TIME-INTEGRATED, FLUX-BASED MONITORING USING SEMIPERMEABLE MEMBRANE DEVICES TO ESTIMATE THE CONTRIBUTION OF INDUSTRIAL FACILITIES TO REGIONAL POLYCHLORINATED BIPHENYL BUDGETS

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Abstract—Passive monitoring of polychlorinated biphenyls (PCB) using semipermeable membrane devices (SPMD) was employed to evaluate the contribution of point and nonpoint sources to the flux of PCB in a drainage system encompassing three U.S. Department of Energy (U.S. DOE) industrial and research facilities in eastern Tennessee, USA. Polychlorinated biphenyls concentrations were highest at outfalls containing process waste from the DOE industrial facilities. The significance of these releases was evaluated by calculating the PCB flux (mass per unit time) at different monitoring locations. The flux was calculated from the time-integrated estimates of the aqueous concentrations of PCB and estimates of the volumetric flow rates of discharges and receiving streams during the deployment period. The DOE discharges accounted for most of the flux of PCB entering the Clinch River from the DOE drainage areas, but these sources constituted only 10% of the flux in the Clinch River about the DOE sources. Principal components analysis was helpful in attributing sources of PCB. In a stream receiving multiple inputs of PCB, congener profiles from upstream sources and discrete discharges were consistent with a mixture of those congener profiles in the downstream receiving water. In another stream with a single upstream source of PCB, changes in PCB flux and congener profiles suggested an apparent steady-state distribution between dissolved PCB and PCB adsorbed to organic matter on the streambed. The flux of dissolved PCB along different stream reaches reflected changes in the sediment organic content. Subtle alterations in congener profiles moving downstream suggested preferential desorption of less chlorinated congeners and sorption of more highly chlorinated congeners to sediment. Time-integrated, flux-based monitoring can be useful across a range of spatial scales for evaluating the significance of point and nonpoint contaminant sources and can help identify and prioritize feasible remedial alternatives.

Keywords—Semipermeable membrane devices Polychlorinated biphenyls Principle components analysis Surface water Budget

INTRODUCTION

Semipermeable membrane devices consisting of a thin film of neutral lipid (triolein) enclosed in a thin-walled lay-flat tubing made of low-density polyethylene have been used for passive monitoring of hydrophobic organic contaminants [1]. The SPMD have allowed investigators to detect the presence of specific compounds in air or water [2–5], compare apparent availability of a contaminant to realized accumulation in biota [6–9], estimate the relative contribution of water and sediment on bioaccumulation [10], and determine the spatial trends of contamination in aquatic environments [5,11]. The goal of this study is to demonstrate the application of the SPMD technique to evaluate the contribution of contaminant discharges from specific facilities to the overall PCB budget on a broader spatial scale. Concerns are justifiedly raised when monitoring of specific industrial discharges exceed permitted levels. However, the broader significance of those releases may dwindle beyond a limited area downstream of the outfall if the volumetric flow rate of problematic discharges is small [12]. Some widely distributed contaminants, such as polychlorinated biphenyls, can enter surface-water systems from various point and nonpoint sources. The combined effects of numerous small inputs can lead to consequences affecting large areas of a drainage system. For example, PCB contamination can lead to health adversities concerning consumption of fish over significant portions of several river systems. If a single major industry is situated in an otherwise undeveloped area, the source of the contaminant inputs may be obvious. More often, however, an array of potential point sources exists, including major industrial facilities, small factories, known or unknown disposal areas, and contaminated storm drain networks, as well as more broadly distributed nonpoint source terms. The contribution of each of those sources to the total flux of contaminant is usually unknown. This uncertainty may be a major limitation to long-term efforts to reduce contaminant inputs regionally. If the magnitude of the major sources were known, the benefits and costs of reducing those inputs could be objectively evaluated, allowing more effective involvement of community and regulatory perspectives in contaminant reductions.

