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Polychlorinated Biphenyl (PCB) Profiles, Degradation, and Aroclor Origin in Sediments of Escambia Bay, Florida

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Polychlorinated biphenyls (PCBs) are anthropogenic substances that have been detected in many parts of the environment and can have major negative impacts on ecosystem and human health. A documented release of PCBs from a nylon plant occurred in 1969 on the Escambia River just upstream of the Escambia Bay estuary along the north coast of the Gulf of Mexico. Other unreported releases of PCBs also likely occurred in the river and bay. The present study sampled sediments in the river and bay and assessed the predominant parent Aroclor of PCBs, and the changes in congener profile and toxic equivalents (TEQ) since the release. United States Environmental Protection Agency (US EPA) method 1668A, which provides quantitative data for 168 elutions, was employed for the analysis according to National Environmental Laboratory Accreditation Program procedures. Correlation analysis and principal component analysis of the PCB congener profiles for the sediments and Aroclors showed that the sedimentary PCB congeners are most similar to that of early production Aroclor 1254 made prior to 1971. Chronologically the use of the early production Aroclor 1254 corresponds to the time of the release. Since the release, overall chlorination of the sedimentary PCBs has decreased by 3% as a result of a shift in chlorination homolog profile to lesser-chlorinated congeners that presumably originated from dechlorination of Aroclor PCBs and from non-Aroclor source(s) of PCB 11, a dichlorobiphenyl. Despite a likely overall decrease in the quantity of dioxin-like PCBs, the TEQ/mole of sediment PCBs, did not substantially change because of a highly toxic congener (PCB 126) that was present at trace amounts in the sediments. There was a modest increase in lesser-chlorinated O,P-congeners that are suspected to have some toxicity to mammals. These findings have relevance for the evolution of environmental PCBs, which has not been studied in this system.

Keywords: polychlorinated biphenyls (PCBs), Aroclors, PCB dechlorination, PCB toxic equivalents (TEQ), environmental toxicology

Introduction

Polychlorinated biphenyls (PCBs) are a group of chemicals that are of special concern because they have been demonstrated to have major negative environmental and human health impacts (Agency for Toxic Substances and Disease Registry [ATSDR], 2006; Safe, 1992). Researchers studying pesticides detected a release of PCBs into the waters of the lower Escambia River in northwest Florida, United States, in 1969 (Duke et al., 1970). The PCBs were found to have originated from a nylon manufacturing facility and the release may have occurred over period of several months to 1 year. Subsequent investigations have shown the presence of PCBs throughout Escambia Bay (Olinger et al., 1975; Mohrherr et al., 2009) presumably transported there by the Escambia River that is the major tributary of the bay and perhaps from other sources. The PCBs have had an impact on shellfish (Karouna-Renier et al., 2007). The Florida Department of Health (2009) has posted a consumption advisory for Escambia Bay for the stripped mullet (*Mugil cephalus*). PCBs have persisted in the sediments for approximately 40 years (Duke et

al., 1970; Mohrherr et al., 2009) but have been the subject of few systematic scientific studies. Some studies of sediments in the bay by several agencies in the 1990s were conducted, with results compiled in a geographic information system (GIS) format by DeBusk et al. (2002). Some additional information is in a report related to a dredging study for barge channel maintenance (EA Engineering, Science, and Technology, 1999). However, no assessment has been made of the rate of degradation, changes in congener profile, or changes in toxic equivalents (TEQ) of the sediment PCBs in the Escambia System. The present study aims to fill that gap in knowledge, including the potential origin of PCBs in Escambia Bay.

The present study covers the Escambia Bay (9324 ha) and lower River (85 km portion of the Escambia River that is in the State of Florida), which are situated on the northeast coast of the Gulf of Mexico (Figure 1). No attempt was made in this study to directly assess spatial and temporal variability in PCB concentrations. The bay and lower river sediments, and associated pollutants, are subject to currents (Olinger, 1975) and strong tidal surges during hurricanes and floods that confound the precise origin of the sediments. Additionally, there has been repeated dredging of a barge channel from the nylon plant through the bay's length (EA Engineering, Science, and Technology, 1999) and the spoils have been disposed about

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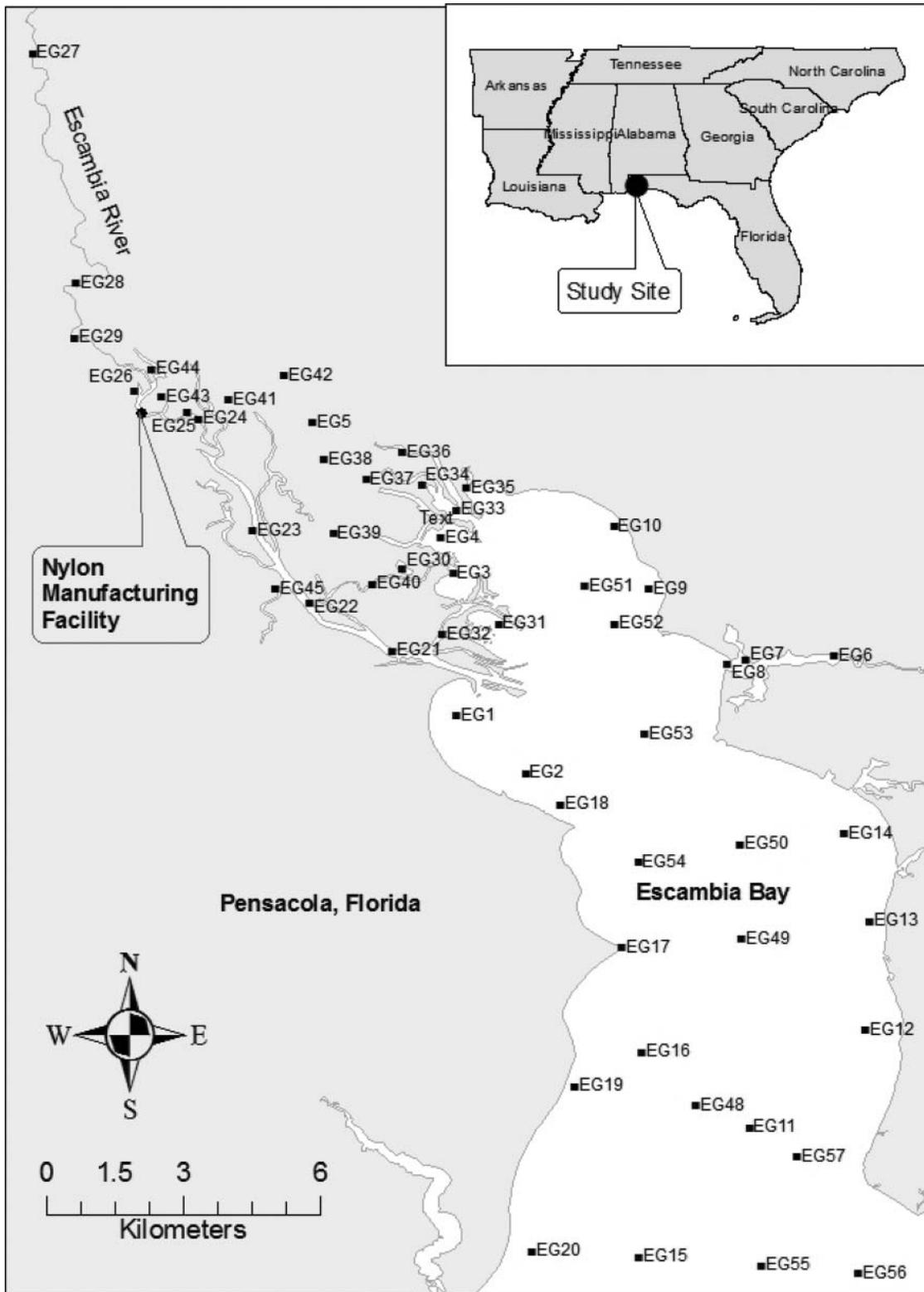
Figure 1. Map of the study area and sampling sites.

