Polychlorinated Dibenzo-p-dioxin and Dibenzofuran Concentration Profiles in Sediments and Flood-Plain Soils of the Tittabawassee River, Michigan

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Concentrations of polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) in sediments and floodplain soils collected along the Tittabawassee River in Michigan ranged from 102 to 53 600 pg/g, dry wt. Mean PCDD/PCDF concentrations in downstream sediment and soil were from 10- to 20-fold greater than those found at locations upstream of Midland, Michigan. Concentrations of PCDD/PCDF in sediments collected upstream of Midland and in the Tittabawassee watershed were comparable to those found in industrialized areas such as the Housatonic and lower Passaic Rivers in the U.S. Concentrations of PCDDs/PCDFs in soil and sediment were not correlated with total organic carbon (TOC) in sediments or soils. OCDD and 2,3,7,8-TeCDD were the predominant congeners in sediment/soil collected from locations downstream of Midland, Michigan. Principal component analysis of the PCDD/PCDF congener profile suggested the presence of sources originating from a mixture of chlorophenol and other chlorinated compound production. Mass balance analysis of TCDD equivalents (TCDD-EQs) derived from H4IE-luc bioassay of sediment extracts and 2,3,7,8-tetrachlorodibenzop-dioxin equivalents (TEQs) estimated from instrumental analysis suggested that PCDDs/PCDFs were the major dioxin-like compounds present in sediments. A significant correlation existed between bioassay-derived TCDD-EQs and instrumentally measured TEQs (r² = 0.94).

Introduction

Water and sediment quality in Saginaw Bay and its tributaries in Michigan has been demonstrably impacted by historical industrial activities within the Saginaw Bay watershed (1). The U.S. Environmental Protection Agency (EPA) has identified the Saginaw River and Bay as an Area of Concern (1) as part of the Assessment and Remediation of Contaminated Sediments Program (ARCS). The Saginaw River and Bay receives discharges from 87 industrial facilities and 127 wastewater treatment plants, including those of the cities of Flint, Saginaw, Bay City, and Midland in Michigan. The Tittabawassee River is the largest tributary to the Saginaw River (Figure 1). It drains 5426 km² and contributes nearly 50% of the tributary flow to the Saginaw River. The Tittabawassee River watershed is mainly woodland (41%) with scattered agricultural areas (37%). The Chippewa and Pine Rivers are two of the major tributaries to the Tittabawassee River. The city of Midland is the major industrial and population center on the Tittabawassee River. The Michigan Department of Public Health has issued fish advisories on the basis of elevated levels of polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) and polychlorinated biphenyls (PCBs) found in fish tissues in the Tittabawassee and Saginaw Rivers downstream of Midland.

The objectives of this study were to elucidate spatial differences in concentrations of PCDDs and PCDFs in sediment and floodplain soils collected along the Tittabawassee River. Sediments collected upstream of Midland and in the Chippewa and Pine Rivers were used as references for comparison. Absolute and relative (congener profile) concentrations and 2,3,7,8-tetrachlorodibenzop-dioxin equivalents (TEQs) were evaluated to describe possible sources and potential for effects. In addition, the H4IE-luc bioassay was used to determine total dioxin-like activity (TCDD-EQs) in sediments. A mass balance analysis of dioxin-like activity derived from instrumental (i.e., TEQs) and bioassay (i.e., TCDD-EQs) analyses was used to test for the presence of other dioxin-like compounds that can bind to the aryl hydrocarbon receptor (AhR). Earlier studies have demonstrated that the H4IE-luc bioassay coupled with instrumental analysis is useful in integrated assessments of dioxin-like activity in sediments (2–4). The instrumental and bioanalytical approaches provide different and complementary information. Whereas instrumental analyses are useful for identifying the compounds of interest and evaluating concentrations of specific compounds, they provide little information regarding the integrated biological relevance of a complex mixture of compounds associated with environmental samples such as sediment. Where appropriate, bioassay-directed fractionation and mass balance analyses are powerful tools for characterizing the causative agents responsible for bioassay responses observed. Studies have indicated that organic extracts of sediments elicited significant AhR-mediated responses in vitro, although the chemical concentrations often did not explain the activities observed in bioassays (2, 5, 6). Empirical bioassay results and mass balance analyses can suggest the magnitudes of the contributions of target organic compounds to total AhR-mediated activity. Thus, bioassay-based toxicity identification and evaluation (TIE) and mass balance analyses are important approaches in the assessment of sediment contamination.
Laboratory at Michigan State University, East Lansing, MI. and TOM were analyzed at the Soil and Plant Nutrient analysis, and TOM was determined by loss on ignition. TOC TOC was determined by dry combustion microcarbon prior to analysis. Pebbles and twigs were removed, and of Midland. Sediment samples were homogenized thoroughly for the study, “upstream” refers to those samples collected upstream Chippewa Rivers upstream of Midland (Figure 1). In this study, samples of composite and transect sediments collected along the river were also analyzed. For comparison, transect samples are composites of Ponar grab samples from several locations along a transect perpendicular to the bank of the river. Transect sediments include both surface sediments collected using a Ponar sampler (0–10 cm) and subsurface (40–60 cm) sediments collected using a PVC corer. In addition, flood-plain soils collected along the river were also analyzed. For comparison, corresponding samples of composite and transect sediments and flood-plain soils were collected from the Pine and Chippewa Rivers upstream of Midland (Figure 1). In this study, “upstream” refers to those samples collected upstream of Midland. Sediment samples were homogenized thoroughly prior to analysis. Pebbles and twigs were removed, and portions of sediments were analyzed for moisture content, total organic carbon (TOC), and total organic matter (TOM). TOC was determined by dry combustion microcarbon analysis, and TOM was determined by loss on ignition. TOC and TOM were analyzed at the Soil and Plant Nutrient Laboratory at Michigan State University, East Lansing, MI.