The focus of the current study are three Department of Energy (DOE) facilities located on tributaries of the Tennessee River system in Anderson and Roane Counties, Tennessee, USA. These facilities, established as part of the Manhattan Project during World War II, include the following:

- Oak Ridge Y-12 Plant. A former nuclear weapons facility that discharges into East Fork Poplar Creek (EFPC) and Bear Creek (Fig. 1). EFPC flows north and then west through the City of Oak Ridge, a town of about 29,000 people. East Fork Poplar Creek is joined by Bear Creek before flowing into Poplar Creek about 10 km upstream of the East Tennessee Technology Park.
- East Tennessee Technology Park (ETTP). Formerly a ura-
nium isotope enrichment facility known as the K-25 Gaseous Diffusion Plant, ETTP currently serves as a waste storage area. Effluents from ETTP are released to Poplar Creek, which joins the Clinch River about 2 km downstream.

Oak Ridge National Laboratory (ORNL). This multidisciplinary research facility discharges to White Oak Creek and its tributaries and then into the Clinch River about 1 km beyond the boundary of the facility.

The drainage for all the DOE facilities flow into the Clinch River, which joins the Tennessee River about 18 km downstream of the ETTP. These rivers are arms of Watts Bar Reservoir, a large Tennessee Valley Authority impoundment. Polychlorinated biphenyl contamination in fish within the Clinch River has led to health advisories warning against consumption of several fish species. The sources of the PCB in the Clinch River may be related to several hydroelectric facilities built upstream of the DOE facilities by the Tennessee Valley Authority in the 1930s in addition to DOE facilities and communities along the river. Polychlorinated biphenyl contamination has also led to health advisories in the Tennessee River in Roane and Anderson Counties and in upstream Knox and downstream London Counties. There are several major industrial and government facilities as well as numerous other potential current and historic sources along the Tennessee River that are thought to have contributed to PCB contamination of the river. The contributions of PCB by the different sources are unknown. Although reductions in pollution could presumably return the river to its full environmental and recreational uses, it is unlikely that this goal could be realized unless the principal contributors to pollution can be identified and the feasibility of cost-effective remediation evaluated.

The goal of the current study was to demonstrate the application of passive monitoring with SPMD to identify the contribution of potential contaminant sources to the total PCB flux in a regional drainage system. The principal objective of this study was to use using time-integrated estimates of the aqueous concentrations of PCB, along with estimates of mean annual volumetric flow rates of discharges and streams, to characterize the PCB flux (mass of PCB per unit time) contributed by the three DOE facilities and to compare the discharges to both nonpoint inputs and to the total flux of PCB in the Clinch River. A secondary objective was to further identify the contribution of potential PCB sources using principal components analysis of PCB congeners to distinguish changes in congener profiles above and below suspected sources.

MATERIALS AND METHODS

Semipermeable membrane devices (SPMD) were prepared as described by Lebo et al. [13] using polyethylene lay-flat tubing (86 cm long, 2.6 cm wide, and 0.05 mm thick). The tubing was immersed for 48 h in hexane to remove any contaminants before use. One milliliter of triolein lipid (95% purity, Sigma Chemical, St. Louis, MO, USA) was pipetted into each piece of tubing and spread to a thin layer. The tubing was then heat-sealed at both ends. The SPMD were stored in metal cans under an argon atmosphere before being deployed. Additional SPMD were prepared for use as laboratory blanks (stored in the metal cans until the field-deployed samples were returned for analysis) or field blanks (taken to the field and opened while samples were deployed and retrieved but not deployed in the water). Each SPMD was suspended in a 5.1-cm-diameter steel or aluminum pipe using plastic-coated wires. Stainless-steel wire mesh (6-mm grid) was placed on both ends of each pipe, and the devices were deployed in the water so that the water flowed through the length of the pipe and contacted the SPMD. Six devices were deployed at each of the locations described in Table 1 and Figure 1 for a 28-d period during December 1995 to January 1996. The SPMD retrieved from each site were wiped clean and stored in metal cans in an argon atmosphere. In the laboratory, SPMD were inspected for leaks, and damaged SPMD were discarded. The remaining SPMD were washed in distilled water, rinsed briefly with acetone, and dialyzed in hexane for 2 d. Polychlorinated biphenyl isomers 30 and 209 were added to the hexane as matrix spikes. Dialysates were concentrated using Kuderna-Danish apparatus with a three-ball column and argon blowdown techniques. The concentrate was subjected to gel permeation chromatography using a Phenomenex Phenogel (100-Å, 10-μm) column (Phenomenex, Torrance, CA, USA). The solvent fraction containing PCB was reconcentrated to approx. 1 ml as above and further
Table 1. Description of monitoring locations, mean volumetric flow rates, estimated PCB concentrations, and PCB fluxa

