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Statistical Comparison of Residential Soil Concentrations of PCDDs, PCDFs, and PCBs from Two Communities in Michigan

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The University of Michigan dioxin exposure study was undertaken to address concerns that the industrial discharge of dioxin-like compounds in the Midland, MI area had resulted in contamination of soils in the Tittabawassee River floodplain and downwind of the incinerator. The study was designed in a rigorously statistical manner comprising soil measurements of 29 polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and polychlorinated biphenyls (PCBs) from 766 residential properties, selected probabilistically, in the Midland area and in Jackson and Calhoun Counties (Michigan) as a background comparison. A statistical comparison determined that the geometric mean toxic equivalent (TEQ) levels in samples from the target populations were statistically significantly above background. In addition, the probabilities of being above the 75th and 95th percentiles of background were also greater. Congener contributions to the TEQ were dominated by 2,3,4,7,8-PeCDF and 2,3,7,8-TCDF in the floodplain and by 2,3,7,8-TCDD in the incinerator plume. However, PCB 126 was the top congener contributing to the background TEQ. On the basis of statistical inference to the total population, it was estimated that about 36% of the properties in the floodplain and incinerator plume have at least one soil sample over the Michigan Department of Environmental Quality's soil direct contact criterion of 90 pg/g TEQ.

Introduction

The University of Michigan dioxin exposure study (UMDES) was undertaken in response to concerns among residents in the Midland, MI area that the historic discharge of polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) from the Dow Chemical Company facilities had resulted in soil contamination in the Tittabawassee River floodplain and in the City of Midland leading to an increase in residents' body burdens of these compounds. Dow Chemical has operated in Midland, MI since 1897 manufacturing a wide range of chemical products such as chlorine through the electrolysis of brine (since its founding (*1*)) and chlorinated phenols by reacting chlorine gas and phenol (from 1937 to 1982 (*2*)). Historically, wastes from these manufacturing operations were incinerated, resulting in aerial deposition in the City of Midland, discharged directly to the Tittabawassee River or discharged to waste ponds that were periodically breached during flooding events. To analyze the relationship between soil contamination and area residents' body burdens, UMDES was a large multidisciplinary undertaking including measurements of dioxin-like compounds not only in soil but also in household dust and serum from populations in Midland, Saginaw, and Bay Counties (Michigan) as the target areas and from Jackson and Calhoun Counties (Michigan) as a background comparison. To account for additional factors that might impact levels of dioxin-like compounds in serum, the study also comprised the administration of a questionnaire covering age, weight, and smoking habits; residential, occupational, and dietary histories; and recreational habits including hunting, fishing, and water activities. This paper details the soil measurements as the fundamental issue from an exposure perspective in the degree of contamination of the soil with dioxin-like compounds, a concern that has received international attention (*3*, *4*).

The establishment of the degree of soil contamination in the Midland/Saginaw area has been the subject of several studies. Hilscherova et al. (*5*) analyzed soil and sediment samples from about 100 locations along the Tittabawassee River finding that the toxic equivalent (TEQ), on the basis of 17 PCDDs and PCDFs using the 1998 World Health Organization (WHO) toxic equivalency factors (TEFs) (*6*) designated here as $TEQ_{DF\text{-}1998}$, ranged from 4 to 1980 pg/g, similar to concentrations at other industrially impacted sites (*7*). Yet, these were targeted samples and included both river sediment and floodplain soil and, as such, they may not be representative of the concentrations to which the population is exposed. The Agency for Toxic Substances and Disease Registry (ATSDR) completed a health consultation (*8*) looking at 22 residential properties of which 15 were determined to have TEQ levels above Michigan Department of Environmental Quality's (MDEQ) soil direct contact criterion of 90 pg/g TEQ. These values were higher than the mean $TEQ_{DF\text{-}1998}$ obtained by MDEQ from sampling 52 urban and rural locations in the lower peninsula of Michigan of 6.7 pg/g (*9*) comparable to the value of 7.0 pg/g obtained in the Denver Front Range Study (*10*) as well as to those obtained in other industrial countries (*11*). The health consultation concluded that, although there was evidence of soil contamination, the

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study was too limited to determine the extent or impact. These sampling efforts have emphasized contamination from the Tittabawassee River. In addition, there is evidence of soil contamination in the Midland City area resulting from incineration. MDEQ (*12*) summarized concentrations from about 67 soil samples from both residential and industrial areas in the Midland City area and found a range of 0−6100 pg/g TEQ-$_{1998}$ (the analytes varied), with a mean of 278 pg/g. Yet, the sampling in these studies, as in others (*3, 4*), was not randomly distributed or population-based and, as such, cannot define statistically valid concentrations for population exposure assessments.

To investigate the degree of soil contamination relative to background in a statistically rigorous manner, this study sampled 572 residential properties in Midland, Saginaw, and Bay Counties and another 194 residential properties in Jackson and Calhoun Counties selected as a comparison group because they represented similar demographics and economics as the target counties but lacked a known industrial source of dioxin-like compounds. Properties were selected using a two-stage area probability household sample design (*13*). The soil samples taken from the properties were analyzed for 29 dioxin-like compounds including not only the 17 PCDDs and the PCDFs listed by the WHO but also 12 nonortho substituted and mono-ortho substituted PCBs which display dioxin-like activity giving a more complete picture of the total TEQ of the soil and satisfying an identified need for more extensive information on dioxin-like PCB concentrations in soil, particularly background levels (*11*). Since the data were originally collected, the WHO has adjusted the TEFs for 14 of these compounds (1 PCDD, 3 PCDFs, and 10 PCBs) (*14*); thus, the impact of the modifications in TEFs needs to be evaluated. This study presents an extensive, comprehensive, and statistically rigorous set of residential measurements of soil concentrations of dioxin-like compounds, both in the vicinity of an industrial source and in the absence of one, that can be compared to data obtained in other locations to determine the impact of incinerators and chemical industries on the levels of these compounds in soil. This research also identifies a method for defining statistically significant concentrations above background for population-based studies.

