

## RELATIONSHIP BETWEEN CONCENTRATIONS OF PCDDS, PCDFS AND DIOXIN-LIKE PCBS IN VEGETATION AND SOIL ON RESIDENTIAL PROPERTIES

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### Introduction

The University of Michigan Dioxin Exposure Study (UMDES) was undertaken in response to concerns among the population of Midland and Saginaw Counties in Michigan, USA, that the discharge of dioxin-like compounds from the Dow Chemical Company facilities in Midland, Michigan, USA, had resulted in contamination of soils in the Tittabawassee River flood plain and areas of the City of Midland, leading to an increase in residents' body burdens of dioxin-like compounds. To analyze the relationship between soil contamination and residents' body burden, soil samples were taken from residential properties in Midland, Saginaw and Bay Counties (Michigan, USA), and in Jackson and Calhoun Counties (Michigan, USA), located about 180 km to the southwest, as a comparison. A total of about 2081 soil samples from 766 residential properties were analyzed for the World Health Organization (WHO) 29 PCDD, PCDF and dioxin-like PCB congeners. Even if soil contact had not resulted in exposure for the residents of this area, there may have been exposure through the vegetation. Consequently, 579 vegetation samples obtained from a subset of the 766 properties were also analyzed for the same congeners.

The transport of dioxin-like compounds into vegetation from contaminated soil can occur through a variety of mechanisms: adsorption onto the root surface; root uptake and transport into the plant shoot; volatilization from the soil surface and adsorption onto the plant surface; and contamination of the plant's foliage by soil<sup>1</sup>. It appears that volatilization and adsorption may be a major transport pathway in greenhouses, but in the field, this mechanism is of minor importance<sup>2,3</sup>. Similarly, root uptake and transport into the plant shoot may be important in some circumstances, notably in the cases of zucchini and pumpkin<sup>2</sup>, but in the case of most plants, this is not a significant mechanism<sup>4</sup>. Based on the similarities between the congener pattern in plant material and that in the atmosphere<sup>5</sup> and the fact that partitioning between the atmosphere and plants, like corn for example, is a function of the saturated vapor pressure<sup>6</sup>, the deduction is that adsorption from the gas phase is the key process for the contamination of vegetation by the lower chlorinated (tetra-hexa) PCDD and PCDFs<sup>7</sup>. As such, the contamination of the plant material shows little correspondence to the contamination in the soil<sup>8</sup>, with the vegetation showing a higher abundance of lower chlorinated congeners<sup>9</sup>. Yet, in laboratory experiments, the experimental plants were often watered from below<sup>7,10</sup>, rather than above, as in natural precipitation. Furthermore, in field surveys, the contaminants often entered the environment via the atmosphere such as from incinerators<sup>8</sup>, and not via flooding as in the Tittabawassee River floodplain. Thus, contamination of foliage by soil particles cannot be ruled out for grass around people's residences, for example. In fact, models based on atmospheric deposition have been noted to underpredict the concentrations of PCDDs and PCDFs in grass<sup>11,12</sup> whereas they work well for fresh fruit and above-ground green vegetables<sup>11</sup>.

### Materials and Methods

Vegetative samples were collected concurrently with soil samples from properties selected from five areas designated as Floodplain (located in the 100-year FEMA [Federal Emergency Management Agency] 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 contained a portion of the 100-year FEMA floodplain), Plume (located downwind of the Dow Chemical facility in the City of Midland), Other Midland/Saginaw (located in Midland, Saginaw or Bay Counties, but outside the above areas) and Jackson/Calhoun (located in Jackson or Calhoun Counties).

Up to four sampling stations were located around the perimeter of the house. If there were soil contact activities, samples were also taken at those locations (maximum of two), usually a vegetable garden and/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: 4 house perimeter, 2 soil contact and 1 near river. Individual soil cores were composited as described elsewhere<sup>13</sup>. Ultimately, each residence yielded all or some of the following composite samples: house perimeter set 0-1 inch composite (HP 0-1 inch); house perimeter set 1-6 inch composite (HP 1-6 inch); soil contact set 0-6 inch composite (Garden); near river set 0-1 inch composite (NR 0-1 inch); and near river set 1-6 inch composite (NR 1-6 inch). Approximately 500 mL of vegetation, typically grass, was collected from each house perimeter sampling station and placed in Ziploc® bag. Approximately 1000 mL of vegetation were collected from the near river and soil contact stations, to ensure sufficient sample mass. Vegetation was rarely procured from the soil contact (Garden) stations. Only a small fraction of the field sampling occurred during the time frame during which garden vegetation was available. Furthermore, a decision was made not to seek permission to sample landscaping. Thus, most of the vegetative samples consisted of weeds and grass. The vegetation was cut just above ground level. Any soil clods attached to the vegetation were removed during compositing, but no washing occurred. The samples were composited by set (HP, Garden, NR) using a balance to ensure approximately equal masses from each station. The proportionate aliquots were then mixed by tossing in stainless steel bowls. Both soil and vegetation samples were shipped to Vista Analytical Laboratory (El Dorado Hills, CA) where they were analyzed by high-resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS) using US Environmental Protection Agency (EPA) methods 8290<sup>14</sup> and 1668<sup>15</sup> for the 29 PCDF, PCDD, dioxin-like PCB congeners listed by WHO. If the concentration of a particular congener was below the limit of detection, the concentration was recorded as the limit of detection divided by  $\sqrt{2}$ <sup>16</sup>.

