

PCDDs and PCDFs in Aquatic and Terrestrial Food Webs of the Tittabawassee River, Michigan, USA

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Introduction

In risk assessment, when measured concentrations are not available for the receptors of concern, concentrations of contaminants of concern are often predicted. Here we address the uncertainty of predicting these concentrations, by comparing concentrations of TEQ measured in tissues with those predicted based on default assumptions. The Tittabawassee River is located in central Michigan, USA. The general area investigated in this study includes 38 km of the river from the upstream boundary delineated by The Dow Chemical Company in Midland, Michigan to the confluence of the Tittabawassee and Shiawassee Rivers. Previous studies have reported that this section of the Tittabawassee River contains elevated concentrations of polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) in sediments, floodplain soils, and fish.^{1,2} A preliminary sampling of aquatic and terrestrial food web items was conducted by Michigan State University at two locations on the Tittabawassee River downstream of Midland (Imerman Park and Tittabawassee Township Park) and from one reference location located upstream at Sanford, Michigan. The results for concentrations and congener profiles of PCDDs and PCDFs in the aquatic and terrestrial food webs are summarized here. The measured concentrations in biota were then compared to biota concentrations that were previously predicted from sediment and soil concentrations.

Materials and Methods

Concentrations of PCDDs and PCDFs in the sediments and floodplain soils near the reference location are consistent with statewide background concentrations of TEQs which range from <1 to 35 ng/kg dry weight (dw) and average 6 ng/kg (dw).² Thus, this area was considered to be relatively uncontaminated and served as a reference location for sediment, soil, and lower food web samples. Land use at Sanford and Tittabawassee Township Park sampling locations can be described as mixed agriculture and emergent forest. Land use at Imerman Park, the second downstream location, is similar to Sanford and Tittabawassee Township Park but with the addition of maintained grass.

Representative samples of the terrestrial and aquatic food webs of the Tittabawassee River and floodplain were collected between September 5 and October 11, 2003. Samples were collected synoptically (e.g., same time and location) to the extent practical and included soils, terrestrial plants, terrestrial invertebrates, earthworms, small mammals, sediments, aquatic plants, benthic invertebrates, crayfish, aquatic emergent insects, and fish. All samples were collected with the approval and permitting of appropriate state and federal agencies and in accordance with Michigan State University's All-University Committee on Animal Use and Care.

Samples of soils, plants, terrestrial invertebrates, earthworms, and small mammals were collected simultaneously within a 30 x 30-meter terrestrial sampling grid. Aquatic samples were collected from areas in the river adjacent to the terrestrial sampling grids. Sediments, aquatic plants, and benthic invertebrates were collected simultaneously by grab sampling sediment to a depth of 5 cm. Sediment samples were pooled for a given transect and placed into clean, labeled buckets. The forage fish composite was a representative sample of a targeted size class of fish (<25 cm) and thus included multiple species.

Analyses of PCDD, and PCDF, concentrations in samples were conducted at AgriQuality Limited (Lower Hutt, New Zealand) using EPA method 8290. The TEQ concentrations presented in this report were calculated by assigning a proxy value of ½ the detection limit (DL) for congeners below the DL. All TEQ values were based on mammalian World Health Organization toxicity equivalency factors.³ Concentrations of TEQ in all biota are expressed as ng/kg

on a wet weight basis. Sediment values are reported as ng/kg on a dry weight basis.

Results and Discussion

Concentrations of the seventeen 2,3,7,8 substituted PCDD/Fs congeners were used to calculate the TEQ concentrations in the sediment, soil, and biota of the aquatic and terrestrial food webs at each of the sampling locations (Tables 1 & 2).

Table 1. Concentrations of TEQ (ng/kg) measured in components of the aquatic food web of the Tittabawassee River.

| | Sanford reference location | | | Tittabawassee Township Park | | | Imerman Park | | |
|------------------------------------|----------------------------|--------------|----------|-----------------------------|-------------|--------|--------------|-------------|--------|
| | N | Mean | SD | N | Mean | SD | N | Mean | SD |
| Sediment | 2 | 1.03 | ± 0.621 | 7 | 46.1 | ± 43.0 | 2 | 197 | ± 241 |
| Benthic invertebrate ¹ | 7 | 1.64 | ± 3.20 | 3 | 14.0 | ± 7.59 | 1 | 45.7 | |
| Aquatic emergent insect | | | | 2 | 19.4 | ± 5.33 | 1 | 20.6 | |
| Aquatic plant | | | | 1 | 4.40 | | 1 | 9.74 | |
| Crayfish | 1 | 0.150 | | 1 | 11.6 | | 1 | 44.3 | |
| Northern pike ² | 1 | 2.89 | | | | | 1 | 66.9 | |
| Composite forage fish ² | 2 | 0.447 | ± 0.0009 | | | | 2 | 54.0 | ± 13.2 |

¹Benthic invertebrates excluding crayfish.

²Whole fish.

