Exposure Dynamics of Polycyclic Aromatic Hydrocarbons and Polychlorinated Biphenyls in the Food Web of Western Lake Erie and the Detroit River

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Abstract

This thesis investigated the processes regulating the exposure dynamics of polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) in the western Lake Erie and the Detroit River biota. First, the freshwater mussel, *Elliptio complanata*, was calibrated as a biomonitor of PAH and PCB water concentrations and used to assess bioavailable water concentrations along the Detroit River and western Lake Erie. Concentrations of the more hydrophobic PAHs and more water soluble PCBs were present at elevated concentrations at the Detroit Edison Generating Station, in the Trenton Channel. Elevated PAH concentrations were also detected at 3 other sites in the Detroit River.

Since it was found that PAHs and PCBs were present at high concentrations in the water of the study region, the distribution patterns of PAHs and PCBs were further determined in 4 benthic invertebrate species of western Lake Erie. Significant differences in the sum of 17 PAH compounds were observed among the 4 species, with mayflies containing the highest concentrations of PAHs followed by dreissenid mussels, amphipods, and crayfish. For PCBs, mayflies contained significantly higher concentrations of the sum of 39 PCB congeners than the other organisms and dreissenids had higher concentrations than crayfish. For PCBs, the relationship between the biota-sediment accumulation factors (BSAFs) and log octanol/water partition coefficients (K_{ow}) followed a parabolic pattern while the BSAFs for PAHs were inversely related to log K_{ow} suggesting that metabolism of the higher K_{ow} PAH compounds was occurring.

Overall, the results of this study suggest that many factors regulate the exposure dynamics of PAHs and PCBs in aquatic systems, such as chemical hydrophobicity, metabolic degradation, route of chemical uptake, and organism habitat, diet, feeding strategy, and lipid content. A modeling approach is needed to mathematically quantify the influence of different processes on the accumulation of PAHs in aquatic food webs.

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Chapter 1.0: General Introduction

1.1 Chemicals in the Environment

In 1962, Rachel Carson wrote "For the first time in the history of the world, every human being is now subjected to contact with dangerous chemicals, from the moment of conception until death" (Carson, 1962, p. 24). In her book, *Silent Spring,* Carson (1962) drew attention to the link between the exposure to chemicals and the risk of effects in both humans and wildlife. At the time her ideas did not have a large impact on societal behavior since people had become highly dependent on chemicals which were persistent in the environment.

In recent years, due to increasing research in the field of ecotoxicology, more people are becoming aware of the dangers of toxic chemicals. Such research includes studies providing evidence that persistent organic chemicals are responsible for toxic effects and population declines of wild populations of birds (Gilbertson *et al.*, 1991; Donaldson *et al.*, 1999) and fish (Black, 1983; Baumann, 1984; Leadley *et al.*, 1998) and for behavioral effects observed in children (Jacobson and Jacobson, 1996; Lonky *et al.*, 1996; Guillette *et al.*, 1998). In response to public concern, the governments of Canada and the United States revised the Great Lakes Water Quality Agreement in 1978 and in 1987 to include a policy that advocated the virtual elimination of the discharge of all persistent toxic chemicals. However, for appropriate regulatory actions to be taken, government officials require information on causal relationships between exposure to contaminants and their effects (Gilbertson, 1997). Thus, an important focus of ecotoxicology is to evaluate the exposure dynamics of chemicals in aquatic ecosystems. Information on the exposure and accumulation of contaminants in the biota, together with

toxicity data, will allow the hazards associated with specific chemicals to be quantified and enable regulatory officials to make decisions on how to allocate resources for remediation projects.

1.2 Polycyclic Aromatic Hydrocarbons

Polycyclic aromatic hydrocarbons (PAHs) are important contaminants in the aquatic environment and are a threat to both human and animal health (Neff, 1979). PAHs consist of a group of hydrophobic organic compounds composed of two or more non-halogenated fused benzene rings. Although there are many different PAHs present in the environment (Neff, 1979), only 17 PAHs were analyzed in this project. These compounds were selected because they have been identified as "priority PAHs" by the United States Environmental Protection Agency (Mackay, 1991). The 17 PAHs include: naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[*a*]anthracene, chrysene, triphenylene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, indeno[*1,2,3-c,d*]pyrene, dibenzo[*a,h*]anthracene, and benzo[*g,h,i*]perylene. These compounds have different physical-chemical properties, causing variable congener exposure dynamics. Their molecular weights range from 128 to 268 g/mol, and their log octanol/water partition coefficients (log K_{ow}s) range from 3.4 to 6.8.

PAHs are produced primarily through the incomplete combustion of carbon compounds (Neff, 1979). However, PAHs can also be synthesized by bacteria and plants (Neff, 1979). The majority of PAHs that enter the aquatic environment are a result of anthropogenic sources (Neff, 1985). For example, PAHs are produced in large quantities by the pyrolysis of fossil fuels and are thus are generated by automobiles, electrical

generating facilities, waste incinerators, coke and asphalt production, and aluminum smelting. Cigarette smoke and human food such as smoked food products and charcoal-broiled meats, contain high concentrations of PAHs (Panalaks, 1976; Neff, 1979).

Once released into the environment, PAHs become sorbed onto fine particles. These chemicals can reach aquatic systems though spills, runoff water from land, industrial and domestic wastewater effluent, or though wet or dry precipitation (Neff, 1979). In the waters of the Great Lakes, transportation of PAHs is regulated primarily by suspended solids. However, these compounds can also partition into the dissolved aqueous phase, especially in areas of low particulate matter, increasing their mobility within the aquatic environment (Metcalfe *et al.*, 2000).

PAHs are chronically toxic to aquatic organisms, and are known to cause carcinogenic, genotoxic and teratogenic effects (Neff, 1979). Parent PAHs are not very hazardous but can be metabolically transformed to more toxic substances (Neff, 1979). The major enzyme system responsible for the biotransformation of PAHs is the cytochrome-P450-dependent Mixed Function Oxidase (MFO) system. The number, type, toxicity, and rate of production of metabolites differ for each animal species and PAH compound (Neff, 1979). Toxic effects are initiated when the metabolites form covalent bonds with macromolecules of cells, such as DNA, RNA, and protein (Neff, 1979). For example, a metabolic product of benzo(a)pyrene is "bay-region" diol-epoxide, which has been shown to be highly carcinogenic (Varanasi *et al.*, 1989a). Vertebrates possess MFO systems and rapidly metabolize PAH compounds (Varanasi *et al.*, 1989a). Invertebrates generally have poorly developed MFO systems and metabolism is slower (James, 1989), although the rate of metabolism varies among species (Landrum, 1982; Leversee *et al.*,

1982; Landrum and Scavia, 1983; Varanasi *et al.*, 1985; Frank *et al.*, 1986; Borchert *et al.*, 1997). As a result, PAH body burden tends to be lower in fish than in invertebrates because conventional monitoring programs only reveal concentrations of the parent compounds. However, PAHs are generally more hazardous to fish than to invertebrates (Neff, 1979).

Data collected during the past two decades have provided evidence that PAHs in contaminated regions of the Great Lakes are hazardous to fish populations. In 1977, Black *et al.* (1980) found a high incidence of neoplasia in several benthic fish species of the Buffalo River, near eastern Lake Erie. Since tubificid worms, a food source to fish, and sediment collected at this site contained elevated PAH burdens it was hypothesized that PAHs may have induced the neoplasms (Black *et al.*, 1980). Tumour frequencies in freshwater drum were significantly higher at 5 sites of high PAH contamination in eastern Lake Erie and the upper Niagara River compared with 2 reference stations (Black, 1983). Baumann *et al.* (1982) found high liver tumour incidences in brown bullheads from the Black River, near Lake Erie. This area was previously shown to contain elevated PAH concentrations in sediment (Brass *et al.*, 1974). In an *in vitro* study, Ali *et al.* (1993) showed that the PAH fraction of sediment extracts from the Trenton Channel, in the Detroit River, caused an increase in DNA repair in brown bullhead cells. This indicated that the PAH concentrations present in this area were sufficiently high to cause cytotoxic and genotoxic effects to fish. In order to directly assess PAH metabolites in fish, Krahn *et al.* (1984) developed a technique to estimate the concentration of metabolites in fish bile collected under field conditions by quantifying the fluorescent aromatic compounds in the sample with an HPLC system. This technique has recently

been applied in several field studies which have demonstrated links between PAH metabolites and teratogenic stress in wild fish populations from the Buffalo River (Maccubbin *et al.*, 1988), the Detroit River (Leadley *et al.*, 1998; Leadley *et al.*, 1999; Arcand-Hoy and Metcalfe, 1999), and Hamilton Harbour and the Black River (Arcand-Hoy and Metcalfe, 1999).

1.3 Polychlorinated Biphenyls as a Tool for Understanding PAH Dynamics

Since PAH metabolites are much more toxic than parent PAH compounds, it is important to evaluate the rate of PAH metabolism in different species. The direct quantification of PAH metabolites is difficult because metabolites are usually lost in the extraction and cleanup phases of chemical analysis procedures (McElroy *et al.*, 1989). Further, metabolite fractions that are extracted in field samples typically contain many other compounds which makes detection of specific metabolites difficult (McElroy *et al.*, 1989). One way to quantify the metabolism of PAHs in the field is to compare PAH distribution with chemicals of similar hydrophobicity that are more persistent in the food web (McElroy *et al.*, 1989). Polychlorinated biphenyls (PCBs) are synthetic chemicals that were used widely in industry between the years 1929 and 1979 due to their high chemical stability (Tanabe, 1988; Metcalfe and Haffner, 1995). Even though they were banned in the 1970s by most western countries, high concentrations are still detected in aquatic food webs (Tanabe, 1988; Koslowski *et al.*, 1994; Metcalfe and Haffner, 1995; Morrison *et al.*, 1997). PCBs have similar size and hydrophobicity as PAHs, however they are more resistant to degradation processes such as metabolism (Sanborn *et al.*, 1975; Sundstrom *et al.*, 1976; Neff, 1979; Conner, 1984). Thus comparisons of relative concentrations of PAHs and PCBs in the food web will yield information as to the

relative rate of PAH metabolism in different species. In this project, 39 PCBs were analyzed along with the PAHs in order to get a better understanding of the processes affecting PAH accumulation under field conditions. This group of PCBs includes both mono-*ortho*-substituted and non-coplanar compounds and their log K_{ow} values range from 5.6 to 7.5.

1.4 Study Area

The Detroit River and Western Lake Erie have received considerable attention from the public, researchers, and government officials. The Detroit River, a busy transportation channel joining Lake St. Clair and Lake Erie, is heavily affected by anthropogenic chemicals (Fallon and Horvath, 1985; Furlong *et al.*, 1988; Metcalfe *et al.*, 1997; Leadley *et al.*, 1998; Metcalfe *et al.*, 2000). The majority of chemical toxins in western Lake Erie originate from the Detroit River (Kelly *et al.*, 1991). Approximately 73% of sediment-bound pollutants from the Detroit River entering Lake Erie are accumulated within the sediment of the western basin, resulting in potentially high concentrations of chemical exposure to the biota of this system (Carter and Hites, 1992). Management strategies have been developed to focus remedial efforts in both the Detroit River and western Lake Erie. The Detroit River was identified as an Area of Concern (AOC) by the International Joint Commission and restoration plans are being coordinated by a Remedial Action Plan (RAP). A Lake Wide Management Plan (LaMP) has been initiated for Lake Erie to focus protection and restoration programs in this lake. In order to ensure continued progress of the RAP and LaMP projects, it is important to assess and monitor chemical concentrations in the biota of the Detroit River and Lake Erie.

1.5 Thesis Objectives

The overall objective of this project was to investigate the processes regulating the dynamics of PAHs in the water and biota of the Detroit River and western Lake Erie. Three separate studies, described in Chapters 2, 3, and 4, were performed in order to achieve this objective.

The objective of the study presented in Chapter 2 was to calibrate the freshwater water mussel, *E. complanata*, as a biomonitor of PAH water concentrations by determining the elimination rate constants (k_2) of 16 PAHs from this mussel to water in a laboratory elimination study. Previously published k_2 values of PCBs were compared to the results in order to assess the relative importance of metabolism and passive depuration of PAHs from mussels to the water phase. If metabolism was not affecting the toxicokinetics of PAHs in mussels, it was predicted that the rate of elimination of PAHs would be regulated by hydrophobicity (Landrum, 1988; Hattum and Montanes, 1999), and k_2 values would be similar to that of PCBs. Mussels are known to possess mixed function oxidase systems (Moore *et al.*, 1989), although their rate of PAH metabolism is typically much slower than in fish and in other invertebrates (Stegeman, 1981; Varanasi *et al.*, 1985). It was assumed that metabolism would play a limited role in the elimination rates detected for parent PAH compounds.

The objective of the study presented in Chapter 3 was to evaluate bioavailable PAH and PCB water concentrations at 11 sites and at 4 times in the Detroit River and in western Lake Erie using *E. complanata*, introduced in cages, as a surrogate for direct water measurements. With the k_2 values calculated in Chapter 2, bioavailable water chemical concentrations can be calculated as a function of chemical uptake by the

mussels, while correcting for the time it takes the mussels to achieve steady state with their environment. It was hypothesized that significant differences would be detected among sites due to spatial variability of contaminant inputs from both point sources and non-point sources along the Detroit River (Detroit River Canadian Cleanup Committee, 1999). Further, it was hypothesized that significant differences would be found among sampling dates. Previous studies have found that PAH exposure to brown bullheads changed through time as a result of temporal variations in chemical inputs related to storm events (Leadley *et al.*, 1999).

Since PAHs were detected at significant concentrations in the water phase of the Detroit River and Lake Erie it was critical to examine the exposure of this class of contaminants to aquatic organisms. The objective of the study presented in Chapter 4 was to assess the dynamics of PAHs in the lower trophic levels of the biota at Middle Sister Island, in western Lake Erie. The distribution patterns of PAHs and PCBs were determined in sediment, and in 4 benthic invertebrates: mayfly larvae (*Hexagenia limbata* and *Hexagenia rigida*), dreissenid mussels (*Dreissena polymorpha* and *Dreissena bugensis*), amphipods (*Gammarus fasciatus*, *Echinogammarus ischnus*, and *Hyalella azteca*), and crayfish (*Orconectes propinquus*). These benthic invertebrates are major components of the diet of many top predators and thus are important vectors for contaminant transfer in aquatic food webs (Morrison *et al.*, 1997; Morrison *et al.*, 1998). Biota-sediment accumulation factors (BSAFs), which are equal to the ratio of the lipid-normalized concentration in an organism divided by the organic carbon-normalized concentration in sediment, were calculated. The BSAF values can be used to measure the dynamics of contaminant uptake from sediment since under conditions of chemical

equilibrium, the BSAF for each chemical, and in each species, should approach 1 (Bierman, 1990; Di Toro *et al.*, 1991). It was hypothesized that significant differences among species would be detected for PAHs due to species-specific differences in the rate of PAH metabolism and that PAH BSAF values would be less than 1 because metabolic degradation of PAHs would prevent equilibrium conditions between sediment and biota from being achieved. I further hypothesized that no significant differences in PCB compounds among species would be found because PCBs are less susceptible to metabolism by invertebrates (Sundstrom *et al.*, 1976) and that PCB BSAF values would be greater than 1 due to biomagnification of chemicals from food.

Chapter 2.0: Calibration of the Freshwater Mussel, *Elliptio complanata*, as a Biomonitor of Bioavailable Water Concentrations of PAHs

2.1 Abstract

The elimination rate constants (k_2) of 16 polycyclic aromatic hydrocarbons (PAHs) were determined for the freshwater mussel, *Elliptio complanata*. Naphthalene, acenaphthylene, acenaphthene, benzo[*a*]pyrene, and benzo[*g,h,i*]perylene were not frequently detected in mussels after 5 days of exposure, which suggested that *E. complanata* was capable of rapidly metabolizing these chemicals. The k_2 values of non-metabolized PAHs ranged from 0.05 to 0.22 day^{-1} and showed a significant inverse relationship with log K_{ow}. The k_2 vs. K_{ow} regression equation in *E. complanata* was similar to the kinetic models developed for PCBs in other bivalve mollusks as well as to kinetics relationships for PAHs in other types of organisms.

2.2 Introduction

Polycyclic aromatic hydrocarbons (PAHs) are commonly released into the environment by anthropogenic activities as a result of the incomplete combustion of carbon compounds (Neff, 1979). PAH compounds taken up by many species, especially vertebrates, are rapidly metabolized and metabolites can cause genotoxic and carcinogenic effects (Neff, 1979). A major source of PAHs to aquatic organisms is the direct partitioning of contaminants to the animal from the water phase (Thomann and Komlos, 1999). It is therefore important to quantify PAH exposure dynamics in aquatic systems in order to assess the risk associated with PAHs. Direct water measurements, such as large volume water analysis with a Goulden continuous extractor, are costly, time-consuming, require large sample sizes, can miss periods of high contamination, and

do not necessarily reflect the bioavailable fraction (Phillips and Segar, 1986; Morrison *et al.*, 1995).

Mussels have been shown to be effective surrogates of direct water assessments (Morrison *et al.*, 1995; Neff and Burns, 1996). As a result of slow PAH metabolism and intensive filter feeding activity, mussels can rapidly accumulate contaminants to detectable concentrations (Livingstone and Farrar, 1984; James, 1989). Although mussels are exposed to contaminants from both water and suspended sediment, several studies have shown that water is the predominant source (Obana *et al.*, 1983; Pruell *et al.*, 1986; Tanabe *et al.*, 1987; Muncaster *et al.*, 1989; Muncaster *et al.*, 1990; Kauss and Hamdy, 1991; Bruner *et al.*, 1994). Thus mussels effectively track water chemical concentrations. Biomonitors such as *E. complanata*, provide information on the amount of chemical that is available to be taken up by the biota, thus eliminating the need for studies on chemical speciation to determine bioavailable fractions (Phillips and Segar, 1986). Finally, the broad distribution of *E. complanata* makes this species ideal for biomonitoring studies in freshwater systems.

The primary objective of this study was to calibrate *E. complanata* in order to quantify the elimination kinetics of the 16 priority PAH compounds in aquatic ecosystems. Although *E. complanata* has been calibrated for hexachlorobenzene and octachlorostyrene (Russell and Gobas, 1989), the PAH kinetics in this organism have not yet been evaluated. A second objective was to compare the results with previously published elimination rate constant (k_2) values of polychlorinated biphenyls (PCBs), which are less sensitive to metabolic degradation (Sanborn *et al.*, 1975; Sundstrom *et al.*, 1976; Neff, 1979; Tanabe, 1988; Metcalfe and Haffner, 1995), to assess the relative

importance of metabolism and passive depuration of PAHs from mussels to the water phase. Elimination data were further compared with different organisms to evaluate species-specific differences in PAH kinetics.

2.3 Methods

2.3.1 Experimental

E. complanata was collected from Balsam Lake using SCUBA in 1998. This lake, located in central Ontario, contains relatively low concentrations of hydrophobic organic contaminants (Curry, 1977/78; Kauss and Hamdy, 1985; Muncaster *et al.*, 1989). Mussels were maintained in a carbon-filtered aquarium until the initiation of the kinetics study.

The exposure of PAHs to the mussels occurred in a clean 30 L glass aquarium with a removable glass lid, that was spray painted black and covered with black cardboard to prevent photolysis of PAH compounds from occurring during the uptake phase of the study. The aquarium was filled with dechlorinated tap water at a temperature of 17°C. The PAH compounds used in this study were obtained from Supelco Inc. (Bellefonte, PA) and included: acenaphthene, acenaphthylene, anthracene, benzo[*a*]anthracene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*g,h,i*]perylene, benzo[*a*]pyrene, chrysene, dibenzo[*a,h*]anthracene, fluoranthene, fluorene, indeno[*1,2,3-c,d*]pyrene, naphthalene, phenanthrene, and pyrene. Exposure of chemicals to the mussels was performed similar to the methods used by Gobas *et al.* (1989) and Russell and Gobas (1989). Four thousand µg of each of the PAHs were dissolved in 100 mL dichloromethane (DCM). The PAH/DCM solution was then evaporated onto glass wool so that the PAHs were sorbed onto the wool. The wool was then placed in 2 Fluval

Aquarium Power Filters (HAGEN Inc., Montreal, Quebec), that were put in the aquarium. The system was allowed to equilibrate for 1 week. After 1 week, 21 mussels were placed in the aquarium and exposed to the PAHs for 5 days.

