Sediment Concentrations of PCDD/PCDF: Casco Bay, Maine, USA

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1. Introduction

Casco Bay has a wealth of natural resources including marine habitats that support a rich and diverse ecology. Casco Bay's natural beauty, clean water, fish and waterfowl, and its deep and protected waters have made it a sought-after location for residences, business, industry, and recreation. However these same activities may add contaminants that pose a threat to the environmental integrity of the bay. Casco Bay has been designated an estuary of national significance and included in the U.S. EPA's National Estuary Program (NEP). The NEP goal is to protect and improve the water quality and enhance living resources by developing comprehensive conservation and management plans that work to ensure the ecological integrity of designated estuaries.

Casco Bay receives freshwater from rivers that discharge directly into the bay (Fore, Presumpscot, Cosins and Royal Rivers). It also appears that the Androscoggin and Kennebec Rivers, which discharge just north of Casco Bay, may be a source of contaminants to the bay. The most densely populated portion of the Casco Bay watershed are Portland, the Fore, and Presumpscot Rivers, and Back Cove. These areas may receive higher inputs of selected contaminants than other regions of Casco Bay.

An assessment of sediment contamination for trace metals, hydrocarbons, chlorinated pesticides and PCB was recently reported for 65 sites throughout Casco Bay[1]. The objective of the present research was to extend the contaminants measured to include polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/PCDF). PCDD/PCDF have been detected in other near-shore ecosystems and are highly toxic. Addition of PCDD/PCDF data makes the contaminant assessment of Casco Bay sediments more complete.

2. Experimental

Sediment samples from 30 sites were collected during November 15-17, 1994 and analyzed for PCDD/PCDF. Sediment samples were collected from locations where PCDD/PCDF concentrations were suspected to be highest. Known depositional areas were sampled in all regions of the bay, and efforts were made to sample fine-grained sediments (mud). The sampling included Cape Small in order to capture the plume of the Kennebec/Androscoggin Rivers. Sediment samples were collected using the Maine University Research Vessel the *LEE*. Some shallow sites required sampling from shore and/or use of a smaller boat. Samples were collected with a Smith-McIntyre grab sampler and the top 2 cm were removed, placed in a clean glass jar, frozen and shipped to the laboratory for analyses.

The QA/QC procedures included analyses of matrix spikes, duplicates and laboratory blanks with each batch of samples. In addition a marine reference sediment, SRM 1941a from the National Institute of Standards and Technology (NIST) was analyzed as a laboratory reference material. This SRM does not currently have certified PCDD/PCDF concentrations. However, previous analyses of this SRM have proven its value as a homogeneous estuarine reference sediment (collected from Baltimore Harbor) that contains PCDD/PCDF[2].

The method used for PCDD/PCDF sediment analyses has been reported[3,4]. The method determines the concentrations of 7 PCDD and 10 PCDF isomers having chlorine substitution in the 2,3,7,8 positions. Sediments (10 to 25 g dry weight) were spiked with the appropriate internal standards and were extracted for at least 24 hours with toluene in a soxhlet extractor fitted with a Dean-Stark trap. PCDD/PCDF were separated from interfering compounds in sample extracts by mixed-bed silica, basic alumina, and AX-21 Super Activated Carbon column chromatography. The extracts were reduced to a final volume of 20 µL and the appropriate recovery standards added.

Two µL of the concentrated extract were injected into an HRGC/HRMS system capable of performing selected ion monitoring at resolving powers of at least 10,000. The identification of the sixteen 2,3,7,8-substituted isomers for which a ^{13}C-labeled standard is available was based on their elution order from a DB-5MS analytical column with the corresponding retention time and the simultaneous detection of the two most abundant ions in the molecular ion region. The identification of OCDF was based on its retention time relative to ^{13}C-OCDD. Confirmation was based on a comparison of the ratios of the integrated ion abundance of the molecular ion species to their theoretical abundance ratios. Quantitation of the individual congeners was achieved with the establishment of a multipoint calibration curve for each analyte. Concentrations of 2,3,7,8-TCDF were confirmed on a DB-225 analytical column[4].