Materials and Methods

Five areas, designated as "floodplain" (located in the 100-year Federal Emergency Management Agency (FEMA) floodplain of the Tittabawassee River or answering yes to the question, "Has your property ever been flooded by the Tittabawassee River?"), "near floodplain" (located in a census block that contains a portion of the 100-year FEMA floodplain), "plume" (located in the incinerator plume downwind of the Dow facility, determined as outlined in Goovaerts et al. (*15*)), "other Midland/Saginaw" (located in Midland, Saginaw, or Bay Counties but outside the above areas and any other river floodplain), and "Jackson/Calhoun" (located in Jackson or Calhoun Counties about 100 miles to the southwest of the Midland Area) were sampled (Figure S1). Within each area, the census blocks to be sampled were first selected randomly followed by the random selection of households within each census block.

The locations of soil-sampling stations at each residence are shown in Figure S2. Up to four stations were located around the perimeter of the house. If the interview indicated soil contact activities, samples were also taken at those locations (maximum of two), usually a vegetable garden or a flower garden. For properties located in the Tittabawassee River floodplain, one additional station, near the river, was sampled. Thus, there were a maximum of seven sampling stations at each residence: four house perimeter, two soil contact, one near river. Each sampling station was defined by laying out a 3 ft diameter ring. Three equally spaced cores were collected around the interior of the ring using custom-made, 2 in. inside diameter (I.D.), polycarbonate sample tubes driven into the ground using a slide hammer (AMS, American Falls, ID).

The collected soil cores were pushed out of the tubes using a Geotest core extruder (Model E-267, Evanston, IL). Vegetation, if present, was separated from the soil and was discarded. The cores from the house perimeter and the near river stations were then separated into two strata, 0−1 in. and 1−6 in., to distinguish between surface and subsurface contamination. The respective strata from the house perimeter and near river stations were then combined and homogenized. The cores from the soil contact stations were not separated into strata as it was assumed that soil in gardens is routinely turned over during planting. Ultimately, each residence yielded some or all of the following soil composites for analysis:

- House perimeter set 0−1 in. composite (HP 0−1 in.)
- House perimeter set 1−6 in. composite (HP 1−6 in.)
- Soil contact set 0−6 in. composite (garden)
- Near river set 0−1 in. composite (NR 0−1 in.)
- Near river set 1−6 in. composite (NR 1−6 in.)

The HP 0−1 in., garden, and NR soil composites were analyzed for all residences if collected. If any part of the property was in the floodplain, the HP 1−6 in. composite was also analyzed. Otherwise, this composite was analyzed only if the $TEQ_{DFP-1998}$ (where the subscript P refers to the 12 PCBs listed by the WHO (*6*) as having dioxin-like activity) of the HP 0−1 in. composite was >8 pg/g. This value represents the 75th percentile (*16*) of the background distribution for the lower peninsula of Michigan on the basis of MDEQ sampling (*9*). Soil samples were analyzed by high-resolution gas chromatography/high-resolution mass spectrometry (HRGC/HRMS) using Environmental Protection Agency (EPA) methods 8290 (*17*) and 1668 (*18*) by Vista Analytical Laboratory (El Dorado Hills, CA). If a concentration of a particular congener was below the limit of detection (LOD), the concentration was recorded as the LOD divided by $\sqrt{2}$ (*19*). About 4% of the soil samples were submitted as blind duplicates. The measured concentrations were adjusted using population-sampling weights to reflect the fact that the soil samples were obtained from a probabilistic subset of the areas' households.

Results and Discussion

A total of 766 residences were sampled in the five counties in Michigan with a total of 2081 samples submitted for analysis. Another 84 samples were submitted as duplicates with the average relative percent difference equaling 15%, at the low end of the range of typical errors (*14*). The arithmetic mean, median, 75th and 95th percentiles, and range of the population-weighted TEQs (in terms of $TEQ_{DFP-2005}$, $TEQ_{DF-2005}$, and $TEQ_{DFP-1998}$) are shown in Table 1. Often, only the mean and range are given (*3, 5*), but these statistics may not present an accurate picture of the distribution as the distributions may be highly skewed (Figure S3 shows a representative histogram) with a long tail at high concentrations resulting in mean values that are as high or even higher than the 75th percentile. The mean $TEQ_{DFP-1998}$ of the HP 0−1 in. soil samples from Jackson and Calhoun Counties of 8.3 pg/g is similar to the mean value computed for the residential properties in the Denver Front Range study (*10*) of 8.8 pg/g $TEQ_{DFP-1998}$ suggesting that Jackson and Calhoun Counties are a suitable background comparison group.

Rather than relying on a qualitative comparison to evaluate whether the soil concentrations were above background, this study compared the TEQs of the HP 0−1 in. soil

TABLE 1. Number of Samples, Arithmetic Mean TEQ, Standard Error (in Parentheses), Median, 75th and 95th Percentiles (in Italics), and Range for Each Soil Composite Type for the Five Areas (in pg/g)[a]

(A) $TEQ_{DFP-2005}$	HP 0–1 in.	HP 1–6 in.	garden	NR 0–1 in.	NR 1–6 in.
floodplain	$N = 203$ 56.5 (9.7) *11.4, 35.4, 223.1* 1.1–1881.4	$N = 198$ 56.2 (11.1) *10.3, 25.6, 214.4* 1.1–2164.7	$N = 132$ 50.7 (11.0) *9.1, 31.5, 218.4* 1.6–2199.3	$N = 191$ 238.5 (40.5) *14.5, 242.5, 1041.8* 1.1–7258.2	$N = 191$ 286.6 (52.3) *11.8, 298.5, 1242.3* 0.7–5356.8
plume	$N = 37$ 109.2 (31.0) *58.2, 111.9, 257.2* 6.3–745.5	$N = 36$ 101.1 (35.9) *54.2, 70.8, 251.1* 7.0–849.9	$N = 27$ 64.0 (15.1) *53.8, 59.7, 323.9* 19.6–323.9	NA	NA
near floodplain	$N = 164$ 52.0 (36.7) *3.9, 10.4, 102.9* 0.8–2299.8	$N = 75$ 64.7 (28.3) *11.2, 36.8, 306.3* 1.3–705.5	$N = 100$ 20.4 (4.9) *5.4, 11.6, 90.5* 0.7–547.0	NA	NA
other Midland/Saginaw	$N = 168$ 13.5 (2.0) *5.3, 13.2, 59.4* 0.8–157.7	$N = 87$ 114.3 (99.6) *11.1, 18.2, 64.6* 1.1–11219.1	$N = 101$ 9.8 (1.0) *4.2, 12.1, 37.3* 0.4–89.4	NA	NA
Jackson/Calhoun	$N = 194$ 6.9 (0.8) *3.6, 7.6, 22.6* 0.4–186.2	$N = 53$ 11.2 (1.1) *8.8, 13.2, 29.9* 0.9–35.3	$N = 124$ 4.9 (1.4) *2.5, 5.2, 14.5* 0.3–72.8	NA	NA

