Direct and Indirect Contributions of Atmospheric PCDDs and PCDFs to Hudson River National Estuarine Research Reserve Sediment Cores

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Introduction

Few data exist on the occurrence of PCDD/PCDF compounds in New York's Hudson River System even though this system may be susceptible to high PCDD/PCDF concentrations owing to its location in the highly populated and industrialized northeastern United States. The present study of PCDD/PCDF concentrations in Hudson sediment cores, air, precipitation, soil, and storm runoff particulates was undertaken to assess the PCDD/PCDF contamination and determine the contribution of these compounds from non-point atmospheric sources to the Hudson River National Estuary Research Reserve system located on the lower(southern) Hudson.

Methods

Dated sediment cores from four estuary reserves and New York harbor were collected and analyzed to determine the historical record of PCDD/PCDF concentrations in the Hudson sediments and the PCDD/PCDF deposition to sediment at a given time interval. The locations and distances from the mouth of the Hudson at New York City were: Stockport(SFE) 120 mi, Tivoli(TSE,TND) 90 mi, Iona(IIC) 50 mi, Piermont(PMB) 25 mi, and New York Harbor(NYH) 0 miles.

To determine the recent direct atmospheric component, air was sampled continuously for 28 days at the rural Tivoli and urban Piermont locations using a glass fiber filter and polyurethane foam. Rain was also collected as weather permitted at the Stockport location for later analysis. Soil cores and composites from locations near the estuaries and storm runoff particles from Hudson River tributaries were also collected and analyzed for PCDD/PCDFs to determine their importance as an indirect source.

Samples were dried, extracted by Soxhlet extraction, cleaned up using acid/base, alumina and carbon chromatography, and analyzed by SIM GC/High Resolution Mass Spectrometry or GC/Low Resolution Mass spectrometry as needed. Principal-components analysis was used to interpret the data.

Results and Conclusions

The sediment was found to be highly stratified. PCDDs and PCDFs were found in all research reserve sediment sections in concentrations that ranged from 800 to 47,800 pg/g, depending on the depth of core section (Table 1) and consisted mostly of OCDD and hepta-CDD. The upper sediment from all four locations had a relatively uniform concentration and composition of PCDDs and PCDFs, indicating a general dispersion of these compounds throughout the recent sediments of the lower Hudson. The highest concentrations of PCDD/PCDFs were found in sub-surface sediments dated at between 1950 and 1980. The oldest sediment had the lowest PCDD/PCDF concentrations of <1100 pg/g.

The average ambient air concentration during 1993 was 1.2 pg/m^3 total PCDD+PCDF at rural Tivoli and 2.0 at near-urban Piermont. The average concentration in precipitation was 94 pg/L. Based on these values, the recent direct atmospheric deposition of PCDDs and PCDFs to the Hudson was estimated to be 194 ng/m^2 or only about 1% of the recent total deposition found in the sediment cores, which ranged from 26,200 to 34,100 ng/m^2 (Table 2).

Principal components analysis showed that the homolog group totals profile and 2,3,7,8-substituted isomer profile of the sediment were consistent with the composition of soil and sewage sludge[1-5]. The profiles were dominated by OCDD, had relatively small quantities of the tetra- to hexa-CDDs and CDFs, and had significant quantities of hepta- and octa-CDFs. The homolog ratios were inconsistent with other PCDD/PCDF sources including municipal waste combustion[6], wood combustion[7], vehicle emissions[8], paper plant discharges[9], air particulates, rain, air, urban runoff[5], PCBs[10], and chlorinated phenols[11]. Therefore, we considered the erosion of soil particles from land surrounding the river and the release of sewage-containing effluent to be the most likely sources of PCDDs and PCDFs to the Hudson estuaries, although these are secondary sources. Specific isomers, found in soil and estuary sediment, were those generally associated with combustion, which have been detected in air, sediment, soil and sewage sludge[3,12,13]. The primary sources of PCDDs and PCDFs found in soil and sewage sludge have not been quantitatively determined, although studies have implicated combustion, bioformation, pentachlorophenol, and household wastewater[2-5].

Using Ellsworth's[14] estimate of particle sources to the lower Hudson as a basis for our calculations, we attempted a mass-balance estimate for PCDDs and PCDFs in recent and lower layers of Hudson estuary sediment. Our soil concentration data, used in these calculations, has been multiplied by an organic enrichment factor of 1.6 that was reported by Ellsworth for particles from tributaries which we assumed were mostly eroded soil. For the PCDD/PCDF content of sewage particles, an average of literature data was used as few actual measurements have been made. The results are given in Table 3. We calculated the relative contribution to sediment deposition from each particle source by multiplying the measured or estimated PCDD/PCDF concentrations for each type of particle times its abundance, and compared the total to measured deposition from core data for 1990-1993 and 1970. We estimate that the most important contributors of PCDDs and PCDFs to Hudson estuary sediment were tributary particles, which contributed 76%; anthropogenic wastes, which contributed 19%; and direct atmospheric deposition, which we estimated at 4%. The predicted recent deposition of PCDDs and PCDFs, 4470 pg/g, was found to compare favorably with the observed range of 4100 to 5600 pg/g.

