

**PCDDs AND PCDFs IN SURFICIAL SEDIMENTS
FROM THE LOWER PASSAIC RIVER AND NEWARK BAY**

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ABSTRACT

The relative distributions of polychlorinated dibenzo-p-dioxin (PCDD) and dibenzofuran (PCDF) measured in sediments from the lower Passaic River and Newark Bay, New Jersey were evaluated in order to assess whether these compounds were likely to have originated from a single source. Nineteen surficial (0-6 in.) sediment samples collected near industrial outfalls were analyzed for total congeners and 2,3,7,8-substituted isomers. The distribution of congener groups in all of the samples were similar to those observed in other environmental samples, such as fish and other aquatic biota, sediments, soils, fly ash, automobile exhaust, sewage sludge, and the adipose tissue of non-occupationally exposed humans. The concentration of total 2,3,7,8-TCDD equivalents in sediments, using USEPA toxic equivalents factors, ranged from 0.04 to 618 ng/kg (dry weight), with a geometric mean concentration of 5 ng/kg. Significant variations in congener and isomer patterns were observed among sediment samples using the multivariate data analysis techniques of principal components and cluster analysis. These analyses indicate that sediments from different locations in the watershed possess unique dioxin fingerprint patterns, suggesting that several sources have contributed to the presence of PCDDs and PCDFs in these two waterways.

KEY WORDS

sediments, dioxins, furans, Newark Bay, principal components analysis

INTRODUCTION

The lower Passaic River flows through a heavily industrialized watershed within the New York City - Newark, New Jersey metropolitan area. Previous studies of this watershed have shown that polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) are present in the soils of several industrial sites along the river (NJDEP, 1989), as well as in sediments and aquatic biota collected from the lower Passaic River and Newark Bay (Belton, 1985; Bopp, 1988). Despite the presence of several likely sources, it has been suggested that most or all of the PCDDs and PCDFs measured in sediments, fish, and invertebrates from the Passaic River and Newark Bay may be associated with a single source near the river's confluence with Newark Bay.

The purpose of the study described in this paper was to examine the relative distributions of PCDDs and PCDFs in sediments from the lower Passaic River and Newark Bay in order to assess whether the presence of these compounds were likely to be associated with a single source. Surficial sediments (0-6 in. depth) were collected near industrial outfalls throughout the lower Passaic River, Newark Bay, and their adjoining waterways. Concentrations of total PCDD and PCDF congeners and 2,3,7,8-substituted isomers were determined in each sample. Variations in the relative distributions of congener groups and 2,3,7,8-substituted isomers observed in sediments were analyzed using the multivariate data analysis techniques of principal components and cluster analysis. These are powerful statistical tools that can be combined to characterize the unique chemical fingerprint of dioxin-contaminated sediments and soils and to differentiate sources of these compounds in the environment (Townsend, 1986; Stalling et al., 1986; Swerev and Ballschmiter, 1989).

METHODS

A total of 19 sediment samples were collected from Newark Bay and the lower Passaic River, between its confluence with the Bay to above the Dundee Dam, between February 21 and 23, 1990. Sediment sampling sites were chosen on the basis of 1) a literature review of industrial processes from which PCDDs and PCDFs could be produced; and, 2) a historical survey of chemical and manufacturing facilities within the Newark Bay watershed which used the industrial processes of interest. Samples were collected primarily from areas proximate to active or inactive industrial outfalls where deposition and accumulation of sediment materials was visually evident. At each location, sediments were collected to an approximate depth of 6 in. with a stainless steel petite Ponar grab sampler. After thorough homogenization, sediments were transferred to pre-cleaned 8 oz. amber glass jars with teflon-lined caps. Samples were stored at 4°C prior to laboratory analysis.

Sediment samples were analyzed according to a modified version of U.S. Environmental Protection Agency (USEPA) Method 1613 and Method 8290 by Twin City Testing Corporation (St. Paul, MN). The laboratory reported 15 specific PCDD/PCDF 2,3,7,8-substituted isomers and 10 total congeners (tetra- through octa-chlorinated PCDD/PCDF) for each sample.

