Bull. Environ. Contam. Toxicol. (1999) 62:239-246


Bulletin of Environmental Contamination and Toxicology

# Polychlorinated Dibenzo-p-dioxin and Polychlorinated Dibenzofuran Congener Profiles in Fish, Crayfish, and Sediment Collected near a Wood Treating Facility and a Bleached Kraft Pulp Mill

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Received: 6 October 1998/Accepted: 25 January 1999

Polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) are chlorinated organic environmental contaminants that have been extensively studied. Congeners with 2,3,7,8 chlorine substitution are toxic at low doses and have been shown to cause cancer (Kociba et al. 1978), reproductive (Murray et al. 1979) and developmental toxicity (Walker and Peterson 1991). Because of their physical chemical properties these compounds are frequently found in sediments and they can bioaccumulate. Sediments contaminated with PCDD or PCDDF can be an important exposure route for aquatic life (Kuehl et al. 1987).

Point and nonpoint sources of pollution release PCDD/PCDF into the environment. Congeners of PCDD/PCDF have been detected in municipal sewage treatment plant sludge, bleached kraft pulp mill effluent, soils and sediments around wood treating facilities, and flue-gas from municipal and medical incinerators. Sediment PCDD and PCDF homologue and congener profiles have been used to identify sources of these pollutants (Fattore et al. 1997; Eitzer 1993). There has been interest in using PCDD/PCDF profiles in fish tissue to identify contaminant sources, and sediment PCDD/PCDF concentrations have been used to predict fish tissue concentrations (Comber et al. 1996). However, recent field studies have shown that fish tissue and sediment collected from the same areas have different PCDD/PCDF homologue profiles (Bonn 1998).

This study reports PCDD/PCDF congener concentrations and profiles in carp, crayfish, catfish and sediment samples collected from near a wood treating facility and near the discharge of a bleached-kraft pulp mill.

## MATERIALS AND METHODS

Sediment and tissue samples were collected in September and October 1991 near a wood treating facility (WTF) located on a side channel of the Columbia River and near the discharge of a bleached-kraft pulp mill (BKM) located on the main

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stem Columbia River. The WTF sediment samples were collected approximately 1 km upstream, adjacent to the facility (2 samples), and 1 km downstream from the WTF. The WTF carp and crayfish samples were collected 1 km upstream, adjacent to the facility, and 1 km and 3 km downstream from the WTF. The BKM sediment samples were collected approximately 4 km upstream, near the effluent discharge, and 1 km downstream from the BKM discharge. The BKM carp and channel catfish samples were collected 4 km upstream, near the effluent discharge, and 1 and 4 km downstream from the BKM discharge.

Surface sediment samples were collected with a stainless steel 0.23 $m^2$ Eckman dredge. Sediment samples were composites with three to five grabs combined from a sample area, homogenized in a stainless steel bucket with a teflon spatula, and placed in glass jars for storage at 4°C until analysis. Fish were collected by electroshocking and gill nets and crayfish were collected with baited traps. Tissue samples were composites from a sample area using the whole body from two to eight carp, tail meat from four to twenty-six crayfish, and fillets with skin on from three to twelve channel catfish. Carp weighed 420 to 2900 g, crayfish weighed 1 to 3 oz, and catfish weighed 1000 to 5000 g. Tissue samples were wrapped in aluminum foil, stored on wet ice for shipment to the laboratory, and then frozen at -20°C.

