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FACTORs REGULATING ORGANOCHLORINE CONTAMINANT LEVELS
IN FORAGE FISH FROM THE ST. CLAIR AND DETROIT RIVERS

by

Craig Edwards Hebert

A Thesis
submitted to the
Faculty of Graduate Studies and Research
through the Department of Biological Sciences
in Partial Fulfillment of the requirements
for the Degree of Master of Science at
the University of Windsor

Windsor, Ontario, Canada

1990
Abstract

This study examined the factors which regulate levels of hydrophobic organic contaminants in forage fish. Whole body levels of pentachlorobenzene (QCB), hexachlorobenzene (HCB) and octachlorostyrene (OCS) in two species of forage fish: Notropis hudsonius and Pimephales notatus similarly reflected the spatial bioavailability of these compounds in the St. Clair River during 1987. A third species, Labidesthes sicculus, did not show spatial changes in contaminant exposure as consistently. These spatial patterns were contaminant specific reflecting the hydrophobicity of the compound. Contaminant levels in P. notatus most accurately reflected changes in sediment contamination.

Interspecific differences in lipid normalized contaminant levels were examined in fish from the St. Clair and Detroit Rivers. Four species of forage fish: L. sicculus, a surface feeder; N. atherinoides, a facultative surface feeder; N. hudsonius, a facultative benthivore; and P. notatus, a benthivore were collected during 1987-88 from the two sites. Whole body levels of QCB, HCB, OCS, DDE and PCB congeners #31, #52, #87, #101, #118, #138, #153, #180 were determined. Significant interspecific differences in contaminant concentrations were observed for compounds with a log octanol-water partition coefficient greater than 6.0. Highest mean contaminant levels
were seen in *P. notatus* and lowest levels were observed in *L. sicculus*. Food and habitat utilization were important factors regulating body burdens in these fish species.

Differences in metabolism may also play a role in regulating interspecific differences in contaminant levels therefore elimination rate constants were determined for *P. notatus* and *L. sicculus*. Significant interspecific differences in elimination rate constants for QCB and OCS were observed. However, no difference was observed in the rate at which HCB was eliminated.
Acknowledgements

I must thank Dr. Rodica Lazar and the other members of the Great Lakes Institute laboratory for weighing, grinding, boiling, and smelling what must have seemed an interminable number of fish samples. Without their assistance I would have been unable to complete this study. In addition, I want to thank Bernie Muncaster and Diane Laviolette for their help in the field and the laboratory. Finally, I need to thank Dr. Doug Haffner for his advice and encouragement over the last few years. Fortunately, Doug's enthusiasm for biology is contagious and I owe him for renewing my interest in science. Cheers, Doug.
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CHAPTER ONE

General Introduction

The threat to wildlife and humans posed by chemical contaminants in the environment is presently perceived to be a major concern by the public. Society is inundated by reports of the potential effects of compounds such as polychlorinated biphenyls (PCBs) and dioxins. However, human cultures have been familiar with the toxic properties of chemicals for thousands of years. Paracelsus's quote, "Sola dosis fecit venenum" or "Only the dose makes the poison" is as important to modern ecotoxicology as it was to Renaissance alchemists. An understanding of the processes that regulate an organism's contaminant 'dose' is essential in predicting those species most at risk. The mechanisms responsible for the transfer of contaminants to aquatic organisms, thereby regulating their chemical dose, are still debated. Laboratory microcosm studies examining the transfer of chlorinated hydrocarbons (CHCs) indicated that CHC accumulation was not food chain dependent but resulted from the direct partitioning of the compounds between the water and the study organisms (Scura and Theilacher 1977, Macek et al. 1979). These results are consistent with what would be predicted by a thermodynamic model of contaminant bioconcentration. A model of this type uses the concept of
fugacity to predict how a contaminant is transferred and where and at what level it will accumulate. Fugacity is a measure of the 'escaping tendency' of a chemical substance from a particular 'phase'. The environment is divided into a number of phases such as water, sediment, soil, atmosphere and biota. The distribution of a chemical in a compartment is considered to be homogeneous and sufficient time has elapsed such that the compartments are in chemical equilibrium. In such a scenario, the fugacities of all the phases are equal and there is no net transfer of contaminants. The fugacity \( f \) of a chemical in any phase can be defined as:

\[
 f = \frac{c}{Z} \quad \text{Eq.1}
\]

where
- \( c \) = concentration of chemical in the phase
- \( Z \) = fugacity capacity of the phase

The fugacity of a chemical in water is equal to the inverse of Henry's law constant:

\[
 Z_w = \frac{1}{H} \quad \text{Eq.2}
\]

therefore the chemical's fugacity in water is:

\[
 f_w = c_w H \quad \text{Eq.3}
\]

Two assumptions are required to obtain a formula for fugacity in biota: 1) organic chemicals are stored in lipid and 2) the fugacity capacities of lipid and octanol are identical. At equilibrium, during an octanol-water partitioning experiment, the fugacities of the chemical in the two phases are equal. Therefore:

\[
 K_{ow} = \frac{Z_o}{Z_w} \quad \text{Eq.4}
\]
where $K_{ow} =$ ratio of chemical concentration in the 2 phases

$Z_o =$ fugacity capacity of octanol
$Z_w =$ fugacity capacity of water

and if assumption 2) is correct, then $Z_o = Z_a$ and the animal's fugacity capacity ($Z_a$) will be:

$$Z_a = K_{ow}Z_w = K_{ow}/H$$  \hspace{1cm} \text{Eq.5}$$

and the organism's fugacity will be:

$$f_a = c_aH/K_{ow}$$  \hspace{1cm} \text{Eq.6}$$

where, $c_o =$ lipid normalized chemical concentration in the animal. At equilibrium, environmental phases can have different contaminant concentrations because each phase has its own fugacity capacity. If the compartments are not in equilibrium then fugacity can be used to predict the direction of contaminant movement. Contaminants will always diffuse from areas of high to low fugacity.

As described above, each phase is considered to be homogeneous and therefore differences between the various components of one phase are not taken into account. This may be of particular importance in the biotic phase where there are significant differences between species in their feeding habits and trophic positions. If the transfer of contaminants is primarily a passive process dominated by equilibrium partitioning then this assumption should not be important. At equilibrium, all species should exhibit similar contaminant levels normalized to their fugacity capacity. Interspecific differences in fugacity capacity can be taken into consideration by lipid normalizing wet
weight contaminant data. Because most organic contaminants are lipophilic they will be stored in the fat of the organism. Therefore, comparisons between species should take into account interspecific differences in fat content. This assumes, of course, that the fugacity capacity of fat tissue is identical between aquatic species. Therefore, at equilibrium, a fugacity model would predict that there should not be interspecific differences in lipid normalized contaminant levels. However, field studies have shown that significant interspecific differences in contaminant levels do occur and these differences cannot be explained by standard fugacity models. Highest contaminant levels are generally observed in species at the highest trophic levels (Thomann 1979, Connolly and Pederson 1988, Oliver and Niimi 1988) and this phenomenon has been explained by models incorporating food chain transfer of contaminants. At this point, it is useful to distinguish between intake of a contaminant from the abiotic environment and from food. Three terms are commonly used to distinguish among the major pathways of contaminant transfer: 1) bioconcentration is accumulation directly from water, primarily across the gills in fish 2) bioaccumulation is accumulation from both water and food. 3) biomagnification is the increase in contaminant concentration in successive levels of a food chain. Previous studies have indicated that, for hydrophobic contaminants (log Kow > 5.0), uptake from food accounts for a much greater proportion of the organism's contaminant burden than uptake from water (Connolly
and St. John 1989). Interspecific differences in feeding habits should then be of primary importance in determining species specific contaminant levels. Persistent, hydrophobic contaminants generally have a strong affinity for particulate matter. As a result, sorption onto particles and settling into sediments is an important, temporary removal mechanism. It is temporary due to the possible recycling out of the sediments and accumulation by benthic organisms (Reynoldson 1987).

To begin to understand the toxicological implications of contaminants in the environment, the scientist needs information concerning: the types of substances entering the environment as well as their quantities, sources, and distribution. A vital step in obtaining these data is to initiate studies involving environmental monitoring. Monitoring of contaminants in the environment can be accomplished by sampling and analyzing abiotic compartments such as water and sediment. However, the usefulness of results obtained from such analyses is limited. For example, levels of hydrophobic contaminants in water are often extremely low and well below the limit of detection for routine analytical techniques. Contaminant levels in water may also fluctuate greatly, reflecting temporal changes in contaminant inputs. Consequently the timing of water column sampling may effect the results. Levels in sediments can also be used to measure contaminant levels in the environment (Oliver and Pugsley 1986, Furlong et al. 1988). Sediment contaminant concentrations may vary greatly because of the physical properties of the sediment.
such as organic carbon content and particle size. Thus, spatial variability in sediment levels may reflect the physical patchiness of the sediment itself, not only the levels of contaminants to which it has been exposed.

The use of living organisms to measure contaminants in the environment is now generally accepted as an important component of any monitoring program. Only by analyzing these organisms do we get a direct measure of contaminant bioavailability and hence, exposure. Thus, biomonitors provide vital information regarding environmental quality. Compliance monitoring is normally undertaken to determine compliance with regulations, that is, to determine whether the discharge of contaminants into the environment is within legislated limits. Biomonitors can be used to provide this type of information. For example, chemical analysis of plant material can give an indication of low level contamination of water that otherwise would not have been detected (Say et al. 1981). The levels of contaminants accumulated in animal tissue have also been used to indicate environmental contamination. Sessile animals, especially those that have a wide distribution, are particularly useful for this purpose (Goldberg et al. 1978). Although biological monitoring may be expensive, its justification lies in the limitations of purely physical and chemical monitoring (Moriarty 1988). As stated earlier, the concentration of pollutants in receiving waters may fluctuate greatly. Even if samples are taken on a regular basis it is highly probable that peak concentrations may
be missed. Biotic samples, however, do not only give an indication of water quality at the time of sampling but also reflect the organisms' integration of past environmental conditions.