<table>
<thead>
<tr>
<th>Facility/site</th>
<th>Code</th>
<th>Location</th>
<th>Description</th>
<th>Flow (million L/d)</th>
<th>Concentration (ng/L)</th>
<th>Standard error</th>
<th>n</th>
<th>PCB flux (mg/d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y-12 Plant</td>
<td>UEFPC</td>
<td>Upper EFPC</td>
<td>Several sites along EFPC within the Y-12 Plant</td>
<td>10</td>
<td>29.3 B</td>
<td>2.5</td>
<td>10</td>
<td>290</td>
</tr>
<tr>
<td>EFK2</td>
<td>EFPC, km 23.4</td>
<td>Outfall of a retention pond exiting offsite to EFPC</td>
<td>14</td>
<td>27.9 B</td>
<td></td>
<td>1</td>
<td>390</td>
<td></td>
</tr>
<tr>
<td>EFK14</td>
<td>EFPC, km 13.8</td>
<td>Downstream of the City of Oak Ridge</td>
<td>41</td>
<td>5.4 C</td>
<td>1.4</td>
<td>3</td>
<td>220</td>
<td></td>
</tr>
<tr>
<td>EFK2</td>
<td>EFPC, km 2.1</td>
<td>In EFPC above its confluence with Bear Creek</td>
<td>97</td>
<td>8.7 D</td>
<td>0.3</td>
<td>2</td>
<td>840</td>
<td></td>
</tr>
<tr>
<td>BC</td>
<td>Bear Creek</td>
<td>In Bear Creek above its confluence with EFPC</td>
<td>19</td>
<td>7.3</td>
<td>2.8</td>
<td>3</td>
<td>140</td>
<td></td>
</tr>
<tr>
<td>Poplar Creek</td>
<td>PCK13</td>
<td>Poplar Creek, km 13</td>
<td>Above the confluence of Poplar Creek with EFPC</td>
<td>240</td>
<td>1.4 E</td>
<td>0.01</td>
<td>2</td>
<td>350</td>
</tr>
<tr>
<td>PCK8</td>
<td>Poplar Creek, km 8.2</td>
<td>Below the confluence of Poplar Creek with EFPC, but above ETTP</td>
<td>360</td>
<td>3.3 F</td>
<td>0.3</td>
<td>3</td>
<td>1200</td>
<td></td>
</tr>
<tr>
<td>ETTP</td>
<td>PCK2</td>
<td>Poplar Creek, km 1.8</td>
<td>Poplar Creek immediately below ETTP</td>
<td>370</td>
<td>4.3 G</td>
<td>0.6</td>
<td>3</td>
<td>1600</td>
</tr>
<tr>
<td>MB</td>
<td>Mitchell Branch</td>
<td>An outfall of several waste streams and storm sewers within ETTP</td>
<td>2.3</td>
<td>35.6</td>
<td>3.3</td>
<td>3</td>
<td>82</td>
<td></td>
</tr>
<tr>
<td>KPO</td>
<td>K1007 Pond Outfall</td>
<td>Outfall of a retention pond draining a portion of ETTP</td>
<td>11</td>
<td>18.6</td>
<td>0.7</td>
<td>2</td>
<td>210</td>
<td></td>
</tr>
<tr>
<td>ORNL</td>
<td>WOC</td>
<td>White Oak Creek</td>
<td>Just above its confluence with the Clinch River</td>
<td>38</td>
<td>4.3</td>
<td></td>
<td>3</td>
<td>160</td>
</tr>
<tr>
<td>Clinch River</td>
<td>CRK32</td>
<td>Clinch River, km 32</td>
<td>Above all U.S. DOE facilities</td>
<td>10,000</td>
<td>2.1 H</td>
<td>0.3</td>
<td>2</td>
<td>21,000</td>
</tr>
<tr>
<td>CRK15</td>
<td>Clinch River, km 15</td>
<td>Below all U.S. DOE facilities</td>
<td>11,000</td>
<td>1.7 H</td>
<td>0.4</td>
<td>3</td>
<td>19,000</td>
<td></td>
</tr>
</tbody>
</table>

