

CHARACTERIZATION OF POLYCHLORINATED DIBENZO-P-DIOXINS AND DIBENZOFURANS IN WHITE-TAILED DEER ALONG THE TITTABAWASSEE AND SAGINAW RIVERS NEAR MIDLAND MICHIGAN

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Introduction

Starting in the early to mid-1990s, polychlorinated dibenzo-p-dioxins (PCDDs) and furan (PCDFs) were input into the Tittabawassee River (TR) near Midland, MI, USA. This activity resulted in PCDD/PCDF concentrations that were 10- to 20-fold greater in soils downstream of Midland when compared to upstream concentrations. Ecological studies have shown that PCDD/PCDF concentrations in mink, small mammals, and birds collected downstream of Midland have concentrations that are greater than animals collected from upstream locations. Given these results, concerns have been expressed about the consumption of wildgame harvested downstream of Midland, Michigan. In response, wildgame studies were conducted in 2003 and 2007 that collected several game species, including the white-tailed deer (*Odocoileus virginianus*). This species is a herbivore and an important resident game species with an extensive home range that includes the floodplains of both the Tittabawassee and the Saginaw (SR) Rivers.

Objectives

- Examine the distribution and magnitude of PCDD and PCDF congeners in muscle and livers from white-tail deer within the Tittabawassee and Saginaw River floodplains;
- Evaluate sex-related differences in PCDD and PCDF concentrations in white-tailed deer;
- Examine percent contribution of PCDD and PCDF congeners to the total Toxic Equivalents concentrations in muscle and liver tissue upriver and downriver of Midland;
- Conduct a Principle Component Analysis to evaluate potential differences in PCDD/PCDF congener patterns in reference and study site locations.
- Evaluate the potential for PCDD/PCDF sequestration in the liver of deer downriver of Midland

Study Area

The study area is in central Michigan. The TR flows southeast through Midland and into the SR, and eventually into the Saginaw Bay of Lake Huron. Sampling areas include Sanford (reference area), Smith's Crossing (Smith's), Imerman Park Area (IPA), Shiawassee National Wildlife Refuge (SNWR), and Crow Island State Game Area (CISGA).