Biological monitoring, in conjunction with surveillance of abiotic factors such as those mentioned above, may provide complementary data which indicate the relationship between chemical conditions and the biological characteristics of the water (Abel 1989). Surveillance and effects monitoring is undertaken to determine whether ecologically significant changes are occurring in an ecosystem. If a change in a biological community is detected then a detailed screening of pollutants can be made (Mason 1981). For example, in 1969 a large, unexplained mortality of seabirds occurred in the Irish Sea. It was discovered, after chemical analyses were performed, that high levels of polychlorinated biphenyls were responsible for this seabird mortality (Natural Environmental Research Council 1977). Prior to this incident, PCBs had received little attention. This underlines the importance of living organisms as vital environmental "sentinels". Reliance on contaminant measurements alone, without also examining biological effects, ignores the biological significance of the contaminant levels and how combinations of pollutants may interact to either enhance or reduce the toxic effect.

A wide variety of organisms has been used as aquatic biomonitors including: plants (Say et al. 1981), invertebrates
(Oliver 1984, Pugsley et al. 1985, Oliver 1987, Knezovich and Harrison 1988), reptiles (Olafsson et al. 1983, Bryan et al. 1987), and fish (Seelye et al. 1982, Suns et al. 1981, 1985a, 1985b, Castonguay et al. 1989). Each of these organisms must meet a number of similar requirements to be effective biomonitors (Price 1979). As mentioned earlier, the species should give an indication of not only the water quality at the time of sampling but also over a more extended period. A biomonitor should be relatively abundant to facilitate sample collection and its life history should be understood so that the primary routes of contaminant transfer can be quantified. In addition, it is important that the biomonitor indicate the environmental quality at the point of sampling rather than in the watercourse as a whole. Being relatively mobile animals, fish, in general, do not meet this last requirement as satisfactorily as, for example, the macroinvertebrates. However, this problem can be ameliorated to some extent by examining contaminant levels in young-of-the-year forage fish species. Forage fish have much smaller home ranges than game fishes and young-of-the-year are known to restrict their movements to an area of approximately two Km² (Suns et al. 1985b). Using forage fish as biomonitors has other advantages as well. They generally accumulate higher levels of contaminants than some other biomonitoring species, such as macroinvertebrates (Muncaster et al. 1990). Forage fish are also important intermediates in the food web linking benthic and pelagic communities.
The spottail shiner (*Notropis hudsonius*) has been used extensively by the Ontario Ministry of the Environment in its biomonitoring studies (Suns et al. 1981, 1985a, 1985b). This species has been used to identify Areas of Concern in the Great Lakes and, due to its preference for near-shore habitat, has proven to be useful in compliance monitoring. Yearly collections of *N. hudsonius* have also provided information on temporal changes in contaminant levels in the Great Lakes (Suns et al. 1985b). This species does meet the requirements for an effective biomonitor but very little is known of the degree to which contaminant levels in this species are comparable to those in other forage fish species. Although research has shown that *N. hudsonius* bioaccumulates contaminants, it is unclear how an examination of these levels can assist in defining the primary routes of contaminant transfer in aquatic ecosystems. Hence, the relationship between exposure and contaminant level in this species needs to be quantified. This has important implications for biomonitoring studies in which only one or two species may be used to evaluate the overall health of an ecosystem. The levels of contaminants in these monitored species cannot be expected to reflect contaminant levels in all species of biota. However, if the objective of the biomonitoring program is to assess the degree to which an area is contaminated then biomonitors must be chosen so that they incur maximal exposure to the contaminants present at that site. The consumption of contaminated benthic prey by some forage fish species may be an important factor
regulating exposure to these maximum concentrations (Eadie et al. 1988).

This study examined contaminant levels in several species of forage fish to resolve three questions concerning the applicability of forage fish as biomonitors:

1) Chapter 2 examines if different forage fish species reflect spatial differences in contaminant bioavailability in a similar manner as *N. hudsonius*. Null hypothesis: There is no difference in the way in which each fish species reflects the spatial distribution of contaminants.

2) Chapter 3 examines if there are interspecific differences in contaminant levels in four species of forage fish and if there are, why do they occur? Null hypothesis: There are no interspecific differences in lipid normalized contaminant levels.

3) In Chapter 4, the possible mechanisms regulating interspecific differences in contaminant levels are examined. Are these differences caused by interspecific differences in toxicokinetics or exposure? Null hypothesis: There is no difference in interspecific chemical elimination rates.
CHAPTER TWO

Forage Fish As Indicators of the Spatial Distribution of Organic Contaminants in the St. Clair River

Introduction

Monitoring of contaminants in the aquatic environment has included the analysis of abiotic components such as water and sediments. Contaminant levels in water samples, however, are often extremely difficult to measure because they are so low and below the detection capability of available instrumentation (Kauss et al. 1983). Due to the hydrophobic nature of many organic contaminants, only minute quantities of these chemicals are found in the aqueous phase. Thus, water samples do not give a good indication of the potential for bioaccumulation because they underestimate levels of hydrophobic contaminants in the environment. Contaminant levels in water samples may also vary temporally because of changes in contaminant discharge. Sediment samples have much higher contaminant concentrations than water but they too may be highly variable and do not yield information on the bioavailability of the chemical. Linear partition coefficients (Kp) can be used to predict the degree to which a chemical will sorb to sediments and other particulate matter
(Swackhammer and Armstrong 1987). Contaminants with high Kp values will have a high affinity for sediments. Kps have been shown to be relatively independent of sediment chemical concentrations but they are directly related to the sediment's organic carbon content. The greater the amount of organic carbon in the sediment the greater the sediment's ability to sorb contaminants (Karickhoff et al. 1979, Swindoll 1987). When the amount of organic carbon in the sediment is taken into consideration (Koc = Kp/fraction organic carbon) the size of the particles also has an important effect on sorption (Karickhoff et al. 1979, Swindoll 1987). Particles that are greater than 50 um in size, such as sand, are much less effective sorbents than smaller particles (<50 um). Accurate estimates of Koc can be made from the Kow of the compound (Karickhoff et al. 1979) according to the equation:

\[
Koc = 0.63 \text{ Kow}
\]  

Eq.7

Therefore, different sediment types will differentially bind contaminants and the levels observed in those sediments may not reflect the sediment's degree of chemical exposure. Sediment levels also may not give an accurate estimate of bioavailability as the proportion of contaminant available for biological uptake may be overestimated. Bioavailability is directly related to the amount of dissolved contaminant that is present. The fraction of contaminant associated with particulate matter can be estimated as follows:

\[
fp = \frac{Kp(\text{SPM})}{1+Kp(\text{SPM})}
\]  

Eq.8
where, \( fp \) = fraction of contaminant associated with particulates
\( SPM \) = suspended particulate matter

As the amount of particulate matter increases so will the proportion of contaminant associated with it, thus reducing the amount of bioavailable contaminant (Eadie and Robbins 1984).

It has become increasingly evident that the use of biomonitors may lead to a more accurate understanding of the factors that regulate the distribution and bioavailability of contaminants in the environment. Organisms integrate contaminant exposure over an extended period and therefore better represent the "typical" exposure to contaminants in an impacted area. Aquatic invertebrates, such as oligochaetes and bivalve molluscs, have proven to be useful in this respect (Oliver 1984, Oliver 1987, Kauss et al. 1981, Kauss and Hamdy 1985, Foster et al. 1987). Vertebrate species have also been used. One of the most successful biomonitors currently utilized in the Great Lakes is a forage fish species, *Notropis hudsonius*, the spottail shiner. The Ontario Ministry of the Environment has used young-of-the-year *N. hudsonius* since 1975 to identify Areas of Concern for organochlorine contaminants in the Great Lakes. Residues of these compounds in the fish are considered to reflect the water quality of the area and indicate local bioavailable forms of contaminants. Because these fish remain in nearshore waters they are particularly useful in compliance monitoring and for the early detection of introduced contaminants from land-based sources (Suns et al. 1981, Suns et al. 1985a, Suns et al. 1985b).
"Notropis hudsonius" has also been used to monitor temporal trends in organochlorine contaminants. Although the usefulness of this species as a biomonitor is evident, it is not known whether the spatial patterns of contaminant concentrations in "N. hudsonius" are a reflection of biological processes or of chemical properties of the compounds, such as their hydrophobicities. Increased hydrophobicity will cause a compound to have a greater affinity for particulate matter and hence that contaminant may be removed from an aquatic system rapidly due to sedimentation. This may limit more hydrophobic compounds to the localized geographic area in which the contaminant is being discharged.

