LEVELS IN THE ENVIRONMENT

PCDD/PCDFs In Storm Water Outfalls Adjacent to Urban Areas and Petroleum Refineries in San Francisco Bay, California, USA

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1. Introduction

Polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) have been recognized as persistent and ubiquitous sediment contaminants in industrialized waterways [1, 2]. Non-point sources such as urban runoff, combined sewer outfalls (CSOs), and atmospheric deposition have been identified as significant sources of these compounds [2,3,4]. More recently, attention has been drawn to whether urban street runoff is a significant environmental source of PCDD/Fs in San Francisco Bay, California, as well as in other parts of the world [5,6].

In this paper the results of two separate storm water investigations are described. The first investigation involved the collection of storm water samples from two outfall locations to the San Francisco Bay, Oakland and Benicia, which represented storm water discharges from urban and mixed urban-industrial land uses, respectively [5]. The second investigation, involving the Regional Water Quality Control Board, San Francisco Bay Region (RWQCB), involved the collection of storm water samples from 13 locations in the San Francisco Bay Area [6]. The distribution of homologues and 2,3,7,8-substituted congeners at different locations were analyzed to estimate PCDD/F loadings to San Francisco Bay. Dioxin fingerprint patterns representative of each location were also characterized to examine the effect of different dominant land uses, if any, on PCDD/F concentrations in storm water.

2. Methods

Sampling. In the first investigation, storm water samples were collected each hour over a 12-hour period simultaneously from outfalls in the Cities of Oakland and Benicia during the first rainstorm of the 1995/1996 winter season. Eleven storm water samples were collected at the Oakland outfall and ten samples were collected at the Benicia outfall using methods described previously [5]. In the second investigation, storm water samples were collected during two storm events of the 1995/1996 winter season. A total of thirteen locations were included in this study. Runoff at six of the locations is from areas considered a mixture of developed, undeveloped, residential, commercial,

light industrial and heavy industrial land uses (hereafter referred to as "urban"). The remaining seven locations consist of areas within or adjacent to petroleum refineries (hereafter referred to as "refinery"). Two one liter grab samples were collected at each outfall, by submerging a bottle under the surface of the water and allowing the bottle to fill. Samples from both investigations were stored on ice at 4°C until laboratory analysis.

PCDD/F Analysis. The cleanup, extraction and quantification of PCDD/F homologues and 2,3,7,8-substituted congeners in storm water by high resolution gas chromatography / mass spectrometry was performed by Alta Analytical Laboratory (El Dorado Hills, CA) according to USEPA method 1613A[7]. The method detection limits for 2,3,7,8-substituted congeners and homologue groups ranged from 0.29 pg/L to 3.8 pg/L in the first investigation and from 0.83 pg/L to 10 pg/L in the second investigation.

PCDD/F Pattern Recognition. The principal components analysis (PCA) technique used to characterize the relative distributions of PCDD/Fs in storm water samples has been described elsewhere[8]. PCA modeling was conducted using Pirouette (version 1.4, InfoMetrix, Seattle, WA). The data were autoscaled to minimize any statistical bias associated with the orders of magnitude differences in the concentrations of different PCDD and PCDFs. For the purpose of the PCA analysis, PCDD/F concentrations below the detection limit were assumed to be present at the detection limit.

3. Results

PCDD/F concentrations in storm water. The results of storm water sampling conducted during both investigations are summarized in Tables 1 and 2. In general, the concentrations of 2,3,7,8-substituted congeners and homologue groups were higher in Oakland storm water than in Benicia storm water. The ΣPCDD and ΣPCDF concentrations in Oakland storm water ranged from 27 to 7562 pg/liter (arithmetic mean of 2602 pg/liter) and 15 to 2970 pg/liter (arithmetic mean of 831 pg/liter), respectively. In Benicia storm water, ΣPCDD and ΣPCDF concentrations ranged from 11 to 2978 pg/liter (arithmetic mean of 480 pg/liter) and 7 to 207 pg/liter (arithmetic mean of 49 pg/liter), respectively.

