MECHANISMS OF CONTAMINATION OF SOILS WITH DIOXIN-LIKE COMPOUNDS IN BACKGROUND AREAS 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 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 PCB congeners.

Most contamination of residential property soil with dioxin-like compounds occurs as a result of proximity of industrial activity that produces such compounds. It is generally assumed that residential properties outside these industrially impacted zones are at background levels. However, as part of The University of Michigan Dioxin Exposure Study (UMDES), residential properties were identified that were located far enough from the known sources of these compounds that the soil concentrations should have been at background levels and yet some properties had a soil toxic equivalence (TEQ) greater than two and half standard deviations above the mean background level. This study examined seven of these cases to elucidate the mechanisms by which these properties became contaminated.

Materials and Methods

Soil samples were collected from 766 residential properties selected from five populations, 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 and Calhoun (located in Jackson or Calhoun Counties). A more detailed description of the populations and respondent selection methodology is reported on UMDES's website (www.umdioxin.org).

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 flood plain, 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, 1 flood plain). Individual cores were composited as described elsewhere[1]. Ultimately, each residence yielded all or some of

the following composite samples for analysis: 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).

The composites that were analyzed 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 [2] and 1668 [3] 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 $\sqrt{2}$ [4].

The arithmetic mean total toxic equivalence (TEQ), calculated using the 29 WHO congeners and the toxic equivalency factors (TEFs) promulgated by the WHO in 2005 [5], designated here as $TEQ_{DFP\text{-}2005}$, for the HP 0-1 inch composites in Jackson and Calhoun Counties was 6.9 pg/g. If recalculated using the 1998 TEFs [6], the value was 8.3 pg/g, very similar to the value measured by the US EPA in the Denver Front Range Study[7] of $TEQ_{DFP\text{-}1998}$ = 8.6 pg/g. Thus, it appeared that, on the average, soil concentrations in Jackson/Calhoun Counties were at background. To determine whether the soil concentrations in the target areas were above background, the mean of the HP 0-1 inch composites from the various geographic areas were compared statistically. Because of the skewness of the data, the data were log-transformed to obtain an approximately normal distribution and the geometric means of the $TEQ_{DFP\text{-}2005}$ values were compared using a t-test (SAS PROC Surveyreg, SAS Institute, Cary, NC). The results showed that all the sets of HP 0-1 inch samples from Midland and Saginaw Counties had statistically higher geometric mean TEQs than the set from Jackson and Calhoun Counties, suggesting statistically significantly higher concentrations of dioxin-like chemicals above background levels[1]. This result was anticipated for the Floodplain and the Plume areas, since these areas have been impacted by historic discharges from the Dow Chemical Company. That the soil samples from the Near Floodplain and the Other Midland/Saginaw areas had mean TEQs that were statistically higher than background was unexpected, given that these areas are neither in the floodplain of the Tittabawassee River nor located downwind from Dow Chemical. In addition, some properties in Jackson/Calhoun had TEQs significantly above the area's mean. Thus, a follow-up study was undertaken to elucidate reasons for the anomalously high TEQs in these areas that had no known industrial source.

To be eligible for the follow-up study, the participant must have elected to receive his soil sampling results and have at least one composite total TEQ value greater than 2.5 standard deviations above the arithmetic mean of the HP 0-1 inch samples in the Other Midland/Saginaw and Jackson/Calhoun areas. This follow-up study did not consider residents from the Floodplain or Plume populations since these areas were known to be contaminated by historic industrial discharges. Seven respondents who met these criteria were recruited to participate. These respondents completed an open-ended interview covering questions about house characteristics (age of house, history of flooding, location relative to industrial activity, prior use of property, etc.), soil movement (onto or off property during construction, renovation, landscaping, etc.), habits of residents (hobbies, trash burning, pesticide spraying, etc.). Also, uncomposited soil samples from the original soil sampling survey were submitted for analysis to help elucidate any hypotheses drawn from the responses to the interview questions.

Results and Discussion

Of the seven selected respondents, four lived in the Other Midland/Saginaw area and seemed to represent a consistent trend, with the TEQ dominated by the PCDFs. In the case of the respondent selected from the Near Floodplain, the soil contamination seemed to be located on only one side of the house and to comprise substantially more PCDDs than other samples from the area. The remaining two respondents of the seven lived in the Jackson/Calhoun area. These cases had anomalously high PCB levels. In one case, the source was clear; however in the second, the source of the PCBs remains unknown.

