PCBs IN FRESHWATER AND MARINE SEDIMENTS: TRANSPORT, TRANSFORMATION AND TREATMENT

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STATISTICAL METHOD TO EVALUATE THE OCCURRENCE OF PCB TRANSFORMATIONS IN RIVER SEDIMENTS

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Introduction

Polychlorinated biphenyls (PCBs) were commercially produced from the 1930s to the 1970s as complex mixtures for a variety of uses. The bulk of the PCB contamination in the United States traces back to PCB mixtures produced by the Monsanto Industrial Chemicals Company. The term PCBs refers to 209 theoretically possible discrete chemical compounds called congeners. Each PCB congener consists of two benzene rings carrying one to ten substituted chlorine atoms, and is named based on the number of attached chlorines and their attachment location. Congeners with the same number of substituted chlorines, regardless of location, are referred to as isomers and are considered members of the same homolog group.

PCB Aroclors (such as A1242) were synthesized in a batch process by heating biphenyl and adding anhydrous chlorine in the presence of ferric chloride. The average degree of chlorination of the Aroclor batch was controlled by the reaction time to yield the desired physical and chemical properties. These PCB mixtures were designated with the Aroclor trademark (1). The total percent weight chlorine is indicated in the last two digits of the Aroclor designation, except in the case of Aroclor 1016 (41 percent chlorine by weight) (1). Based on the properties of the biphenyl molecule, as it is chlorinated and transformed into PCB congeners, some of the PCB congeners continue to accept chlorine at the same rate, or some predictable rate, thus fixing the ratio of some of the congeners with respect to others in the commercially manufactured Aroclors.

Dechlorination, the process by which one or more of the chlorines on the PCB molecule are removed, has been the subject of much research over the past several decades. Understanding if, and to what extent dechlorination is occurring in river sediments can have important implications for remedial design strategies. Due to the historical PCB reporting methods, it has been difficult to develop an in-depth understanding of the dechlorination process in field samples. Much of the confusion stems from not knowing the specific Aroclor (such as A1242) or Aroclors (such as a mixture of A1242 and A1254) that represent the original source contamination at a field location, thus providing no clear starting point for comparison.

This study broadens the definition of the starting point from knowing which Aroclors were present, to needing only know that the source contaminants were Aroclors by focusing only on PCB congeners that maintain a constant relative proportion in sequentially more-highly chlorinated commercial Aroclors. The percentages of one such pair of correlated congeners are shown in Figure 1.

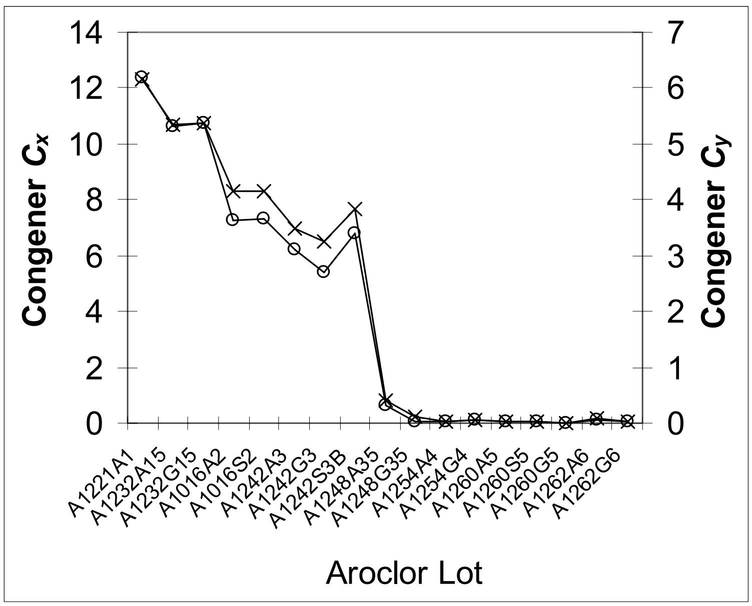

Figure 1: The Mass Weight Percentages of Correlated Congeners C_x and C_y

In Figure 1 the mass weight percentages of congeners C_x and C_y are plotted for each of the 17 Aroclor lots published by Frame and colleagues (2). Aroclor lot names are summarized below in Table 1. It is clearly evident in Figure 1 that the congeners maintain the same ratio relationship ($C_x \sim 2C_y$) in the commercial Aroclors. This suggests that congener C_x was preferentially formed in the synthesis process, as compared to congener C_y, by a factor of two. The methods for identifying correlated congener pairs are detailed below.

Data and Methods

The identification of correlated congener pairs in commercial Aroclors is made using data published by Frame and colleagues (2). The Aroclor data consists of characterized congener distributions in multiple lots (totaling 17) of eight different commercial Aroclors. Table 1 lists the commercial Aroclors and the lot names used in the published literature (2).