Tissue lipid and PCDD/PCDF analysis were performed by Alta Analytical (El Dorado Hills, CA). Sediment sample PCDD/PCDF analysis were performed according to USEPA Method 1613A (U.S. Environmental Protection Agency 1990a). Briefly, 10 g of sediment was soxhlet extracted for 16 hr with toluene. Initial sample cleanups were performed by mini-silica gel filtration using 200 mm x 15 mm glass chromatographic columns and were eluted with hexane. The final cleanup was by charcoal/silica gel columns using 200 mm x 15 mm glass columns. The samples were eluted with 5 ml 1:1 $MeCl_2$:Cyclohexane and 5 ml 75:20:5 $MeCl_2$:MeOH:Benzene and the rinses discarded. The column was inverted and eluted with 25 ml toluene into a 50 ml round bottom flask. Quantification was performed by gas chromatography (GC) with mass spectrometry (MS) verification. Fish tissue PCDD/PCDF analysis was performed according to USEPA Method’8290 (U.S. Environmental Protection Agency 1990b). Approximately 25 g of tissue was extracted with toluene in a soxhlet/Dean extractor. Cleanup was as described above. Quantification and verification were by GC/MS. Tissue lipids were analyzed according to USEPA Method 8290. Sediment organic carbon was analyzed by the Oregon Department of Environmental Quality (Portland, OR) according to the Walkly-Black method (Allison 1965).

Congener profiles were developed by normalizing PCDD/PCDF congener concentrations to total PCDD/PCDF. Significant differences between mean concentrations of PCDD/PCDF congeners for locations and species were determined using Mann-Whitney U test with a significant difference at a two-tailed p-value of <0.05.

## RESULTS AND DISCUSSION

Carp, channel catfish, and crayfish are bottom feeders and PCDD/PCDF accumulation from contaminated sediments would be expected. Carp from the WTF had significantly higher concentrations of 1,2,3,7,8-PeCDD and 1,2,3,4,6,7,8- HpCDD than carp from the BKM (Table 1).

**Table 1.** Mean PCDD concentrations and lipid normalized concentrations in fish samples collected from near a wood treating facility (WTF) and a bleached kraft pulp mill (BKM). Means are from upstream and downstream samples. n=4 (SE).

| | pg/g-tissue-dry wt | | | | pg/g-lipid-dry wt | | | |
|---|---|---|---|---|---|---|---|---|
| | Carp WTF | Carp BKM | Cray WTF | Catf BKM | Carp WTF | Carp BKM | Cray WTF | Catf BKM |
| 2,3,7,8-TCDD | 1.0 | 4.7 | 0.0[2] | 12.7 | 5.6 | 18.9 | 0.0[2] | 45.3 |
| | (0.4) | (2.3) | (na)[4] | (3.8) | (1.7) | (8.5) | (na)[4] | (15.2) |
| 1,2,3,7,8-PeCDD | 1.1 | 0.0[1] | 0.1[2] | 0.0 | 6.3 | 0.0[1] | 0.3[2] | 0.0 |
| | (0.2) | (na)[4] | (0.0) | (na)[4] | (0.8) | (na)[4] | (0.2) | (na)[4] |
| 1,2,3,4,7,8-HxCDD | 0.6 | 0.3 | 0.0[2] | 0.1 | 3.8 | 1.2[1] | 0.0[2] | 0.5 |
| | (0.1) | (0.1) | (na)[4] | (0.0) | (0.5) | (0.2) | (na)[4] | (0.1) |
| 1,2,3,6,7,8-HxCDD | 3.0 | 0.9 | 0.1[2] | 0.8 | 18.1 | 3.6[1] | 0.6[2] | 2.9 |
| | (0.6) | (0.4) | (0.1) | (0.1) | (2.5) | (1.3) | (0.4) | (0.5) |
| 1,2,3,7,8,9-HxCDD | 0.4 | 0.1 | 0.0[2] | 0.1 | 2.4 | 0.4[1] | 0.0[2] | 0.4 |
| | (0.1) | (0.1) | (na)[4] | (0.0) | (0.5) | (0.3) | (na)[4] | (0.0) |
| 1,2,3,4,6,7,8-HpCDD | 5.8 | 1.9[1] | 0.7[2] | 0.6[3] | 36.6 | 8.3[1] | 4.2[2] | 2.2[3] |
| | (0.7) | (0.6) | (0.3) | (0.1) | (7.2) | (2.0) | (1.6) | (0.2) |
| OCDD | 11.2 | 7.5 | 11.7 | 6.5 | 70.5 | 34.5 | 58.6 | 20.5 |
| | (3.1) | (1.9) | (2.8) | (4.5) | (21.2) | (11.4) | (18.9) | (13.0) |
| % lipid | 16.6 | 23.2 | 22.8 | 28.9 | (na)[4] | (na)[4] | (na)[4] | (na)[4] |

[1] Significant difference between locations for carp.
[2] Significant difference between carp and crayfish (Cray) from the same location.
[3] Significant difference between carp and channel catfish (Catf) collected from the same location (two-tailed p-value <0.05 for [1,2,3]).
[4] Not applicable.

