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1-4 NOVEMBER GSA 2015 Baltimore, Maryland, USA

Volatilization of polychlorinated biphenyls: Implications for their distribution, forensics and toxicity in urban environments

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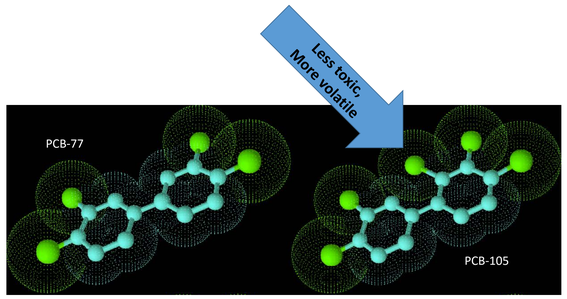

Figure 1: Chlorine substitution for a PCB congener with no ortho-chlorines (IUPAC 77), and a congener (PCB-105) with one ortho substitution that is less toxic and more volatile than PCB-77.

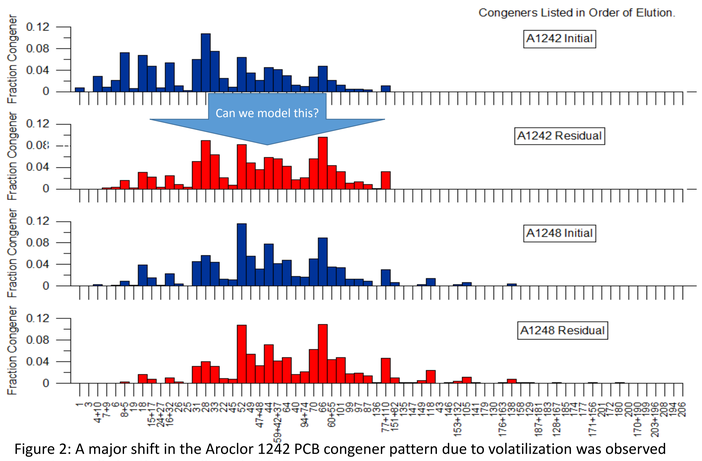

Figure 2: A major shift in the Aroclor 1242 PCB congener pattern due to volatilization was observed experimentally by Chiarenzelli et al. (1997).

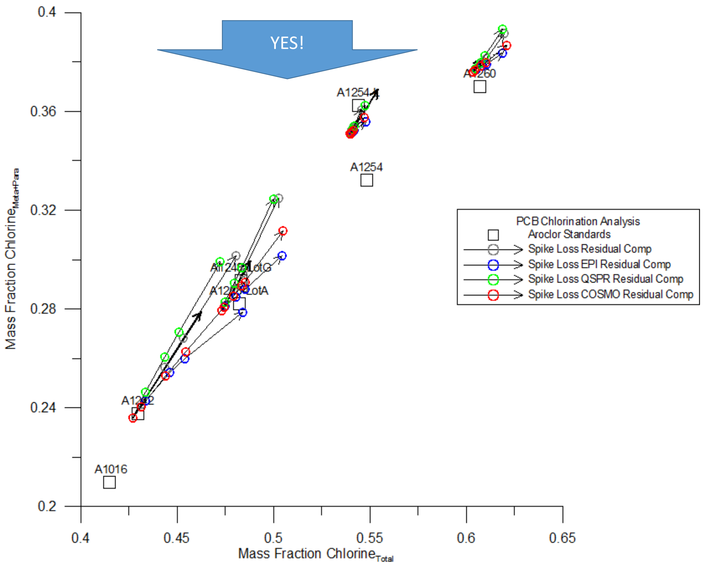

Figure 3: The volatilization loss observed by Chiarenzelli et al. (1997) is shown as dark arrows. Three types of volatilization models span this observation. Vapor pressure estimation methods are estimates to be able to include all congeners in each Aroclor mixture: "EPI" refers to a modified Gran method estimate from the EPI Suite software (EPA, 2015); "QSPR" is a molecular modeling method from van Noort (2009); "COSMO" is a molecular modeling method from Phillips et al. (2008).