a EFPC = East Fork Poplar Creek; ETTP = East Tennessee Technology Park; ORNL = Oak Ridge National Laboratory; U.S. DOE = U.S. Department of Energy.
b Letters indicate the results of pairwise t tests comparing estimates of PCB concentrations between pairs of up- and downstream sites. Pairs with the same letters are not significantly different from each other.

cleaned using concentrated H₂SO₄. Octachloronaphthalene was added as a volume spike, and 1 μL of sample was injected on a DB-5 column in a Hewlett-Packard 5890 gas chromatography (Avondale, PA, USA) with electron capture detection using hydrogen as the carrier gas and argon/methane as the makeup gas. The temperature program started at 40°C and rose at 10°C/min to 120°C, at 2°C/min to 260°C, held at 260°C for 2 min before increasing at 10°C/min to 320°C, and held at that temperature for 5 min. A mixed Arochlor standard with known concentrations of approx. 80 isomers (mixture of Arochlor 1242, 1248, 1254, and 1260; K. Echols) was used for quantifying the total PCB content and for quantifying individual isomers used in the principal components analysis (PCA). The identity of most congeners was confirmed using individual congener standards.

A pairwise t test [14] was used to evaluate the statistical significance of differences in estimated PCB concentrations at pairs of up- and downstream sites in EFPC, Poplar Creek, and the Clinch River.

For the PCA, congener profiles were adjusted for concentration differences between samples by dividing congener concentrations by the sum of all congeners, excluding added spikes. In cases where pairs of congeners coeluted, the pairs were treated as a single congener for purposes of this analysis. The PCA involved analysis of site congener profiles using SAS® [15]. The principal components were plotted to reveal separation of geographic groups of replicates.

Average daily flows at the monitoring sites during the period when the SPMD were deployed were obtained from stream gauging stations at sites on White Oak Creek, upper EFPC, Mitchell Branch (MB), K-1007 discharge, and Melton Hill Dam. Flows at the other sites were estimated as follows. The estimated long-term average daily flow at each ungauged site was calculated by multiplying the watershed area by the average daily runoff (18.5 L/s/km²) for streams in the Oak Ridge area [16]. This long-term average was adjusted to reflect conditions during the deployment period by multiplying it by the ratio of the average daily flow during the deployment period to the long-term average daily flow in West Fork Walker Branch, a well-characterized gauged research station on the Oak Ridge Reservation [17]. Watershed areas and estimates of inputs from the Oak Ridge Municipal Waste Water Treatment Plant were obtained from the Tennessee Valley Authority [18] and Loar et al. [19].

RESULTS

Polychlorinated biphenyl concentrations

For each site, the aqueous concentration of PCB (Cₚ) was estimated from the concentration of PCB accumulated in the SPMD:

$$C_p = \frac{C_i V_i}{R \cdot t}$$

where Cᵢ is the concentration in the SPMD lipid, Vᵢ is the volume of lipid in the SPMD, Rᵢ is the SPMD uptake rate or sampling rate, and t is the exposure time [11,20]. For convenience, it is assumed that all of the chemical recovered by the SPMD is in the triolein lipid. In reality, Rᵢ includes the contribution of both the lipid and the membrane [20]. A value of 3.5 L/d was used for Rᵢ on the basis of measurements on uptake of selected congeners from water ([20], A.L. Rantalainer, per-
Table 2. Calculation of PCB fluxes from groups of sites

