmentalization has been based solely on the observation of two distinct rate constants, one being slower than the other. Yet, it is not clear how increased contact time between contaminant and sediment (or ageing) influences the distribution of chemicals between compartments. One hypothesis is that rapid desorption occurs from the fraction of chemical nearest to the organic carbon – pore water interface. Diffusion from this accessible pool would be fast due to the proximity of chemicals to the porewater, resulting in higher desorption rate constants. As contact time increases, chemicals would move from the accessible compartment towards a deeper, less accessible compartment, in an attempt to reach equilibrium with the total organic matter. In this deeper compartment, diffusion is associated with a greater resistance and measured desorption rate constants are subsequently slower than those measured in the accessible or "fast" compartment (Pignatello and Xing 1996). Figure 3.11 illustrates this phenomenon.

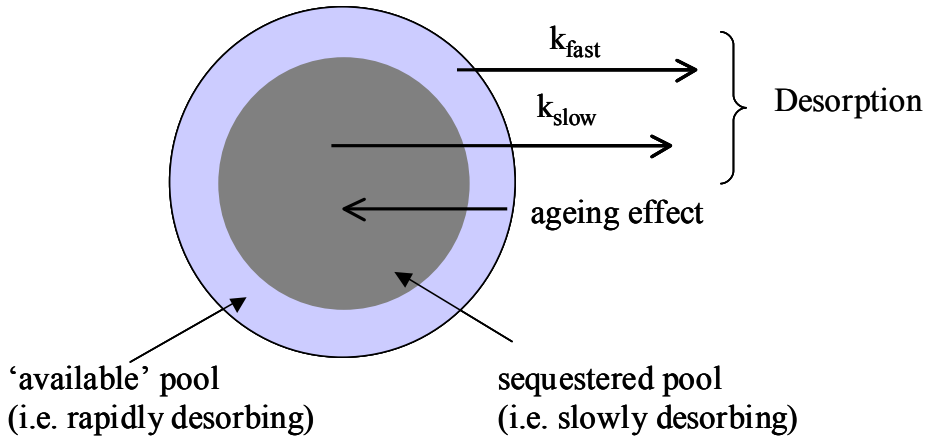

Figure 3-11 The effect of ageing on a sediment particle with rapidly and slowly desorbing compartments

Therefore, as sediment-contaminant contact time increases, we would expect a reduction in the fraction of contaminants associated with rapid desorption. This trend has been observed in several studies (Cornelissen et at 1997, Kraaij 2002, ten Hulscher et al 2003). In these studies, contaminants were stripped from sediment particles by adding large volumes of the strong sorbant, tenax. Using this method, the authors were able to measure the desorption rate constants as well as the fraction of chemical present in each of the compartments. In the present experiment, extraction of contaminants from the sediment is non-depletive, meaning the sediment concentrations are not expected to change over time. Consequently, we cannot determine the absolute distribution of contaminants between compartments, and detection of changes in these distributions is not possible. Because our method cannot detect chemicals associated with very slow desorption (sequestered fraction), a movement of chemicals into very slowly desorbing compartments would instead appear as a drop in EVA concentration or fugacity.

3.4 Fugacity

It is beneficial to use fugacity when expressing the bioavailability of sediment-associated contaminants. Fugacity can be calculated based on the results of EVA thin-film extractions. Fugacity capacities for EVA were calculated using the chemicals' octanol-air partitioning coefficient (Koa) (using equation 13). Estimated equilibrium concentrations (C_{EVA}) from the two-compartment uptake model were used to calculate the fugacity in EVA at equilibrium, which is equal to the fugacity in the sediment. Tables 3.6 -3.8 summarize the results of the fugacity calculations, including equilibrium EVA concentration and Z_{EVA}s.

Table 3-6 EVA Fugacity capacities Z_{EVA} (mol/m^{3}Pa) and fugacities (nPa) calculated using equilibrium EVA concentrations (C_{EVA}) for chlorobenzenes and PCBs in Port Moody sediment (1 standard error in parentheses)

			21 days		*102 days*	
Chemical	**log Koa**	**Z_{EVA} (mol/m^{3}Pa)**	**C_{EVA} (mol/m^3)**	**f (nPa)**	**C_{EVA} (mol/m^3)**	**f (nPa)**
4CB	5.81	1.04 x10^3	0.484 (0.072)	4.64 x10^5 (6.94 x10^4)	0.309 (0.033)	2.96 x10^5 (3.15 x10^4)
5CB	6.46	4.66 x10^3	0.850 (0.073)	1.82 x10^5 (1.56 x10^4)	0.488 (0.029)	1.05 x10^5 (6.17 x10^3)
6CB	6.78	9.73 x10^3	0.434 (0.033)	4.46 x10^4 (3.36 x10^3)	0.361 (0.037)	3.71 x10^4 (3.82 x10^3)
PCB52	9.30	8.67 x10^5	0.952 (0.072)	1.10 x10^3 (8.26 x10^1)	0.995 (0.075)	1.15 x10^3 (8.65 x10^1)
PCB155	9.52	5.35 x10^6	0.330 (0.035)	6.17 x10^1 (6.51 x10^0)	0.308 (0.041)	5.76 x10^1 (7.68 x10^0)

Table 3-7 EVA Fugacity capacities Z_{EVA} (mol/m^{3}Pa) and fugacities (nPa) of chlorobenzenes and PCBs in Robert's Bank sediment (1 standard error in parentheses)

			17 days		*52 days*	
Chemical	**log Koa**	**Z_{EVA} (mol/m^{3}Pa)**	**C_{EVA} (mol/m3)**	**f (nPa)**	**C_{EVA} (mol/m3)**	**f_{EVA} (nPa)**
4CB	5.81	1.04 x10^3	1.47 (0.044)	1.40 x10^6 (4.20 x10^4)	1.07 (0.08)	1.02 x10^6 (8.00 x10^4)
5CB	6.46	4.66 x10^3	2.72 (0.086)	5.83 x10^5 (1.84 x10^4)	1.91 (0.11)	4.10 x10^5 (2.51 x10^4)
6CB	6.78	9.73 x10^3	4.11 (0.570)	4.22 x10^5 (5.85 x10^4)	2.60 (1.17)	2.67 x10^5 (1.25 x10^5)
PCB26	8.20	2.56 x10^5	5.03 (0.808)	1.96 x10^4 (3.16 x10^3)	2.67 (0.96)	1.04 x10^4 (3.90 x10^3)
PCB52	9.30	8.67 x10^5	6.35 (1.03)	7.32 x10^3 (1.19 x10^3)	3.13 (1.22)	3.61 x10^3 (3.94 x10^2)
PCB101	9.60	6.43 x10^6	2.77 (0.431)	4.30 x10^2 (6.70 x10^1)	1.66 (0.52)	2.58 x10^2 (8.40 x10^1)
PCB155	9.52	5.35 x10^6	4.05 (0.735)	7.57 x10^2 (1.37 x10^2)	2.10 (0.89)	3.92 x10^2 (1.74 x10^2)
PCB180	11.43	4.35 x10^8	1.15 (0.122)	2.64 x10^0 (2.81 x10^{-1})	0.96 (0.16)	2.21 x10^0 (3.88 x10^{-1})
PCB194	12.48	4.88 x10^9	0.934 (0.059)	1.92 x10^1 (1.21 x10^{-2})	0.71 (0.74)	1.45 x10^{-1} (1.57 x10^{-1})

Table 3-8 Fugacity capacities (mol/m^{3}Pa) and fugacities for PCB congeners in Sydney Harbour sediment (1 stardard error in parentheses)

Congener Number	log Koa[a]	Z_{EVA} (mol/m^{3}Pa)	C_{EVA} (mmol/m^3)	fugacity (nPa)
17	7.88	1.23 x10^5	0.064(0.019)	0.525(0.156)
18	7.83	1.09 x10^5	0.146(0.056)	1.34(0.509)
31	8.29	3.15 x10^5	0.114(0.049)	0.363(0.155)
44	8.85	1.14 x10^6	0.178(0.026)	0.156(0.023)
49	8.7	8.10 x10^5	0.142(0.019)	0.175(0.0240)
59/42	8.9	1.28 x10^6	0.094(0.008)	0.0731(0.0060)
71/41/64	8.94	1.41 x10^6	1.59(0.051)	1.13(0.0363)
85	9.8	1.02 x10^7	0.053(0.007)	0.00523(0.0007)
89			0.162(0.016)	
91	9.4	4.0 x10^6	0.056(0.009)	0.0139(0.0022)
92/84	9.53	5.47 x10^6	0.277(0.011)	0.0507(0.0019)
95	9.35	3.62 x10^6	2.20(0.116)	0.61(0.032)
97/86	9.75	9.08 x10^6	0.136(0.007)	0.0149(0.0007)
99	9.67	7.56 x10^6	0.190(0.019)	0.0251(0.0026)
101/90	9.61	6.58 x10^6	2.30(0.12)	0.350(0.0182)
110	9.94	1.41 x10^7	1.00(0.04)	0.071(0.0026)
115/87	9.84	1.12 x10^7	0.336(0.025)	0.0301(0.0023)
118	10.2	2.56 x10^7	0.494(0.025)	0.0193(0.0010)
119	9.72	8.48 x10^6	0.030(0.005)	0.00351(0.0006)
128	10.9	1.28 x10^8	0.204(0.009)	0.00159(0.0001)
130	10.6	6.43 x10^7	0.208(0.010)	0.00323(0.0002)
132/153	10.5	5.11 x10^7	5.28(0.22)	0.103(0.0044)
133	10.4	4.06 x10^7	0.671(0.035)	0.0165(0.00087)
135/144	10.3	3.22 x10^7	1.07(0.04)	0.033(0.0013)
136	10	1.62 x10^7	0.819(0.044)	0.051(0.0028)
141	10.6	6.43 x10^7	1.16(0.04)	0.0180(0.0006)
149	10.2	2.56 x10^7	5.13(0.17)	0.200(0.0068)
151	9.97	1.51 x10^7	2.13(0.12)	0.142(0.0079)
158	10.6	6.43 x10^7	0.346(0.011)	0.0054(0.00017)
160/163/164/138	10.6	6.43 x10^7	4.12(0.11)	0.064(0.00171)
168	10.5	5.11 x10^7	0.860(0.026)	0.0168(0.00050)
170/190	11.7	8.10 x10^8	1.74(0.11)	0.00215(0.00013)
171	11.2	2.56 x10^8	0.438(0.027)	0.00171(0.00011)
174/181	11.1	2.03 x10^8	1.95(0.10)	0.0096(0.00051)
175	10.9	1.28 x10^8	0.084(0.004)	0.00066(0.00003)
176	10.7	8.10 x10^7	0.391(0.017)	0.0048(0.00021)
177	11.1	2.03 x10^8	1.02(0.04)	0.0050(0.00022)
178	10.8	1.02 x10^8	0.391(0.022)	0.0038(0.00021)
179	10.7	8.10 x10^7	1.02(0.05)	0.0126(0.00059)
180	11.4	4.06 x10^8	3.72(0.25)	0.0092(0.00062)
183	10.9	1.28 x10^8	1.07(0.07)	0.0083(0.00052)
185	10.9	1.28 x10^8	0.253(0.014)	0.00197(0.00011)
187/182	11.0	1.62 x10^8	2.43(0.12)	0.0150(0.00076)
191	11.6	6.43 x10^8	0.068(0.012)	0.00011(0.00002)