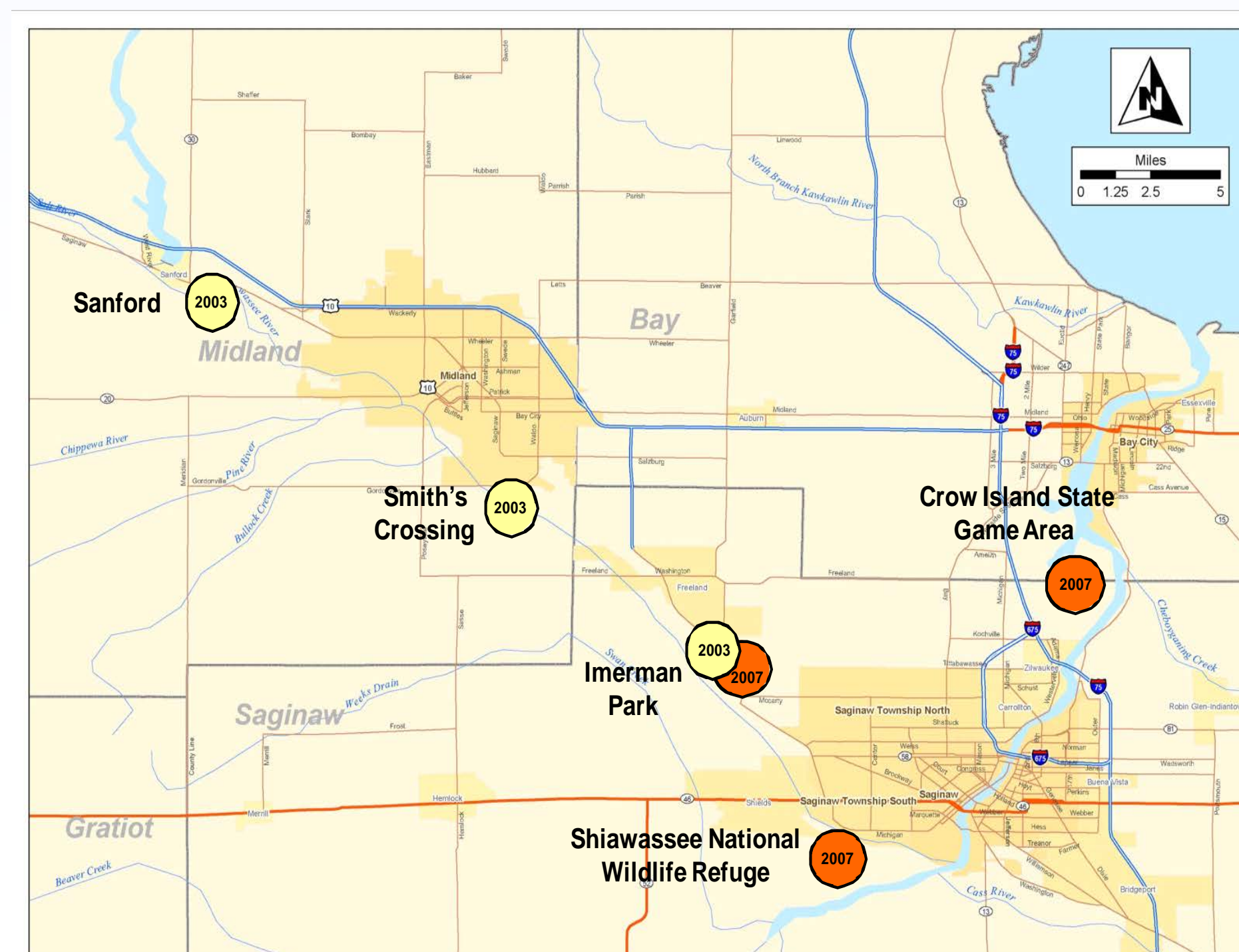


Figure 1: White-tailed deer sampling locations along the Tittabawassee and Saginaw Rivers. Sampling events are indicated by yellow (2003) and orange (2007) circles.

Methods

- Animals were collected from locations upstream and downstream of Midland (Figure 1) by use of traps and firearms in 2003 and 2007
- Whole animals were removed from collection locations (i.e., entrails removed at laboratory) to prevent contamination from other media such as floodplain soils
- Tissues commonly consumed by humans were removed from each animal and freeze-fractured (i.e., cryogenic homogenization)
- Tissue samples were analyzed for 17 PCDD/PCDFs. Toxic Equivalency (TEQ) concentrations were based on mammalian Toxic Equivalency factors (TEF) were compared between species, locations, and tissue types (van den Berg et al. 2006)
- Soil PCDD/PCDF data was taken from studies conducted by Michigan State University and from studies conducted by the MDEQ.

Results and Discussion

Deer Tissue Concentrations

- No statistically significant differences were observed between male and female deer were observed for $\sum\text{TEQ}_{\text{PCDD}}$, $\sum\text{TEQ}_{\text{PCDF}}$ or $\sum\text{TEQ}_{\text{Total}}$, thus sexes were pooled for all subsequent analyses.
- Deer muscle $\sum\text{TEQ}_{\text{Total}}$ concentrations at Sanford ranged from 0.034 to 0.16 ng/kg ww while concentrations in the study areas ranged up to 0.83 ng/kg ww (Table 1).
- Liver $\text{TEQ}_{\text{Total}}$ concentrations were statistically greater than corresponding muscle concentrations. Reference liver $\text{TEQ}_{\text{Total}}$ concentrations ranged from 0.20 to 1.04 ng/kg while at the down river sites concentrations ranged from 0.15 to 98 ng/kg ww.
- Deer muscle and liver $\text{TEQ}_{\text{Total}}$ concentrations at Smith, IPA and SNWR were statistically greater than the Reference and CISGA locations.
- PCDD/PCDF concentrations in deer muscle are comparable to meats analyzed in the U.S. Food and Drug Administration's Total Diet Study (www.cfsan.fda.gov/~lrd/dioxdal2.html). These concentrations range from 0.09 to 0.3 TEQ (ND = 1/2 DL, as consumed, i.e., cooked), considering a 50% cooking and trimming loss this range is similar to that identified in deer muscle.