References
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Polychlorinated biphenyls (PCBs) are a group of man-made organic chemicals found virtually everywhere in the environment due to their widespread use historically, with higher concentrations around urban and industrial areas. There are 209 possible PCB congeners each with a unique chlorine substitution pattern, they tend to be quite stable under environmental conditions, and 12 have been assigned a Toxic Equivalency Factor (TEF) to relate their concentrations to a highly toxic dioxin compound. The volatilization of PCBs has been shown through previous experiments to have a potentially large effect on congener composition due to differences in vapor pressures among the congeners. In addition to the expected overall loss of lower molecular weight congeners, it was observed that the less toxic ortho-substituted congeners were more volatile, potentially leaving the residual relatively more toxic. The original investigators did not report concentrations of the congeners with TEFs, but recent work on congener-specific vapor pressure estimates allows us to model the changes in the relative toxicity of a congener mixture during volatilization. Here we test whether the observations can be reproduced using three vapor pressure estimating methods. We found that all although all methods captured the general compositional changes, but that a quantitative structure-property relationship method best matched the observed preferential loss of ortho-substituted PCBs. In order to see these changes, a large portion of the starting material has to be lost. For example, in order for Aroclor 1242 (42 wt% chlorine) to approach the 48 wt% chlorine composition of Aroclor 1248, at least 70% of the original Aroclor 1242 mass must be lost. The rate of this loss is highly variable, depending on temperature, surface area and interactions with water or other solvents. However, if this degree of fractional mass loss is achieved, the residual Aroclor 1242 reaches approximately 46% chlorine, has a congener composition very similar to Aroclor 1248, and its relative toxicity increases. The weighted mean TEF approximately doubles, but is still an order of magnitude lower than the weighted mean TEF of Aroclor 1248. These changes have been shown experimentally with very small amounts of PCBs, and their practical importance remains to be demonstrated.

Modeling volatile losses

- PCB congeners exhibit substantially different properties based on chlorine substitution patterns (Figure 1)
- Chiarenzelli et al. (1997) showed (1) that volatile losses led to a residual Aroclor 1242 congener pattern that was similar to Aroclor 1248 (Figure 2), and (2) preferential loss was found in ortho-substituted congeners
- We compiled vapor pressure estimates and were able to model both of these findings (Figure 3)
- Vapor pressure estimates can model observed Aroclor vapor pressure dependency on temperature (Figure 4), which is important for estimating volatile losses in environmental and industrial settings.
- Of the three vapor pressure methods, QSPR best matches observed variability within homolog groups (Figure 5), and ranges across 6 orders of magnitude
- Here we focus on volatile losses from pure phase Aroclors, making vapor pressure the key parameter (Figure 5). Henry's Law constants show a much smaller overall shift (around 1 order of magnitude) across the congeners (Figure 6).

Toxicity

The toxicity of PCB congeners is measured in relative to a tetra-chloro dioxin (2,3,7,8-TCDD).

- Planar, or mostly planar PCBs with few to no ortho-substituted chlorines interact in a similar manner to dioxins (which are planar).
- These Toxicity Equivalency Factors, or TEFs, may then be used to calculate the Toxicity Equivalency Quotient, or TEQ.
- As a PCB mixture volatilizes, the shifting congener mixture affects the mean weighted TEQ (Figure 7)
- Wide ranges in volatilization rates (Figure 8) means that it is not clear whether these theoretical changes in TEQ are realistic

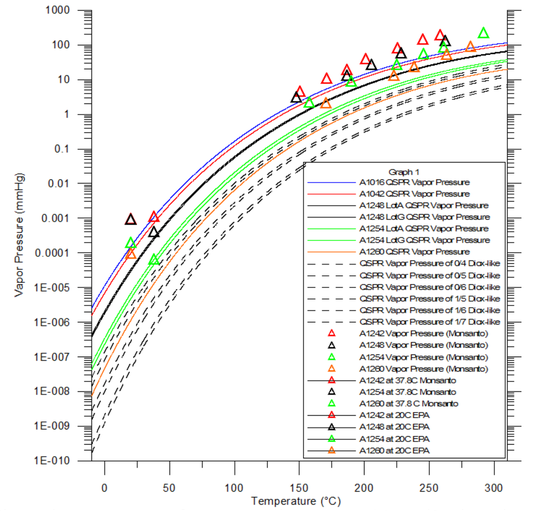

Figure 4: Observed vapor pressures for commercial congener mixtures (Aroclors, shown as triangles) can be matched by QSPR estimation (van Noort, 2009). Note the systematically lower vapor pressure for non-ortho congeners (dashed lines).