Congener Number	log Koa[a]	Z_{EVA} (mol/m^{3}Pa)	C_{EVA} (mmol/m^3)	fugacity (nPa)
192/172	11.4	4.06 x10^8	0.274(0.019)	0.00068(0.00005)
193	11.4	4.06 x10^8	0.158(0.010)	0.00039(0.00002)
195	12.0	1.62 x10^9	0.304(0.064)	0.00019(0.00004)
197	11.2	2.56 x10^8	0.041(0.013)	0.00016(0.00005)
199	11.9	1.28 x10^9	0.107(0.010)	0.00008(0.00001)
200	11.6	6.43 x10^8	0.227(0.028)	0.00035(0.00004)
201	11.3	3.22 x10^8	0.713(0.148)	0.00221(0.00046)
202	10.7	8.10 x10^7	0.249(0.057)	0.00307(0.00071)
203/196	11.9	1.28 x10^9	0.989(0.207)	0.00077(0.00016)

a- Harner and Bidleman (1996)

3.4.1 Sediment fugacities

Fugacities (in nPa) of the spiked chemicals in the Port Moody and Robert's Bank sediment are plotted in Figure 3.12. In the Port Moody sediment, fugacities range from 57.6 nPa for PCB52 to 464,000 nPa for tetrachlorobenzene (4CB), and in the Robert's Bank sediment, from 0.145 nPa for PCB194 to 1,400,000 nPa for 4CB. The fugacities in both sediments decrease significantly as the chemicals' Kow increases. The observed fugacity is a function of the chemical's concentration in the sediment as well as the fugacity capacity of the sediment for that contaminant (Z_{sed}). Given that sediment concentrations (spiking concentrations reported in Table 2.3) did not vary much between chemicals, the differences in resulting fugacities can be attributed to differences in sediment fugacity capacity. Sediment tends to have a high affinity for hydrophobic contaminants, with Z_{sed} being a function of Kow, so it is not surprising that we see a decrease in fugacity with increasing Kow.

Equilibrium concentration and fugacities are plotted in Figure 3.15 as a function of log Kow for the PCB congeners in the Sydney Harbour sediment. While the sediment concentrations (total sediment concentration reported in Appendix A), are not

significantly related to Kow (Pearson's coefficient = 0.051 , p= 0.655), the fugacities show a clear negative trend (Pearson's coefficient = -0.60, p = 0.00000258) with increasing log Kow.

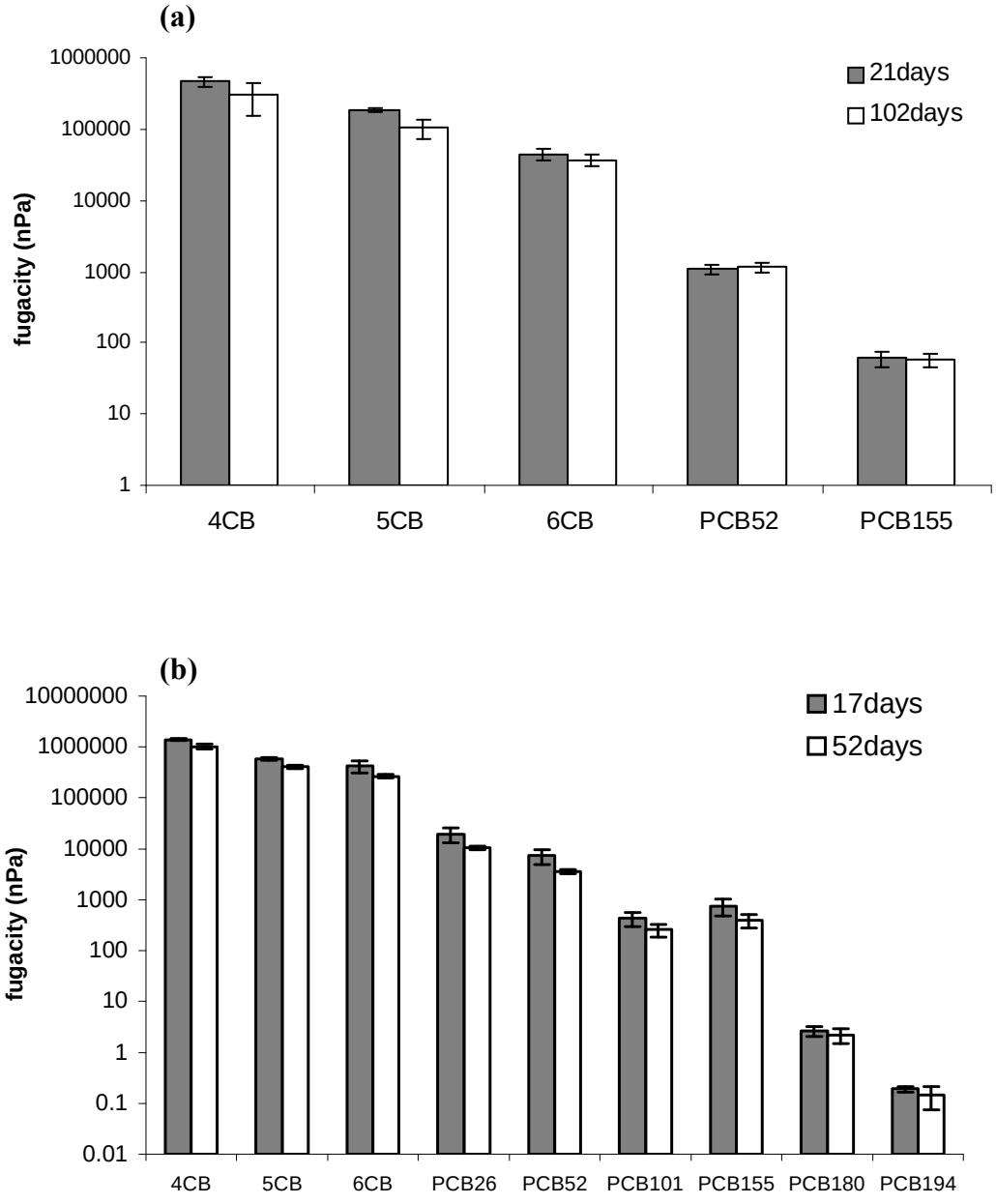

Figure 3-12 Fugacities (nPa) of chlorobenzenes and PCBs in (a) Port Moody sediment and (b) Robert's Bank sediment (error bars represent +/- 2 standard errors)

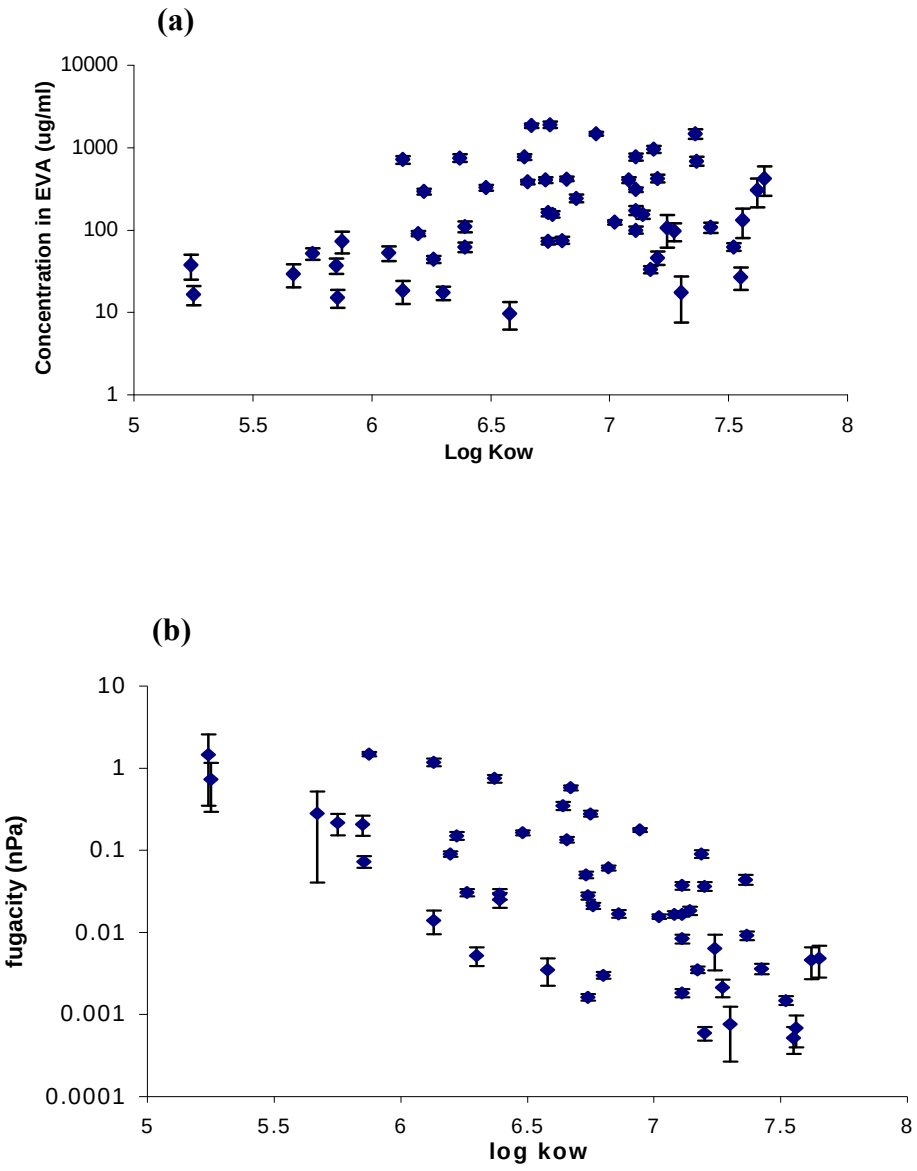

Figure 3-13 (a) EVA concentrations (µg/ml) and (b) sediment fugacities (nPa) for individual PCB congeners in the Sydney Harbour sediment (error bars represent 2 standard errors)

3.4.3 Sediment fugacity capacities

The fugacity capacity of sediment (Z_{sed}) is an important parameter in the bioavailability of sediment-associated contaminants. The fugacity, and subsequent bioavailability, of a chemical is based on the amount of chemical in the sediment as well as the sediment's ability to hold that chemical (measured as Z_{sed}). The apparent fugacity capacities of the test sediments were calculated using the following equation:

$$Z_{sed(app)} = C_{sed} / f_{sed} \quad (19)$$

where C_{sed} is the sediment concentration (in mol/m^3), and f_{sed} is the sediment fugacity (in units of Pa). For the Port Moody and Robert's Bank sediments, the dry weight spiking concentrations were used to estimate C_{sed}. For the Sydney Harbour sediment, dry weight concentrations from the Axys analytical report were used (concentrations are summarized in Appendix A).

