

## SOURCES OF ERROR IN SAMPLING AND ANALYSIS OF PCBS IN INDOOR AIR

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### Introduction

Indoor air exposure to polychlorinated biphenyls (PCBs) from building materials, such as caulk and joint sealants, has recently been receiving increased attention in the United States (US), although it has been recognized as an issue in Europe for a number of years<sup>1</sup>. In September 2009, the US Environmental Protection Agency (USEPA) issued guidance, which included sampling and analysis methodologies<sup>2</sup>. Although this guidance contains useful information, investigators need to be aware of a number of potential issues with the sampling and analysis of air for PCBs. This paper discusses available sampling and analysis methodologies for PCBs in indoor air with their associated uncertainties and provides some recommendations on how to avoid potential pitfalls while obtaining needed information in a cost efficient manner.

Historically, air sampling for PCBs in indoor air was performed using active air sampling methods based on ambient air methods. Solid phase media phases, such as Tenax®, Florisil®, polyurethane foam (PUF) or XAD<sup>tm</sup> resin, are used as sorbents with pumps drawing in air at typical flow rates of 1-2 L/minute with sampling times of 1-8 hours. Most sampling was performed for occupational exposure evaluation. The three main US regulatory agency sampling methods include the National Institute for Occupational Safety and Health (NIOSH) 5503<sup>3</sup>, the Occupational Safety and Health Administration (OSHA) PV2088<sup>4</sup>, and USEPA TO-4 and TO-10<sup>5</sup>. In the last 10 years, the use of passive air sampling (PAS) techniques have been developed and validated for PCBs. These include the use of polyurethane foam (PUF) disks<sup>6</sup>, XAD canisters<sup>7</sup>, and thin film on indoor window glass<sup>8</sup>. These PAS techniques provide time averaged concentrations. An important concern with any sampling type is the capacity of the media. When active sampling has run for too long at a given air concentration, a breakthrough can result. When PAS sampling has run for too long, re-equilibration of the sample can result, which is undesirable.

The USEPA, NIOSH and OSHA sampling documents are all based on work originally carried out during the 1970's and 1980's. At that time, the principal concern was for occupational exposures from the use of Aroclor<sup>tm</sup> containing liquids or high concentration solid materials. Aroclor<sup>tm</sup> analysis, based on Webb-McCall quantitation, was the state of the art at that time<sup>9</sup> and the concentrations of concern (NIOSH recommended exposure limits (RELs) or OSHA permissible exposure limits (PELs)) were greater than 1000 ng/m<sup>3</sup>. More recent exposure concerns are for vapor phase PCBs or indoor dust. Vapor phase PCBs will have a different air pattern than the oil or solid phase and are at levels much lower than those found in an occupational exposure setting. In addition, analytical method advances have also occurred, including the use of High Resolution Gas Chromatography (HRGC) with detection by electron capture detection (ECD), low resolution mass spectrometry (LRMS), and high resolution mass spectrometry (HRMS), all of which have much greater sensitivity and selectivity. Homolog level analysis is available using mass spectrometry MS. Congener specific analysis can be performed with ECD or MS detection. The congener or homolog type analysis allows for a more accurate determination of the air concentration and allows for the "fingerprinting" of a sample which can be useful in source identification. As a result of the changing exposure scenarios and analytical advances, Aroclor<sup>tm</sup> analysis of indoor air samples is no longer an acceptable methodology,

despite its widespread use. The importance of this type of information and problems with the use of Aroclor<sup>™</sup> analysis are illustrated with example data below.

### Materials and Methods

The equilibrated vapor phase concentration of PCBs over solids (sand or soil) spiked with varying concentrations of PCBs oil (Aroclor<sup>™</sup> 1260) was determined using the USEPA flux chamber technology. Air was sampled using PUF/XAD-2/PUF sorbent, and those air samples were analyzed for all 209 congeners using HRGC-HRMS with isotope dilution (ID) (USEPA Method 1668A)<sup>10</sup>. A total of six different concentrations were tested to provide a range of air concentrations. Further details are provided elsewhere<sup>11</sup>.

### Results and Discussion

The congener patterns of spiked solid samples closely matched published patterns for Aroclor<sup>™</sup> 1260<sup>12</sup>. However, the air sample (vapor phase) congener (and homolog patterns) differed significantly from the original oil in the solid samples (Figure 1). Furthermore, the air patterns observed did not match any Aroclor<sup>™</sup>. A predictive model for vapor phase congener patterns was developed based on the congener vapor pressure and observed relative mole fraction. The predicted patterns agree reasonably well with the observed (Figure 1). The predictive model was then applied to published Aroclor<sup>™</sup> data to produce predicted vapor phase patterns for each of the five major Aroclors<sup>™</sup>. Figures 2 and 3 illustrate these patterns for congeners and homologs. Using this information for Aroclor<sup>™</sup> oil and predicted vapor phase (congener or homolog patterns), the observed vapor phase data (congener or homolog) can be fit to predict the original source Aroclor<sup>™</sup> type(s) using techniques such chemical mass balance (CMB) or principal component analysis (PCA). Figure 4 shows that there is little correlation (poor  $R^2$ ) between the vapor phase of soil to its original parent Aroclor<sup>™</sup> although a better  $R^2$  was observed comparing the vapor phase to Aroclor<sup>™</sup> 1221. Similar changes in PCB congener distributions compared to the parent Aroclor<sup>™</sup> sources have been observed by others<sup>13</sup>. More recently the existence of PCB-11, a “non-Aroclor” PCB, has been reported in air<sup>14</sup>. This congener would not be quantified by Aroclor<sup>™</sup> analysis. Thus, the use of Aroclor<sup>™</sup> based analysis with Webb-McCall quantitation would miss specific congeners and would provide erroneous quantitation and little useful pattern information.

