

# EVALUATION OF CONGENER-SPECIFIC CONCENTRATIONS OF POLYCHLORINATED BIPHENYLS (PCBS) AND PATTERNS IN AN AQUATIC-BASED FOOD WEB AT THE KALAMAZOO RIVER SUPERFUND SITE, MICHIGAN



ENTRIX

A. Blankenship<sup>1,2</sup>, K. Coady<sup>1</sup>, M. Zwiernik<sup>2</sup>, C. Parks<sup>2</sup>, R. Holem<sup>1</sup>, P. Bradley<sup>2</sup>, A. Neigh<sup>2</sup>, D. Kay<sup>1</sup>, and J.P. Giesy<sup>2</sup> <sup>1</sup>ENTRIX, Inc., Okemos, MI and <sup>2</sup>Michigan State University, East Lansing, MI



National Food Safety and Toxicology Center

MICHIGAN STATE UNIVERSITY

## ABSTRACT

Approximately eighty miles of the Kalamazoo River has been designated a Superfund site with PCBs as the primary contaminant. As part of a comprehensive field study on exposure to PCBs and potential ecological risks of PCBs, several different aquatic-based food items were collected and analyzed for PCB congeners from the former Trowbridge impoundment. Representative species of fish (including smallmouth bass, various suckers, carp, and a forage fish composite), aquatic plants, representative invertebrates (e.g., benthic representative invertebrates (e.g., benthic invertebrates, crayfish, and several taxa of aquatic emergent invertebrates), and co-located sediments were collected from up to six areas along the Kalamazoo River. Four of the sampling grids were located within the submerged portions of the former Trowbridge impoundment. The remaining two sampling grids were located at an upstream reference location at Fort Custer State Recreation Area. Total concentrations of PCBs in sediments and smallmouth bass from the former Trowbridge impoundment ranged from 0.017 to 5.2 mg PCB/kg dw and from 3.5 to 10.2 mg PCB/kg ww, respectively. Concentrations of PCBs in all other aquatic-based biota from the former Trowbridge impoundment were less than the maximum concentration observed in smallmouth bass. Total concentrations of PCBs from the reference area ranged from 0.014 to 0.023 mg PCB/kg dw and from 0.4 to 1.4 mg PCB/kg ww, respectively. Finally, a comparison of congener patterns and total PCB concentrations will be presented and discussed across trophic levels.



Figure 1. Site Map - Trowbridge Grids

## INTRODUCTION

Due to selective volatilization, degradation, accumulation, sorption and metabolism (i.e., collectively termed "environmental weathering"), the relative concentrations of PCB congeners in a mixture or matrix change as a function of time. As a result of weathering, biological samples contain PCB congener patterns that are often statistically distinct from any Aroclor or mixture of Aroclors (Erickson, 1997; Schwartz et al., 1987; Stalling et al., 1987; Schwartz and Stalling, 1991). In KRAOC samples, the weathering of congeners as they pass through the various steps in the food chain results in congener mixtures in biota which are often highly variable (Blankenship et al., 2002). The purpose of this study was to evaluate differences in absolute concentrations of total PCBs and congener patterns for an aquatic food web.

## METHODS AND MATERIALS

Samples were collected from locations within the Trowbridge impoundment, Kalamazoo River, MI (Figure 1). Specifically, carp, sucker, and smallmouth bass were collected at the Trowbridge impoundment during Fall, 1999. Sediments, aquatic plants, benthic invertebrates, aquatic emergent invertebrates, crayfish, and tree swallow eggs were collected at Trowbridge grid 1 from 2000-2002. Mink livers and muskrat (whole body) were collected in winters of 1999/2000 and 2000/2001 from the Trowbridge impoundment and associated areas within the Kalamazoo River Area of Concern.

PCB congener patterns are presented for representative samples collected from the former Trowbridge impoundment within the Kalamazoo River Area of Concern (Figure 2). Data (expressed as a weight percent relative to total PCBs) are from Michigan State University's Aquatic Toxicology Laboratory. Concentrations of total PCBs in samples is also presented (Figure 3).

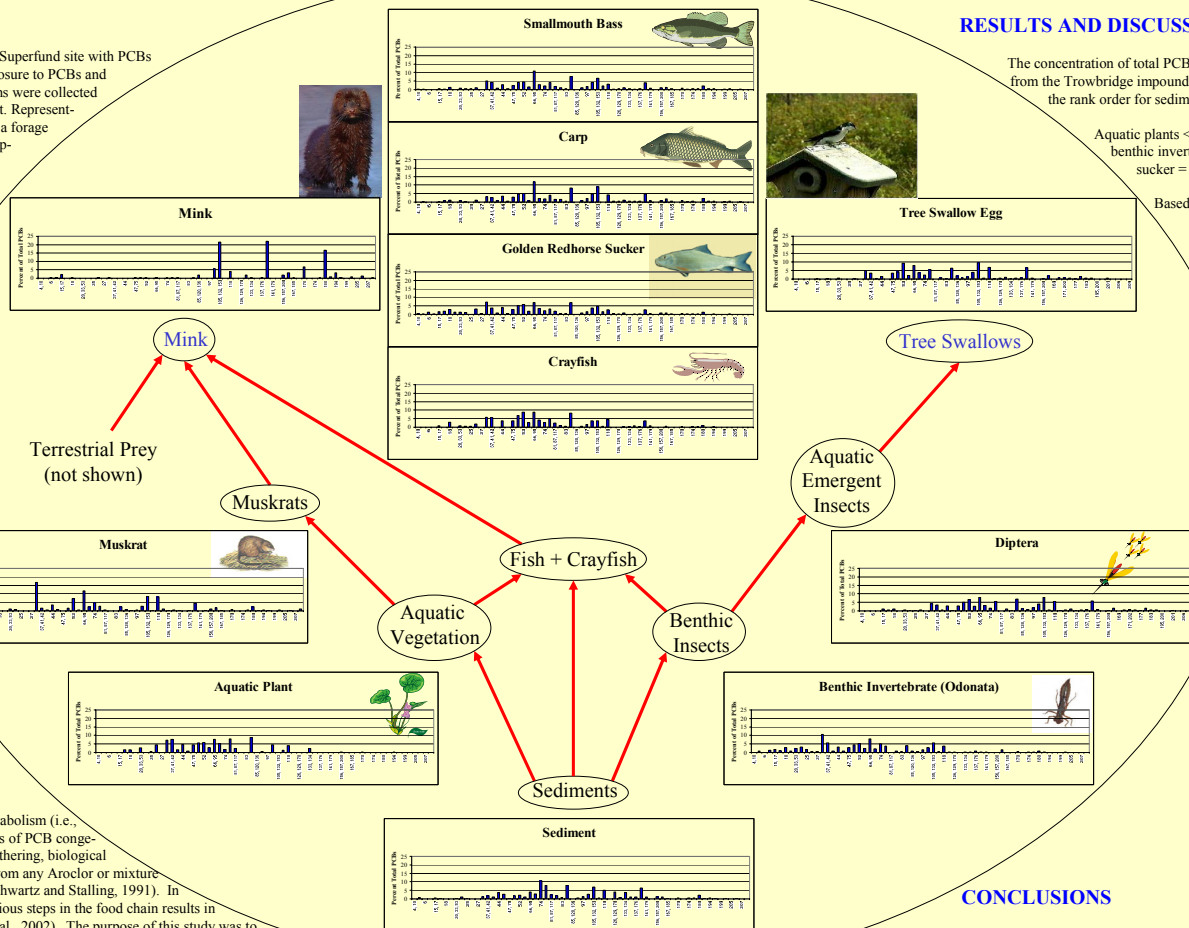


Figure 2. PCB Congener Patterns

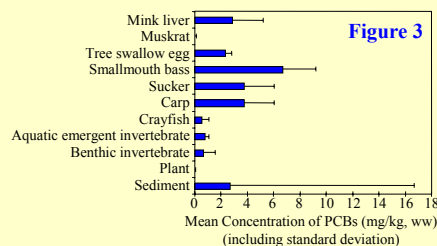


Figure 3

## RESULTS AND DISCUSSION

The concentration of total PCBs and the PCB congener patterns were evaluated for samples collected from the Trowbridge impoundment along the Kalamazoo River. Based on total PCB concentrations, the rank order for sediments and food web items are as follows:

Aquatic plants < muskrat < crayfish < aquatic emergent insects < benthic invertebrates < tree swallow eggs < sediments < mink liver < sucker = carp < smallmouth bass

Based on these concentration data and site-specific data on dietary composition of mink (based on stomach content analysis), site-specific dietary exposures have been estimated for mink (Pastva et al., 2002). If mink were only eating fish, one might expect that the concentrations of total PCBs in mink liver would be greater than that of fish. Taken together, these data indicate that mink eat a varied diet of fish, muskrat (and other small mammals), and crayfish. For tree swallows, the diet is predominantly composed of aquatic emergent invertebrates and terrestrial invertebrates (Neigh et al., 2002). Variations in total PCB concentrations and congener patterns among individual orders are the subject of a companion poster (PH 112).

As trophic levels increase, there is a general trend towards greater concentrations of total PCBs. Changes in congener patterns are relatively subtle among the lower levels of the aquatic-based food web in contrast to previous results on the terrestrial food web. Some notable observations are that in aquatic plants, the congener distribution is dominated by lighter chlorinated PCBs. However, there is a marked shift in congener patterns as one moves up the food web to mink.



## CONCLUSIONS

- Concentration of total PCBs generally increase with increasing trophic level as expected, except that concentrations of total PCBs in mink liver are less than that of fish, likely due to site-specific dietary composition of mink which includes crayfish, fish, and muskrat
- Congener patterns change dramatically as expected with enrichment of higher chlorinated congeners and diminution of lighter chlorinated congeners
- In mink liver, 60% of the total PCB concentration was based on only a few highly chlorinated congeners: 105, 132/153, 138/158, and 180

## LITERATURE CITED

Blankenship, A.L., Zwiernik, M.J., Park, C.S., Holom, R., Klemm, G., Bradley, P., Neigh, A., Kay, D.P., Kanan, K., and Giesy, J.P. 2002. Accumulation of PCBs and an evaluation of ecological risk for birds and other small mammals at the Kalamazoo River Superfund site, Michigan. Presented at the 2002 Annual Meeting of SETAC, Salt Lake City, UT.  
 Erickson, M.D. 1997. Analytical Chemistry of PCBs. Lewis Publishers, New York, 1,667.  
 Neigh, A., M.A. MacCarroll, M.J. Zwiernik, C.S. Park, P.W. Bradley, D. Kim, R. Adams, K.D. Strause, S. Pastva, and J.P. Giesy. PCB Dietary Exposure and Body Burden in Prairie Mink at the Kalamazoo River Superfund Site Presented at the 2002 Annual Meeting of SETAC, Salt Lake City, UT.  
 Pastva, S.D., Blankenship, A.L., Bradley, P., Holom, R., Jones, P., K. Kanan, Kay, D.P., Neigh, A., Park, C.S., Strause, K.D., Zwiernik, M.J., and Giesy, J.P. 2002. Assessment of risks of PCBs to mink (Mustela vison) at the Kalamazoo River, Michigan. Presented at the 2002 Annual Meeting of SETAC, Salt Lake City, UT.  
 Schwartz, T. R., D.L. Stalling, and C.L. Rice. 1987. Are Polychlorinated Biphenyl Residues Adequately Described by Aroclor Mixture Equivalents? Isomer-Specific Principal Component Analysis of Such Residues in Fish and Turtles. Environ Sci Technol 21: 72-76.  
 Schwartz, T. R. and D. L. Stalling. 1991. Chemometric Comparison of Polychlorinated Biphenyl Residues and Toxicologically Active Polychlorinated Biphenyl Congeners in the Eggs of Common Terns (Sterna Hirundo). Arch Environ Contam Toxicol 20: 183-199.  
 Stalling, D. L., T. R. Schwartz, W. J. Dani, and S. Wolf. 1987. Classification of Polychlorinated Biphenyl Residues: Isomers vs. Homologue Concentrations in Modeling Aroclors and Polychlorinated Biphenyl Residues. Anal Chem 59: 1833-1839.



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