Figures 3.14 illustrates the Z_{sed} for chemicals in the Port Moody and Robert's Bank spiked sediments. In the Port Moody sediment, sediment fugacity capacities appear slightly greater in the second (102 day) ageing period than the first (21 days) for the chlorobenzenes. This is likely due to sequestration of contaminants into an unavailable compartment, resulting in decreases in fugacity between the two periods. However, because the fugacity differences were not significant (i.e., EVA concentration did not differ significantly between the two ageing period, except for pentachlorobenzene), we cannot conclude that the apparent Z_{sed} is significantly greater between the two ageing periods. In the Robert's Bank sediment, apparent Z_{sed} appears higher in the later ageing period, which again can be attributed to increased sequestration of chemicals with the increased contaminant sediment contact time

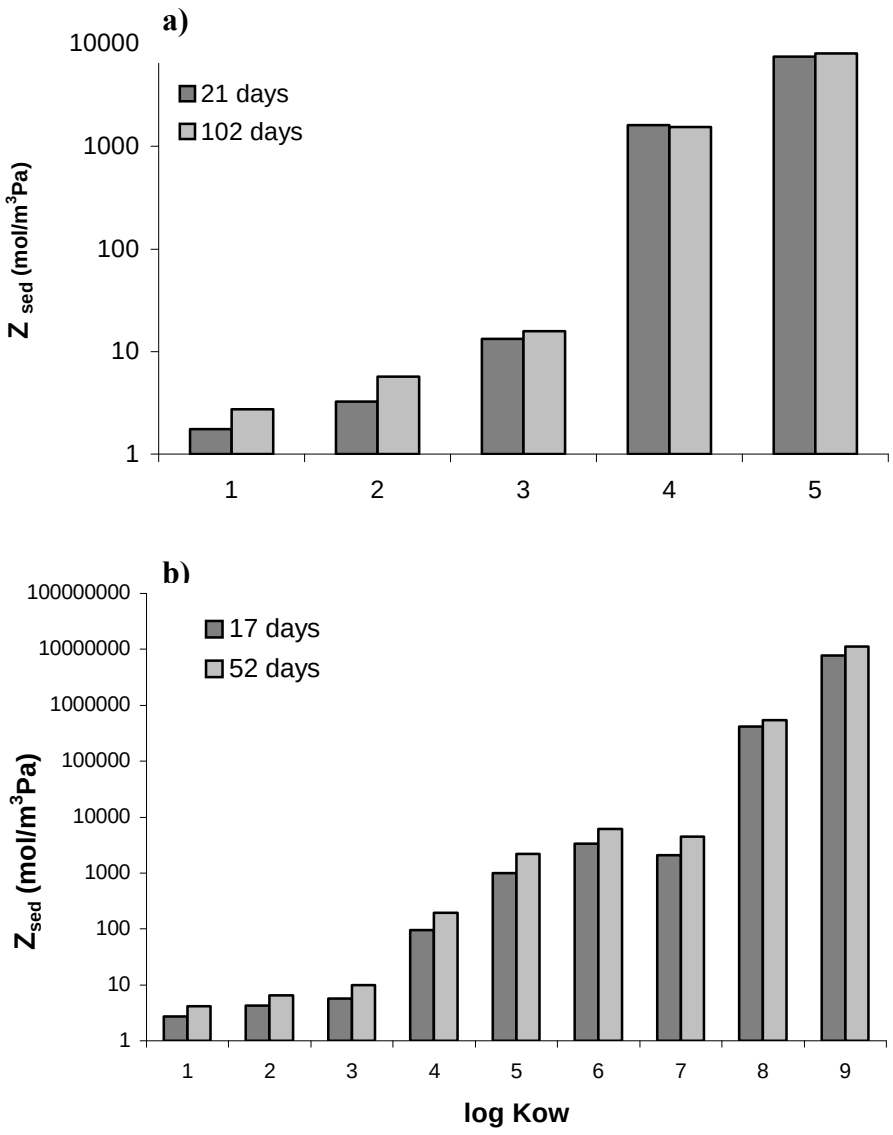

Figure 3-14 Observed sediment fugacity capacities for the (a) Port Moody experiments (at 21 and 102 days) and the (b) Robert's Bank experiments (at 17 and 52 days)

To examine differences among the test sediments' ability to 'hold' contaminants (contributing to decreases in bioavailability), sediment fugacity capacities were compared. By comparing fugacity capacities instead of fugacities, we are controlling for

difference in sediment concentrations (e.g., the Robert's Bank sediment was spiked at roughly twice the concentration at the Port Moody sediment). Fugacity capacities for chemicals all three of the test sediments are plotted as a function of Kow in figure 3.15. For the two spiked sediments, apparent Z_{sed}s from the longest ageing period (102 days for Port Moody and 52 days for Robert's Bank) were used. The fugacity capacities of chemicals in the Port Moody and Robert's Bank sediment appear similar for matching congeners. This is surprising, because the organic carbon content in the Robert's Bank sediment (at 0.0035) is much lower than in the Port Moody sediment (at 0.038). Given these differences in organic carbon content, we would expect the capacity of the Port Moody sediment to be approximately 10 times greater than that of the Robert's Bank sediment for chemicals with the same Kow (see equation 4). This implies that factors aside from organic carbon content are important in determining sediment's ability to hold organic contaminants. Potential factors include the particle size distribution, nature of the organic carbon (diagenetically young versus old material), and difference in sequestration status (i.e., perhaps the Robert's Bank sediment has a much larger chemical fraction associated with very slow desorption). The field contaminated Sydney Harbour sediment appears to have a much greater capacity than the two spiked sediment, which would be expected given the high amount of organic carbon and the longer ageing period in comparison to the two spiked sediments.

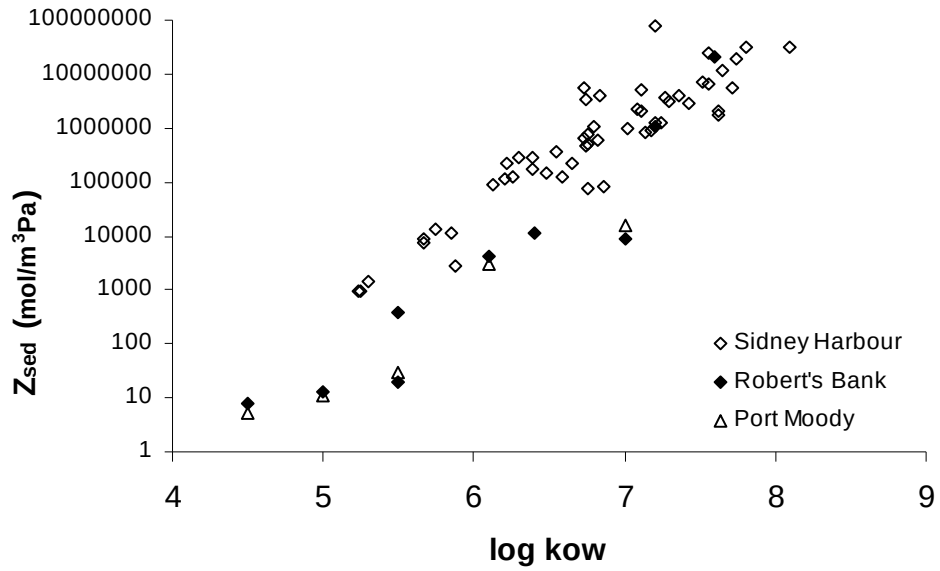

Figure 3-15 Sediment fugacity capacites (mol/m^{3}Pa) for chlorobenzenes and PCBs in the three test sediments

3.5 Implication for bioavailability

The estimates of bioavailability obtained through application of thin-film solid phase extraction reflect the amount of chemical that is able to partition from the sediment into an organic matrix (i.e. the EVA thin film). The resulting EVA concentrations offer a more biologically relevant measure of sediment contamination than the traditionally used total sediment concentrations. To illustrate this, we plotted the ratios between EVA concentration (our measurement of "available concentration") and total sediment concentration (dry weight) for chemicals in the three test sediments in Figure 3.16a. The available fraction of contaminant appears much greater (over one order of magnitude) in the two laboratory-spiked sediments (Port Moody and Robert's Bank) than it is in the field collected Sydney Harbour sediment. This significant discrepancy between the

availablility of contaminants among test sediment would not be recognized when considering only the total concentrations

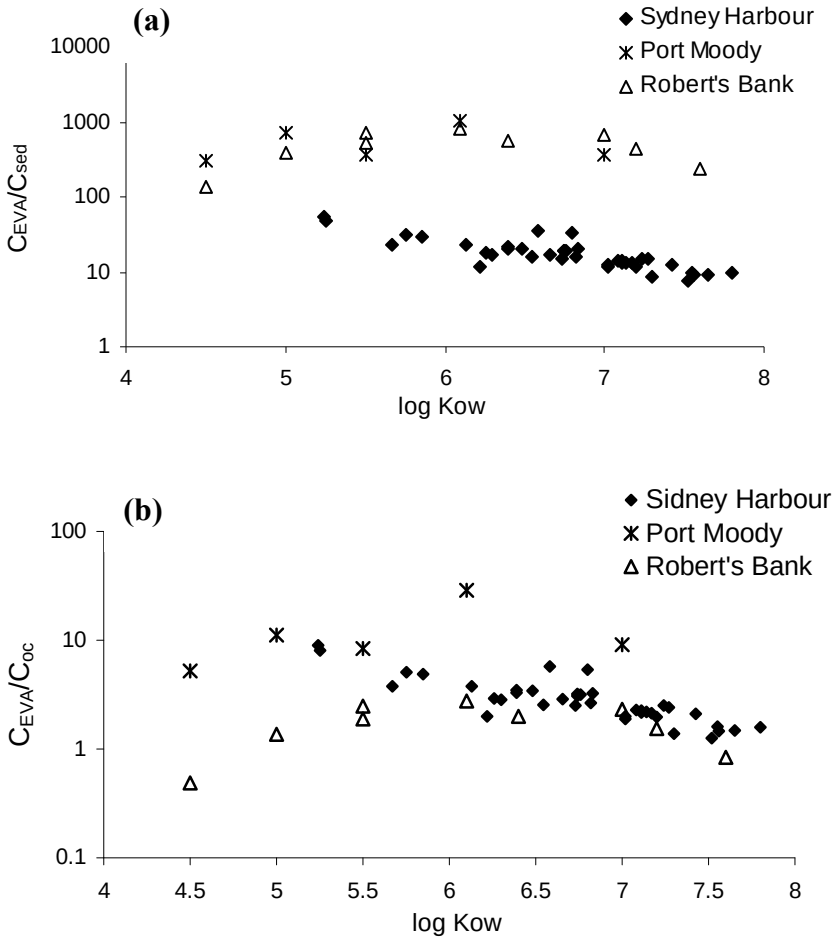

Figure 3-16 Ratio of EVA concentration (available concentration) to (a) total sediment concentration and (b) sediment organic carbon concentration for contaminants in the Sydney Harbour, Port Moody (aged for 102 days) and Robert's Bank (aged for 52 days) sediment.