<table>
<thead>
<tr>
<th>Sources</th>
<th>Calculation method</th>
<th>Sites used in calculation</th>
<th>Flux (mg/d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a. Flux from the Y-12 Plant</td>
<td>addition</td>
<td>EFK24 + BC</td>
<td>530</td>
</tr>
<tr>
<td>b. Flux from unknown sources along EFPC</td>
<td>subtraction</td>
<td>EFK2 - EFK24</td>
<td>450</td>
</tr>
<tr>
<td>c. Flux into Poplar Creek from EFPC and Bear Creek</td>
<td>addition</td>
<td>EFK2 + BC</td>
<td>980</td>
</tr>
<tr>
<td>d. Flux from ETTP to Poplar Creek</td>
<td>subtraction</td>
<td>PCK8 - PCK13</td>
<td>850</td>
</tr>
<tr>
<td>e. Flux from Poplar Creek and WOC to the Clinch River</td>
<td>addition</td>
<td>MB + KPO</td>
<td>290</td>
</tr>
<tr>
<td>f. Total flux from the three U.S. DOE facilities</td>
<td>addition</td>
<td>PCK2 + WOC</td>
<td>400</td>
</tr>
</tbody>
</table>

Sources: the flux at EFK24 and the flux at Bear Creek. Bear Creek Valley is undeveloped except for the Y-12 Plant, so the total flux observed near the mouth of Bear Creek (site BC) can be used to estimate the PCB flux from the Y-12 Plant along this drainage. Alternately, total flux from a source can be calculated by subtracting the flux upstream of a source from the flux downstream. As an example, the total PCB flux entering Poplar Creek from EFPC can be calculated as the difference in the flux above and below their confluence (PCK13 and PCK8, respectively; Table 2c). The flux computations revealed several interesting features. Calculations of PCB flux into Poplar Creek from EFPC and Bear Creek (Table 2c) by addition (EFK2 + BC) or subtraction (PCK8 - PCK13) are in good agreement, suggesting that time-averaged concentrations derived from the SPMD deployments accurately reflected PCB fluxes. Polychlorinated biphenyl discharges directly attributable to the Y-12 Plant (Table 2a) account for only about half the total PCB flux entering Poplar Creek from EFPC and Bear Creek. The source of the additional PCB flux arising between EFK14 and EFK2 is not known. There may be additional sources of PCB that are not associated with the Y-12 Plant, potentially including discharge from the Oak Ridge Municipal Sewage Treatment Plant and Tennessee Valley Authority power transformers. However, as will be discussed further in conjunction with PCB congener profiles, the changes in PCB flux along EFPC can be interpreted as sorption of PCB between EFK24 and EFK14 (flux along this reach decreases from 390 mg/d to 220 mg/d; Table 1), followed by increased inputs between EFK14 and EFK2 (PCB flux increased to 840 mg/d) due to desorption from sediments contaminated with PCB historically released from the Y-12 Plant.

The spatial pattern of decreasing and then increasing PCB flux correlates well with the organic content of the streambed. The levels of organic matter on surfaces of the rocks is twice as high in the upstream reach compared to that below EFK14 (53 and 26%, respectively; [21]). Because of the composition of the discharges from the Y-12 Plant, light, rather than nutrients, limit productivity in EFPC [21]. As a result, the changes in the organic content reflect differences in the canopy cover over the stream. The reach between EFK24 and EFK14 is characterized by limited canopy and a high amount of photosynthetically active radiation (PAR) reaching the stream (averaging 21 mol/m²/d measured at three sites along this reach in August 1988; [20]). In contrast, the lower reach (EFK14–EFK2) is wooded, and PAR is much lower (averaging 1.2 mol/m²/d measured at three sites along this reach in August 1988).
Thus the high levels of organic matter act as a PCB sink along the reach between EFK24 and EFK14. The 60% increase in the aqueous PCB concentration farther downstream could be related to the 50% lower organic content at EFK2, possibly suggesting that the dissolved PCB concentration is in steady state with the organic matter in the streambed. The sediment concentrations of PCBs reflect the differences in the organic content and sorption affinity of the streambed. Polychlorinated biphenyl concentrations in the sediments are higher in the organic-rich reach between EFK24 and EFK14 (averaging 1.1 mg/kg at three sites) than in the lower reach (averaging 0.5 mg/kg at four sites between EFK14 and EFK2) [21].