Carp, channel catfish, and crayfish are resident animals but are mobile and could be used as spatial integrators of contamination. Upstream and downstream sample were considered to be representative for the area and the results were pooled for determining mean PCDD/PCDF congener differences between location. However, upstream samples had fewer detections and lower concentrations of PCDD/PCDF congeners than downstream samples.

Carp samples from the WTF had significantly higher concentrations of 1,2,3,4,7,8-HxCDF and 1,2,3,4,7,8,9-HpCDF than carp samples from the BKM site (Table 2). Carp samples from the BKM location had significantly higher concentrations of 2,3,7,8-TCDF than WTF carp samples (Table 2). Carp and channel catfish samples collected from the BKM site had similar levels of PCDD/PCDF congeners while crayfish had significantly lower concentrations of PCDD/PCDF congeners than carp collected from the WTF site (Table 1 and 2). Lipid normalization increased the number of congeners with significantly higher concentrations for Carp from the WTF site. Although carp, channel catfish, and crayfish are all omnivores and occupy similar trophic levels the data could be confounded by uncontrolled variables such as age and diet. Lipid content is an important variable for organic contaminants and lipid normalization can reduce species to species and tissue to tissue variability. However, contaminant disposition may be influenced by tissue specific characteristics separate from lipid content. Congener concentration differences between carp and channel catfish could be due to different tissue types instead of species.

**Table 2.** Mean PCDF concentrations and lipid normalized concentrations in fish samples collected at the WTF and the BKM locations. n=4 (SE).

| | pg/g-tissue-dry wt | | | | pg/g-lipid-dry wt | | | |
|---|---|---|---|---|---|---|---|---|
| | Carp WTF | Carp BKM | Cray WTF | Catf BKM | Carp WTF | Carp BKM | Cray WTF | Catf BKM |
| 2,3,7,8-TCDF | 2.8 | 22.1[1] | 0.1[2] | 3.7[3] | 15.8 | 90.5[1] | 0.4[2] | 12.9[3] |
| | (1.2) | (9.9) | (0.1) | (0.3) | (5.3) | (35.2) | (0.4) | (1.0) |
| 1,2,3,7,8-PeCDF | 0.5 | 0.4 | 0.1[2] | 0.2 | 2.9 | 1.9 | 0.6[2] | 0.6[3] |
| | (0.5) | (0.2) | (0.1) | (0.0) | (0.5) | (0.7) | (0.3) | (0.0) |
| 2,3,4,7,8-PeCDF | 0.9 | 1.5 | 0.1[2] | 2.1 | 5.2 | 6.1 | 0.5[2] | 7.7 |
| | (0.1) | (0.7) | (0.0) | (0.5) | (0.7) | (2.5) | (0.2) | (2.0) |
| 1,2,3,4,7,8-HxCDF | 0.4 | 0.1[1] | 0.1[2] | 0.0 | 2.6 | 0.4[1] | 0.4[2] | 0.0 |
| | (0.1) | (0.0) | (0.0) | (na)[4] | (0.5) | (0.2) | (0.2) | (na)[4] |
| 1,2,3,6,7,8-HxCDF | 0.3 | 0.1 | 0.0[2] | 0.0 | 1.9 | 0.4[1] | 0.2[2] | 0.0 |
| | (0.1) | (0.0) | (0.0) | (na)[4] | (0.5) | (0.2) | (0.1) | (na)[4] |
| 1,2,3,7,8,9-HxCDF | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| | (na)[4] | (na)[4] | (na)[4] | (na)[4] | (na)[4] | (na)[4] | (na)[4] | (na)[4] |
| 2,3,4,6,7,8-HxCDF | 0.3 | 0.2 | 0.1[2] | 0.2 | 2.2 | 0.9[1] | 0.8[2] | 0.6 |
| | (0.0) | (0.0) | (0.0) | (0.0) | (0.4) | (0.1) | (0.3) | (0.1) |
| 1,2,3,4,6,7,8-HpCDF | 0.6 | 0.3[1] | 0.1[2] | 0.1[3] | 4.0 | 1.2[1] | 0.7[2] | 0.4 |
| | (0.1) | (0.1) | (0.0) | (0.0) | (0.7) | (0.2) | (0.3) | (0.0) |
| 1,2,3,4,7,8,9-HpCDF | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| | (na)[4] | (na)[4] | (na)[4] | (na)[4] | (na)[4] | (na)[4] | (na)[4] | (na)[4] |
| OCDF | 0.4 | 0.0 | 0.8 | 0.2 | 2.3 | 0.0 | 4.7 | 0.6 |
| | (0.2) | (na)[4] | (0.8) | (0.1) | (1.5) | (na)[4] | (4.7) | (0.4) |

