STATISTICAL FINGERPRINTING OF PCBs USING THE SUBSET WITH DIOXIN-LIKE ACTIVITY

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Introduction

Polytopic vector analysis (PVA) is a multivariate statistical fingerprinting technique that was used to better understand the distribution of congeners in the University of Michigan Dioxin Exposure Study (UMDES) soil and dust datasets. This paper presents results of statistical fingerprinting using the 12 polychlorinated biphenyl (PCB) congeners included in the WHO 29 dioxin-like compounds. Although these 12 compounds are a small subset of the 209 PCB congeners, this analysis demonstrates that the resulting fingerprints may be linked to Aroclor sources. Distributions of the contributions of each Aroclor to the dust and soil of the different study populations were compared, and limitations of the approach were considered.

Materials and Methods

Sample Collection

As part of the UMDES, soil and dust samples were collected from five study populations: 1) Individuals whose property is in the floodplain of the Tittabawassee River (Floodplain - FP); 2) Individuals who live in census blocks that intersect the Tittabawassee River floodplain, but whose property is outside of the floodplain (Near Floodplain - NFP); 3) Residents of Midland and Saginaw counties living outside of the Tittabawassee River floodplain census blocks and incinerator plume (Other Midland/Saginaw - MS); 4) Residents of the City of Midland living downwind of a former Dow incinerator (Plume - PL); 5) Residents of Jackson and Calhoun counties, which served as the comparison population (Jackson/Calhoun - JC). A total of 2081 soil samples (from 766 properties) and 764 indoor dust samples (1 sample per property) were collected and analyzed. Details of respondent selection, sample collection methodologies, and summary statistics of analytical results are presented elswhere[1,2].

Samples were analyzed for the 29 WHO designated dioxin, furan, and PCB congeners. However, preliminary analysis using all 29 congeners indicated that the variability of the PCB congeners was greater than the variability in the dioxin and furan congeners, and patterns of dioxins and furans were obscured. Therefore, the PCB congeners were analyzed separately.

Data Treatment

Values below detection limits can affect correlations between congeners and, therefore, impact the results of PVA. In order to minimize the effect of values below limit of detection (LOD), congeners with greater than 50% of the values below LOD were excluded from the analysis. Samples with greater than 50% of the remaining congeners below LOD were also excluded.

Polytopic Vector Analysis

PVA is a type of factor analysis that has been demonstrated to be useful in determining source contributions in environmental systems[3,4,5]. PVA uses the correlations among congeners to establish which occur together in stable patterns. Each sample is decomposed into these stable patterns, yielding fingerprints that have contributed to the mix in each sample. The stable congener patterns that emerge from PVA and represent potential exposure sources are referred to as end-members (EMs). The contribution of each EM to the congener pattern of an individual sample is referred to as a loading.

PVA was performed using Matlab[6]. The important steps in the PVA algorithm are: a constant row sum and range transformation of the dataset; principal components analysis; varimax rotation of the principal components axes; oblique rotation towards extreme values; and iterative rotations until end-members and loadings satisfy a positivity constraint. Further details regarding the PVA process can be found elsewhere[3,4].

The PVA algorithm is run using a range of different numbers of end-members. Determining the appropriate number of EMs to retain is based on a number of criteria, including: parsimony, stability of EMs across different model sizes, interpretability of EMs, percent of variance explained, coefficient of determination (reproducibility of each congener), and communality (reproducibility of each sample).

Results and Discussion

Comparison of end-members to known Aroclor patterns

The results from the PVA demonstrate that the subset of 12 PCB congeners can be used to make comparisons to, and differentiate between, some Aroclor patterns. Figure 1 shows the congener profiles from the three end-member soil and dust models. The profiles show each PCB congener as a fraction of the total of the dioxin-like PCBs. For comparison, profiles based on published analysis[7] of multiple lots of the three most common Aroclors[8] (1242, 1254, and 1260) are also included. The presence of PCB-77 differentiates Aroclors 1242 and 1254. Aroclor 1260 is differentiated because it includes contributions from a several PCBs with higher chlorination levels, specifically PCB-156, PCB-167, and PCB-189.