The petrochemical industries along the Canadian shoreline of the St. Clair River, south of Sarnia, have been identified as the primary sources of QCB, HCB, and OCS in the St. Clair River (Pugsley et al. 1985, Oliver and Pugsley 1986, O.M.O.E. 1987). This study examined how contaminant levels in forage fish, collected from the St. Clair River in 1987, reflected spatial changes in contaminant bioavailability. The null hypothesis being that species have similar home ranges and therefore the spatial heterogeneity of contaminant distribution should be reflected in the same manner between "N. hudsonius" and two other forage fish species: "Labidesthes sicculus" and "Pimephales notatus."
Methods and Materials

Field

Three species of forage fish: *Labidesthes sicculus* (brook silverside), *Notropis hudsonius* (spottail shiner), and *Pimaphales notatus* (bluntnose minnow) were collected from 8 sites along the St. Clair River system (Figure 1). Collections of each species were made in July, August, and September 1987. Site 1 (SC1) was located north of Sarnia's petrochemical industries on Lake Huron and was the control site. Site 2 (SC2) was located near Stag Island immediately south of Sarnia's Chemical Valley. Sites 3 and 4 (SC3 + SC4) were located on the Canadian and American sides of the lower St. Clair River respectively. Sites 5-8 (CE1-CE4) were located from north to south on the Chenal Ecarte, one of the main branches of the St. Clair River. Fish were collected in shallow waters (1-1.5 m) using a 10 m, 0.6 cm mesh bagseine. They were measured (total length) and immediately wrapped in hexane-rinsed aluminum foil. These samples were kept frozen at -20°C until they were analyzed.

Sediment samples were also taken from all of the sites except CE4. The top 3 cm of sediment were collected and placed in hexane-rinsed amber glass jars. Jars were stored at -20°C.
Figure 1. Fish collection sites from the St. Clair River and the Chenal Ecarte
Laboratory

1) Preliminary Treatment of Fishes

Pooled samples of whole fish were analyzed according to the protocol developed by the Canadian Wildlife Service (1982). Each sample consisted of approximately 5 fish and the composite wet weight was not less than 3 g. The sample was placed into a mortar and 30 g of anhydrous sodium sulphate (ACS) was added. The mixture was ground to a free-flowing powder using a glass pestle. The resulting sodium sulphate mixture was poured into a 2.1 cm x 35 cm long glass column, with teflon stopcock, which had been plugged with glass wool (previously rinsed with 1:1 methylene chloride and hexane and air-dried) and 2 cm of sodium sulphate. It was then heated to 400°C for 1-2 h. The mixture in the column was then topped with 1 cm of sodium sulphate and the column was tapped to settle the mixture. A 500 mL evaporating flask was placed under the column. The mortar and pestle were rinsed with 50 mL of 50/50 dichloromethane (DCM) and hexane (distilled-in-glass Caledon) and this was transferred to the column using a Pasteur pipet. The stopcock was opened and enough DCM/hexane was added to expel any air in the column. The DCM/hexane was allowed to sink only into the top sodium sulphate layer. A reservoir was placed on the column and 250 mL of DCM/hexane were added without disturbing the top sodium sulphate layer. The column was eluted at 5-10 mL/min. (a steady drip). The eluate was evaporated to less than 20 mL on a rotary evaporator (Buchi Rotavapor-R) with a
water bath at 33°C. The eluate was transferred to a 50 mL graduated cylinder with a ground glass stopper. It was made up to a volume of 25 mL with DCM/hexane, mixed, and then allowed to stand so that any sodium sulphate sediment settled out. Lipid determinations were made by pipetting 2.5 mL of the DCM/hexane extract into a pre-weighed aluminum dish. The DCM/hexane was evaporated to dryness in a fume hood and the dish was placed into a drying oven at 105°C for 10-20 min. The dish was removed from the oven, cooled, and reweighed. The difference in weight was the weight of the lipid. Percent lipid was calculated as follows:

\[
\% \text{ lipid} = \frac{W_l}{W_t} \times \frac{V_t}{V_e} \times 100
\]

Eq. 9

where,  
\( W_l \) = weight of lipid  
\( W_t \) = total weight of sample extracted  
\( V_t \) = total volume of extract  
\( V_e \) = volume of extract used for lipid determination

2) Contaminant Determinations

The remaining 22.5 mL of the sample extract underwent the following Florisil column clean-up. 35 g of 1.2% deactivated Florisil (60-100 mesh PR, Floridin Co.) were poured into a 2.1 cm x 35 cm glass column, with teflon stopcock, that had been plugged with glass wool. The column was gently tapped after the addition of the Florisil and then the column was topped with 1 cm of sodium sulphate. The column was prewetted with petroleum ether and, as the petroleum ether reached the top of the sodium sulphate, the stopcock was closed. The receiving vessel was replaced with a 250 mL evaporating flask. 150 mL of petroleum
ether were measured out to be used as the eluant. The sample extract (22.5 mL) was transferred to a 250 mL evaporating flask and evaporated to 2 mL using a rotary evaporator. It was then transferred to the top of the column using a Pasteur pipet. This aliquot did not contain more than 0.5 g lipid. The sample was allowed to sink into the column and the evaporating flask was rinsed with 3 x 2 mL portions of petroleum ether. The washings were transferred to the column using a Pasteur pipet. The sides of the column were rinsed with 3 x 2 mL portions of petroleum ether. A 250 mL glass reservoir was placed on top of the column and the remainder of the petroleum ether was added. The column was eluted at 5-100 mL/min. In this study only the first fraction through the column was collected as it contained the compounds of interest. It was evaporated to 2 mL in the Rotavapor and transferred with a Pasteur pipet to a 12 or 15 mL centrifuge tube with ground glass stopper. The flask was rinsed with small, 1-2 mL, portions of petroleum ether. The volume of this fraction was adjusted to 2 mL/g. This fraction contained chlorobenzenes, octachlorostyrene, polychlorinated biphenyls, pp'-DDE, mirex and photomirex. Pentachlorobenzene (log Kow = 5.2), hexachlorobenzene (log Kow = 5.5) and octachlorostyrene (log Kow = 6.3) were examined in detail due to their presence in all of the samples and because they are produced near the sample sites (M.O.E. 1987). Recovery efficiencies for this method were determined to be 87% for QCB, 89% for HCB, and 91% for OCS. Reported values were not corrected for recovery efficiencies. Sediment samples
were analyzed using Soxhlet procedures.

The samples were injected into a Hewlett-Packard Model 5790A GC-ECD fitted with a 30 m x 0.25 mm DB-5 capillary column (J+W Scientific). Standards (QCB, HCB – Chemservice, OCS – Health and Welfare Canada) and a solvent blank, which had undergone the entire isolation procedure, accompanied each set of six samples. For QCB, HCB, and OCS the limit of quantification was 0.1 ug/kg.

Results

Figures 2-4 show the spatial distribution of pentachlorobenzene, hexachlorobenzene and octachlorostyrene for L. sicculus, N. hudsonius, and P. notatus respectively. No significant intraspecific differences in lipid levels were observed during these months (ANOVA, L. sicculus p>0.1, N. hudsonius p>0.1, P. notatus p>0.1). Lipid levels ranged from 2.5-3.0%. Because the contaminants examined are highly lipophilic, changes in lipid levels might have an important impact on contaminant levels. Lipid levels in each of the species are similar in July, August and September therefore contaminant analyses for those 3 months were pooled. For all three species the concentration of the 3 compounds at the 'background' site (SC1) were significantly lower than the levels observed at SC2 (Scheffe's test p<0.05). At SC2, the site immediately south of Sarnia's Chemical Valley, the highest contaminant levels were observed for HCB and OCS for all 3 species (Scheffe's test.
Figure 2. Mean pentachlorobenzene levels in whole fish from sites 1-8 (+1 standard error). a) *Labidesthes sicculus*  
b) *Notropis hudsonius*  c) *Pimephales notatus*
Figure 3. Mean hexachlorobenzene levels in whole fish from sites 1-8 (± 1 standard error). a) *Labidesthes sicculus*
b) *Notropis hudsonius* c) *Pimephales notatus*
Figure 4. Mean octachlorostyrene levels in whole fish from sites 1-8 (± 1 standard error). a) Labidesthes sicculus
b) Notropis hudsonius  c) Pimephales notatus
p<0.05). For QCB, levels were highest at SC2 (Scheffe's test p<0.05) with two exceptions: there were no significant differences between levels at CE1 and SC2 for *L. sicculus* or between levels at SC3 and SC2 for *N. hudsonius* (Scheffe's test p>0.1). Continuing down the St. Clair River and into the Chenal Ecarte there was a gradual decline in contaminant levels in *N. hudsonius* and *P. notatus*. Although contaminant levels between adjacent sites were not statistically different there was a trend of diminishing contaminant levels downstream, away from the sources of contamination. Levels of the 3 contaminants did not show as consistent a decline in *L. sicculus*. Levels of all 3 contaminants are highest in *P. notatus*, followed by *N. hudsonius* and then *L. sicculus*.

Although no statistical analyses were completed I also examined the spatial decline of QCB, HCB and OCS for the 3 fish species from SC2 to CE4 and for sediment from SC2 to CE3 (Figures 5-7) and the following trends were observed. It was evident that sediment levels declined to the greatest degree. For example, from site SC2 to site CE3 sediment OCS levels declined 92.4%. Among the fish species, levels of the 3 contaminants generally declined to the greatest degree in *P. notatus* followed by *N. hudsonius* and then *L. sicculus*. This was particularly true for the higher Kow compounds, HCB and OCS. For example, from site SC2 to site CE4 OCS levels decline 89.9% in *P. notatus*, 83.5% in *N. hudsonius*, and 47.5% in *L. sicculus*. It should be noted that Figures 5-7 represent a preliminary examination of spatial
Figure 5. Spatial decline in pentachlorobenzene levels:
percent of SC2 QCB concentration at downstream sites
for sediment, P. notatus, N. hudsonius, L. sicculus.