the river and bay system without records being kept. Previous studies for this region have reported up to a maximum of 28 separate PCB elutions depending on the method of analysis used (Debusk et al., 2002; EA Engineering, Science, and Technology 1999), yielding incomplete PCB congener information. While most PCB methods analyze only a small number of congeners, reports of studies using United States Environmental Protection Agency (US EPA) Method 1668A, which yields more accurate quantitative and qualitative information for all 209 PCBs, have appeared in the literature (e.g., Howell et al., 2008; Martinez et al., 2009). We used this more inclusive method in this study to assess the congener profiles of sediment PCBs in the Escambia System.

PCB impact on biota is based on dioxin-like (DL) toxicity of 12 of the PCBs, which is typically expressed as toxic equivalents (TEQ), and on total PCB quantity within the sediments (Buchman, 2008; MacDonald, 1994a; 1994b). Other concerns are reports of para, ortho-(O,P) chlorinated non-DL PCB toxicity (Ganey and Boyd, 2005) resulting from remediation activities (Bae et al., 2001; Ganey et al., 2000; Mousa et al., 1998). It has been suggested that DL PCBs transformed to non DL O,P-PCB congeners may pose additional health risks to mammals (Ganey and Boyd 2005; Ganey et al., 2000) and it seems possible that this toxicity could extend to other taxonomic groups. An important local issue is if similar accumulation of potentially toxic byproducts is occurring from natural PCB degradation in the Escambia System.

The current study utilized the full suite of PCB congeners obtained from US EPA Method 1668A and determined the predominant Aroclor released to the Escambia System, congener profile transformation, and toxicological changes related to TEQ and the changes of O,P-chlorinated PCB congener profiles. These findings have implications for impacts of DL PCB and non-DL PCB toxicity upon the biota of other estuarine systems elsewhere.

Materials and Methods

Sediment samples were collected at 57 sites with a stainless steel ponar dredge (Figure 1). At each site, five local grab samples were composited. The composited samples were placed into pre-cleaned dedicated sampling containers, preserved on wet ice, and sent to the analytical laboratory the day of sampling. Columbia Analytical Services in Houston, TX, performed the PCB analyses. US EPA and State of Florida Department of Environmental Protection (FDEP) approved sample handling, sample extraction, and sample analytical methodologies were used as specified for National Environmental Laboratory Accreditation Program (NELAP) accredited laboratories. All laboratory quality assurance / quality control (QA/QC) procedures had results within acceptable limits as specified in a US EPA-approved Quality Assurance Protection Plan (QAPP) and NELAP guidelines. US EPA Method 1668A was employed to detect the concentrations of the 209 PCB congeners with isotope dilution-high

resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS).

For comparative purposes and when feasible, profile components were expressed as mole% composition rather than the more often used weight percent composition. Changes in mole % give a better accounting for change of total PCBs because the molecular weight of the PCBs is not constant and ranges from 188.0 (mono-CB) to 493.7 (deca-CB). SYSTAT statistical package was used to determine correlations and principal component analysis (PCA). There were a total of 168 elutions detected for Escambia PCB congeners. Aroclor 1254 data derived from Johnson et al. (2008) that were obtained from a version of US EPA Method 1668a that yielded an elution pattern that was very similar to the one of the present study were recalculated and expressed in mole%. The results from the present study were also correlated with the 209 elutions published by Frame et al. (1996) by combining when needed the separate elutions of Frame et al. (1996) to match multiple congener elutions of this current study. Each correlation was thereby based on 168 data points. The PCA was run on the $\log_{10}$ transformed relative proportions (%) of the 168 elutions in the individual samples and Aroclors, similar to procedures used by Zhang et al. (2007) and Cachada et al. (2009). No rotation was performed. For TEQ calculations, the updated 2005 World Health Organization TEF values (Van den Berg et al., 2006) were used. The contribution of an individual congener to the total TEQ of the DL-PCBs was calculated by multiplying the congener's TEF value with its proportional contribution, on a mole basis, to the DL-PCBs.