Table 2. Concentrations of TEQ (ng/kg) measured in components of the terrestrial food web of the Tittabawassee River.

| | Sanford reference location | | | Tittabawassee Township Park | | | Imerman Park | | |
|---------------------------------|----------------------------|--------------|---------|-----------------------------|-------------|--------|--------------|-------------|--------|
| | N | Mean | SD | N | Mean | SD | N | Mean | SD |
| Soil | 1 | 2.04 | | 2 | 2530 | ± 116 | 1 | 2450 | |
| Earthworm depurate | 1 | 0.612 | | 1 | 83.5 | | 1 | 76.1 | |
| Earthworm fresh | 1 | 0.686 | | 1 | 129 | | 1 | 96.4 | |
| Terrestrial plant | 1 | 1.47 | | | | | 2 | 1.52 | ±0.208 |
| Terr. invertebrate ¹ | 5 | 1.13 | ±0.415 | 6 | 15.8 | ±17.6 | 5 | 28.7 | ±33.0 |
| Shrew | 2 | 0.892 | ± 0.923 | 3 | 69.4 | ± 102 | | | |
| Small mammal ² | 10 | 0.664 | ± 0.254 | 13 | 93.2 | ± 81.4 | 19 | 85.5 | ± 85.3 |

¹ Terrestrial invertebrates excluding earthworms.

² Small mammals excluding shrews.

The downstream locations exhibited similar congener profiles. Using Imerman park as an example, six congeners accounted for more than 80% of the TEQ in both the aquatic and terrestrial food web items (Figure 1). The remaining congeners accounted for less than 5% of the TEQ when considered separately. In general, 2,3,4,7,8-PeCDF made the greatest contribution to the total TEQ concentrations across all matrices studied. At Sanford, the reference location, the same six congeners generally accounted for >70% of the TEQ with a more even distribution between 2,3,7,8-TCDD, 1,2,3,7,8-PeCDD, and 2,3,4,7,8-PeCDF.

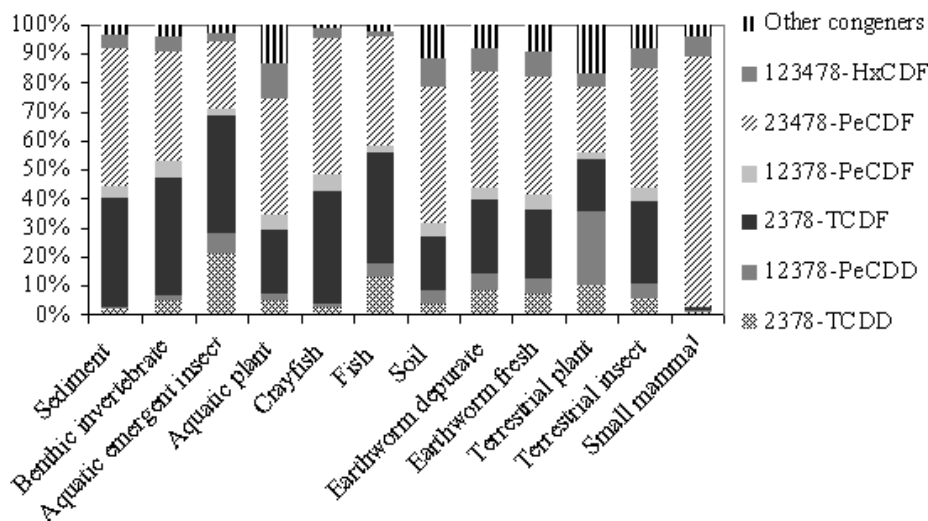


Figure 1. Percent contribution of PCDD and PCDF congeners to the total TEQ concentration in Imerman Park aquatic and terrestrial food web items.

A comparison of the current study results was made to predicted residue data presented previously by GES/MDEQ.⁴ In the report entitled, "Tittabawassee River Floodplain Screening-Level Ecological Risk Assessment", soil data were utilized to predict concentrations of TEQs in invertebrates, small mammals, and birds using a conservative bioaccumulation model. Based on the soil data from the Michigan State University preliminary food web study and using the parameters from the GES/MDEQ model, predicted results and actual data were compared (Table 3). The model parameters resulted in an overestimate of the actual measured TEQ concentrations by more than 10-fold for invertebrates and 100-fold for small mammals. This comparison of predicted to measured values illustrates the importance of collecting site specific data to reduce uncertainty when considering food web exposures in environmental risk assessments.

Table 3. Comparison of modeled and actual TEQ (ng/kg, ww) data for the terrestrial food web for the floodplain along the Tittabawassee River.

| | Predicted data ^A | | | Measured data | |
|---------------|-----------------------------|--------------|----------------------------|-----------------------------|--------------|
| | Tittabawassee Township Park | Imerman Park | | Tittabawassee Township Park | Imerman Park |
| Invertebrates | 343 | 705 | Terr. inverts ^B | 15.8 | 28.7 |
| | | | Earthworms ^C | 83.5 | 76.1 |
| Small mammals | 13,633 | 12,063 | Small mammals | 93.2 | 85.5 |

^A Predicted data was obtained by applying model parameters from GES/MDEQ to the Michigan State University measured soil values.

^B Terrestrial invertebrates excludes earthworms.

^C Depurated earthworms

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