Evaluation of Polychlorinated Biphenyl Contamination in the Saginaw River Using Sediments, Caged Fish and SPMDs

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ABSTRACT

The Saginaw River is contaminated with a number of industrial pollutants including polychlorinated biphenyls (PCBs). Understanding of the risk posed by PCBs in the aquatic system requires measurement of the dissolved, bioavailable levels of PCBs. In this study, three means of assessing bioavailability were compared: sediments, caged fish, and semipermeable membrane devices (SPMDs). Caged channel catfish and SPMDs were placed in the river for one month at five sites where sediments were also sampled. PCBs were analyzed by congener specific methods to determine PCB concentrations and patterns. Total PCB concentrations ranged 33 - 277 ng/g in sediments, 46 - 290 ng/g in caged fish, and 77 - 792 ng/g in SPMDs. SPMD and sediments provide complementary PCB information: sediments reflecting long term accumulation while SPMDs indicate what was present in the water at the site during the sampling period. Differences in PCB patterns in caged fish and SPMDs are due to lower chlorinated PCBs having reached steady state with the fish but not with the SPMD. Sediments were assumed to have reached equilibrium with PCBs in the water. Concentrations and patterns of dissolved PCB congeners were estimated from sediment data using an equilibrium model. The SPMD-based dissolved concentrations were estimated by using SPMD accumulation rates for 86 PCBs that were determined in an earlier SPMD calibration study. Steady-state bioconcentration factors for PCB congeners were used to estimate times required to reach steady state; congener concentrations in the fish were then normalized to steady state, and an equilibrium model was applied. The three methods indicated that similar patterns and concentrations of dissolved PCBs were present in the Saginaw River.

INTRODUCTION

Polychlorinated biphenyl (PCB) pollution in the Great Lakes region, in particular Saginaw Bay and Lake Huron has been documented for many years (Michigan DNR, 1988). Fish consumption advisories have been issued because of high concentrations of PCBs in sport fishes. Effects on wildlife have included increased reproductive failure in fish-eating birds and elevated mink kit mortality (Alan, 1991; Giesy and others, 1997). Comprehensive risk assessment of an aquatic system requires information about the bioavailable aqueous fraction of the contaminant burden– that concentration of a contaminant which is accessible to organisms at each trophic level. Currently there are no accurate procedures to assess the bioavailability of contaminants (Dickson and others, 1994). Exposure of organisms that have minimal capability for biotransformation approaches the criterea for defining bioavailability, but few organisms meet such criteria for a great number of contaminant classes. Therefore, regulatory agencies must rely on modeling efforts.

The objective of this study was to compare the semipermeable membrane device (SPMD) method of water sampling with sediment-based and fish-based biomonitoring methods. The SPMD method utilizes a passive sampler that combines membrane diffusion and liquid/liquid partitioning to concentrate low to moderate molecular mass (<600 Da) lipophilic compounds

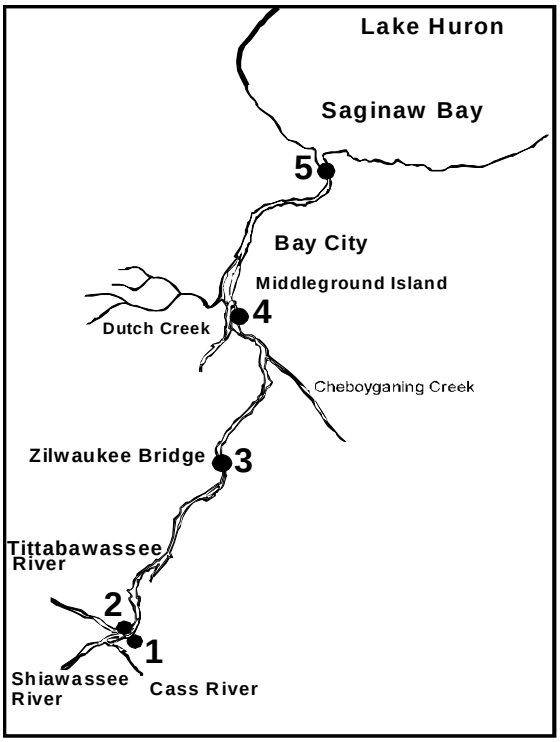
from water. (Huckins and others, 1996). Five sites along the Saginaw River were sampled using these methods and the resulting congener specific PCB concentrations in each of these sample types were interpreted so concentrations of bioavailable PCBs could be estimated. Concentrations of PCB congeners were estimated from previously determined SPMD uptake rates, bioconcentration factors (BCFs) and sediment partition coefficients.