Proponents of Equilibrium Partitioning theory would argue that the differences in availability observed in Figure 3.16a could be explained by the differences in organic carbon content between the sediments. To acknowledge this we present the ratio of EVA

concentration to organic carbon normalized concentrations for the test sediments in Figure 3.16b. Normalizing for organic carbon content has effectively removed much of the variation in availability among the sediment. However, differences still remain. The available fraction in the Port Moody sediment appears nearly one order of magnitude greater than the available fraction in the Robert's Bank and Sydney Harbour sediments for several of the test chemicals. This suggests that less chemical is available for partitioning in the Robert's Bank and Sydney Harbour sediments compared to the Port Moody sediment. The reduction in availability could be due to sequestration of chemicals (e.g. an ageing effect was observed for several chemicals in the Robert's Bank sediment), or perhaps to differences in the organic matter structure among the sediments. Whatever the case may be, the use EVA concentrations (or fugacity) as a measure of contaminant bioavailability eliminates the need to correct for all of these unknowns (e.g. extent of sequestration, nature of organic matter, etc.).

Our uptake experiments have demonstrated that movement of contaminants may occur on a long time scale due to slow desorption rates and resistance to diffusion through the pore water phase. Therefore, it is possible that a given organism is not exposed to the whole fugacity, but rather a time dependent fraction of the total sediment fugacity. The extent of accumulation is then a function of the period that the organism is exposed to the contaminated sediment. In order to address the kinetic constraints on equilibrium, it may be beneficial to define bioavailability in terms of exposure period. Our uptake experiments have provided us with equations that can facilitate the estimation of contaminant uptake over time. What remains is to choose a relevant exposure period. Finding a universal exposure period is difficult because exposure time is likely to vary

from organism to organism, and is also dependent on the route of exposure. In deposit feeding organisms (e.g. Mussels and clams) the primary exposure route is through ingestion of sediment particles. Thus, for sediment ingestors, exposure may be limited to the period of time that the sediment resides in the gut prior to being egested. Typical gut residence times for benthic invertebrates include 6 hours for the clam *Macoma balthica* and 2.5 hours for the mussel *M. edulis* (Decho 1991, Wang 1996). For organisms that are exposed through contact with pore water, contaminant accumulation may take place during the entire life span of the organism, making the attainment of equilibrium feasible. This is, of course, reliant on the organism remaining sedentary in order to reach equilibrium with the fraction of contaminants that are desorbing at slow rates.

Several authors have acknowledged that desorption of contaminants from sediment particles directly limits uptake of chemicals by biota. Kraaij et al (2001), found that the accumulation of sediment-associated PAHs in the amphipod *Corophium volutator* was well correlated with the rapidly desorbing fraction of contaminants. Others found that it was the amount desorbed in 48 hours (Lamoureux and Brownawell 1999) or 6 hours (Cornelissen et al 2000, ten Hulscher et al 2003) that was best correlated with the bioavailable fraction. To explore the effects exposure time in our sample sediments, we substituted the exposure periods of 2 hours, 6 hours and 48 hours into the uptake equations for PCB congeners found in the Sydney Harbour sediment. Figure 3.17 illustrates the fraction of the effective fugacity sensed by the EVA film after these different exposure periods.

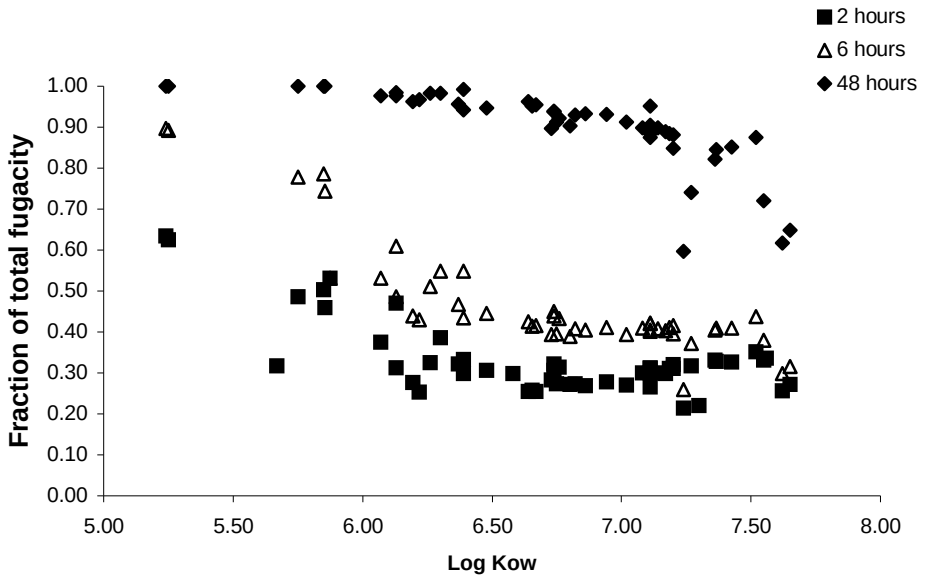

Figure 3-17 Fraction of the total "effective" sediment fugacity in EVA film after an exposure period of 6 hours and of 48 hours, for PCB congeners in the Sydney Harbour sediment

The fugacity sensed by the film after 2 hours of exposure is only 20 to 60% of the total available fugacity across all chemicals. After 6 hours of contact with the sediment, the EVA has sensed nearly 90% of the available fugacity for lower Kow congeners, dropping to approximately 40% of the available fugacity for the highest Kow congeners. After 48 hours of exposure, the EVA has reached equilibrium with congeners of Kow lower than 10^6, and near-equilibrium (60-90%) with congeners of Kow greater than 10^6. The lower availability of the highest Kow congeners can be explained by the decreased uptake rate constants associated with these slowly diffusing, hydrophobic chemicals. From this exercise, we gain insight into the availability of organic chemicals over time. For exposures of less than 6 hours (representative of typical gut residence times), an organism may only be exposed to a fraction of the total sediment fugacity, but when the exposure exceeds 6 hours, contribution from the slowly desorbing compartment becomes

significant as well, and the concentration in the organisms may reach equilibrium with the sediment concentrations in both sediment compartments. These trends are, of course, based on the parameters of this particular sediment-contaminant system. Nevertheless, thin-film solid phase extraction may be applied in other sediments to examine the availability of hydrophobic organic contaminants over time. Once the parameters of the uptake curves are known, the model can be used with any given exposure time to determine relevant bioavailable concentrations.

We must acknowledge, however, that an organism's interaction with the sediment environment is more complex than our sediment-pore water-EVA system. For example, when investigating exposure through ingestion, it may be important to consider the environment of the organism's gut, which is different than that of the external environment. Additional breakdown of the sediment organic carbon by digestive enzymes and surfactants may play a role in changing the capacity of the sediment, triggering the release of sequestered contaminants. This may result in magnification of chemical fugacities in the gut, akin to both the magnification observed during carbon mineralization and the gastro-intestinal magnification observed between diet and consumer. To approximate the availability of contaminants during digestion, some authors have extracted chemicals from sediment using digestive fluids, in what is termed a biomimetic extraction (Mayer et al 1996, Ahrens et al 2001). Mayer et al (1996) found that the amount of PAHs solubilized by digestive fluid was between 9 and 235 times greater than the amount that partitioned into seawater. Still, finding the ideal biomimetic solution is difficult because the composition of digestive fluid, including the amount of enzymes and surfactants and the gut residence time, are variable from species to species.

Therefore, the application of thin-film extraction may provide a reasonable first approximation of bioavailable concentration, or fugacity.

4 Conclusions

Thin film solid phase extraction may prove to be a useful and powerful tool for examining sediment contamination. The method is simple to conduct, reproducible, and can easily be applied to measure fugacity of hydrophobic organic contaminants in both field-collected and laboratory-spiked sediments. In addition, the chemical analysis of thin-films (i.e., analysis of the hexane extract) is faster and more cost effective than the measurement of bulk sediment concentrations, which require an exhaustive extraction procedure and clean up. Our experiments have demonstrated that it is possible to quantify the presence of contaminants at levels as low as 0.28 ppb (sediment dry weight) in field-collected samples. Should the application require identification of contaminant concentrations much lower than this, the experimental system can be altered to increase the volume of EVA. It is recommended, however, that a high surface area to volume ratio be maintained to prevent creating additional resistance to diffusion in the EVA matrix. Also, because this method is meant to be non-depletive, the sediment to EVA ratio should remain reasonably high.

By applying thin-film solid-phase extraction to contaminated sediments, it is possible to obtain direct estimates of bioavailable concentration or fugacity without having to measure a multitude of sediment properties (e.g., particle size distribution, composition of organic carbon etc.), and without any prior information of sediment-contaminant history (i.e., contact time). Additionally, the information provided by the method can be much more useful than bulk sediment concentrations alone. For the purpose of ranking contaminated sites, sediment fugacities could be compared from site to site. By comparing fugacity, we are taking into account the sequestration of contaminants as well as the differences in quantity and quality of organic matter across sediments. These factors are not considered when comparing total sediment concentrations. Unfortunately, most toxicity data is not available in relation to fugacity exposures. Once further research is conducted relating fugacity to toxic effects, thin-film measurements would become very useful in the assessment of sediment contamination. For example, guidelines could be created based on fugacity that would explicitly consider bioavailability and could be applicable in any environmental medium (e.g. sediment, water, air, etc). Once the method has been calibrated (i.e., EVA-tissue partition coefficients are known), it may also be used to estimate expected concentrations in biota. Thus, a relevant research extension would be to compare uptake by the EVA films with uptake by biota. In addition, when the uptake equation is known (through model fitting), exposure can be customized to the time frame relevant to the study (i.e., exposure periods could be altered for different species). By obtaining quick and accurate measurements of contaminant uptake, thin-film solid phase extraction could be applied to produce

exposure profiles for risk assessments. Furthermore, to account for food web transfer, thin film measurement can be used in conjunction with biomagnification factors.

Appendix A

PCB congener concentrations

in Sydney Harbour sediment

Table A-1 Total sediment concentrations for PCB congeners in Sydney Harbour sediment (ug/g dry weight)

Congener #	CAS NO.	CO-ELUTIONS	CONC. FOUND	DETECTION LIMIT
17	37680-66-3		0.341	0.340
18	37680-65-2		0.692	0.340
31	16606-02-3		1.28	0.258
41	52663-59-9	41 + 64 + 68 + 71	2.33	0.499
44	41464-39-5		1.69	0.499
49	41464-40-8	43 + 49	n/d	
59	74472-33-6	42 + 59	n/d	
84	52663-60-2		1.76	0.0713
85	65510-45-4	85 + 120	1.01	0.0777
86	55312-69-1	86 + 97	2.49	0.0777
87	38380-02-8	87 + 115 + 116	5.49	0.0777
89	73575-57-2	89 + 90 + 101	37.3	0.187
91	68194-05-8		0.805	0.0813
92	52663-61-3		3.52	0.0713
93	73575-56-1	93 + 95	29.7	0.215
99	38380-01-7		2.94	0.0663
106	70424-69-0	106 + 118	8.30	0.0542
110	38380-03-9		15.8	0.0552
119	56558-17-9		0.280	0.0777
128	38380-07-3		3.96	0.151
129	55215-18-4		1.45	0.151
130	52663-66-8		2.03	0.151
132	38380-05-1	132 + 168	15.2	0.141
133	35694-04-3		1.04	0.207
135	52744-13-5	135 + 144	22.2	0.207
136	38411-22-2		24.6	0.226
138	35065-28-2	138 + 163 + 164	119	0.174
139	56030-56-9	139 + 149	136	0.203
141	52712-04-6		25.9	0.181
148	74472-41-6			0.226
151	52663-63-5		55.7	0.217
153	35065-27-1		142	0.162
158	74472-42-7	158 + 160	10.9	0.181
170	35065-30-6	170 + 190	69	0.404
171	52663-71-5		13.2	0.101
172	52663-74-8	172 + 192	8.51	0.101
174	38411-25-5	174 + 181	56.8	0.334
175	40186-70-7		2.58	0.101
176	52663-65-7		8.09	0.0803
177	52663-70-4		29.2	0.100
178	52663-67-9		11.6	0.101
179	52663-64-6		26.7	0.0803
180	35065-29-3		140	0.343
182	60145-23-5	182 + 187	82.9	0.348

