

Analysis of PCB Congeners vs. Aroclors in Ecological Risk Assessment

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Abstract

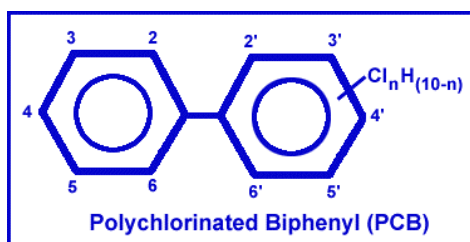
An issue of growing interest in the field of ecological risk assessment is whether analyses of polychlorinated biphenyl (PCB) contamination in environmental media should focus on Aroclors, which are commercial mixtures of PCB compounds, or more specifically on congeners, which are individual PCB compounds. As is often the case in such debates, the answer seems to boil down to "It depends." This issue paper presents a general description of PCBs and then discusses the differences in costs, data quality, and significance of results for the two analytical methods, as well as their pros and cons as tools in ecological risk assessment.

What are PCBs and why are they important in assessing risk?

Polychlorinated biphenyls (PCBs), all of which are man-made, are among the most stable organic compounds known. Each PCB consists of a biphenyl molecule with a specific number of attached chlorine atoms (see diagram on the next page). There are 209 distinct PCB compounds (known as congeners) with from 1 to 10 chlorine atoms on a biphenyl molecule. The number and placement of the chlorine atoms on the biphenyl molecule determines how the congener is named and dictates its environmental fate and toxicity. PCBs generally occur as mixtures of congeners; the most common commercial mixtures are called Aroclors. Aroclor names reflect the percent chlorine (by weight) of the mixture (e.g., Aroclor 1242 is 42% chlorine by weight), with the more chlorinated mixtures generally being the most persistent and toxic.

Two mechanisms allow PCB concentrations to change in the environment: degradation and weathering. Under normal environmental conditions, PCBs are slow to degrade. Microbial degradation depends on the position of the chlorine atom on the biphenyl molecule and the degree of chlorination. Higher chlorinated compounds (those with five or more chlorine atoms) are more persistent in the environment and are not readily transformed by bacteria. The number and position of the chlorine atoms on the biphenyl rings also influence how biological organisms incorporate and are affected by exposure to PCBs. PCBs with hydrogen atoms on two adjacent carbon atoms are more readily metabolized than those with hydrogen atoms adjacent to the chlorine atoms. PCBs are highly soluble in lipids and are known to biomagnify in upper trophic levels. Congeners with higher chlorine contents (and higher $\log K_{ow}$ values) tend to bioaccumulate the most and, depending on structure, metabolize the least. The toxicity is influenced by the presence or absence of chlorines ortho to the phenyl ring. Since congeners tend to bioaccumulate and biomagnify, evaluations of potential adverse effects to ecological receptors are generally focused on upper trophic level organisms. Because of the persistence of PCBs in environmental media, analyzing the presence and concentration of PCBs is important in conducting ecological risk assessments. The growing issue, however, is whether such analyses

should focus on mixture of PCBs (Aroclors) or on individual PCB congeners. As discussed here, a number of factors need to be considered in making that decision.



What are the Differences between Aroclor and Congener Analyses?

Analytical methods for Aroclors include the EPA approved Method 8082, using capillary column with GC/ECD. This method typically has quantitation limits in the range of 36 to 540 $\mu\text{g}/\text{kg}$ wet weight in sediment. Lower reporting limits can be achieved through improved sample cleanup, and concentration steps. On the other hand, homologue-based¹ quantification methods using GC/MS and congener-specific analyses can achieve lower quantitation limits (0.02 to 0.6 $\mu\text{g}/\text{kg}$) but at generally higher costs. Table 1 compares the various methods, quantitation limits, and approximate costs associated with these various PCB analyses.

Table 1. Methods, Quantitation Limits, and Costs Associated with PCB Analysis

| Method | Quantitation Limits in Sediments ($\mu\text{g}/\text{kg}$) ** | Approximate Cost (\$/sample) | Comments |
|-------------------------|---|------------------------------|---|
| Aroclor using GC/ECD | 36 - 540 | 75 - 300 | May not meet DQOs. Aroclor analysis may over- or underestimate PCB concentrations because it is not a measurement of individual congeners but is instead is a pattern recognition estimate. Individual congeners will weather, degrade, and bioaccumulate at different rates. Aroclor analysis may severely underestimate toxicity. |
| Homologues using GC/MS | 0.02 - 0.2 | 1,000 | |
| Homologues using GC/ECD | 0.5 - 5 | 500 | Interferences may overestimate total PCB concentration |

¹ Homologue-based methods are defined by the chlorination of the molecule (e.g., monolog).