The outfalls monitored at ETTP (K1007 Pond Outfall [KPO] and MB) appeared to account for the majority of the total PCB flux that could be attributed to ETTP, if that total flux is computed by subtracting fluxes in Poplar Creek above and below ETTP (Table 2d). However, because the PCB concentrations in Poplar Creek do not increase by a statistically significant amount between PK8 and PK2 (Table 1), quantitative estimates of the potential contribution of unmonitored discharges or nonpoint sources are not possible. Although discharges at KPO and MB contained some of the highest PCB concentrations in this study, the small volume of ETTP discharges into Poplar Creek makes it very difficult to use changes in PCB concentration in Poplar Creek to evaluate the total flux of PCB from the facility. Given the standard error observed in the replicate samples from the up- and downstream sites in Poplar Creek, the concentrations of PCB in discharges at KPO and MB would have to be more than threefold greater than those observed in order to have created a measurable increase in PCB concentrations in Poplar Creek. Interpretation of the importance of unmonitored discharges is further complicated by the hydrology of Poplar Creek. Poplar Creek enters Watts Bar Reservoir in an embayment, and water can temporarily flow upstream in Poplar Creek when the Tennessee Valley Authority raises water levels in the reservoir. Thus, PCB-contaminated deposits farther downstream in the embayment may be subject to resuspension and dissolution of sorbed PCB.

Of the three DOE facilities, the Y-12 Plant contributes the greatest flux of PCB, followed by ETTP (Table 2a and d). Oak Ridge National Laboratory (White Oak Creek [WOC]; Table 1) appears to contribute only about 15% of the total PCB flux discharged by the three facilities. White Oak Creek, which flows near ORNL, encounters two impoundments that may create sinks for PCB before White Oak Creek water reaches the Clinch River. Alternately, the lower flux of PCB from ORNL may be related to the fact that ORNL is a research facility, not a manufacturing or production facility.

The total PCB flux directly attributable to discharges from all three DOE facilities (Table 2f) accounts for approx. 60% of the total PCB entering the Clinch River from Poplar Creek and White Oak Creek. However, if the increased PCB flux between EFK14 and EFK2 is the result of desorption of PCB from sediments contaminated by historic discharges from the Y-12 Plant, then these facilities may be ultimately responsible for almost all the PCB flux to the Clinch River.

The total PCB flux from all the sources entering the Clinch River through Poplar and White Oak Creeks (Table 2e) is an order of magnitude lower than the PCB flux in the Clinch River upstream of the DOE facilities (CRK32; Table 1). Although the concentrations of PCB in the Clinch River are low, the river has a large discharge. Thus, the Clinch River transports a significant mass of PCB. The flux of PCB in the Clinch River appears to decrease between CRK32 and CRK15. However, the measured PCB concentrations between the two sites are not significantly different. Because the flow volume is similar at the two sites, no conclusions can be drawn with respect to the impact of the DOE facilities on PCB flux in the Clinch River.

**Principal components analysis**

The relative contribution of PCB sources was further investigated by analysis of PCB congener profiles at different sites using PCA. Approximately 80 individual congeners or congener pairs could be identified and quantified by gas chromatography/electron-capture detector. The relative contribution of each congener to the total of all the identified congeners in a sample differed because of Aroclor ratios and different rates of transformation and transport. The resulting congener profiles were used as a basis of comparison between sites. In this analysis, the concentration of nondetected congeners within a sample was assumed to be half the detection limit concentration for that congener. Principal components analysis is used to explain the variance–covariance structure of a complex multivariate data set through a few linear combinations of the original variables (in this case, the relative concentration of 80 congeners). The first few principal components summarize the majority of the differentiation of the samples originally represented by the 80-variable congener profiles.