For investigations of indoor air where building materials or indoor dust are a suspected source, it is recommended that sampling be performed using active sampling with PUF/XAD-2/PUF sorbent or PAS with PUF disks. These sampling materials are well established and readily available. The use of field surrogate(s) (for active air sampling) or performance reference compounds (PRCs) for PAS is strongly recommended. One advantage of using PUF PAS disks is that samples can be collected from multiple locations in a building, and/or over longer time periods more affordably than using active air sampling methods. Extraction of the air sample media can be performed using several well characterized methods, including soxhlet or pressurized liquid extraction. Analysis of sample extracts should be performed using HRGC-ECD (congener specific), HRGC-LRMS (congener specific or homolog), or HRGC-HRMS (congener specific). The use of Aroclor<sup>™</sup> analysis with Webb-McCall quantitation is not recommended. The analysis of homologs (which will require a minimum of 19 congeners)<sup>15</sup> should only be undertaken using MS and will provide accurate totals but less pattern information. Where congener specific analysis is performed, the exact congener list may vary depending on the type of information being collected. For HRGC-ECD, the use of dual columns or a PCB analysis optimized column, such as the HT-8 PCB, will reduce uncertainties due to coelutions of congeners. One of the issues that has hampered adoption of congener specific analysis has been the availability of standards for calibration; however, a congener solution containing 144 congeners is commercially available (Accustandard mix 1-5) and has been used successfully with both ECD and MS methods<sup>16</sup>. Where very accurate total quantitation and/or fingerprinting are required, a longer list of congeners (up to 209) should be used. Routine quality assurance/quality control (QA/QC) protocols should include field and lab blanks, duplicate samples and extractions, and the use of recovery, cleanup and injection standards and second source standards. While there is no SRM currently available for air samples, the analysis of an SRM such as NIST sediment or urban dust can provide additional confidence in the results.

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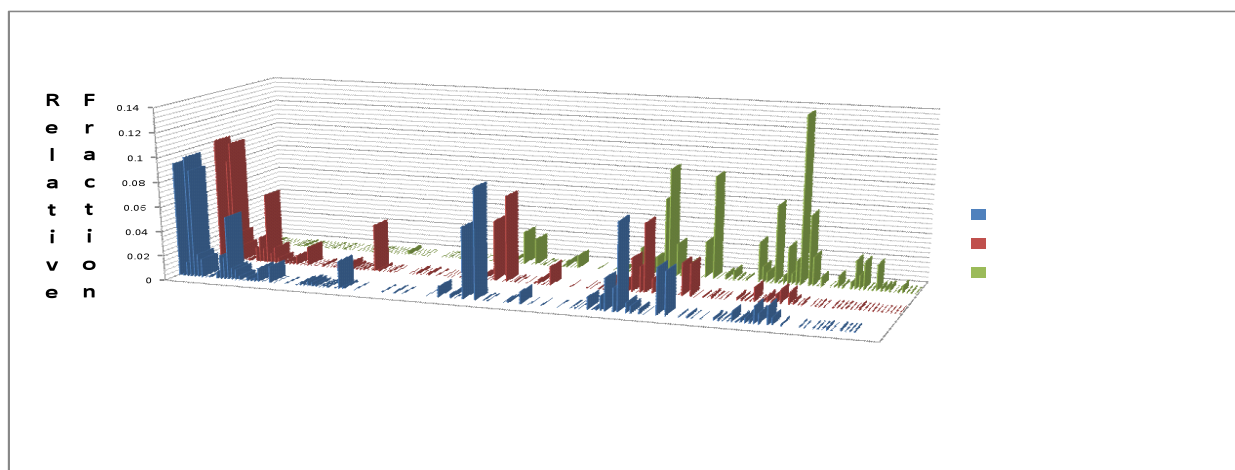