Consistent trends in the four cases in the Other Midland/Saginaw area included that the properties had no prior industrial use and that the residences had been built on farmland. The properties had never been flooded by the Tittabawassee River (or any other river), even during the historic flood of 1986, when the Tittabawassee River crested at nearly 10 feet above flood stage[8] and yet, the contamination on the properties contained a preponderance of furans, a pattern typical of the floodplain contamination in that area[1]. In one case, the contamination was limited to the garden, but in other cases, the contamination seemed to be around the entire residence. Since a number of the property owners had brought in commercial top soil for landscaping, a sample of commercial top soil was analyzed, and its TEQ was dominated by dioxins, not furans. Because of the distinctive floodplain signature of the samples and based on the topography of some of the houses' sites, it was surmised that contaminated soil had been brought in during the preparation of the site for the construction of the houses.

As the UMDES was a randomized, population-based study, we could estimate the frequency with which contaminated materials had been used on residential properties outside the floodplain. Since it was apparent from the soil sampling in UMDES that the geographic area over which the contaminated soil was distributed was limited, these calculations focused on properties within 8 km of the floodplains of the Tittabawassee and Saginaw Rivers. Having Floodplain contamination was defined as having at least one composite soil sample with a $TEQ_{DFP\text{-}2005}$ above 22.6 pg/g (the 95th percentile of the distribution of the HP 0-1 inch samples from Jackson/Calhoun), with at least 50% of it attributable to furans. Using these criteria, it was estimated (SAS PROC Freq, SAS Institute, Cary, NC) that 23.0% (with a 95% confidence interval of 15.4% to 30.6%) of properties within 8 km of the floodplains showed contamination with a Floodplain pattern, most likely through the anthropogenic movement of contaminated soil or other materials. Furthermore, 4.2% (with a 95% confidence interval of 0.2% to 8.2%) of properties were estimated to have at least one soil sample with a TEQ above 90 pg/g, which is the direct soil contact criterion promulgated by Michigan's Department of Environmental Quality. This finding has significant implications, as there are numerous sites historically contaminated with persistent chemicals, from which materials may have been moved.

In the case of the property from Jackson and Calhoun, the congener profile of the soil composites was suggestive of Aroclor 1254, a PCB mixture that was a constituent of paint, caulk, ink and adhesives[9]. From the interview, we learned that the homeowner had sandblasted his swimming pool to remove layers of paint, creating a fine particulate cloud over his property. Contamination of soil through power sanding of paint has often been noted in the case of lead and other metals[10]; consequently, there is an awareness of the public health hazards of lead paint removal. There does not seem to be a comparable level of awareness of the potential hazards of physical removal of non-lead based paints that may be contaminated with other hazardous materials, such as PCBs. Although soil contamination of residential properties with PCBs by power sanding has not been commonly reported, building materials containing PCBs such as joint sealants, caulks and plaster are being investigated as sources of soil contamination[11-14]. Herrick et al.[12] called for a random probability-based survey of masonry buildings constructed or renovated during the time when PCB-containing caulking was in use in order to assess the public health risk from this source. The results reported here suggest that such a survey should perhaps also include facilities in which PCB-containing paint was used.

This study reports two mechanisms by which residential soil can become contaminated outside of zones impacted by industrial sources: through the anthropogenic relocation of contaminated materials and through the sandblasting of paint containing PCBs. Thus, the delineation of a zone of contamination around an industrial source based on the transition of soil concentrations to background may not be valid.

Acknowledgements
Financial support for this study comes from the Dow Chemical Company through an unrestricted grant to the University of Michigan. The University of Michigan has complete independence to design, carry out and report the results of the study. The authors are grateful to Drs. Linda Birnbaum, Paolo Boffetta, Ronald A. Hites, David Kleinbaum and Marie Haring Sweeney for their guidance as members of University of Michigan Dioxin Exposure

Study (UMDES) Scientific Advisory Board. Opinions contained in this report are those of the authors and do not necessarily reflect those of the Dow Chemical Company or members of the UMDES Scientific Advisory Board.

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