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PhD Thesis, May 2005

Abstract

Polychlorinated biphenyls (PCBs) were manufactured in the mid 1900s for industrial use. PCBs were subsequently introduced into the environment and are now considered ubiquitous pollutants, found in most animal and human adipose samples, milk, sediment, and numerous other matrices. The term PCBs refers to 209 chlorinated compounds of the biphenyl molecule (*congeners*). The number and location of the chlorines govern both the environmental fate and toxicity of each congener. Exposure to PCBs is reported to be the cause of cancer and non-cancer related health problems, including problems with the immune system, reproductive system, nervous system, and endocrine system.

In the first part of this study, the relationship of the congeners in the commercially manufactured PCB mixtures (*Aroclors*) are evaluated to identify congeners that maintain a constant relative proportion in sequentially more-highly chlorinated *Aroclors* (*tracker pairs*). Focusing on the correlated congeners eliminates the need to know the source contaminating *Aroclors*. This is useful in tracking the fate of PCBs in the environment. Using the congener distributions of eight *Aroclors*, 276 pairs of correlated congeners, constructed from 95 individual congeners, are identified.

In the next part of the study, congener distributions from Hudson River sediments are evaluated to determine if the relationships of the correlated congener pairs are statistically distinguishable from those found in the *Aroclors*. Conclusive evidence of a shift in the congener proportions, such as by biotransformation, occurred in more of the 276 correlated congener pairs than expected, based on a rigorous statistical test, if no *in situ* PCB weathering had occurred in the sediments.

The final part of the study examines the changes in correlated congener distributions in Hudson River sediments to determine the likely pathways of *in situ* PCB dechlorination. Starting with eight initial *Aroclor* distributions, ten theoretically possible pathways of dechlorination are modeled and compared to the field weathered congener distributions. The results indicate that flanked chlorines are the most likely to be removed during *in situ* dechlorination in the Hudson River sediments studied. No systematic difference in the preferred dechlorination pathway is observed across the sampling sites in the study area. Qualitatively similar results are obtained using a shortlist of 53 dechlorination indicator congeners.