Results and Discussion

General Composition

Detected PCB concentrations ranged from 0.9 to 125.9 mg/kg with a mean of 17.9 mg/kg. Of the 57 samples, 12 exceeded the FDEP threshold effects level (TEL) of 21.6 mg/kg (MacDonald et al., 1996). The mean concentration for the samples in the upper bay (EG18 and north thereof, Figure 1) was 26.7 mg/kg, which exceeds the FDEP TEL. The highest concentrations were observed in the northern part of the upper bay. For the lower bay (south of EG18, Figure 1) the mean concentration was 11.9 mg/kg. This value is less than half of the average concentration for the upper bay. The overall lower concentrations of the lower bay may be due to their greater distances away from sources of PCBs. However, spatial trends in PCB concentrations that could help identify a PCB release point are not present in the bay, potentially because the distribution of sediments is affected by local transporting mechanisms. It appears likely that PCBs have accumulated in the northern part of the upper bay due to its proximity to fluvial input of sediments and suspended particles, but surface water transport from adjacent drainages, stormwater, and industrial outfalls, and other regional sources may also have contributed to sediment PCB concentrations. On the basis of spatial patterns it is not readily apparent if there is only a single

source or if there are multiple source origins for the PCBs of the upper Escambia Bay.

The Escambia River is the major source of fresh water and sediments for Escambia Bay (Olinger et al., 1975). Samples taken in the Escambia River near and south of the nylon manufacturing facility (Figure 1) ranged in total PCB concentration from 1.0 to 43.9 mg/kg with three samples exceeding the FDEP TEL. The mean concentration was 28.8 mg/kg. The PCB concentrations have a spotty spatial distribution that is likely determined by sediment characteristics, which are influenced by natural erosion and deposition, prop wash from tugboats, and dredging. PCB concentrations in sediments north of the facility were reduced compared to those in the lower river. They had a mean of 5.06 mg/kg and ranged from 1.54 to 16.0 mg/kg. The detection of PCBs in this stretch of the river suggests that at least some PCBs may be entering the system from upriver sources, or possibly from atmospheric deposition (Eisler, 1986).

Table 1 shows average data derived from 168 elutions representing the spectrum of 209 PCB congeners in the Escambia System sediments. Many of the elutions consist of multiple congeners and are not as useful for determining origins as single congener elutions. For example, the maximum elution of 5.96 mole% consists of three PCB congeners (2,2′,3,3′,4,5 + 2,2′,3,4,4′,5′ + 2,3,3′,4′,5,6) and several of the other top concentrations are also multiple elutions. The three congeners of the maximum elution are most plentiful in Aroclors 1254 and 1260 where on a weight basis they compose 6.34 and 6.18% in early and late A1254, respectively, and 6.62, 6.55, and 6.85% in three tested lots of A1260. This finding suggests that either A1254 or A1260 could be sources for Escambia System PCBs but other more definitive elutions must be looked at to assess the main Aroclor source. Three of the higher elutions (more than 3 mole% of the total) consist of single congeners: 2,3′,4,4′,5 (5.42 mole%, PCB 118 a DL PCB), 2,3,3′,4′,6 (4.83 mole%, PCB 110), and 3,3′ (3.64 mole%, PCB 11). PCB 118 routinely varies from 7.4 mole% to 13.6 mole% in the two known A1254 formulations and PCB 110 is also present in its highest amounts of 8.48 mole% to 9.63 mole% in the A1254 formulations (Frame et al., 1996; Johnson et al., 2008). This suggests that Aroclor 1254 may be the dominant source for the sediment PCBs in the studied sections of Escambia Bay and River, which is consistent with the contention of Duke et al., (1970) that A1254 was released from a nylon facility into the lower part of the river in 1969. There are two distinct forms of A1254, an early and a late form, which due to a change in the manufacturing process in 1971 have differing proportions of PCB congeners, but with identical total chlorination (Frame et al., 1996, Johnson et al., 2008). The presence of PCB 11 in surface sediments appears to be inconsistent with an origin in A1254, or any other Aroclor. PCB 11 is only present in A1221 (Frame et al., 1996) and at a mass% that is approximately 25 times less than the observed concentrations in sediments of the Escambia System. Due to its higher volatility (Hanson, 1999), any PCB 11 present in the original source(s) would be expected to diminish more quickly than the more fully chlorinated congeners in the absence of new

input. It appears that there is a more recent source(s) of PCB 11. Possible origins of PCB 11 include yellow pigments used in paints (Basu et al., 2009). For the Escambia watershed there are no known sources for the diarylide dyes used in yellow paint or other dyes that could serve as a source of PCB 11 other than what is present on painted structures. The presence of a paper mill on the upper Escambia River seems important because there is a report of such a mill being a source of PCB 11 (Rodenburg et al., 2010). Rodenburg et al. (2010) state that, for formation of PCB 11 to occur by dechlorination, the precursors PCB 77, 126, and 169 are required. These PCBs are not plentiful in A1254s or in Escambia sediments and could not serve as a basis for significant PCB 11 formation in the present study area. The origin of PCB 11 in Escambia River and bay thus remains unclear.

Dioxin-Like PCBs

Table 2 shows average DL PCB and TEQ proportions on a mole% basis. The TEQ proportion is the contribution of an individual congener to the total TEQ of the DL PCBs. The sedimentary DL PCBs on the basis of mole composition constitute 8.77% of the total PCBs (Table 2). Congener 118, at 5.42% of total PCBs on a mole basis, composes approximately 62% of the DL PCBs and the highly toxic congener 126 at 0.0096 mole% of total PCBs composes 0.11% of the DL PCBs (Table 2). The contribution of these congeners to TEQ is reversed as the more scarce congener PCB 126 is responsible for approximately 76% (9.6E-06 TEQ contribution/mole) of the total DL PCB TEQ, due to its high TEF, and the more abundant congener PCB 118 accounts for only approximately 13% (1.6E-06 TEQ contribution/mole) of total DL PCB TEQ. In two nearby estuaries that are connected to the bay PCB 126 is also responsible for a higher percentage of the TEQ (Liebens et al., 2011). In general, DL PCB proportions on a mole% basis are lower in sediment than in A1254 (Table 2). The decline is 3.56% compared to the early form of A1254 and 14.8% compared to late form of A1254, showing that the early A1254 form is closest in profile to that of the sediment profile. For both forms of A1254 the major differences in mole% are due to PCB 118 and PCB 105 that have lower concentrations in the sedimentary PCB profile. Interestingly, the TEQ for early production A1254 is less than that of the sediments due to PCB 126 being somewhat higher in the sediment, even though the total DL PCB mole% is higher for early production A1254. The PCB 126 concentrations are trace detections that must be estimated, possibly resulting in poor accuracy. It is also possible that there are minor differences between Aroclor standards and the Aroclors that were released to the Escambia Bay system.