To evaluate whether differentiation among the congener profiles in lower EFPC were consistent with the flux results, suggesting additional sinks and sources downstream from the Y-12 Plant, we plotted principal components on the basis of congener distributions from several sites in upper and lower EFPC (Fig. 2). The first and second principal components for several sites along EFPC are shown in Figure 2a. The two sites in lower EFPC (EFK2 and EFK14) cannot be distinguished on the basis of the first two principal components. However, this pair of sites had distinctly different congener profiles, compared to congener profiles from EFK24 and other sites in upper EFPC. Only one SPMD sample was available from EFK24, where EFPC exits the Y-12 Plant. Sites in upper EFPC occupied a wide region within the plot of principal components, suggesting multiple sources from specific outfalls and from historic contamination within the streambed. The sources and sinks for PCB in upper EFPC are complex [22] and will not be discussed further here, but our results for congener profiles confirm that PCB from the Y-12 Plant are not identical to those present in lower EFPC. The two sites in lower EFPC can be distinguished on the basis of the first and
third principal components (Fig. 2b). The congener profile for EFK14 appears to be closer to profiles for sites in upper EFPC than to the profile of EFK2. This pattern of increasing differences in congener profile moving downstream from the Y-12 Plant is consistent with the hypothesis that the Y-12 Plant is the main source of PCB in EFPC. The lower flux of PCB between EFK24 and EFK14 suggests negligible inputs of new PCB sources from the City of Oak Ridge. Conversely, although a large increase in PCB flux was seen between EFK14 and EFPC, the change in congener profiles was minor (profiles could not be distinguished from the first and second principal components only; their resolution required the third principal component). As mentioned previously, we hypothesized a steady-state condition between dissolved PCB and PCB adsorbed to organic matter in the streambed. The relatively subtle changes in congener patterns with distance downstream in EFPC are likely due to abiotic processes, including volatilization of less chlorinated congeners and preferential adsorption of the more highly chlorinated congeners. This hypothesis was evaluated further by identifying the changes in chlorinated content for PCB congeners at three locations in EFPC (Fig. 3). On the basis of the concentration of individual congeners identified by GC/ECD, the concentration of congeners with different abundances of chlorine was calculated and expressed as a fraction of the total PCB concentration within a sample. Downstream from EFK24, we noted a progressive increase in the abundance of less chlorinated congeners (<4 chlorines) and a decrease in the more highly chlorinated congeners (>4 chlorines; Fig. 3). This pattern could reflect preferential desorption of the less chlorinated congeners and preferential adsorption of the more highly chlorinated PCB.

As might be expected, the congener profiles for PCB sites in upper EFPC also differed from those of PCB in Bear Creek (Fig. 4). Unlike EFPC, Bear Creek does not receive direct discharge from the Y-12 Plant. Instead, the PCB in Bear Creek are thought to originate from a number of other sources, including Bear Creek Valley. The differences between the sites revealed by PCA of PCB congeners confirms the effectiveness of this method for distinguishing differences in PCB sources.

The PCA for the ETTP site is shown in Figure 5. On the basis of a comparison of the first principal component with either the second or the third principal component, the congener profiles upstream of ETTP are different than those downstream of the facility. The profiles of the two ETTP outlets that were monitored, KPO and MB, were distinct from each other and from those of Poplar Creek (PCK2 or PCK8). However, the principal components of the downstream Poplar Creek site (PCK2) were situated between those of the upstream site (PCK8) and the two ETTP discharges, suggesting that facility discharges were responsible for the shift in the congener profiles in Poplar Creek. Thus, PCA appeared to be a more sensitive indicator of PCB sources than were the statistically insignificant changes in the concentration and flux of PCB at Poplar Creek sites above and below ETTP.

**DISCUSSION**

Semipermeable membrane devices offer a number of advantages in studies to quantify sources of PCB and other hydrophobic organic contaminants. Semipermeable membrane devices permit time-integrated measurements of PCB concentration. Because concentrations of contaminants can vary widely in time, grab sampling is not a reliable method for obtaining samples representative of the average flux of contaminant at a sampling location. Variations in aqueous concentration may be related to changes in the discharge of a stream, such as occurs as a result of storm events. However, the temporal linkages between hydrologic events and contaminant levels can vary, depending on the size of the storm, antecedent moisture conditions, distances of contaminant sources from the monitoring location, and other variables. These linkages are usually not known, making it virtually impossible to relate data for flow and concentration measured at
any one point in time to a meaningful representation of the overall flux of contaminant from a source. In contrast, contaminant flux estimates based on time-integrated concentrations at a site during an SPMD deployment period are a more representative measure of flux.