Table 1. Methods, Quantitation Limits, and Costs Associated with PCB Analysis (Continued)

| Method | Quantitation Limits in Sediments ($\mu\text{g}/\text{kg}$) ** | Approximate Cost (\$/sample) | Comments |
|---|---|------------------------------|--|
| NIST 18 congeners using GC/ECD | 0.5 - 5 | 250 | Interferences may overestimate total PCB concentration |
| Congener NIST/WHO ² list using GC/MS | 0.02 - 0.2 | 1,000 | |
| Congener NIST/WHO list using GC/ECD | 0.5 - 5 | 250 | May not be able to detect non-ortho (indicates position of chlorine molecule on the ring-clockwise ortho, meta, para) congeners. |

** Reporting limits can often be altered by cleanup and concentration, often with increased cost.

What are the pros and cons of the different methods?

PCB congener data offer many advantages over Aroclor data for environmental risk analysis. Congener-specific analyses generally offer lower detection limits and a higher information content from the analytical technique than do Aroclor analyses. The specific advantages of congener analysis are:

- It is easier to detect and discard results biased by interference caused by chemicals that coelute (come out of the column at the same time and therefore make it hard to determine type of compound) with PCBs;
- Quantitation of individual congeners is more accurate than estimating Aroclors;
- Composition of weathered, degraded, and metabolized PCB mixtures can be measured and interpreted easier using congener versus Aroclor analysis;
- Aroclor concentrations can be estimated using congener concentrations (dependent on the list of congeners);
- The toxicity of PCBs is congener-specific, and, therefore, measurement on an Aroclor basis may not accurately measure toxicity. Estimated risk based on congeners versus Aroclors may indicate the areal extent of contamination is substantially reduced. This finding may lead to significantly reduce cleanup costs.

The cons of using congener-specific analyses include cost and the general lack of toxicity data for most congeners. Most of the currently available ecotoxicity data are for Aroclor mixtures. However, toxicity equivalency factors (TEFs) for fish, birds, and mammals have been developed for one dozen congeners (i.e., PCB-77, 81, 105, 114, 118, 123, 126, 156,

² NIST list refers to National Institute of Standards and Technology; WHO refers to World Health Organization.

157, 167, 169, 189). Congener-specific analyses demand greater effort in terms of data reduction, quality assurance, and processing. A problematic area in congener analyses is comparability between laboratories. Sources of this variability include differences in coelution patterns, different lists of congeners are analyzed at different laboratories (labs are not yet synchronized with similar lists of analytes), and normal interlaboratory variation. Coelution of analytes is a major impediment in PCB congener-specific analyses. The use of dual column chromatography ECD or single column GC/MS-SIM (selective ion monitoring) screens out interferences, minimizes coelution of PCB congeners, and increases reliability of the data. Congener data generated by a single column GC-ECD should be interpreted cautiously. A strong quality assurance program, including reference materials (matrix specific when possible), is essential in conducting reliable congener-specific analyses.

When should Aroclor and/or Congener Analyses be performed?

The history, potential remedies, and risk management issues for each site being evaluated should be considered before selection of either Aroclor or congener-specific methods. The data quality objectives should be defined, including analytical reporting limits (not detection limits) and methods needed to achieve these limits. In addition, the intended end use of the data should be defined. Actual toxicity data exist for Aroclors, but congener-specific methods generally require the use of TEFs to determine potential adverse effects to ecological receptors (using total PCB equivalents).

Aroclor analyses may be appropriate when:

- The area will have a presumptive remedy to prevent exposure to ecological receptors (precluding use of any PCB analyses);
- The historical information suggests there are no sources of PCBs (precluding use of any PCB analyses);
- The Aroclors are detected at non-site-related sources;
- The use of TEFs is not defensible when used to predict adverse effects (e.g. using TEFs based on ingestion to predict dermal toxicity);
- The project is in the initial stages of investigation to determine presence or absence of PCBs or a preliminary estimation of risk.

Congener analyses may be appropriate when:

- PCB hot spots have been identified;
- Weathering, biotransformation (metabolism and variable bioaccumulation) have occurred;
- Lower reporting limits are required;
- Fingerprinting to determine source is necessary;
- Adverse effects (toxicity) have been observed and retrospective analysis using TEFs will help determine causation;
- Cleanup will be based on congener-specific TEFs.