Five days prior to the elimination phase of the experiment, a transparent, clean 30 L glass aquarium was filled with dechlorinated tap water at a temperature of 17°C. A Fluval Aquarium Power Filter, containing activated filter carbon, and 2 nylon bags filled with activated filter carbon, were placed in the aquarium so that any freely dissolved PAH contaminants present in the system would be removed from the water phase. At this time, 3 mussels were placed in this aquarium and removed at the start of the elimination study, to determine if PAH concentrations in the water were below the detection level.

After 5 days of exposure to the PAHs, 3 mussels were sampled from the exposure aquarium to determine initial PAH body burdens of the organisms. The remaining dosed mussels were placed in the second aquarium for the elimination phase of the study. Three additional unexposed mussels were placed into the second aquarium for the duration of the elimination study to determine if PAHs were being recycled within the system. Three mussels were sampled after 1, 2, 4, 8, 16, and 32 days of depuration into the clean water. Water temperature was monitored throughout the experiment and ranged from 16.5 to 18°C. Sampled mussels were wrapped in hexane rinsed foil and stored at -20°C until chemical analysis.

2.3.2 Chemical Analysis

Chemical analysis was performed at the analytical laboratory at the Great Lakes Institute for Environmental Research at the University of Windsor, which has been

accredited by the Canadian Association for Environmental Analytical Laboratories (CAEAL). The PAH analysis technique is approved by CAEAL and annual reference CAEAL sediment samples are run. Sample preparation was done according to Lazar *et al.* (1992). Each mussel was shucked and the tissue was homogenized with anhydrous sodium sulfate using a mortar and pestle. The samples were then poured into 35 cm × 2 cm glass columns that were plugged with glass wool, filled with 30 mL of DCM:hexane (1:1) and 2 cm of Na_2SO_4. Internal standards of tribromobenzene, tetrachloro-m-xylene, and decachlorobiphenyl were added to the column. After one hour, the samples were eluted with 250 mL of DCM:hexane (1:1). Five mL of isooctane was added to each sample, which were then rotoevaporated to 5 mL using a Büchi Rotoevaporator. The samples were made up to 25 mL with hexane. Lipid determination was done by evaporating 2 mL of each sample for an hour at 105°C and percent lipid was calculated gravimetrically. The remaining portion of the samples was rotoevaporated to 1.5-2 mL and transferred to 35 cm × 1 cm glass columns that were plugged with glass wool, filled with 6 g of activated florisil, 2 cm of Na_2SO_4, and hexane. PAHs were eluted with 100 mL of DCM:hexane (3:2). Extracts were then rotoevaporated to less than 1 mL and then made up to a final volume of 1 mL with isooctane.

2.3.3 Gas Chromatography

Gas chromatographic analysis was performed on a Hewlett-Packard (HP) 5890/5979 equipped with a mass selective detector, a HP-7673A autosampler, and a 30 m × 0.25 mm DB-5 column. Injection was 1 μL spitless at 250°C and the oven temperature was programmed from 100 to 270°C at 3°C /min. Carrier gas was ultra-high purity helium at 30 cm/s flow rate. The detection level was 0.5 ng/g wet weight and

contaminants that were not at quantifiable levels were replaced with the detection limit value. The percent recoveries of internal standards were 88.75 ± 3.369, 88.67 ± 1.953, and 88.77 ± 1.311 (mean ± SE) for tribromobenzene, tetrachloro-m-xylene, and decachlorobiphenyl respectively. Concentrations were not corrected for the recovery of internal standards.

2.3.4 Elimination Rate Constants

When a contaminated organism is placed into clean water, the rate of chemical depuration can be expressed as follows:

$$\frac{dC_{org}}{dt} = -k_2 C_{org} \tag{2.1}$$

This equation can be integrated:

$$\ln C_{org} = \ln C_{org,t=0} - k_2 t \tag{2.2}$$

where C_{org} is the lipid normalized PAH concentration in the organism at a specific time and $C_{org,t=0}$ is the initial lipid normalized PAH concentration. Thus for a particular PAH compound, k_2 will equal the absolute value of the slope of a plot of the natural logarithm of concentration versus time. The k_2 values of PAHs in the mussels were thus determined through linear regression with the ln lipid normalized PAH mussel concentration and time as the dependent and independent variables respectively.

Equation (2.2) assumes that the elimination kinetics of mussels can be described by first-order rate constants. Several other studies have found that the depuration of individual PAHs approximate a first-order reaction (Pruell *et al.*, 1986; Sericano *et al.*, 1996; Hattum and Montanes, 1999). This equation also assumes that the only route of chemical elimination is from water to gills, and that depuration via feces and metabolism

is not occurring. The mussels were not fed for the duration of the study to minimize chemical elimination through feces. In addition, it was assumed that lipid was the predominant storage phase of the mussels.

The time it takes the mussels to achieve 95% steady-state concentrations of PAHs was calculated as follows:

$$t_{95} = -\frac{\ln 0.05}{k_2} \tag{2.3}$$

2.4 Results

For most PAH compounds, concentrations decreased throughout the depuration experiment and elimination rates of 14 PAHs are presented in Fig. 2.1. Elimination data for naphthalene and benzo[*a*]pyrene are not shown because they were only detected at low concentrations, and in most mussels, concentrations were below the detection level, even at the start of the experiment. Acenaphthylene, acenaphthene, and benzo[*g,h,i*]perylene were not further evaluated because more than half their concentrations were below the detection limit. Measurable concentrations of these compounds were infrequently observed after the first 8 days of elimination and concentrations were not detected in any of the mussels on the last day of the study. It was concluded that the data for acenaphthylene, acenaphthene, and benzo[*g,h,i*]perylene were not sufficient to quantify elimination rate constants.

The slopes of the linear regression of mussel concentration versus time for 9 PAHs were significantly different from zero ($p < 0.05$) (Table 2.1), whereas the slopes for benzo[*k*]fluoranthene and dibenzo[*a,h*]anthracene were not significantly different from zero ($p > 0.05$) (Table 2.1). These non-significant k_2 values were still employed in

the calibration of *E. complanata* because it is legitimate to use non-significant best estimates of elimination kinetics (ASTM, 1983; Landrum, 1988) since best estimates are more appropriate than zero when some loss is observed (Landrum, 1988). The k_2 values for *E. complanata* ranged from 0.05 to 0.22 day^{-1} (Table 2.1).

To assess the role of equilibrium partitioning on the elimination kinetics of PAHs, k_2 values of the 11 PAHs were plotted against log K_{ow} (Fig. 2.2). The k_2 values displayed a significant inverse relationship with log K_{ow}. The regression equation was:

$$k_2 = 0.39(\pm 0.083) - 0.05(\pm 0.015)\log K_{ow},\ r^2 = 0.52,\ n = 11 \qquad (2.4)$$

The relationship between k_2 and log K_{ow} obtained in this study was compared with the elimination kinetics of PCBs in other bivalve mollusks to determine if metabolism was contributing to the depuration of the 11 PAHs in *E. complanata* (Table 2.2). Since PCBs are more resistant to metabolism (Neff, 1979; Tanabe, 1988), the regression equation for PAHs and PCBs would only be similar if metabolism of PAHs was not a significant source of chemical elimination in mussels. The relationship between k_2 and log K_{ow} for PCBs in zebra mussels (*Dreissena polymorpha*) reported by Morrison *et al.* (1995) was identical to the equation obtained in this project, and the relationship in green-lipped mussels (*Perna viridis*) was also very similar (Tanabe *et al.*, 1987).

The elimination kinetics of PAHs in *E. complanata* were further compared with the depuration of PAHs in other species (Table 2.2). Elimination kinetics of PAHs in amphipods (Landrum, 1988), oligochaetes (Frank *et al.*, 1986), mysids (Frez and Landrum, 1986), oysters (Bender *et al.*, 1988) and zebrafish (Djomo *et al.*, 1996) were similar to those observed in this study. Isopods were also similar although the k_2 vs. log K_{ow} regression equation had a steeper slope and a larger intercept (Hattum and Montanes,

1999). *Daphnia pulex* had a substantially greater slope and intercept compared with other types of organisms (Southworth *et al.*, 1978). Results published for PAH elimination kinetics in 3 bivalve species (Pruell *et al.*, 1986; Bender *et al.*, 1988; Tanacredi and Cardenas, 1991; Sericano *et al.*, 1996) and in rainbow trout (Niimi and Palazzo, 1986), however, were substantially different from this study.

No PAH compounds were detected in the 3 clean mussels placed in the elimination aquarium 5 days before the start of the study and sampled at $t = 0$. This supports the conclusion that the elimination tank water initially contained no detectable PAH compounds. PAHs in the 3 clean mussels left in the elimination aquarium for the duration of the experiment were either not detected or detected at low concentrations (< 2.4 μg/g lipid), which suggests that PAHs were efficiently removed from the water once they had been eliminated from the mussels. Recycling of PAHs in the experimental tank was therefore concluded to be minimal.

2.5 Discussion

The k_2 values of the 11 PAHs shown in Table 2.1 showed a significant inverse relationship with log K_{ow}. Hydrophobicity explained 52% of the variation in k_2, and thus had a major influence on the elimination rates of PAHs. Since the regression equation (equation (2.4)) observed in this study was very similar to the equations published for PCBs in other bivalve mollusks (Tanabe *et al.*, 1987; Morrison *et al.*, 1995), metabolic degradation was likely not a significant route of elimination of these 11 PAH compounds in mussels.

Benzo[*a*]pyrene and naphthalene were rarely detected, even at the end of the 5 day exposure, which suggests that these chemicals were rapidly metabolized. Since

naphthalene was the most water soluble compound analyzed, it would have definitely partitioned from the glass wool to the water phase during the uptake period. Although benzo[*a*]pyrene is more hydrophobic, compounds with higher K_{ow}s partitioned highly into the mussels. It was therefore concluded that naphthalene and benzo[*a*]pyrene were taken up by the exposed mussels, but were being rapidly metabolized, which resulted in little net uptake. This might have toxicological significance for mussels as metabolites of benzo[*a*]pyrene are among the most carcinogenic compounds (IARC, 1983; Krahn *et al.*, 1984; Leadley *et al.*, 1999).

Acenaphthylene, acenaphthene, and benzo[*g,h,i*]perylene were frequently detected at the start of the elimination study, but not during the latter part of the experiment. This indicates that metabolism likely had a significant role in the depuration of these chemicals, which resulted in a higher rate of elimination being detected for the parent PAH compounds.

Mussels are known to possess mixed function oxidase systems (Moore *et al.*, 1989), although their benzo[*a*]pyrene hydroxylase activities are less than in fish and in other invertebrates (Stegeman, 1981). Borchert *et al.* (1997) found, using an HPLC system, that the freshwater mussel, *Sphaerium corneum*, metabolized 26% of benzo[*a*]pyrene after 20 h of exposure, whereas Varanasi *et al.* (1985) found, using thin-layer chromatography, that the marine mussel, *Macoma nasuta*, metabolized less than 5% of benzo[*a*]pyrene in 4 weeks. Comparing these results with those of this study leads to the conclusion that mussels might have very species-specific metabolic potentials.

The relationship between k_2 and log K_{ow} of PAHs in *Pontoporeia hoyi* (Landrum, 1988), *Stylodrilus heringianus* (Frank *et al.*, 1986), *Mysis relicta* (Frez and Landrum,

1986), and in *Crassostrea virginica* (Bender *et al.*, 1988) were similar to *E. complanata* and to the equations published by Morrison *et al.* (1995) and Tanabe *et al.* (1987) for PCBs in mussels (Table 2.2). In each of these studies, it was concluded that limited metabolic degradation was occurring. Thus it is likely that the elimination kinetics of hydrophobic contaminants are similar among invertebrates when metabolism is not significantly contributing to chemical elimination. These results suggest that contaminant kinetics are not strongly regulated by organism size as compared with chemical hydrophobicity. For example, although the mussels used in this study ranged from 7-10 cm and the *Dreissena polymorpha* used by Morrison *et al.* (1995) were much smaller (approximately 1-2 cm), these two bivalve species had similar k_2 values. Small fish species, such as guppies (Gobas *et al.*, 1989) and zebrafish (Fox *et al.*, 1994), also have PCB elimination rate constants that are similar to invertebrates. However larger fish, such as rainbow trout, typically have slower PCB elimination kinetics due to lower gill surface to volume ratios (Oliver and Niimi, 1985; Coristine *et al.*, 1996).

The kinetics of PAHs in freshwater isopods (Hattum and Montanes, 1999) were generally more rapid, but still comparable to the results obtained with *E. complanata* and with other invertebrates (Frank *et al.*, 1986; Frez and Landrum, 1986; Landrum, 1988; Bender *et al.*, 1988). Although Hattum and Montanes (1999) argued that PAH biotransformation in isopods was not an important process, the isopods might have been more susceptible to metabolism than other invertebrates. Gewurtz *et al.* (2000) reported that different invertebrate species varied in their ability to metabolize PAH compounds. PAH elimination in *Daphnia* (Southworth *et al.*, 1978) was much more rapid than in other species (Table 2.2). Daphnids are very small compared to the other organisms

listed in Table 2.2, thus their larger surface area to volume ratio likely caused the high elimination kinetics. The PAH data for the 3 bivalve species *Crassostrea virginica* (Sericano *et al.*, 1996), *Mytilus edulis* (Pruell *et al.*, 1986), and *Mercenaria mercenaria* (Bender *et al.*, 1988; Tanacredi and Cardenas, 1991), contrasted greatly from the toxicokinetics of PAHs in *E. complanata* and in other invertebrates (Frank *et al.*, 1986; Frez and Landrum, 1986; Landrum, 1988; Bender *et al.*, 1988). This large discrepancy among mussel data may be due to differences in experimental conditions, but species-specific differences in metabolic potentials cannot be ruled out. PAH elimination kinetics in zebrafish (Djomo *et al.*, 1996) were similar to those in *E. complanata* and in other invertebrates (Frank *et al.*, 1986; Frez and Landrum, 1986; Landrum, 1988; Bender *et al.*, 1988). Further, the PAH kinetics in zebrafish were comparable to those of PCBs (Fox *et al.*, 1994). However, Djomo *et al.* (1996) employed a series of ^{14}C-labelled PAHs and thus they were not able to differentiate between parent PAH compounds and PAH metabolites. In rainbow trout, elimination rates for PAHs (Niimi and Palazzo, 1986) were substantially greater than for PCBs (Niimi and Oliver, 1983; Coristine *et al.*, 1996), which suggests that metabolism was an important factor in the depuration of PAHs in this fish species.

2.6 Conclusions

The results of this study demonstrate that the kinetics of non-metabolized PAHs and PCBs in *E. complanata* and in other invertebrates can be predicted by hydrophobicity. Metabolic degradation likely had a major influence on the overall elimination of benzo[*a*]pyrene, naphthalene, acenaphthylene, acenaphthene, and

benzo[*g,h,i*]perylene. With these data, *E. complanata* can be used to effectively quantify PAH and PCB exposure dynamics in aquatic ecosystems.

Table 2.1. Elimination rate constants (k_2) and time to 95% steady-state (t_{95}) of 11 PAHs in *Elliptio complanata*.

PAHs[a]	Log K_{ow}[b]	k_2 (day^{-1}) (n=3) Mean ± SE	r^2	p-level	t_{95} (day)
FL	4.18	0.217 ± 0.0370	0.65	< 0.001	13.8
PHE	4.57	0.177 ± 0.0291	0.66	< 0.001	16.9
AN	4.54	0.163 ± 0.0432	0.43	< 0.01	18.4
FLT	5.22	0.130 ± 0.0242	0.61	< 0.001	23.0
PY	5.18	0.144 ± 0.0226	0.68	< 0.001	20.8
B(a)A	5.91	0.148 ± 0.0377	0.45	< 0.001	20.2
C	5.86	0.105 ± 0.0262	0.46	< 0.001	28.6
B(b)F	5.80	0.103 ± 0.0287	0.40	< 0.01	29.1
B(k)F	6.00	0.037 ± 0.0631	0.02	0.57	81.8
IP	6.50	0.162 ± 0.0459	0.40	< 0.01	18.5
D(ah)A	6.75	0.048 ± 0.0468	0.05	0.32	63.0

[a]FL = fluorene, PHE = phenanthrene, AN = anthracene, FLT = fluoranthene, PY = pyrene, B(a)A = benzo[*a*]anthracene, C = chrysene, B(b)F = benzo[*b*]fluoranthene, B(k)F = benzo[*k*]fluoranthene, IP = indeno[*1,2,3-c,d*]pyrene, D(ah)A = dibenzo[*a,h*]anthracene.
[b]PAH values from Mackay *et al.* (1992) except IP which was reported in Maruya *et al.* (1996).

Table 2.2. Relationship between elimination rate constants (k_2) and log K_{ow} of PCB and PAH compounds in different species.

Species	Compound	n	Regression equation	r^2	Ref.
Eastern Elliptio (*Elliptio complanata*)	PAH	12	$k_2 = 0.39 - 0.05 \log K_{ow}$	0.55	*a*
Zebra mussel (*Dreissena polymorpha*)	PCB	36	$k_2 = 0.39 - 0.05 \log K_{ow}$	0.59	*b*
Green-lipped mussel (*Perna viridis*)	PCB	72	$k_2 = 0.25 - 0.02 \log K_{ow}$	0.50	*c*
Asian clam (*Corbicula fluminea*)	PAH	4	$k_2 = 0.50 - 0.08 \log K_{ow}$	0.46	*d*
Amphipod (*Diporeia hoyi*, formerly *Pontoporeia hoyi*)	PAH	5	$k_2 = 0.24 - 0.03 \log K_{ow}$	0.51	*e*
Oligochaete (*Stylodrilus heringianus*)	PAH	8	$k_2 = 0.74 - 0.07 \log K_{ow}$	0.62	*f*
Mysid (*Mysis relicta*)	PAH	3	$k_2 = 0.35 - 0.01 \log K_{ow}$	0.03	*g*
Isopod (*Asellus aquaticus*)	PAH	5	$k_2 = 4.24 - 0.68 \log K_{ow}$	0.96	*h*
Eastern oysters (*Crassostrea virginica*)	PAH	12	$k_2 = 0.60 - 0.09 \log K_{ow}$	0.75	*i*
Eastern oysters (*Crassostrea virginica*)	PAH	7	$k_2 = -0.08 + 0.02 \log K_{ow}$	0.38	*j*
Blue mussels (*Mytilus edulis*)	PAH	9	$k_2 = -0.04 + 0.01 \log K_{ow}$	0.33	*k*
Hard clam (*Mercenaria mercenaria*)	PAH	12	$k_2 = 0.14 + 0.003 \log K_{ow}$	0.00	*i*
Hard clam (*Mercenaria mercenaria*)	PAH	9	Not significantly depurated		*l*
Water flea (*Daphnia pulex*)	PAH	7	$k_2 = 73.1 - 12.2 \log K_{ow}$	0.80	*m*
Zebrafish (*Brachydanio rerio*)	PAH	4	$k_2 = 0.52 - 0.07 \log K_{ow}$	0.58	*n*
Rainbow trout (*Salmo gairdneri*)	PAH	6	$k_2 = -1.54 + 0.36 \log K_{ow}$	0.82	*o*

[a]this study, [b]Morrison *et al.*(1995), [c]Tanabe *et al.* (1987), [d]Narbonne *et al.* (1999), [e]Landrum (1988), [f]Frank *et al.* (1986), [g]Frez and Landrum (1986), [h]Hattum and Montanes (1999), [i]Bender *et al.* (1988), [j]Sericano (1996), [k]Pruell *et al.* (1986), [l]Tanacredi and Cardenas (1991), [m]Southworth *et al.* (1978), [n]Djomo *et al.* (1996), [o]Niimi and Palazzo (1986).

