BIOMONITORS OF DIOXIN/FURAN AND COPLANAR PCB CONTAMINATION IN THE SACRAMENTO AND SAN JOAQUIN RIVERS IN NORTHERN CALIFORNIA

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INTRODUCTION

A study was designed to investigate the extent, magnitude and source of polychlorinated dibenzodioxin and furan (PCDD/PCDF) and coplanar polychlorinated biphenyl (PCB) contamination using aquatic life as biomonitors. The study focused around two suspected sources of dioxin contamination: a bleached pulp and paper mill and a pentachlorophenol (PCP) wood treatment plant. These two facilities operated, along with other industrial plants, near the confluence of the Sacramento and San Joaquin Rivers (Delta) in Northern California.

The objectives of the study were:

1. To select appropriate and representative locations bracketing each suspected source.
2. To collect target fish and sediment samples and to transplant bivalves for a two-month period.
3. To analyse sediment, bivalve and fish samples for PCDD/PCDFs and coplanar PCBs.
4. To compare and contrast congener profiles and concentrations among species and sampling sites.
5. To compare analyte concentrations in fish filets to those in whole body samples of the same species.

METHODOLOGY

During the first year of the study sampling and analytical efforts focused around the pulp mill in Antioch, while during the second year the focus shifted to the PCP plant near the Port of Stockton. Several locations were selected for sampling around each of the two plants.

In Antioch, site of the pulp mill, two locations were selected upstream from the plant

(one on each river), one in the vicinity of the plant and one downstream from the plant. Because of the salinity gradient of the riverine system, no single fish or bivalve species could be collected, but multiple comparisons were made instead. The target species, selected on the basis of their abundance and localized feeding range, were: white catfish (Ictalurus catus), channel catfish (Ictalurus punctatus), Pacific staghorn sculpin (Leptocottus armatus) and yellowfin goby (Acanthogobius flavimanus). Clams (Corbicula fluminea) were transplanted in the three freshwater locations and retrieved two months later, while resident mussels (Mytilus edulis) were collected from the estuarine location. Surface sediment samples were collected from each location.

In Stockton, site of the PCP plant, fish were collected from two locations: the Deep Channel near the port, and the slough bordering the plant. These fish included both bottom feeding, resident species such as goldfish (Carassius auratus), carp (Cyprinus carpio), bluegill (Lepomis macrochirus), green sunfish (Lepomis cyanellus) and redear sunfish (Lepomis microlophus) and sportsfish such as striped bass (Morone saxatilis) and large mouth bass (Micropterus salmoides). In addition, surface sediment samples were collected from 10 locations, extending beyond the above areas. Clams were deployed for a period of 2 months at the same 10 locations.

All samples were freeze-dried prior to extraction. Fish from the pulp mill phase of the study were analysed as whole body, while both whole body and filet measurements were conducted on the larger fish from the PCP plant phase. Bivalves were shelled following freeze-drying. All freeze-dried samples (sediments, fish and bivalves) were blended and homogenized in 1:1 CH_2Cl_2/n-Hexane (sediments) or 1:1 CH_2Cl_2/Cyclohexane (bivalves and fish); spiked with ^{13}C-labeled internal standards; cleaned up by Carbon/SiGel followed by potassium silicate/acid silica and Super I basic alumina. The final extract was spiked with the mixture of $^{13}C_6$-labeled recovery standards. The samples were analysed by High Resolution Gas Chromatography/ High Resolution Mass Spectrometry (HRGC/HRMS) (Varian 3400, Finnigan MAT 90) with a 60m, 0.25mm, DB-5 column, using a temperature program (220°C for 2 min, then 5°C/min to 260°C, followed by 1°C/min to 300°C). The MS operated in the EI mode (50 eV) with a 0.8 mA emission current and a minimum resolution of 8000 amu.

RESULTS and DISCUSSION

Overall, the coplanar PCB levels found in fish from the pulp mill phase of the study rivaled the highest concentrations found in fish from Green Bay, Lake Michigan[1], a site of acute PCB contamination where reproductive impairment and teratogenicity in fish-eating birds has been observed. No single source for the PCB contamination is envisioned; rather, multiple sources and processes over the years may have contributed to the observed levels.