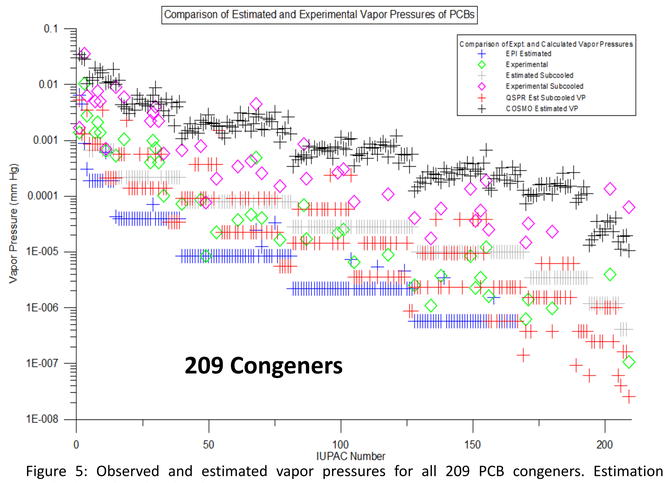

Figure 5: Observed and estimated vapor pressures for all 209 PCB congeners. Estimation methods are listed with references in Figure 3.

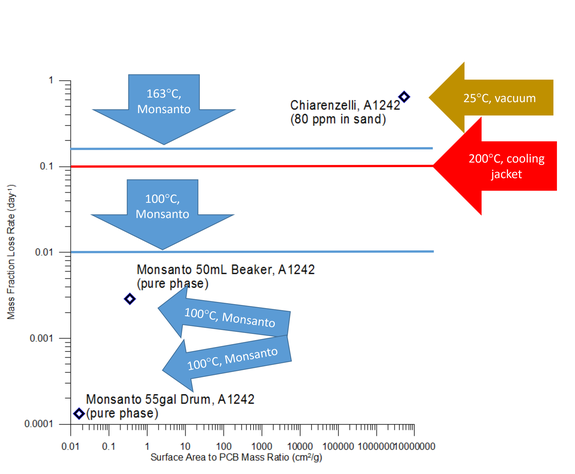

Figure 8: Reported mass fraction losses at various temperatures and surface area to mass ratios.

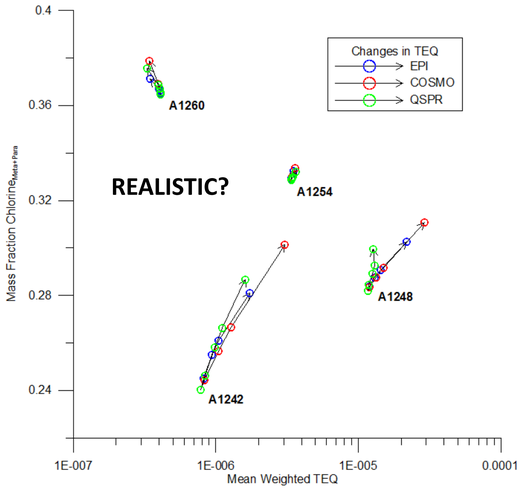

Figure 7: Theoretical shifts in mean weighted Toxicity Equivalency Factor (TEQ) due to the same shifts in ortho substitution shown in Figure 3.0

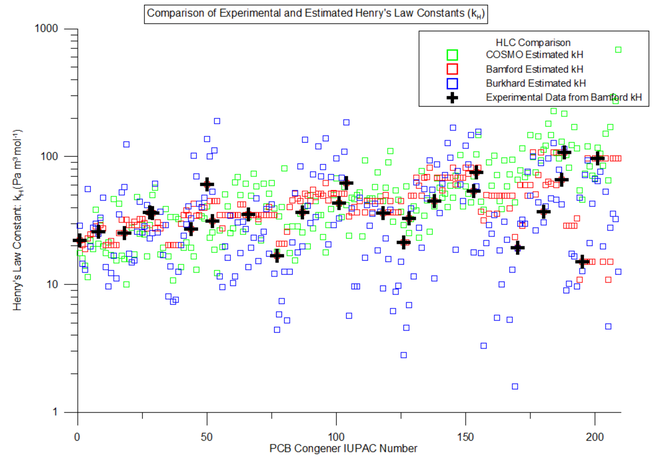

Figure 6: Observed and estimated Henry's Law constants.