Table 1: FACDD Aroclor Relative Abundance Data Lots

Commercial Aroclor	*Number of Lots*	*Lot Names*	*Aroclor Lot Number*	*Aroclor Number (at a specific chlorination level)*
A1221	1	A1	1	1
A1232	2	A1.5 G1.5	2 3	2
A1016	2	A2 S2	4 5	3
A1242	3	A3 G3 S3B	6 7 8	4
A1248	2	A3.5 G3.5	9 10	5
A1254	2	A4 G4	11 12	6
A1260	3	A5 S5 G5	13 14 15	7
A1262	2	A6 G6	16 17	8

Identifying correlated congener pairs is a multi-step, computationally intensive procedure. Congeners are screened in a four step process. In step one, for each congener, the number of lots containing that congener is determined and congeners that are present in seven or more lots move to the next step. In step two, congeners that are present in three or more of the eight Aroclor chlorination levels move to the next step. Unlike steps one and two, in step three, data from a first congener (C_x) are examined in relation to data from a second congener (C_y). For each congener pair the correlation coefficient between the relative abundances of the congeners is computed and pairs with a coefficient greater than 0.97 continue to the next step. Step four confirms that the correlation coefficients generated were based on overlapping detections (those where the percent weight of C_x is greater than the detection limit and the percent weight of C_y is greater than the detection limit in the same Aroclor lot); this assures that the correlation coefficient reflects an actual correlation between the congeners, not a relationship between the detection limits of the congeners (one-half the minimum percent detected was used in computing the correlation coefficient in cases were the congener was not detected).

Results and Discussion

There are 276 congener pairs that meet all four screening requirements. These pairs are plotted in Figure 2.

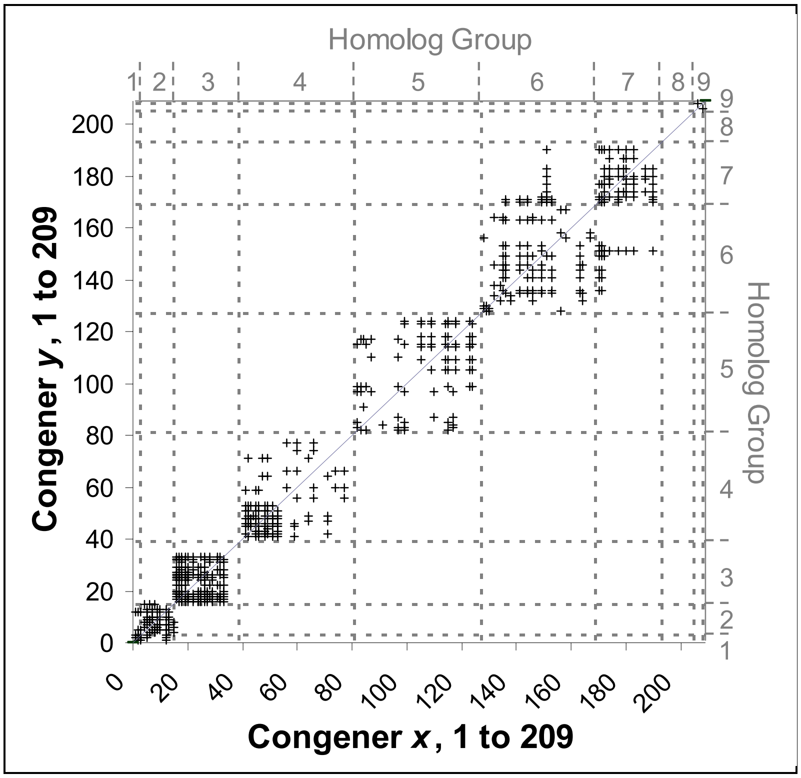

Figure 2: Correlated Congener Pairs in the FACDD (276)

Figure 2 consists of 552 points, 276 where each correlated pair is graphed as (C_x, C_y) and 276 where each pair is graphed as (C_y, C_x). The dashed lines throughout the graph divide the space into groupings by the number of substituted chlorines on the biphenyl molecule; the homolog number is indicated on the top and right side of the chart. This figure shows, with few exceptions, that a correlated pair consists of two congeners with the same number of substituted chlorines. It is expected that the physical/chemical properties governing the acceptance of a chlorine molecule in the PCB commercial production process would be similar in cases where the congeners are isomers. Finding this to be the case in most of the correlated pairs further validates the premise of the method.

These correlated congener pairs are being exploited to help identify shifts in congener distributions in river sediments. Ongoing research is focusing on elucidating dechlorination pathways in sediment samples collected from the Hudson River.

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