Semipermeable membrane devices take up only the dissolved concentration of contaminant, which is also the most bioavailable form [23–25]. Thus, PCB concentration and flux measurements obtained using SPMD are directly relevant to the health and environmental effects of the contaminant.

Flux measurements based on dissolved concentrations of PCB provide more useful information for identifying the location and nature of PCB sources than do measurements that include particle-associated contaminants. In most cases, fresh inputs of PCB involve dissolution of the sparingly soluble compounds from transformer oil at a point source. However, PCBs have a high affinity for organic matter on suspended particles and sediment, and their desorption is not rapid. Thus, large concentrations of dissolved PCB from a point source might be expected to decrease over a short distance downstream if the receiving system contains particles or sediment. This phenomena might increase the spatial resolution with which the point source could be identified. Conversely, a gradual increase in the flux of dissolved PCB downstream of a historic source of PCB discharges might suggest that desorption from contaminated sediment is a continuing source of PCB input to the system, as appears to be occurring between EFK14 and EFK2.

Sorption also imposes some limitations on this SPMD-based approach to identifying PCB sources. The magnitude of sources of dissolved contaminant could be underestimated if sorption to particles is significant near the discharge. Furthermore, by excluding particle-associated contaminants in flux estimates, SPMD will underestimate the total mass of mobile contaminant. Significant transport of PCB attached to suspended particles or sediment can occur in some systems during storms. However, established approaches exist to modeling transport of particles and particle-associated contaminants in streams [26]. The measurement of the flux of dissolved contaminants using SPMD is a valuable new tool that can be coupled with sediment models to provide a better understanding of contaminant dynamics.

SUMMARY AND CONCLUSIONS

Polychlorinated biphenyls were monitored using SPMD to identify and evaluate the contribution of point and nonpoint sources to the total PCB flux in a drainage system encompassing three DOE facilities. Polychlorinated biphenyl concentrations were highest at outfalls from ETTP and in the upper EFPC within the Y-12 Plant. The relative magnitude of these releases was determined by calculating the flux of PCB at different sites from time-integrated estimates of the aqueous concentrations of PCB along with measurements or estimates of flow rates of discharges and streams during the deployment period. The time-averaged mass of PCB released from the Y-12 Plant to the watershed was greater than that from ETTP; ORNL releases were lower. The flux of current PCB discharges from all the DOE facilities accounted for approx. 60% of the total PCB entering the Clinch River from Poplar Creek and White Oak Creek, but the combined flux from these sources was only 10% of that in the Clinch River above these sources. Principal components analysis was helpful in attributing sources of PCB to the receiving system. Congener profiles changed between sites in a manner consistent with the evidence from flux measurements. In the case of ETTP, different congener profiles from upstream sources and discrete discharges were consistent with a mixture of those congener profiles in the receiving water. For the Y-12 Plant, PCB congener profiles along EFPC changed only slightly with distance downstream, suggesting that the Y-12 Plant was the principal source of PCB. Subtle changes in congener patterns for sites in EFPC may have been caused by preferential adsorption and desorption of different congeners to the sediment.

More generally, this study illustrates an approach for identifying point and nonpoint sources of contamination and comparing the relative importance of different sources to the overall PCB budget of a region. This approach may guide more effective remediation strategies for specific PCB sources. Our study focused on PCB at a fairly broad geographic scale and encompassed several industrial facilities and municipalities. An approach of this type would be equally applicable to other hydrophobic organic contaminants that can be accumulated by SPMD, such as polycyclic aromatic hydrocarbons and dioxins. Furthermore, the same time-integrated, flux-based approach can be very useful on a smaller spatial scales to identify sources of contaminant releases within a single facility [22]. Ongoing work is attempting to identify the sources of PCB discharging to EFPC by monitoring the storm sewer network within the Y-12 Plant as well as several sites in upper EFPC. This monitoring is expected to localize the source of discharges within the Y-12 Plant and determine the relative contribution of current discharges from waste streams compared to possible historic sources from past releases.

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