(B) $TEQ_{DF-2005}$	HP 0–1 in.	HP 1–6 in.	garden	NR 0–1 in.	NR 1–6 in.
floodplain	$N = 203$ 55.7 (9.7) *10.6, 35.1, 220.0* 1.0–1878.3	$N = 198$ 55.4 (11.1) *9.9, 24.4, 213.9* 1.0–2159.6	$N = 132$ 49.5 (11.0) *8.8, 31.2, 217.7* 1.0–2197.5	$N = 191$ 237.2 (40.4) *12.7, 240.5, 1038.3* 1.0–7242.0	$N = 191$ 285.0 (52.2) *11.2, 295.8, 1231.7* 0.7–5335.3
plume	$N = 37$ 103.3 (30.6) *57.6, 96.1, 245.7* 4.5–742.9	$N = 36$ 97.6 (35.7) *53.3, 69.9, 249.3* 6.8–847.5	$N = 27$ 60.1 (12.1) *53.0, 58.7, 260.9* 19.3–260.9	NA	NA
near floodplain	$N = 164$ 51.7 (36.7) *3.6, 10.1, 102.7* 0.8–2298.6	$N = 75$ 64.3 (28.3) *11.0, 32.7, 305.4* 1.1–704.8	$N = 100$ 20.1 (4.9) *5.0, 11.5, 90.3* 0.7–546.7	NA	NA
other Midland/Saginaw	$N = 168$ 12.8 (2.0) *4.5, 11.9, 56.7* 0.8–157.4	$N = 87$ 113.4 (99.5) *10.1, 17.2, 64.1* 1.0–11217.4	$N = 101$ 9.3 (1.0) *3.7, 11.1, 36.8* 0.4–88.8	NA	NA
Jackson/Calhoun	$N = 194$ 4.8 (0.5) *2.9, 5.7, 12.2* 0.3–64.1	$N = 53$ 8.1 (1.2) *6.8, 8.7, 22.2* 0.7–31.9	$N = 124$ 3.1 (0.3) *2.0, 4.0, 9.4* 0.2–18.5	NA	NA

(C) $TEQ_{DFP-1998}$	HP 0–1 in.	HP 1–6 in.	garden	NR 0–1 in.	NR 1–6 in.
floodplain	$N = 203$ 72.2 (12.7) *12.6, 41.6, 294.0* 1.2–2483.5	$N = 198$ 71.9 (14.6) *11.8, 30.8, 276.5* 1.2–2841.1	$N = 132$ 64.4 (14.5) *10.3, 40.4, 250.1* 1.8–2951.8	$N = 191$ 302.1 (52.1) *15.0, 283.3, 1329.6* 1.2–9351.0	$N = 191$ 363.4 (67.5) *12.6, 393.0, 1469.0* 0.8–6758.9
plume	$N = 37$ 121.2 (38.7) *59.2, 114.1, 270.7* 6.9–925.8	$N = 36$ 114.4 (45.5) *58.0, 71.4, 294.7* 7.1–1070.9	$N = 27$ 68.4 (17.1) *54.7, 62.5, 363.1* 19.9–363.1	NA	NA
near floodplain	$N = 164$ 67.8 (48.7) *4.3, 11.0, 135.3* 0.9–3055.9	$N = 75$ 83.2 (36.9) *12.1, 47.8, 403.7* 1.3–919.4	$N = 100$ 25.3 (6.5) *6.0, 12.6, 117.6* 0.8–730.3	NA	NA

TABLE 1. Continued

(C) $TEQ_{DFP-1998}$	HP 0−1 in.	HP 1−6 in.	garden	NR 0−1 in.	NR 1−6 in.
other Midland/Saginaw	N = 168 15.6 (2.4) *5.5, 14.6, 74.3* 0.9−205.0	N = 87 152.9 (135.8) *12.9, 22.5, 83.7* 1.1−15308.7	N = 101 10.7 (1.1) *4.5, 12.6, 37.9* 0.4−115.9	NA	NA
Jackson/Calhoun	N = 194 8.3 (1.3) *3.6, 8.5, 23.8* 0.4−329.7	N = 53 13.2 (1.4) *10.3, 14.5, 35.5* 1.0−45.1	N = 124 5.5 (1.6) *2.7, 5.7, 14.8* 0.3−87.9	NA	NA

[a] $TEQ_{DFP-2005}$ is calculated using the 29 PCDD, PCDF, and PCB congeners specified by the WHO and the 2005 TEFs (*14*); TEQ $_{DF-2005}$ is calculated using the 17 PCDD and PCDF congeners specified by the WHO and the 2005 TEFs (*14*); TEQ $_{DFP-1998}$ is calculated using the 29 PCDD, PCDF, and PCB congeners specified by the WHO and the 1998 TEFs (*6*). HP = house perimeter; NA = not applicable; NR = near river.