Figure 1. Patterns of observed air and oil with predicted vapor phase

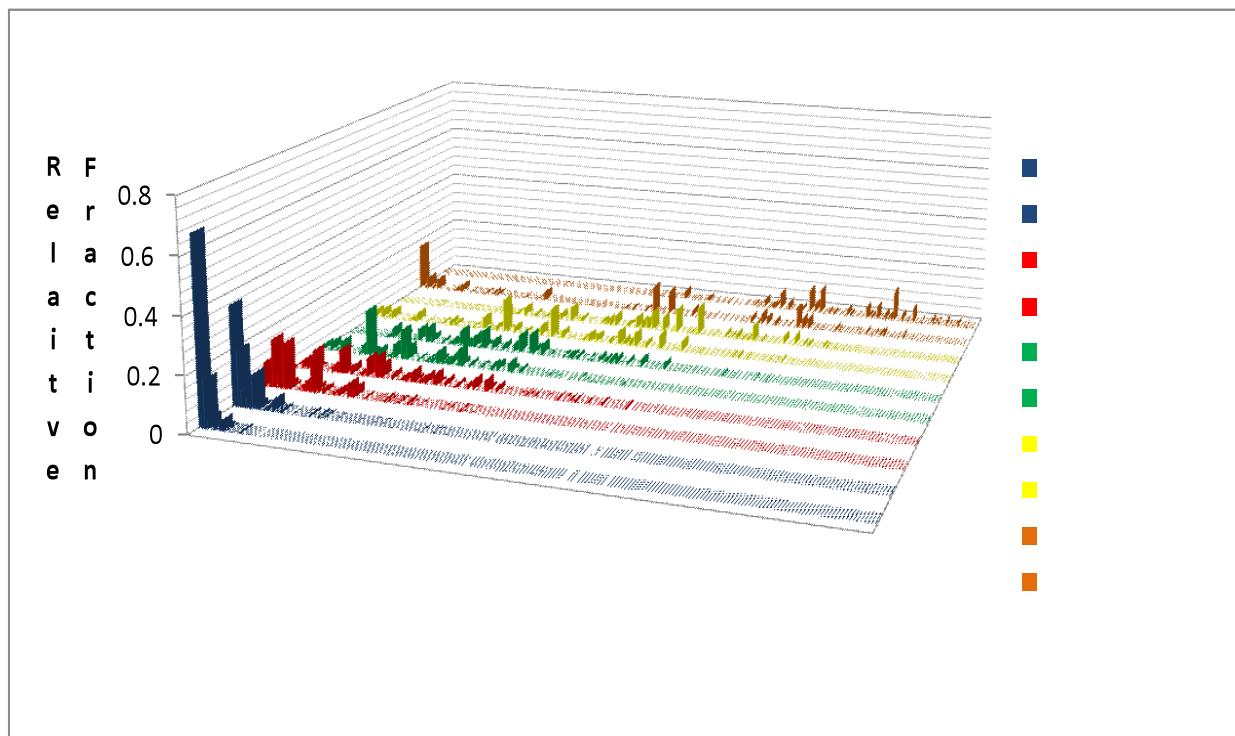


Figure 2. Comparison of selected Aroclor™ oil and predicted vapor phase

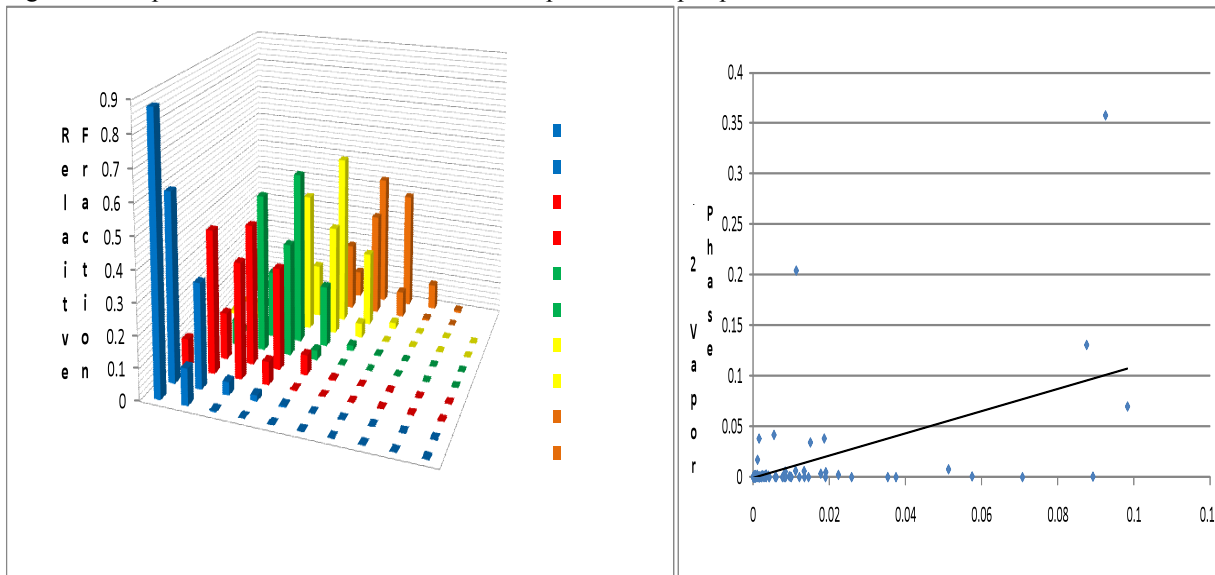


Figure 3. Comparison of selected Aroclor™ oil and predicted vapor phase

Figure 4. Correlation plot for soil 2 vapor phase vs. Aroclor™<sup>14</sup> 1221 Oil 1