### Chemical Analysis

Concentrations of 17, 2,3,7,8-substituted PCDDs and PCDFs were analyzed by modifications of previously described methods (7–9). Sediment and soil samples (40–50 g wet) were homogenized with anhydrous sodium sulfate, Soxhlet extracted using 400 mL of toluene, and concentrated to 10 mL. Extracts were treated with activated copper to remove sulfur. Portions of sediment samples were dried at 80°C for the determination of moisture content. Two-milliliter aliquots of extracts were taken for in vitro bioassays using H4IIE-luc cells to estimate total dioxin-like activity. 13C-labeled PCDDs and PCDFs were added as internal standards to the remaining extracts before they were passed through 6 g of multilayer silica gel (100–200 mesh) column packed in a glass column (10 mm i.d.). The silica gel column was prepared by packing 2 g of silica gel followed by 2 g of 40% acidic silica and then 2 g of silica gel. The silica gel bed was washed with 100 mL of hexane prior to loading of the sample extract. Extracts were then eluted with 10% dichloromethane in hexane. Samples were concentrated and passed through 1 g of activated-carbon-impregnated silica gel column (Wako Pure Chemical Industries, Tokyo, Japan). The first fraction eluted with 150 mL of hexane was discarded, and the second fraction eluted with 200 mL of toluene was concentrated and analyzed by high-resolution gas chromatography and high-resolution mass spectrometry (HRGC/HRMS). A Hewlett-Packard 6890 GC interfaced with a JEOL JMS-700 HRMS was used for the determination of hepta- and octa-chlorinated congeners. A Hewlett-Packard 6890 Series II gas chromatograph coupled with a JEOL Autospec-Ultima instrument was used for the determination of the second fraction eluted with 200 mL of toluene was concentrated and analyzed by high-resolution gas chromatography and high-resolution mass spectrometry (HRGC/HRMS).

### Figure 1

Map of the Tittabawassee River and its tributaries in Michigan. Sampling area is shaded.
was observed in sediment collected from surface (0 cm) transect sediment (overall) although mean PCDF concentrations were greater in subsurface (4830 pg/g) whereas concentrations reported for sediments in the lower Passaic River and Newark Bay, New Jersey, ranged from 160 to 5400 pg/g, dry wt, except in one sample that contained a concentration of 82,000 pg/g, dry wt. Nevertheless, the mean concentration of PCDDs was greater than that of PCDDs even when the outlier was removed. Concentrations of PCDDs/PCDFs were 6–10-fold greater in flood-plain soils than in sediments collected along the Tittabawassee River. The greatest PCDD/PCDF concentration (53,600 pg/g, dry wt) was found in a flood-plain soil collected from the middle sections of the river (SSS). Total PCDD and PCDF concentrations in flood-plain soil and sediment samples collected upstream of Midland in the Tittabawassee River and in the Chippewa and Pine Rivers were 10–20-fold less than those collected downstream of Midland (Table 1). These results suggest the existence of potential sources near Midland. Previous studies have reported the occurrence of PCDDs/PCDFs arising from historical industrial operations at Dow Chemical Company in Midland (12, 13).