Table 1. Mean concentrations of TEQs in white tailed deer collected from the upstream reference area and locations downstream of Midland, MI, USA.¹

	Reference ²	Smith	IPA	SNWR	CISGA
Deer Muscle ²	(n=13)	N=10	(n=10)	(n=11)	(n=11)
Lipid	2.54 A (2.12-2.96)	2.36 A (2.09-2.64)	2.36 A (1.74-2.98)	1.42 B (1.27-1.57)	1.23 B (1.01-1.46)
\sum PCDD	0.044 A (0.033-0.054)	0.048 A (0.038-0.059)	0.060 A (0.048-0.072)	0.11 B (0.10-0.11)	0.11 B (0.10-0.11)
\sum PCDF	0.014 A (0.011-0.017)	0.078 C (0.062-0.095)	0.25 D (0.14-0.36)	0.052 BC (0.041-0.062)	0.040 B (0.039-0.041)
Total	0.058 A (0.044-0.070)	0.13 B (0.10-0.15)	0.33 C (0.21-0.43)	0.16 B (0.15-0.18)	0.44 A (0.29-0.57)
Deer Liver	(n=13)	N=10	(n=10)	(n=11)	(n=11)
Lipid	3.35 A (2.91-3.78)	3.09 A (2.60-3.57)	3.58 A (2.97-4.18)	3.27 A (2.31-4.23)	2.66 A (1.52-3.80)
\sum PCDD	0.27 A (0.20-0.33)	0.61 B (0.39-0.83)	1.08 B (0.52-1.65)	0.19 A (0.13-0.26)	0.15 A (0.10-0.19)
\sum PCDF	0.18 A (0.13-0.23)	5.98 B (4.02-7.94)	26.6 C (7.89-45.2)	2.56 B (1.37-3.75)	0.27 A (0.14-0.39)
Total	0.45 A (0.35-0.56)	6.62 B (4.47-8.78)	27.8 C (8.51-47.1)	2.78 B (1.52-4.03)	0.44 A (0.29-0.57)

¹ Lipid values are given as percent lipid while TEQ concentrations are given as ng TEQ/kg, wet weight. All values are presented as geometric means and 95% confidence limits. Proxy value used to calculate TEQ was: Non-detects (ND) = 0.5x Detection Limit.

² Different letters indicate statistically significant differences (p<0.05) from Reference values

Percent Contribution of PCDD/PCDF Congeners to $\sum\text{TEQ}$

Muscle

- In the Reference location, 2,3,7-TCDD, 1,2,3,7,8-PeCDD, 2,3,7,8-TCDF, and 2,3,4,5,6-PeCDF in deer muscle accounted for approximately 30%, 35%, 2% and 7% of the $\text{TEQ}_{\text{Total}}$ in deer muscle, respectively
- At two downriver location, Smith's and IPA, TCDD, PeCDD, TCDF and PeCDF in deer muscle accounted for approximately 10%, 15%, 7% and 56% of the $\text{TEQ}_{\text{Total}}$, respectively.
- Due to the high number of non-detects in muscle tissue from SNWR and CISGA, the percent contribution of these congeners could be determined. However, PeCDF was measured in approximately 40% of the samples collected at SNWR.

Liver

- Percent contributions to $\text{TEQ}_{\text{Total}}$ in deer liver from the Reference location for TCDD, PeCDD, TCDF and PeCDF were approximately 16%, 34%, 1% and 24%, respectively
- For Smith, IPA and SNWR, percent contributions of TCDD, PeCDD, TCDF, and PeCDF TEQs to $\text{TEQ}_{\text{Total}}$ were approximately 2.5%, 3.4%, 3.5% and 74%, respectively.
- The percent contribution of TCDD, PeCDD, TCDF, and PeCDF TEQs in livers from deer from CISGA differed from that observed in tissues from the other downriver locations and were approximately 14%, 18%, 1.2% and 46%, respectively. Thus, while PCDFs still dominated the $\text{TEQ}_{\text{Total}}$, the percentage decreased in relation to PCDDs.

Results and Discussion

Principle Component Analysis

- For muscle, Factors 1, 2 and 3 accounted 36%, 29% and 16% of the explained variation, respectively. Significant loadings on Factor 1 were (values > 0.7) for Hexa-, Penta- and Tetra PCDDs while for Factor 2 it was Hexa-, Penta- and Tetra PCDFs (Figure 2).
- For liver, Factors 1, 2, and 3 accounted 36%, 34% and 22% of the explained variation, respectively. Significant loadings on Factor 1 were Hepta-, Hexa-, and Penta- PCDFs while for Factor 2 it was Hepta-, Hexa-, Penta- and Tetra PCDDs.
- For soil, Factors 1 and 2 accounted for 51% and 44% of the total explained variation respectively. Significant loadings on Factor 1 were Octa-, Hexa-, Penta- and Tetra- PCDDs while Factor 2 it was Hepta-, Hexa-, Penta- and Tetra- PCDFs. This distribution of loadings was similar to that observed for muscle loading factors.
- Overall, these results indicate that presence and magnitude of PCDFs in tissues and soils are the most important variable that account for differences between locations.