3. Results and Discussion

PCDD/PCDF are by-products of many processes that include chlorination steps. Paper mills, wood treatment facilities that use pentachlophenol, steel mills, and incinerators are some of the potential sources of dioxin/furan to the environment. Environmental loadings are sometimes associated with high levels of other environmental contaminants, such as PCBs.

No historical PCDD/PCDF data is available for sediments from Casco Bay; however, there is data for the 2,3,7,8-tetrachloro dibenzo-p-dioxin and dibenzofurans (TCDD/TCDF) for Androscoggin River sediments[5]. The Androscoggin River effluent enters the Atlantic Ocean via the Sheepscot Bay estuary, which is just to the northeast of Cape Small. Since the average daily flow rate to the Sheepscot Bay estuary is more than eight times the flow rate into the Casco Bay estuary, it is possible that effluent from the Androscoggin River containing particulate materials could exit Sheepscot Bay and enter Casco Bay where they may be deposited[6]. Androscoggin River sediments had a median concentration of 2,3,7,8-TCDD of 23.1 and 5.3 pg/g for samples collected in 1985 and 1991, respectively. The median concentration of 2,3,7,8-TCDF in 1991 (the only year it was measured) was 168 pg/g. The analyses did not include the other 2,3,7,8- substituted polychlorinated dioxins and furans[5]. Concentrations of 2,3,7,8-TCDD and 2,3,7,8-TCDF in bass, suckers, and lobsters from the Presumpscot River have been reported[5]. The meat of the bass had no detectable TCDD and TCDF was less than 1 pg/g. Suckers did contain TCDD and TCDF with an average 2,3,7,8-TCDD toxicity equivalent (TEQ)[7] of 2.3 pg/g. Lobster meat had an average TEQ of 0.8 pg/g, however the tomalley or hepatopancreas of the lobster had an average TEQ of 18.7 pg/g.

TEQ at these levels resulted in the Maine Bureau of Health issuing an advisory in 1994 regarding human consumption of lobster tomalley[6].

The total PCDD/PCDF concentrations for Casco Bay ranged from 342 to 3,350 pg/g. The spatial pattern observed for total PCDD/PCDF (Figure 1) shows highest median concentrations in East Bay (2010 pg/g) inner bay (1645 pg/g) and Outer Bay (1358 pg/g) with lower concentrations in West Bay (735 pg/g) and Cape Small (342 pg/g). The TEQ for all 2,3,7,8-substituted congeners of PCDD/PCDF, have a similar distribution. The TEQ were highest in East Bay (12.4 pg/g), Inner Bay (12.4 pg/g) and Outer Bay (9.4 pg/g) and lower in West Bay (3.8 pg/g) and Cape Small (1.8 pg/g). The highest TEQs are associated with the Presumpscot River. Inner Bay sediments to the south of the river have higher TEQ indicating they may be influenced by the river effluent.

The percentage that TCDF contributes to the total PCDF for most sites is 5% or less. The percentage of TCDF for sites on the Royal River (SW07B) and the Cousins River (SW07A) are 26.7% and 18.0%, respectively. This suggests a different source for the furans from these two sites. Inner Bay sites IB09 and IB08, to the south of the effluence of the Royal and Cousins Rivers also exhibit slightly elevated TCDF percentages of 8.3% and 6.1%, respectively.

There is a gradient for 2,3,7,8-TCDD (Figure 2) with higher concentrations in and near the Presumpscot River, lower concentrations in the Outer Bay, and no detectable 2,3,7,8-TCDD in East Bay, Cape Small or West Bay. This suggests a source of 2,3,7,8-TCDD in the drainage basin of the Presumpscot River. The source may be the SD Warren's bleached kraft pulp and paper mill near Westbrook and 10 miles from Casco Bay where 2,3,7,8-TCDD has been reported in the sludge from their waste water treatment plant[5]. The concentration of 2,3,7,8-TCDD has decreased in sludge samples from the SD Warren plant between 1985 and 1992. However, previous discharges may be moving down the Presumpscot River as evidenced by the detections of 2,3,7,8-TCDD in sediments in this study and in lobster tomalley samples collected just south of the mouth of the Presumpscot River[5].