See Table 1 for symbol notation.

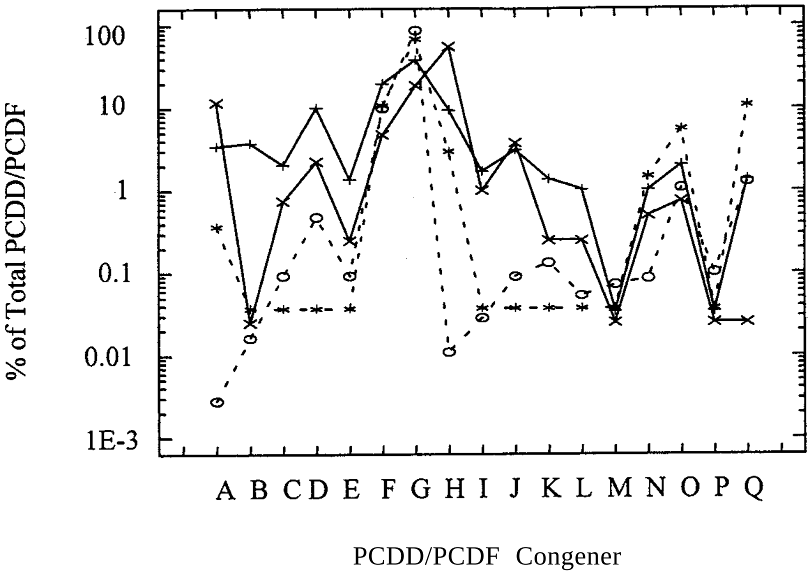


**Figure 1.** Mean PCDD/PCDF congener profiles in carp from the WTF (-+-) and BKM (-×-) sites and for sediment from the WTF (-o-) and the BKM (-*-) sites. A=2,3,7,8-TCDD; B=1,2,3,7,8-PeCDD; C=1,2,3,4,7,8-HxCDD; D=1,2,3,7,8,9-HxCDD; E= 1,2,3,7,8,9-HxCDD; F=1,2,3,4,6,7,8-HpCDD; G=OCDD; H=2,3,7,8-TCDF; I=1,2,3,7,8-PeCDF; J=2,3,4,7,8-PeCDF; K=1,2,3,4,7,8-HxCDF; L=1,2,3,6,7,8-HxCDF; M=1,2,3,7,8,9-HxCDF; N=2,3,4,6,7,8-HxCDF; O=1,2,3,4,6,7,8-HpCDF; P=1,2,3,4,7,8,9-HpCDF; Q=OCDF.