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Table 1. PCDD and PCDF Results for Samples from the Hudson River National Estuary Research Reserve

SEDIMENT CORE SECTIONS, PG/G, Homolog Group Totals Including 2,3,7,8-substituted congeners
N = 41

NO.	LOCATION	DEPTH, CM	137CS DATE	TCDD	PCDD	HXCDD	HPCDD	OCDD	PCDD	TCDF	PCDF	HXCDF	HPCDF	OCDF	PCDF	PCDD+F	I-TEQ
	Upper sediment																
1	SFE	0-2	1991	0	0	0	900	4400	5300	0	0	0	0	0	0	**5300**	9.9
2	TND	0-2	1990	9	0	70	400	3300	3800	110	20	20	60	60	270	**4100**	8.1
3	TSE	0-2	1991	10	14	130	700	2900	3700	300	40	40	110	100	590	**4300**	17
4	IIC	0-2	1990	15	11	160	800	3400	4400	330	60	60	110	80	640	**5000**	25
5	PMB	0-2	1990	17	24	200	800	3800	4900	300	70	70	160	130	730	**5600**	9
6	NYH	0-2		48	26	230	1100	5800	7200	360	210	90	280	260	1200	**8400**	57
	Maximum PCDD/F layer																
7	SFE	24-28	1962	0	60	1000	8500	34800	44300	870	80	250	1380	950	3530	**47800**	161
8	TND	20-22	1950	0	0	730	5000	16700	22400	820	60	80	450	580	1990	**24400**	65
9	TSE	22-24	1960	19	53	910	6300	22800	30200	770	160	210	740	520	2400	**32600**	108
10	IIC	8-12	1968	9	10	200	1200	4700	6100	500	70	60	150	100	880	**7000**	29
11	PMB	4-6	1982	41	14	210	1100	5100	6400	340	80	90	190	160	860	**7300**	38
12	NYH	52-56		165	39	660	3700	19100	23700	1260	770	330	670	960	3990	**27700**	141
	Lowest layer																
13	TSE	54-56	1917	0	0	0	0	900	900	0	0	0	0	0	0	**900**	0.9
14	IIC	32-38 5	1907	0	0	0	100	1000	1100	0	0	0	0	0	0	**1100**	1.1
15	PMB	32-36	1924	0	0	30	100	900	1000	0	0	0	0	0	0	**1000**	1.2
	SOIL, PG/G																
	AVERAGE, N = 9:			7	7	31	230	2000	2300	43	29	36	120	97	330	**2600**	8.6
	MAXIMUM:			13	16	71	470	6100	6200	91	57	89	460	270	960	**6200**	16
	MINIMUM:			0	0	0	48	100	200	0	0	0	0	0	0	**300**	2.3
	AIR, PG/M3																
	AVERAGE, N = 14:			0.03	0.07	0.15	0.23	0.45	0.93	0.23	0.15	0.15	0.09	0.04	0.67	**1.59**	
	MAXIMUM:			0.07	0.16	0.33	0.48	1.41	2.24	0.48	0.35	0.44	0.23	0.10	1.43	**3.35**	
	MINIMUM:			<0.02	0.02	0.04	0.09	0.21	0.37	0.06	0.04	0.05	0.07	<0.005	0.25	**0.64**	
	STD DEVIATION			0.02	0.04	0.06	0.11	0.28	0.44	0.13	0.09	0.10	0.05	0.02	0.32	**0.68**	
	Piermont (PMB) average:			0.05	0.10	0.19	0.21	0.50	1.05	0.33	0.22	0.22	0.10	0.05	0.92	**1.97**	0.048
	Tivoli (TSE) average:			0.01	0.03	0.10	0.25	0.40	0.80	0.13	0.08	0.08	0.08	0.04	0.41	**1.21**	0.022
	PRECIPITATION , PG/L																
	AVERAGE, N=5			0.06	0.09	3.7	12.0	52	68	0.35	1.6	4.2	9	11	27	**94**	
	SEWAGE (Literature avg), PG/G			66	204	386	1889	8957	11500	426	431	710	1821	1664	5050	**16650**	
	STORM RUNOFF PARTICLES, PG/G																
	AVERAGE, N=5			nd	nd	nd	830	10800	11600	nd	nd	800	220	600	1720	**13200**	

SFE = Stockport, TND = Tivoli north, TSE = Tivoli south, IIC = Iona, PMB = Piermont, NYH = New York Harbor

Table 2. RECENT RATES OF DEPOSITION (in ng/m2 y)

From Sediment Core data:		From Direct Air and Precipitation data:
Tivoli location, 1990-1992	D = 26,200	1993 averages
Stockport, 1990-1992	D = 32,300	
Iona, 1990-1992	D = 30,400	D (dry) = 100
Piermont, 1990-1992	D = 34,100	D (wet) = 94
NY Harbor	D = 51,200	D (total) = 194

Table 3. MASS BALANCE ESTIMATE: DEPOSITION OF TOTAL PCDD AND PCDF TO THE HUDSON RIVER NATIONAL ESTUARY RESERVE SEDIMENT (>150 km upstream)

	1990-1993				1970			
	Particulate %*	D+F Conc	P x C	% Contribution	Partic. %	D+F Conc	P x C	% Contribution
Shoreline erosion	0.56	4160	23	0.5	0.44	2496	11	0.1
Tributaries	82	4160	3410	76	64	2496	1670	15
Biological Production	12.6	0	0	0	12.6	0	0	0
Anthropogenic Wastes	4.8	18000	870	19	22	36000	7850	70
Atmospheric, direct	0.40	43000	170	4	0.8	215000	1660	15
TOTAL:	100		**4470**	100	100		**11200**	100
Experimentally found:			**4100-5600**				**7000-47800**	

Particle estimate is from: Ellsworth, 1986