Figure 2.1. Elimination of PAHs (ln μg/g lipid) over 32 days. The lines represent the linear regression equations. Error bars represent ± 1 SE. AL = acenaphthylene, AE = acenaphthene, FL = fluorene, PHE = phenanthrene, AN = anthracene, FLT = fluoranthene, PY = pyrene, B(a)A = benzo[*a*]anthracene, C = chrysene, B(b)F = benzo[*b*]fluoranthene, B(k)F = benzo[*k*]fluoranthene, IP = indeno[*1,2,3-c,d*]pyrene, D(ah)A = dibenzo[*a,h*]anthracene, B(ghi)P = benzo[*g,h,i*]perylene.

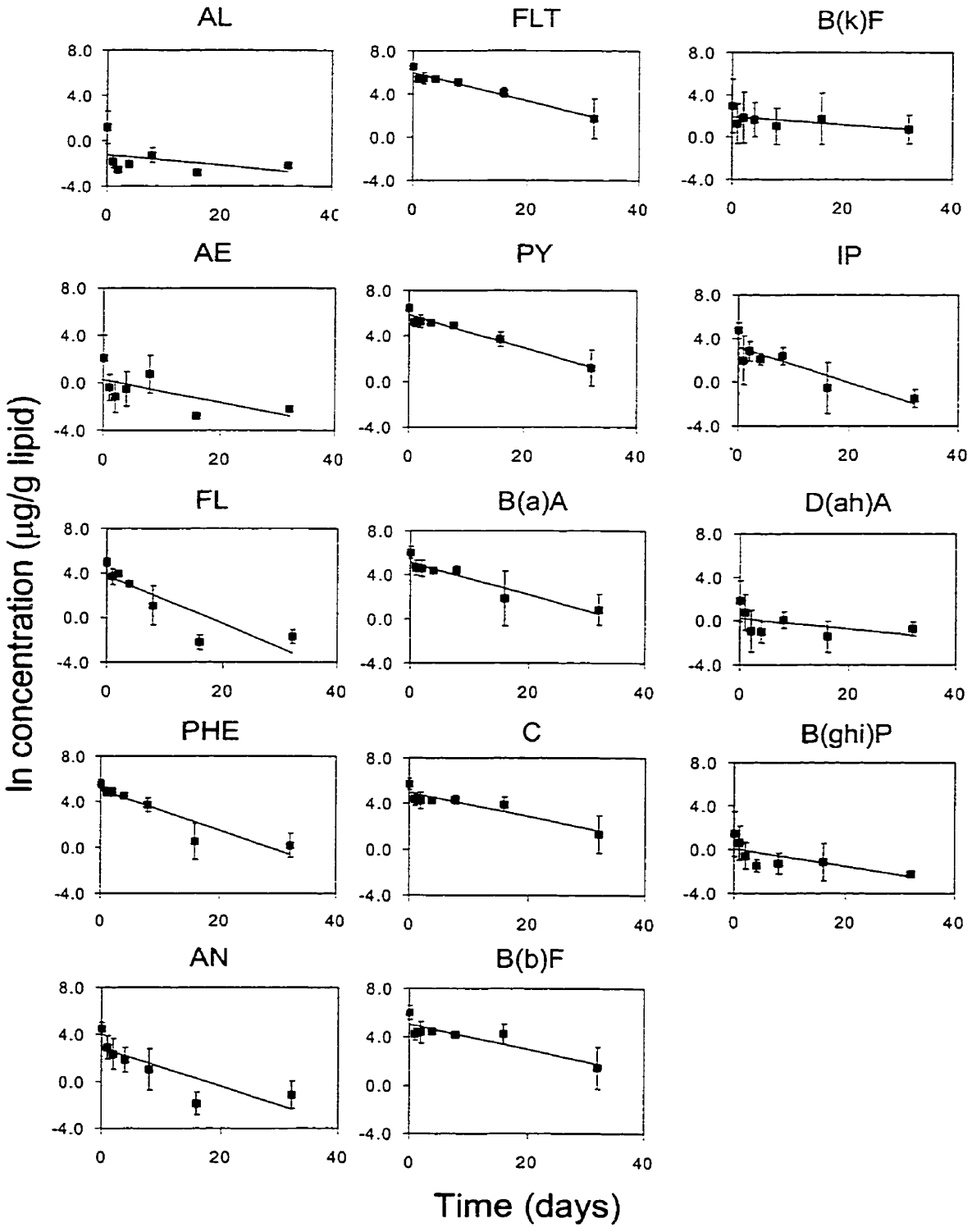
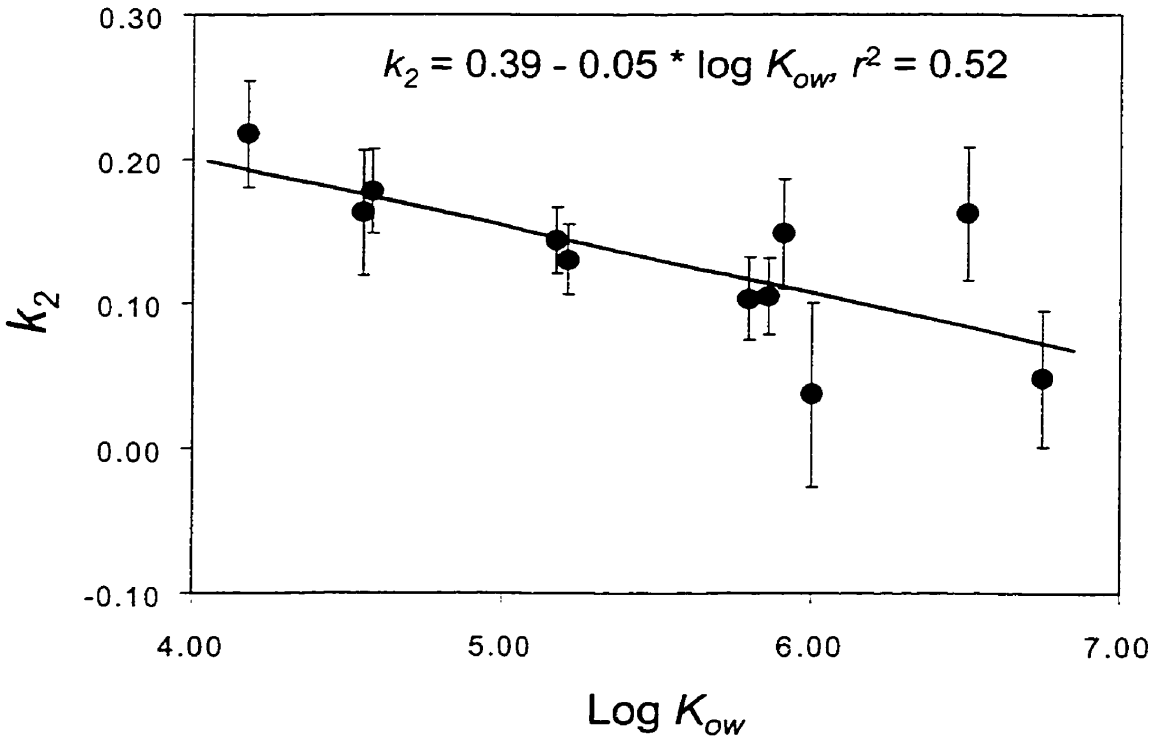

AL
FLT
B(k)F
AE
PY
IP
FL
B(a)A
D(ah)A
PHE
C
B(ghi)P
AN
B(b)F
8.0
4.0
0.0
-4.0
0
20
40
ln concentration (µg/g lipid)
Time (days)

Figure 2.2. Elimination rate constants (k_2) of 11 PAH compounds in *Elliptio complanata* versus log K_{ow}. The line represents the linear regression equation. Error bars represent ± 1 SE.


$k_2 = 0.39 - 0.05 * \log K_{ow}$, $r^2 = 0.52$
0.30
0.20
0.10
0.00
-0.10
k_2
4.00
5.00
6.00
7.00
Log K_{ow}

Chapter 3.0: Biomonitoring of Bioavailable PAH and PCB Water Concentrations in the Detroit River Using the Freshwater Mussel, *Elliptio complanata*

3.1 Abstract

Bioavailable PAH and PCB water concentrations were evaluated along the Detroit River using the freshwater mussel, *Elliptio complanata*. Water concentrations of the sum of 10 PAH compounds ranged from 64.2 to 620.7 ng/L while concentrations of the sum of 35 PCB congeners ranged from 0.11 to 3.01 ng/L. Water concentrations of the low K_{ow} compounds were much higher than the high K_{ow} compounds. A principal component analysis grouped contaminants primarily on the basis of hydrophobicity, indicating that physical-chemical properties regulate the relative concentrations and distributions of PAHs and PCBs among sites. Concentrations of the more hydrophobic PAHs and more water soluble PCBs were present at elevated concentrations at the Detroit Edison Generating Station, in the Trenton Channel. High PAH concentrations were also detected at 3 other sites along the Detroit River. This study supports the conclusion that *E. complanata* is an effective biomonitor of water PAH and PCB concentrations in aquatic systems. In addition, the results indicate that areas of high contamination are present in the Detroit River which reflect the continued loading of these chemicals to the lower Great Lakes.

3.2 Introduction

Polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) are important contaminants in aquatic systems. Although PAHs do not biomagnify, PAH metabolites are genotoxic and carcinogenic (Neff, 1979). PCBs are known to biomagnify to high concentrations up the food chain (Koslowski *et al.*, 1994; Morrison *et al.*, 1997)

and coplanar congeners are highly toxic to the biota because they are similar to 2,3,7,8-tetrachlorodibenzo-*p*-dioxin in molecular configuration (Metcalfe and Haffner, 1995). Since water is a major exposure route of PAHs and PCBs to aquatic organisms (Morrison *et al.*, 1997; Thomann and Komlos, 1999), it is important to measure bioavailable contaminant concentrations in the water to quantify the relative importance of direct chemical uptake from water. Direct water measurements are costly, time-consuming, require large sample sizes, can miss periods of high contamination, and do not necessarily reflect the bioavailable fraction (Phillips and Segar, 1986; Morrison *et al.*, 1995).

Mussel species are often used as surrogates of direct water measurements (Morrison *et al.*, 1995; Neff and Burns, 1996). The use of the freshwater mussel, *Elliptio complanata*, as a surrogate of PAH and PCB water concentrations, has several advantages. First, *E. complanata* is abundant at many locations (Curry, 1977/78). Since *E. complanata* is an intensive filter feeder (Pennak, 1978) with limited ability for chemical metabolism (James, 1989), this organism can rapidly bioconcentrate contaminants that are undetectable in the water phase to quantifiable concentrations. The contaminant burden in mussels represents a time averaged exposure concentration for the period of uptake (Phillips and Segar, 1986). Thus mussels are able to continuously track contaminant discharges. Although mussels are exposed to contaminants from both water and suspended sediment, water has been shown to be the predominant source (Obana, *et al.*, 1983; Pruell, *et al.*, 1986; Tanabe and Tatsukawa, 1987; Muncaster *et al.*, 1989; Muncaster *et al.*, 1990; Kauss and Hamdy, 1991; Bruner *et al.*, 1994). Being sessile organisms, contaminant body burdens of mussels are representative of specific areas.

Finally, biomonitors such as *E. complanata* provide information on the amount of chemical that is available to be taken up by the biota, thus eliminating the need for studies on chemical speciation to determine bioavailable fractions (Phillips and Segar, 1986).

The Detroit River is a highly industrialized shipping channel, connecting Lake Erie with Lake St. Clair. This river is heavily affected by anthropogenic chemicals including PAHs and PCBs (Fallon and Horvath, 1985; Furlong *et al.*, 1988; Metcalfe *et al.*, 1997; Leadley *et al.*, 1998). The Detroit River was identified as an Area of Concern by the International Joint Commission and a Remedial Action Plan (RAP) has been initiated to focus protection and restoration efforts. Frequent monitoring of contaminant water concentrations is needed to ensure continued progress of the RAP program.

The objective of this study was to assess PAH and PCB water concentrations within the Detroit River using the contaminant body burden of *E. complanata*, introduced in cages. Although *E. complanata* has been previously employed in several studies to monitor PAH (Heit *et al.*, 1980; Kauss and Hamdy, 1991) and PCB (Koenig and Metcalfe, 1990; Metcalfe and Charlton, 1990) concentrations, few studies have used mussels as a direct alternative to water measurements. *E. complanata* has been calibrated as a biomonitor of PAH and PCB water concentrations (Chapter 2) by determining elimination rate constants (k_2) of PAHs and PCBs from this organism to water. With this information water chemical concentrations can be directly calculated as a function of chemical accumulation by the mussels.

3.3 Materials and Methods

3.3.1 Field Methods

In April 1998, *E. complanata* was collected from Balsam Lake, which is located in central Ontario, using SCUBA. The mussels were maintained in a carbon-filtered aquarium until the start of the study. At the beginning of May, the mussels were introduced to 10 sites along the Detroit River (Fig. 3.1). Mussels were contained in galvanized steel minnow traps of 1/4″ square mesh that were 16.5″ long × 9″ wide at the largest diameter. All cages, except by Grassy Island, were suspended in the water column and thus not in contact with sediment. The cage at the Grassy Island site was situated on hard sediment because the water at this location was very shallow. Three mussels from each cage were sampled after 3 weeks (end of May/beginning of June), 9 weeks (July), 18 weeks (September) and 32 weeks (December). Additional caged mussels were placed at Middle Sister Island in western Lake Erie at the end of July and sampled after 3 weeks. In some cases, mussels could not be retrieved because the cages were lost as a result of vandalism or storms. Mussels by Ambassador Bridge, Fighting Island South Light, Grassy Island, and the Detroit Edison Generating Station were not sampled in December as these sites were not accessible at this time of year. Sampled mussels were placed in hexane rinsed foil and stored at –20°C until analysis.

3.3.2 Chemical Analysis

Chemical analysis was performed at the analytical laboratory at the Great Lakes Institute for Environmental Research at the University of Windsor, which has been accredited by the Canadian Association for Environmental Analytical Laboratories (CAEAL). The PAH and PCB analysis techniques are approved by CAEAL and annual

reference CAEAL sediment samples are run. Sample preparation was performed according to Lazar *et al.* (1992). Briefly, each mussel was shucked and the tissue was homogenized with anhydrous sodium sulfate using a mortar and pestle. Preliminary results showed that the combined tissues of 3 mussels were necessary to quantify PAHs. Therefore, the tissues from the 3 mussels for each cage per sampling date were composited. The weight of the composite samples were 10.10 ± 2.056 g (mean ± SE). The samples were poured into 35 cm × 2 cm glass columns that were plugged with glass wool, filled with 30 mL of dichloromethane (DCM):hexane (1:1) and 2 cm of Na_2SO_4. Internal standards of tribromobenzene, tetrachloro-m-xylene, and decachlorobiphenyl were added to the columns. After one hour, the samples were eluted with 250 mL of DCM:hexane (1:1). Five mL of isooctane was added to each sample, which were then rotoevaporated to 5 mL using a Büchi Rotoevaporater. The samples were made up to 25 mL with hexane. Lipid determination was done by evaporating 2 mL of each sample for an hour at 105°C and percent lipid was determined gravimetrically. The remaining portion of the samples was rotoevaporated to 1.5-2 mL and transferred to 35 cm × 1 cm glass columns that were plugged with glass wool, filled with 6 g of activated florisil, 2 cm of Na_2SO_4, and hexane. Fraction 1 (containing PCBs) was eluted with 50 mL of hexane. Fraction 2 (containing PAHs) was eluted with 100 mL of DCM:hexane (3:2). Extracts were then rotoevaporated to less than 1 mL. Fraction 1 was made up to a final volume of 5 mL with isooctane and Fraction 2 was made up to a final volume of 1 mL.

3.3.3 Gas Chromatography

Gas chromatographic analysis of Fraction 1 was performed on a Hewlett-Packard (HP) (Avondale, PA, USA) 5890, Series II Plus Model, equipped with an electron

capture detector, a HP-3396 integrator, a HP-7673A autosampler, and a 30 m × 0.25 mm DB-5 column. Injection was 1 μL spitless at 250°C and oven temperature was programmed from 100 to 270°C at 3°C /min. Carrier gas was ultra-high purity helium at 30 cm/s flow rate and makeup gas as Ar/CH_4 (95%/5%) at 50 mL/min. Gas chromatographic analysis of Fraction 2 was performed on a HP 5890/5979 equipped with a mass selective detector, a HP-7673A autosampler, and a 30 m × 0.25 mm DB-5 column. Injection was 1 μL spitless at 250°C and oven temperature was programmed from 100 to 270°C at 3°C /min. Carrier gas was ultra-high purity helium at 30 cm/s flow rate. Fraction 1 was analyzed for 39 PCB compounds and Fraction 2 was analyzed for 17 PAHs. The PCBs have a wide range of water solubilities and include both mono-*ortho*-substituted and non-coplanar compounds. The PAHs have been identified as priority compounds by the United States Environmental Protection Agency and are often considered the most bioavailable and mobile aromatic hydrocarbons within aquatic environments due to their relatively small molecular size. The detection level was 0.5 ng/g wet weight for PAHs and 0.05 ng/g wet weight for PCBs. The percent recoveries of internal standards were 99.08 ± 4.852, 95.28 ± 3.143, and 101.91 ± 3.114 (mean ± SE) for tribromobenzene, tetrachloro-m-xylene, and decachlorobiphenyl respectively. Concentrations were not corrected for the recovery of internal standards. For both PAH and PCB gas chromatographic analysis, a Canadian Wildlife Service herring gull (*Larus argentatus*) egg homogenate standard was run every tenth sample, and a method blank was run every sixth sample.

3.3.4 Calculation of Water Contaminant Concentrations from Mussel Body Burden

The two-compartment model that describes chemical uptake by mussels from water is:

$$\frac{dC_{mu}}{dt} = k_1 C_w - k_2 C_{mu} \tag{3.1}$$

where C_{mu} is the lipid-normalized chemical concentration in the mussels, C_w is the bioavailable water concentration, k_1 is the uptake rate constant, and k_2 is the elimination rate constant. If C_w is constant, which is a valid assumption under field conditions, equation (3.1) can be integrated as follows:

$$C_{mu} = C_w\left(\frac{k_1}{k_2}\right)\left(1 - e^{-k_2 t}\right) \tag{3.2}$$

Under steady-state conditions, using equation (3.1), the octanol-water partition coefficient (K_{ow}) can be related to the rate constants:

$$K_{ow} = \frac{k_1}{k_2} \tag{3.3}$$

Combining equations (3.2) and (3.3), C_w can be expressed as:

$$C_w = \frac{C_{mu}}{(K_{ow})\left(1 - e^{-k_2 t}\right)} \tag{3.4}$$

where C_w represents the average bioavailable water concentration during the time it takes the mussels to achieve steady-state with the water phase. The C_{mu} values were determined in this study and the log K_{ow} of each chemical are listed in Table 3.1 and Table 3.2. The k_2 values of PAHs and PCBs in *E. complanata* were determined in Chapter 2, where k_2 was related to K_{ow} as follows:

$$k_2 = 0.39(\pm 0.083) - 0.05(\pm 0.015)\log K_{ow},\ r^2 = 0.52,\ n = 11 \tag{3.5}$$

This relationship is only valid for contaminants whose rate of elimination by the mussels is not being significantly affected by metabolism.

Equation (3.4) can be used to calculate water concentrations even if the mussels have not yet achieved steady-state conditions at the time of sampling. However, after longer exposure periods, the term $1-e^{-k_2 t}$ in equation (3.4) approaches 1 and simplifies the equation to:

$$C_w = \frac{C_{mu}}{K_{ow}} \tag{3.6}$$

which is the relationship used by Morrison *et al.* (1995) to calculate water concentrations using zebra mussels which were at steady-state with their environment.

3.4 Results

Prior to analysis, acenaphthylene, acenaphthene, benzo[*a*]pyrene, and benzo[*g,h,i*]perylene were deleted because the calibration study revealed that these compounds were being metabolized by the mussels (Chapter 2). Dibenzo[*a,h*]anthracene, and PCB 158 were not further analyzed as these compounds were not frequently detected in samples. Other contaminants that were not consistently quantified, yet known to be present, were replaced with the detection limit value.