End-member loading

Figure 2 presents the distribution of loadings of the three EMs by study population for soil and dust. The whiskers in the box-and-whisker plots represent the 5th and 95th percentiles, the edges of the box represent the 25th and 75th percentiles, the line in the box between colors represents the median, and the hollow dot indicates the mean. For all study populations, for both dust and soil, the Aroclor 1254 pattern has the greatest loading.. The most obvious difference between the sample matrices is that, across all study populations, the contribution of 1242 is higher in the soil than in the dust.

There are slight regional differences in the loadings of the patterns associated with Aroclors 1242 and 1260 for both dust and soil; however, these differences are inconsistent between the two matrices. For soil, the contribution of 1260 is slightly higher in Jackson/Calhoun compared to the other populations. Conversely, in the dust samples, the contribution of 1260 is slightly higher for the Other Midland/Saginaw population, and the contribution of 1242 is higher for the Jackson/Calhoun population. This suggests that the sources of the Aroclors found in dust and the sources found in soil differ to some degree. These minor differences may be within the range of model variability that will be evaluated in future work. However, this finding is consistent with results from the UMDES dust outlier study, which showed that the highest dust PCB levels did not usually correspond with high soil levels[9].

Interestingly, the end-member loadings for the Plume population are similar to those of the other populations. The soils from Plume properties have mean PCB concentrations four to five times higher than soils from the other populations[2]. This analysis suggests that although the Plume soils have much higher levels of PCBs, the mix of PCB sources present in the Plume is similar to that found in other regions.

Limitations

Although the subset of 12 dioxin-like PCB congeners may be sufficient to distinguish between the three most common Aroclors, using this limited subset does present some difficulties. For example, another common Aroclor, 1248, was not extracted even when the models were expanded to include additional end-members. This could be a result of the fact that its congener pattern, when limited to the dioxin-like PCBs, can be reasonably reproduced as a combination of 1242 and 1254. Therefore, some fraction of the loading attributed to 1242 and 1254 may actually be due to 1248. Also, Aroclor 1016, the most commonly produced PCB mixture in the US after 1971[10], contains none of the subset of 12 PCBs with dioxin-like activity.

An additional consideration related to PCB fingerprinting is that linking a particular Aroclor to a particular source in a broad, population-based study such as UMDES is problematic. Each Aroclor was used in a variety of different applications (e.g., transformers, hydraulics, synthetic resins, paints, and adhesives) and there is substantial overlap between Aroclors in their applications[10].

Finally, it should be noted that the results presented here are preliminary. A bootstrapping analysis will be completed to evaluate the sensitivity of the end-member patterns and their associated loadings.

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Figure 1. Soil and dust end-members with comparison to Aroclor patterns based on 12 PCBs with dioxin-like activity.