TABLE 2. Statistics for Pair-Wise Comparisons of $TEQ_{DFP-2005}$ for HP 0−1 Inch Soil Composites[d]

area	geometric mean $TEQ_{DFP-2005}$ (pg/g)	percent above 7.6 pg/g[a]	percent above 22.6 pg/g[b]
floodplain	15.7	68	31
plume	73	98	97
near floodplain	5.9	33	14
other M/S	6.6	41	15
Jackson/Calhoun	3.5	24[c]	5

[a] $TEQ_{DFP-2005}$ = 7.6 pg/g is the 75th percentile of the Jackson/Calhoun distribution. [b] $TEQ_{DFP-2005}$ = 22.6 pg/g is the 95th percentile of the Jackson/Calhoun distribution. [c] The 75th percentile for Jackson/Calhoun is actually 7.5800 pg/g, which was rounded to 7.6 pg/g for the purposes of the Wald chi-square test. Because of the multiple values between 7.5800 and 7.600, actually 24.07% is above 7.600 pg/g in Jackson/Calhoun. [d] HP = house perimeter; J/C = Jackson/Calhoun; M/S = Midland Saginaw.

samples among the five areas using a *t* test (SAS PROC Surveyreg, SAS Institute, Cary, NC) for the geometric mean and a Wald chi-square test (SAS PROC Surveylogistic, SAS Institute, Cary, NC) using the 75th ($TEQ_{DFP-2005}$ = 7.6 pg/g) and 95th ($TEQ_{DFP-2005}$ = 22.6 pg/g) percentiles of the Jackson/Calhoun samples as cutpoints (Table 2). Because of their skewness (Figure S3), the data were log-transformed, which resulted in a normal distribution, an assumption underlying the *t* test. The *p*-values presented in Table 3 indicate that the HP 0−1 in. samples from all the target areas have statistically significantly higher geometric means than the corresponding samples from Jackson and Calhoun Counties indicating statistically significant concentrations of dioxin-like chemicals above background levels. In addition, the probability that the $TEQ_{DFP-2005}$ of the HP 0−1 in. sample is above the cutpoints is greater in the target areas (with the exception of the probability of being above 7.6 pg/g in the near floodplain) than in Jackson/Calhoun. Furthermore, the comparison between the plume and the floodplain HP 0−1 in. samples shows that the $TEQ_{DFP-2005}$ in the plume has a higher geometric mean as well as a greater probability of being above the cutpoints than in the floodplain. The differences in the geometric mean and probabilities of being above the cutpoints between the near floodplain and the other Midland/Saginaw samples are not statistically significant. On the basis of previous sampling campaigns, it was expected that the plume and the floodplain areas had higher levels than background; this study indicates that the difference is statistically significant and is not based on convenience or targeted sampling. The higher levels in the near floodplain and other Midland/Saginaw samples were unanticipated and suggest either the movement of contaminated soils to those areas or the presence of additional sources other than the Tittabawassee River or the Dow incinerator.

Because of the statistical sampling design, these results could be used to develop inferences for households in these areas. Perhaps of greatest concern to the area residents is the possibility of contamination on their property. Table 4 shows the percentages of properties estimated to have at least one soil sample above MDEQ's soil direct contact criterion of TEQ = 90 pg/g or above EPA's screening level of TEQ = 1000 pg/g. Over one-third of the properties in the floodplain and the plume (36.5% and 35.8%, respectively) were estimated to have a soil sample with a TEQ over 90 pg/g. Furthermore, an appreciable number of properties outside the floodplain and the plume, 9.7% for the near floodplain and 1.7% for other Midland/Saginaw, were estimated to have a soil sample that exceeds 90 pg/g. Even 0.3% of the properties in Jackson/Calhoun, the background comparison area, were estimated to have a soil sample over MDEQ's criterion.

In addition to the data for the HP 0−1 in. composites, Table 1 presents the mean and median $TEQ_{DFP-2005}$ values for the other types of soil composites. The NR composites for the floodplain population, both the 0−1 in. and the 1−6 in., have decidedly higher mean TEQ values than the HP composites; yet, they have similar medians. This observation indicates that the more heavily contaminated soil is concentrated adjacent to the river rather than around the exterior of the houses; it also suggests that the distribution of the contamination is heterogeneous. The high mean $TEQ_{DFP-2005}$ for the HP 1−6 in. composites for the other Midland/Saginaw samples of 114.3 pg/g is primarily due to an outlier as the maximum value for this composite type is 11 219 pg/g, almost 2 orders of magnitude higher than the maximum value of the HP 0−1 in. composites for this area. The mean $TEQ_{DFP-2005}$ of the garden composites in the floodplain is 50.7 pg/g, similar to the mean TEQs of the HP composites (56.5 pg/g for HP 0−1 in. and 56.2 pg/g for HP 1−6 in.), suggesting that the gardens are generally constructed of soil from around the house rather than from soil adjacent to the river. In contrast, the mean TEQ of the garden composites from the plume is 64.0 pg/g, considerably lower than that of the plume's HP composites of about 101−109 pg/g, yet the median values are again similar. This discrepancy may be due to the mixing in of less contaminated soil in the garden, either commercial soil or underlying soil.

TABLE 3. p-Values for Pair-Wise Comparisons of $TEQ_{DFP-2005}$ Among the HP 0−1 Inch Soil Composites from the Five Areas[a]

area		plume	near floodplain	other M/S	Jackson/ Calhoun
floodplain	geometric mean	<0.0001−	<0.0001+	<0.0001+	<0.0001+
	odds > 7.6 pg/g	0.0015−	<0.0001+	<0.0001+	<0.0001+
	odds > 22.6 pg/g	<0.0001−	0.0016+	0.0043+	<0.0001+
plume	geometric mean		<0.0001+	<0.0001+	<0.0001+
	odds > 7.6 pg/g		<0.0001+	<0.0001+	<0.0001+
	odds > 22.6 pg/g		<0.0001+	<0.0001+	<0.0001+
near FP	geometric mean			0.6162−	0.0098+
	odds > 7.6 pg/g			0.2702−	0.1378+
	odds > 22.6 pg/g			0.8480−	0.0112+
other M/S	geometric mean				<0.0001+
	odds > 7.6 pg/g				0.0018+
	odds > 22.6 pg/g				0.0075+

[a] HP = house perimeter; FP = floodplain; M/S = Midland/Saginaw. Geometric means were compared using a *t* test, and the results are given in the first row for each area. The probabilities of being above 7.6 pg/g [Jackson/Calhoun's 75th percentile] or 22.6 pg/g [Jackson/Calhoun's 95th percentile] were compared using a Wald chi test, and the results are given in the second and third rows, respectively, for each area. *p*-values of <|0.05| indicate statistical significance. "+" after the *p*-value indicates that the samples from the area listed in the row have a higher geometric mean or a higher probability of being above the cutpoints than the samples from the area listed in the column. "−" after the *p*-value indicates that the samples from the area listed in the row have a lower mean or a lower probability of being above the cutpoint than the samples from the area listed in the column.