No spatial gradient in PCDD/PCDF concentrations was evident, although the midsections of the river contained greater concentrations than did the upper or lower sections (Figure 2, Supporting Information). Concentrations of total PCDDs/PCDFs were not significantly correlated with organic carbon content in sediment or soils (p > 0.05) (Figure 3, Supporting Information). The greater total concentrations of PCDDs/PCDFs in certain locations could be explained by the hydrological and geological characteristics (e.g., sedimentation) of the river.

Concentrations of total PCDDs and PCDFs in Tittabawassee River sediments were greater than those reported for Housatonic River sediments in Massachusetts, which ranged from 160 to 5400 pg/g, dry wt, except in one sample that contained a concentration of 82,000 pg/g, dry wt. Concentrations of PCDDs/PCDFs in surficial sediments from the lower Passaic River and Newark Bay, New Jersey, ranged from 370 to 24,000 pg/g, dry wt. Total concentrations of PCDDs/PCDFs in sediments from the rivers in the United Kingdom ranged from 446 to 9310 pg/g, dry wt. In Korea, concentrations of PCDD/PCDF ranged from 102 to 6490 pg/g, dry wt, whereas concentrations reported for sediments in

**TABLE 1. Mean and Range of 2,3,7,8-Substituted PCDD and PCDF Concentrations in Sediments from Upstream (Tributary Rivers) and Downstream Locations of the Tittabawassee River**

<table>
<thead>
<tr>
<th>sediment</th>
<th>n</th>
<th>TOC (%)</th>
<th>TOM (%)</th>
<th>PCDDs (pg/g, dry wt)</th>
<th>PCDFs (pg/g, dry wt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>composite sediment</td>
<td>16</td>
<td>0.64</td>
<td>1.11</td>
<td>2400</td>
<td>3790</td>
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<tr>
<td>transect sediment (overall)</td>
<td>14</td>
<td>0.41</td>
<td>0.71</td>
<td>(0.36–1.3)</td>
<td>(0.61–2.24)</td>
</tr>
<tr>
<td>transect (upper)</td>
<td>7</td>
<td>0.37</td>
<td>0.64</td>
<td>(0.11–1.27)</td>
<td>(0.19–2.19)</td>
</tr>
<tr>
<td>transect (lower)</td>
<td>6</td>
<td>0.43</td>
<td>0.74</td>
<td>(0.26–0.71)</td>
<td>(0.45–1.22)</td>
</tr>
<tr>
<td>flood-plain soil</td>
<td>7</td>
<td>3.2</td>
<td>5.4</td>
<td>(0.11–1.27)</td>
<td>(0.19–2.19)</td>
</tr>
<tr>
<td>individual sediment</td>
<td>12</td>
<td>0.89</td>
<td>1.53</td>
<td>(1.2–6.5)</td>
<td>(2.1–11.1)</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>(0.11–4.05)</td>
<td>(0.19–6.98)</td>
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<tr>
<td>composite sediment</td>
<td>3</td>
<td>0.72</td>
<td>1.23</td>
<td>120</td>
<td>59</td>
</tr>
<tr>
<td>transect sediment</td>
<td>4</td>
<td>0.76</td>
<td>1.2</td>
<td>(0.58–0.95)</td>
<td>(1–1.65)</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(0.41–1.28)</td>
<td>(0.71–2.21)</td>
</tr>
<tr>
<td>flood-plain soil</td>
<td>3</td>
<td>4</td>
<td>6.9</td>
<td>(3.6–4.4)</td>
<td>(6.1–7.5)</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(0.23–0.6)</td>
<td>(0.4–1.04)</td>
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<tr>
<td>individual sediment</td>
<td>2</td>
<td>0.42</td>
<td>0.72</td>
<td>116</td>
<td>145</td>
</tr>
</tbody>
</table>

respectively. Reported concentrations were corrected for the recoveries of corresponding 13C-labeled congeners.

