METHODS FOR SAMPLING AND ANALYZING SOIL FOR THE UNIVERSITY OF MICHIGAN DIOXIN EXPOSURE STUDY

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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, Michigan (USA) has 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 PCDDs, PCDFs and PCBs. To analyze the relationship between soil contamination and resident's body burden, soil 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. The descriptive statistics, distributions, and congener patterns of the soil samples are presented in Adriaens et al. (2006a)[1]. The objective of this presentation is to describe the sampling and analysis strategy used in the collection and processing of the soil samples in the UMDES.

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 soil sampling in UMDES, the respondent had to have lived in the residence at least five years and had to be an owner of the property. A more detailed description of the populations and respondent selection methodology is reported in Olson et al. (2006)[2].

Sampling Technique: The locations of soil sampling stations at each residence are shown in Figure 1. Up to four sampling stations were located around the perimeter of the house. If responses to interview questions indicated 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 flood plain, one additional station in the flood plain was sampled. The flood plain station was placed at the lowest, safely accessible location on the respondent's property in the direction of the river. Thus, there were a maximum of seven sampling stations at each residence (4 house perimeter, 2 soil contact, 1 flood plain). Each sampling station was defined by laying out a 3-foot diameter sampling ring. Three equally spaced cores around the ring were collected using custom-made single-use polycarbonate sample tubes pushed into the ground using a slide hammer (AMS, American Falls, Idaho). This procedure allowed for direct sample collection in the tube, sealing of the tube, and the minimization of cross-contamination between samples. The locations of the sample cores were brought back to grade using commercial top soil. The time and date of collection, location of samples, and additional observations (e.g., location of combustion areas) were recorded as field notes on a preprinted field data sheet. All sample location coordinates were established using global positioning system (GPS) (GeoXT, Trimble, Sunnyvale, California) procedures. All sealed sample cores were stored on ice (4°C) in coolers before transport to the University of Michigan for compositing. Chain of custody forms were completed and kept with the samples at all times.

The soil cores were pushed out of the polycarbonate tubes using a Geotest core extruder (Model E-267, Evanston, Illinois). The extruded cores from the house perimeter and the floodplain stations were then separated into two strata: the 0-1 inch and 1-6 inch. The cores from the soil contact stations were not separated into strata. If vegetation was present, the leaf cover and roots were separated from the 0-1 inch stratum. The strata from each station were first combined and homogenized and then the stratum composites were combined and homogenized. The collected vegetation was composited unwashed separately from the soil. The details on vegetation compositing are reported in Adriaens et al. (2006b)[3].

