

PCBs and PCDD/Fs in a historically polluted estuary along the northern Gulf of Mexico.

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Abstract

Escambia Bay is a large shallow estuary in northwest Florida, US. It receives most of its waters from the Escambia River which originates to the north in Alabama. Starting in the 1950's several industrial facilities were constructed on the bay and river. Prior to the 1970's there were unregulated releases from these facilities and from domestic sewage facilities that lead to a catastrophic environmental collapse of the system in the early 1970s. The present study assesses the current profiles of PCBs and PCDD/Fs in sediment of Escambia Bay and River and examines the concentrations, spatial patterns, and potential origin of these pollutants relative to environmental and human health concerns. Fifty-seven composite samples were collected with a ponar grab sampler. PCBs and PCDD/Fs were extracted with USEPA Method 3550. USEPA Method 1668A was employed to detect the concentrations of the 209 PCB congeners and USEPA 1613B was used to detect PCDD/Fs. Sediment PCBs have a mean concentration of 15.6 ug/kg and a range from 1.0 to 93.3 ug/kg. Twelve (21%) out of the 57 samples exceed the FDEP TEL of 21.6 ug/kg and no sample exceeds the FDEP PEL of 189 ug/kg. In spite of these relatively low concentrations, bioaccumulation of PCBs in seafood from the bay has resulted in advisories for seafood consumption. The 17 PCDD/F congeners that are considered to have significant toxicity have a mean of 1.9 ug/kg and a range of 0.022-11.0 ug/kg. The mean total TEQ of PCDD/Fs and dioxin-like PCBs combined is 2.6 ng/kg. PCDD/Fs contribute about 92% and PCBs about 8% of the total TEQ. About 33% of the samples exceed the NOAA TEL for total TEQ but not the AET and an additional 23% of the samples exceed the AET. This implies that about 56% of samples exhibit total TEQ toxicities that could impact sediments adversely. The current PCB profile most closely resembles Aroclor 1254 produced prior to 1972. This is consistent with the composition of a spill on the Escambia River in 1969 and suggests that the PCBs have persisted in the sediments for at least 40 years with only moderate degradation of the original profile. An overall decline of 3% in the chlorination of the PCBs is associated with a shift to the lesser-chlorinated congeners, however, the total TEQ did not decline. The PCDD/F congener profile is similar to what has been observed in local bayous in that octachlorodibenzo-p-dioxin (OCDD) is the dominant congener in the sediment but does not unequivocally point to a specific source.

1. Introduction

Escambia Bay came to the attention of the newly formed United States Environmental Protection Agency (USEPA) in the late 1960's and early 1970's (USEPA, 1972) when there were environmentally stressed conditions in the Bay resulting in very large fish kills and the collapse of the white shrimp fishery (Olinger et al., 1975). At that time, the upper part of Escambia Bay had two chemical facilities on its eastern shore and there was a coal fired electrical power plant and a nylon facility several km upstream from the Bay on the banks of the Escambia River, which drains into the Bay. A release of polychlorinated biphenyls (PCBs) from the nylon plant was detected in 1969 (Duke et al., 1970). There was severe dissolved oxygen depletion resulting from industrial and municipal discharges and poor circulation in upper Escambia Bay, which resulted in the large fish kills (Olinger et al., 1975). The condition of Escambia Bay gained national media attention and has become a classical example for introductory environmental text books (Laws, 2000). Federal and state actions took place during the following years and resulted in a diminution of point source releases to the Escambia Bay and River System (USEPA, 1980). There was extensive investigation of the sediments during the early 1970's (Olinger et al., 1975) and in the 1990's (DeBusk et al., 2002). The presence of the organochlorine pollutants is of major interest because these compounds were still detected in sediments by studies from the 1990's (DeBusk et al., 2002) more than 20 years after the initial releases and recently PCBs and polychlorinated dibenzodioxins/furans (PCDD/Fs) were detected in shellfish and mullet in the Bay (Karouna-Renier et al., 2007; 2011) and the Florida Department of Health has issued advisories for the consumption of mullet since 2007 (FDOH, 2014). These persistent organochlorines are also a concern because the bay and river currently provide habitat for several listed species including the Gulf Sturgeon that is listed as a threatened species under the Endangered Species Act (Federal Register, 1998). Additionally, the wetlands adjacent to Escambia Bay and River serve as a nursery for commercially valuable species such as the white shrimp.