**In vitro Bioassay Analysis.** For all of the samples, raw extracts, after Soxhlet extraction, were assessed for AhR-mediated activity by use of the in vitro H4IE-luc recombinant cells. Solvent was transferred to hexane prior to dosing of the cells. Test and control wells were dosed with appropriate extract or solvent. For selected samples, raw extracts were treated with concentrated sulfuric acid for at least 12 h and then assessed for AhR-mediated activity. The procedures applied to conduct the bioassays have been described in detail previously (6, 10, 11). Luciferase and protein assays were conducted after 72 h of exposure. Sample responses, expressed as mean relative luminescence units (RLU) over three replicate wells, were converted to relative response units, expressed as a percentage of the maximum response observed for 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD; % TCDD max) standard curves generated on the same day. Potencies of samples relative to TCDD were estimated. Mass balance analysis (or potency balance analysis) was used to examine whether the known composition of a sample (identified by instrumental analysis) can account for the magnitude or potency of biological response observed. Further details of the bioassay procedures and mass balance analysis are presented elsewhere (2, 5, 6, 10).

Data were analyzed statistically by principal component analysis (PCA). For PCA, concentrations of PCDD/PCDF isomers were normalized to percentages of the total concentrations. PCA was performed using a statistical package supplied by Esumi Co. Ltd., Tokyo, Japan.

**Results and Discussion**

**Chemical Analysis.** Mean concentrations of 17 2,3,7,8-substituted PCDD and PCDF congeners in sediment collected from the Tittabawassee River downstream of Midland were 2400 and 3790 pg/g, dry wt, respectively (Table 1). Concentrations of total PCDD/PCDFs in surficial transect sediments were comparable to those found in composite sediment samples. No significant difference in PCDD concentration was observed in sediment collected from surface (0–10 cm) or subsurface (40–60 cm) transects although mean PCDD concentrations were greater in subsurface layers (4830 pg/g) than in surface layers (1560 pg/g). The greater concentration of PCDDs in subsurface layers is due to an elevated concentration in one of the subsurface sediment samples collected at the lower (downstream) sections of the river (17,700 pg/g, dry wt). Nevertheless, the mean concentration of PCDFs was greater than that of PCDDs even when the outlier was removed. Concentrations of PCDDs/PCDFs were 6–10-fold greater in flood-plain soils than in sediments collected along the Tittabawassee River. The greatest PCDD/PCDF concentration (53,600 pg/g, dry wt) was found in a flood-plain soil collected from the middle sections of the river (SSS). Total PCDD and PCDF concentrations in flood-plain soil and sediment samples collected upstream of Midland in the Tittabawassee River and in the Chippewa and Pine Rivers were 10–20-fold less than those collected downstream of Midland (Table 1). These results suggest the existence of potential sources near Midland. Previous studies have reported the occurrence of PCDDs/PCDFs arising from historical industrial operations at Dow Chemical Company in Midland (12, 13).
Japanese ranged from 377 to 15,800 pg/g, dry wt (7, 9, 16–18). In general, the concentrations of PCDDs/PCDFs measured in sediments and floodplain soils from the Tittabawassee River were similar to those reported in industrialized areas (15).

Concentrations of PCDFs were greater than those of PCDDs in approximately 50% of the sediments/soils collected from the Tittabawassee River. Ratios of concentrations of PCDDs to PCDFs in sediments collected from the Tittabawassee River ranged from 0.32 to 1.82. In contrast, sediments collected from the Pine and Chippewa Rivers (upstream reference locations) contained 6–16-fold greater concentrations of PCDDs compared to PCDFs. Profiles of PCDD and PCDF congeners in sediment and soil from sampling locations upstream and downstream of Midland are presented in Figure 4. OCDD accounted for 30–60% of the total PCDD/PCDF concentrations in downstream sediment/soils and 60–80% in upstream samples. Sediment/soil samples from upstream locations contained relatively greater proportions of OCDD and lesser proportions of PCDFs than those from the downstream sampling locations. Among PCDF congeners, 2378-TCDF was the most abundant congener in downstream sediments accounting for 12–25% of the total PCDD/PCDF concentration. This was followed in order by PeCDF > HxCDF > OCDF > HpCDF. The distributions of PCDD/PCDF isomers in the majority of sediment/soil from the Tittabawassee River were similar to those from New Bedford Harbor and the lower Passaic River (15).