To analyze the relationship between the contamination in the soil and in the vegetation, linear regression was carried out using SAS statistical software (version 9.1; SAS Institute, Cary, NC), employing the concentrations in the various soil composites, information drawn from the UMDES questionnaire, such as property use (e.g., use of weed killers, trash or yard waste burning), information drawn from field notes (e.g., sampling season), as well as weather information (e.g., elapsed time since last rain) as predictor variables. These analyses were performed to predict the TEQ<sub>DFP-2005</sub> (based on the 29 congeners listed by WHO and the 2005 TEFs<sup>17</sup>) of the vegetation as well as to predict the concentrations of 2,3,7,8-TCDD, the top contributor to the TEQ in the Plume; 2,3,4,7,8-PeCDF, the top contributor to the TEQ in the Floodplain; and PCB 126, the top contributor to the TEQ in Jackson/Calhoun<sup>13</sup>.

## Results and Discussion

The average, median, 75<sup>th</sup> percentile, 95<sup>th</sup> percentile and range of TEQ<sub>DFP-2005</sub> for the soil HP 0-1 inch composites and the vegetation HP composites are shown in Tables 1 and 2, respectively. The mean TEQ for the HP 0-1 inch soil composites was 56.5 pg/g in the Floodplain and 109.2 pg/g in the Plume, the two areas known to be contaminated, whereas the mean TEQ for the HP vegetation composites was 14.2 pg/g and 37.5 pg/g for the same areas. These data show that the mean TEQ in the vegetative samples is 0.25 and 0.34 of that in the soil for these areas. These ratios roughly correspond to that of 0.27 reported by Meneses et al. (based on I-TEQ) for grass and weeds<sup>12</sup>. Figure 1 shows the profiles for the Floodplain HP 0-1 inch soil composites and the Floodplain HP vegetation composites. A comparison of these profiles shows that they are similar, with the top contributor to the TEQ in both instances being 2,3,4,7,8-PeCDF. Thus, this figure does not show the discrepancy often cited between soil and vegetation profiles<sup>8,9</sup>. The similarity of the profiles is supported by the results of the linear regression, in that the greatest amount of the variance of the vegetation congener concentration is explained by that in the soil. Based on these results, it is

inferred that the primary mechanism for the transport of these compounds into the grass samples was by deposition of soil particles; the same conclusion was reached by Hulster and Marschner<sup>1</sup> for hay samples. Thus, on grassy residential properties, the possibility of soil particle deposition as the primary means of contamination of vegetation by dioxin-like compounds should be taken into account.

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Table 1. TEQ<sub>DFT29-2005</sub> of the Soil Composites (NR = near river; HP = house perimeter)

| Soil Composites             | TEQ <sub>DFP29-2005</sub> ( pg/g) |       |      |        |                       |                       |     |        |
|-----------------------------|-----------------------------------|-------|------|--------|-----------------------|-----------------------|-----|--------|
| Zone                        | N                                 | Mean  | S.E. | Median | 75 <sup>th</sup> %ile | 95 <sup>th</sup> %ile | Min | Max    |
| Floodplain HP 0-1 inch      | 203                               | 56.5  | 9.7  | 11.4   | 35.4                  | 223.1                 | 1.1 | 1881.4 |
| Near Floodplain HP 0-1 inch | 164                               | 52.0  | 36.7 | 3.9    | 10.4                  | 102.9                 | 0.8 | 2299.8 |
| Other M/S HP 0-1 inch       | 168                               | 13.5  | 2.0  | 5.3    | 13.2                  | 59.4                  | 0.8 | 157.7  |
| Plume HP 0-1 inch           | 37                                | 109.2 | 31.0 | 58.2   | 111.9                 | 257.2                 | 6.3 | 745.5  |
| Jackson/Calhoun HP 0-1 inch | 194                               | 6.9   | 0.8  | 3.6    | 7.6                   | 22.6                  | 0.4 | 186.2  |

Table 2. TEQ<sub>DFP29-2005</sub> of the Vegetation Composites (NR = near river; HP = house perimeter)

| Vegetation Composites<br>Zone | TEQ <sub>DFP29-2005</sub> (pg/g dry wt) |       |       |        |                       |                       |     |        |
|-------------------------------|-----------------------------------------|-------|-------|--------|-----------------------|-----------------------|-----|--------|
|                               | N                                       | Mean  | S.E.  | Median | 75 <sup>th</sup> %ile | 95 <sup>th</sup> %ile | Min | Max    |
| Floodplain HP                 | 188                                     | 14.2  | 3.4   | 3.4    | 7.4                   | 50.2                  | 0.4 | 1427.2 |
| Near Floodplain HP            | 69                                      | 376.6 | 354.1 | 3.3    | 10.1                  | 152.0                 | 0.6 | 7994.9 |
| Other M/S HP                  | 71                                      | 4.2   | 0.4   | 3.3    | 5.1                   | 10.1                  | 1.0 | 27.5   |
| Plume HP                      | 361                                     | 37.5  | 12.7  | 18.3   | 31.1                  | 125.4                 | 0.8 | 268.9  |
| Jackson/Calhoun HP            | 52                                      | 4.5   | 0.6   | 3.3    | 6.7                   | 8.7                   | 0.6 | 25.9   |

Figure 1. Congener Contributions to TEQ<sub>DFP29-2005</sub> for Vegetation and Soil Composites from the Floodplain. The plus sign indicates the arithmetic mean. The horizontal line across the box indicates the 50<sup>th</sup> percentile (median), the lower and upper margins of the box indicate the 25<sup>th</sup> percentile and 75<sup>th</sup> percentile, respectively; the upper ticked line extends to the 99<sup>th</sup> percentile and the lower ticked line extends to the 1<sup>st</sup> percentile. The stars show the values above the 99<sup>th</sup> percentile and below the 1<sup>st</sup> percentile.

