ESHID-602837

R. Ryti, W. Swanson, T. Kostrubala, A. White, A. Groffman, S. Veenis
rryti@neptuneinc.org

Statistical Evaluations of Polychlorinated Biphenyl Storm Water Background for a Large Federal Facility

ABSTRACT

Since 2000, Los Alamos National Laboratory (LANL) and the New Mexico Environment Department (NMED) have collected polychlorinated biphenyl (PCB) storm water samples to comply with the Clean Water Act. Historical activities at LANL have resulted in the release of PCBs into the environment (e.g. releases from PCB transformers and outfalls from processing facilities at LANL during historic operations). However, LANL and NMED studies have shown that the natural background landscape and the developed landscape are also sources of PCBs, likely from global cycling and PCBs contained in building materials. This analysis presents statistical comparisons of the LANL impacted PCB data population with both natural and developed background PCB populations. LANL impacted PCB data was collected from watersheds that contained potential sources of PCB contamination. Natural background sampling was conducted from watersheds that contained no development or known LANL releases, but may have been impacted from grazing or fires. Development is assessed using information on land cover types, the presence or absence of roads, and the presence or absence of source areas of constituents such as copper sourced from developed landscapes. We also evaluate the homolog data from U.S. Environmental Protection Agency (EPA) 608 and congener data from EPA Method 1668 using a variety of multivariate data-mining techniques to help determine the source of the PCBs. These statistical analyses, taken in concert with the conceptual model for PCB distribution in the environment, identify sampling locations associated with natural or developed background.

This poster is publication LA-UR-17-27465 of the Los Alamos National Laboratory and has been cleared for unlimited release.

Introduction

PCBs are widely distributed in the environment. There are 209 PCB congeners that group into 10 homolog groups. Each of the Aroclor™ mixtures differs in the fraction of these homologs (Figure 1). As PCBs persist in the environment, they are subject to weathering, which leads to dechlorination. The purpose of this paper is to determine if we can identify statistical groupings of storm water sampling locations associated with sources, and also find homolog patterns that can be associated with background levels of PCBs. This evaluation is not limited to samples specifically collected to represent background. Instead, we evaluate all data to determine if a background population can be established in a cost-effective and defensible manner.

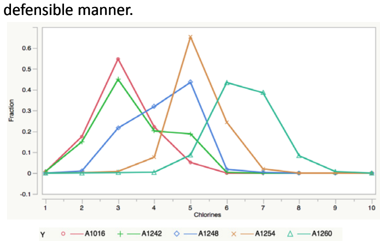

Figure 1. Plot of homolog fractions for Aroclor™ mixtures based on Frame et al. 1996

Methods

Data Preparation. The period of record for storm water samples collected by LANL and NMED was obtained. Because concentrations of congeners vary widely with the amount of suspended sediments, it was decided to normalize these results by the total PCBs reported for the sample. Some of the total PCBs were reported as non-detects; these sample results were removed from the data set for statistical analyses. These non-detects total PCB results accounted for 36 of the 39 samples excluded. The other three samples were reported with the incorrect units and were excluded, as the sum of homologs did not agree with the total PCB result. After these samples were excluded, 1528 samples (910 LANL, 628 NMED) collected from 2003 to 2016 remained for the statistical analyses.

The Effects of Fire on Water Quality Parameters. The Jemez Mountains and Pajarito Plateau were substantially burned by the Cerro Grande wildfire from May 3 to July 20, 2000. From June 26 to August 3, 2011, the Las Conchas fire severely burned portions of Water Canyon, Cañon de Valle, Pajarito Canyon, and Guaje Canyon. Based on previous studies, it is known that forest fires can impact surface water quality for a period of approximately 3 yr (Gallaher and Koch 2004, 088747). Following a forest fire, the volume of storm water increases, the amount of sediment and ash transported by storm water increases, and water chemistry changes. Samples collected post-fire were flagged; 461 of 1528 samples were collected post-fire.

Cluster analysis (CA) statistical methods. These multivariate statistical analyses determined if water-quality patterns exist within the storm water sampling stations that could identify natural groupings. The multivariate statistical techniques were used to reduce the large amounts of data to decipher patterns within the data that might not otherwise be observed. Ultimately, this approach allows for partitioning water chemistry samples into like groups. The general procedures recommended by Güler et al. (2002, 094417) for classification of water chemistry data were followed in this study. The statistical analyses performed on the data included hierarchical CA ([HCA], also known as CA), using Ward's minimum variance method based on standardized data.

Results

Figures 2–10 display the results of the CA using the PCB homolog data. Figure 2 is the "dendrogram," or tree diagram, that lists each observation, and shows which cluster it is in and when it entered its cluster. The scree plot beneath the dendrogram has a point for each cluster join. The ordinate is the distance that was bridged to join the clusters at each step. Often there is a natural break where the distance jumps up suddenly. These breaks suggest natural cutting points to determine the number of clusters. We used two-way clustering, so a color map is included with the column dendrogram at its base. The columns must be measured on the same scale (e.g. the congener fractions as on a scale of 0 to 1). Another term for this component is heat map. We identified four clusters of sample IDs for homologs. These cluster signatures are displayed using the parallel coordinates plots displayed in Figure 3 (four panels). Figure 4 is a map showing the clusters by location. Figures 5 and 6 show a lack of difference in total PCB concentrations over time or by data source, respectively. Figure 7 compares the homolog profiles of Clusters 1, 2, and 3 to Aroclor mixtures. Figure 8 shows the total PCB concentrations of the cluster. Cluster 3 has total PCB concentrations most similar to background (Figure 8). Figures 9 and 10 evaluate cluster 3 results only and show an apparent post-fire increase in total PCBs and a distance affect for this background homolog cluster.