Contaminant water concentrations along the Detroit River and at Middle Sister Island in Lake Erie were calculated using equations (3.4) and (3.5) and are summarized in Tables 3.1 and 3.2. Tables 3.1 and 3.2 reveal that the less hydrophobic compounds, such as naphthalene and fluorene, are present at much higher concentrations than the more hydrophobic chemicals with higher K_{ow}s.

Although in Chapter 2 it was found that the mussels were metabolizing naphthalene, this compound was included in the analysis because it was detected in all samples at concentrations considerably above detection limit values. However, since the k_2 value used for naphthalene was predicted assuming passive elimination from the mussels, the estimates of water concentrations of naphthalene as determined by equation (3.4) are biased low.

Statistical analyses were performed to test for differences among sites for PAHs and PCBs. Mussels collected after 3 and 9 weeks of exposure were the only samples statistically analyzed because of the completeness of the data sets for these occasions. Sites included in the analysis were: Lake St. Clair, Riverside Marina, Ambassador Bridge, Outfall of West Windsor Pollution Control Plant, Downstream of West Windsor Pollution Control Plant, Goyers Marina, Grassy Island, Fighting Island South Light, and Detroit Edison Generating Station. Data were log transformed to control heteroscedasticity. To reduce autocorrelation among contaminants, Principal Component Analysis (PCA) was performed using STATISTICA '98 Edition. PCA increases the power of statistical tests by grouping congeners into orthogonal components, thereby reducing the number of variables. The results of the PCA are shown in Table 3.3. For both PAHs and PCBs, 3 components were determined and contaminants were classified into these components primarily on the basis of hydrophobicity.

The PAH and PCB factor scores were analyzed in 9 × 2 non-replicated multivariate analysis of variances (MANOVAs) to test for differences among sites and dates. The MANOVAs were performed with the general linear model procedure of the SAS statistical package. For both classes of compounds, there was an overall significant

difference among sites (for PAHs, Wilks' Lambda = 0.013, $p = 0.02$, for PCBs, Wilks' Lambda = 0.022, $p = 0.002$). For PAH compounds, there were significant differences present among sites for component 1 ($p < 0.01$) but not for component 2 or component 3 ($p > 0.05$). For PCBs, there were significant differences present for component 1 ($p < 0.05$) and component 2 ($p < 0.01$). There were no overall significant differences among sampling dates (for PAHs, Wilks' Lambda = 0.58, $p > 0.05$, for PCBs, Wilks' Lambda = 0.64, $p > 0.05$). Unplanned multiple comparisons were performed with the Tukey test ($\alpha = 0.05$) and results are indicated in Fig. 3.2. The Tukey test detected differences in factor scores among sites only for PAH component 1 and PCB component 2, which consisted of congeners with similar K_{ow}s (Table 3.3). For both these components, factor scores were elevated at the Detroit Edison Generating Station.

3.5 Discussion

Contaminant concentration in the water depended highly on hydrophobicity. Water concentrations of the sum of 10 PAH compounds ranged from 64.2 to 620.7 ng/L while concentrations of the sum of 35 PCB congeners ranged from 0.11 to 3.01 ng/L. Water concentrations of the low K_{ow} compounds were several orders of magnitude higher than the high K_{ow} compounds. This indicates that the sum of total PAHs and PCBs is only representative of the more water soluble compounds, such as naphthalene, and does not reflect the spatial and temporal variability of the other chemicals.

In many cases, PAH compounds were present at much higher concentrations than PCB congeners of comparable hydrophobicity. Lower PCB concentrations are likely a result of the ban imposed on the use and production of PCBs by most western countries in the late 1970s. Presently, the major source of PCBs into aquatic systems is thought to

be from previously contaminated sediments (Koslowski *et al.*, 1994) and landfills (Tanabe, 1988). In contrast, PAHs are still being released in large quantities by industrial processes along the Detroit River.

The PCA grouped contaminants together with similar hydrophobicity. This suggests that the relative concentrations and distributions of PAHs and PCBs among sites in the Detroit River depended principally on the physical-chemical properties of the contaminants. PCAs from previous studies have also grouped organic contaminants primarily on the basis of hydrophobicity (Koslowski *et al.*, 1994; Morrison *et al.*, 1995; Mazak *et al.*, 1997; Haffner *et al.*, 1997). PAH component 1 and PCB component 2, which contained compounds of similar K_{ow}s (Table 3.3), were distributed similarly along the Detroit River (Fig. 3.2). Therefore, for the contaminants evaluated in this study, bioavailable chemical concentrations are strongly determined by the hydrophobicity of the chemical.

Significant differences among sites (Tukey test, $p < 0.05$) were observed for PAH component 1 and PCB component 2. Contaminants associated with these components were most elevated at the Detroit Edison Generating Station. This location is along the Trenton Channel, which has been previously identified as a region of high contamination (Fallon and Horvath, 1985; Kauss and Hamdy, 1985; Ali *et al.*, 1993; Leadley *et al.*, 1998). Elevated concentrations of PAH contaminants, compared to other sites, that were associated with component 1 were also detected Downstream of West Windsor Pollution Control Plant, Grassy Island, and Ambassador Bridge.

For PCB compounds, only the lower K_{ow} compounds were elevated at the Detroit Edison Generating Station. This suggests that there are ongoing sources of PCBs into the

Trenton Channel. There are several landfill sites located in this area, and it is possible that during storms the more water soluble PCBs stored at these sites would preferentially partition into the rainwater and be transported to the river. If contaminated sediment was the major source of PCBs to the mussels deployed in the Trenton Channel, a higher proportion of the more hydrophobic compounds would have been detected as observed at other sites along the river.

For PAHs, no significant differences in the concentrations of the more water soluble compounds were found among sites. These PAH compounds, which have K_{ow}s that are lower than any of the PCBs, are more mobile in the water phase compared with other chemicals, thus becoming more evenly distributed along the Detroit River.

Although PAH and PCB concentrations at Middle Sister Island were not included in the statistical analysis, Table 3.1 and Table 3.2 indicates that concentrations for many compounds at this site were remarkably similar to those in the Detroit River. This suggests that Detroit River contaminants are being transported directly into the western Lake Erie system, and thus are likely influencing the health of the Lake Erie biota. Other studies have also found that Detroit River derived hydrophobic chemicals are a major source of contaminants to western Lake Erie (Kelly *et al.*, 1991; Carter and Hites, 1992; Corkum *et al.*, 1997). Some compounds, such as naphthalene, PCB 171, and PCB 180, were considerably elevated at Middle Sister Island compared with the Detroit River. It was thus hypothesized that storm events might also contribute to the high PAH and PCB concentrations observed at this island. Storms cause resuspension of contaminated sediment particles into the water column (Scheffer, 1998), which would increase partitioning of sediment-associated chemicals into the water phase. Storms have a

greater effect on Lake Erie than on the Detroit River because of the larger fetch distance in this shallow lake.

The water concentrations measured in this study were comparable to previous data. In 1995 and 1996, Froese *et al.* (1997) found, using XAD-2 resin extracts, that the dissolved concentration of the sum of 110 PCBs ranged from < 5 to 13 ng/L at different locations in the Trenton Channel. In 1994, Metcalfe *et al.* (2000) found, using semi-permeable membrane devices, that the water concentration of the total of 26 PCBs at Elizabeth Park in the Trenton Channel was 9.8 ng/L. In this study, it was found that the sum of 35 PCBs at the Detroit Edison Generating Station was 1.7 ng/L in June and 3.0 ng/L in July 1998. In 1994, Morrison *et al.* (1995) calculated water concentrations as a function of zebra mussel contaminant burden and they found that at Middle Sister Island the water concentration of the sum of 33 PCBs was 0.94 ng/L. It was determined in this study that the sum of 35 PCB congeners at Middle Sister Island was 0.71 ng/L. Water PCB concentrations were also evaluated by large volume analysis with a Goulden continuous extractor and the concentrations were within an order of magnitude of water concentrations derived from zebra mussels for PCB congeners with log K_{ow} < 6.6 (Morrison *et al.*, 1995). The contribution of particle-bound PCBs became more significant for more hydrophobic PCB congeners, which potentially caused the mussels to over estimate water measurements.

3.6 Conclusions

The freshwater mussel, *E. complanata*, was shown to effectively monitor PAH and PCB bioavailable water concentrations in the Detroit River. The data confirms that the physical-chemical properties of hydrophobic organic contaminants have a major

influence on chemical behavior in the water phase of aquatic systems. The Trenton Channel remains an area of high PAH and PCB contamination, which is likely causing significant toxicological stress to native species in this channel and in western Lake Erie. Remediation efforts should continue to focus in this area and begin to take note of the potential toxicological stress related to exposure of PAHs.

Table 3.1. Bioavailable PAH water concentrations estimated from *Elliptio complanata* chemical body burden along the Detroit River and western Lake Erie.

Site[b]	Date sampled	Exposure time (d)	PAH[a] water concentration (ng/L)									
			NA	FL	PHE	AN	FLT	PY	B(a)A	C/T	B(b)F	IP
Log K_{ow}[c]			3.37	4.18	4.57	4.54	5.22	5.18	5.91	5.86	5.80	6.50
CL	19-May-98	21	119.61	8.79	13.90	*1.31	4.83	*0.31	*0.06	0.48	*0.08	*0.02
CL	6-Jul-98	69	152.12	*3.44	8.03	*1.50	2.49	*0.34	*0.06	0.51	*0.08	*0.02
CL	10-Sep-98	135	317.43	*4.72	6.91	*2.06	3.21	*0.47	*0.09	0.10	*0.11	*0.02
CL	11-Dec-98	227	337.02	*5.80	30.56	*2.53	9.38	*0.58	*0.11	1.30	*0.14	*0.03
RS	20-May-98	21	131.52	*2.90	6.38	*1.28	3.24	0.80	*0.06	0.47	*0.07	*0.02
RS	6-Jul-98	68	219.72	11.26	16.61	*2.09	5.07	0.55	*0.09	1.54	*0.11	*0.02
RS	10-Sep-98	134	78.21	2.60	4.54	*1.14	1.97	0.26	*0.05	0.31	*0.06	*0.01
RS	11-Dec-98	226	141.86	4.79	10.93	*2.09	3.83	0.48	*0.09	1.00	*0.11	*0.02
AB	11-Jun-98	21	326.55	9.36	21.33	*1.87	15.00	13.52	0.76	3.27	0.44	0.05
AB	27-Jul-98	63	60.94	11.15	38.80	8.61	27.63	29.09	3.20	7.19	3.69	0.40
GL	6-Jul-98	48	71.42	*2.45	9.18	*1.07	3.60	*0.24	*0.05	0.33	*0.06	*0.01
GL	10-Sep-98	115	357.85	*3.71	11.10	*1.62	3.92	*0.87	*0.07	0.31	*0.09	*0.02
GL	11-Dec-98	207	146.44	*5.60	26.73	*2.44	7.28	*1.38	*0.10	1.18	*0.13	*0.03
WO	20-May-98	21	340.72	41.80	61.69	1.46	4.21	0.96	*0.03	0.34	*0.04	*0.01
WO	6-Jul-98	68	106.97	8.01	11.33	0.82	2.46	0.60	*0.03	*0.04	*0.04	*0.01
WO	10-Sep-98	134	457.81	2.92	16.75	1.28	2.07	0.29	*0.05	*0.06	*0.07	*0.01
WO	11-Dec-98	226	164.33	33.53	63.62	2.29	7.60	2.09	*0.10	*0.83	*0.13	*0.03
WD	19-May-98	21	319.53	*2.61	15.26	*1.15	3.44	*0.27	*0.05	0.13	*0.07	*0.01
WD	31-Jul-98	94	154.76	*5.70	22.69	*2.49	8.79	1.45	*0.11	2.14	*0.14	*0.03
WD	10-Sep-98	135	231.63	*4.18	11.24	*1.83	2.84	1.12	*0.08	0.20	*0.10	*0.02
GY	20-May-98	21	73.25	7.88	17.52	*1.28	6.76	2.17	0.07	0.76	0.11	*0.02
GY	31-Jul-98	93	354.21	12.55	27.17	*2.22	8.52	2.01	*0.09	2.05	*0.12	*0.02
GY	10-Sep-98	134	109.10	4.57	13.72	*1.72	6.74	2.36	*0.09	0.71	*0.11	*0.02
GY	11-Dec-98	226	85.71	10.13	26.15	*1.70	7.95	2.90	*0.07	1.28	*0.09	*0.02
GI	11-Jun-98	21	235.05	9.86	19.89	*1.97	15.46	18.96	1.02	3.96	1.57	0.04
GI	27-Jul-98	63	29.08	6.01	13.76	*1.64	10.61	13.44	0.69	2.46	0.34	0.04
GI	28-Sep-98	126	503.15	25.41	71.43	*1.85	8.81	6.44	0.77	1.70	1.16	0.03

Table 3.1. continued.

Site[b]	Date sampled	Exposure time (d)	PAH[a] water concentration (ng/L)									
			NA	FL	PHE	AN	FLT	PY	B(a)A	C&T	B(b)F	IP
Log K_{ow}[c]			3.37	4.18	4.57	4.54	5.22	5.18	5.91	5.86	5.80	6.50
FI	11-Jun-98	21	151.07	*4.54	5.97	*2.00	2.66	0.84	*0.09	0.47	*0.12	*0.03
FI	27-Jul-98	63	49.22	*3.18	5.95	*1.39	2.67	1.14	0.06	0.45	0.09	0.02
FI	28-Sep-98	126	245.61	*6.01	11.83	*2.18	4.02	1.90	0.09	0.67	0.50	*0.02
DE	11-Jun-98	21	78.18	14.27	41.45	2.69	29.48	48.76	3.47	9.50	3.34	0.13
DE	27-Jul-98	63	36.86	10.60	30.57	6.41	29.09	52.70	4.12	11.99	15.31	0.23
MSI	19-Aug-98	21	309.27	5.90	5.82	*2.60	1.89	*0.61	*0.12	0.48	0.15	0.03

[a] NA = naphthalene, FL = fluorene, PHE = phenanthrene, AN = anthracene, FLT = fluoranthene, PY = pyrene, B(a)A = benzo[*a*]anthracene, C/T = chrysene/triphenylene, B(b)F = benzo[*b*]fluoranthene, IP = indeno[*1,2,3-c,d*]pyrene.
[b]Location of sites shown in Fig. 3.1. CL = Lake St. Clair, RS = Riverside Marina, AB = Ambassador Bridge, GL = Great Lakes Institute for Environmental Research, University of Windsor, WO = Outfall of West Windsor Pollution Control Plant, WD = Downstream of West Windsor Pollution Control Plant, GY = Goyers Marina, GI = Grassy Island, FI = Fighting Island South Light, DE = Detroit Edison Generating Station, MSI = Middle Sister Island.
[c] log K_{ow} values from Mackay *et al.* (1991) except IP which was reported in Maruya *et al.* (1996).
Asterisk (*) indicates that PAH compound was not detected in mussels and was substituted with detection limit of 0.5 ng/g on a wet weight basis.

Table 3.2. Bioavailable PCB water concentrations estimated from *Elliptio complanata* chemical body burden along the Detroit River and western Lake Erie.

			PCB Water Concentration (ng/L)											
Site[a]	Date sampled	Exposure time (d)	PCB 31/28	PCB 52	PCB 49	PCB 44	PCB 42	PCB 64	PCB 74	PCB 70	PCB 66/95	PCB 60	PCB 101	PCB 99
Log K_{ow}[b]			5.6	6.1	6.1	6	5.6	6.1	6.1	5.9	5.8	5.9	6.4	6.6
CL	19-May-98	21	0.075	0.063	0.068	0.030	0.046	0.005	*0.004	0.015	0.073	0.019	0.025	0.006
CL	6-Jul-98	69	0.049	0.028	0.042	0.026	0.035	*0.004	*0.004	0.014	0.050	0.023	0.013	0.004
CL	10-Sep-98	135	*0.018	0.021	*0.006	0.011	*0.018	*0.006	*0.006	*0.009	0.031	0.012	0.010	0.002
CL	11-Dec-98	227	0.085	0.055	0.068	0.038	0.054	0.007	*0.007	0.022	0.062	0.034	0.020	0.006
RS	20-May-98	21	0.024	0.023	0.007	0.010	*0.012	*0.004	*0.004	0.009	0.047	0.016	0.019	0.003
RS	6-Jul-98	68	0.059	0.039	0.084	0.028	*0.019	0.006	*0.006	0.032	0.142	0.045	0.040	0.011
RS	10-Sep-98	134	*0.010	*0.003	*0.003	0.009	*0.010	*0.003	*0.003	*0.005	0.026	0.014	0.015	0.003
RS	11-Dec-98	226	0.018	0.017	0.038	0.011	*0.019	*0.006	*0.006	0.010	0.051	0.019	0.023	0.005
AB	11-Jun-98	21	0.099	0.105	0.046	0.043	0.105	*0.006	0.031	0.080	0.233	0.082	0.089	0.026
AB	27-Jul-98	63	*0.016	0.080	0.049	0.042	0.046	*0.005	0.017	0.051	0.171	0.087	0.074	0.019
GL	6-Jul-98	48	0.045	0.060	0.032	0.032	0.038	0.005	0.008	0.054	0.119	0.038	0.032	0.011
GL	10-Sep-98	115	0.036	0.037	0.011	0.034	*0.016	0.005	*0.005	0.030	0.085	0.034	0.029	0.008
GL	11-Dec-98	207	0.113	0.072	0.076	0.047	0.079	0.008	0.015	0.046	0.149	0.060	0.051	0.015
WO	20-May-98	21	0.018	0.013	0.009	0.010	*0.007	*0.002	*0.002	*0.004	0.015	0.007	0.003	0.001
WO	6-Jul-98	68	0.091	0.040	0.006	0.030	0.016	0.004	0.008	0.018	0.049	0.013	0.010	*0.001
WO	10-Sep-98	134	0.058	*0.004	*0.004	0.016	*0.011	*0.004	*0.004	*0.006	0.042	0.023	0.008	*0.001
WO	11-Dec-98	226	0.112	0.053	0.032	0.042	0.047	0.007	0.013	0.034	0.081	0.030	0.022	0.005
WD	19-May-98	21	0.069	0.050	0.010	0.029	0.023	0.005	*0.004	0.026	0.052	0.020	0.011	0.004
WD	31-Jul-98	94	0.056	0.067	0.040	0.052	0.065	0.008	*0.008	0.047	0.116	0.038	0.029	0.010
WD	10-Sep-98	135	0.060	0.030	0.016	0.026	0.022	*0.005	*0.005	0.026	0.058	0.025	0.016	0.005
GY	20-May-98	21	0.068	0.051	0.031	0.048	0.087	0.004	0.010	0.031	0.077	0.036	0.022	0.006
GY	31-Jul-98	93	0.087	0.072	0.065	0.057	0.047	0.006	*0.006	0.040	0.122	0.049	0.039	0.010
GY	10-Sep-98	134	0.037	0.036	0.019	0.036	0.047	0.005	0.007	0.025	0.069	0.033	0.027	0.007
GY	11-Dec-98	226	0.051	0.037	0.032	0.026	0.031	*0.005	*0.005	0.015	0.063	0.028	0.024	0.007
GI	11-Jun-98	63	0.100	0.095	0.033	0.055	0.133	*0.006	0.014	0.077	0.149	0.031	0.045	0.011
GI	27-Jul-98	126	0.066	0.053	0.027	0.043	0.037	0.005	0.034	0.063	0.137	0.053	0.043	0.013

Table 3.2. continued.