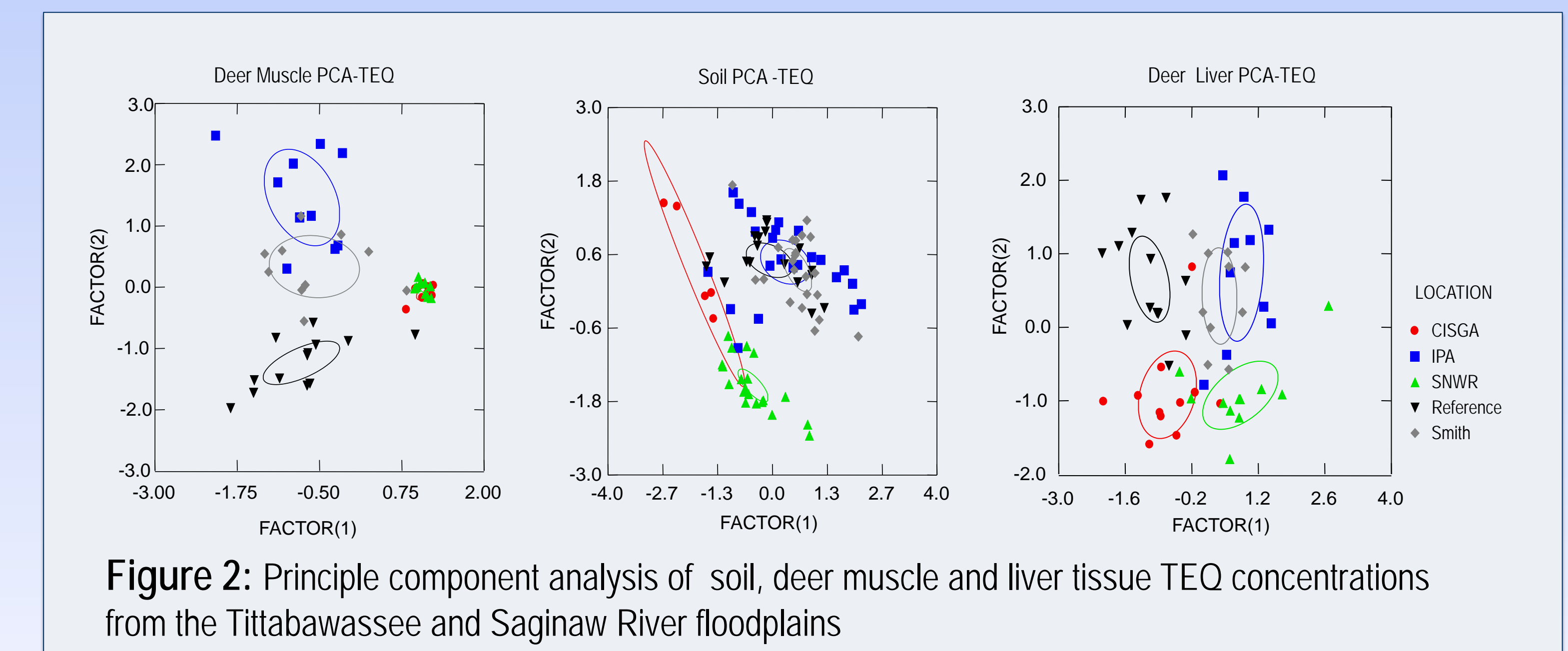


Figure 2: Principle component analysis of soil, deer muscle and liver tissue TEQ concentrations from the Tittabawassee and Saginaw River floodplains

Muscle and Liver Concentration Ratios

- The slopes of the regression models for both lipid normalized TEQ concentrations of TCDD and PeCDD slopes were negative. These results may indicate that the accumulation of these two congeners in deer liver is most likely dominated by partitioning and metabolism.
- In contrast, the slopes of both regression models for lipid normalized TCDF and PeCDF TEQ concentrations were positive and statistically greater than one. This may indicate possible partitioning and sequestration of TCDF and PeCDF in deer liver.
- The difference in the slope of the regression models for TCDF and PeCDF may be due to the metabolism of TCDF in the liver that has been observed in other mammalian and avian species.