Figure 6. Spatial decline in hexachlorobenzene levels:
percent of SC2 HCB concentration at downstream sites
for sediment, P. notatus, N. hudsonius, L. sicculus.
Figure 7. Spatial decline in octachlorostyrene levels:
percent of SC2 OCS concentration at downstream sites
for sediment, P. notatus, N. hudsonius, L. sicculus.
decline in contaminant concentrations in the St. Clair River system. The lines on these figures are not meant to indicate that contaminant levels are declining in a linear fashion but have been added to facilitate interpretation.

Examining percent decline Km\(^{-1}\) of river section emphasizes differences in the capacity of the river sections to bind contaminants. Percent decline Km\(^{-1}\) of river section was calculated by comparing contaminant levels at adjacent sites. This resulted in an estimate of percent decline per river section which was then divided by the distance between the 2 sites. The greatest decline in sediment and fish concentrations took place in the Chenal Ecarte between sites CE2 and CE3 (Figures 8-10). For example, OCS levels in sediment and \textit{P. notatus} declined 1.6\% and 1.8\% Km\(^{-1}\) from SC2-CE1, 0.3\% and 4.4\% Km\(^{-1}\) from CE1-CE2, and 13.0\% and 5.1\% Km\(^{-1}\) from CE2-CE3. In river section CE2-CE3 levels of HCB and OCS declined to a greater extent than levels of QCB. For example, sediment levels of QCB, HCB and OCS declined 12.6\%, 14.5\% and 13.0\% Km\(^{-1}\) respectively. Similarly, from CE2-CE3 levels of QCB, HCB and OCS in \textit{P. notatus} declined 4.6\%, 7.3\% and 5.1\% Km\(^{-1}\) respectively.
Figure 8. Percent decline in pentachlorobenzene levels per kilometer of river section for *L. sicculus*, *N. hudsonius*, *P. notatus* and sediment.

Figure 9. Percent decline in hexachlorobenzene levels per kilometer of river section for *L. sicculus*, *N. hudsonius*, *P. notatus* and sediment.
Figure 10. Percent decline in octachlorostyrene levels per kilometer of river section for *L. sicculus*, *N. hudsonius*, *P. notatus* and sediment.
Discussion

Levels of QCB, HCB and OCS in each of the three species examined in this study were highest at the site closest to the contaminant sources. However, contaminant levels in N. hudsonius and P. notatus exhibited a more consistent pattern of contaminant decline with increasing distance from these point sources than did levels in L. sicculus. In addition, the decline in contaminant concentrations was not constant along the course of the river. Greatest contaminant declines were observed in fish and sediment between sites CE2 and CE3. This may occur because in this section of the Chenal Ecarte there is more natural shoreline allowing for extensive macrophyte growth. Further upstream, much of the original shoreline has been replaced with dykes and steel siding designed to prevent erosion. Therefore, in this river section the amount of organic material available to bind contaminants was greatly enhanced. This may have resulted in the observed reduction in fish and sediment contaminant levels as the chemicals were sorbed onto this vegetative matter. The ability of aquatic macrophytes to accumulate organic contaminants has been demonstrated in the Walpole Island marsh (Haffner et al. unpublished data). Thus, wetlands may play an important role in reducing contaminant availability. Their high productivity and resultant large organic carbon pool can act to bind bioavailable forms of contaminants lessening biological exposure.
As described earlier, the fate and distribution of contaminants in the environment can be predicted, in part, by the physical properties of the chemicals. Amongst the more useful of these characteristics is the chemical's n-octanol-water partition coefficient or Kow. The Kow of a compound measures the degree to which that compound partitions between water and octanol. As many persistent environmental contaminants are highly hydrophobic, they will partition from the aqueous phase into the lipid compartment. Octanol acts as a lipid surrogate and hence the Kow of a compound measures the hydrophobicity of the chemical. The greater the Kow the greater the chemical's hydrophobicity and the lower its aqueous solubility. Therefore, for very hydrophobic contaminants (log Kow > 6.0) only a small fraction of that chemical will be found in water. Instead, these compounds will partition to organic material. The compounds examined in this study have Kows ranging over an order of magnitude: QCB (log Kow = 5.2), HCB (log Kow = 5.5), and OCS (log Kow = 6.3). Thus, QCB is the least hydrophobic and OCS shows the greatest hydrophobicity. Compounds with high Kows would also be expected to have high Kocs (Karickhoff 1981). It would be expected that a compound such as OCS would partition more readily to sediments and other particulate matter than a relatively less hydrophobic compound such as QCB. This was reflected in the relative decline of the contaminants from CE2 to CE3. Levels of the higher Kow compounds HCB and OCS declined to a greater extent than QCB indicating that HCB and OCS may have partitioned to organic
matter, such as submersed macrophytes, to a greater extent than
QCB. This is consistent with observations of Gobas et al. (1990)
that showed a linear relationship between macrophyte
bioconcentration factor and chemical Kow. However, differences
among these compounds were not as great as might have been
expected considering their different Kows. One might have
expected that the higher Kow compounds would have been
distributed within a narrow geographic region around their point
sources because rapid partitioning to organic matter would have
precluded extensive transport in the aqueous phase. However, this
hypothesis does not take into consideration processes such as
sediment transport, biotic dispersal, or transport of
contaminants associated with the dissolved organic carbon
fraction of the aqueous phase. Thus, the physical and biological
characteristics of a waterway may complicate the understanding of
contaminant transport.

In general, *P. notatus* tracked changes in sediment levels
more accurately than the other two fish species. For instance,
the levels of OCS in *P. notatus* from the Chenal Ecarte declined
more rapidly than OCS levels in the other two species, reflecting
the decline in sediment concentrations. Levels of OCS declined in
an intermediate fashion in *N. hudsonius*, and to an even lesser
degree in *L. sicculus*. This may have been because of the
differences among species with respect to habitat utilization and
feeding behaviour. *P. notatus* makes use of benthic food resources
and habitat to a much greater extent than the other two fish
species (Hebert and Haffner 1989b). Thus, declining sediment levels of OCS were most clearly reflected in the species most closely associated with the contaminated sediments.

There was evidence that interspecific differences in contaminant levels existed. Since the three species showed similar responses in their contaminant levels to changes in the spatial distribution of contaminants, other factors must have been responsible for regulating these interspecific differences. The importance of resource and habitat partitioning in determining contaminant levels in forage fish has been documented (Hebert and Haffner 1989b).

Summary

This study indicated that: 1) *N. hudsonius* and *P. notatus* exhibited similar spatial patterns of bioaccumulation and that *L. sicculus* reflected changes in environmental contamination in a less consistent manner 2) these spatial patterns were contaminant specific, reflecting the hydrophobicity of the compound. However, interspecific differences in contaminant levels were indicated. The current use of *N. hudsonius* as the Ontario Ministry of the Environment's forage fish biomonitor may underestimate the potential bioavailability of contaminants in sediment. Benthic species track organic sediments and will therefore be exposed to the greatest concentrations of persistent, hydrophobic
contaminants. The sampling of benthic species, such as P. notatus, will focus on organisms most likely to be impacted by hydrophobic contaminants and will therefore result in a better approximation of in place pollutants.
CHAPTER THREE

Habitat Partitioning and Contaminant Exposure in Forage Fish

Introduction

Debate exists concerning the role that biomagnification plays in regulating contaminant distribution in aquatic ecosystems. The thermodynamic approach, based on fugacity models, predicts that organisms in equilibrium with their environment should show similar levels of contaminants in their lipid fractions, regardless of their trophic status or habitat utilization (Connolly and Pederson 1988). An alternate model based on food web dynamics incorporates the process of biomagnification thereby allowing for interspecific differences in lipid normalized contaminant levels (Thomann and Connolly 1984).

The fugacity approach divides the environment into phases such as biota, sediment, suspended solids, water, and air. If transfer of a chemical is to occur passively among these compartments then a gradient in chemical potential, or fugacity, must exist. At equilibrium, the fugacity of all phases is assumed to be equal, with no net transfer of contaminants. In such a balanced aquatic ecosystem one would not predict any differences
in lipid-normalized contaminant levels among aquatic organisms. When differences in contaminant levels have been observed between trophic levels, these differences have been dismissed as being relatively small and only occurring for a few very hydrophobic compounds (Thomann and Connolly 1984). Such differences have also been attributed to non-equilibrium conditions which assume that organisms are moving towards equifugacity, possibly at different rates, but have not yet reached that state. Non-equilibrium dynamics, for example, would also result from the slow uptake rates of highly hydrophobic compounds compared with organism growth rates. Therefore, large species at higher trophic levels would have the greatest chemical body burdens not because feeding provides additional exposure to the chemical but because exposure duration would be greatest and chemical elimination would be slowest for these species.

Other work has suggested that an alternate model based on food web dynamics can better explain the distribution of contaminants in aquatic ecosystems. Borgmann and Whittle (1983) illustrated that larger organisms had higher contaminant levels than smaller organisms, but as their data were not lipid normalized it is not possible to demonstrate biomagnification. Their results did suggest, however, that biomagnification could occur. Thomann and Connolly (1984) developed an age-dependent food chain model for polychlorinated biphenyls in the Lake Michigan food chain and concluded that the major route of PCB uptake was from food. This mechanism was further substantiated
by Oliver and Niimi (1988) who demonstrated the importance of 'trophodynamics' in contaminant partitioning in the Lake Ontario ecosystem. Similar observations have been made by Connolly and Pederson (1988) and Gobas et al. (1988), resulting in considerable evidence that food resources play an important role in determining the distribution and levels of selected organic contaminants in aquatic food webs.