Site[a]	Date sampled	Exposure Time (d)	PCB Water Concentration (ng/L)											
			PCB 31/28	PCB 52	PCB 49	PCB 44	PCB 42	PCB 64	PCB 74	PCB 70	PCB 66/95	PCB 60	PCB 101	PCB 99
Log K_{ow}[b]			5.6	6.1	6.1	6	5.6	6.1	6.1	5.9	5.8	5.9	6.4	6.6
GI	28-Sep-98	21	0.039	0.038	0.019	0.033	*0.016	*0.005	0.014	0.031	0.082	0.030	0.021	0.008
FI	11-Jun-98	63	*0.018	*0.006	*0.006	0.012	*0.018	*0.006	*0.006	0.019	0.028	*0.009	0.007	0.003
FI	27-Jul-98	126	*0.012	*0.004	*0.004	0.016	*0.012	*0.004	*0.004	0.011	0.024	*0.006	0.006	0.001
FI	28-Sep-98	21	*0.019	0.013	0.007	0.024	*0.019	*0.006	*0.006	*0.010	0.029	*0.010	0.008	0.003
DE	11-Jun-98	21	0.408	0.173	0.070	0.112	0.101	0.016	0.057	0.154	0.282	0.115	0.067	0.022
DE	27-Jul-98	63	0.530	0.262	0.111	0.180	0.189	0.021	0.126	0.319	0.558	0.154	0.136	0.039
MSI	19-Aug-98	21	*0.024	0.047	0.014	0.025	*0.024	*0.008	*0.008	0.024	0.133	0.041	0.049	0.014

Table 3.2. continued.

Site[a]	Date sampled	Exposure time (d)	PCB Water Concentration (ng/L)											
			PCB 97	PCB 87	PCB 110	PCB 151	PCB 149	PCB 118	PCB 146	PCB 153	PCB 105	PCB 138	PCB 129	PCB 182/187
Log K_{ow}[b]			6.6	6.5	6.5	6.9	6.8	6.4	6.9	6.9	6.4	7	7.3	7.2
CL	19-May-98	21	0.004	*0.002	0.014	0.002	0.011	0.007	*0.001	0.006	0.004	0.007	*0.000	0.002
CL	6-Jul-98	69	0.003	*0.002	0.010	0.001	0.005	0.010	0.001	0.005	0.006	0.006	0.000	0.001
CL	10-Sep-98	135	*0.002	*0.002	0.007	0.001	0.005	0.005	0.001	0.005	*0.003	0.006	*0.000	0.002
CL	11-Dec-98	227	0.004	*0.003	0.015	0.002	0.007	0.016	0.001	0.008	0.004	0.011	0.000	0.002
RS	20-May-98	21	0.002	*0.002	0.009	0.004	0.017	0.005	0.002	0.012	0.007	0.011	0.001	0.004
RS	6-Jul-98	68	0.004	0.004	0.025	0.016	0.065	*0.003	0.008	0.049	0.030	0.041	0.003	0.019
RS	10-Sep-98	134	0.001	*0.001	0.007	0.004	0.019	*0.002	0.003	0.018	0.009	0.016	0.001	0.008
RS	11-Dec-98	226	0.004	*0.002	0.013	0.006	0.027	0.011	0.004	0.031	0.014	0.024	0.001	0.012
AB	11-Jun-98	21	0.006	0.016	0.033	0.017	0.054	*0.003	0.006	0.042	0.040	0.041	0.002	0.012
AB	27-Jul-98	63	0.007	0.012	0.036	0.016	0.053	*0.003	0.007	0.046	0.048	0.041	0.002	0.015
GL	6-Jul-98	48	0.006	0.014	0.019	0.003	0.009	0.019	0.001	0.007	0.006	0.008	0.000	0.002
GL	10-Sep-98	115	0.006	0.006	0.020	0.003	0.009	0.025	0.001	0.007	0.007	0.010	0.000	0.002
GL	11-Dec-98	207	0.010	0.019	0.036	0.004	0.015	0.038	0.002	0.012	0.011	0.016	0.001	0.003
WO	20-May-98	21	0.001	*0.001	0.003	*0.000	0.002	0.003	*0.000	0.002	*0.001	0.002	*0.000	0.000
WO	6-Jul-98	68	0.001	*0.001	0.005	0.000	0.002	*0.001	*0.000	0.002	*0.001	0.002	*0.000	0.000
WO	10-Sep-98	134	*0.001	*0.001	0.005	*0.001	*0.001	*0.002	*0.001	0.001	*0.002	0.002	*0.000	*0.000
WO	11-Dec-98	226	0.004	0.003	0.012	0.002	0.007	0.017	0.002	0.010	0.004	0.010	0.000	0.002
WD	19-May-98	21	0.003	*0.002	0.007	0.001	0.003	0.008	*0.001	0.003	*0.002	0.003	*0.000	0.001
WD	31-Jul-98	94	0.006	0.011	0.021	0.003	0.009	0.022	0.001	0.007	0.006	0.008	*0.000	0.002
WD	10-Sep-98	135	0.002	0.005	0.011	0.001	0.005	0.013	*0.001	0.004	0.003	0.005	*0.000	0.001
GY	20-May-98	21	0.004	0.007	0.014	0.003	0.009	0.014	0.001	0.007	0.009	0.007	0.000	0.002
GY	31-Jul-98	93	0.005	0.010	0.024	0.007	0.024	0.024	0.003	0.019	0.018	0.018	0.001	0.006
GY	10-Sep-98	134	0.004	0.008	0.016	0.005	0.017	0.020	0.002	0.015	0.019	0.014	0.001	0.005
GY	11-Dec-98	226	0.004	0.007	0.013	0.004	0.014	0.017	0.002	0.012	0.010	0.013	0.001	0.004
GI	11-Jun-98	63	0.004	0.012	0.021	0.007	0.024	*0.003	0.003	0.020	0.022	0.020	0.001	0.006
GI	27-Jul-98	126	0.006	0.012	0.028	0.005	0.033	*0.002	0.005	0.032	0.035	0.029	0.002	0.010
GI	28-Sep-98	21	0.005	0.009	0.017	0.006	0.022	*0.003	0.003	0.022	0.022	0.021	0.001	0.007

Table 3.2. continued.

Site[a]	Date sampled	Exposure time (d)	PCB Water Concentration (ng/L)											
			PCB 97	PCB 87	PCB 110	PCB 151	PCB 149	PCB 118	PCB 146	PCB 153	PCB 105	PCB 138	PCB 129	PCB 182/187
Log K_{ow}[b]			6.6	6.5	6.5	6.9	6.8	6.4	6.9	6.9	6.4	7	7.3	7.2
FI	11-Jun-98	63	*0.002	0.004	0.003	*0.001	0.003	*0.003	*0.001	0.003	*0.003	0.003	*0.001	0.001
FI	27-Jul-98	126	*0.001	*0.002	0.003	0.001	0.002	*0.002	*0.001	0.003	0.002	0.003	*0.000	0.001
FI	28-Sep-98	21	0.002	0.004	0.007	0.002	0.006	*0.003	0.001	0.006	0.007	0.007	*0.000	0.002
DE	11-Jun-98	21	0.009	0.021	0.037	0.007	0.018	*0.003	0.002	0.013	0.018	0.015	0.001	0.004
DE	27-Jul-98	63	0.020	0.043	0.082	0.016	0.045	*0.002	0.006	0.034	0.044	0.040	0.002	0.009
MSI	19-Aug-98	21	0.008	0.014	0.035	0.013	0.037	*0.004	0.006	0.033	0.044	0.033	0.002	0.011

Table 3.2. continued.

Site[a]	Date sampled	Exposure time (d)	PCB Water Concentration (ng/L)										
			PCB 183	PCB 185	PCB 174	PCB 171	PCB 180	PCB 170/190	PCB 201	PCB 203	PCB 195	PCB 194	PCB 206
Log K_{ow}[b]			7	7	7	6.7	7.4	7.3	7.5	7.1	7.1	7.1	7.2
CL	19-May-98	21	*0.001	*0.001	0.001	*0.001	0.001	0.001	0.001	0.001	*0.001	*0.001	0.001
CL	6-Jul-98	69	*0.001	*0.001	0.001	*0.001	0.001	0.001	0.000	0.000	*0.000	0.001	0.000
CL	10-Sep-98	135	*0.001	*0.001	0.001	*0.001	0.002	0.001	0.000	0.001	*0.001	0.001	0.001
CL	11-Dec-98	227	*0.001	*0.001	0.002	*0.002	0.003	0.001	0.001	0.001	0.001	0.001	0.001
RS	20-May-98	21	0.002	0.001	0.005	0.002	0.004	0.002	0.001	0.001	0.001	0.001	0.001
RS	6-Jul-98	68	0.009	0.003	0.024	0.010	0.018	0.011	0.005	0.006	0.003	0.007	0.005
RS	10-Sep-98	134	0.002	0.001	0.009	0.004	0.009	0.005	0.003	0.003	0.002	0.004	0.001
RS	11-Dec-98	226	0.002	0.001	0.014	0.003	0.015	0.005	0.004	0.004	0.002	0.006	0.002
AB	11-Jun-98	21	0.005	0.002	0.016	0.012	0.013	0.008	0.003	0.003	0.002	0.003	0.002
AB	27-Jul-98	63	0.008	0.002	0.019	0.013	0.015	0.008	0.003	0.004	0.002	0.004	0.001
GL	6-Jul-98	48	0.001	*0.000	0.002	0.001	0.001	0.001	0.000	0.000	*0.000	0.001	0.000
GL	10-Sep-98	115	*0.001	*0.001	0.002	*0.001	0.002	0.001	0.001	0.001	*0.001	0.001	0.001
GL	11-Dec-98	207	*0.001	*0.001	0.003	0.002	0.002	0.001	0.001	0.001	0.001	0.001	0.001
WO	20-May-98	21	*0.000	*0.000	0.000	*0.001	0.001	0.000	0.000	0.000	*0.000	0.000	0.000
WO	6-Jul-98	68	*0.000	*0.000	0.000	*0.001	0.001	0.000	0.000	0.000	*0.000	*0.000	0.000
WO	10-Sep-98	134	*0.000	*0.000	*0.000	*0.001	0.000	*0.000	*0.000	*0.000	*0.000	*0.000	*0.000
WO	11-Dec-98	226	*0.001	*0.001	0.002	*0.002	0.002	0.001	0.001	0.001	0.001	0.001	0.001
WD	19-May-98	21	*0.001	*0.001	0.001	*0.001	0.001	0.000	0.000	0.000	*0.000	*0.000	0.000
WD	31-Jul-98	94	0.001	*0.001	0.002	0.002	0.001	0.001	0.001	0.001	0.001	*0.001	0.001
WD	10-Sep-98	135	*0.001	*0.001	0.001	*0.001	0.001	0.001	0.000	0.000	*0.001	0.000	0.000
GY	20-May-98	21	0.001	*0.001	0.002	0.002	0.002	0.001	0.000	0.001	*0.000	0.001	0.000
GY	31-Jul-98	93	0.003	0.001	0.007	0.003	0.005	0.003	0.001	0.001	0.001	0.001	0.001
GY	10-Sep-98	134	0.002	0.001	0.006	0.005	0.004	0.002	0.001	0.001	0.001	0.001	0.001
GY	11-Dec-98	226	0.001	0.001	0.005	0.001	0.004	0.002	0.001	0.001	0.001	0.002	0.001
GI	11-Jun-98	63	0.002	*0.001	0.006	0.003	0.006	0.003	0.001	0.001	0.001	0.002	0.001
GI	27-Jul-98	126	0.006	0.001	0.011	0.007	0.009	0.005	0.002	0.003	0.002	0.002	0.001
GI	28-Sep-98	21	0.003	*0.001	0.008	0.008	0.008	0.004	0.002	0.002	0.001	0.002	0.001

Table 3.2. continued.

Site[a]	Date sampled	Exposure time (d)	PCB Water Concentration (ng/L)										
			PCB 183	PCB 185	PCB 174	PCB 171	PCB 180	PCB 170/190	PCB 201	PCB 203	PCB 195	PCB 194	PCB 206
Log K_{ow}[b]			7	7	7	6.7	7.4	7.3	7.5	7.1	7.1	7.1	7.2
FI	11-Jun-98	63	*0.001	*0.001	*0.001	*0.002	0.001	*0.001	0.000	*0.001	*0.001	0.001	*0.001
FI	27-Jul-98	126	*0.000	*0.000	0.001	*0.001	0.001	0.000	0.000	*0.000	*0.000	*0.000	0.000
FI	28-Sep-98	21	*0.001	*0.001	0.002	0.002	0.002	0.001	0.001	0.001	0.001	0.001	0.001
DE	11-Jun-98	21	0.001	*0.001	0.005	0.002	0.003	0.002	0.001	0.001	0.001	0.001	0.001
DE	27-Jul-98	63	0.003	0.002	0.012	0.004	0.008	0.005	0.002	0.002	0.001	0.002	0.001
MSI	19-Aug-98	21	0.004	0.001	0.011	0.010	0.011	0.005	0.003	0.003	0.002	0.003	0.002

[a]Location of sites shown in Fig. 3.1. CL = Lake St. Clair, RS = Riverside Marina, AB = Ambassador Bridge, GL = Great Lakes Institute for Environmental Research, University of Windsor, WO = Outfall of West Windsor Pollution Control Plant, WD = Downstream of West Windsor Pollution Control Plant, GY = Goyers Marina, GI = Grassy Island, FI = Fighting Island South Light, DE = Detroit Edison Generating Station, MSI = Middle Sister Island.

[b] log K_{ow} values from Shiu and Mackay (1986) except for congeners 110, 182/187, 180, and 170/190, which are from Hawker and Connell (1988).

Asterisk (*) indicates that PCB compound was not detected in mussels and was substituted with detection limit of 0.05 ng/g on a wet weight basis.

Table 3.3. Principle component analysis of PAH and PCB water concentrations along the Detroit River, derived from *Elliptio complanata* contaminant burden.

Component	% Variance Explained	PAH[a]/PCB Congener	Log K_{ow} range
PAHs			
1	60	AN, FLT, PY, B(a)A, C/T, B(b)F, IP	4.5 – 6.5
2	21	FL, PHE	4.2 - 4.6
3	11	NA	3.4
PCBs			
1	51	151, 149, 146, 153, 105, 138, 129, 182/187, 183, 185, 174, 171, 180, 170/190, 201, 203, 195, 194, 206	6.4 – 7.5
2	40	31/28, 52, 49, 44, 42, 64, 74, 70, 66/95, 60, 101, 97, 87, 110	5.6 – 6.6
3	3.5	118	6.4

[a]AN = anthracene, FLT = fluoranthene, PY = pyrene, B(a)A = benzo[*a*]anthracene, C/T = chrysene/triphenylene, B(b)F = benzo[*b*]fluoranthene, IP = indeno[*1,2,3-c,d*]pyrene, FL = fluorene, PHE = phenanthrene, NA = naphthalene.

Figure 3.1. Sampling locations in the Detroit River and western Lake Erie.

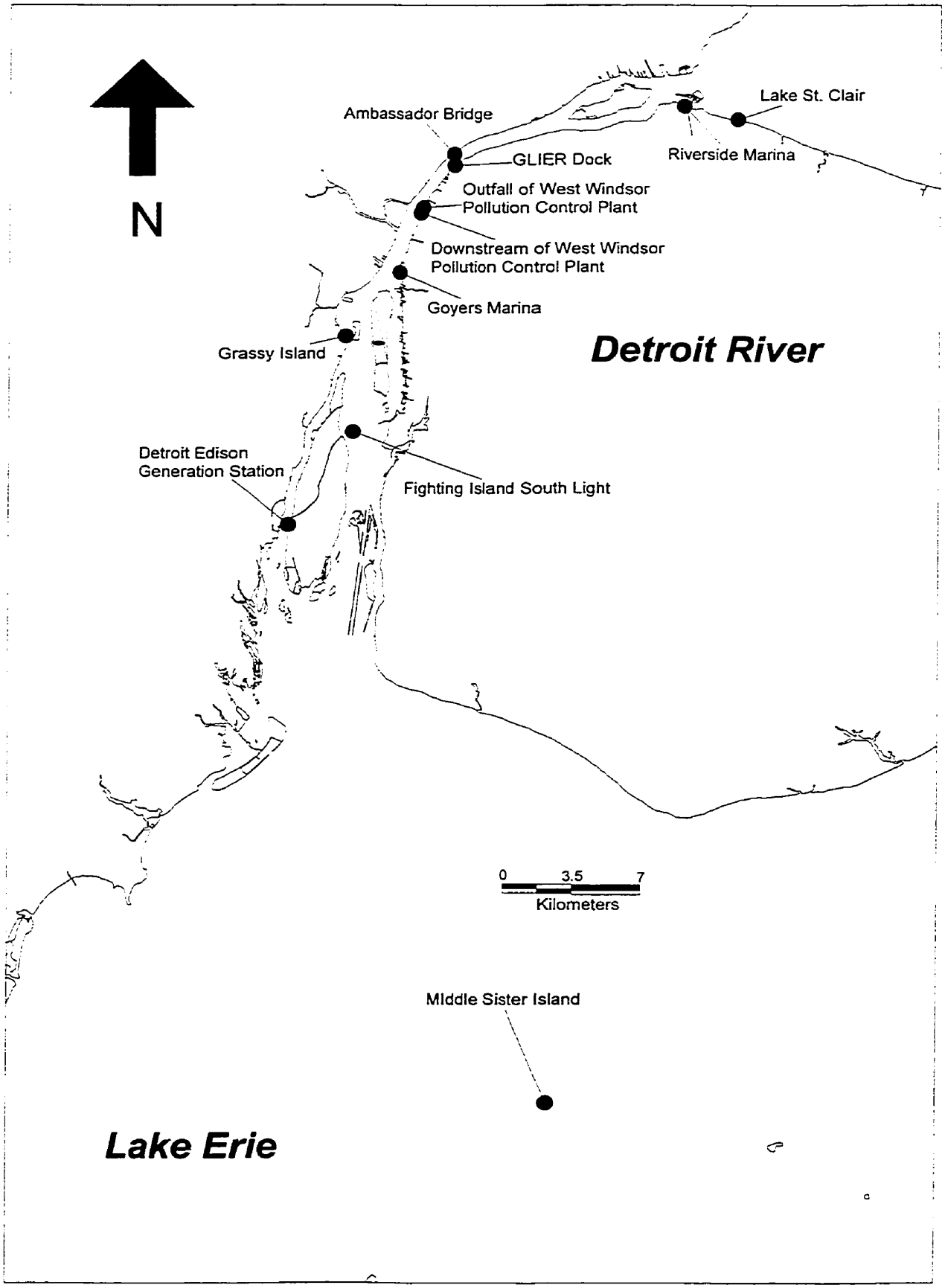
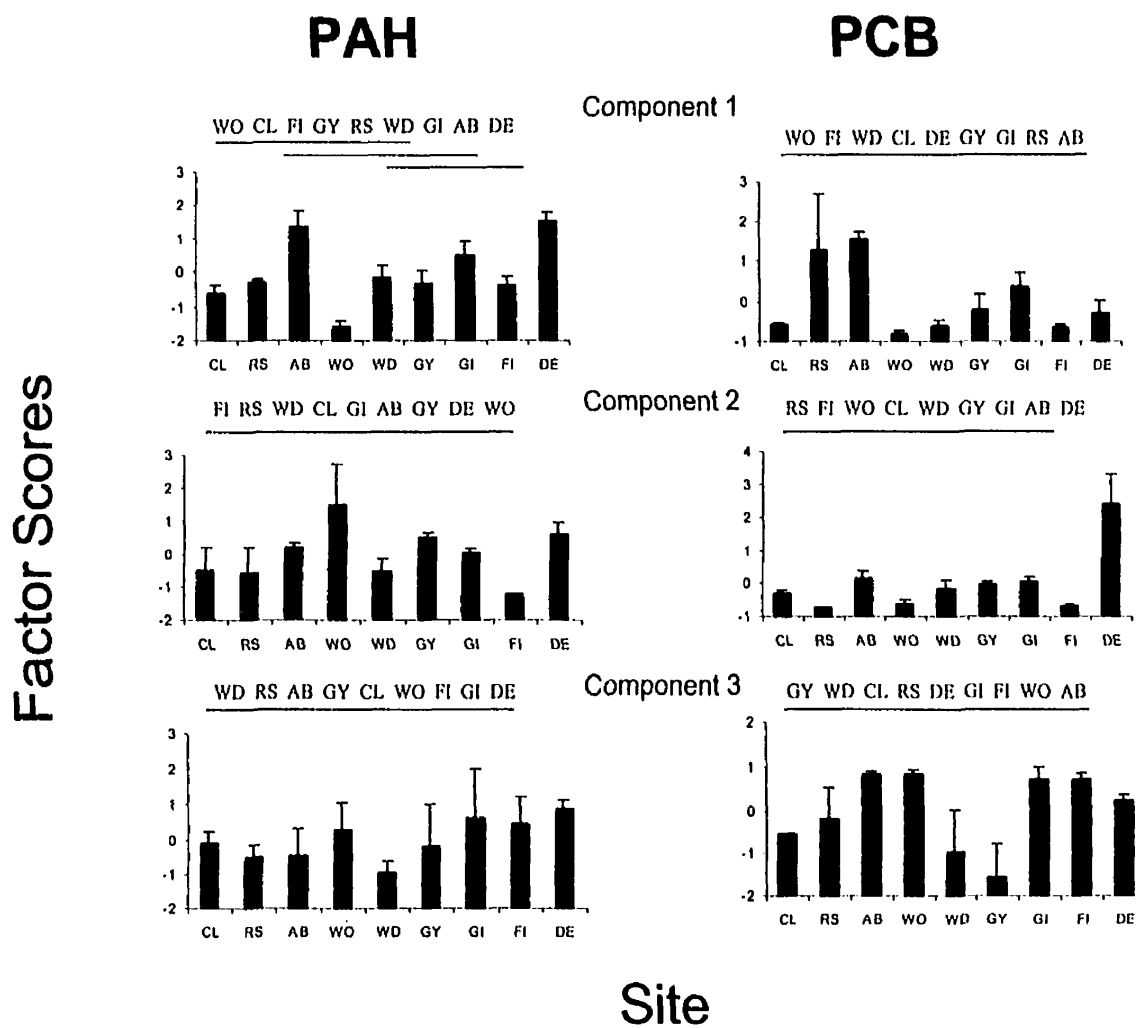

N
Ambassador Bridge
Lake St. Clair
GLIER Dock
Riverside Marina
Outfall of West Windsor
Pollution Control Plant
Downstream of West Windsor
Pollution Control Plant
Goyers Marina
Grassy Island
Detroit River
Detroit Edison
Generation Station
Fighting Island South Light
0
3.5
7
Kilometers
Middle Sister Island
Lake Erie

Figure 3.2. Factors scores for the 3 components extracted from the principal component analysis for PAH and PCB water concentrations at sites along the Detroit River. Error bars represent ± 1 SE. Sites listed above graphs are in order of least to most contaminated. No significant differences are present between underlined sites (Tukey, $p < 0.05$). CL = Lake St. Clair, RS = Riverside Marina, AB = Ambassador Bridge, WO = Outfall of West Windsor Pollution Control Plant, WD = Downstream of West Windsor Pollution Control Plant, GY = Goyers Marina, GI = Grassy Island, FI = Fighting Island South Light, DE = Detroit Edison Generating Station.