In the present study we determine the concentrations and congener profiles of PCBs and PCDD/Fs in surface sediments of the Florida segment of the Escambia Bay and River. We also assess spatial patterns and potential origin of these pollutants relative to environmental health. The Florida segment of the river is approximately 85 km long and consists of multiple channels. The river has a total length of about 370 km (Thorpe et al., 1997). Escambia Bay is a large (93 km²), shallow, micro-tidal estuary with an average tidal range of 50 cm that is often augmented by strong winds (Schroeder et al., 1999; Murrell et al., 2004). It receives most of its waters from the Escambia River which originates to the north in Alabama. The watershed is mostly rural with extensive tracts of forest land and some urban centers.

2. Methods

Sediment samples were collected at 57 sites with a stainless steel ponar dredge sampler during December 2007 to May 2008. Coordinates were determined by WAAS enabled GPS. At each site five ponar grab samples were joined and mixed thoroughly prior to placing composited samples into certified cleaned sampling containers for shipment to the analytical laboratory the day of sampling. The study operated under approved QA/QC protocols of the USEPA, including

an approved quality assurance project plan (QAPP) that detailed the guidelines for the sampling plan and laboratory analyses that are in accord with USEPA, NELAP (National Environmental Laboratory Accreditation Program) accredited laboratories, and State of Florida Department of Environmental Protection (FDEP) requirements. CAS (Columbia Analytical Services) in Jacksonville, FL performed all analyses except for PCB and PCDD/F analyzes that were performed by CAS Houston, TX.

The PCDD/Fs, and PCBs were extracted using USEPA Method 3550. USEPA Method 1668A was employed to detect the concentrations of the 209 PCB congeners and USEPA 1613B was used to detect tetra-octa PCDD/PCDFs with isotope dilution-high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS). The toxicities of PCDD/Fs and dioxin-like PCBs (dl-PCBs) were calculated using the updated 2005 WHO TEF values (Van den Berg et al., 2006). For toxicity assessment SQAGs (sediment quality assessment guidelines) were assessed according to MacDonald (1994a,b) for the TEL (threshold effects level) and the PEL (probable effects level) for PCBs. For dioxin toxicity the NOAA TEL and AET (apparent effects level) were used to assess sediment toxicity to benthic organisms (Buchman, 2008).

3. Results and Discussion

The sampled area was divided into six sections (Figure 1) to help assess the potential origin of the pollutants: the lower Escambia River (LR) as the 11 km segment between the river's mouth and the nylon facility where a documented PCB release occurred; upper Escambia River (UR) going from the nylon facility north to the Alabama state border; upper wetlands (UW) consisting of riverine forested wetland to the north and east of the nylon facility; lower (LW) wetlands with herbaceous vegetation to the south southwest of the facility and downstream of it; and the upper (UB) and lower (LB) Escambia Bay artificially separated for discussion purposes by the I-10 interstate bridge (Figure 1).

3.1. PCBs

PCBs in Escambia Bay and River sediment had a mean concentration of 15.6 ug/kg and a range from 1.0 to 93.3 ug/kg. Twelve (21%) out of the 57 samples exceeded the FDEP TEL of 21.6 ug/kg and no sample exceeded the FDEP PEL of 189 ug/kg. In spite of these relatively low concentrations relative to SQAGs, bioaccumulation of PCBs in seafood from the Bay has resulted in advisories for seafood consumption (FDOH, 2014).

The mean concentrations of the PCBs varied among the six study areas. Regions of the watershed upstream of the nylon plant had lower PCB concentrations than those downstream of the nylon plant, supporting the assertion that this stretch of the river is the main source of the PCBs. However, the presence of PCB detections upriver of the nylon facility suggests that the origin of the PCBs is not solely caused by the 1969 release at the nylon facility (Duke et al., 1970). The upper river region is under the influence of small metropolitan areas (Century, FL and Brewton, AL) that could be sources of the PCBs in that segment of the river.