If food is an important exposure route, then differences in resource utilization among species may play an important role in regulating their contaminant body burdens (Flint et al. 1988). To further resolve the factors regulating contaminant levels in aquatic organisms, I examined contaminant levels in forage fish. Within this component of the foodweb, benthic, pelagic, and allochthonous food sources are differentially utilized by philopatric species of similar size and age. Should chemical properties, related to the bioconcentration potential of contaminants, be singularly important (Neely et al. 1974, Veith et al. 1979) one would expect negligible interspecific differences among these organisms. The importance of chemical hydrophobicity in determining contaminant levels in fish has been demonstrated (Johnston et al. 1988). Similarly, other chemical factors such as aqueous solubility, which regulates the bioavailability of a compound, should also result in equivalent body burdens. Should, however, differences in lipid normalized contaminant levels be observed, other regulating factors such as metabolic differences and/or differences in exposure dynamics
would need to be examined.

Few studies have examined the relative importance of ecological factors in determining both contaminant levels and distribution in aquatic food webs. Many species, for which ecological data are lacking, have been considered by monitoring programs to be ecological equivalents. As a result, different biomonitors are often expected to integrate system changes in contaminant levels in a similar manner. This assumption might not be justified for organisms that differ either ecologically or metabolically.

Forage fish populations provide an opportunity to test this assumption. Within this group, minor morphological differences among species can correspond to major differences in habitat utilization (Keast and Webb 1966). Forage fish are useful biomonitors in that they have limited home ranges and are accurate indicators of the local bioavailability of contaminants (Hebert and Haffner 1990a). For example, the spottail shiner (Notropis hudsonius), has been used to monitor the spatial distribution of contaminants in the Great Lakes as well as to evaluate long-term trends in contaminant levels (Suns et al. 1985b, Suns et al. 1985). However, little is known regarding the factors that regulate contaminant accumulation in this species or if this species represents contaminant levels in forage fish in general.

Four species were examined in this study: Labidesthes sicculus (Cope) (brook silverside), Notropis atherinoides
Rafinesque (emerald shiner), *Notropis hudsonius* (Clinton) (spottail shiner), and *Pimephales notatus* Rafinesque (bluntnose minnow). There are major anatomical differences between surface, water-column, and bottom feeding fishes. These physical differences determine their partitioning of food resources (Keast and Webb 1966). *Labidesthes sicculus* is primarily a surface feeding species (Scott and Crossman 1973), with a beak-like snout and dorso-terminal mouth designed to seize prey at the surface. Analysis of stomach contents reveals that its diet consists primarily of small flying insects and some cladocerans (Scott and Crossman 1973). *Notropis atherinoides* has a terminal mouth and is a facultative surface feeder whose diet consists primarily of zooplankon (Scott and Crossman 1973). *N. hudsonius* has a terminal mouth, but analysis of gut contents, as summarized in Scott and Crossman (1973), indicates that this species consumes a wide variety of organisms including Cladocera, aquatic insect larvae, and algae. It could therefore be classified as a facultative benthivore. *P. notatus* possesses a ventro-terminal mouth designed for benthic feeding (Scott and Crossman 1973), and subsists almost entirely on chironomid larvae and organic detritus from the bottom. The diet of these species represents an integration of allochthonous, pelagic, and benthic foodwebs. The partitioning of food resources between *N. hudsonius* and *N. atherinoides* has been previously documented. Muth and Busch (1989) found little dietary overlap between the two species, with *N. atherinoides* mainly feeding on Cladocera. As these two species are generalists
in the sense that they both consume benthic and pelagic food items, it would be expected that specialists such as *P. notatus* and *L. sicculus* would have pronounced differences in diet based upon their morphological adaptations to feed primarily in the benthic and pelagic food webs respectively. In this study, the relative importance of chemical and ecological factors in determining contaminant burdens in forage fish species is examined.

Materials and Methods

Fish were collected from two nearshore sampling locations (Figure 11). The first site was located in the St. Clair River approximately 1.5 km south of Sarnia's Chemical Valley, and was close to important sources of organochlorine contamination on the Canadian side of the river (Kauss and Hamdy 1985). Water was shallow (1-1.5 meters) and well mixed. Sediment consisted of a mixture of silt and coarse sand. A second site, located in the Trenton Channel of the Detroit River near the southern tip of Grosse Ile was chosen because it is also heavily contaminated (Kauss and Hamdy 1985) with a variety of organochlorines.

The St. Clair River site was sampled during August and September, 1987. Young-of-the-year of the 4 fish species were caught in nearshore waters using a 10 m, 0.6 cm mesh bagseine. Immature fish were collected to minimize intersexual differences.
Figure 11. Fish collection sites from the St. Clair and Detroit Rivers (boxes).
Fish were measured (total length), grouped according to length and immediately wrapped in hexane-rinsed aluminum foil. Samples were kept frozen at -20°C until they were analyzed. This site was sampled again in September 1988 and at this time both fish and sediment samples were collected. The top 3 cm of sediment was collected and placed in hexane-rinsed amber glass jars. Jars were also stored at -20°C.

During October 1988, _L. sicculus_ and _P. notatus_, were collected from the Detroit River site. Sediment samples were also collected as previously described.

The compounds we examined varied over two orders of magnitude in their 1-octanol water partition coefficients (Kow). Pentachlorobenzene (log Kow = 5.2), hexachlorobenzene (5.5), octachlorostyrene (6.3) and PCB congeners 101 (6.38) and 180 (7.36) were examined at both sites. In addition, at the Detroit River site, p,p′DDE (log Kow = 5.69) and PCB congeners 31 (5.7), 52 (5.84), 87 (6.29), 118 (6.74), 138 (6.83), and 153 (6.92) were examined. Fish from the St. Clair River had low levels of PCBs; therefore, we examined the wide range of congeners only in 1988 so that bioaccumulation factors could be calculated for fish from both locations.

Whole fish were analyzed according to extraction and clean up protocols developed by the Canadian Wildlife Service (1982). All samples consisted of approximately 5 individuals and the composite wet weight was not less than 3 g. The only deviation from CWS methodology was that during the Florisil column clean-
up, petroleum ether (Caledon, distilled-in-glass) was used as the eluant instead of hexane.

Sediment samples were analyzed using Soxhlet procedures. For all samples, only the first fraction from the Florisil column was collected. This fraction contained chlorobenzenes, octachlorostyrene, and various PCB congeners. Recovery efficiencies for this method were 87% for QCB, 89% for HCB, and 91% for OCS. Recovery efficiencies for the PCB congeners were 90%. Reported values were not corrected for recovery efficiencies. To determine if the existing gut content could affect body burden, gutted fish were analyzed and compared with body burdens of whole fish samples. Lipid determinations were made on each sample. The organic carbon content of each of the sediment samples was determined using loss on ignition.

The samples were injected into a Hewlett-Packard Model 5790A GC-ECD fitted with a 30m x 0.25mm DB-5 capillary column (J+W Scientific). Standards (QCB, HCB-Chemservice, OCS-Health and Welfare Canada, PCB congeners-Environment Canada) and a solvent blank, which had undergone the entire isolation procedure, accompanied each set of six samples. For QCB, HCB, and OCS the limit of quantification was 0.1 ug kg\(^{-1}\). For the PCB congeners the limit of quantification was 0.2 ug kg\(^{-1}\).

Rudimentary gut contents analysis was completed for P. notatus and L. siccus to verify diet partitioning. Three food types were included: chironomid larvae (benthic), bosmina (pelagic) and chironomid adults (allochthonous). Other food items
were not included.

Bioaccumulation factors (BAFs) were estimated for each of the species at both sites during 1988 to determine the relationship among contaminant levels in fish and sediment and the 1-octanol water partition coefficient. BAFs were calculated by dividing the lipid-normalized contaminant levels in the fish by the organic carbon normalized contaminant levels in the sediment (dry weight).

Results

Considerable interspecific compartmentalization of the contaminants occurred in fish from the St. Clair River (Figure 12). Significant interspecific differences in log\(_{10}\) transformed, lipid normalized contaminant levels were detected using ANOVA (p<0.05) followed by Tukey's test (p<0.05). A similar pattern of chemical compartmentalization for _L. sicculus_ and _P. notatus_ was seen in the Detroit River (Figure 13). Significant interspecific differences in log\(_{10}\) transformed, lipid normalized contaminant levels were detected using Student's t-test (p<0.05). In both the St. Clair and Detroit Rivers, _P. notatus_ generally had the highest mean contaminant levels and _L. sicculus_ the lowest. In the St. Clair River mean contaminant levels in _P. notatus_ were followed by _N. hudsonius_ and then by _N. atherinoides_. Significant interspecific differences were only seen for the higher Kow compounds (Figures 12 and 13). No significant differences in
Figure 12. 1987 $\log_{10}$ lipid normalized mean contaminant levels from the St. Clair River site. Error bars represent 1 standard deviation. Bars with different letter are significantly different ($p<0.05$).
Figure 13. 1988 $\log_{10}$ lipid normalized mean contaminant levels from the Detroit River site. Error bars represent 1 standard deviation. Significance levels indicated (** p<0.01, * p<0.05, open* p<0.06).
length or lipid content were observed among the species at the St. Clair River site (ANOVA p>0.1) or at the Detroit River site (t-test p>0.1). Therefore, contaminant distribution in these species was not a function of allometric differences.