On the other hand, PCDD/PCDF levels measured in the all samples from the same phase were low, ranging from 2-5 pg/g I-TEQ (wet weight) in fish and bivalves and from 3-51 pg/g I-TEQ (dry wt) in sediments. These measurements can be compared with other measurements in fish from the Sacramento River that were part of the National Dioxin Study[1]. In comparing these data, however, differences in species, fish size, lipid content,

feeding range and sampling method (filet vs. whole body; composite vs. individual fish) should be taken into account. The levels reported in this study are lower than the concentrations measured[1] in the Sacramento River near Anderson (12.5 pg/g I-TEQ in a composite of four whole body Sacramento suckers; 22.5 pg/g I-TEQ in a composite of four Rainbow trout fillets). They are, however, in the same range as the levels measured[2] near Antioch in a single Sacramento squawfish (Ptychocheilus grandis) fillet (1.5 pg/g I-TEQ) and in a single Sacramento sucker (Catostomus occidentalis) (8 pg/g I-TEQ whole body). The latter had a 2,3,7,8-TCDF to 2,3,7,8-TCDD ratio of approximately 10, a ratio associated with bleach pulp activities[3]. No such "bleach pulp" profile was evident in any of the samples analysed in this study. In addition, because of the low overall levels of PCDD/PCDF measured in all samples, no differences between sites could be seen, and therefore, no special impact could be attributed to the pulp mill discharge.

Difficulties were encountered in catching target fish in the selected areas around the pulp mill and the majority of the fish caught were extremely small in size. The small size and the inferred young age of the fish may have biased the sample towards brief exposures to the contaminants of interest. The effect of age (expressed as size) on concentration was explored by comparing subgroups of the same species collected at the same location. In the San Joaquin River, the number and sizes of the collected White Catfish allowed three subsamples: A composite (WCF1) of the 8 smallest fish, ranging in weight from 3.7 to 4.7 g; the largest individual (WCF3) weighing 86 g; and a composite (WCF2) of the 4 largest fish, excluding WCF3, ranging in weight from 15.4 to 33.6 g. The larger fish (WCF2 and WCF3) had more than three times the lipid content of the smaller fish (WCF1) and, with the exception of HpCDD and OCDD, higher concentrations than the larger fish. The differences were greatest in the case of the coplanar PCBs.

Sediment samples in the vicinity of the pulp mill had a PCDD/PCDF pattern consistent with pentachlorophenol contamination (high HpCDD and OCDD levels relative to other congeners). Sediments and bivalves had both 2,3,7,8-substituted and non-2,3,7,8-substituted congeners. In contrast, with few exceptions, only 2,3,7,8-substituted PCDD/PCDF congeners were found in fish. This is consistent with reports showing selective bioconcentration of these congeners in fish [4,5] as opposed to mollusks and crustaceans[6].

Similar PCDD/PCDF patterns were observed in freshwater clams and estuarine mussels associated with the pulp mill phase of the study. All bivalves had relatively high levels of total tetradioxins compared to total pentadioxins or total hexadioxins. The profile of tetradioxins was similar in all field bivalves, but differed in the control clams. This difference indicates that clams are sensitive to changes in their environment and within a two month period reflect the tetradioxins in their new environment. This finding supports the use of transplanted clams in biomonitoring programs for PCDD/PCDFs.

In all locations near the pulp mill, the concentrations of PCB #77 and #126 increased at least tenfold from sediments to bivalves. No similar increase was observed with any of the PCDD/PCDFs. In fact, the high HpCDD and OCDD levels measured in the San Joaquin sediment were not reflected in the corresponding clams.

In all samples, the ratio of 1,2,3,7,8 PeCDD to 2,3,7,8 TCDD was always greater than 1, a finding already reported in the literature for fish and human samples from Sweden[7].

No particular source has ever been associated with 1,2,3,7,8 PeCDD, however, low levels have been measured in pentachlorophenol formulations and in incinerator emissions[7]. Among the PeCDFs, the 2,3,4,7,8 PeCDF was consistently higher than the 1,2,3,7,8 PeCDF, but its ratio to the 1,2,3,7,8 PeCDD fluctuated around 1. It has been reported that 2,3,4,7,8 PeCDF predominates in fish from northern Europe, but not in fish from North America[7,8].

The toxicity attributed to PCDD/PCDFs, in I-TEQs, was greater than that attributed to the three coplanar PCBs (expressed as PCB-TEQs[9]) in all the sediments associated with the pulp mill phase of the study, primarily because of the high OCDD and HpCDD levels. On the other hand, the PCB-TEQs were greater than the I-TEQs for all fish and bivalves. This finding is in agreement with the observation of a tenfold increase in PCB concentration, from the sediments to the bivalves. The toxicity contribution of the coplanar PCBs clearly points to the need to monitor these contaminants in aquatic species.

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