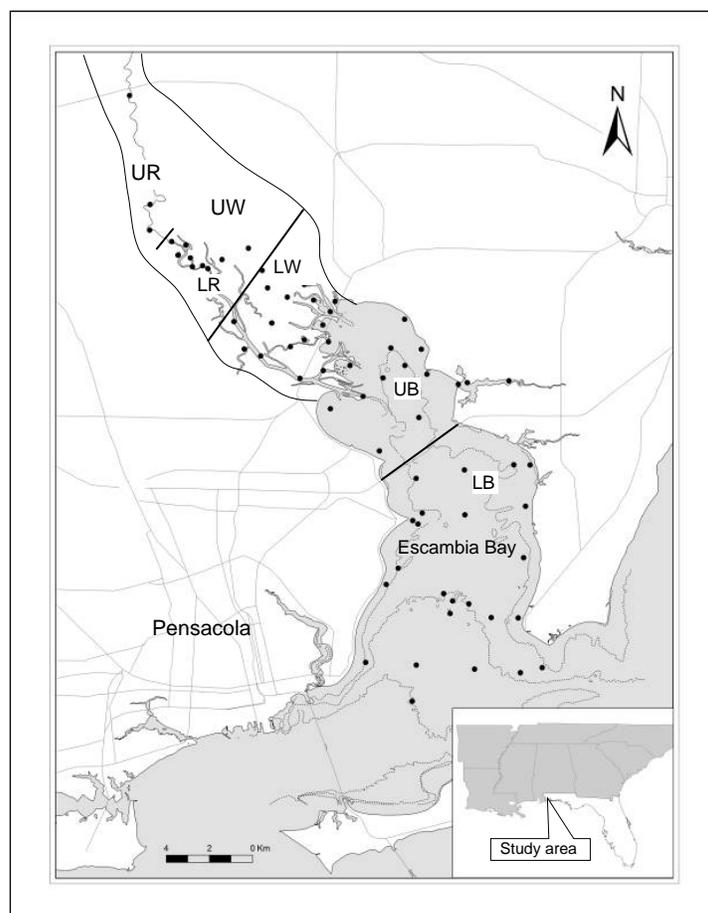


Figure 1. Map of the Florida portion of Escambia River and Escambia Bay depicting the areas of study: LB (Lower Bay), UB (Upper Bay), LR (lower river), UR (upper river), LW (lower wetland), UW (upper wetlands). Black dots mark sampling sites. Two sites are located upriver from northern edge of map.

Sediments in the lower Escambia River and upper Escambia Bay have higher mean PCB concentrations than in the lower Escambia Bay. River transportation is the probable source for the higher PCB concentrations in sediment in the upper Bay. It is possible that some of the PCBs in the upper Bay were released from other sources such as the chemical facilities on the northeastern shore of the upper Bay. Previous studies have shown that water borne pollutants originating from the eastern shore of the upper Bay can be transported throughout the upper Bay (Olinger et al., 1975). The PCBs in the lower wetlands, adjacent to the upper Bay, likely originate at least in part from transport of polluted sediments from the upper Bay by tidal currents and during tropical storms (Hagy et al., 2006) because concentrations in the upper wetlands were very low. The lower concentrations in the lower Bay are due to being further away from the PCB source(s) and to being closer to the influences of the lesser contaminated Pensacola Bay.

The maximum sediment PCB concentrations in Escambia Bay seem to have been higher in the past. After the 1969 spill the concentrations for the upper Bay were in the lower parts per million with 30 ppm recorded at the mouth of the river (Nimmo et al., 1975). The concentrations have declined over the years. Debusk et al. (2002) observed maxima of 152 ug/kg and 168 ug/kg for data collected in the 1990's compared to a maximum of 71.2 ug/kg for the current study and 118.1 ug/kg in a related study for the Bay (Smith et al., 2009). These minor differences between the maximum concentrations of the present studies and those of the 1990's may in part be due to the different sampling site locations, varying analytical methods, and different groups of reported PCB congeners (Debusk et al., 2002), but nevertheless, they suggest declining PCB concentrations for Escambia Bay. A decline in the maximum PCB concentration would be in agreement with studies that show PCBs can degrade under natural conditions via aerobic and anaerobic mechanisms (Abramowicz, 1990).

PCB Aroclor Origin and Degradation: Aroclor 1254 is the only Aroclor that was documented to have been released into the Escambia bay and River system (Duke, 1970). A recent study (Mohrherr et al., 2012) on the profile of Escambia River and Escambia Bay sediment PCBs showed that the congener profiles of the current sediment PCBs are most similar to that of early production Aroclor 1254 made prior to 1972. Chronologically the early production form of Aroclor 1254 corresponds to the time of the release. Overall chlorination of the sediment 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 (Mohrherr et al., 2012).