Homologue patterns for PCDD/PCDF in sediments can differ between pollution sources (Fattore et al. 1997) and land use types (Bonn 1998). Sediment homologue profiles for PCDD/PCDF have been used to distinguish between nonpoint and point sources of pollution (Eitzer 1993). Sediment samples from the WTF site had significantly higher concentrations of 1,2,3,4,7,8-HxCDD, 1,2,3,6,7,8-HxCDD, and 1,2,3,7,8,9-HxCDD than sediment samples from the BKM site (Table 3). Generally, there were more detections and higher concentrations of PCDD/PCDF, especially the more highly chlorinated congeners, at the WTF site. Organic carbon normalization did not affect significant differences with location for PCDD/PCDF concentrations (Table 3). The mean concentrations for the more highly chlorinated dioxins and furans were orders of magnitude higher at the WTF but there were only three congeners that were significantly different between the sites (Table 3). The lack of significance was probably due to the low number of samples analyzed.

Homologue profiles of PCDD/PCDF can differ between fish tissue and sediments with higher concentrations of highly chlorinated PCDD/PCDF in sediments (Bonn 1998). This is consistent with the results of this study that showed sediment congener profiles were different from those for carp (Fig. 1) and

**Table 3.** Mean PCDF and PCDD concentrations and organic carbon (oc) normalized concentrations in sediment samples collected from the WTF (n=4) and the BKM locations (n=3). (SE).

| | pg/g-sediment dry-wt | | pg/g-oc dry-wt | |
|---|---|---|---|---|
| | WTF | BKM | WTF | BKM |
| 2,3,7,8-TCDF | 5.5 | 0.8 | 5.66E5 | 1.41E5 |
| | (4.19) | (0.6) | (4.50E5) | (7.82E4) |
| 1,2,3,7,8-PeCDF | 14.2 | 0.0 | 1.45E6 | 0.0 |
| | (12.0) | (na)[2] | (1.29E6) | (na)[2] |
| 2,3,4,7,8-PeCDF | 45.2 | 0.0 | 4.64E6 | 0.0 |
| | (38.6) | (na)[2] | (4.14E6) | (na)[2] |
| 1,2,3,4,7,8-HxCDF | 65.9 | 0.0 | 6.75E6 | 0.0 |
| | (55.2) | (na)[2] | (5.93E6) | (na)[2] |
| 1,2,3,6,7,8-HxCDF | 26.6 | 0.0 | 2.71E6 | 0.0 |
| | (22.0) | (na)[2] | (2.36E6) | (na)[2] |
| 1,2,3,7,8,9-HxCDF | 36.0 | 0.0 | 3.71E6 | 0.0 |
| | (31.5) | (na)[2] | (3.37E6) | (na)[2] |
| 2,3,4,6,7,8-HxCDF | 42.9 | 0.4 | 4.40E6 | 1.04E5 |
| | (36.0) | (0.0) | (3.86E6) | (4.01E4) |
| 1,2,3,4,6,7,8-HpCDF | 541 | 1.5 | 5.55E7 | 3.63E5 |
| | (457) | (0.2) | (4.90E7) | (1.02E5) |
| 1,2,3,4,7,8,9-HpCDF | 50.9 | 0.0 | 5.22E6 | 0.0 |
| | (43.4) | (na)[2] | (4.65E6) | (na)[2] |
| OCDF | 638 | 2.9 | 6.46E7 | 6.29E5 |
| | (496) | (1.4) | (5.33E7) | (2.36E5) |
| 2,3,7,8-TCDD | 1.4 | 0.1 | 1.22E5 | 1.03E4 |
| | (0.8) | (0.1) | (7.20E4) | (1.03E4) |
| 1,2,3,7,8-PeCDD | 8.2 | 0.0 | 7.80E5 | 0.0 |
| | (5.1) | (na)[2] | (5.27E5) | (na)[2] |
| 1,2,3,4,7,8-HxCDD | 46.8 | 0.0[1] | 4.77E6 | 0.0[1] |
| | (38.2) | (na)[2] | (4.10E6) | (na)[2] |
| 1,2,3,6,7,8-HxCDD | 241 | 0.0[1] | 2.46E7 | 0.0[1] |
| | (201) | (na)[2] | (2.16E7) | (na)[2] |
| 1,2,3,7,8,9-HxCDD | 46.4 | 0.0[1] | 4.53E6 | 0.0[1] |
| | (30.2) | (na)[2] | (3.21E6) | (na)[2] |
| 1,2,3,4,6,7,8-HpCDD | 5017 | 2.9 | 5.09E8 | 6.48E5 |
| | (4054) | (0.8) | (4.35E8) | (1.62E5) |
| OCDD | 43,370 | 18.3 | 4.34E9 | 4.06E6 |
| | (33,122) | (5.5) | (3.56E) | (1.02E6) |
| organic carbon (mg/g) | 9.9 | 5.1 | (na)[2] | (na)[2] |
| | (1.2) | (1.5) | | |