TABLE 4. Estimate of Percentages of Properties with at Least One Soil Composite[a] Over TEQ = 90 pg/g or Over TEQ = 1000 pg/g

	$TEQ_{DFP-2005}$ (pg/g)		$TEQ_{DF-2005}$ (pg/g)		$TEQ_{DFP-1998}$ (pg/g)	
area	over 90	over 1000	over 90	over 1000	over 90	over 1000
floodplain	36.5	7.0	36.5	7.0	38.0	10.7
plume	35.8	0.0	35.8	0.0	38.1	4.2
near floodplain	9.7	1.6	9.7	1.6	10.8	1.6
other M/S	1.7	0.4	1.7	0.4	2.4	0.4
Jackson/Calhoun	0.3	0.0	0.0	0.0	1.8	0.0

[a] The soil composite may be any of the five types of composites. $TEQ_{DFP-2005}$ is calculated using the 29 PCDD, PCDF, and PCB congeners specified by the WHO and the 2005 TEFs (*14*); $TEQ_{DF-2005}$ is calculated using the 17 PCDD and PCDF congeners specified by the WHO and the 2005 TEFs (*14*); $TEQ_{DFP-1998}$ is calculated using the 29 PCDD, PCDF, and PCB congeners specified by the WHO and the 1998 TEFs (*6*). M/S = Midland/Saginaw.

The percent contributions to the $TEQ_{DFP-2005}$ of the 29 individual congeners for the HP 0−1 in. composites are shown in Figure 1 with the arithmetic mean, standard error, median, and LOD for the individual congener concentrations (unweighted by TEFs) given in Table S1. Figure 1 shows three major patterns. In the floodplain composites, the majority of the $TEQ_{DFP-2005}$ (on the basis of the arithmetic mean) is attributable to 2,3,4,7,8-PeCDF, 2,3,7,8-TCDF, 2,3,7,8-TCDD, 1,2,3,7,8-PeCDD, and 1,2,3,4,7,8-HxCDF in that order (the same order occurs using $TEQ_{DFP-1998}$). This ranking differs from that in Hilscherova et al. (*5*) in which the top five congeners in the downstream soil samples were ($TEQ_{DF-1998}$): 2,3,4,7,8-PeCDF, 1,2,3,7,8-PeCDF, 2,3,7,8-TCDF, 1,2,3,4,7,8-HxCDF, and 1,2,3,4,6,7,8-HpCDF with no dioxins making the list. The discrepancy may be attributable to the difference in sampling strategies employed in the two studies. Hilscherova et al. (*5*) analyzed seven downstream soil samples taken from known locations of contamination (minimum $TEQ_{DF-1998}$ measured was 250 pg/g). This study analyzed 203 composites taken from a random sampling of properties located in the Tittabawassee River floodplain. Even though located in the floodplain, the specific soil sample locations may not have been flooded with contaminated water. Thus, the pattern observed here represents more of a floodplain average than a pattern symptomatic of the floodwater contamination. In contrast, the TEQ in the plume is dominated by 2,3,7,8-TCDD with a mean contribution of 43%. The next highest contributor is 1,2,3,7,8-PeCDD with a mean contribution of about 19%. The dominance of the pattern in the plume by these two congeners is at the high end of the range obtained in the targeted sampling performed by MDEQ in which these two congeners together comprised about 35−65% of the $TEQ_{DF-1998}$ (*20*).

The near floodplain and other Midland/Saginaw samples exhibit a somewhat similar pattern to that in the floodplain but with the important variation that the contributions from 2,3,4,7,8-PeCDF and 2,3,7,8-TCDF have diminished and those from 2,3,7,8-TCDD and 1,2,3,7,8-PeCDD have increased. In fact, the congener pattern in the other Midland/Saginaw samples has some features of the pattern in Jackson/Calhoun with larger contributions from 1,2,3,4,6,7,8-HpCDD and PCB 126. Thus, the patterns in these samples seem to be a mixture of the floodplain pattern and a background pattern represented by Jackson/Calhoun. The fact that these areas' samples have elements of the floodplain pattern suggests that some properties in these areas may have been flooded, although they were located outside the 100-year FEMA floodplain of the Tittabawassee River and were not known to have been flooded or that contaminated soil had been moved to these areas.

The top five congeners contributing to the $TEQ_{DFP-2005}$ in the Jackson/Calhoun samples are PCB 126 (16.5%) followed by slightly lower contributions of 1,2,3,7,8-PeCDD, 1,2,3,4,6,7,8-HpCDD, and 2,3,4,7,8-PeCDF and again by a slightly lower contribution of 2,3,7,8-TCDD. Similarly, the Denver Front Range study (*10*) found that PCB 126 was usually the biggest contributor to the $TEQ_{DFP-1998}$ in residential soils, accounting for an average of 18.2% commensurate with 1,2,3,7,8-PeCDD (at 18.5%), followed by 1,2,3,4,6,7,8-HpCDD, 2,3,4,7,8-PeCDF, and 2,3,7,8-TCDD. Since the highest mean