Congener #	CAS NO.	CO-ELUTIONS	CONC. FOUND	DETECTION LIMIT
183	52663-69-1		35.4	0.100
185	52712-05-7		7.31	0.100
191	74472-50-7		2.76	0.101
193	69782-91-8		8.22	0.101
195	52663-78-2		14.7	0.0876
196	42740-50-1	196 + 203	47.2	0.0854
197	33091-17-7		2.08	0.0854
198	68194-17-2		2.08	0.0854
199	52663-75-9		39.7	0.0854
200	52663-73-7		6.67	0.0854
201	40186-71-8		7.23	0.0854
202	2136-99-4		7.03	0.0640

Appendix B

EVA concentration from spiked and

field-collected sediment extraction

Table B -1 EVA concentrations (μg/ml) for chlorobenzenes and PCBs thin-film extracted from the Port Moody spiked sediment (aged for 21 days)

Extraction time (h)	4CB	5CB	6CB	PCB52	PCB155
0.25	36.0	36.4	23.6	45.0	35.7
0.25	26.8	51.3	46.9	39.0	47.1
0.25	27.6	50.9	39.0	38.2	44.4
1	40.6	83.9	55.5	69.4	60.6
1	46.9	82.1	45.0	65.0	34.8
1	40.5	83.3	66.2	67.1	45.6
3	64.1	110	47.9	87.5	72.6
3	67.8	111	60.3	76.0	68.2
3	73.1	107	47.7	79.3	29.3
7	66.5	116	57.6	97.7	43.1
7	79.9	126	47.9	119	48.2
7	74.8	121	58.4	99.4	34.3
24			89.3	219	95.5
24			63.6	179	73.9
24			91.6	249	95.5
74	139	244	102	255	
74	88.1	186	87.8	214	
74	111	191	78.8	219	
288	105	244	133	309	105
288	95.6	192	118	288	130
288	90.0	206	123	316	120

Table B-2 EVA concentrations (μg/ml) for chlorobenzenes and PCBs thin-film extracted from the Port Moody spiked sediment (aged for 102 days)

Extraction time (h)	4CB	5CB	6CB	PCB52	PCB155
0.167	15.8	20.7	18.1	17.8	24.1
0.333	20.5	25.0	17.2	25.4	23.7
0.667	23.9	39.0	42.2	38.3	
1	31.0	39.6	30.0	37.7	41.3
2	41.3	46.6	30.6	43.8	41.3
4	41.0	60.8	45.0	74.4	57.0
6	42.2	73.0	57.9	90.8	44.2
6	39.5	64.1	51.2	84.6	51.2
6	41.7	71.0	57.0	87.2	47.2
8	56.2	89.1	74.2	117	47.1
28	63.1	108	83.0	154	69.6
28	66.9	111	82.2	150	56.5
28	68.8	119	107	154	66.3
53	70.2	119	91.7	187	65.6
104	68.6	130	103.1	225	85.8
194	57.5	122	114.4	275	98.1

Table B-3 EVA concentrations (μg/ml) for chlorobenzenes and PCBs thin-film extracted from the Robert's Bank spiked sediment (aged for 17 days)

extraction time (h)	4CB	5CB	6CB	PCB 26	PCB 52	PCB 101	PCB 155	PCB 180	PCB 194
0.167	66.1	90.7	114	86.8	111	32.3	53.7	10.2	8.82
0.333	83.7	128	177	131	164	52.2	97.5	16.5	12.6
0.667	117	159	201	153	195	67.8	109	23.0	17.2
1	135	211	281	216	264	91.1	151	32.5	25.9
2	242	544	858	863	1140	370	716	121	71.6
2	302	625	955	962	1250	390	774	126	74.1
2	309	581	843	843	1080	354	686	114	69.7
4	319	629	921	913	1200	452	819	162	93.5
6	336	732	1098	1100	1470	580	1040	213	126
6	338	708	1070	1090	1480	559	1020	199	114
8	344	712	1130	1200	1650	682	1230	253	144
28	335	687	1110	1207	1690	695	1240	276	174
28	245	571	995	1130	1650	810	1330	337	208
28	306	666	1070	1140	1560	739	1210	319	201
50	300	672	1130	1220	1730	857	1410	374	235
98	316	723	1240	1390	1970	891	1510	394	257
336	305	672	1130	1220	1760	893	1400	456	371

Table B-4 EVA concentrations (μg/ml) for chlorobenzenes and PCBs thin-film extracted from the Robert's Bank spiked sediment (aged for 52 days)

extraction time (h)	4CB	5CB	6CB	PCB 26	PCB 52	PCB 101	PCB 155	PCB 180	PCB 194
0.17	31.8	54.7	86.2	58.1	83.7	27.4	41.8	9.82	9.19
0.33	45.5	77.9	117	82.2	115	39.3	61.5	13.2	10.3
0.67	46.4	92.1	145	107	145	51.6	80.9	17.9	14.4
2	86.3	153	226	173	232	87.4	138	30.8	22.3
4	98.0	191	290	234	316	127	198	46.0	33.2
6	106	223	342	281	371	156	244	60.1	44.2
6	101	196	287	236	327	143	170	99.2	50.9
6	91	208	331	273	364	150	235	57.2	41.2
8	119	241	372	334	451	203	307	89.8	70.7
18	158	291	410	323	424	177	277	73.5	59.6
28	164	344	517	449	583	268	405	120	90.6
28	175	345	517	454	591	268	407	119	91.4
28	169	343	515	442	573	257	391	112	84.7
53	227	455	636	551	706	322	484	152	120
102	203	437	681	615	795	370	551	183	155
194	243	495	765	707	936	462	678	247	211

Table B-5 EVA concentrations (ng/ml) for PCB congeners thin-film extracted from the Sydney Harbour sediment

extraction time (h)	5/8	16/32	17	18	24/27	25	26	28	31	41
0.25	10.8	12.5	4.9	13.4	ND	1.7	7.9	10.8	11.1	22.0
0.25	12.3	14.3	7.1	15.0	2.4	ND	4.2	14.7	13.0	21.7
1	ND	18.6	7.8	19.1	ND	ND	3.8	12.3	14.4	26.0
4	14.0	27.4	10.8	24.8	3.1	2.6	5.5	32.0	27.7	50.9
4	20.7	31.7	14.8	29.7	3.2	1.8	5.7	31.7	25.5	42.5
8	18.9	30.1	14.7	33.4	4.9	2.2	6.5	31.0	24.2	47.4
8	33.6	50.3	18.3	47.7	5.5	3.5	7.5	45.9	34.4	51.5
24	20.2	35.8	16.3	35.5	ND	2.7	7.5	33.5	33.4	58.1
24	24.2	43.8	18.4	41.8	5.6	2.4	7.6	36.4	30.3	55.4
75	21.8	37.7	16.4	34.7	5.2	2.9	6.2	33.3	28.4	62.0

extraction time (h)	42/59	44	47/75/48	49	82	84/92	85	86/97	87/115	89	90/101
0.25	3.4	12.5	13.0	9.8	2.2	14.9	5.6	9.0	19.2	9.8	141.5
0.25	4.3	13.8	8.8	10.7	2.1	13.9	4.7	8.7	21.1	9.7	160.2
1	4.6	18.4	12.1	13.8	4.1	20.2	4.0	11.5	23.6	15.7	199.3
4	12.4	41.4	16.7	28.4	5.7	31.6	11.1	19.0	37.7	24.6	297.8
4	8.2	32.2	16.3	25.9	6.9	33.4	8.8	18.6	40.7	25.8	291.0
8	9.7	38.3	18.9	26.0	7.7	42.5	9.8	24.6	55.8	25.9	376.3
8	13.4	45.7	19.2	34.2	11.7	50.8	10.8	28.2	67.6	36.3	457.5
24	15.2	50.2	ND	35.5	11.0	71.3	16.4	36.5	77.9	41.8	579.5
24	16.8	51.4	16.2	32.9	10.4	76.0	13.4	40.6	84.8	49.9	620.3
75	14.7	51.9	20.1	37.9	15.2	89.9	18.6	43.7	107.3	54.1	747.3
75	14.0	55.0	30.6	43.3	12.4	90.4	16.8	45.2	112.4	51.6	752.2

extraction time (h)	91	95	99	103	110	118	119	128	129	130	131/142
0.25	2.9	112.3	12.3	ND	50.9	34.0	2.1	17.8	3.8	13.3	ND
0.25	4.1	118.1	13.1	ND	56.2	34.4	2.4	18.9	2.5	20.3	ND
1	4.8	173.8	14.7	ND	82.9	42.1	ND	19.1	5.1	18.1	ND
4	12.3	283.7	30.9	2.7	119.6	61.2	4.8	26.3	5.9	22.6	2.7
4	8.9	288.1	26.2	2.3	121.5	63.6	ND	23.3	3.2	22.1	ND
8	11.0	381.3	34.9	5.3	161.9	81.9	4.5	37.0	12.4	31.2	4.0
8	13.1	457.3	46.4	6.5	186.1	95.8	2.8	42.8	11.7	39.6	5.1
24	16.5	586.4	53.2	ND	251.9	122.1	7.7	56.3	5.7	53.2	6.5
24	16.6	612.5	54.6	7.1	258.0	125.1	6.0	56.2	10.7	54.6	5.4
75	19.3	710.7	60.7	7.1	323.6	161.8	9.5	75.1	14.3	74.1	7.3
75	17.6	734.9	66.5	10.4	325.7	161.8	8.6	70.5	14.1	71.7	7.8

extraction time (h)	132/153	133	134/143	135/144	136	137	138/160/163/164	141	147	149	151
0.25	383.1	48.1	5.2	71.1	45.6	ND	304.7	79.2	ND	326.7	129.9
0.25	443.4	56.0	5.2	71.9	52.0	2.5	341.9	97.0	ND	349.4	148.3
1	472.9	60.2	6.6	88.0	63.5	3.3	358.8	105.4	ND	391.8	165.8
4	574.5	68.9	7.0	121.3	93.2	3.0	475.3	130.1	ND	571.2	244.6
4	555.5	67.9	5.7	108.0	87.8	ND	471.9	127.6	ND	526.3	215.4
8	886.1	115.1	20.5	200.4	162.9	ND	706.3	197.7	1.1	998.7	421.4
8	992.3	126.9	11.0	190.5	154.1	4.1	768.8	215.7	2.0	911.1	384.7
24	1430.9	196.1	19.0	312.2	253.1	5.5	1133.2	313.3	1.5	1508.9	661.7
24	1310.7	173.7	28.4	299.1	234.9	6.7	1107.0	321.9	1.9	1448.2	604.0
75	1864.3	227.4	17.4	385.1	307.1	9.5	1471.2	419.0	3.9	1854.9	787.8
75	1862.9	248.2	31.2	376.6	281.9	9.5	1456.6	403.4	2.7	1819.0	739.8