[1]Significant difference between locations (two-tailed p-value <0.05).
[2]Not applicable.

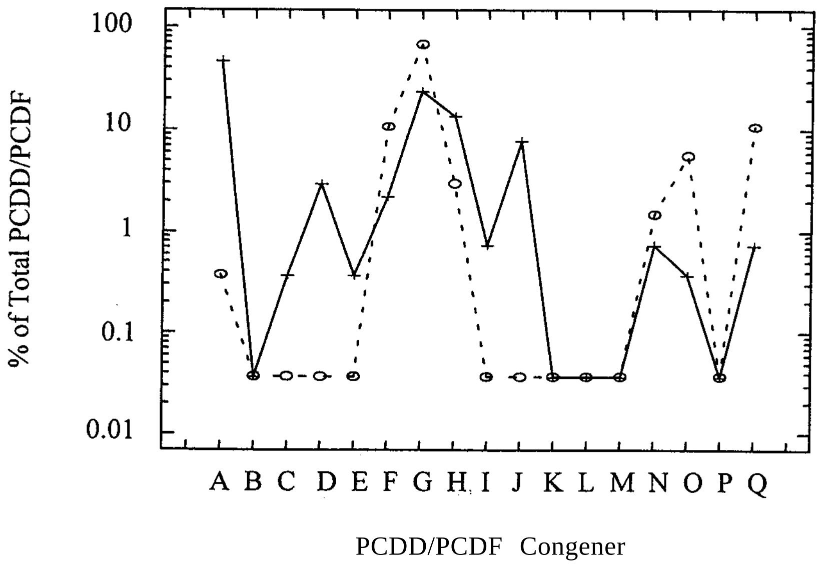


**Figure 2.** Mean PCDD/PCDF congener profiles in catfish (-+-) and for sediment (-o-) from the BKM site. A=2,3,7,8-TCDD; B=1,2,3,7,8-PeCDD; C=1,2,3,4,7,8-HxCDD; D=1,2,3,7,8,9-HxCDD; E= 1,2,3,7,8,9-HxCDD; F=1,2,3,4,6,7,8-HpCDD; G=OCDD; H=2,3,7,8-TCDF; I=1,2,3,7,8-PeCDF; J=2,3,4,7,8-PeCDF; K=1,2,3,4,7,8-HxCDF; L=1,2,3,6,7,8-HxCDF; M=1,2,3,7,8,9-HxCDF; N=2,3,4,6,7,8-HxCDF; O=1,2,3,4,6,7,8-HpCDF; P=1,2,3,4,7,8,9-HpCDF; Q=OCDF.

cattish (Fig 2.). In this study, sediments did not accurately predict fish tissue concentrations of PCDD/PCDF congeners (Fig. 1 and Fig. 2). Sediment results would potentially underestimate the lower chlorinated congeners and over estimate the higher chlorinated congeners in fish. Differences between fish and sediment congener profiles may be attributed to preferential uptake of lesser chlorinated PCDD/PCDF (Muir et al. 1992), the route of accumulation was not linked to bed sediments (Owens et al. 1994), preferential metabolism and clearance of higher chlorinated PCDD/PCDF, or variability in sediment contamination yielding variable tissue accumulation.

*Acknowledgments.* We thank the U.S. Environmental Protection Agency Region X Office for financial support of this project.

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