Samples were spiked with $^{13}\text{C}_{12}$ -labeled PCDD/PCDF internal standards and continuously extracted with benzene for 18 hrs in a Soxhlet Dean-Stark extractor. Extract volumes were reduced using a Kuderna Danish concentrator and the solvent exchanged to hexane. Sample interferences were minimized by additional extractions with sodium hydroxide, concentrated sulfuric acid, and distilled water. The hexane extracts were eluted on a liquid chromatography column containing alternating layers of silica gel impregnated with sulfuric acid and sodium hydroxide. Extracts were then fractionated on separate columns containing activated alumina or 5% AX-21 activated carbon on silica gel. Congener and 2,3,7,8-substituted isomer quantifications were conducted by high resolution gas chromatography / high resolution mass spectrometry (HRGC/HRMS) using a Hewlett Packard Model 5890 GC and VG Model 70SE HRMS. The PCDD/PCDF isomers were quantified from relative response factors as described in USEPA Method 8290. The recoveries of $^{13}\text{C}_{12}$ -labeled PCDD/PCDF internal standards ranged from 70 - 110%. Detection limits ranged from 0.15 to 5.3 parts per trillion (ppt) in sediments for individual 2,3,7,8-substituted isomers.

Principal components and cluster analyses were conducted on a Compaq DeskPro 386/20e microcomputer using the statistical software program Ein*Sight (Version 2.5, Infometrix Inc., Seattle, WA). Total congener and 2,3,7,8-substituted isomer data were organized into a 19 (samples) \times 25 (concentrations) matrix. Isomer concentrations identified by the analytical laboratory as non-detect (ND) were assumed to be one-half the reported detection limit from each individual sample analysis. The highest detection limit reported among 2,3,7,8-substituted isomers measured within a homologue group was assumed for any congener group identified as ND.

Principal components analysis was used as an exploratory data analysis technique in order to estimate the variability of the data set. Log-transformed data were autoscaled by Ein*Sight to have a mean value of 0.0 and a constant variance of 1.0 in order to eliminate any statistical bias associated with the orders of magnitude differences in chemical concentrations. Eigenvectors of the log-transformed/scaled data matrix were computed and used to determine principal component scores and loadings for each sediment sample. Principal components scores were calculated to factor or group the sediment samples, while loadings were calculated to factor or group the concentration variables.

Cluster analysis was performed on the log-transformed/scaled data in order to identify samples with similar distributions of PCDDs and PCDFs. A hierarchy of clusters (i.e., groups of similar samples) were generated by seven different sorting algorithms (single linkage, complete linkage, centroid, incremental sum of squares, median, group average, and Lance and Williams flexible), which depend primarily on the definition of a distance-measure between groups of data points. The distance between any one sample or group from each of the other samples or groups is a measure of the similarity between the samples. Results were produced graphically in the form of a dendrogram.

RESULTS AND DISCUSSION

The concentrations of total tetra- through octa-chlorinated PCDD and PCDF congeners and 2,3,7,8-substituted PCDD and PCDF isomers in sediments are presented in Tables 1 through 4. All samples contained congener profiles that were characteristic of environmental samples. For example, octa-chlorinated PCDDs and PCDFs were the predominant congener groups measured in sediment samples, followed by hepta-, hexa-, tetra-, and penta-chlorinated compounds. This distribution has

been observed by many researchers in fish and other aquatic biota, sediments, soils, fly ash, automobile exhaust, sewage sludge, and the adipose tissue of non-occupationally exposed humans (Hutzinger and Blumich, 1985; Rappe et al., 1987; 1989; Swerev and Ballschmiter, 1989).