extraction time (h)	154	158	168	170/190	171	172/192	173	174/181	175	176	177
0.25	1.0	24.6	62.7	193.9	44.7	32.1	2.2	189.8	6.5	37.2	98.8
0.25	1.7	30.2	60.0	230.3	52.7	37.1	3.9	215.1	7.9	48.4	114.7
1	1.2	30.1	69.1	197.5	48.5	29.8	ND	203.0	9.6	43.4	101.1
4	1.7	38.9	98.8	229.6	51.6	34.9	3.4	241.8	11.7	51.4	132.6
4	ND	36.9	100.9	224.1	54.2	34.0	2.1	231.9	9.2	48.5	127.8
8	2.5	57.7	159.3	307.9	80.2	47.4	2.6	364.0	16.3	81.2	187.1
8	3.7	59.7	150.8	361.8	92.4	57.1	3.8	402.6	16.1	79.1	210.2
24	5.1	89.9	240.2	472.1	124.7	71.6	8.4	537.6	23.3	118.2	283.7
24	3.9	93.2	258.4	434.5	111.5	73.5	6.7	520.7	23.0	115.5	291.7
75	7.3	125.7	317.6	642.6	170.7	107.5	10.4	754.8	32.6	154.9	392.1
75	5.1	118.0	296.3	648.6	160.3	95.9	9.5	727.4	31.5	147.2	390.3

extraction time (h)	178	179	180	182/187	183	185	191	193	194	195	196/203
0.25	37.7	88.0	421.4	245.7	112.7	28.0	5.8	20.4	112.0	40.3	96.2
0.25	44.2	99.8	507.3	283.9	134.0	31.7	8.8	23.0	145.2	56.4	132.1
1	35.7	97.7	427.2	258.8	114.4	22.4	8.7	16.2	116.6	44.8	114.6
4	48.8	125.3	494.9	313.4	137.6	32.6	9.7	24.2	102.9	40.1	103.4
4	48.8	125.1	472.1	317.7	133.6	32.6	8.3	24.1	113.6	41.5	102.4
8	75.6	193.1	656.5	450.2	208.6	49.4	12.9	28.2	148.5	62.6	160.8
8	83.6	203.2	752.1	498.8	229.0	51.4	10.0	32.3	182.0	60.9	154.1
24	110.8	277.9	970.8	674.3	289.4	75.1	13.9	45.3	173.9	73.5	217.5
24	104.7	282.6	892.8	660.2	290.3	69.8	15.4	43.2	156.0	75.6	193.2
75	155.3	404.4	1385.2	967.4	415.5	97.9	21.6	62.3	236.5	113.9	325.0
75	145.2	380.6	1316.7	879.2	397.7	96.0	22.8	56.8	258.1	104.3	330.2

extraction time (h)	197	198	199	200	201	202	205	206	207	208
0.25	3.1	3.0	13.3	24.2	70.6	19.7	4.9	26.4	4.6	4.6
0.25	5.0	3.8	14.7	36.1	90.6	23.8	5.0	33.7	4.6	6.9
1	5.5	3.8	9.3	26.9	73.8	20.4	4.5	24.7	5.5	3.4
4	4.9	3.0	16.1	30.9	76.9	22.8	6.5	22.3	3.9	4.4
4	3.3	2.0	12.2	30.8	68.0	22.5	3.9	25.8	5.0	5.1
8	6.6	6.6	25.6	45.0	107.7	33.9	5.4	23.8	3.9	7.4
8	3.6	4.0	21.9	38.7	96.6	32.1	5.1	29.2	4.9	7.0
24	9.7	4.6	30.6	57.6	144.9	50.9	6.6	35.9	7.1	8.2
24	8.1	6.2	28.1	51.9	137.9	39.3	6.6	28.2	6.1	7.4
75	13.4	10.0	42.6	83.4	223.7	75.0	8.6	44.5	8.5	10.1
75	14.0	12.5	44.4	82.9	229.2	80.7	10.5	47.2	7.9	11.0

Appendix C

Resdiuals from 1- and 2-compartment model fitting

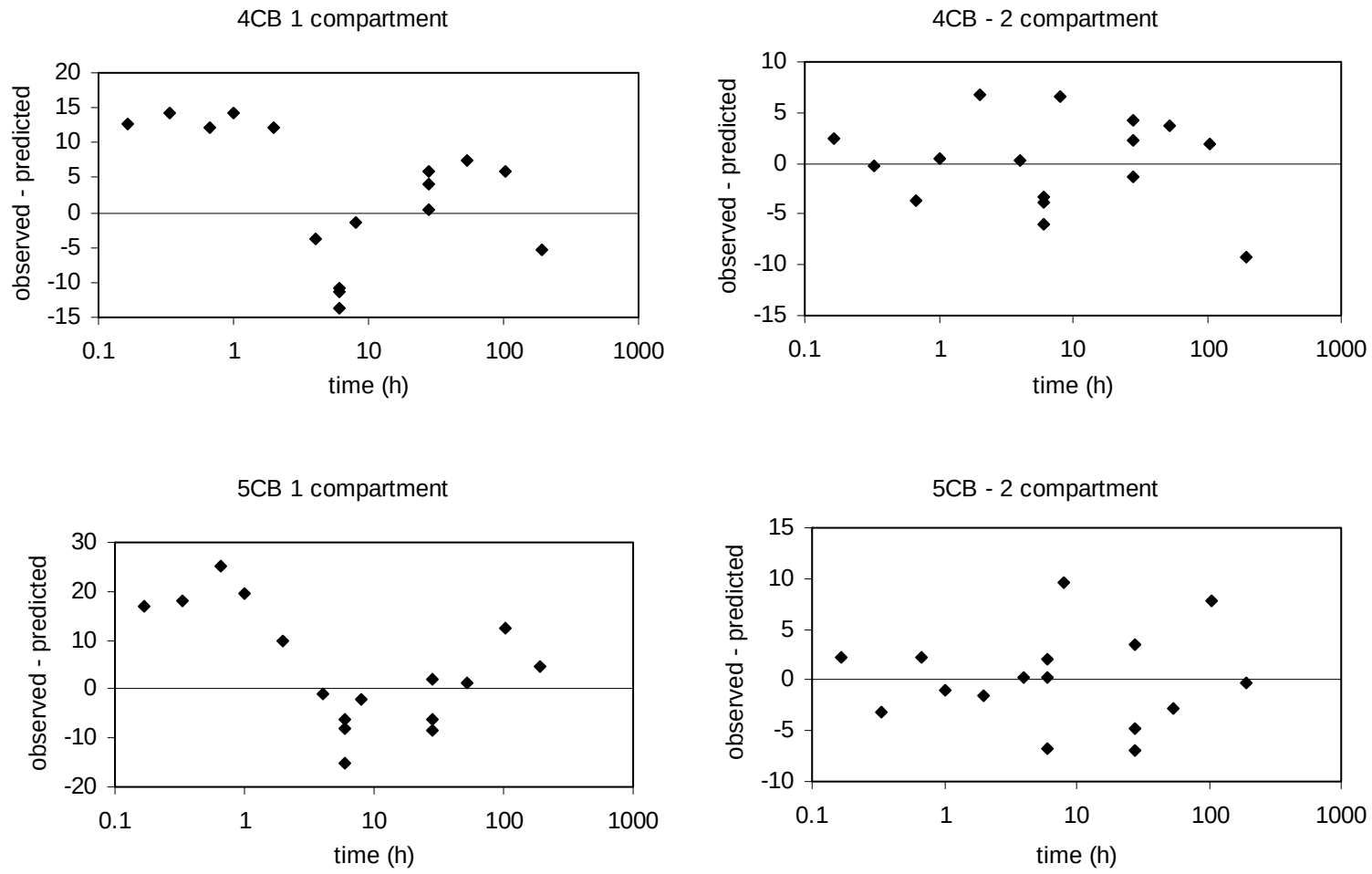

Figure C-1a Residuals (CEVA(t) observed – CEVA (t) predicted) from the 1 and 2 compartment model fit for tetrachlorobenzene (4CB) and pentachlorobenzene (5CB), extracted from the Port Moody spiked sediment, aged for 102 days

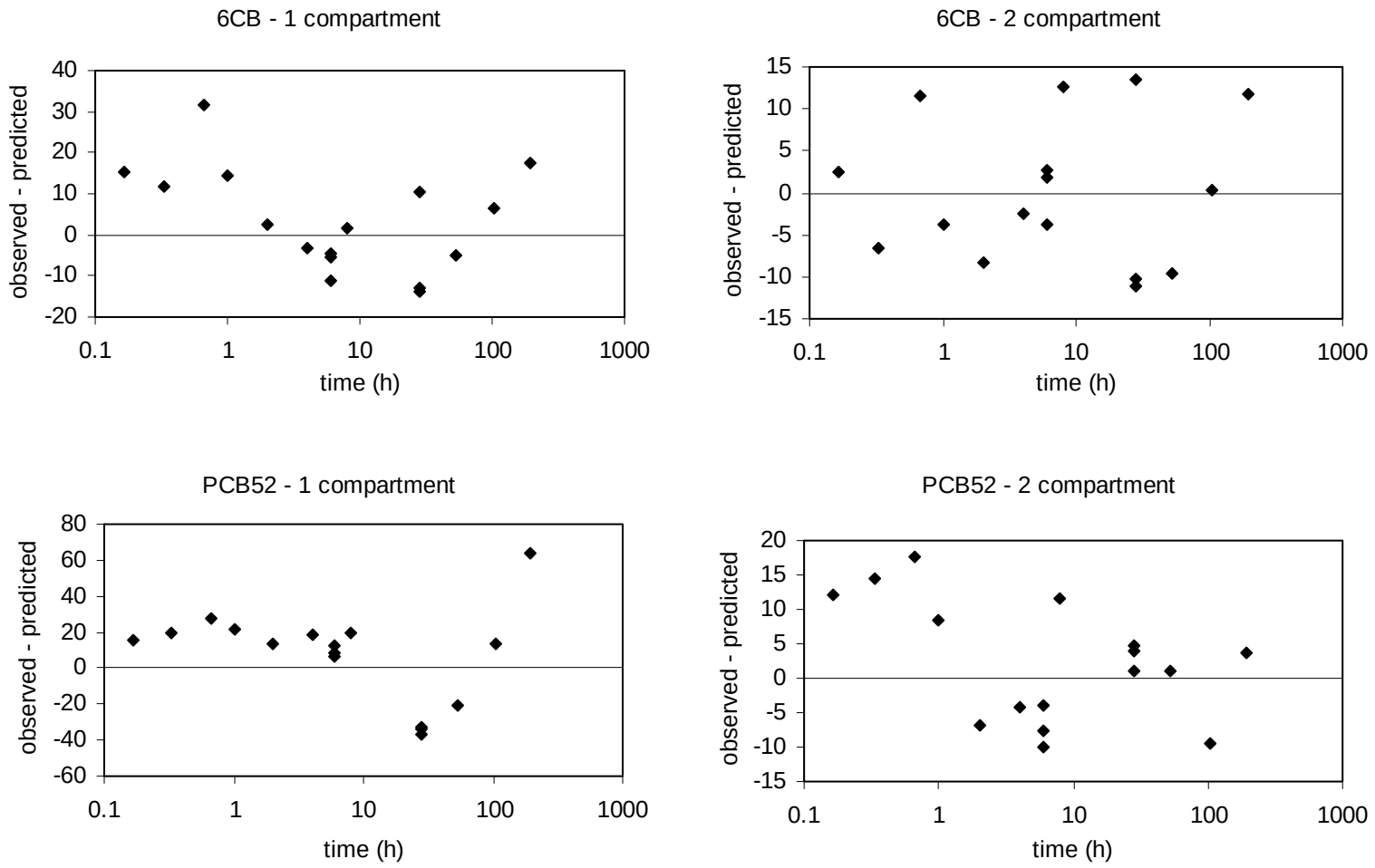

Figure C-1b Residuals ($C_{EVA}(t)$ observed – $C_{EVA}(t)$ predicted) from the 1 and 2 compartment model fit for pentachlorobenzene (5CB) and PCB 52, extracted from the Port Moody spiked sediment, aged for 102 days