PAH
PCB
Component 1
WO CL FI GY RS WD GI AB DE
WO FI WD CL DE GY GI RS AB
Component 2
FI RS WD CL GI AB GY DE WO
RS FI WO CL WD GY GI AB DE
Component 3
WD RS AB GY CL WO FI GI DE
GY WD CL RS DE GI FI WO AB
CL RS AB WO WD GY GI FI DE
Factor Scores
Site

Chapter 4.0: A Comparison of PAH and PCB Dynamics in Benthic Invertebrates of Lake Erie

4.1 Abstract

The distribution patterns of PAHs and PCBs were determined in 4 benthic invertebrate species of western Lake Erie to assess and compare the processes governing the exposure dynamics of these two classes of contaminants. Significant differences in the sum of 17 PAH compounds were observed among the 4 species, with mayflies containing the highest PAH body burden followed by dreissenid mussels, amphipods, and crayfish. For PCBs, mayflies contained significantly higher concentrations of the sum of 39 PCB congeners than the other organisms and dreissenids had higher concentrations than crayfish. There were no significant differences in the ΣPCB concentrations between dreissenids and amphipods or between amphipods and crayfish. For PCBs, the relationship between BSAF and log K_{ow} followed a parabolic pattern, indicative of selective bioaccumulation. In contrast, BSAFs for PAHs were inversely related to log K_{ow}, suggesting that metabolism of the higher K_{ow} compounds was occurring. The results of this study support the conclusion that mayflies and dreissenid mussels play major roles in the transfer of PAHs and PCBs to upper trophic levels, and demonstrate that the exposure dynamics of PAHs and PCBs are different in the benthic components of aquatic food webs.

4.1 Introduction

Much work has been done to study and model the exposure dynamics of polychlorinated biphenyls (PCBs) and other organochlorine contaminants in aquatic food webs (Gobas, 1993; Morrison *et al.*, 1997; Camphens and Mackay, 1997; Harrad and

Smith, 1998; Morrison *et al.*, 2000). Less has been published on polycyclic aromatic hydrocarbons (PAHs) because they are rapidly metabolized by vertebrates and thus are often not detected in higher organisms (Varanasi *et al.*, 1989b). However, it was found that PAH water concentrations in the Detroit River and at Middle Sister Island in western Lake Erie were elevated compared to PCBs (Chapter 3) which indicates that significant PAH exposure to the biota is likely occurring. PAHs are frequently found in benthic invertebrates (Eadie *et al.*, 1982; Metcalfe *et al.*, 1997). Since benthic invertebrates are important components of aquatic food webs (Gobas, 1993; Morrison *et al.*, 1996), accumulated PAHs can be directly transferred to higher trophic levels, such as fish and birds, that utilize benthic invertebrates as part of their diet. Therefore, these contaminants should be considered as a potentially important component of quantifying toxicological stress in aquatic ecosystems.

Polycyclic aromatic hydrocarbons are produced primarily through the incomplete combustion of carbon compounds (Neff, 1979). Although parent PAHs are not very toxic, some metabolites can form covalent bonds with DNA, RNA, and protein, causing genotoxic and carcinogenic effects (Neff, 1979). The major enzyme system responsible for the biotransformation of PAHs is the mixed function oxidase (MFO) system. Fish possess MFO systems and rapidly metabolize PAH compounds (Varanasi *et al.*, 1989b). Invertebrates generally have poorly developed MFO systems and metabolism is slower (James, 1989), although the rate of biotransformation varies among species (Landrum, 1982; Varanasi *et al.*, 1985; Borchert *et al.*, 1997). Low PAH concentrations in higher trophic levels do not necessarily imply that they are not at risk because if an organism is

exposed to PAHs but subsequently metabolizes the compounds at a rapid rate, the body burden will be low, but the potential hazard will be high.

The assessment of PAH metabolism is typically confined to laboratory settings by studying individual radiolabeled compounds in different species (Landrum, 1982; Varanasi *et al.*, 1985; Borchert *et al.*, 1997). Though the detailed information generated in these experiments are necessary for the study of contaminant transfer in aquatic food webs, the results are not easily extrapolated to field conditions where the interactions of many species, chemicals, and environmental variables can affect chemical behaviour (Varanasi *et al.*, 1985). One way to quantify the exposure dynamics and metabolism of PAHs in the field is to compare PAH distribution with chemicals of similar hydrophobicity that are more persistent in the food web (McElroy *et al.*, 1989). Polychlorinated biphenyls are synthetic chemicals that were used widely in industry between the years 1929 and 1979 due to their non-flammable and insulating properties (Metcalfe and Haffner, 1995). Even though they were banned in the 1970s by most western countries, high concentrations are still detected in aquatic food webs (Koslowski *et al.*, 1994; Morrison *et al.*, 1997). Polychlorinated biphenyls have similar size and hydrophobicity as PAHs, however they are more resistant to degradation processes such as metabolism and photolysis (Sanborn *et al.*, 1975; Sundstrom *et al.*, 1976; Conner, 1984; McElroy *et al.*, 1989). Thus comparisons of relative concentrations of PAHs and PCBs in the food web will yield information as to whether degradation processes enhance the toxicological stress imposed by PAHs.

Biota-sediment accumulation factors (BSAFs) are commonly used as measures of chemical bioavailability and uptake from sediment (Hope *et al.*, 1997; Thomann and

Komlos, 1999; Epplett *et al.*, 2000). The BSAF is equal to the ratio of the lipid-normalized concentration in an organism divided by the organic carbon–normalized concentration in sediment. Lipid or organic carbon normalization is necessary to account for the capacities of different compartments to accumulate chemicals (Connolly and Pedersen, 1988). Under conditions of chemical equilibrium, and assuming organic carbon and lipid have similar capacities to sorb chemicals, the lipid-normalized concentration in an organism should approximate the organic carbon-normalized concentration in sediment. Thus the BSAF for each chemical should approach 1 (Connell, 1989; DiToro *et al.*, 1991). Biota-sediment accumulation factor values that vary consistently from 1 indicate that chemicals are not achieving equilibrium. In this case, processes such as metabolism (BSAF<1) or biomagnification (BSAF>1) may be playing significant roles in the transfer of organic contaminants in the benthic food web.

The environmental quality of Lake Erie is of concern because it supports a population of 13 million people and contains valuable commercial and sport fisheries (Fuller *et al.*, 1995). Western Lake Erie has recently received a lot of attention due to changes, such as invasion of dreissenid mussels, which may be causing elevated biological exposure of organic contaminants to top predators as a result of increased benthic-pelagic coupling (Haffner and Koslowski, 1999). The Detroit River, one of the more polluted aquatic ecosystems in the world, is the major source of PAHs and PCBs into Lake Erie (Kelly *et al.*, 1991). Approximately 73% of sediment-bound pollutants from the Detroit River entering Lake Erie are accumulated within the sediment of the western basin, resulting in potentially high concentrations of chemical exposure to the biota of this system (Carter and Hites, 1992).

The objective of this study was to assess the mechanisms governing the accumulation of PAHs in western Lake Erie benthic invertebrate species. To achieve this objective, the distribution and BSAFs of PAHs in 4 benthic invertebrate species were investigated. Because PCBs are generally more persistent than PAHs and because the distribution and dynamics of PCBs in the Lake Erie food web has been extensively studied (Koslowski *et al.*, 1994; Morrison *et al.*, 1997), the accumulation patterns of PAHs were compared with PCBs in order to better understand PAH dynamics.

4.3 Materials and Methods

4.3.1 Sample Collection

All samples were obtained near Middle Sister Island (41°51'N 83°00'W), located in the western basin of Lake Erie (Fig. 4.1). Middle Sister Island is continuously exposed to organic contaminants from the Detroit River (Kelly *et al.*, 1991). During the summer of 1997, composite samples of mayfly larvae (*Hexagenia limbata* and *Hexagenia rigida*) (n=3), dreissenid mussels (*Dreissena polymorpha* and *Dreissena bugensis*) (n=3), and crayfish (*Orconectes propinquus*) (n=3) were collected. In 1998, samples of sediment (n=3), dreissenid mussels (n=3), amphipods (*Gammarus fasciatus, Echinogammarus ischnus*, and *Hyalella azteca*) (n=3), and crayfish (n=4) were obtained. Within each invertebrate group, species were pooled to ensure that there was adequate tissue for chemical analysis. Although there may be differences in the biotransformation of PAHs among species, these differences were likely minimal for the mayfly and dreissenid species since they belonged to the same genus and thus were taxonomically similar. Further, the pooling of the 3 amphipod species was not deemed problematic since 98% of the amphipods present at Middle Sister Island in 1998 were *E. ischnus* (C. Van Overdijk,

personal communication). All samples weighed between 5 and 20 g wet weight. Crayfish were gathered by snorkeling, amphipods were rinsed off rocks, and mussels were scraped off the same rocks and shucked. Sediment and mayfly larvae were collected with a Petite Ponar grab. Mayflies were separated from the sediment with a 625 μm mesh sieving bucket. Sediment was placed in amber jars and stored at -20°C until analysis. All other samples were placed in hexane rinsed foil and stored at -20°C until analysis.

4.3.2 Sample preparation

Chemical analysis was performed at the analytical laboratory at the Great Lakes Institute for Environmental Research at the University of Windsor, which has been accredited by the Canadian Association for Environmental Analytical Laboratories (CAEAL). The PAH and PCB analysis techniques are approved by CAEAL and annual reference CAEAL sediment samples are run. Sample preparation was done according to Lazar *et al.* (1992). Briefly, each biological sample was homogenized with anhydrous sodium sulfate using a mortar and pestle. The samples were then poured into 35 cm × 2 cm glass columns that were plugged with glass wool, filled with 30 mL of dichloromethane (DCM):hexane (1:1, v/v) and 2 cm of Na_2SO_4. Internal standards of tribromobenzene, tetrachloro-m-xylene, and decachlorobiphenyl were added to the columns. After one hour, the samples were eluted with 250 mL of DCM:hexane (1:1, v/v). Five mL of isooctane was added to each sample, which were then rotoevaporated to 5 mL using a Büchi Rotoevaporater. The samples were made up to 25 mL with hexane. Lipid determination was done by evaporating 2 mL of each sample for an hour at 105°C. Percent lipid was determined gravimetrically. The remaining portion of the samples was

rotoevaporated to 2 mL and transferred to 35 cm × 1 cm glass columns that were plugged with glass wool, filled with 6 g of activated florisil, 2 cm of Na_2SO_4, and hexane. Fraction 1 (containing PCBs) was eluted with 50 mL of hexane. Fraction 2 (containing PAHs) was eluted with 100 mL of DCM:hexane (3:2, v/v). Extracts were then rotoevaporated to a volume of less than 1 mL. Fraction 1 was made up to a final volume of 5 mL with isooctane and Fraction 2 was made up to a final volume of 1 mL.

Sediment samples were combined with 100 g of Na_2SO_4. Each sample was extracted using a Soxhlet extractor for 16 hours with acetone:hexane (1:1, v/v). The extracts were then rotoevaporated to 50 mL. The samples were poured into 2 cm × 35 cm glass columns that were filled with anhydrous Na_2SO_4, and then eluted with 200 mL of hexane. Sediment extracts were cleaned-up using the same method as the biological samples. Organic carbon content of sediment was determined by loss on ignition according to Hakanson and Jansson (1983). Five g of each sample were dried at 105°C for 24 hours and then were placed in a muffle furnace at 450°C for 24 hours.

4.3.3 Gas chromatography

Gas chromatographic analysis of Fraction 1 was performed on a Hewlett-Packard (Avondale, PA, USA) 5890 Gas Chromatograph with Electron Capture Detector equipped with a Hewlett-Packard-3396 integrator, a Hewlett-Packard-7673A autosampler, and a 30 m × 0.25 mm DB-5 column. Injection was 1 μL spitless at 250°C and oven temperature was programmed from 100 to 270°C at 3°C /min. Carrier gas was ultra-high purity helium at 30 cm/s flow rate and makeup gas as Ar/CH_4 (95%/5%) at 50 mL/min. Gas chromatographic analysis of Fraction 2 was performed on a Hewlett-Packard 5890/5979 Gas Chromatograph with Mass Selective Detector equipped with a

Hewlett-Packard-7673A autosampler, and a 30 m × 0.25 mm DB-5 column. Injection was 1 µl spitless at 250°C and oven temperature was programmed from 100 to 270°C at 3°C /min. Carrier gas was ultra-high purity helium at 30 cm/s flow rate. Fraction 1 was analyzed for 39 PCB compounds and Fraction 2 was analyzed for 17 PAHs. The PCBs have a wide range of water solubilities and include both mono-*ortho*-substituted and non-coplanar compounds. The PAHs have been identified as priority compounds by the United States Environmental Protection Agency and are often considered the most bioavailable and mobile aromatic hydrocarbons within aquatic environments due to their relatively small molecular size. The detection level was 0.5 ng/g wet weight for PAHs and 0.05 ng/g wet weight for PCBs. The percent recoveries of internal standards were 94.25 ± 2.338, 94.21 ± 5.677, and 104.29 ± 2.953 (mean ± SE) for tribromobenzene, tetrachloro-m-xylene, and decachlorobiphenyl respectively. Concentrations were not corrected for the recovery of internal standards. For both PAH and PCB gas chromatographic analysis, a Canadian Wildlife Service herring gull (*Larus argentatus*) egg homogenate standard was run every tenth sample, and a method blank was run every sixth sample.

4.3.4 Data analysis

Concentrations of PAHs and PCBs in benthic invertebrate and sediment samples were lipid normalized and organic carbon normalized respectively. Acenaphthylene, acenaphthene, anthracene, benzo[*k*]fluoranthene, and PCB #118 were deleted from the analysis because they were infrequently detected in the samples. Other contaminants that were not present at quantifiable concentrations were replaced with the detection limit value. Since there were few significant differences in log-transformed congener

concentrations among years (t-test, $p < 0.05$) (Table 4.1), data from 1997 and 1998 were compiled to increase sample size.

4.4 Results

PAH and PCB concentrations in mayflies, dreissenid mussels, amphipods, and crayfish are reported in Table 4.1. To investigate interspecific differences of chemical concentration between PAHs and PCBs, 2 analysis of variance (ANOVA) tests were conducted, one on the sum of PAH compounds and one on the sum of PCB compounds. The ΣPAH and ΣPCB data were log transformed prior to analysis so that the variances would not be significantly heterogeneous (Bartlett's test for homogeneity of variances, $p > 0.05$). Unplanned multiple comparisons were performed with the Tukey test. There were significant differences among species for both ΣPAHs (ANOVA, $p < 0.001$) and ΣPCBs (ANOVA, $p < 0.001$). For PAH compounds, there were significant differences among all species (Tukey, $p < 0.05$). Mayflies contained the highest PAH body burden, followed by mussels, amphipods, and crayfish. For PCBs, mayflies contained significantly higher concentrations than the other 3 species (Tukey, $p < 0.001$) and dreissenid mussels had higher concentrations than crayfish (Tukey, $p < 0.01$). There were no significant differences in ΣPCBs between mussels and amphipods or between amphipods and crayfish (Tukey, $p > 0.05$).

To assess species differences in the distribution of individual compounds, the proportion of each PAH compound relative to total PAHs were evaluated in the 4 invertebrate groups and in sediment (Fig. 4.2). PAHs were not distributed similarly among the samples. Sediment had elevated concentrations of the more hydrophobic compounds. Mayfly larvae contained higher proportions of compounds with middle to

high octanol/water partition coefficients (K_{ow}s) whereas crayfish had greater concentrations of the more water soluble PAHs, especially naphthalene. Dreissenid mussels and amphipods had high proportions of the PAHs with low to middle K_{ow}s.

The proportion of 12 PCB compounds relative to total PCBs were also assessed (Fig. 4.3). These representative PCBs were present at concentrations well above the detection limit and include compounds with a wide range of K_{ow}s. The more water soluble PCBs, which have similar hydrophobicity as the PAHs with middle to high range K_{ow}s, were found at higher proportions in sediment compared with the invertebrate organisms. In most cases, the 4 invertebrate groups contained higher proportions of the high K_{ow} PCBs compared with sediment.

Biota sediment accumulation factors were calculated for PAH and PCB compounds and plotted against log K_{ow} (Fig. 4.4) to assess the influence of hydrophobicity on contaminant accumulation. For PCBs, BSAF values followed a parabolic relationship with log K_{ow} and most values were above 1 in all organisms except crayfish (Fig. 4.4). In contrast, PAH BSAFs were inversely related to log K_{ow} and most chemicals were considerably below equilibrium values, especially those that were more hydrophobic (Fig. 4.4). Regression analysis was performed so that the relationships could be statistically quantified (Fig. 4.4). Due to detection limit problems, indeno[*1,2,3-c,d*]pyrene, dibenzo[*a,h*]anthracene, and benzo[*g,h,i*]perylene were not included in the analysis for amphipods and crayfish, and in addition, benzo[*a*]anthracene, chrysene/triphenylene, benzo[*b*]fluoranthene, and benzo[*a*]pyrene were not included for crayfish. Log BSAFs were significantly related to log K_{ow} for both PAH and PCB compounds (ANOVA, $p < 0.001$). However, the slopes of the two regression lines were

significantly different (t-test, $p < 0.001$). The PAH regression coefficient was negative whereas the PCB regression coefficient was positive (Fig. 4.4). Since the PCB curve seemed parabolic rather than linear, a quadratic curve was also fit to the PCB data (Fig. 4.4), which significantly improved the accuracy of the regression curve (t-test, $p < 0.001$) and was the optimum regression function for the data.