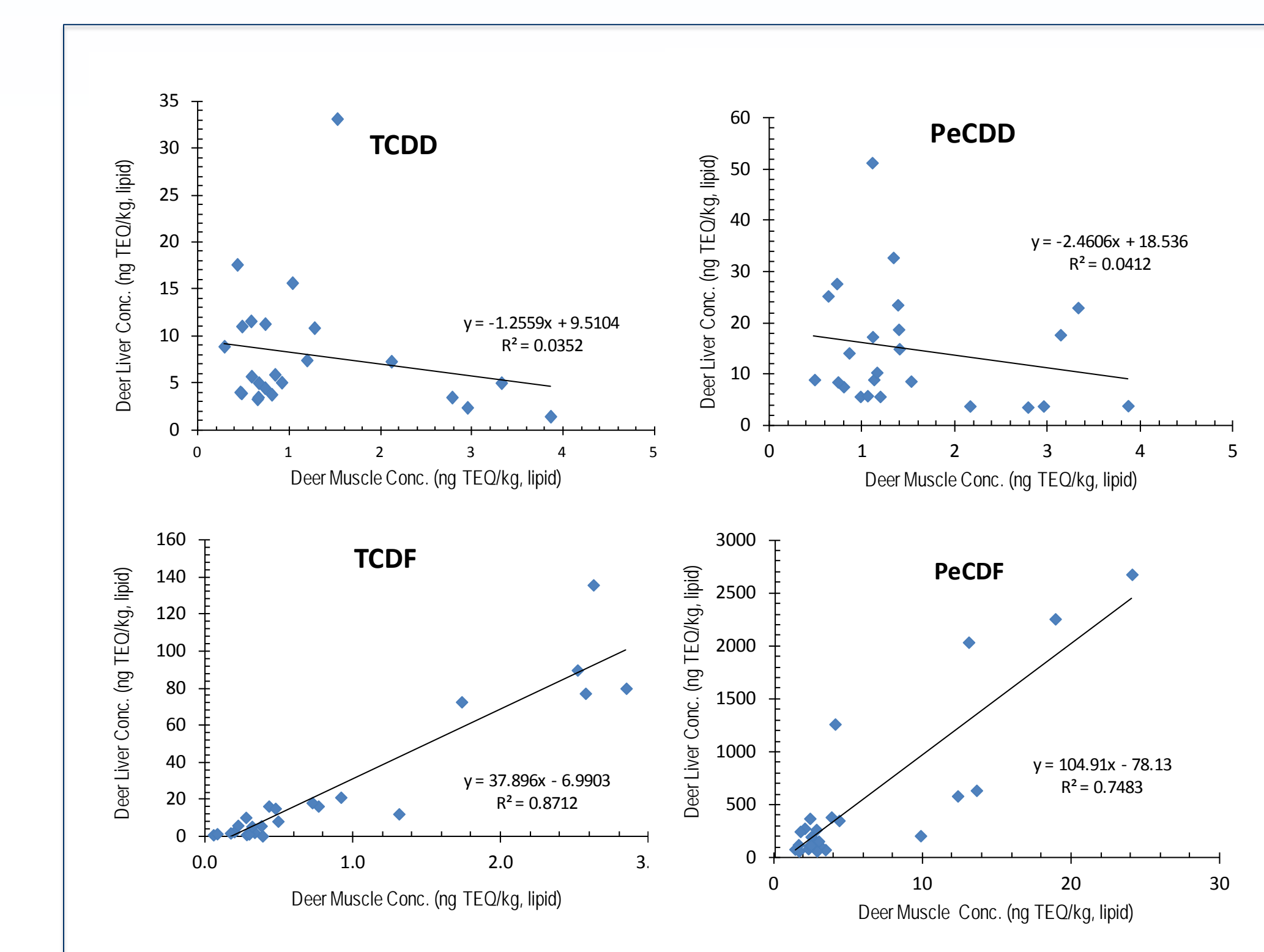


Figure 3: Comparison of lipid normalized PCDD/PCDF congener TEQ concentrations in muscle and liver of deer collected from the Tittabawassee and Saginaw River floodplains. Muscle non-detect data were excluded from regression analyses.

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