A comparison shown in Figure 2 shows the relative mass composition of the common Aroclors for DL PCBs 118 and 105 (Frame et al., 1996). Non-degraded early and late form Aroclors A1254 have 7.35% and 13.59% by mass of PCB 118 and 3.04 and 7.59% of PCB 105 respectively. These two congeners have a range of non-detection to 2.35% mass composition in the other Aroclors. A1248 that has the next highest PCB 118

Table 1. *Mean composition of polychlorinated biphenyl (PCB) elutions [mole%] for Escambia System sediments.*

Congener(s)	% M	Congener(s)	% M
2,2′,3,3′,4,5+ 2,2′,3,4,4′,5′+ 2,3,3′,4′,5,6	5.96	2,2′,3,4,5′,6	0.11
2,3′,4,4′,5 -118[a]	5.42	2,2′,3,3′,4,4′,5,5′,6,6′	0.10
2,2′,4,4′,5,5′ + 2,3′,4,4′,5′,6	4.94	2,2′,3,5,6 + 2,2′,4,4′,6	0.10
2,3,3′,4′,6 -110	4.83	2,2′,4,5′,6	0.09
2,2′,3,4′,5+ 2,2′,4,5,5′+ 2,3,3′,5′,6	4.80	2,3,4′,5,6	0.09
3,3′ -11	3.64	2,2′,4,4′,5,6′	0.09
2,2′,4,5′ + 2,3′,4,6	3.32	2,2′,3,3′,4,4′,5,6′	0.09
2,2′,3,4′,5,6 + 2,2′,3,4′,5′,6	3.32	2,3,3′,4,5	0.08
2,2′,3,5′ + 2,2′,4,4′ + 2,3,5,6	3.00	2,2′,3,3′,5,5′	0.08
2,2′,3,5′,6	2.95	2,3′,5,5′	0.07
2,2′,5,5′	2.91	2,2′,3,3′,5,5′,6,6′	0.07
2,2′,3,3′,5	2.70	2,3,4′,5	0.07
2,3′,4′,5 + 2,3,4,5 + 2,4,4′,5 + 2′,3,4,5	2.58	2,2′,3,3′,4,6,6′	0.07
2,2′,3,4,5+ 2,2′,3,4,5′+ 2,2′,3′,4,5+ 2,3,3′,4,5′ + 2,3 ′,4,4′,6+ 2′,3,4,5,6′	2.40	2,3′,4,5	0.07
2,4′	2.36	2′,3,4,4′,5 123	0.06
2,3′,4,4′	2.28	2,3	0.06
2,3,4 + 2′,3,4	1.96	2,2′,3,3′,4,4′,5,6	0.06
2,2′,4,4′,5	1.89	2,3′,4,5,5′	0.06
2,3,3′ + 2,4,4′	1.71	2,2′,3,3′,4,4′,5,5′,6	0.06
2,3,3′,4,4′ - 105	1.69	2,3,4,4′,5 114	0.06
2,2′,3,4 + 2,3′,4′,6 + 2,2′,3,3′	1.51	2,2′,3,4,4′,6 + 2,2′,3,4,4′,6′	0.05
2,4′,6	1.46	2,3,3′,5′	0.05
2,2′,3,4,4′,5,5′+ 2,3,3′,4′,5,5′,6	1.31	2,2′,6,6′	0.05
2	1.23	3,3′,4	0.05
2,2′,3,3′,5,6′ + 2,2′,3,5,5′,6	1.11	3,4 + 3,4′	0.04
2,2′,3,3′,4,6′	1.07	2,2′,3,3′,4,5,5′,6,6′	0.04
2,2′,3,3′,4,4′ + 2,3,4,4′,5,6	1.07	2′,3,5	0.04
2,2′,3,4,6+ 2,2′,3,4′,6	1.00	3,3′,4,5′	0.04
2,4′,5	0.98	2,2′,3,3′,4,5′,6,6′	0.03
2,2′,4	0.92	2,2′,3,5,6′	0.03
2,2′,3,3′,4,4′,5	0.87	2,2′,3,4,5,5′,6	0.03
2,2′,3,3′,6	0.87	2,2′,3,3′,4,6	0.03
2,2′,3,5,5′	0.80	2,4	0.03
2,2′,3,4′,5,5′,6	0.79	2′,3,3′,4,5	0.03
4,4′	0.79	2,2′,3,5 + 2,3′,5′,6	0.03
3,4,4′	0.75	2,3,3′,4,4′,5,5′ 189	0.03
2,2′,5 + 2,4,6	0.72	2,2′,3,3′,4,5,6,6′	0.02
2,3,3′,4,4′,5+ 2,3,3′,4,4′,5′ 156&157	0.72	2,3,3′,4,4′,5′,6	0.02
2,2′,3,4′,5,5′	0.71	2,2′,3,6,6′	0.02
2,2′	0.69	2,2′,3,3′,4,5′,6	0.02
2,2′,4,6 + 2,2′,5,6′	0.65	2,3,3′,4′,5,5′	0.02
2,3,3′,4′	0.63	3	0.02
2,2′,3,4′	0.60	2,3,4,4′,6	0.02
2,3,3′,4,6	0.59	2,3,3′,4	0.01
2,2′,3,4,4′ + 2,3,4,5,6	0.57	3,3′,5,5′	0.01
2,2′,3,4,5,5′	0.56	3,3′,4,4′,5 - 126	0.01
3,3′,4,4′ 77	0.54	2,2′,3,4′,6,6′	0.01
2,2′,3,6 + 2,2′,4,6′	0.53	2,2′,3,4,6′	0.01
2,2′,3,3′,4,5,6′	0.50	2,3,3′,4,5,5′	0.01
2,2′,3,3′,6,6′	0.47	2,2′,3,3′,4,4′,5,6,6′	0.01
2,2′,3,3′,4,5,6	0.45	2,3,6	0.01
2,3′	0.40	2,2′,3,4,4′,5,6	0.01
2,3,3′,4,4′,6	0.40	2,2′,3,3′,4,4′,6,6′	0.01
2,3,4′,6	0.38	3,4,4′,5 81	0.00
2,2′,6	0.36	2,3,3′,5	0.00
2,2′,3,3′,4,5′	0.35	2,2′,3,4′,5,6′	0.00
2,2′,3,4,4′,5′,6	0.35	2,3,3′,4,4′,5,5′,6	0.00
2,3,4′	0.29	2,2′,4,6,6′	0.00
2,3,3′,4′,5′,6	0.28	2,2′,3,4,4′,5,6′	0.00
2,3′,5 + 2,4,5	0.27	2,2′,3,5,6,6′	0.00
2,2′,3	0.26	3,3′,4,5,5′	0.00
2,3′,4	0.25	2,3,3′,5,5′	0.00
2,2′,3,3′,4,4′,6 + 2,2′,3,3′,4,5,6	0.25	2,5	0.00
2,2′,3,3′,4	0.24	3,3′,5 36	0.00
2,3′,6	0.24	2,2′,3,4,5,6′	0.00