Different sources of PCDDs/PCDFs are characterized by different congener and homologue patterns (15, 19). Furthermore, differences in the physicochemical (mobility, solubility, etc.) and biological (biodegradation, bioaccumulation, etc.) properties can alter the congener profiles. The profiles of PCDD and PCDF congeners in sediment from the Tittabawassee River downstream of Midland were different from that in samples collected from upstream reference locations. A large proportion of OCDD and HpCDF has been suggested to be due to the sources originating from chlorophenol-related inputs (20). Greater proportions of TCDFs suggest sources originating from PCB mixtures, chlorobenzenes, the chlor-alkali process, or the incineration of PCBs and PVC (19–23). Total concentrations of PCBs in sediments from the Tittabawassee River were less than 150 ng/g, dry wt (24). This suggests that PCBs were not likely to be a source of PCDD/PCDFs, but rather, that other sources such as chlorophenol and chlorobenzene production, incineration-related activities, and/or chlor-alkali processes are likely sources of PCDFs found in Tittabawassee River sediments collected below Midland.

The profiles of relative concentrations of PCDD/PCDF congeners were characterized by use of principal component analysis (PCA). The relative orderings of profiles of concentrations of PCDD/PCDF congeners, normalized to the total concentration of PCDD and PCDF, in sediments or soils from the Tittabawassee River and some representative source materials are plotted as a function of the first two principal components (Figure 5). The first and second principal components explained 31 and 16%, respectively, of the original variance of the normalized congener dataset. The first principal component (PC1) contained greater positive eigenvectors for congeners 123478- and 12378-TCDF, whereas the vectors were negative for OCDD and 1234678-HpCDD. The second principal component (PC2) contained positive eigenvectors for congeners 123789-HxCDF and 12378-PCDF, whereas the vectors were negative for OCDD and 1234678-HpCDD. The second principal component (PC2) contained positive eigenvectors for congeners 123789-HxCDF, OCDF, 2378-OCDF, and 12378-PCDF, whereas a negative vector was obtained for 2378-TCDF. In a plot of PC1 versus PC2, the pattern for Aroclors 1242 and 1248, graphite sludge, and PVC/PCB pyrolysis, ordered them toward the right side of the graph, whereas pentachlorophenol (PCP), sodium pentachlorophenate, and municipal solid waste incineration-related sources were placed toward the left (Figure 5). The PCDD/PCDF profiles of Aroclors, graphite sludge, and chlorobenzenes are dominated by PCDFs, whereas those in PCP or other chlorophenol-related sources are dominated by PCDDs, particularly HpCDD and OCDD (15, 19–23). PCDD/PCDF homologue profiles in tri- and tetrachlorobenzenes were in the order TeCDF > PeCDF > HxCDF, which resembled the order of PCDF profiles found in sediments. Whereas homologue profiles of PCDD/PCDF have been reported for chlorobenzenes (22), profiles of individual isomers have not been reported. Because of the lack of isomer-specific information on PCDD/PCDF profiles in chlorobenzenes, only homologue profiles were plotted as a function of principal components. PCA of homologue profiles of tri- and tetrachlorobenzenes exhibited a greater negative loading of PC2 as a result of the lack of OCDD and HpCDD in these mixtures. Tri- and tetrachlorobenzenes (not shown) were ordered toward the right near Aroclor 1242.

The majority of the soil and sediment samples collected along the Tittabawassee River were positioned at the intersection of the two principal components intermediate between the patterns of PCP, Aroclors 1242 and 1248, and graphite sludge. Therefore, PCDDs/PCDFs in Tittabawassee River sediments/
flood-plain soils are likely to have come from these sources and others. Soils/sediments from locations upstream of Midland exhibited greater negative loading on PCl because of their greater proportions of HpCDD and OCDD. Although the patterns of relative concentrations of PCDD/PCDF congeners alone are insufficient to determine the exact source of PCDDs/PCDFs (as PCDD/PCDFs undergo congener-specific degradation in soil/sediments and volatilization in the environment), the results of the principal components analysis of relative proportions of congeners, combined with the absolute concentrations, indicate that the Midland area is the source of PCDDs/PCDFs found in sediments collected from the Tittabawassee River.