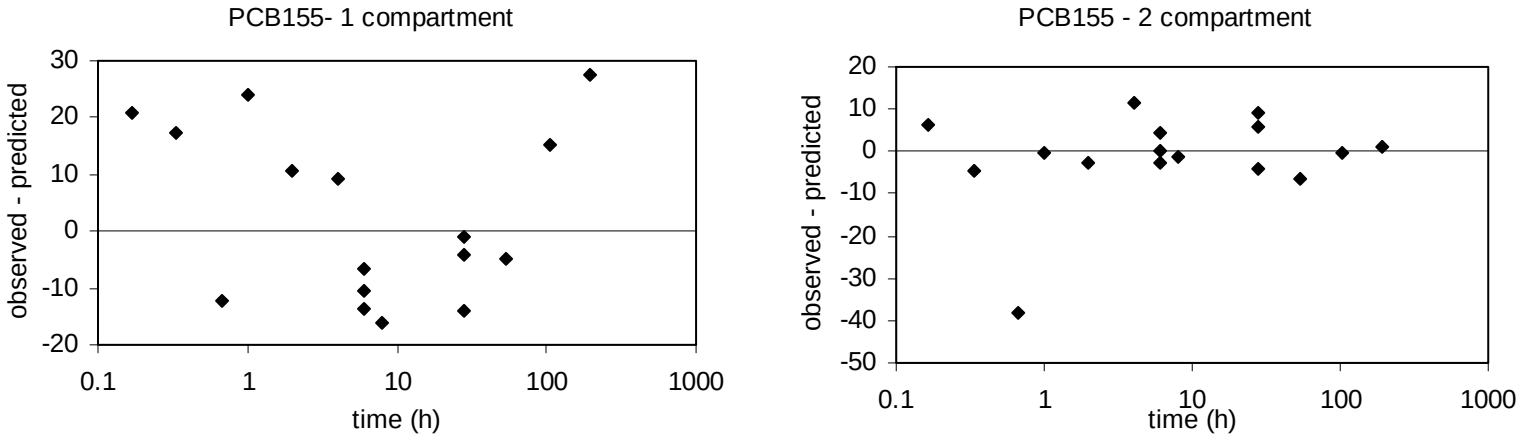

Figure C-1c Residuals (C_{EVA}(t) observed – C_{EVA}(t) predicted) from the 1 and 2 compartment model fit for PCB 155, extracted from the Port Moody spiked sediment, aged for 102 days

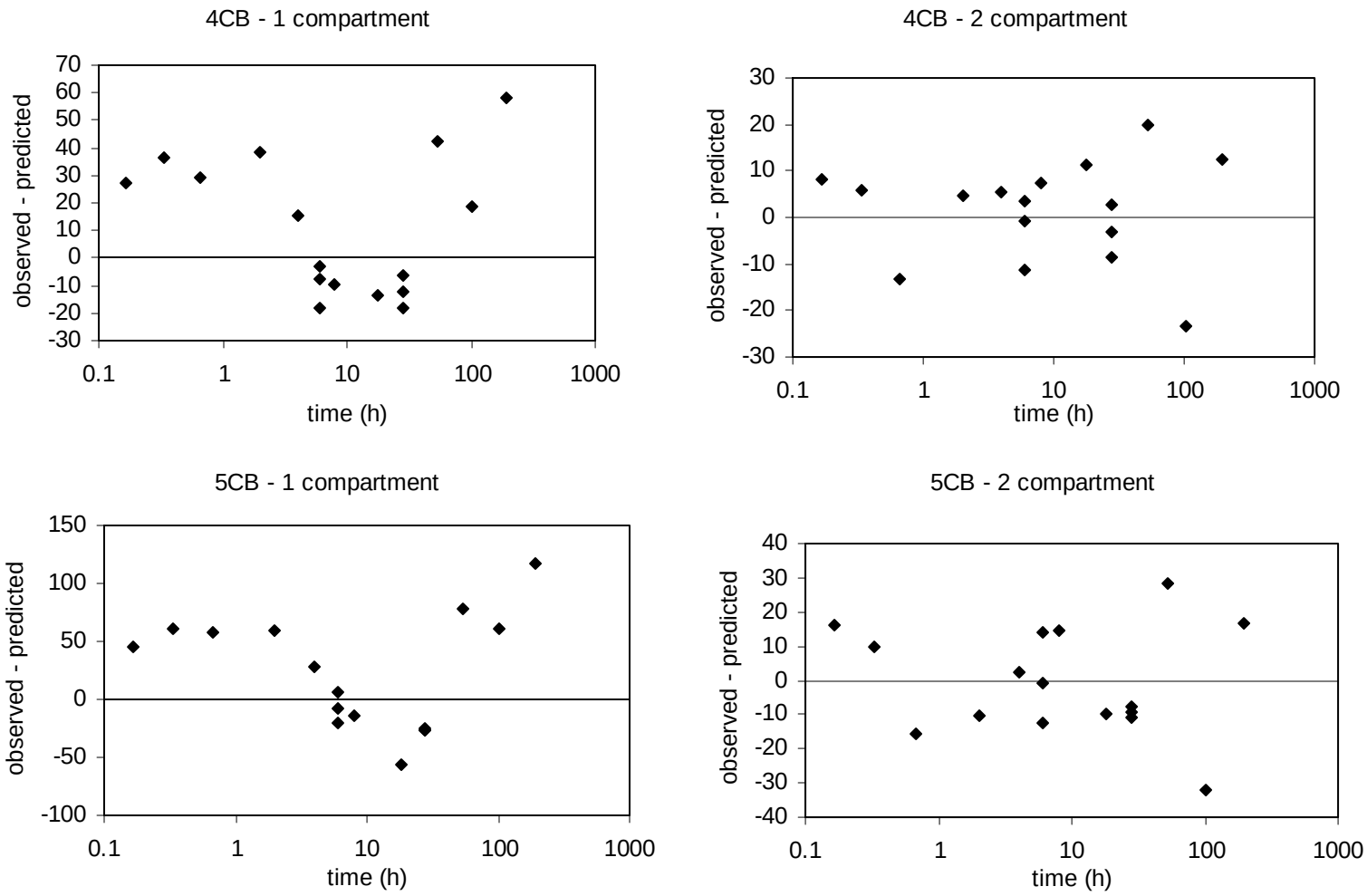

Figure C-2a Residuals ($C_{EVA}(t)$ observed – $C_{EVA}(t)$ predicted) from the 1 and 2 compartment model fit tetrachlorobenzend (4CB) and pentachlorobenzene (5CB), extracted from the Robert's Bank spiked sediment, aged for 52 days

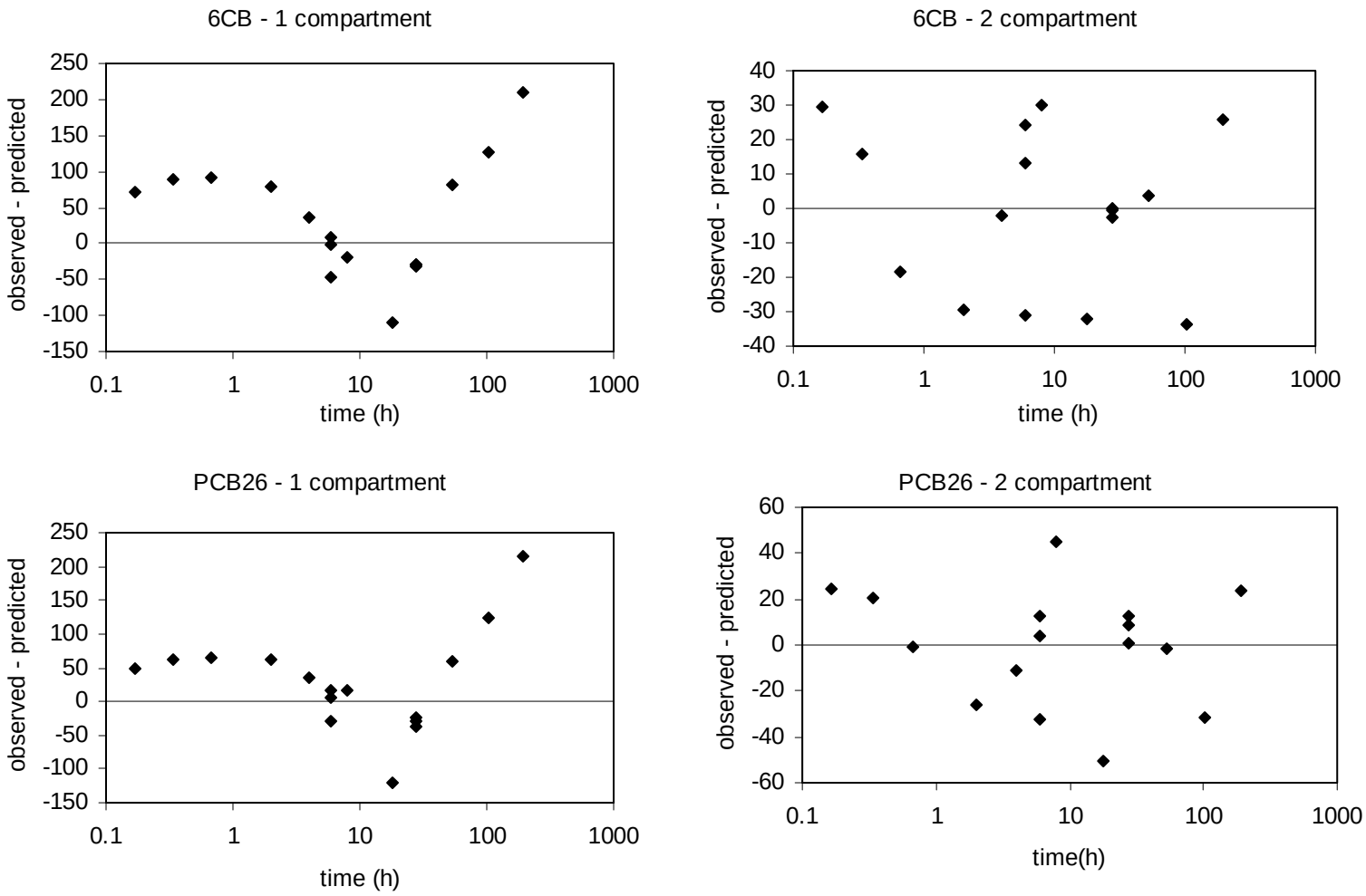

Figure C-2b – Residuals ($C_{EVA}(t)$ observed – $C_{EVA}(t)$ predicted) from the 1 and 2 compartment model fit hexachlorobenzene (4CB) and PCB 26, extracted from the Robert's Bank spiked sediment, aged for 52 days