(Continued on next page)

Table 1. Mean composition of polychlorinated biphenyl (PCB) elutions [mole%] for Escambia System sediments. (Continued)

Congener(s)	% M	Congener(s)	% M
2,3′,4,4′,5,5′ - 167	0.24	2,2′,3,4′,5,6,6′	0.00
2,2′,3,3′,5,6,6′	0.23	2,3,3′,5,5′,6	0.00
4	0.22	2,6	nd
2,2′,3′,4,6 + 2,2′,4,5,6′	0.22	3,5	nd
2,2′,3,3′,4,5,5′,6 + 2,2′,3,3′,4,5,5′,6′	0.20	2,3,5	nd
2,2′,3,3′,5,6	0.20	3,4′,5	nd
2,2′,3,4,4′,5	0.18	3,4,5	nd
2,2′,4,5	0.18	3,3′,4,5	nd
2,3,4,4′	0.17	2,3′,4,5′,6	nd
2,2′,3,3′,4,4′,5,5′	0.16	2,2′,4,4′,6,6′	nd
2,3,3′,4,4′,5,6	0.15	2,2′,3,4,6,6′	nd
2,2′,3,6′	0.15	2,2′,3,4,5,6	nd
2,2′,3,3′,5,5′,6	0.14	2,3,3′,4,5′,6	nd
2,3,3′,4′,5 + 2′,3,4,5,5′	0.14	2,3,3′,4,5,6	nd
2,3,3′,5,6	0.13	3,3′,4,4′,5,5′ - 169	nd
2,2′,3,4,4′,5,5′,6	0.12	2,2′,3,4,4′,6,6′	nd
2,3′,4,5′	0.12	2,2′,3,4,5,6,6′	nd
2,3,3′,6 + 2,3,4,6 + 2,4,4′,6	0.12	2,3,3′,4,5,5′,6	nd
2,2′,3,3′,4,5,5′	0.11	2,2′,3,4,4′,5,6,6′	nd

[a]Dioxin-like polychlorinated biphenyl (DL PCBs) and three dominant PCBs are listed also by IUPAC number.

concentrations contains only 17% to 32% of the PCB 118 that is present in the A1254s. A similar trend is seen for PCB 105 except that the differences between A1254 and A1248 are not as pronounced. This information corroborates that A1254 is the predominant, but not necessarily the only, Aroclor that was released to the Escambia System.

Correlations Between Sediment PCBs and Aroclors

To compare the full suite of PCBs in sediments of the Escambia System with Aroclors, an approach was used similar to that utilized by Martinez et al. (2009) to show that A1248 was the best match for PCBs in Indiana Harbor and Ship Canal sediment. For

this comparison single elutions from Frame et al. (1996) were combined when needed to make the 209 elutions comparable to the 168 elutions of the present study. Pearson correlations were obtained (Table 3) to compare all elutions including the lower chlorinated and the more fully chlorinated congeners. For the Escambia System the least chlorinated Aroclor, A1221, has the lowest correlation with sediment PCBs (Table 3). The correlation increases with increasing chlorination until the chlorination percentage reaches 54% by weight in A1254. When the 54% chlorination found in A1254 is surpassed the correlation coefficient declines (Table 3). The absence of a near perfect correlation with A1254, or any of the other Aroclors, is due to the degradation that must have affected the PCBs, the presence

Table 2. Dioxin-like polychlorinated biphenyl (DL PCB) elutions (mole % of total PCBs) and toxic equivalents (TEQ) proportion (TEQ contribution/mole) for sediments and A1254 Aroclors[a]. Aroclor 1254G4 is early form, 1254A4 is late form.

Congener(s)	Sediments[b]		A 1254, early form		A1254, late form	
	% M	TEQ prop[c]	% M	TEQ prop[c]	% M	TEQ prop[c]
2,3′,4,4′,5 - PCB **118**	5.42	1.6E-06	7.73	2.3E-06	13.15	3.9E-06
2,3,3′,4,4′ - PCB **105**	1.69	5.1E-07	3.04	9.1E-07	7.59	2.3E-06
2,3,3′,4,4′,5+ 2,3,3′,4,4′,5′ - PCB **156&157**	0.72	2.2E-07	0.98	2.9E-07	1.47	4.4E-07
3,3′,4,4′ - PCB **77**	0.54	5.4E-07	0.02	1.8E-08	0.23	2.3E-07
2,3′,4,4′,5,5′ - PCB **167**	0.24	7.2E-08	0.25	7.4E-08	0.32	9.6E-08
2′,3,4,4′,5 - PCB **123**	0.064	1.9E-08	0.10	3E-08	0.26	7.8E-08
2,3,4,4′,5 - PCB **114**	0.055	1.7E-08	0.19	5.7E-08	0.49	1.5E-07
2,3,3′,4,4′,5,5′ - PCB **189**	0.025	7.5E-09	0.02	6.4E-09	0.03	7.7E-09
3,3′,4,4′,5 - PCB **126**	0.0096	9.6E-06	0.003	3.2E-06	0.026	2.6E-05
3,4,4′,5 - PCB **81**	0.0034	1E-08	0.007	2E-08	0.013	3.9E-08
3,3′,4,4′,5,5′ - PCB **169**	nd[d]	0.0	0.002	1.5E-07	0.002	1.5E-07
Sum	8.77	1.3E-05	12.33	7.1E-06	23.57	3.3E-05