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Acronyms

| | |
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| DQO | data quality objective |
| ECD | electron capture detector |
| GC/ECD | gas chromatography / electron capture detector |
| GC/MS | gas chromatography / mass spectrometer |
| GC/MS-SIM | gas chromatography / mass spectrometer - selective ion monitoring mode |
| NIST | National Institute of Standards and Technology |
| PCB | polychlorinated biphenyl |
| TEF | toxicity equivalency factor |
| WHO | World Health Organization |

Glossary

Aroclor: A common trade name for mixtures of PCBs. The mixtures have been widely used as coolants and lubricants in transformers, insulators, and other electrical equipment because of their highly stable properties. Because of their stability in the environment together with the toxicity and their propensity to biomagnify up the food chain, Aroclor mixtures can cause severe impacts to human and ecological systems.

Biomagnification: A measure of cumulative bioaccumulation from the media source through two or more steps in a food chain.

Coelute: More than one compound comes out of the column at the same time, making it difficult to determine the type of compound analyzed. Coeluting compounds can make it difficult to accurately measure specific compounds. Often coelution can be eliminated as a problem if different ions for each coeluting peak can be monitored.

Congener: Any single, unique, well-defined chemical compound in the PCB category is called a "congener." The name of a congener specifies the total number of chlorine substitutes and the position of each chlorine. There are a total of 209 congeners.

GC/ECD (Gas Chromatography / Electron Capture Detector): Analyzes Aroclor compounds but not individual congeners. One of the many instruments used in analytical measurement. It is very powerful in analyzing chlorinated compounds, but weak in quantifying specific congeners. The electrons emitted from ECD ionize the carrier gas eluded from GC, and the ionized gas subsequently reduces the current and is expressed as a response curve.

GC/MS (Gas Chromatograph / Mass Spectrometer): An instrumental analysis especially useful in analyzing for specific PCB congeners. The instrument consists of is a gas chromatograph coupled with a mass spectrometer to produce a 3-D dataset that is not available with traditional GC detectors (i.e., GC-ECD). The gas chromatography separates samples into fractions, and the mass spectrometer produces characteristic spectra. GC/MS operates under scan mode or selective ion monitoring mode (SIM). The scan mode produces the maximum qualitative information of the mass data, while SIM samples at a predetermined mass value to give maximum quantitative information.

GC/MS-SIM (Gas chromatography / Mass Spectrometry - Selective Ion Monitoring mode): A mode to run a GC/MS that increases sensitivity of the instrument by looking for only specific ions as opposed to scanning through a broad range. Spending more time looking for a few ions as opposed to hundreds increases the instrument sensitivity.

Homolog: Subcategories of PCB congeners having equal numbers of chlorine substituents. For example, the "Tetrachlorobiphenyls" (or "Tetra-PCBs" or "Tetra-CBs" or just "Tetras") are all PCB congeners with exactly 4 chlorine substituents that may be in any arrangement.

Log K_{ow} : Quantification of the degree of partitioning of a contaminant between a mixture of octanol and water (i.e., immiscible liquids). A chemical's propensity to biomagnify up the food chain is proportion to the log K_{ow} .

Meta: Indicates the position of a chlorine molecule on the ring. Meta indicates the second carbon (clockwise direction) and para indicates the third carbon location.

Ortho: Indicates the position of chlorine molecule on the ring. The ortho position indicates the chlorine is located on the first available carbon on the ring.

Para: Indicates the position of chlorine molecule on the ring. Para indicates the third carbon location.

Quantitation Limit: The lowest concentration of an analyte that can be reliably quantified within specified limits of precision and accuracy.

Toxicity Equivalency Factors (TEF): Scaling factors that estimates the toxicity of dioxin-like PCBs to that of dioxin (2,3,7,8-tetrachlorodibenzodioxin).

Trophic level: A functional classification of taxa within a community food web that is based on feeding relationships.

Informative Web Page Links:

For more information on PCBs and congener-specific analyses, the following links are provided:

<http://www.epa.gov/pcb>

<http://www.epa.gov/toxteam/pcb/pcbindex.html>

Laboratories

It is imperative when selecting a lab for PCB analyses to use one that not only performs congener-specific analyses, but that also has experience with delivering quality products. The cleanup procedures and concentration steps make congener-specific analysis very lab dependent. Find a lab that has a good reputation performing these analyses. Two examples of quality labs include Battelle Marine Sciences Lab in Washington State and the CH2M HILL Applied Sciences Lab in Oregon. Identification of these two examples does not constitute official Navy endorsement of these laboratories.