Contaminant burdens in gutted P. notatus were not significantly different from comparable samples consisting of whole fish (t-test p>0.1). Analysis of gut contents revealed that the diet of L. sicculus consisted primarily of prey associated with surface waters. P. notatus, however, fed primarily on benthic organisms (Figure 14).

Figure 15a shows a plot of log BAF versus log Kow for three of the four species at the St. Clair River site. These fish were collected in September 1988 along with sediment from that site. N. atherinoides was not present in the collections. There was a linear relationship between log BAF and log Kow for the three species (L. sicculus, $r^2=0.81$; N. hudsonius, $r^2=0.88$; P. notatus, $r^2=0.93$). Analysis of covariance indicated that the slopes of these lines were not significantly different (p>0.1), but the intercepts differed (p<0.05). P. notatus and N. hudsonius had significantly greater BAFs than L. sicculus. At the Detroit River site (Figure 15b) a linear relationship existed between log BAF and log Kow for both species (L. sicculus, $r^2=0.45$; P. notatus, $r^2=0.64$). Analysis of covariance indicated that there was no significant difference in the slopes or intercepts (p>0.1) of the lines for the two species. However, this may be because of the relatively poor fit of log BAF to log Kow on a linear scale.
Figure 14. Gut contents analysis (uncoloured - *P. notatus*,
  coloured - *L. sicculus*). Error bars represent 1
  standard error.
Gut Contents

- Pimephales notatus, Labidesthes sicculus

<table>
<thead>
<tr>
<th>Prey</th>
<th>No. of Individuals / Fish</th>
</tr>
</thead>
<tbody>
<tr>
<td>chir.larva</td>
<td>2</td>
</tr>
<tr>
<td>basmina</td>
<td>4</td>
</tr>
<tr>
<td>chir.cault</td>
<td>5</td>
</tr>
</tbody>
</table>

60
Figure 15a. Log bioaccumulation factor versus log octanol-water partition coefficient – St. Clair River site 1988 (compounds examined, from left to right – QCB, HCB, PCB #52, #87, OCS, #101, #118, #138, #153, #180). Dotted line (diamond) – P. notatus, dashed line (triangle) – N. hudsonius, solid line (square) – L. sicculus.

Figure 15b. Log bioaccumulation factor versus log octanol-water partition coefficient – Detroit River site 1988 (compounds examined, from left to right – HCB, PCB #52, #87, #101, #118, #138, #153, #180). Dashed line (triangle) – P. notatus, solid line (square) – L. sicculus.
Discussion

This study is among the first to present evidence of interspecific differences in contaminant levels in species of fish of the same size, lipid content, and trophic status. Earlier studies, indicated that food can play an important role in determining contaminant levels (Thomann and Connolly 1984; Oliver and Niimi 1988). When sediment or sediment-associated organisms are an important component of the diet, exposure via food can be of particular importance (Schindler 1987). The role that sediments play in contaminant transfer has often been downplayed because of the assumption that chemicals associated with sediments are tightly sorbed, and therefore not biologically available (Neff 1984). In most ecosystems, however, both physical and biological processes may re-introduce these compounds into aquatic food chains (Reynoldson 1987; Riedel 1987). Previous studies have shown the potential for contaminant uptake from sediments by invertebrates (Oliver 1984; Larsson 1986; Oliver 1987) and fish. Larsson (1986) concluded that sediment-mediated uptake by fishes could occur by: 1) bioturbation, desorption, and gas convection allowing contaminants to move across the sediment-water interface and be bioconcentrated and 2) food chain transfer which initially involves bioaccumulation by benthic invertebrates followed by transfer to predatory fishes. Seelye et al. (1982) and Wilford et al. (1987) indicated that contaminant transfer to
fish need not be limited to a food-chain mechanism but that accumulation by detritivores can occur directly from the sediment.

The interspecific differences in contaminant burdens I found indicate that food and habitat selection, may be major factors contributing to contaminant levels in forage fish. In the St. Clair and Detroit Rivers, interspecific differences were associated primarily with the higher Kow compounds. There were no significant differences among levels of low Kow compounds, such as pentachlorobenzene, which would be relatively water soluble compared with the other compounds studied. In the Detroit River no interspecific differences were seen between the surface and benthic feeders for any chemical with a log Kow less than 6.0, indicating that for these lower Kow compounds exposure through water may be the primary route of transfer. Exposure to chemicals through water would be more homogeneous than through food because low Kow compounds would be uniformly distributed in the aqueous phase whereas individual prey items may vary in their chemical concentrations. High Kow compounds with low aqueous solubility, such as OCS and PCB 180, tend to be associated more with the particulate phase than the water phase. When feeding, P. notatus comes into contact with the sediment and may ingest organic detritus. As a possible result of feeding on benthic organic detritus and zoobenthos, P. notatus had consistently higher levels of the higher Kow contaminants. Notropis hudsonius, a facultative benthivore, also had significantly higher contaminant
burdens than *L. sicculus* and *N. atherinoides* but lower levels than *P. notatus*. This difference might have been because of this species selection of a wider variety of food items and less dependence on organic detritus, than *P. notatus*. The levels of contaminants in *L. sicculus* were lower than in the two benthic species because a large proportion of its diet consists of terrestrial invertebrates. There is little or no direct contact between *L. sicculus* and the organic carbon pool of the sediments.

Species associated with the benthic community had higher bioaccumulation factors than the surface feeding species. Because the slopes of the lines were similar the uptake and depuration mechanisms regulating bioaccumulation are probably similar among species. Hebert and Haffner (1990c) have shown that the chemical elimination rate constant for HCB is similar for *L. sicculus* and *P. notatus*. Thus, interspecific differences in HCB levels at the St. Clair River site cannot be explained by differences in HCB metabolism. Therefore, different BAFs observed among species of forage fish imply that exposure dynamics are species dependent.

In the St. Clair River, significant differences were observed between the intercepts of the lines for the benthivores versus the surface feeder. In the Detroit River, however, no significant difference between the intercepts of *P. notatus* and *L. sicculus* were observed. The latter was predicted for the lower Kow compounds as exposure to these less hydrophobic compounds should be more similar among species, with water playing a more important role as a source of contamination (Haffner et al. 65
1990). The interspecific differences for low Kow compounds observed at the St. Clair River site may be a result of the nearby source of the contaminants. In the St. Clair River, inputs of the lower Kow compounds, such as QCB and HCB, are from nearby point sources, and therefore levels in the sediment are very high and perhaps have not equilibrated with the water column. In the St. Clair River point sources of PCBs are not as important as in the Detroit River. Therefore, at the St. Clair River site the primary source of the higher Kow compounds may have been through atmospheric deposition. In the Detroit River there is evidence of the expected pattern of low Kow compounds being more homogeneously distributed in the food web, and considerable compartmentalization being observed for the higher Kow compounds. Levels of QCB and HCB are much lower in the Detroit River than in the St. Clair River and PCB contamination is higher as a result of point source contamination from Michigan. Thus, the source of a contaminant may have a role in regulating interspecific differences in these fish species.

Summary

Four species of forage fish: *Labidesthes sicculus*, a surface feeder; *Notropis atherinoides*, a facultative surface feeder; *Notropis hudsonius*, a facultative benthivore; and *Pimephales notatus*, a benthivore; were found to have significantly different
levels of high Kow organochlorine contaminants. Body burdens were generally greatest in P. notatus, possibly reflecting its greater exposure to contaminated sediments. The interspecific differences observed suggest that habitat or food differences may be major factors regulating contaminant levels in these forage fish species. These interspecific differences in contaminant levels have important implications for fugacity models which would predict that these differences should not exist. Although chemical and physiological parameters may determine which contaminants have the potential to bioaccumulate, I postulate that it is the regulation of exposure through ecological processes that determines the degree to which that potential is realized.
CHAPTER FOUR

Toxicokinetics of Three Organochlorine Contaminants in Two Species of Forage Fish

Introduction

Interspecific differences in contaminant levels, particularly for compounds with high octanol-water partition coefficients, were observed in young-of-the-year L. sicculus, N. atherinoides, N. hudsonius and P. notatus (Hebert and Haffner 1990b). These differences were consistent in different sampling areas and were not attributed to variations in lipid content or size of the fish (Hebert and Haffner 1990a). A linear relationship between the log bioaccumulation factor (log BAF) and log octanol-water partition coefficient (log Kow) for all species suggested that the mechanisms regulating contaminant elimination were similar in each of the species. Interspecific differences were attributed to different chemical exposures in the environment, and not to different elimination processes such as chemical metabolism. Further interpretation of the environmental significance of interspecific differences in contaminant levels in forage fish requires an assessment of whether different forage fish species reflect changes in the chemical environment in similar time frames. This is important in that interspecific differences can
be attributed not only to species specific exposure dynamics, but also to differences in the time required for the different species to reach chemical equilibrium with their environments. The following model (Thomann and Connolly 1984) can be used to address factors regulating chemical body burdens in forage fish:

\[ \frac{dC_f}{dt} = K_1 C_w + K_A C_A - K_2 C_f - K_E C_f - K_R C_f \]  

Eq.10

Where \( \frac{dC_f}{dt} \) = change in fish concentration through time

- \( K_1 \) = uptake rate constant from water
- \( K_A \) = uptake rate constant from food
- \( K_2 \) = elimination rate constant to water
- \( K_E \) = elimination rate constant through feces
- \( K_R \) = elimination rate constant through metabolism
- \( C_w \) = chemical concentration in water
- \( C_A \) = chemical concentration in food
- \( C_f \) = chemical concentration in fish

In a homogeneous environment, the concentration of a chemical in water and food will be the same for all species. At equilibrium, all species should have the same body burden. For highly hydrophobic chemicals \( C_w \) approaches 0 such that \( K_1 C_w = 0 \) (Connolly and St. John 1989) and chemical exposure will primarily be a function of food \( (K_A C_A) \) uptake dynamics. The existence of interspecific differences in feral forage fish communities (Hebert and Haffner 1989b) can be a function of:

1) \( K_A C_A \) is species specific in that the trophodynamics of one species can be significantly different from a second species.
2) the species have similar trophodynamics, but track the
chemical environment at different rates (even though at equilibrium there will be no interspecific differences).