METHODS

Caged fish, SPMDs, and sediments were used to sample PCBs at five sites along the Saginaw River as shown in Figure 1:

1) the terminus of the Shiawassee River,
2) terminus of the Tittabawassee River
3) Saginaw River- Zilwaukee Bridge,
4) near the wastewater treatment plant and industrial wastewater inlets at Middleground Island at Buoy 26 (site of dredge spoil disposal)
5) downstream of Bay City at Buoy 10

Figure 1. Map of Saginaw River Sampling Sites



SPMD Method

SPMDs (2.5-cm x 152-cm, 85 Φm membrane thickness) with a total mass of 8.35 g each were made of a thin film of 95% pure triolein (1.64 g) sealed inside low-density polyethylene lay-flat tubing. Each analytical sample, consisting of four SPMDs, was transported to the field sites in new, airtight, hexane-rinsed, metal cans. At the site, SPMDs were placed inside stainless steel cages, and placed in the Saginaw River 2-10 meters above the sediment for 35 days. Field blank SPMDs accompanied the analytical samplers to the sampling sites, were replaced in their airtight containers, and returned to the laboratory.

Caged Fish Method

Juvenile hatchery-reared channel catfish (*Ictalurus punctatus,* 8-10 cm) were deployed in cages at each site for 30 days, at the same level as the SPMD cages. Negative control samples of the catfish were obtained at the beginning of the study as quality control matrix samples.

Sediment Sampling Method

Sediment samples were collected in triplicate from each site by stainless steel Ponar® dredge. Sediments were composited and homogenized from each site to insure a representative sample was analyzed.

Analytical Methods

Fish and sediment samples were extracted with methylene chloride, while SPMDs were dialyzed twice in hexane. Percent lipid determinations of fish samples were determined gravimetrically. Extracts and dialysates were treated by two-stage reactive cleanup, high performance gel-permeation chromatography (Feltz and others, 1995). Sediment extracts and SPMD dialysates were copper treated to remove sulfur. PCB congeners were analyzed by capillary GC/ECD to quantify 86 peaks. Total organic carbon in sediment was determined by coulometry.

PCB Water Concentration Estimations

Sediment-based water concentrations were calculated by the equation:

$$Cw_{sed} = C_{sed} f_{oc}^{-1} K_{oc}^{-1}, \quad (1)$$

where

Cw_{sed} is the sediment-based water concentration

C_{sed} is concentration in the sediment

f_{oc} is fraction of organic carbon in the sediment

K_{oc} is the sediment-water partition coefficient

The K_{oc} values for PCB congeners were estimated using K_{ow} values (Hawker and others, 1988) and the approximation that K_{oc} is $0.41K_{ow}$ (Karickhoff, 1981).

Caged fish PCB concentrations were used to estimate dissolved PCB concentrations by normalizing to steady state PCB concentrations:

$$Cw_{fish} = f_{ss} \; C_{fish} \; BCF^{-1}, \quad (2)$$

where

Cw_{fish} PCB water concentration is the caged fish-based

f_{ss} is the fraction of steady state reached in 28 days

C_{fish} is the calculated steady state PCB congener concentration in the fish

BCF is the steady-state bioconcentration factor for fish

Specific channel catfish steady-state *BCFs* for PCB congeners were not found in the literature, so selected *BCFs* from several studies with other species of fish were used (Mackay and others, 1992; Bruggeman and others, 1984; and Fox and others, 1994). The rates at which each PCB homolog group reached equilibrium was estimated from the *BCF* data.

SPMD-based water concentrations were calculated as follows:

$$Cw_{spmd} = C_{spmd} \, m_s R_s^{-1} \, t^{-1}, \quad (3)$$

where

Cw_{spmd} is SPMD-based PCB concentration in the water

C_{spmd} is the PCB concentration in the SPMD

m_s is mass of the SPMD

R_s is SPMD accumulation rate constant for the PCB

t is time

R_s values were obtained from a previous exposure study where SPMD uptake of 86 PCB congeners and dissolved PCB water concentrations were measured (Meadows and others, 1998).

PCB Pattern Analysis

Patterns of the PCB congener data were evaluated using SIMCA (Soft Independent Modeling by Class Analogy) principal components analysis (Schwartz and others, 1987; and Wold and others, 1984). PCB data was normalized to fractional composition and univariately transformed. A 95% confidence interval was used.

RESULTS AND DISCUSSION

Total-PCB concentrations in caged fish, sediments and SPMDs are presented in Table 1 as nanograms per gram of matrix. PCB congener data will be presented as SIMCA plots. All matrices suggest that Site 5 has the highest level of PCB contamination. Total PCB concentrations in the sediments at sites 1-5 were not directly related to variations in percent organic carbon values, which were 1.2, 1.0, 3.0, 2.8, 3.5, respectively.

Recoveries of PCBs ranged from 75% to 114% and variability was < 20%. Method detection limits were ~0.2 ng/g per congener or 25 ng/g in terms of total-PCBs.