[a]Aroclor data from Johnson et al. (2008).
[b]Escambia System sediments.
[c]TEQ proportion: Contribution of congener to total TEQ/mole calculated by multiplying congener's TEF with congener's mole % contribution to total DL-PCBs.
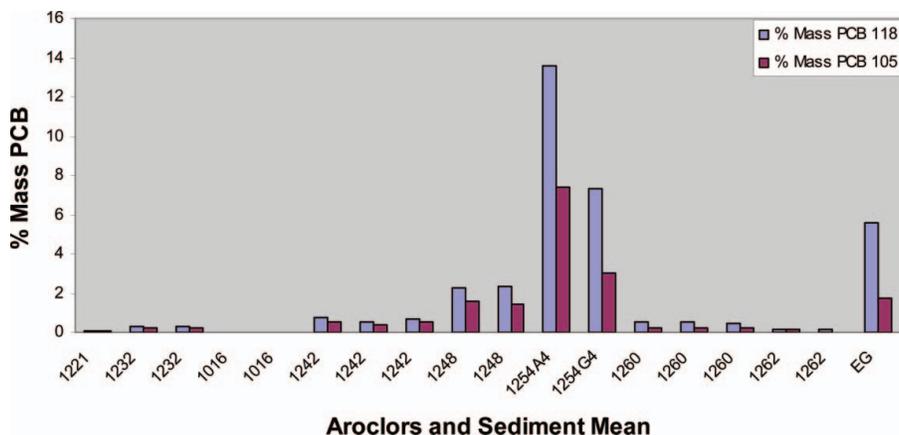[d]nd: non-detectable.

Figure 2. Graph of the mass proportions of dioxin-like polychlorinated biphenyls (DL PCBs) 118 and 105 in common Aroclors (after Frame et al., 1996) and mean for Escambia Bay sediments (EG). Multiple listings of the same Aroclor reflect different forms. (color figure available online.)

of PCB 11 and possibly secondary input of PCB congeners from other Aroclors. It is interesting to observe that the correlation with the sediment PCBs is higher for early form A1254, which agrees with the period that the PCB spill occurred on Escambia River (Duke et al., 1970), than for the more recent form of A1254. These observations further suggest that early production A1254 is the major source of PCBs in sediments of the Escambia System. However, a contribution from other PCB formulations cannot be excluded.

The correlations for heavy and light congeners were determined separately. Correlation coefficients for the lower chlorinated homologs 1, 2 and 3 (congeners 1–37) were determined to assess if input from Aroclors other than A1254 could be present, since this part of the sediment PCB profile differed most from that of A1254. Of special interest were the Aroclors whose pro-

files were dominated by congeners from the less chlorinated homolog groups that could possibly contribute congeners to homologs 1, 2, and 3 of the sediment profile. The correlations showed low to moderate correlations of 0.09 to 0.53 (Table 3). The highest correlations were for the more chlorinated A1260 (two of three lots) and A1262, which are not likely candidates for a source of low chlorinated congeners because of their overall composition. The low correlations observed for A1221 and A1232, the most likely candidates as a source of low chlorinated congeners, suggests that these two Aroclors have not contributed significantly to the profile of Escambia System sediment PCBs and that the increase observed with the exception of PCB 11 for mono-, di-, and tri-chlorinated PCBs is due to degradation of the more fully chlorinated congeners and perhaps to an input from non-Aroclor sources. Congeners in the homologs 7, 8, 9, and 10 (congeners 128–209) in sediments and Aroclors were compared to evaluate if the more heavily chlorinated Aroclor mixtures contributed to Escambia System sediment PCBs. The correlations for the less chlorinated Aroclors could not be calculated for the more chlorinated homologs because of excessive zero values. The strongest correlation of 0.96 again was for the early form of A1254 (Table 3). For A1260 the correlation was also high (0.81) but still lower than that for the A1254. These correlation data suggest that an early form of A1254 is also the major source of the more fully chlorinated congeners.

Principal Component Analysis

Statistical analysis of relatedness was performed to further evaluate to which Aroclor the PCB profiles in the individual sediment samples are most closely related. The 168 elutions were compared to the A1254 data of Johnson et al. (2008) and data for other Aroclors from Frame et al. (1996). The first two components of the PCA represented 78% of the variability in the dataset. A factor-loading plot shows that there is little variability among the PCB congener profiles of the sediments (Figure 3). The congener profiles in the sediments are much more similar to the early form of A1254 than to any other of the Aroclors,
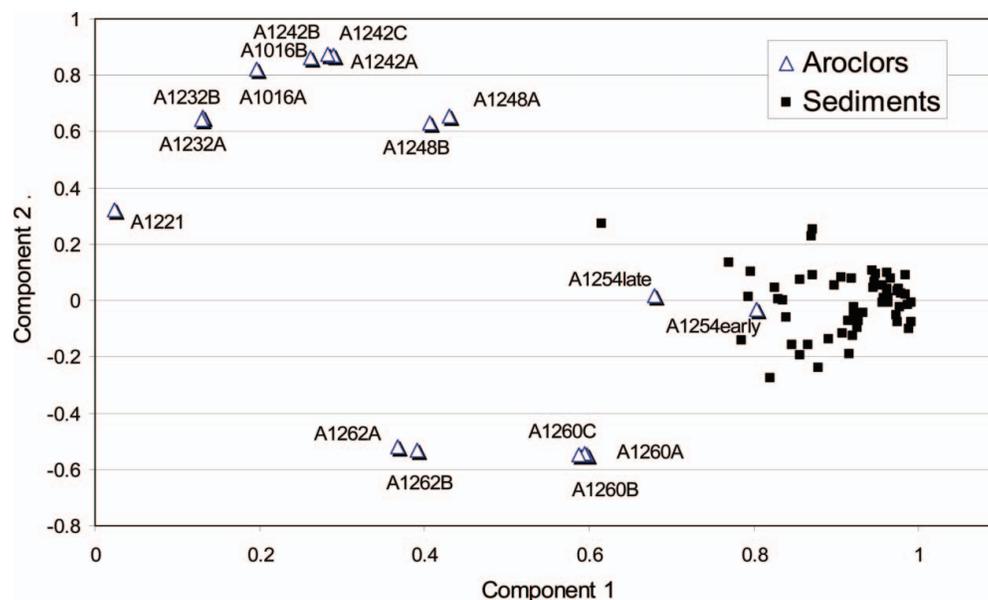
Table 3. Pearson correlation coefficients for Aroclors[a] and mean sediment polychlorinated biphenyls (PCB).