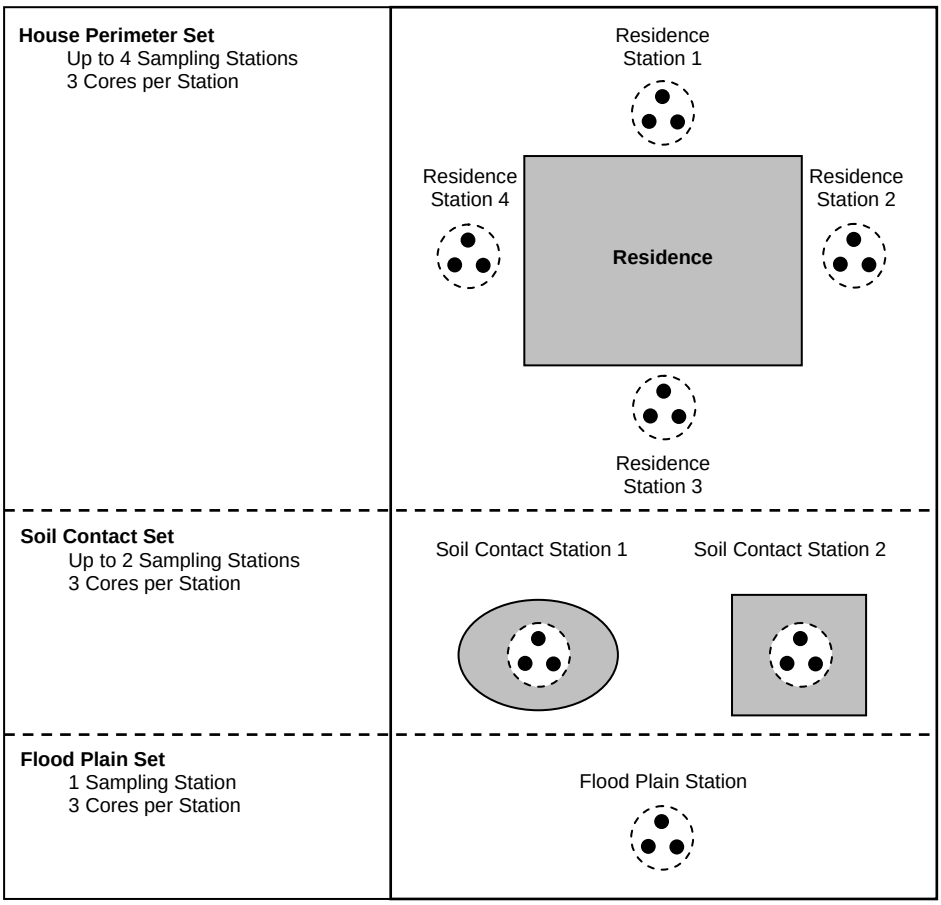


Figure 1. Soil sample locations

All reused utensils were scrubbed in water containing 2% Liquinox solution, followed by rinsing with distilled (DI) water, methanol, DI water, acetone, and then a third DI rinse.

Ultimately, each residence yielded the following composite samples for analysis:

- House perimeter set 0-1 inch composite;
- House perimeter set 1-6 inch composite; and
- House perimeter set surface vegetation composite.

If there was a soil contact station or stations, the residence yielded the following additional samples:

- Soil contact set 0-6 inch composite; and
- Soil contact set surface vegetation composite (if available).

In addition, residences in the Tittabawassee River flood plain yielded the following samples:

- Flood plain set 0-1 inch composite;
- Flood plain set 1-6 inch composite; and
- Flood plain set surface vegetation composite.

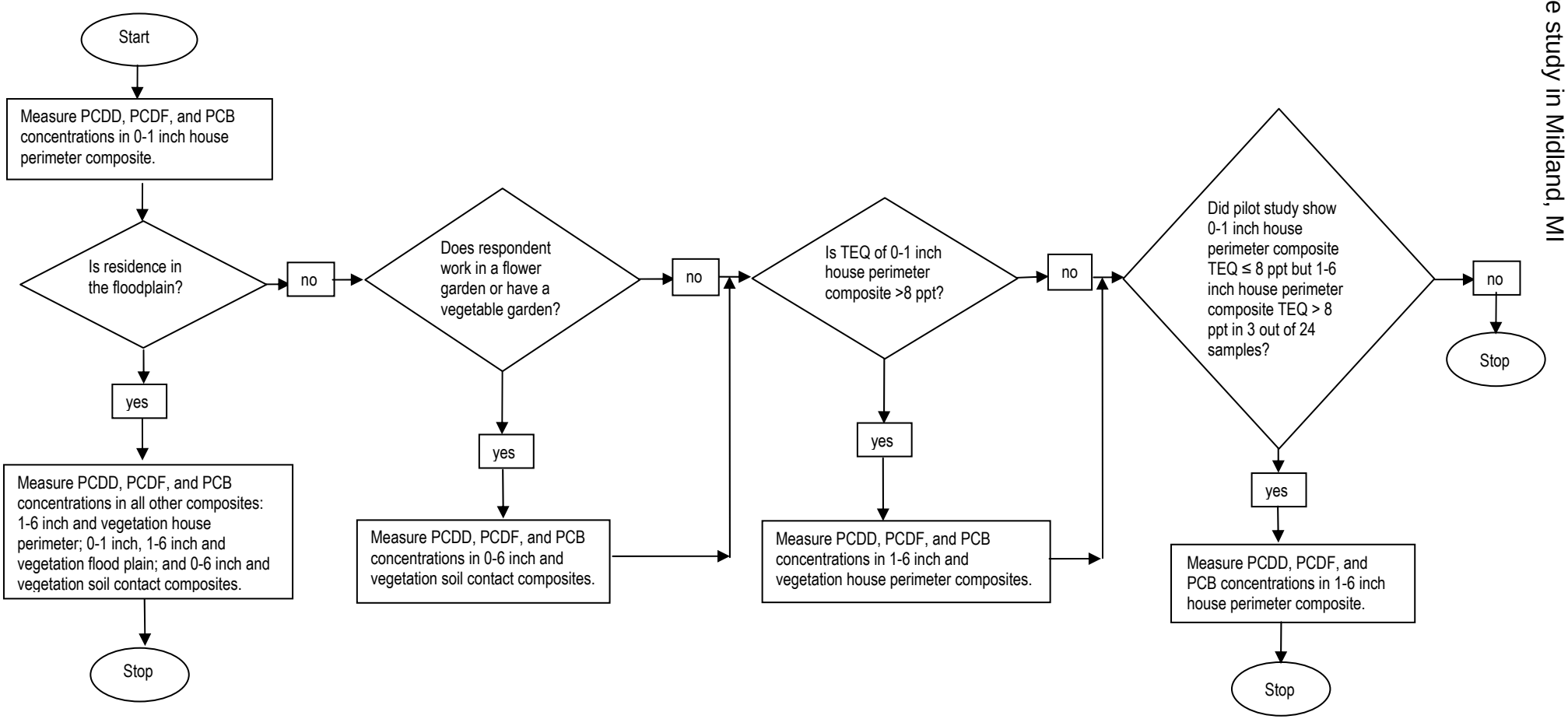
The soil samples were archived in 4 oz dioxin-grade amber glass jars to avoid photolytic degradation, and stored in dedicated 4° C cold rooms prior to analysis.