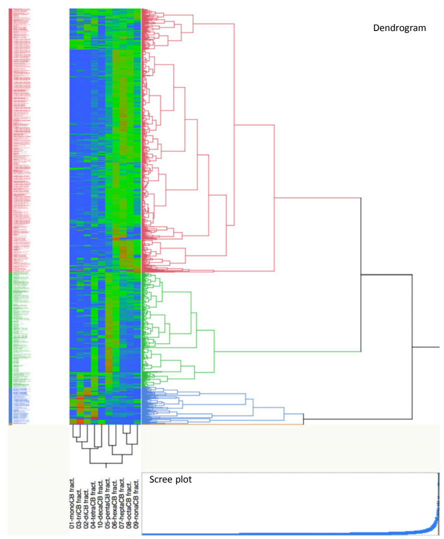

Figure 2. Dendrogram, or tree diagram, with two-way clustering color or heat map. The coloring indicates the relative concentration of the homologs. The homologs are ordered by the number of chlorines

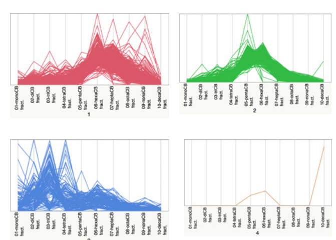

Figure 3. Parallel coordinate plots for clusters 1–4. The homologs are ordered by the number of chlorines

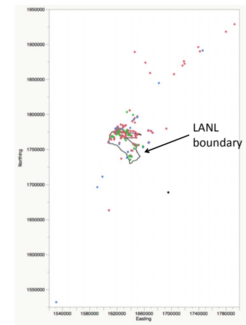

Figure 4. Posting plot showing the locations marked by homolog cluster. Same symbols are used in Figures 5 and 6.

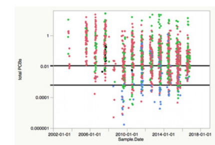

Figure 5. Time series plot of total PCBs marked by the homolog clusters. Same symbols are used in Figures 4 and 6. Upper line is background (0.0117 ug/L); lower line is the standard (0.00064 ug/L).

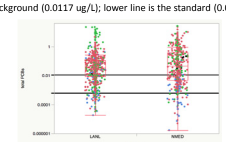

Figure 6. Box plot of total PCBs by data source and marked by the homolog clusters. Same symbols are used in Figures 4 and 5. Upper line is background (0.0117 ug/L); lower line is the standard (0.00064 ug/L).

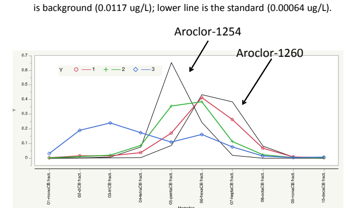

Figure 7. Overlay plot of the average homolog fractions for clusters 1, 2, and 3 compared to Aroclor™ mixtures for Aroclor-1254 and Aroclor-1260 (Frame et al. 1996).

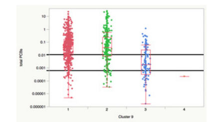

Figure 8. Box plot of total PCBs for clusters 1, 2, 3, and 4. Upper line is background (0.0117 ug/L); lower line is the standard (0.00064 ug/L).

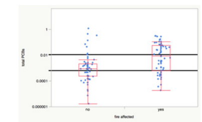

Figure 9. Box plot of cluster 3 (dechlorinated) comparing fire-affected to not fire-affected. Upper line is background (0.0117 ug/L); lower line is the standard (0.00064 ug/L).

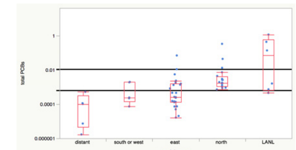

Figure 10. Box plot of total PCBs for cluster 3, not fire-affected only. Boxes are sorted by distance from LANL groups (from distant to LANL on-site). Upper line is background (0.0117 ug/L); lower line is the standard (0.00064 ug/L).

Conclusions

Multivariate statistical analysis were used to define groups that can be associated with sources and non-sources. The dechlorinated cluster group was widely distributed both on-LANL and off-site, and may reflect environmental weathering and possibly background. Concentrations of the dechlorinated cluster were greater in post-fire samples. We removed post-fire effects and observed greater total PCB concentrations on-LANL compared to distant locations. The reasons for this trend are not clear and could reflect real trends or be related to a substantially reduced sample size. Homolog cluster analysis may be a useful tool to independently establish background levels of PCBs in storm water.

References

Frame, G.M., J.W. Cochran, and S.S. Bøwadt, December 1996. "Complete PCB Congener Distributions for 17 Aroclor Mixtures Determined by 3 HRGC Systems Optimized for Comprehensive, Quantitative, Congener-Specific Analysis," Journal of High Resolution Chromatography, Vol. 19, pp. 657668. (Frame et al. 1996, 106797)

Gallaher, B.M., and R.J. Koch, September 2004. "Cerro Grande Fire Impacts to Water Quality and Stream Flow near Los Alamos National Laboratory: Results of Four Years of Monitoring," Los Alamos National Laboratory report LA-14177, Los Alamos, New Mexico. (Gallaher and Koch 2004, 088747)

Güler, C., G.D. Thyne, J.E. McCray, and A.K. Turner, August 2002. "Evaluation of Graphical and Multivariate Statistical Methods for Classification of Water Chemistry Data," Hydrogeology Journal, Vol. 10, pp. 455-474. (Güler et al. 2002, 094417)

LANL (Los Alamos National Laboratory), May 2012. "Polychlorinated Biphenyls in Precipitation and Stormwater within the Upper Rio Grande Watershed," Los Alamos National Laboratory document LA-UR-12-1081, Los Alamos, New Mexico. (LANL 2012, 219767)

LA-UR-17-27465