**Bioassay Analysis.** Both raw extracts after Soxhlet extraction and acid-treated extracts of several sediment and soil samples were examined for their ability to elicit AhR-mediated activity in vitro using H4IIE-luc cells. All of the tested sediment extracts, both raw and acid-treated, elicited significant AhR-mediated activity. TCDD-EQs were calculated on the basis of the amount of sample needed to produce a response equivalent to EC20 = EC0 of TCDD. The estimate of a range is more appropriate than the estimate of a single point because of the nonparallelism of the dose–response curves (the lower the range, the more parallel the curves) (25). The values on the basis of the response equivalent to EC0 were used for statistical comparisons between instrumental and bioassay results. TCDD-EQs estimated on the basis of an EC0 are presented (Table 2). EC0 values are used because all of the samples reached 20% of the efficacy and, therefore, extrapolations were not needed to calculate EC20 concentrations. Concentrations of TCDD-EQs in sediments ranged from 17 to 1860 pg/g dry wt, whereas those in flood-plain soils ranged from 290 to 2550 pg/g dry wt. Concentrations of TCDD-EQs in upstream sediment were 10–100-fold less than those in downstream sediments. Similarly, TCDD-EQs in upstream soils were approximately 5–10-fold less than those in downstream sediment samples.

On the basis of the results of instrumental analysis of PCDD/PCDF, concentrations of 2,3,7,8-tetrachlorodibenzo-p-dioxin equivalents (TEQs) were calculated using H4IIE-luc cell line-specific relative potencies (REPs-EC20) (26). The use of REPs instead of toxic equivalency factors (TEFs) was necessary to perform mass balance analyses of TCDD-EQs derived using the H4IIE cell bioassay and TEQs calculated on the basis of instrumental analysis. Concentrations of TEQs in sediments from the Tittabawassee River ranged from 4 to 1980 pg/g dry wt (Table 2). The mean concentration of TCDD-EQs in flood-plain soils was 800 pg/g dry wt. As observed for TCDD-EQs, concentrations of TEQs in upstream soils and sediments were 50 to 100-fold less than those in downstream soils and sediments. A significant correlation existed between concentrations of TCDD-EQs derived from H4IIE-luc bioassay and TEQs estimated from instrumental analysis.
Midland (see Table 3 and Figure 8). Among PCDFs, 23478-PeCDF was the major contributor to TEQs in sediments, accounting for 40–50% of the TEQs, followed in order by 12378-PeCDF, 2378-TeCDF, and 123478-HxCDF (Figure 7). These four congeners collectively accounted for 85–90% of the total TEQs.

These results suggest that the concentrations of PCDDs/PCDFs in sediments and flood-plain soils collected downstream of Midland were comparable to those observed in several other industrialized regions. OCDD and TCDF were the predominant congeners in soil and sediments, which suggests a unique pattern. Concentrations of PCDD/PCDF in sediment/soil were not correlated with TOC. Bioassay-derived TCDD-EQs were similar to those derived from instrumental analysis of PCDDs/PCDFs, which suggests that PCDDs/PCDFs were the critical contaminants that contribute to dioxin-like activity in sediments from the Tittabawassee River.

The present study has not addressed the issue of the risks of PCDDs/PCDFs to humans or wildlife. Risk is a factor of both exposure and hazard (toxicity). An assessment of the risks posed by PCDDs/PCDFs would need to consider the bioavailability of each congener as well as other factors that would affect the potential exposure. The Agency for Toxic Substances and Disease Registry in the United States (28) has adopted interim policy guidelines for PCDDs/PCDFs in residential soils near or on hazardous waste sites. When concentrations of TEQs exceed 50 pg of TEQ/g, dry wt, evaluation of site-specific factors such as pathway analysis and soil cover are needed. Actions to be taken when soil concentrations exceed 1000 pg/g, dry wt, include surveillance and research of exposure investigations. In this study, TEQ concentrations in 42 of 61 soil/sediment samples were greater than 50 pg/g, dry wt. More than 90% of the sediment samples collected downstream of Midland contained TEQ concentrations greater than 50 pg/g, dry wt. Fifteen of the 61 samples contained TEQ concentrations greater than 1000 pg/g, dry wt. These TEQ estimates might be an underestimation because these are based on H4IIE-bioassays rather than WHO guidelines, which have greater TEF values. According to these guidelines additional reconnaissance work would be warranted. Remedial options should be based on sound data on the relative risks now and in the future (29).

Acknowledgments

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Supporting Information Available

Figures showing spatial trends in concentrations of total PCDDs/PCDFs in surface sediment and flood-plain soils and relationship between total PCDD/PCDF concentrations and 
PCDDs/PCDFs in surface sediment and flood-plain soils collected along the Tittabawassee River and its tributaries. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited