PCB CONGENER PROFILES AND BIOMAGNIFICATION FACTORS OF MINK COLLECTED FROM THE KALAMAZOO RIVER, MICHIGAN SUPERFUND SITE

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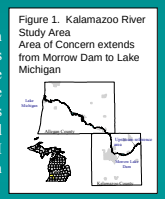
Abstract

Eighty miles of the Kalamazoo River (Figure 1), has been designated a Superfund site with PCBs as the primary contaminant. Mink are of special concern due to their trophic status and sensitivity to PCBs. There were no significant differences among sites for total PCBs or Total TEQs. Questions remained regarding why there would be no significant differences among sites for mink liver tissue, when there were significant differences in prey items. To address this issue, the mean congener profiles for mink liver tissue from FC and TB were compared. The profiles are visually similar to one another. The similarity is most likely a result of weathering and metabolism, making PCB "fingerprinting" at a top trophic level difficult. Site-specific BMFs were calculated for each prey item and an assumed dietary model. BMFs were greatest for mammals and least for fish. BMFs at FC were approximately 4x greater than those observed at KRAOC. The greater BMFs at the reference area resulted in PCB concentrations at FC that were similar to those from KRAOC.

Introduction

125 kilometers (80 miles) of the Kalamazoo River, located in southwestern Michigan, has been designated a Superfund site. It is referred to as the Kalamazoo River Area of Concern (KRAOC). The site extends from Morrow Dam in Kalamazoo County to Lake Michigan (Figure 1). The release of polychlorinated biphenyls (PCBs), resulted primarily from PCB-contaminated waste discharged from the recycling and processing of carbonless copy paper (CDM 1999). During the period of 1957 – 1971, the ink solvent used in carbonless copy paper contained PCBs, primarily Aroclor 1242 (Durfee et al. 1976; EPA report EPA 560/6-76-005). A lesser amount of PCBs may have also been added to inks and other additives, primarily Aroclor 1254 (Durfee et al. 1976).



The mink (*Mustela vison*) is a semi-aquatic carnivore common in the Great Lakes region and was chosen as a wildlife receptor for an ecological risk assessment previously conducted by the authors (Pastva, 2003, PhD dissertation, MSU). For this assessment, mink were trapped from the KRAOC and an upstream reference area called Fort Custer (FC). Total PCB and total toxic equivalency quotient (TEQ) concentrations for each site were calculated and the means compared (Pastva, 2003). There were no significant differences among sites for either total PCBs or TEQs (Figure 2 and Figure 3) . However, PCB concentrations in prey items were significantly greater at sites within the KRAOC. This purpose of this poster is to attempt to explain why mink from a lesser contaminated area can have similar PCB concentrations as mink collected from a more contaminated area.

Methods

Sample Collection

Wild mink were trapped throughout the KRAOC and FC during the winter of 2000-2001. Trapping was conducted by MSU personnel and by local trappers.

Congener-Specific PCB Analysis and TEQ Computation

PCBs were analyzed following methods described elsewhere (Khim et al, 2000, Arch Environ Contam, 39:360-368). Briefly, liver samples were soxhlet extracted, concentrated, and then purified by passage through an acidic silica column. PCBs were quantified using a gas chromatograph-electron capture detector. A standard containing 98 individual PCB congeners was used to resolve peaks and then summed for total PCB concentrations. Concentrations of TEQs in mink livers were calculated by multiplying the concentration of individual PCB congeners by its respective World Health Organization toxic equivalence factor (TEF) (Van den Berg et al. 1998, Environ Health Perspect 106:775-792) and then summed for the total TEQ.

Methods Continued

Congener Profile and BMF Calculations

For each individual mink, PCB congeners were divided by the total PCB amount to determine the relative contribution of individual PCB congeners to total PCB (expressed as a percentage). A mean was then calculated for each site. The mean percent contribution for each congener was then plotted for each site (Figure 4 and Figure 5).

BMF was calculated using the following formula:

$$\frac{\text{Total PCB in prey item/dietary model}}{\text{Total PCB in mink liver}}$$

Data for both individual prey items and three different dietary models are presented. The models offer a continuum of percent fish in the diet. The site-specific diet was obtained by analyzing gut contents of trapped mink.

Statistical Methods

Differences among sites for total PCBs and TEQs used a t-test (unequal variance) using Systat. Power was also determined. The congener profiles were only visually compared.

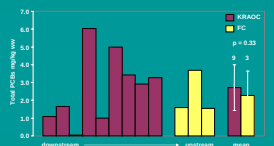


Figure 2. Total PCBs (mg/kg ww) in mink collected from KRAOC and FC

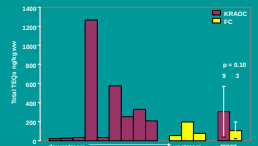


Figure 3. TEQ concentrations (pg/g ww) in mink collected from KRAOC and FC

Results and Discussion

- Difference in mean concentrations was small (0.44 mg PCB/kg) and not statistically significant.
- Statistical power (1- β) based on a type I error (α) of 0.05 and a type II error (β) of 0.2, was< 0.1.
- A 2.5-fold difference in the mean PCB concentrations would have shown a statistical difference between the means, even with the same sample size and variability.
  - The likely reason for the lack of a significant difference was due primarily to the small difference between the two populations, rather than to sample size or variance of the concentrations of PCBs.
- Congener profiles from FC (Figure 4) and KRAOC (Figure 5) appear to be similar.
- Congener profiles from mink liver quite different than Aroclor 1242 (Figure 6).
- Change in PCB profile is due to environmental weathering and metabolism.
  - This change in PCB congener profiles has implications for choosing toxicity reference values for ecological risk assessments.

Some explanations for why the profiles are similar for the two sites include:

- A combination of weathering and metabolism at this trophic level makes it difficult to "fingerprint" the profile.
- The PCB source is the same at FC and KRAOC
- Individuals caught at FC originated from KRAOC

Mink from FC ranged in age from juvenile (< 1 y) to 2 y (average 1.2 y). Therefore, it is possible that some of the mink had emigrated from other areas.

Results and Discussion Continued

Figure 4. Mean congener profile of mink liver tissue collected from FC. Data expressed as percent weight of total PCB.

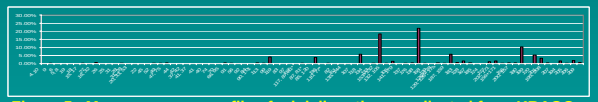


Figure 5. Mean congener profile of mink liver tissue collected from KRAOC. Data expressed as percent weight of total PCB.

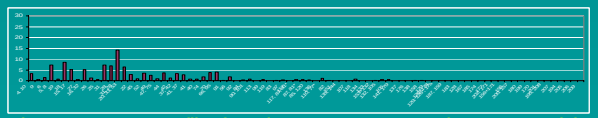


Figure 6. Congener profile of Aroclor 1242. Data expressed as percent weight of total PCB (from Frame, et. al. J. High Resol. Chromatogr., 19:657-668)

- BMFs for fish are least and mammals greatest
- FC has BMFs that are ~4x greater than KRAOC
- Mink from FC bioaccumulate PCBs more efficiently than their KRAOC counterparts.
- The greater BMFs at FC are the most likely reason why PCB concentrations in mink seem elevated.

Table 1. Mean BMFs for each dietary item and dietary model at each site

	Location	
Site-specific dietary item	**KRAOC**	**FC**
suckers	0.72	2.9
smallmouth bass	0.41	2.5
carp	0.72	2.0
forage fish	0.85	3.4
crayfish	5.1	40
muskrats	41	160
small mammals (non shrew)	25	110
Dietary Models		
Literature (85% fish, 9% crayfish, 6% mammals) Alexander, 1977	0.72	3.1
Equally opportunistic (33% fish, 33%mammals, 33%crayfish)	1.6	7.3
Site Specific (71% mammals, 14% fish, 15% crayfish)	3.6	15.8

Conclusions

- PCB congener profiles of mink liver tissue from FC and KRAOC appear similar
- PCB weathering and metabolism at this trophic level makes it difficult to "fingerprint"
- BMFs are ~4x greater at FC than at KRAOC.
- Individuals from less contaminated areas bioaccummulate PCBs more efficiently
- Significantly lower PCB concentrations within lower food chain organisms at a site do not always equate with significantly lower concentrations in higher trophic level organisms such as mink.

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