3.2 PCDD/Fs

The detected concentrations for the 17 toxic PCDD/F congeners have a mean of 1.9 ug/kg and a range of 0.022-11.0 ug/kg. The overall toxic PCDD/F congener profile is similar to what was observed in the local bayous in related studies (Mohrherr et al., 2006; 2008) in that octachlorodibenzo-p-dioxin (OCDD) is the dominant congener on the basis of mass concentration. The 17 toxic congeners comprise from 77 to 99% (mean = 87.3%) of the total PCDD/Fs, showing that the nontoxic component of the tetra-octa chlorinated homolog profile total is a minor fraction of the sediment PCDD/Fs in Escambia Bay and River. The dominance of OCDD in congener profiles may result from post emission alterations rather than a source such as pentachlorophenol, whose profile also contains a predominance of OCDD (USEPA, 2006), because lesser chlorinated congeners that are present during the initial atmospheric release diminish prior to final deposition (Lohmann et al., 1998).

3.3 PCB and PCDD/F toxicity

Degradation of dioxin-like PCBs would be expected to lower the TEQ on a molar basis. Despite an overall decrease in the relative percentage of dioxin-like PCBs, the TEQ of the PCBs did not substantially change on a molar basis over the years. This is due to the presence, at trace amounts, of a highly toxic congener (PCB 126) in the sediments (Mohrherr et al., 2012). Total PCDD/F TEQs ranged from 0 ng/kg to 15.9 ng/kg with a mean of 2.4 ng TEQ/kg. About 42% of the samples had TEQs above the NOAA TEL (0.85 ng/kg, Buchman, 2008) and an additional 21% showed values above the NOAA AET (3.4 ng/kg). No sediment samples exceeded the NOAA PEL (21.5 ng/kg, Buchman, 2008). Even though OCDD makes up nearly 94% of the total toxic PCDD/F mass it is responsible for only about 22% of the TEQ toxicity. Congener

1,2,3,4,6,7,8-HpCDD is 4.6% of the total congener mass and yet makes up about 35% of the total toxicity. The more toxic congeners such as tetra and penta congeners compose about 0.033% of the mass but yet make up approximately 10% of the total TEQ toxicity.

Total sediment TEQ is the summed TEQ of the 12 dioxin-like PCBs and the 17 toxic PCDD/F congeners. The PCDD/Fs account for 92.4% of the total TEQ. About 40% of the samples exceeded the NOAA TEL for total TEQ but not the NOAA AET and an additional 23% of the samples exceeded the NOAA AET. This shows that about 63% of samples could impact benthic organisms adversely (McDonald 1994a, b). Bioaccumulation of the PCDD/Fs and PCBs has already been shown in shellfish (Karouna-Renier et al., 2007) and in fish (Karouna-Renier et al., 2011) in Escambia Bay.

The dlPCB TEQ distribution does not coincide with the PCDD/F TEQ distribution as shown by a Pearson correlation coefficient 0.128. The mass concentrations of total PCB and PCDD/F follow a similar trend. The lack of correlation is likely due to differences in origin and possibly to different interactions with transporting and degradation processes. The total mass of the PCBs was highest for the lower river and upper bay, 21,840 and 21,860 ng/kg respectively, but the mass of the 17 toxic PCDD/F congeners, 1540.7 and 1209.977 ng/kg respectively, is less than the means for the lower wetlands and upper river (3769 and 2962 ng/kg). This suggests that the distributions of these two toxic classes of organic compounds are determined independently of one another and most likely have different origins in the Escambia Bay and River system.

4. Conclusions

Escambia Bay suffered an environmental collapse in the early 1970s that was associated with releases from multiple industrial and municipal sites. The current study shows that PCB concentrations in sediments are higher in proximity to a nylon plant on the lower part of Escambia River and in the upper Escambia Bay. PCBs similar in congener composition to what was originally released in the late 1960's to Escambia River are still dispersed throughout the surficial sediments of the Escambia Bay and River. The concentrations are considerably less than the concentrations detected during the early 1970's showing a decline over time. Currently, the majority of PCB concentrations in sediments are below SQAG but are still of concern in fishes and crabs. PCBs in the sediments have a mean concentration of 15.6 ug/kg and a range from 1.0 to 93.3 ug/kg.

PCDD/Fs were detected throughout Escambia Bay and River, ranging from almost non-detect to 15.9 ng TEQ/kg with a mean of 2.4 ng TEQ/kg and 42% of the samples above the lowest SQAG. OCDD is the most common congener on the basis of mass and represents 21% of the total TEQ. While PCDD/Fs do accumulate in seafood there are no health advisories for them in Escambia Bay and River. The spatial distributions of PCBs and PCDD/Fs are different suggesting differing origins for these two classes of compounds. No specific part of Escambia Bay and River is suggested by the data for the origin of PCDD/Fs. Controlled burns of forests (Gullett and Touati, 2003) and the frequent fires that occur in the lower wetlands may be a significant source of the PCDD/Fs.

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