Aroclors	All congeners	PCB 1 to 37	PCB 128–209
1221	0.01	0.09	NA[b]
1232	0.10	0.28	NA
1232	0.10	0.28	NA
1016	0.16	0.48	NA
1016	0.16	0.48	NA
1242	0.26	0.49	NA
1242	0.23	0.48	NA
1242	0.25	0.51	NA
1248	0.46	0.37	NA
1248	0.43	0.38	NA
1254 A4[c]	0.75	0.44	0.92
1254 G4[c]	0.86	0.45	0.96
1260	0.54	0.50	0.82
1260	0.54	0.51	0.81
1260	0.53	0.08	0.81
1262	0.30	0.52	0.50
1262	0.32	0.53	0.54

[a]Aroclor data from Frame et al. (1996).
[b]Excessive zero values in Aroclor data caused erroneous results.
[c]Aroclor 1254G4 is early form, 1254A4 is late form.

Figure 3. Graph showing the factor-loading plot for congener profiles in individual sediment samples and Aroclors. Aroclor data from Frame et al. (1996) and Johnson et al. (2008). (color figure available online.)

corroborating the above made argument that this early pre-1971 form of A1254 is the main contributor to sediment PCBs in both Escambia River and Bay. These results do not exclude that there may have been contributions from other Aroclors or non-aroclor PCBs but the very strong association between the congener profiles of the early form A1254 and the sediments shows that any such contribution must have been minor. It is also possible that various sources of early form A1254 contributed to the congener profiles in the sediments.

Non-Dioxin Toxicity and Degradation

Table 4 compares the chlorination homolog mole% composition and O, P degradation changes from early and late form A1254 to Escambia System sediment PCBs. Although the percentage of chlorination is equivalent between the two A1254 forms there are differences in PCB congener composition between them. Compared with the early form, the late form has higher proportions of homologs 1, 4 and 5, lower proportions of homologs 2, 3, 6, 7, and 8, and similar homologs but very low proportions of homologs 9 and 10. The sediment profiles have higher, but still low, proportions of homologs 7, 8, 9, and 10. For homologs 1, 2, and 3, there is a more pronounced increase between the Aroclors and the sediments (Table 4). This increase may be caused by dechlorination (Bedard and Quensen, 1995). Overall, on a basis of mole composition there is an approximate 3% decrease in total chlorine content in sediments relative to the profiles of the A1254s. The 3% loss of chlorine from the profile does not indicate an equivalent overall loss of total congeners but corresponds to a shift in the profile. The shift is due to a decline for PCBs 118 and 110 relative to the fresh Aroclor and the presence of PCB 11 in sediments.

It has been postulated that there are non-dioxin toxicities from PCBs associated with microbial dechlorination. Ganey and Boyd (2005) reported that reductive dechlorination occurs during bioremediation. This causes an accumulation of lesser chlorinated congeners substituted at O, P-positions on at least one phenyl. The dechlorination of the meta chlorines also eliminates DL-like toxicity (Ganey and Boyd, 2005). The O, P-chlorinated PCBs did evoke responses in several cellular bioassays showing that non-DL PCBs have the potential to effect toxic responses in mammalian and perhaps other organisms. To evaluate the wider applicability of the observations by Ganey and Boyd (2005) we assessed profile changes of the O, P- chlorinated PCBs for Escambia System sediments relative to early and late manufactured A1254s. A total of 20 elutions containing at least one O, P phenyl ring substitution were assessed. The amounts of O, P- congeners are approximately the same in the sediments as in the early production A1254 (30.7% mole and 29.9 mole% respectively) and are substantially more than in late production A1254 (22.7 mole%) (Table 4). Overall there is a shift of O, P-congeners to the less chlorinated homologs in the sediments. In homologs 1, 2, 3 they represent 2.9 mole% in sediments versus 0.2 mole% and 0.06 mole% in early and late A1254 respectively. The O, P- PCBs in the mono through tetra-chlorinated PCB homologs combined represent 12.76 mole% in the sediments and 4.6 mole% and 5.5 mole% in early and late A1254 respectively. For the remaining 10 O, P- PCBs of the penta to hepta-chloro PCBs the composition is 17.9 mole% for sediments versus 25.2 mole% and 17.2 mole% for the early and late A1254 respectively. These observations show that in the Escambia System there is shift of the O, P- congener profile from more chlorinated homologs to less chlorinated homologs in sediments compared to the parent Aroclor. However, the accumulation of

Table 4. *Mean composition [mole %] of chlorination homologs and ortho and para chlorine substituted polychlorinated biphenyl (PCB) congeners in sediments from Escambia System and in 1254 Arochlors[a].*