Sample Analysis: The decision sequence of which samples were analyzed is shown in Figure 2. The 0-1 inch house perimeter composite samples were analyzed for all properties. If any part of the property was in the floodplain, then all remaining composites (1-6 inch and vegetation house perimeter; 0-1 inch, 1-6 inch and vegetation floodplain; and 0-6 inch and vegetation soil contact) were also submitted for analysis. If the respondent did not live in the flood plain, but had a vegetable garden or worked in a flower garden, the 0-6 inch and vegetation composites for the soil contact set were analyzed. If the TEQ of the 0-1 inch house perimeter composite for any property outside the floodplain was > 8 pg/g, then the 1-6 inch and vegetation house perimeter composites were subsequently analyzed. The trigger value of 8 pg/g TEQ represent the 75th percentile of the background distribution for the lower peninsula of Michigan (i.e., 25% of soil samples are expected to be above 8 pg/g) (Adriaens et al, 2006)[1]. All samples that were subjected to analysis were shipped to Vista Analytical Laboratory (El Dorado Hills, California) according to 40 CFR 761.65 (i)(3) and in accordance with current and applicable D.O.T. standards via express carrier. At Vista, the laboratory personnel completed the chain-of-custody forms by signing and dating to acknowledge receipt of samples. The samples were subsequently analyzed by high-resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS) for the WHO 29 PCDD, PCDF and PCB congeners using internal modifications of USEPA methods 8290 (US EPA, 1994)[4] and 1668 (US EPA, 1999)[5].

Pilot Study: In the design of the study, it was assumed that most of the exposure was from surface soil (except in the gardens where the exposure was assumed to occur from the top 6 inches due to digging) and if contamination existed on the property at a greater depth (1-6 inches), then the 0-1 inch stratum would be above the 8 pg/g TEQ trigger value. To verify this assumption, a pilot study was conducted on the near flood plain and Midland/Saginaw populations. These populations were targeted as there may be a greater likelihood of elevated subsurface concentrations of dioxin-like compounds in those areas because of the reputed use of Tittabawassee and Saginaw River flood plain sediment as fill material. Twenty-four residences were selected from those whose 0-1 inch house perimeter composite yielded a TEQ below the 8 pg/g trigger: 12 properties where reported or observed fill activity had taken place and 12 where no obvious fill activity had taken place. For these properties, the 1-6 inch house perimeter composite was submitted for congener specific chemical analysis.

QA/QC: Four kinds of QA/QC samples were submitted for analysis: wipe samples from floors and counter tops in the compositing lab, rinse blanks from compositing lab equipment, duplicate soil samples, and soil samples containing a known quantity of dioxin obtained from Cambridge Isotope Laboratories (Andover, Massachusetts) or from the International Intercalibration Study (van Bavel, 2004)[6]. Quality control procedures for analytical services were conducted by Vista Analytical Laboratory in accordance with their standard operation procedures and the individual method requirements.

Figure 2: Soil and vegetation analytic sequence



Results and Discussion

A total of 766 residences were sampled in the five counties in Michigan from October – December 2004 and from April – September 2005, with a total of 2081 samples submitted for analysis (not including QA/QC samples). An analysis of PCDD, PCDF and PCB congener concentrations was performed for the soils collected for each of the five populations in the UMDES. A summary of these analyses is presented in Adriaens et al. (2006a). This presentation concentrates on the results of the pilot study and the variability between the top 1 inch and 1-6 inch samples, and the QA/QC samples. These results will be available in August 2006 after the release of the study results to the affected communities.

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