The presence of higher concentrations of PCDD/PCDF in East Bay site sediments is puzzling, but may be due to transport around Cape Small and deposition of fine-grained particulate matter from the Androscoggin River and Sheepscot Bay estuary. The East Bay has no major river input only surface runoff from the surrounding shore area. Other possible sources of PCDD/PCDF responsible for the higher concentrations in East Bay are not apparent at this time. Higher TEQ, and total dioxins are associated with sites near the Presumpscot River and Inner Bay. This may be the result of the influence of the effluent from these rivers.

Sediments from other coastal regions have a wide range of reported values for the concentration of 2,3,7,8-TCDD from not detected (ND) to 1500 pg/g or 2,3,7,8-TCDD TEQ of ND to 2300 pg/g[8]. The concentrations of 2,3,7,8-TCDD in Casco Bay (ND to 1.8 pg/g) are in the lower end of this range. However, sediments with low 2,3,7,8-TCDD concentrations may actually have TEQ values of concern resulting from the presence of other less toxic PCDD/PCDF isomers. The predominance of the 2,3,7,8-octachlorodibenzo-*p*--dioxin in the sludge from a pentachlorophenol (PCP) wood treatment facility has been reported[8].

4. Conclusions

PCDD/PCDF were detected in sediments from all areas of Casco Bay. The concentrations were highest near potential input sources (i.e. the Presumpscot River) with the exception of the higher concentrations in East Bay which may be the result of transport into the bay from the Androscoggin River. The concentrations found in Casco Bay sediments are

not low when compared to other estuarine areas. In spite of the low concentration in sediment, the detection of 2,3,7,8-TCDD/TCDF in lobster tissue and tomalley indicate they are bioavailable and have resulted in an advisory regarding consumption of lobster tomalley. Additional data is needed to determine if other PCDD/PCDF isomers may also pose a human health concern in Casco Bay.

5. References

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6. Acknowledgments

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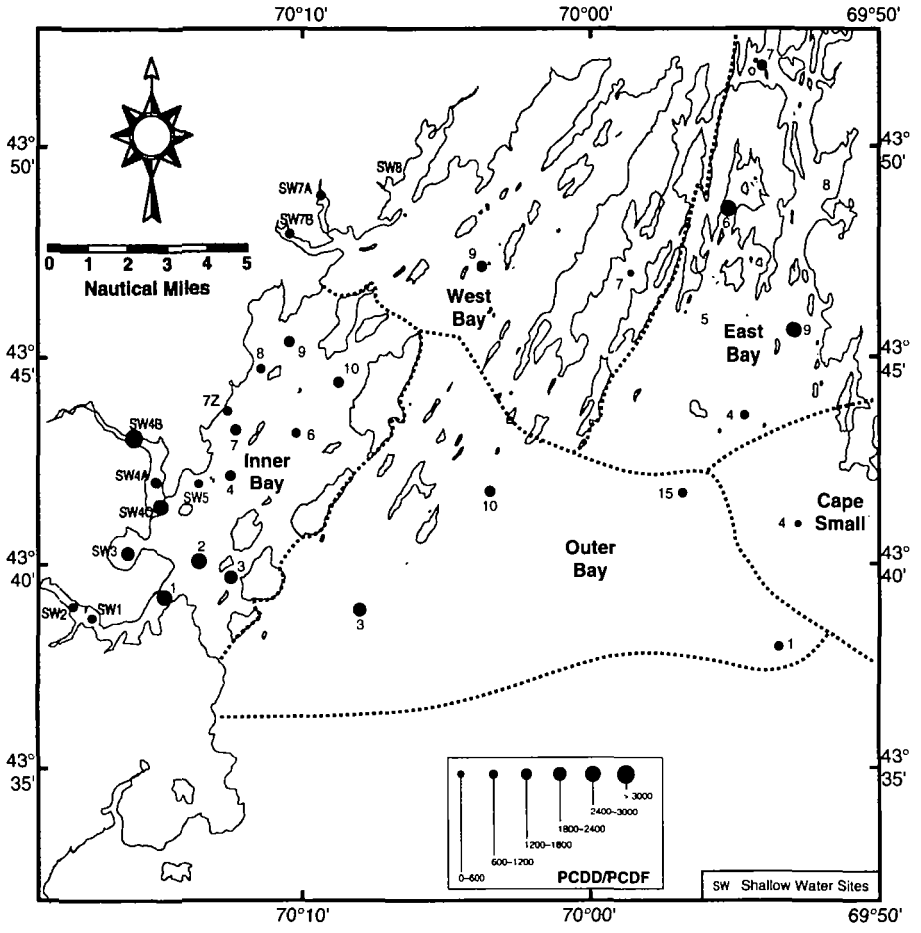