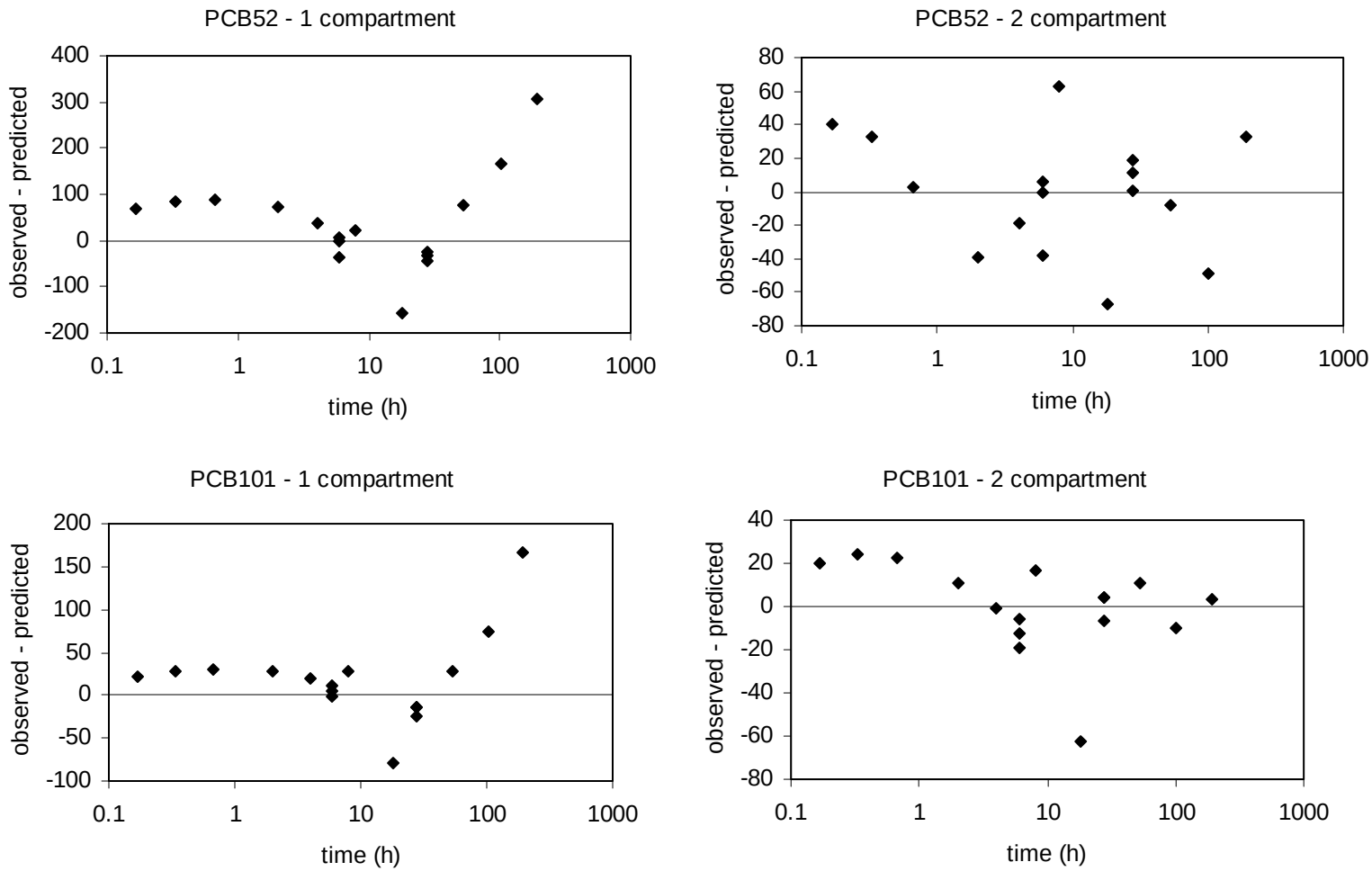

Figure C-2c Residuals (C_{EVA}(t) observed – C_{EVA}(t) predicted) from the 1 and 2 compartment model fit for PCB 52 and PCB 101, extracted from the Robert's Bank spiked sediment, aged for 52 days

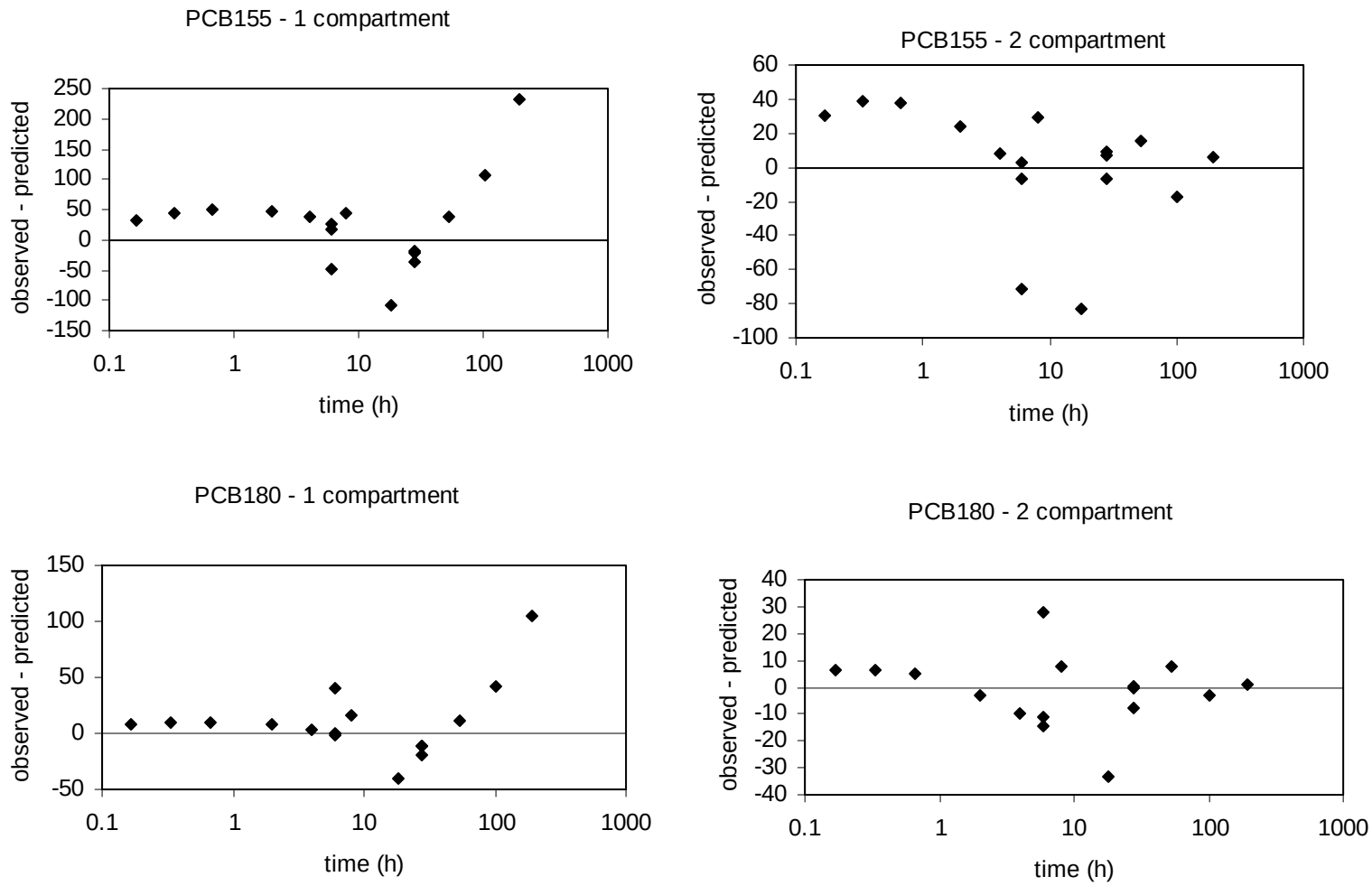

Figure C-2d Residuals (C_{EVA}(t) observed – C_{EVA}(t) predicted) from the 1 and 2 compartment model fit for PCB 155 and PCB 180, extracted from the Robert's Bank spiked sediment, aged for 52 days

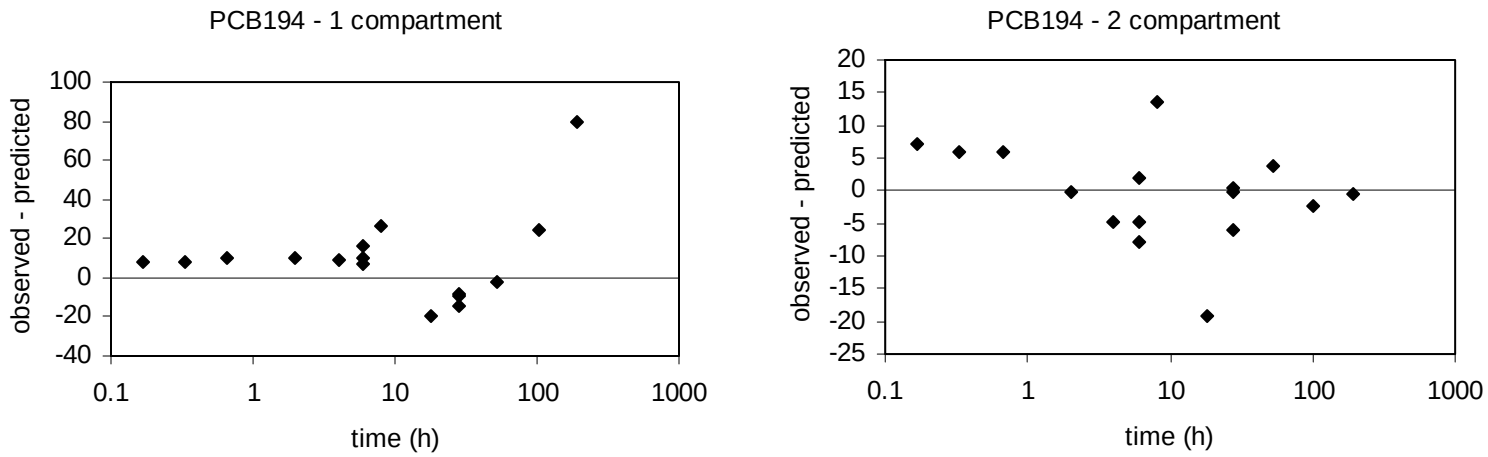

Figure C-2e Residuals (C_{EVA}(t) observed – C_{EVA}(t) predicted) from the 1 and 2 compartment model fit for PCB 194, extracted from the Robert's Bank spiked sediment, aged for 52 day

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