Based on an SPMD uptake model, accumulation of PCBs remained in the linear phase during the one month period (Gale, 1998). The same situation existed for caged fish except for Cl_2 PCBs which reach steady in about 13 days. All other PCBs were well within the linear phase, with Cl_8 PCBs linear uptake into SPMDs being one and a half years.

Table 1. Total PCB concentrations in samples from Saginaw River (ng/g)

Sites	Sedi-ment	Caged Fish	SPMD
1. Shiawasee	33	46	77
2. Tittabawasee	96	58	100
3. Zilwaukee	29	68	85
4. Middle Ground	98	71	156
5. Buoy 10A	277	290	792

PCB patterns were similar in each matrix but differed between matrices. SIMCA plots of the first two principle components are presented for all three matrices in Figure 2. The differences between SPMD and sediment PCB patterns reflect the long term accumulation of higher chlorinated PCBs and weathering of the lower chlorinated PCBs in the sediment. The differences between the SPMD and caged fish patterns can be the result of the lower chlorinated PCBs having reached steady state. Patterns of Cl_6 - Cl_{10} PCBs in the fish and SPMDs were similar. Feral fish from the Saginaw Bay, sampled near the mouth of the River, show slightly different patterns than caged fish, likely because PCBs homologs Cl_{3-5} have reached steady state.

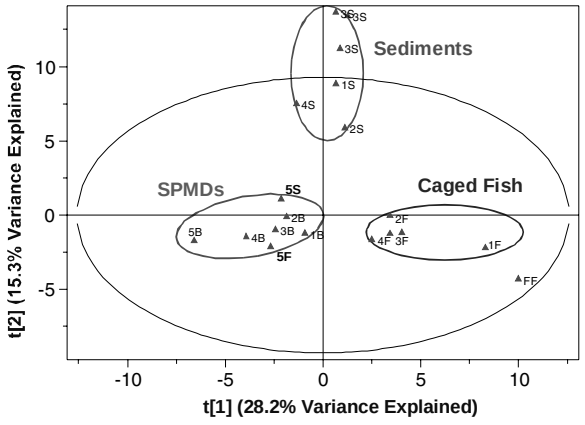


Figure 2. SIMCA plots of PCB congeners in sediments, caged fish and SPMDs. Score t[1]/t[2] using all sites. Large oval boundary line indicates 95% confidence interval.

Bioavailable aqueous concentrations of PCBs were estimated using the models described earlier in the text and are presented in Table 2 in terms of total PCBs. The PCB patterns are represented in the Figure 3 SIMCA plot. All estimated patterns of dissolved PCB are similar at all sites and fall within the 95% confidence interval. There is some separation between methods used to estimate the PCB patterns in the water, however the patterns are very similar.

Table 2. Bioavailable concentrations of total-PCBs in Saginaw River (ng/L) calculated from matrix*

Site	*Sedi-ment	*Caged Fish	*SPMD
1. Shiawasee	8	4	1
2. Tittabawasee	8	5	1.4
3. Zilwaukee	3	6	1.2
4. Middle Ground	18	7	2.2
5. Buoy 10A	38	27	12

A filtered, large volume water sample that was taken two years earlier (Verbruegge and others, 1995) estimated similar dissolved PCBs concentrations (1.9 - 16 ng/L). This similarity may indicate that the PCB sources have not changed or dramatically increased at these sites over the two year period.

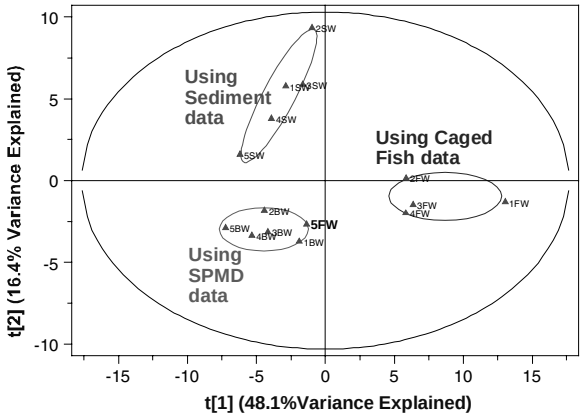


Figure 3. SIMCA plot of dissolved PCB congeners calculated from sediment, caged fish and SPMD PCB concentrations. Scores: t[1]/t[2] Large oval boundary indicates 95% confidence interval.

CONCLUSIONS

The three models using SPMDs, caged fish and sediments predicted similar bioavailable concentrations and patterns of PCBs in the Saginaw River. PCB patterns in each matrix from sites 1-4 were distinctive. Patterns at at Buoy 10A near the mouth of the river (site 5) were slightly different, possibly indicating a different PCB source. All matrices at this site also indicated that PCB levels were higher than the other four sites. Concentrations and patterns of PCBs in sediments reflect longer term accumulation of higher chlorinated PCBs, whereas the fish and SPMDs reflect what is dissolved in the water column at a specific site over a period of time.

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