Figure 1. Total PCDD/PCDF concentrations in Casco Bay surface sediments.

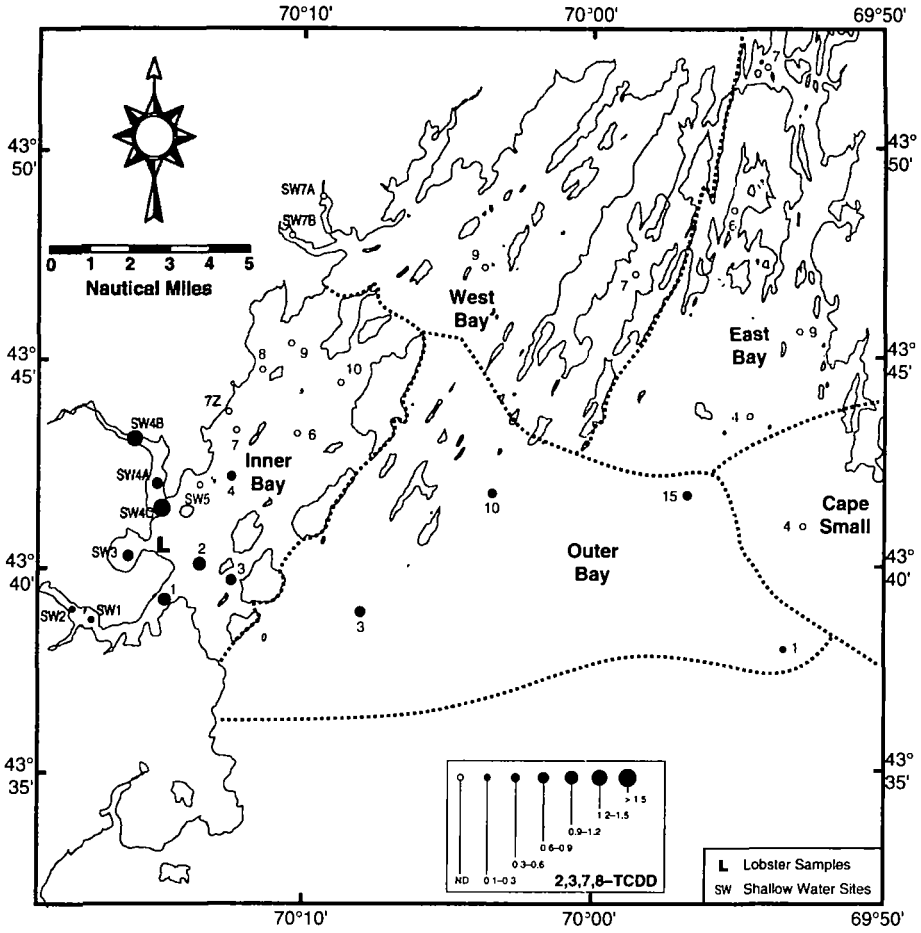

Figure 2. 2,3,7,8-TCDD concentrations in Casco Bay surface sediments.