Total PCDD congener concentrations ranged from ND to 17,000 ng/kg (dry weight) of OCDD. Total PCDF congener concentrations ranged from ND to 2,400 ng/kg of OCDF. TCDF and TCDF congeners ranged from ND to 590 ng/kg and from 0.32 to 1,500 ng/kg, respectively. The concentration of total 2,3,7,8-TCDD equivalents, using USEPA toxic equivalents factors, ranged from 0.04 to 618 ng/kg, with a geometric mean concentration of 5 ng/kg. Forty seven percent (47%) of the sediment samples had no detectable levels of 2,3,7,8-TCDD. The concentrations of 2,3,7,8-substituted TCDF and TCDF isomers ranged from ND to 510 ng/kg (geometric mean = 5.3 ng/kg) and from 0.28 to 480 ng/kg (geometric mean = 12.7 ng/kg), respectively.

Preliminary results of principal components analysis and cluster analysis indicate that surface sediment samples collected from different areas of the lower Passaic River and Newark Bay contain significantly different distributions of PCDDs and PCDFs. It has been well established that PCDD and PCDF fingerprint patterns are source-specific (Townsend, 1986; Rappe et al., 1987; Pitea et al., 1989; Swerev and Ballschmiter, 1989). Accordingly, the identification of unique fingerprint patterns by multivariate data analysis techniques supports the hypothesis that the introduction of PCDDs and PCDFs to the Newark Bay watershed is the result of contamination from several sources.

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Table 1. Total PCDD Congener Concentrations (ng/kg, dry weight) in Surficial Sediments from the Lower Passaic River and Newark Bay.

Sample	Total TCDD Equivalents ^a	Total TCDD	Total PeCDD	Total HxCDD	Total HpCDD	Total OCDD
RS1	3.5	3.5	1.5	23	89	530
RS2	1.6	56	ND ^b	36	140	930
RS3	12.8	11	1.4	27	98	350
RS4	491	590	6.5	280	1800	9000
RS5	618	510	22	1700	4100	17000
RS6	43	100	ND	300	1100	6500
RS7	6	39	ND	120	420	2600
RS8	6.2	52	630	160	660	4200
RS9	1.0	ND	ND	ND	190	1300
RS10	0.2	ND	38	ND	8.9	42
RS11	0.05	0.13	ND	ND	12	67
RS12	0.05	ND	ND	ND	6	35
RS13	0.1	ND	9.5	0.55	5.4	31
RS14	31	27	ND	11	420	2100
RS15	0.8	2.2	ND	23	84	400
RS16	13	60	ND	76	1000	6300
RS17	15	21	ND	84	400	2200
RS18	120	160	ND	140	640	2800
RS19	23	75	ND	140	1100	5900

a. Total 2,3,7,8-TCDD toxic equivalents were calculated based on International TEFs/89 criteria.

b. ND indicates that the congener group was not detected.

Table 2. Total PCDF Congener Concentrations (ng/kg, dry weight) in Surficial Sediments from the Lower Passaic River and Newark Bay.

Sample	Total TCDF	Total PeCDF	Total HxCDF	Total HpCDF	Total OCDF
RS1	22	14	15	46	33
RS2	13	ND ^a	7.9	ND	12
RS3	52	42	86	210	220
RS4	940	890	990	2200	2400
RS5	1500	2300	640	1800	2200
RS6	290	320	260	430	560
RS7	89	33	41	130	160
RS8	93	77	50	210	220
RS9	8.9	ND	ND	59	ND
RS10	0.32	0.34	0.76	3	2.5
RS11	0.42	0.73	1.7	3.5	2.2
RS12	0.42	2.6	0.81	3.3	2.2
RS13	0.5	0.48	1.6	2.7	1.6
RS14	79	69	110	200	200
RS15	19	6.5	9.4	32	30
RS16	220	250	410	490	580
RS17	120	210	250	250	220
RS18	290	370	530	1000	1200
RS19	220	220	260	400	440

a. ND indicates that the congener group was not detected.

Table 3. 2,3,7,8-substituted PCDF Isomer Concentrations (ng/kg, dry weight) in Surficial Sediments from the Lower Passaic River and Newark Bay.