Although it is difficult to measure in situ trophodynamics to assess if \( K_A C_A \) is different for different species, it is possible to test if forage fish track their chemical environment in similar time frames. When a contaminated organism is placed into a clean environment it loses chemical according to equation 1, such that:

\[
\frac{dC_f}{dt} = -(K_z + K_e + K_r)C_f
\]

which when integrated with an initial \( C_f(t=0) \) becomes:

\[
C_f = C_f(t=0) e^{- (K_z + K_e + K_r)t} \tag{Eq. 11}
\]

or

\[
\ln C_f = \ln C_f(t=0) \left[ -(K_z + K_e + K_r) t \right] \tag{Eq. 12}
\]

suggesting that \( C_f \) decreases exponentially with time, the slope of which is the total elimination rate constant.

This study examines the role of chemical elimination in developing and maintaining interspecific differences in contaminant levels. Specifically, the ability of two species of forage fish, \textit{L. sicculus} and \textit{P. notatus}, to depurate three organic contaminants, pentachlorobenzene (log Kow=5.2), hexachlorobenzene (log Kow=5.5) and octachlorostyrene (log Kow=6.3), was examined. A previous study (Hebert and Haffner 1989b) indicated that there were significant differences in contaminant levels between \textit{L. sicculus} and \textit{P. notatus} collected from the same site and that these interspecific differences resulted from differences in chemical exposure. In the present study, depuration rates for three hydrophobic organic
contaminants were measured to determine if interspecific differences in elimination of these compounds could account for the observed interspecific differences in contaminant burdens. I hypothesized that there will be no significant differences in chemical elimination rates between species, and therefore interspecific differences in chemical elimination are not significant. Thus, $C_t(K_z + K_\xi + K_\eta)$ is similar for the species examined in this study.

A second component of the study assesses the importance of sediments in regulating contaminant levels in forage fish. The bioavailability of organic contaminants from sediments is of interest as contaminant levels in sediments are usually much higher than those in the overlying water. Therefore, it is vital to know if sediments act as sinks or sources of these contaminants. By manipulating access to the sediments, it was possible to determine the relative contribution of sediment related pathways in the overall exposure of benthic feeding fish such as P. notatus. Because of the abundance of P. notatus and its consumption by larger piscivores, it can be a significant transfer route of chemicals from the benthic to the pelagic food web.
Methods and Materials

Depuration rates were examined so that interspecific differences in contaminant elimination could be quantified. The effect of habitat use on contaminant burden was examined in the second part of the study.

1) Depuration

Two species of forage fish: Labidesthes sicculus (brook silverside) and Pimephales notatus (bluntnose minnow) were collected from a site in the St. Clair River, south of Sarnia's Chemical Valley, in November 1988 (Figure 16). The fish were caught in nearshore waters using a 10 m, 0.6 cm mesh bagseine. They were immediately transferred to glass aquaria containing aerated river water. They were transported to the University of Windsor where they were sorted according to species and placed in 2 identical 50 L glass aquaria filled with identical volumes of dechlorinated tap water. These tanks had been established 2 weeks prior to the addition of the fish. Water temperature was 20°C in both tanks. The water in each of the tanks was continuously filtered through activated charcoal at a rate of 200 L/hr. The charcoal in each filter was replaced weekly. The charcoal filters provided aeration. The fish were not fed during the study. Triplicate samples of fish were taken from each tank at intervals of 0, 14, 35, 49 (L. sicculus), and 67 days (P. notatus). Each
Figure 16. St. Clair River fish collection site (box) for depuration study.
sample consisted of a pool of individuals with a total wet weight not less than 3 grams. The fish were measured (total length) and wrapped in hexane-rinsed aluminum foil and frozen at -20°C until analyzed by GC-ECD (CWS 1982).

In order to determine if species were tracking their chemical environment in similar time scales, the biological half life of each chemical was determined for each species. The biological half-life was derived from the following equation:

$$t_{1/2} = \ln 2/(K_e + K_t + K_r)$$

$$= 0.693/(K_e + K_t + K_r)$$

Eq.14

2) Accumulation

Fish for the uptake study were collected in September 1988 from Faren Lake in southeastern Ontario. Faren Lake is a relatively uncontaminated waterbody located 60 km north of Kingston, Ontario. Pimephales notatus were collected by bagseine and immediately transferred to 140 L glass aquaria containing aerated lake water. The fish were transported to the University of Windsor where they were acclimated to laboratory conditions for 3 weeks prior to the start of the experiment. Fish were then placed in two 80 L aquaria, both containing sediment from a contaminated site in the St. Clair River, 1.5 Km south of Sarnia's petrochemical industries (Guthrie Park). The sediment was collected in August 1988 from the top 3 cm of the site's sediment profile and it consisted of a fine silt-sand mixture with an organic carbon content of 1.4%. Before the sediment was
transferred to the aquaria it was mixed for 72 hours using a mechanical mixer (Caframo type RZR50). Six L of sediment were transferred to each aquarium. Identical volumes of water were added to each tank and both tanks were covered with glass and aerated for 4 weeks prior to the start of the experiment. In tank 1, 33 fish were added and they were allowed complete access to the contaminated sediments. Immediately after addition, tank 1 became turbid as the fish disturbed the sediments. In tank 2, 33 fish were also added but these fish were caged 5 cm above the bottom and were prevented from having any interaction with the sediments. Tank 2 remained clear throughout the experiment. No food was added to either tank during the study but fish could ingest sediment in tank 1. Triplicate samples were collected from both tanks at intervals of 0, 7, 14, and 25 days.

Whole fish were extracted and analyzed using Canadian Wildlife Service (1982) methodology with minor modifications, which are described in greater detail elsewhere (Hebert and Haffner 1989a). Samples were injected into a Hewlett-Packard Model 5790A GC-ECD with a 30 m x 0.25 mm DB-5 capillary column (J+W Scientific). Recovery efficiencies for this method were 87% for QCB, 89% for HCB and 91% for OCS. The limit of quantification for each compound was 0.1 µg/kg.

Because of logistical problems associated with maintaining large numbers of wild fish in the laboratory no tank replicates were possible and these studies are pseudoreplicated. We felt that it was more important to have replicate samples from each of
the tanks, so that an indication of intra-tank variability through time could be obtained, than it was to have inter-tank comparisons.

Results

Depuration

Figures 17 and 18 illustrate the observed depuration rates of QCB, HCB, and OCS for L. sicculus and P. notatus respectively. In both species, for all three compounds, there is a log linear relationship between declining contaminant concentrations and time. This trend is typical of the two compartment models used to describe chemical elimination (Gobas et al. 1988). Total depuration rate constants ($K_d=K_2+K_t+K_q$) and biological half-lives were calculated for each of the compounds for both species (Table 1). For P. notatus, QCB was depurated most quickly and OCS most slowly. For L. sicculus, HCB was lost most quickly and OCS was again lost at the slowest rate. Comparisons between the two species revealed that P. notatus lost QCB at a faster rate than L. sicculus (ANCOVA, p<0.05). For HCB the rates of loss were not significantly different (ANCOVA, p>0.05). For OCS, loss was approximately twice as fast in L. sicculus as in P. notatus (ANCOVA, p<0.05).
Figure 17. Mean $\log_{10}$ transformed wet weight levels of QCB (open circles), HCB (closed circles) and OCS (triangles) in *L. sicculus* through time. Error bars represent 1 standard error (some error bars are hidden within the symbol).

Figure 18. Mean $\log_{10}$ transformed wet weight levels of QCB (open circles), HCB (closed circles) and OCS (triangles) in *P. notatus* through time. Error bars represent 1 standard error (some error bars are hidden within the symbol).
Table 1. Elimination rate constants and biological half-lives for QCB, HCB and OCS for *L. sicculus* and *P. notatus*.