The slopes of all species-specific PAH and PCB log BSAF versus log K_{ow} linear regression functions were significantly different from zero (ANOVA, $p < 0.001$). In addition, for both PAHs and PCBs, the slopes of the regression lines were significantly different among species (ANCOVA, $p < 0.05$ for PAHs and ANCOVA, $p < 0.001$ for PCBs).

4.5 Discussion

Mayfly larvae accumulated significantly higher concentrations of PAH and PCB contaminants than the other organisms studied. Mayfly larvae live in soft sediment (Pennak, 1978) and their diet consists mostly of sediment and detritus (Morrison *et al.*, 1997). This exposes them to high concentrations of sediment-sorbed hydrophobic contaminants, such as PAHs and PCBs. Although mayflies disappeared from western Lake Erie in the 1950s due to anoxic conditions, populations are now recovering (Krieger *et al.*, 1996). Mayflies are a major food source for many fish and bird species (McCafferty, 1983; Morrison *et al.*, 1998). Thus elevated PAH and PCB burdens in mayflies coupled with growing population size is likely causing increasing contaminant exposure to predators and elevated stress within the trophic levels of Lake Erie and the surrounding terrestrial ecosystem.

Mayflies are commonly used as biomonitors of contaminants in aquatic systems (Clements and Kawatski, 1984; Corkum *et al.*, 1997). Since this organism can accumulate high concentrations of sediment associated chemicals, the results confirm that mayfly larvae would effectively monitor PAHs and PCBs in sediment, although mayflies might not represent exposure and accumulation of organic contaminants in other invertebrate species.

Dreissenid mussels contained significantly lower concentrations of PAHs and PCBs than mayflies but significantly higher concentrations than crayfish. In addition, mussels had significantly higher PAH concentrations than amphipods that were on the same rocks. Mussels are intensive filter feeders, and thus are able to accumulate high concentrations of hydrophobic contaminants from algae and suspended sediment (Bruner *et al.*, 1994). Freely dissolved PAHs and PCBs also contribute to the body burden of mussels if the chemicals are present at high concentrations in the aqueous phase (Bruner *et al.*, 1994). Like mayflies, dreissenid mussels have become an important prey item for many species in Lake Erie (Mazak *et al.*, 1997; Morrison *et al.*, 1998). Thus although contaminant concentrations in mussels are less than in mayflies, dreissenids are likely another important exposure route of PAHs and PCBs to the upper trophic levels of Lake Erie. Dreissenid mussels have also been used as indicators of aquatic contaminants (Morrison *et al.*, 1995; Metcalfe *et al.*, 1997). The results of this study indicate that mussels can effectively monitor PAHs and PCBs present in the water column.

The PCB concentrations in mussels and amphipods were not significantly different. Diet was likely an important factor in the relatively high accumulation of PCBs in amphipods. The amphipods were collected in dreissenid mussel colonies and thus fed

on mussel feces and pseudofeces, which causes elevated contaminant burdens compared to amphipods living in the absence of mussels (Bruner *et al.*, 1994). In contrast to PCBs, PAHs in mussels were significantly higher than in amphipods. Bivalve mussels have limited ability for PAH metabolism (Neff, 1979; Varanasi *et al.*, 1985; James, 1989) and thus are able to accumulate higher concentrations than species that possess greater metabolic capabilities. Since concentrations of PCBs in mussels and amphipods were similar, it was hypothesized that significant differences in PAHs were due to higher rates of PAH metabolism in amphipods as compared with mussels. Laboratory studies have found varying rates of PAH biotransformation in amphipod species. For example, Varanasi *et al.* (1985) reported that the two amphipod species *Eohaustorius washingtonianus* and *Rhepoxynium abronius* metabolized 22% and 74% of benzo[*a*]pyrene respectively in 1 week. Another study found negligible rates of anthracene metabolism after 48 hours in the amphipod *Diporeia hoyi* (formerly *Pontaporeia hoyi*) (Landrum, 1982). Therefore, the results suggest that amphipods probably contribute to the exposure dynamics of PCBs in Lake Erie but are less important in the trophic transfer of PAHs. The amphipod would be a less effective biomonitor of organic contaminants compared with mayflies and mussels.

Crayfish accumulated low concentrations of contaminants. Metabolism was likely an important process contributing to the low crayfish PAH body burden. Since concentrations of PCBs in amphipods and crayfish were similar, significant differences in PAHs may have been due to higher rates of PAH metabolism in crayfish, compared with amphipods. A model developed by Thomann and Komlos (1999) showed that differences between PAH and PCB concentrations in crayfish were due largely to

metabolism. However, it is likely that low exposure rates also contributed to the low contaminant concentrations in crayfish because both PAH and PCB concentrations were diminished in crayfish compared with mayflies and mussels. Overall, the results indicate that crayfish are not a critical part of the PAH/PCB dynamics in Lake Erie and that this organism would be of limited use as a biomonitor of organic contaminants.

Contrasts in PAH distribution among species (Fig. 4.2) demonstrates that there were species-specific differences in congener accumulation. Sediment contained high proportions of the high K_{ow} compounds and it was hypothesized that the major exposure route of the more hydrophobic PAHs to the study organisms was sediment and suspended particles. Mayfly larvae accumulated high proportions of the middle to high K_{ow} compounds, which suggests that sediment was the major source of PAHs to mayflies. Landrum and Poore (1988) found that *H. limbata* accumulated greater than 90% of hydrophobic contaminants from sediment. The major exposure route of the lower K_{ow} compounds was likely the water phase. Crayfish accumulated only the most water soluble PAHs, indicating that the major source was from water. Amphipods and dreissenid mussels had high proportions of the low to middle K_{ow} compounds, which suggests that exposure occurred through both water and sediment.

Differences in the proportion of PCB congeners were also found among samples (Fig. 4.3). Elevated proportions of the more water soluble PCB compounds were found in sediment. These low K_{ow} PCBs have similar hydrophobicity as the more hydrophobic PAHs, which were also present at elevated proportions in sediment. This suggests that sediment and suspended particles were major exposure routes of all PCBs. The elevated

proportions of the higher K_{ow} PCBs in the organisms suggest that these congeners are being biomagnified more than other compounds.

The parabolic relationship between log BSAF and log K_{ow} for PCBs has been demonstrated in other studies (Morrison *et al.*, 1996; Hope *et al.*, 1997; Epplett *et al.*, 2000) and indicates that the benthic invertebrates were selectively bioaccumulating PCB contaminants. The BSAF values above 1 for mayflies, mussels, and amphipods suggest that PCBs in these 3 organisms exceeded equilibrium predictions. The lower BSAFs in crayfish supports the conclusion that crayfish were accumulating low concentrations of sediment-associated contaminants. A model developed by Morrison *et al.* (1996) predicted that chemical disequilibria between water, food, and sediment were important in the accumulation of PCBs in benthic invertebrates.

Although PAHs and PCBs partition in aquatic ecosystems according to their respective hydrophobicities, their BSAFs are quite different due to the susceptibility of PAHs to different degradation processes. In crayfish and sunfish, Thomann and Komlos (1999) also found below equilibrium PAH BSAF values and they determined a similar inverse relationship between log BSAF and log K_{ow}. The model they developed showed that diminished BSAFs for PAHs with log $K_{ow} > 5$ was due primarily to metabolism and decreased efficiency of chemical transfer from the gut to the organism (due to lower bioavailability of PAHs sorbed to ingested sediment or prey and/or metabolism). Other factors, such as photolysis (Arfsten *et al.*, 1996) and slow desorption kinetics from sediment to water (McGroddy *et al.*, 1996; Cornelissen *et al.*, 1997; Lamoureux and Brownawell, 1999) might also have contributed to the below equilibrium values.

Significant differences among species-specific log BSAF versus log K_{ow} regression lines may have been due to a variety of factors such as differences in growth rate, lipid content, feeding preference and strategy, contaminant sources, and metabolic capabilities.

4.6 Conclusions

The results of this study indicate that the rate of PAH exposure to benthic invertebrates varied due to both habitat preference and diet. In addition, the data suggests that species-specific metabolic rates of PAHs were also different. PAH metabolism was highest in crayfish, followed by amphipods and the rates of PAH metabolism in dreissenids and mayflies were lower. Since PAH toxicity is induced primarily by metabolites, PAH exposure is likely resulting in varying degrees of toxicological stress to different benthic invertebrates in western Lake Erie. Increasing mayfly abundance coupled with elevated mayfly contaminant body burdens will likely result in higher PAH and PCB exposure to the Lake Erie food web and the surrounding terrestrial ecosystem in the near future. Dreissenid mussels also likely play a significant role in the transfer of contaminants to upper trophic levels. This project demonstrates the effectiveness of mayflies and dreissenid mussels as indicators of organic contamination. However, these organisms monitor different phases in the environment. Mayflies provide information on sediment contaminant concentrations whereas mussels monitor water column concentrations. The data demonstrates that the exposure dynamics of PAHs and PCBs in the benthic invertebrates of western Lake Erie are different and that equilibrium models are not sufficient to predict chemical accumulation in critical components of aquatic food

webs. A model that incorporates different metabolic processes and rates should be developed to predict PAH behavior in the food web of large aquatic ecosystems.

Table 4.1. PAH and PCB concentrations in benthic invertebrates (μg/g, lipid basis) and sediment (μg/g, organic carbon basis) collected from Middle Sister Island in western Lake Erie.

Compound	Log K_{ow}[a]	Mayfly larvae (n = 3) Mean ± SE	*Dreissenia* (n = 5) Mean ± SE	Amphipods (n = 3) Mean ± SE	Crayfish (n = 7) Mean ± SE	Sediment (n=3) Mean ± SE
%Lipid		1.50 ± 0.052	1.22 ± 0.026	1.53 ± 0.058	2.52 ± 0.155	7.14[b] ± 0.289
%Moisture		73.13 ± 0.221	83.93 ± 1.118	77.47 ± 0.984	69.12 ± 1.37	52.25 ± 1.212
PAHs[c]						
NA	3.4	0.74 ± 0.068	0.74 ± 0.208	0.58 ± 0.274	*0.36 ± 0.073	0.51 ± 0.052
FL	4.2	0.16 ± 0.010	0.04 ± 0.001	0.17 ± 0.003	°0.02 ± 0.001	0.60 ± 0.042
PHE	4.6	0.60 ± 0.060	0.36 ± 0.061	0.53 ± 0.068	*0.07 ± 0.026	3.64 ± 0.156
FLT	5.2	3.52 ± 0.257	0.79 ± 0.079	0.50 ± 0.132	*0.03 ± 0.003	6.85 ± 0.522
PY	5.2	7.60 ± 0.428	0.46 ± 0.052	0.13 ± 0.067	°0.02 ± 0.001	7.56 ± 0.582
B(a)A	5.9	1.03 ± 0.199	0.26 ± 0.037	°0.03 ± 0.001	°0.02 ± 0.001	2.97 ± 0.224
C/T	5.9	3.34 ± 0.464	1.19 ± 0.112	0.21 ± 0.173	°0.02 ± 0.001	5.51 ± 0.368
B(b)F	5.8	0.29 ± 0.195	0.67 ± 0.089	°0.03 ± 0.001	°0.02 ± 0.001	6.74 ± 0.945
B(a)P	6.0	0.93 ± 0.168	0.08 ± 0.042	°0.03 ± 0.001	°0.02 ± 0.001	5.02 ± 0.386
IP	6.5	1.05 ± 0.240	0.20 ± 0.034	°0.03 ± 0.001	°0.02 ± 0.001	3.79 ± 0.106
D(ah)A	6.8	0.22 ± 0.101	0.27 ± 0.234	°0.03 ± 0.001	°0.02 ± 0.001	1.11 ± 0.099
B(ghi)P	6.5	0.69 ± 0.360	0.13 ± 0.028	°0.03 ± 0.001	°0.02 ± 0.001	5.25 ± 0.445
Sum PAHs		20.16 ± 2.549	5.19 ± 0.975	2.31 ± 0.725	0.65 ± 0.096	49.55 ± 3.927
PCBs						
31/28	5.6	0.09 ± 0.006	0.01 ± 0.002	0.02 ± 0.002	*0.02 ± 0.002	0.05 ± 0.003
52	6.1	0.37 ± 0.020	0.09 ± 0.002	0.10 ± 0.013	0.07 ± 0.004	0.08 ± 0.002
49	6.1	0.22 ± 0.015	0.05 ± 0.001	0.05 ± 0.005	*0.04 ± 0.003	0.03 ± 0.001
44	6	0.22 ± 0.013	0.06 ± 0.002	0.06 ± 0.010	0.01 ± 0.000	0.05 ± 0.001
42	5.6	0.12 ± 0.008	*0.04 ± 0.007	0.04 ± 0.003	0.00 ± 0.000	0.04 ± 0.002
64	6.1	0.02 ± 0.001	0.01 ± 0.001	0.01 ± 0.003	0.00 ± 0.000	0.01 ± 0.001
74	6.1	0.09 ± 0.004	0.04 ± 0.002	0.04 ± 0.013	0.04 ± 0.004	0.03 ± 0.001
70	5.9	0.14 ± 0.007	0.05 ± 0.002	0.06 ± 0.015	*0.01 ± 0.002	0.06 ± 0.003
66/95	5.8	0.55 ± 0.074	0.22 ± 0.005	0.16 ± 0.018	0.10 ± 0.008	0.13 ± 0.005
60	5.9	0.25 ± 0.006	0.09 ± 0.006	0.09 ± 0.016	0.03 ± 0.004	0.07 ± 0.002
101	6.4	0.74 ± 0.038	0.30 ± 0.004	0.21 ± 0.018	0.19 ± 0.013	0.10 ± 0.003
99	6.6	0.30 ± 0.016	0.13 ± 0.007	0.13 ± 0.011	0.15 ± 0.012	0.05 ± 0.001
97	6.6	0.16 ± 0.010	0.07 ± 0.007	0.05 ± 0.007	0.03 ± 0.002	0.03 ± 0.001
87	6.5	0.31 ± 0.017	0.09 ± 0.001	0.06 ± 0.008	*0.06 ± 0.007	0.04 ± 0.001
110	6.5	0.59 ± 0.035	0.27 ± 0.007	0.23 ± 0.030	0.04 ± 0.002	0.11 ± 0.004
151	6.9	0.32 ± 0.010	0.19 ± 0.007	0.14 ± 0.018	0.06 ± 0.002	0.04 ± 0.006
149	6.8	0.93 ± 0.043	0.58 ± 0.026	0.36 ± 0.035	0.21 ± 0.008	0.12 ± 0.009
146	6.9	0.19 ± 0.009	*0.12 ± 0.005	0.12 ± 0.011	0.11 ± 0.007	0.02 ± 0.001
153	6.9	1.40 ± 0.062	0.69 ± 0.023	0.65 ± 0.062	0.62 ± 0.050	0.12 ± 0.010
105	6.4	0.39 ± 0.021	0.23 ± 0.009	0.18 ± 0.020	0.02 ± 0.005	0.05 ± 0.003
141		0.27 ± 0.012	0.11 ± 0.026	0.09 ± 0.008	0.09 ± 0.006	0.03 ± 0.002
138	7	1.40 ± 0.060	0.70 ± 0.022	0.64 ± 0.065	0.63 ± 0.052	0.18 ± 0.011
158	7.3	0.04 ± 0.002	*0.02 ± 0.001	0.03 ± 0.002	0.02 ± 0.001	0.01 ± 0.000
129	7.3	0.11 ± 0.003	*0.07 ± 0.003	0.07 ± 0.006	0.06 ± 0.004	0.02 ± 0.001
182/187	7.2	0.50 ± 0.023	*0.41 ± 0.018	0.36 ± 0.036	0.35 ± 0.025	0.07 ± 0.005
183	7	0.31 ± 0.014	*0.17 ± 0.008	0.14 ± 0.013	0.10 ± 0.006	0.03 ± 0.003

Table 4.1. continued.

Compound	Log K_{ow} [a]	Mayfly larvae	*Dreissenia*	Amphipods	Crayfish	Sediment
185	7	0.05 ± 0.002	*0.03 ± 0.002	0.01 ± 0.001	0.01 ± 0.000	0.01 ± 0.000
174	7	0.30 ± 0.013	*0.29 ± 0.014	0.16 ± 0.013	0.12 ± 0.007	0.05 ± 0.006
171	6.7	0.21 ± 0.010	*0.12 ± 0.005	0.08 ± 0.020	0.05 ± 0.003	0.03 ± 0.006
200		0.06 ± 0.003	0.04 ± 0.003	0.03 ± 0.001	0.02 ± 0.001	0.01 ± 0.002
172		0.06 ± 0.003	0.03 ± 0.001	0.03 ± 0.001	0.03 ± 0.002	0.01 ± 0.001
180	7.4	1.30 ± 0.052	0.56 ± 0.023	0.51 ± 0.048	0.58 ± 0.041	0.12 ± 0.013
170/190	7.3	0.60 ± 0.023	0.23 ± 0.010	0.20 ± 0.020	0.18 ± 0.012	0.07 ± 0.007
201	7.5	0.21 ± 0.010	0.17 ± 0.008	0.12 ± 0.009	0.11 ± 0.006	0.04 ± 0.003
203	7.1	0.21 ± 0.010	0.10 ± 0.005	0.07 ± 0.006	0.05 ± 0.002	0.03 ± 0.002
195	7.1	0.09 ± 0.004	0.04 ± 0.001	0.02 ± 0.002	0.03 ± 0.001	0.02 ± 0.001
194	7.1	0.27 ± 0.012	*0.07 ± 0.004	0.05 ± 0.005	0.07 ± 0.003	0.02 ± 0.003
206	7.2	0.08 ± 0.005	0.04 ± 0.002	0.02 ± 0.001	0.01 ± 0.001	0.02 ± 0.001
Sum PCBs		13.46 ± 0.628	6.53 ± 0.221	5.40 ± 0.566	4.34 ± 0.287	1.99 ± 0.125

[a] PAH values from Mackay *et al.* (1992) except IP which was reported in Maruya *et al.* (1996). PCB values from Shiu and Mackay (1986) except for congeners 110, 182/187, 180, and 170/190, which are from Hawker and Connell (1988).
[b] % organic carbon, rather than lipid, for sediment.
[c] NA = naphthalene, FL = fluorene, PHE = phenanthrene, FLT = fluoranthene, PY = pyrene, B(a)A = benzo[*a*]anthracene, C/T = chrysene/triphenylene, B(b)F = benzo[*b*]fluoranthene, B(a)P = benzo[*a*]pyrene, IP = indeno[*1,2,3-c,d*]pyrene, D(ah)A = dibenzo[*a,h*]anthracene, B(ghi)P = benzo[*g,h,i*]perylene.
° indicates that PAH value was not detected and was substituted with detection limit of 0.5 ng/g on a wet weight basis.
Asterisk (*) indicates that logarithm of lipid-normalized concentration significantly different (t-test, $p < 0.05$) among 2 years.

Figure 4.1. Middle Sister Island in western Lake Erie.