Sample	2378 TCDF	12378 PeCDF	23478 PeCDF	123478 HxCDF	123678 HxCDF	123789 HxCDF	234678 HxCDF	1234678 HpCDF	1234789 HpCDF
RS1	6.8	1.4	1.4	3.9	2	1.5	(0.45) ^a	25	2.7
RS2	9.1	(0.95)	(1.5)	4.2	(1.2)	3.7	(1.0)	(2.4)	(1.3)
RS3	15	3.6	3.6	41	7.3	2.6	(0.31)	180	4.6
RS4	280	15	53	370	50	29	(2.1)	1600	48
RS5	480	(9.5)	420	(100)	(75)	(15)	(16)	1200	41
RS6	85	12	18	55	16	16	(1.8)	260	14
RS7	52	(5.5)	(5.0)	(6.0)	(3.2)	(4.1)	(7.0)	74	(8.0)
RS8	19	(1.8)	(1.3)	(3.4)	(2.2)	(2.8)	(4.2)	84	(4.5)
RS9	8.9	(5.0)	(12.0)	(2.7)	(2.0)	(1.5)	(3.6)	30	(6.5)
RS10	0.32	(0.14)	(0.14)	(0.55)	(0.5)	(0.16)	(0.06)	1.4	(0.14)
RS11	0.28	(0.14)	0.14	(0.17)	(0.14)	(0.14)	(0.1)	1.3	(0.08)
RS12	0.42	(0.12)	(0.18)	(0.16)	(0.28)	(0.21)	(0.12)	1.5	(0.14)
RS13	0.5	(0.06)	0.11	(0.1)	(0.11)	(0.15)	(0.10)	1.2	(0.2)
RS14	27	(1.6)	(1.8)	22	(2.6)	(2.6)	(3.6)	120	(2.05)
RS15	4.9	(0.32)	1.2	(1.1)	(1.2)	1.5	(0.34)	13	(0.85)
RS16	35	(2.1)	(3.6)	39	9.8	13	(1.8)	240	(5.5)
RS17	22	(4.6)	9.1	31	12	12	(1.8)	130	10
RS18	120	10	20	200	33	12	(1.8)	900	15
RS19	46	5.3	11	36	15	14	(0.9)	230	(2.8)

a. Data in parentheses () represent non detected measurements and, therefore, one half the detection limit was assumed.

Table 4. 2,3,7,8-substituted PCDD Isomer Concentrations (ng/kg, dry weight) in Surficial Sediments from the Lower Passaic River and Newark Bay.

Sample	2378 TCDD	12378 PeCDD	123478 HxCDD	123678 HxCDD	123789 HxCDD	1234678 HpCDD
RS1	2.1	(0.55) ^a	(0.6)	3	2.4	41
RS2	(1.3)	(1.2)	(2.2)	(2.2)	(1.8)	56
RS3	9.6	(0.5)	0.94	3	(0.8)	38
RS4	440	6.5	9.6	46	21	880
RS5	510	22	(48)	(38)	(20)	2100
RS6	26	(2.4)	(3.4)	31	25	490
RS7	(14)	(9.0)	(7.0)	(6.0)	(6.5)	170
RS8	(5.5)	(2.6)	(3.2)	(8.5)	(4.0)	360
RS9	(7.5)	(16)	(1.9)	(1.4)	(3.1)	80
RS10	(0.08)	(0.12)	(0.24)	(0.22)	(0.18)	4.7
RS11	(0.19)	(0.13)	(0.09)	(0.26)	(0.24)	5.5
RS12	(0.12)	(0.08)	(0.16)	(0.3)	(0.18)	3
RS13	(0.27)	(0.16)	(0.1)	(0.34)	(0.12)	2.8
RS14	27	(1.6)	(1.6)	11	(1.5)	210
RS15	(1.0)	(0.22)	(0.25)	2.4	(1.2)	42
RS16	6.4	(3.4)	(2.2)	16	(6.0)	520
RS17	10	(3.6)	5.5	18	(3.2)	200
RS18	100	(2.4)	(1.9)	15	(2.2)	290
RS19	12	(1.8)	8	24	20	550

a. Data in parentheses () represent non detected measurements and, therefore, one half the detection limit was assumed.