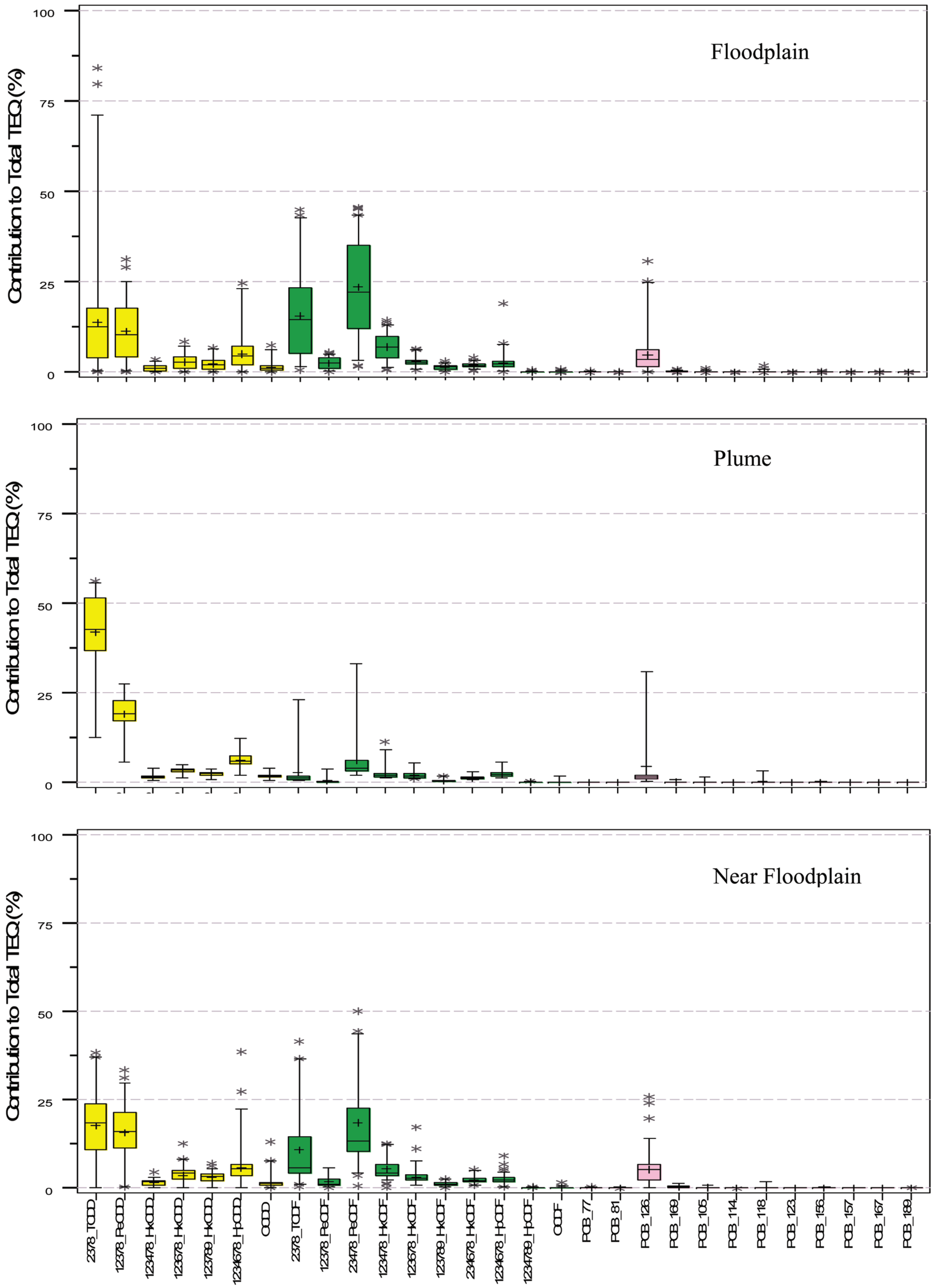

FIGURE 1

contributor to the TEQ is PCB 126, this nonortho PCB, at least, needs to be characterized in examining background TEQs. In this study and in the Denver Front Range Study, the additional contribution of other PCBs is small, 1.9% and 4.3%,

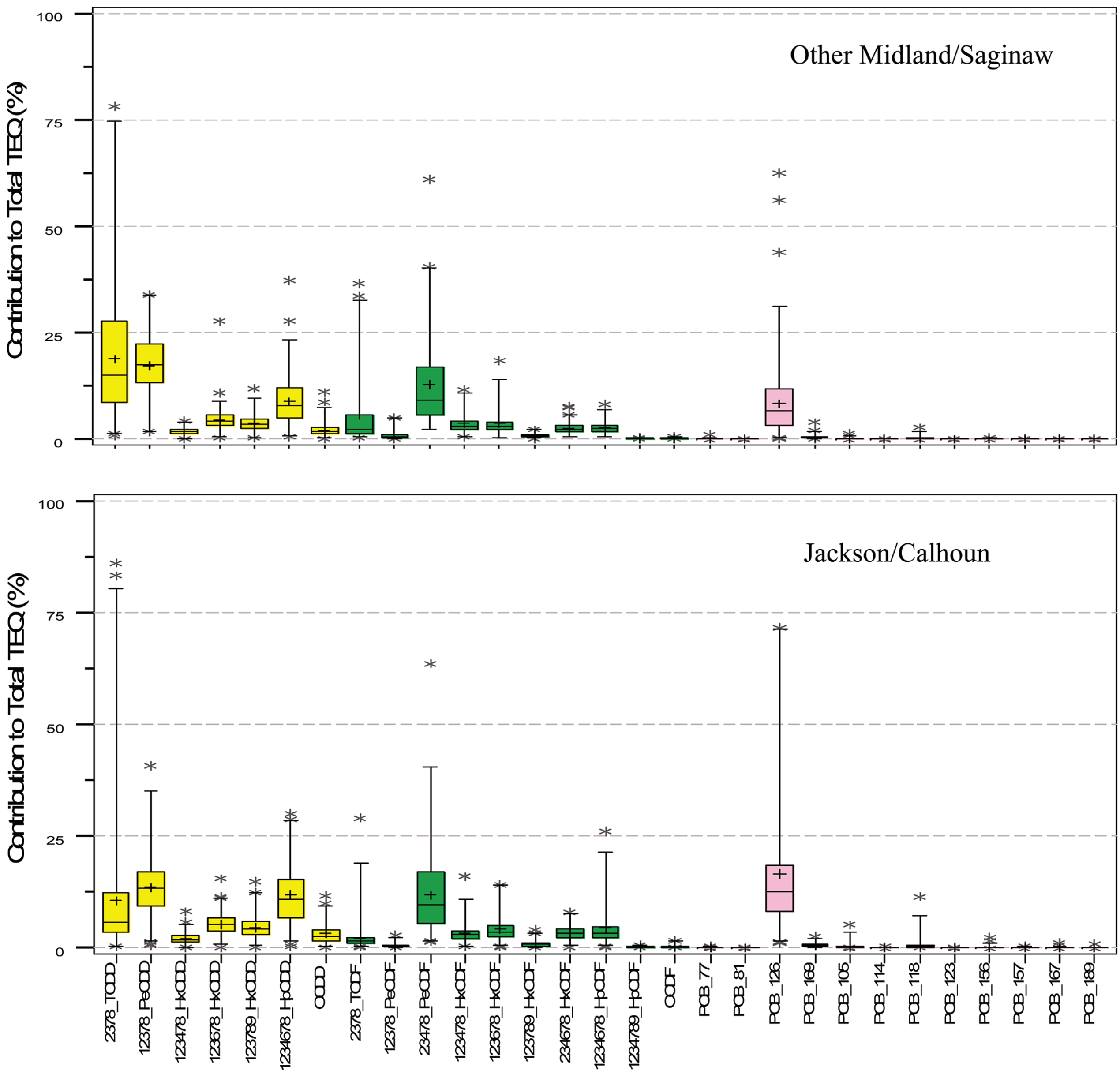

FIGURE 1. Contribution to $TEQ_{DFP\text{-}2005}$ of the individual congeners for the HP 0−1 in. samples. The plus sign indicates the arithmetic mean. The horizontal line across the box indicates the 50th percentile (median), the lower and upper margins of the box indicate the 25th percentile and 75th percentile, respectively; the upper ticked line extends to the 99th percentile, and the lower ticked line extends to the 1st percentile. The stars show the values above the 99th percentile and below the 1st percentile.