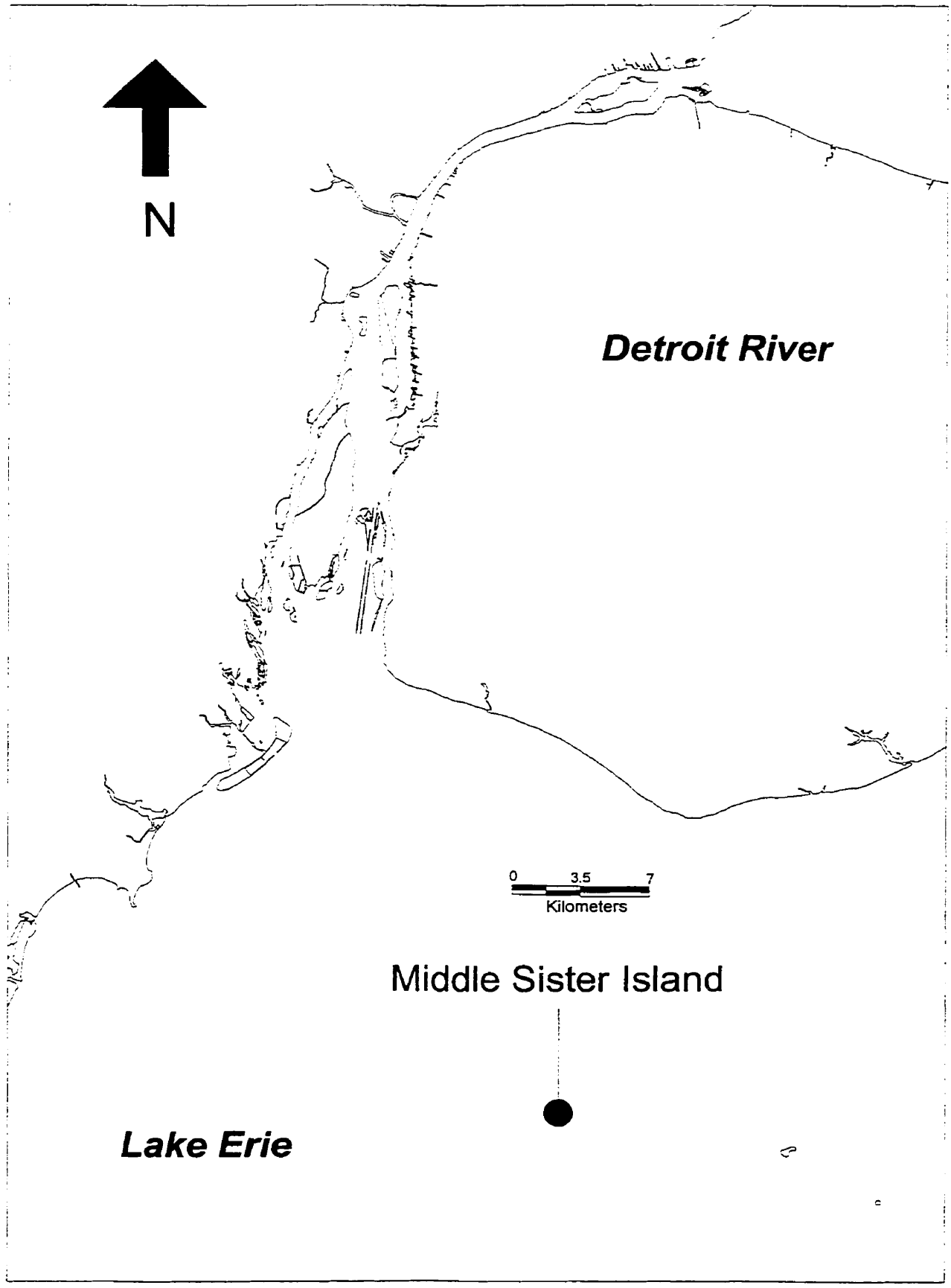

N
Detroit River
0
3.5
7
Kilometers
Middle Sister Island
Lake Erie

Figure 4.2. Proportion of PAH compounds relative to total PAHs in 4 benthic invertebrate species and sediment collected from Middle Sister Island in western Lake Erie. Error bars represent ± 1 SE. NA = naphthalene, FL = fluorene, PHE = phenanthrene, FLT = fluoranthene, PY = pyrene, B(a)A = benzo[*a*]anthracene, C/T = chrysene/triphenylene, B(b)F = benzo[*b*]fluoranthene, B(a)P = benzo[*a*]pyrene, IP = indeno[*1,2,3-c,d*]pyrene, D(ah)A = dibenzo[*a,h*]anthracene, B(ghi)P = benzo[*g,h,i*]perylene.

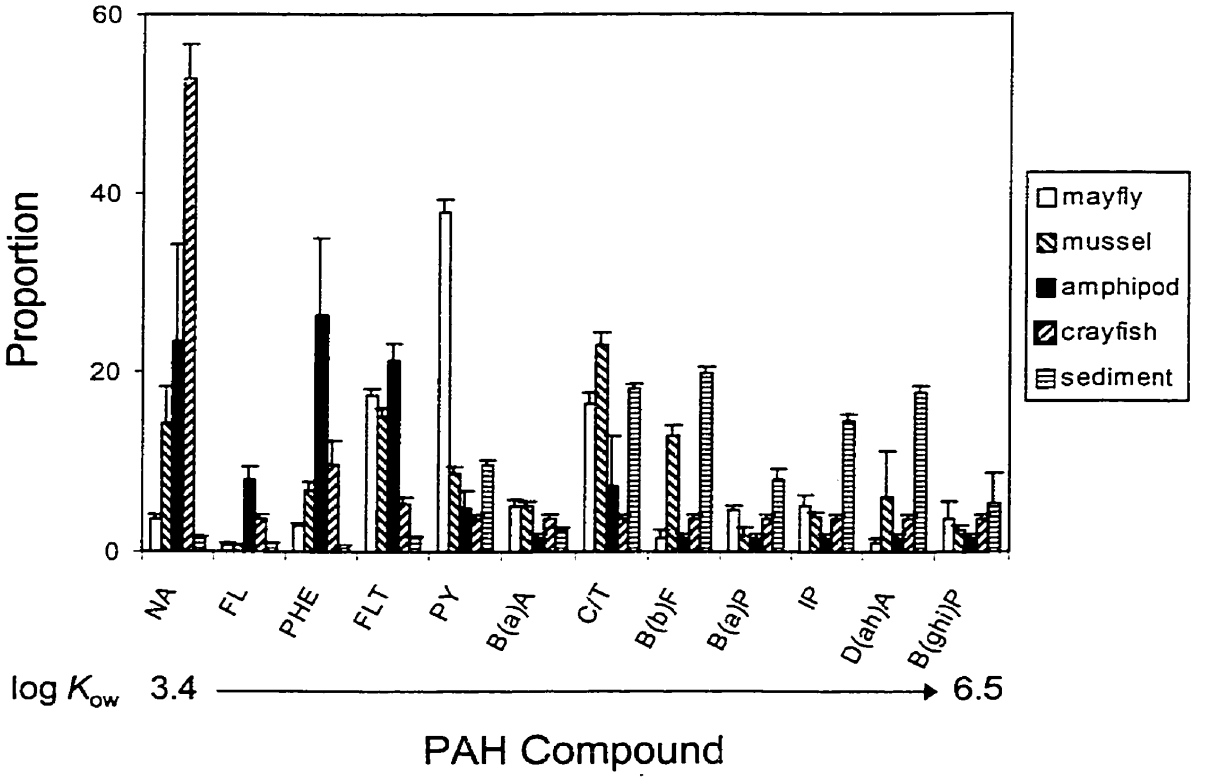

60
40
20
0
Proportion
mayfly
mussel
amphipod
crayfish
sediment
NA
FL
PHE
FLT
PY
B(a)A
C/T
B(b)F
B(a)P
IP
D(ah)A
B(ghi)P
log K_{ow} 3.4
6.5
PAH Compound

Figure 4.3. Proportion of 12 PCB congeners relative to total PCBs in 4 benthic invertebrate species and sediment collected from Middle Sister Island in western Lake Erie. Error bars represent ± 1 SE.

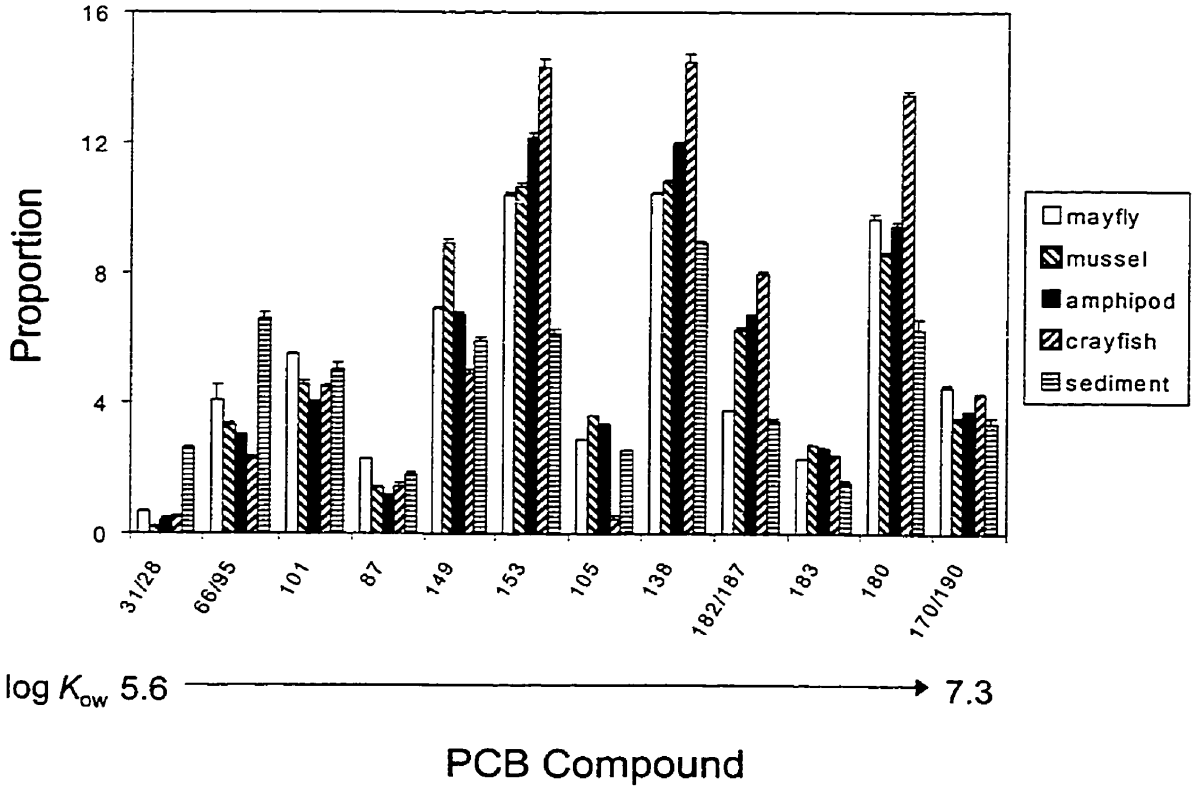
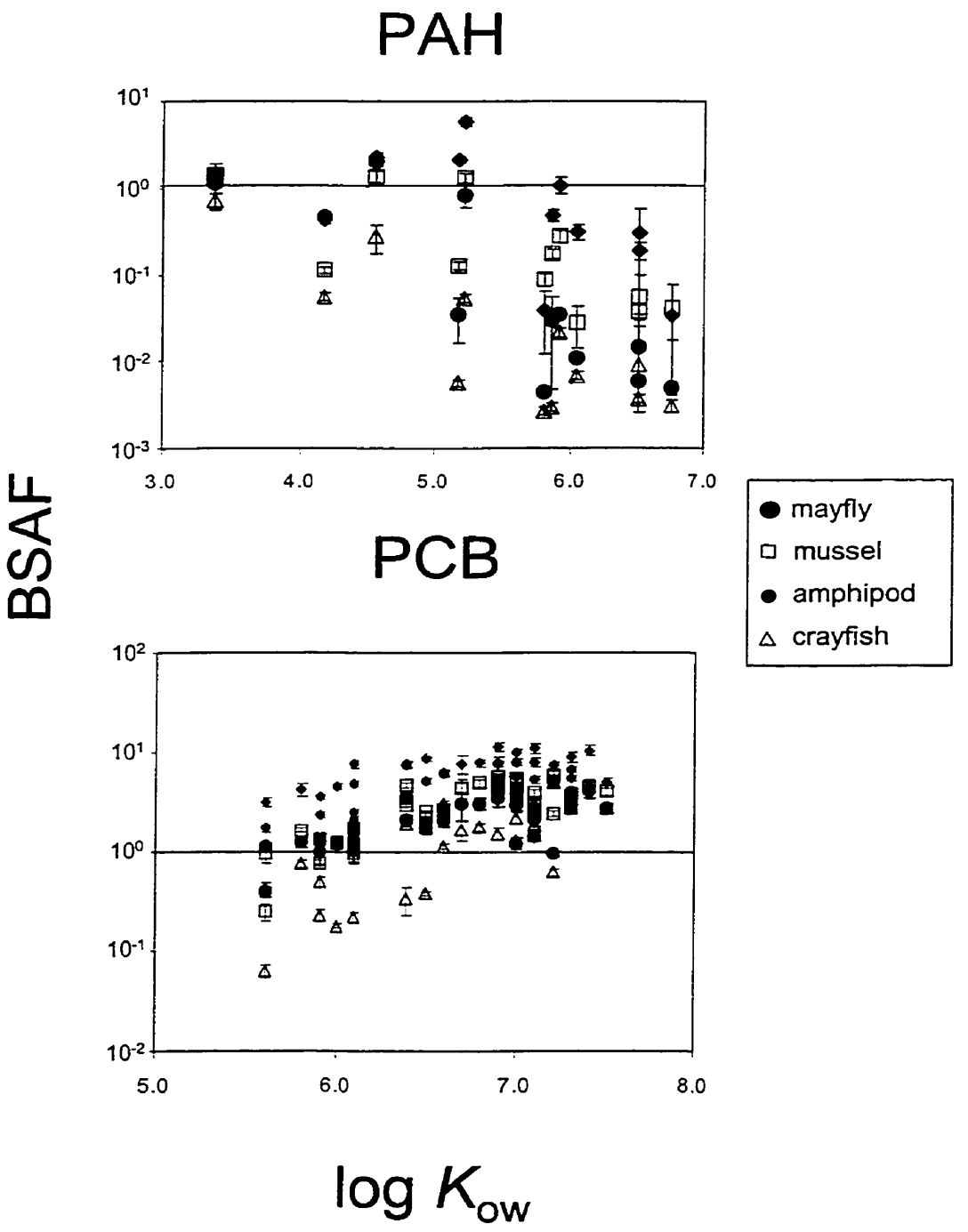

16
12
8
4
0
Proportion
mayfly
mussel
amphipod
crayfish
sediment
31/28
66/95
101
87
149
153
105
138
182/187
183
180
170/190
log K_{ow} 5.6
7.3
PCB Compound

Figure 4.4. Biota Sediment Accumulation Factors (BSAFs) for individual PAH and PCB compounds in 4 benthic invertebrate species collected from Middle Sister Island in western Lake Erie. The line represents predicted equilibrium values. Error bars represent ± 1 SE. Regression analysis of log BSAF versus log K_{ow}s gave the following relationships: PAH linear regression: log BSAF = -0.40 * log K_{ow} + 1.21 (r^2 = 0.22); PCB linear regression: log BSAF = 0.48 * log K_{ow} – 2.86 (r^2 = 0.35); PCB quadratic regression: log BSAF = -0.30 * log K_{ow}^2 + 4.42 * log K_{ow} – 15.66 (r^2 = 0.38).


PAH
PCB
BSAF
log K_{ow}
mayfly
mussel
amphipod
crayfish
10^1
10^0
10^{-1}
10^{-2}
10^{-3}
10^2
3.0
4.0
5.0
6.0
7.0
8.0

Chapter 5.0: General Conclusions

The results of this project demonstrated that there were many processes that regulated the dynamics of PAHs in the Detroit River and western Lake Erie ecosystems. These processes were related to both chemical and food web properties, which has also been found for PCBs (Oliver and Niimi, 1988; Haffner *et al.*, 1994; Russell *et al.*, 1999). Specifically, chemical hydrophobicity, metabolic degradation, route of chemical uptake, and organism habitat, diet, feeding strategy, and lipid content were shown to influence PAH distribution in the lower trophic levels of aquatic food webs.

In Chapter 2 it was found that for non-metabolized PAHs, elimination kinetics in the freshwater mussel, *Elliptio complanata* were similar to PCBs. Further, k_2 could be predicted by the hydrophobicity of the chemicals. The elimination kinetics of non-metabolized PAHs and PCBs were similar in other invertebrates and in small fish species. This indicated that when chemical elimination from an organism was passive, kinetics were dependent on K_{ow}, but were not strongly influenced by the type of organism or the class that a chemical belonged to.

It was also determined in Chapter 2 that the k_2 values of naphthalene, acenaphthylene, acenaphthene, benzo[*a*]pyrene, and benzo[*g,h,i*]perylene could not be predicted by hydrophobicity. This suggested that metabolic degradation significantly contributed to the overall elimination of these parent compounds from *E. complanata*.

In Chapter 3 it was found that *E. complanata* could effectively monitor PAH and PCB water concentrations. This study showed that PAH and PCB water concentrations along the Detroit River and western Lake Erie, calculated as a function of mussel chemical body burden, were influenced by the hydrophobicity of the contaminants.

Significant differences along the Detroit River were only detected for the more hydrophobic PAHs and the less hydrophobic PCBs that had similar log K_{ow}s ranging from 4.5 – 6.6. This group of PAHs and PCBs were especially elevated by the Detroit Edison Generating Station in the Trenton Channel which has been previously identified as an area of high contamination (Fallon and Horvath, 1985; Kauss and Hamdy, 1985; Ali *et al.*, 1993; Leadley *et al.*, 1998). It was hypothesized that storm events contributed to contaminant water concentrations through increased urban and agricultural runoff and by causing resuspension of contaminated sediment particles into the water column. The influence of storms on the exposure dynamics of organic chemicals requires further study. The data showed that in many cases PAHs were present at much higher concentrations than PCBs of comparable hydrophobicity, which provided evidence that PAHs are critical contaminants in aquatic systems that warrant further attention.

In Chapter 4 it was found that PAH and PCB accumulation in benthic invertebrates of Lake Erie were influenced by the habitat preferences and diets of the different organisms. For example, mayflies accumulated high concentrations of contaminants because they live in soft sediment and thus have elevated exposure through ingestion of sediment associated chemicals. However, exposure through water was likely more important for dreissenids due to their intensive filter feeding activity. This study suggested that metabolic degradation of PAH compounds was important in the accumulation of PAHs in the benthic invertebrates. PAH metabolism was possibly highest in crayfish, followed by amphipods, while the rates of PAH metabolism in dreissenids and mayflies were lower. Since mayfly and dreissenid populations in western Lake Erie are abundant and because these organisms are important prey items for many

fish, mayflies and dreissenid mussels are likely an important source of organic contaminants to top predators. This study also showed that mayfly larvae and dreissenid mussels were effective biomonitors of PAHs and PCBs in the sediment and water column respectively of aquatic systems. Both PAH and PCB BSAF values varied consistently from 1, which supported the hypothesis that equilibrium dynamics were not occurring in western Lake Erie. The relationship between log BSAF and log K_{ow} for PCBs followed a parabolic pattern whereas PAH log BSAF values were inversely related to log K_{ow}. Differences among PAH and PCB BSAF values were likely due to PAH metabolism although factors, such as photolysis and slow desorption kinetics of PAHs from sediment to water, may have also been important. It was hypothesized that species-specific differences in log BSAF versus log K_{ow} regression lines were due to factors such as differences in growth rates, lipid content, feeding preferences and strategies, contaminant sources, and metabolic capabilities.

Overall, this thesis has demonstrated that the exposure dynamics of PAHs in the Detroit River and western Lake Erie are very complex. In addition, there are other factors that have not been taken into account in this project, such as climate changes and invasions of exotic species, that can further influence chemical behavior (Morrison *et al.*, 2000). A modeling approach is needed to quantify the relative importance of all these confounding factors in the accumulation of PAHs in different organisms. Several models have been developed to predict PCB distribution in aquatic systems (Gobas, 1993; Morrison *et al.*, 1996; Morrison *et al.*, 1997; Camphens and Mackay, 1997; Harrad and Smith, 1998; Morrison *et al.*, 2000). However, since the dynamics of PAHs and PCBs in food webs are different, PCB models cannot be directly applied to PAH compounds. In a

subsequent study, a PAH food web model will be developed to mathematically evaluate the factors influencing PAH behavior in aquatic systems. This will allow a more comprehensive evaluation of the toxicological stress resulting from PAHs to the Detroit River and western Lake Erie biota.

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