

## ANALYSIS OF VEGETATION CONCENTRATIONS OF PCDD/F/PCBS FROM A COMMUNITY IN MICHIGAN, USA

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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 that the discharge of dioxin-like compounds from the Dow Chemical Company facilities in Midland has resulted in contamination of soils in the Tittabawassee River flood plain and areas of the City of Midland. There is concern that people's body burdens of polychlorinated dibenzodioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and polychlorinated biphenyls (PCBs) may be elevated because of the environmental contamination. A central goal of the UMDES was to determine the factors that explain variation in serum congener levels of PCDDs, PCDFs, and PCBs, and to quantify how much variation each factor explains. Residential vegetation concentrations of PCDDs, PCDFs, and PCBs were included as one of the potentially explanatory factors. To analyze the relationship between vegetation concentration and a resident's body burden, samples were taken from residential properties in Midland, Saginaw and Bay Counties (Michigan, USA), and from Jackson and Calhoun Counties (Michigan, USA) as a comparison. This report describes the sampling methods and results of vegetation analysis conducted as part of UMDES. Overall study results are presented elsewhere.<sup>1</sup>

### Materials and Methods

*Respondent Selection:* Five populations in Midland, Saginaw, Bay, Jackson, and Calhoun Counties, Michigan, USA were sampled using a two-stage area probability household sample design. In order to be eligible for participation in the soil and vegetation sampling portion of the UMDES, subjects had to have lived in their residence at least five years and had to be the owner of their residence and property. A more detailed description of the populations and respondent selection methodology is reported elsewhere.<sup>2</sup>

*Sampling Strategy:* Soil and vegetation samples were collected concurrently. At each respondent's residence, up to seven soil and vegetation sampling stations were identified in three sets: the house perimeter set, the soil contact set, and the flood plain set. Up to four stations were sampled in the house perimeter set, up to two stations were in the soil contact set, and one station was in the flood plain set. Each station was defined by the placement of a 3-foot diameter sampling ring. Vegetation was rarely procured from the soil contact (garden) set. The decision was made to not seek permission to sample desired landscaping, and only a small fraction of the sampling took place during the timeframe in which vegetable garden samples could be procured. A more detailed description of soil and vegetation sampling strategy is given elsewhere.<sup>3</sup>

*Sampling and Compositing Methods:* Approximately 500 mL of vegetation, typically grass, was collected from each residential zone station from the area within the sampling ring and stored in a Ziploc® bag. Approximately 1000 mL were collected from flood plain and soil contact stations, to ensure sufficient sample mass without compositing. Vegetation was procured by severing the vegetation at the ground level, resulting in occasional soil clumps attached to the vegetation. These clumps were removed during the compositing procedure. The compositing was conducted

at the laboratories at the Environmental and Water Resource Engineering building at the University of Michigan. The samples were composited by set (house perimeter, soil contact, and flood plain) using a balance to ensure approximately equal masses from each station. The vegetation was mixed with a tossing action in a stainless steel bowl and stainless steel spoons. Samples of approximately 50 g were created and placed into 500 mL amber jars. Duplicate and triplicate samples were created from the remaining collected vegetation. The samples were stored in dedicated 4°C cold rooms prior to analysis

*Analytic Sequence:* As part of the analytic sequence, vegetation samples were selected for analysis under either of two conditions: the respondent was part of the Tittabawassee River flood plain population or the analysis of the underlying soil sample yielded a value of greater than 8 pg/g TEQ. As a result of this analytic sequence 416 house perimeter set, 163 flood plain set, and 18 soil contact set vegetation samples were selected for analysis. A more detailed description of the soil and vegetation analytic sequence is reported elsewhere.<sup>3</sup>

*Sample Analysis:* Analyses were performed by Alta Analytical Laboratory, Inc. (El Dorado Hills, California, USA) for the WHO designated 29 PCDD, PCDF, and PCB congeners<sup>4</sup> using US EPA methods 8290<sup>5</sup> and 1668<sup>6</sup>. As part of sample preparation, 10 grams (dry weight) or half of the sample are soxhlet extracted with toluene for 16 hours. The extract then goes through 3 cleanup procedures: acid/base silica gel, acid alumina and florisil. The extract is then further concentrated to 20 uL and analyzed using HRGC/HRMS.

*PCDD, PCDF, and PCB concentration distribution vegetation samples:* A descriptive analysis of PCDD, PCDF, and PCB congener concentrations in the vegetation was performed for each of the five geographic regions. Upper quantiles were compared among regions in addition to comparisons of mean levels. SAS<sup>7</sup> statistical software was used to complete the analyses.

*Soil and Vegetation Comparison:* For each vegetation sample, the corresponding soil sample was also analyzed. Using Minitab<sup>8</sup>, a congener specific comparison between each vegetation sample and the underlying soil sample was made. A scatterplot and linear regression was created for each congener. The comparison was repeated separately for the flood plain and plume populations to evaluate whether the deposition mechanism (flooding vs aerial) affects the soil-vegetation relationship.

*Vegetation Precision Calculations:* As part of the UMDES QA/QC procedures, 23 blind duplicate vegetation samples were submitted for analysis. The precision of the collection, compositing, and analysis processes were assessed by the comparison of duplicate samples. The relative percent difference (RPD) was calculated as follows:

$$RPD = \frac{|C_o - C_D|}{0.5(C_o + C_D)} \times 100$$

where  $C_o$  = measured concentration of the original sample  
 $C_D$  = measured concentration of the duplicate sample

The RPD was calculated for each congener of each duplicate pair. Duplicate samples were also submitted for soil samples. The precision of soil and vegetation analytical results were compared.

### Results and Discussion

Results and discussion will not be available until after complete study results have been presented to the affected communities in August of 2006.

## References

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