respectively. Yet in other situations, the contribution may be appreciable as in the study by Pirard et al. (*4*) in rural France where the mono-ortho dioxin-like PCBs contributed an average of 10.8% to the background $TEQ_{DFP\text{-}1998}$.

To evaluate the impact of the multiple conventions for calculating the TEQ, the mean and median TEQ were calculated as $TEQ_{DFP\text{-}2005}$, $TEQ_{DF\text{-}2005}$, and $TEQ_{DFP\text{-}1998}$ (Table 1). (The individual congener concentrations provided in Table S1 allow the calculation of the TEQ using additional conventions, for example, on the basis of the subset of 21 congeners utilized in the National Health and Nutrition Examination Survey (NHANES) (*21*).) In the floodplain, the difference in mean TEQ using the 1998 TEFs (*6*) versus the 2005 TEFs (*14*), across all soil composite types, is a reduction of about 21%, whereas in the plume and in Jackson/Calhoun, the reduction is 10% and 14%, respectively. The difference is attributable to the different congener patterns (Figure 1). In the floodplain, the TEQ is dominated by the PCDFs. The TEFs for three PCDFs changed: 1,2,3,7,8-PeCDF, from 0.05 to 0.03; 2,3,4,7,8-PeCDF, from 0.5 to 0.3; and OCDF, from 0.0001 to 0.0003 (*14*). Since only 2,3,4,7,8-PeCDF figures prominently in the floodplain congener pattern, the reduction in TEQ for these samples is primarily due to the decrease of 40% in this compound's TEF.

In contrast, the mean contribution to the TEQ in the plume is greater for the PCDDs than for the PCDFs. The only PCDD whose TEF changed is OCDD, whose value increased from 0.0001 to 0.0003, yet this compound has a mean contribution of only 1.8% to the TEQ in the plume. In Jackson/Calhoun, of the top five congeners, the TEF only changed for 2,3,4,7,8-PeCDF. Thus, the decreases in the TEQ for the plume and Jackson/Calhoun also stem from the reduction in the TEF for 2,3,4,7,8-PeCDF. Despite the changes in the TEFs for 10 of the 12 PCBs, the impact is minimal here because the TEF for the dominant PCB, PCB 126, did not change. Because of the minor contribution of the PCBs to the TEQ in the samples from Midland and Saginaw Counties, the $TEQ_{DF\text{-}2005}$ is only a bit lower than the $TEQ_{DFP\text{-}2005}$, less than 5%. The only samples where the inclusion of the PCBs make an appreciable difference is in Jackson/Calhoun: a 30.4% decrease in the mean for the HP 0−1 in. composites if the PCBs are not included.

Perhaps of greater importance is the impact of the various ways of calculating the TEQ on the percentage of properties over 90 pg/g and over 1000 pg/g. The percentage of properties in the floodplain and plume over 90 pg/g dropped roughly two percentage points and the percentage over 1000 pg/g dropped about four percentage points with the recalculation of the TEQ using the 2005 TEFs (Table 4) implying that hundreds of properties that might have qualified for remedial action may no longer do so. The percentages did not change with the recalculation of the TEQs without the PCBs except in the case of Jackson/Calhoun because only in these samples was a PCB among the top contributors to the TEQ.

Many studies of soil contamination rely on a qualitative evaluation of whether a particular area is contaminated. This study employed a probabilistic sampling design that allowed for a statistical determination as to whether the soil concentrations in the target areas were above background. On the basis of this analysis, it was determined that the geometric mean soil concentrations in all four target areas in Midland, Saginaw, and Bay Counties, not just the Tittabawassee River floodplain and the incinerator plume in the City of Midland, were elevated relative to background. In addition, the probabilities of a soil sample having a concentration above the 75th and 95th percentiles of background were statistically greater in these areas. Furthermore, the data presented here showed the importance of measuring PCB 126 in determining the total TEQ of the background as this compound contributed about 16.5% to the overall TEQ (Figure 1) in the comparison community of Jackson and Calhoun Counties. This study also showed that the reevaluation of the TEFs by the WHO was not inconsequential as the mean TEQ in the floodplain, for example, decreased by 21% resulting in a substantial decrease in the number of properties that might qualify for remedial action.

With the establishment of statistically significant elevated concentrations of dioxin-like compounds in the soil in the Midland area, the subsequent issue is whether exposure of the area residents to this contamination has resulted in elevated levels of these compounds in the population's serum. UMDES included the collection of serum from the residents whose soil was sampled. The statistical analysis of the relationship between the concentrations of these compounds in soil and in the area residents' serum is presented in Garabrant et al. (*13*).

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Supporting Information Available

The Supporting Information contains a map of the study area (Figure S1), a diagram of sampling locations at each residence (Figure S2), an example histogram of the measured $TEQ_{DFP\text{-}2005}$ showing the skewness of the distribution (Figure S3), and a table giving the individual concentrations of the 29 congeners (Table S1). This information is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) Whitehead, D. *The Dow Story*; McGraw-Hill, New York, 1968.

(2) Collins, J. J.; Bodner, K. M.; Wilken, M.; Haidar, S.; Burns, C. J.; Budinsky, R. A.; Martin, G. D.; Carson, M. L.; Rowlands, J. C. Serum concentrations of chlorinated dibenzo-*p*-dioxins and dibenzofurans among former Michigan trichlorophenol and pentachlorophenol workers. *J. Exposure Sci. Environ. Epidemiol.* **2007**, *17*, 541–548.