<table>
<thead>
<tr>
<th>Species</th>
<th>QCB</th>
<th>HCB</th>
<th>OCS</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>L. sicculus</em> Kd (ng/g/day)</td>
<td>0.065</td>
<td>0.088</td>
<td>0.048</td>
</tr>
<tr>
<td>Half-life (days)</td>
<td>10.7</td>
<td>7.9</td>
<td>14.4</td>
</tr>
<tr>
<td><em>P. notatus</em> Kd (ng/g/day)</td>
<td>0.202</td>
<td>0.080</td>
<td>0.023</td>
</tr>
<tr>
<td>Half-life (days)</td>
<td>3.4</td>
<td>8.7</td>
<td>30.1</td>
</tr>
</tbody>
</table>
Accumulation

Figures 19a-c compare accumulation of contaminants in fish from tank 1 (fish exposed to contaminants through sediment and water - free) to fish from tank 2 (exposure through water only - caged). For all three compounds accumulation was enhanced by direct access to sediments. For QCB (Figure 19a) the fish in tank 1 reached an equilibrium level of approximately 2 ng/g (wet weight) in 5 days. The fish in tank 2, however, reached a steady state of approximately 1 ng/g in the same time period. In both tanks, steady state conditions were reached within 7 days and may have been achieved sooner. As Figure 19b indicates, HCB levels in the free fish reached levels of approximately 60 ng/g after 15 days. This seemed to be the equilibrium value in that levels began to plateau after this time. Levels in the caged fish were much lower, even after 25 days exposure, and a steady state of chemical uptake and loss was not achieved. Figure 19c shows the difference in OCS levels between free and caged fish. After 25 days, levels in the free fish were approximately 15 ng/g whereas levels in the caged fish were 2 ng/g. The levels in both groups were still increasing after 25 days, suggesting that neither had reached steady state. Differences in contaminant levels became more pronounced between fish populations in tanks 1 and 2 as the hydrophobicity of the chemicals increases (as C₅₇ approaches 0). There was no significant difference in the size of the fish from tanks 1 and 2 (t-test p>0.1).
Figure 19. Mean wet weight contaminant levels in P. *notatus* with access to sediment (closed circles) and in P. *notatus* without access to sediment (open circles). Error bars represent 1 standard error (some error bars are hidden within the symbol). a) pentachlorobenzene levels b) hexachlorobenzene levels c) octachlorostyrene levels.
Discussion

Depuration

Previous studies have shown that the rate at which a compound is eliminated from an aquatic organism decreases as the hydrophobicity of the chemical increases (Neely 1979, Opperhuizen et al. 1985, Hawker and Connell 1985). In this study, both L. sicculus and P. notatus lost the compound with the highest Kow, OCS, at the slowest rate. P. notatus lost QCB, the lowest Kow compound examined, at the fastest rate, as expected. L. sicculus, however, lost HCB faster than QCB and this was not expected based upon the relative hydrophobicities of the two chemicals. However, in general terms this study corroborates previous work showing decreased elimination rates with increased chemical hydrophobicity. The rate at which an organism can eliminate a chemical is one of the most important factors governing the accumulation of that compound. Uptake rate constants from food have been shown to be nearly constant for hydrophobic compounds up to a log Kow of 7.0 (Gobas et al. 1988) and hence may be less important in determining steady state chemical concentrations.

The physiology of an organism is important in determining the rate of chemical elimination and therefore will determine the rate at which an organism can respond to changes in its chemical environment. Therefore, physiological differences may be an important factor when examining the cause of observed
interspecific differences in contaminant levels in organisms collected in the field. Comparisons between *P. notatus* and *L. sicculus* indicated that elimination rate constants were not significantly different for HCB. Thus, higher HCB levels in *P. notatus* from the St. Clair River (Hebert and Haffner 1990b) cannot be explained by differences in HCB elimination. The rate at which QCB and OCS were eliminated was different between the two species but there was no consistent pattern to these differences. QCB was eliminated faster from *P. notatus* than *L. sicculus*. However, OCS was lost more quickly from *L. sicculus* than from *P. notatus*. Interspecific differences in QCB levels are not seen in these two species but OCS levels are much greater in *P. notatus* (Hebert and Haffner 1990b). The faster rate of OCS elimination in *L. sicculus* indicates that this species would reach equilibrium twice as fast as *P. notatus*. The effect that this difference would have on regulating interspecific differences in OCS levels is unclear. However, it is apparent that elimination rates do not play a role in regulating interspecific differences in HCB levels. Differential exposure to HCB, resulting from interspecific differences in exposure to contaminated sediments, may play a more important role.

**Accumulation**

The results from this study indicate that direct access to contaminated sediments results in increased body burdens of all three contaminants. For QCB, it was demonstrated that two
different equilibrium levels were achieved during the course of the study. The fish exposed to the sediments accumulated twice as much QCB as the fish exposed through water alone. As illustrated in equation 1, the relative uptake of a chemical from water ($K_w C_w$) and food ($K_a C_a$) is a function of the hydrophobicity of the chemical. If fish species were tracking the water compartment only, they would have similar body burdens. The time to reach steady state conditions, however, would vary with the uptake rate constant ($K_a$). For extremely hydrophobic chemicals, $C_w$ approaches 0, and $K_a C_a$ becomes the primary mechanism of chemical transfer. As the food concentration $C_a$ can vary with prey type, the partitioning of food resources (Muth and Busch 1989) can result in different steady states being established in aquatic ecosystems.

This study emphasizes the importance of contact with contaminated sediment particles as a major route of contaminant transfer, particularly for high Kow compounds. A similar result was obtained by Opperhuizen and Stokkel (1988) in their study examining the influence of contaminated particles on bioaccumulation of hydrophobic pollutants in fish. They found that the relative importance of particles as a source of contaminants depended on the chemical's hydrophobicity. For lower Kow compounds dissolved fractions were more important and therefore water was the major route of exposure. Contaminated particles were a more important source for chemicals with log Kows greater than 5.0. Previous studies have examined the
relative importance of overlying water, pore water, and sediments in regulating contaminant accumulation in a variety of organisms (Larsson 1986, Oliver 1987, Knezovich and Harrison 1988, Schuytema et al. 1988). In this study, it was impossible to distinguish between direct uptake from sediment via ingestion and uptake from interstitial water. Because of the feeding behaviour of P. notatus, bioturbation of the sediments may be an important process increasing the release of chemical from the sediments. A micro-gradient in water concentration might then exist at the sediment-water interface and some of the increased body burdens of benthic fish species could be due to increased water exposure. However, the greatest differences observed between benthic and surface feeding species were with respect to compounds with log Kows greater than 6.0 (Hebert and Haffner 1990b). Because of their low water solubilities these compounds would not be expected to partition into water. Thus, bioaccumulation of these compounds directly from ingestion of sediment particles would be expected to play a more important role.
CHAPTER FIVE

General Conclusions

This study examined some factors which may regulate contaminant levels in forage fish and has given an indication of the applicability of these fish species as biomonitors. A major theme underlining this work is that ecological factors may be as important as physical, chemical, and physiological influences in determining the levels of organic contaminants in these fish species. The unique biological attributes of a species must be considered when examining the potential for bioaccumulation of environmental contaminants (Ramade 1987). There are important interspecific differences regulating the degree of exposure and these intrinsic factors must be taken into account when considering the levels and distribution of contaminants in aquatic food webs.

The hypothesis that water-organism interactions were of primary importance in regulating pollutant concentrations has prevailed in the past (Hamelink 1971, Levin et al. 1984). But Rosenberg (1975) suggested that when water concentrations are extremely low, material suspended in the water can be an important contaminant source. Since then many researchers have shown that organisms living in or on contaminated sediments have higher contaminant burdens than pelagic species (Roesijadi et al. 88)
1978). In these studies, desorption of the contaminant from sediment into the water column, where it could be biocentrated by the organism, was thought to be the primary mechanism controlling pollutant levels (Kobylnski and Livingston 1975). Further studies have indicated the importance of food in determining interspecific differences in contaminant levels in aquatic organisms from different trophic levels (Rubinstein et al. 1984; Oliver and Niimi 1988; Thomann and Connolly 1984). My study also emphasizes the importance of food web dynamics in regulating contaminant levels but in species occupying the same trophic position. Contaminant levels in any one species do not necessarily give an accurate indication of overall contamination at that trophic level, nor do they indicate the extent of ecosystem contamination. Only when that species is placed in an "ecological context" describing life history characteristics such as habitat and food selection can contaminant levels in aquatic species be accurately interpreted and compared. Because of the compartmentalization of contaminants in the environment, exposure will differ between species based upon their utilization of different habitats. Exposure to hydrophobic organic contaminants is potentially greater in benthic species because of the physical and chemical properties of the contaminants, which result in their accumulation in sediment. Recognizing the importance of sediment as a contaminant source is necessary to accurately model the behaviour and distribution of hydrophobic organic chemicals in the environment. Some species of forage fish, such as P.
notatus, may play an important role in the transfer of contaminants from the benthic to the pelagic food web. Their integration of both carbon and contaminant flow may result in the introduction of these contaminants into pelagic predators. Stringent regulations controlling the discharge of contaminants into the environment are being imposed by programs such as the Ontario Ministry of the Environment's Municipal Industrial Strategy for Abatement (MISA). MISA will result in reduced emissions of contaminants into the environment (Ontario Ministry of the Environment 1988). If current inputs are reduced or eliminated, the importance of sediment as a contaminant source will become paramount. Therefore, the extent to which biological transfer of these chemicals contributes to overall ecosystem contamination will also grow in importance.

The ultimate goal of any biomonitoring program is not only to identify and quantify contaminants in the environment but also to warn of the potential for toxic effects. Biomonitoring species are expected to act as environmental "sentinels" warning of the potential for harm in wildlife and human populations. To accomplish this task requires that the biomonitoring species be exposed to a concentration of the contaminant high enough to induce a toxic response. Pharmacokinetic dose-response curves predict that organisms exposed to higher contaminant concentrations might also be the first to be adversely affected. Thus, the importance of choosing a species that will reach maximal exposure is obvious. As indicated in this study, benthic species are exposed to the
greatest chemical concentrations and as a result they may be most susceptible to the toxic actions of these hydrophobic contaminants. A species such as *N. hudsonius* may be a good indicator of the spatial distribution of contaminants in a geographic area but may underestimate the extent of *in situ* contamination and therefore, the threat posed by contaminants to aquatic organisms.
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