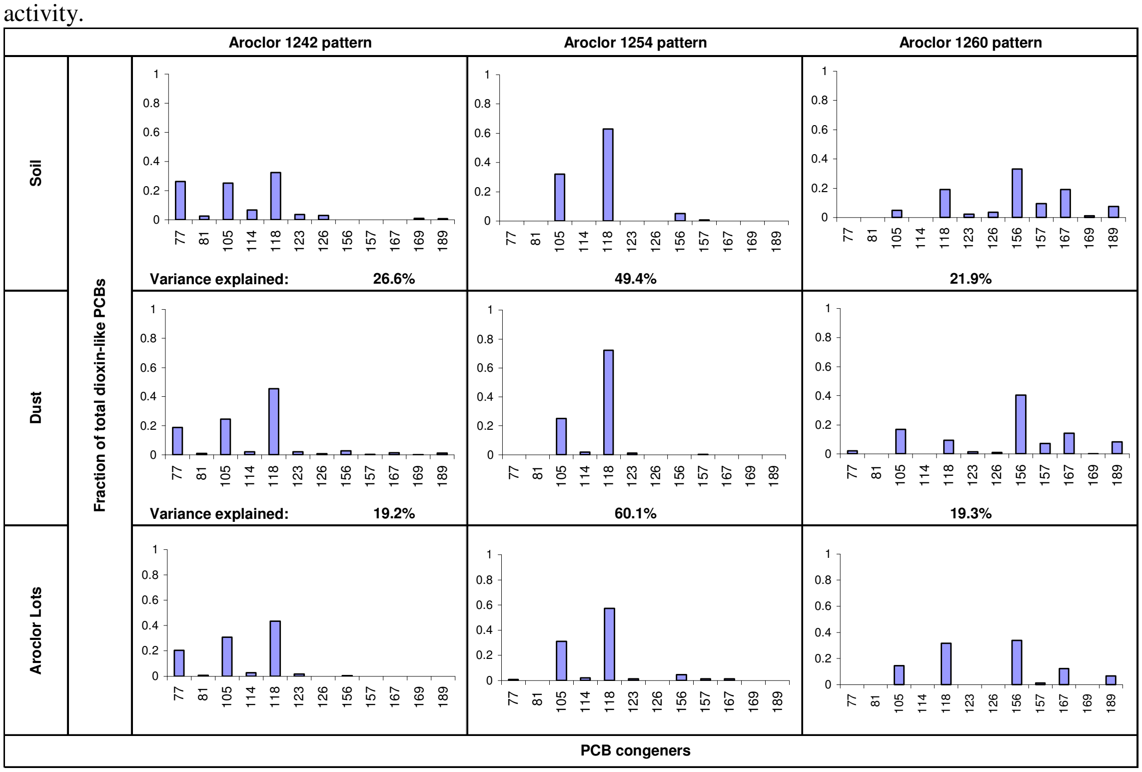
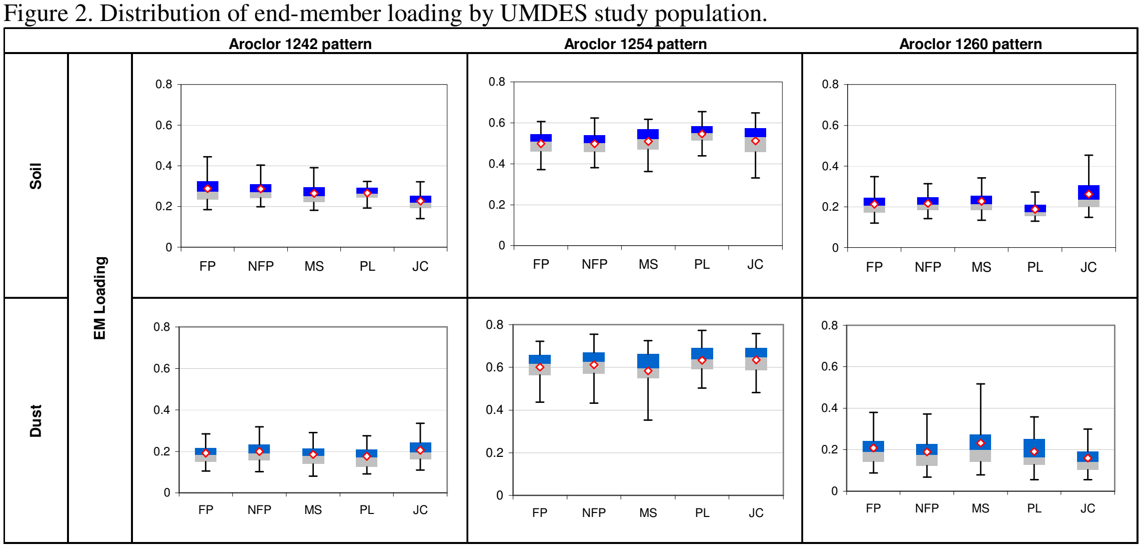


Figure 2. Distribution of end-member loading by UMDES study population.



FP- Floodplain, NFP – Near Floodplain, MS – Other Midland/Saginaw, PL – Plume, JC – Jackson/Calhoun