(3) Schuhmacher, M.; Nadal, M.; Domingo, J. L. Levels of PCDD/Fs, PCBs and PCNs in soils and vegetation in an area with chemical and petrochemical industries. *Environ. Sci. Technol.* **2004**, *38*, 1960–1969.

(4) Pirard, C.; Eppe, G.; Massart, A.-C.; Fierens, S.; De Pauw, E.; Focant, J.-F. Environmental and human impact of an old-timer incinerator in terms of dioxin and PCB level: A case study. *Environ. Sci. Technol.* **2005**, *39*, 4721–4728.

(5) Hilscherova, K.; Kannan, K.; Haruhiko, N.; Nobuyasu, H.; Nobuyoshi, Y.; Bradley, P. W.; McCabe, J. M.; Taylor, A. B.; Giesy, J. P. Polychlorinated dibenzo-*p*-dioxin and dibenzofuran concentration profiles in sediments and flood-plain soils of the Tittabawassee River, Michigan. *Environ. Sci. Technol.* **2003**, *37*, 468–474.

(6) Van den Berg, M.; Birnbaum, L.; Bosveld, A. T. C.; Brunstrom, B.; Cook, P.; Feeley, M.; Giesy, J. P.; Hanberg, A.; Hasegawa, R.; Kennedy, S. W.; Kubiak, T.; Larsen, J. C.; van Leeuwen, F. X. R.; Liem, A. K. D.; Nolt, C.; Peterson, R. E.; Poellinger, L.; Safe, S.; Schrenk, D.; Tillitt, D.; Tysklind, M.; Younes, M.; Warn, F.; Zacharewski, T. Toxic equivalency factors (TEFs) for PCBs, PCDDs, PCDFs for humans and wildlife. *Environ. Health Perspect.* **1998**, *106*, 775–792.

(7) Wenning, R. J.; Harris, M. A.; Ungs, M. J.; Paustenbach, D. J.; Bedbury, H. Chemometric comparisons of polychlorinated dibenzo-*p*-dioxin and dibenzofuran residues in surficial sediments from Newark Bay, New Jersey and other industrialized waterways. *Arch. Environ. Contam. Toxicol.* **1992**, *22*, 397–413.

(8) A Pilot Exposure Investigation: Dioxin Exposure in Adults Living in the Tittabawassee River Flood Plain, Saginaw County, Michigan; U.S. Department of Health and Human Services, Agency for Toxic Substances and Disease Registry, Atlanta, GA, 2005.

(9) Michigan Department of Environmental Quality. http://www.deq.state.mi.us/documents/deq-whm-hwp-mi_soil_bkgd_dioxin_data.pdf (accessed August 2007), Lansing, MI, 1999.

(10) U.S. Environmental Protection Agency, Region 8 *Denver Front Range Study: Dioxins in Surface Soil*. Denver, CO, 2001.

(11) U.S. Environmental Protection Agency *Exposure and Human Health Reassessment of 2,3,7,8-Tetrachlorodibenzo-p-dioxin (TCDD) and Related Compounds. EPA/600/P-00/001Cb,* Washington, D.C., 2003.

(12) Michigan Department of Environmental Quality. http://www.deq.state.mi.us/documents/deq-whm-hw-dow-2005−06−10-midland-summary-map.pdf (accessed August 2007), Lansing, MI, 2005.

(13) Garabrant, D. H.; Hong, B.; Chen, Q.; Franzblau, A.; Lepkowski, J.; Adriaens, P.; Demond, A.; Hedgeman, E.; Knutson, K.; Zwica, L.; Chang, C.-W.; Lee, S.-Y.; Olson, K.; Towey, T.; Trin, H.; Wenger, Y.; Luksemburg, W.; Maier, M.; Gillespie, B. Factors that explain serum dioxin concentrations in Michigan, USA. *Organohalogen Compd.* **2007**, *69*, 206–209.

(14) Van den Berg, M.; Birnbaum, L.; Denison, M.; De Vito, M.; Farland, W.; Feeley, M.; Fiedler, H.; Hakansson, H.; Hanberg, A.; Haws, L.; Rose, M.; Safe, S.; Schrenk, D.; Tohyama, C.; Tritscher, A.; Tuomisto, J.; Tysklind, M.; Walker, N.; Peterson, R. E. The 2005 World Health Organization reevaluation of human and mammalian toxic equivalency factors for dioxins and dioxin-like compounds. *Toxicol. Sci.* **2006**, *93*, 223–241.

(15) Goovaerts, P.; Trinh, H.; Demond, A.; Franzblau, A.; Garabrant, D.; Gillespie, B.; Lepkowski, J.; Adriaens, P. Geostatistical modeling and spatial distribution of soil dioxins in the vicinity of an incinerator: 1, Theory and application to Midland, Michigan. *Environ. Sci. Technol.* **2008**, *42*, 3648–3654.

(16) Barabas, N. Personal communication, Limno-Tech, Ann Arbor, MI, 2004.

(17) Method 8290: Polychlorinated Dibenzodioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs) by High-Resolution Gas Chromatography/High-Resolution Mass Spectrometry (HRGC/HRMS); United States Environmental Protection Agency, Office of Solid Waste and Emergency Response, Washington, DC, 1994.

(18) Method 1668, Revision A: Chlorinated Biphenyl Congeners in Water, Soil, Sediment, and Tissue by High-Resolution Gas Chromatography/High-Resolution Mass Spectrometry (HRGC/HRMS); United States Environmental Protection Agency, Office of Water, Washington, DC, 1999.

(19) Hornung, R. W.; Reed, L. D. Estimation of average concentration in the presence of nondetectable values. *Appl. Occup. Environ. Hyg.* **1990**, *5*, 46–51.

(20) Michigan Department of Environmental Quality. http://www.deq.state.mi.us/documents/deq-rrd-tr-soils-appendix-j.pdf (accessed August 2007), Lansing, MI, 2003.

(21) National Health and Nutrition Survey Laboratory Protocol 28POC; Centers for Disease Control and Prevention, National Center for Health Statistics, Hyattsville, MD, 2005; http://www.cdc.gov/nchs/about/nhanes/lab01_02.htm.

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