Congener(s)[b] or Homologs	Formulas	Escambia System sediments	Early A1254	Late A1254
Homolog 1	$C_{12}H_9Cl$	1.454	0.060	0.000
Homolog 2	$C_{12}H_8Cl_2$	7.898	0.170	0.515
7	2,4-Dichlorobiphenyl	0.028	0.005	0.000
Homolog 3	$C_{12}H_7Cl_3$	10.259	0.607	1.997
17	2,2′,4-Trichlorobiphenyl	0.923	0.064	0.005
25	2,3′,4-Trichlorobiphenyl	0.247	0.013	0.002
28+20	2,3,3′- + 2,4,4′-Trichlorobiphenyl	1.713	0.154	0.049
Homolog 4	$C_{12}H_6Cl_4$	20.093	22.621	20.558
42	2,2′,3,4′-Tetrachlorobiphenyl	0.597	0.145	0.121
44+47+65	2,2′,3,5′- + 2,2′,4,4′- + 2,3,5,6-Tetrachlorobiphenyl	3.003	2.180	0.866
69+49	2,2′,4,5′- + 2,3′,4,6-Tetrachlorobiphenyl	3.319	1.057	0.429
45+51	2,2′,3,6- + 2,2′,4,6′-Tetrachlorobiphenyl	0.526	0.045	0.055
66	2,3′,4,4′-Tetrachlorobiphenyl	2.284	0.950	3.987
68	2,3′,4,5′-Tetrachlorobiphenyl	0.118	0.000	0.000
Homolog 5	$C_{12}H_5Cl_5$	31.963	57.755	53.122
117+116+ 85	2,3,4′,5,6- +2,2′,3,4,4′- + 2,3,4,5,6-Pentachlorobiphenyl	0.656	1.268	2.223
113+90+101	2,2′,3,4,4′-+ 2,3,4,5,6-Pentachlorobiphenyl	4.801	8.256	5.312
88+91	2,2′,3,4,6- + 2,2′,3,4′,6-Pentachlorobiphenyl	1.002	0.971	0.476
83+99	2,2′,4,4′,5- +2,2′,3,3′,5-Pentachlorobiphenyl	4.594	3.929	5.037
95+100+93+102+98	2,2′,3,5′,6- +2,2′,3,5,6- + 2,2′,4,4′,6- +2,2′,3′,4,6- + 2,2′,4,5,6′-Pentachlorobiphenyl	3.269	6.577	1.679
123*	2′,3,4,4′,5-Pentachlorobiphenyl	0.0640	0.102	0.260
Homolog 6	$C_{12}H_4Cl_6$	22.035	17.852	21.951
137	2,2′,3,4,4′,5-Hexachlorobiphenyl	0.181	0.427	0.513
147+149	2,2′,3,4′,5,6 + 2,2′,3,4′,5′,6-Hexachlorobiphenyl	3.318	3.573	1.544
139+140	2,2′,3,4,4′,6- + 2,2′,3,4,4′,6′-Hexachlorobiphenyl	0.054	0.129	0.108
Homolog 7	$C_{12}H_3Cl_7$	5.331	0.916	1.813
181	2,2′,3,4,4′,5,6-Heptachlorobiphenyl	0.006	0.014	0.011
Homolog 8	$C_{12}H_2Cl_8$	0.768	0.000	0.023
Homolog 9	$C_{12}H_1Cl_9$	0.101	0.020	0.020
Homolog 10	$C_{12}Cl_{10}$	0.099	0.000	0.000
Sum of ortho, para PCBs	30.704	29.858	22.676	
Homolog sum		100	100	100

[a]Aroclor data based on Johnson et al. (2008).
[b]International Union of Pure and Applied Chemistry (IUPAC) congener number of ortho- and para-chlorine-substituted PCB congener(s) for each homolog.

O, P- congeners is not as large as that reported to occur during anaerobic bioremediation (Bae et al., 2001; Ganey et al., 2000; Mousa et al., 1998; Zwiernik et al., 1998). This finding suggests that there need not be the degree of concern for possible toxicity from these congeners in Escambia Bay as occurs during some bioremediation. However, the overall impact of toxicity cannot be determined precisely because there are no available data for uptake of these PCBs into biota and no established criteria to assess the toxicity of this form except by total concentration.

Conclusions

PCB analyses with US EPA Method 1668A allowed the construction of congener profiles that give insight into the Aroclor origin and the fates of sediment PCBs that have been exposed to environmental degradation. The current study found a preponderance of data showing that early production Aroclor A1254 produced prior to 1972 is the PCB mixture that is predominantly present in Escambia System surface sediments. PCBs that were discovered in 1969 in the Escambia River have persisted in

the sediments of Escambia Bay for at least 40 years with only moderate degradation of the original profile compared with that of the reference sample Aroclor A1254. The evidence consisted of sediment PCB congener profile assessment matched to those of Aroclors, assessment of transformation by dechlorination, toxicological changes related to TEQ, and the biotransformation to O, P- chlorinated PCB congeners. Three of the dominant Escambia System sediment elutions consist of single congeners, two of which are the dominant PCBs in early form A1254: DL PCB 118 and PCB 110. The third is PCB 11, which is not a major constituent of the early form A1254. Correlation and principal component analysis for the congeners of common Aroclors showed that the highest association for most individual sediment samples was with the A1254 early production form, and then with the similar A1254 late production form.

An overall decline of 3% in the chlorination of the PCBs is associated with a moderate shift to the lesser-chlorinated congeners. There was an observed decrease in the penta-chlorinated congeners and an increase of homologs 1, 2, and 3. The decline in the profile of the two major penta-chlorinated DL PCBs (118

and 105) was 29%. However, the total TEQ did not decline because of a slight increase of the highly toxic DL-PCB 126 that is present at trace quantities. Other toxicologic changes were noted. There was a modest increase of the less chlorinated O, P-congeners that are suspected to be toxic but the accumulation in this study was not as large as had been reported to occur during anaerobic bioremediation (Ganay and Boyd, 2005).

These findings suggest that degradation of the original A1254 PCB mixture has occurred. What is not known is if the current sediment PCB profile is in equilibrium with the rate of dechlorination and input of PCB 11 balanced by loss of the dechlorinated congeners or if there will be a continued increase of the mono-, di-, and tri-chlorohomologs.

Acknowledgement

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