As shown in Table 1, ΣPCDD concentrations in urban outfalls sampled during the first storm event (which occurred in December, 1995) ranged from 119 pg/liter (Fairfield) to 1980 pg/liter (Contra Costa Rheem Channel) with an arithmetic mean concentration of 1250 pg/liter. ΣPCDF concentrations in urban outfalls ranged from 16 pg/liter (Fairfield) to 282 pg/liter (Contra Costa Rheem Channel) with an arithmetic mean concentration of 148 pg/liter. In storm water outfalls sampled adjacent to refineries the ΣPCDD concentrations ranged from 318 pg/liter (Shell) to 2791 pg/liter (Exxon) with an arithmetic mean concentration of 1086 pg/liter. ΣPCDF concentrations in outfalls sampled adjacent to refineries ranged from 33 pg/liter (Shell) to 131 pg/liter (Exxon) with an arithmetic mean concentration of 78 pg/liter. 2,3,7,8-TCDD was not detected in any of the refinery or urban storm water collected during the first storm water sampling event.

Samples collected during the second storm event (which included samples collected between February and April, 1996) were generally lower in 2,3,7,8-substituted congeners and homologue groups than the samples collected during the first storm event. ΣPCDD concentrations in urban storm water outfalls ranged from 68 pg/liter (Fairfield) to 3,933 pg/liter (Alameda) with an

arithmetic mean concentration of 1349 pg/liter. ΣPCDF concentrations in urban storm water outfalls ranged from non-detect (ND) (Fairfield) to 463 pg/liter (Alameda) with an average of 148 pg/liter. The ΣPCDD concentrations in storm water collected adjacent to refineries during the second sampling event ranged from ND (Shell) to 1140 pg/liter (Unocal) with an arithmetic mean concentration of 318 pg/liter. ΣPCDF concentrations in samples collected from outfalls adjacent to refineries ranged from ND (Shell and Chevron) to 171 pg/liter (Unocal) with an arithmetic mean concentration of 49 pg/liter. 2,3,7,8-TCDD was not detected in any of the refinery or urban storm water samples from the second sampling event.

Toxicity Equivalents (TEQs). The total TEQ levels in Oakland storm water ranged from 0.07 pg/L (Oakland 5) to 64.97 pg/L (Oakland 6). The total TEQ levels in Benicia storm water ranged from 0.01 pg/L (Benicia 3 and 4) to 13.86 pg/L (Benicia 8). TEQs in storm water were seen to follow the same temporal trend as the concentrations of ΣPCDD and ΣPCDF discussed previously. The TEQs in refinery and urban storm water outfalls collected during the first sampling event ranged from 1 pg/liter (Shell) to 10 pg/liter (Exxon) and from 0.6 pg/liter (Fairfield) to 15 pg/liter (Guadalupe), respectively. The TEQs in refinery and urban storm water outfalls from the second sampling event ranged from ND (Shell) to 3 pg/liter (Unocal) and from 0.14 pg/liter (Fairfield) to 26 pg/liter (Alameda), respectively.

Fingerprint Patterns. In general, PCA results indicate that the composition of PCDD/Fs were similar among storm water samples collected during the first storm event of the 1995/96 winter season, but different from the composition of PCDD/Fs in storm water collected during subsequent storm events. The differences were primarily attributed to a predominance of hepta- and octa- chlorinated PCDD/Fs in storm water samples collected during the second storm event. Among urban outfalls, unique distributions of PCDD/Fs were observed among several storm water samples. When the results of urban sampling conducted as part of the second study were compared to time course data collected as part of the first study, the distributions of PCDD/Fs in the majority of urban storm water samples were similar to those collected at the onset of hourly sampling conducted at the Benicia and Oakland outfalls. In addition, some differences in the composition of PCDD/Fs were noted among storm water samples collected from outfalls located adjacent to petroleum refineries.

4. Discussion

Despite large differences in land use at the locations evaluated, few differences in PCDD/F concentrations could be identified between samples collected from refinery areas, urban environments (which included runoff from areas consisting of a mixture of developed, undeveloped, residential, commercial and industrial land), and urban areas such as the cities of Benicia and Oakland. The concentrations of PCDD/Fs in storm water from Oakland generally represented the upper range of PCDD/F concentrations found in both investigations, particularly for individual congeners, as well as TEQs. TEQ levels were significantly higher in storm water runoff from Oakland (as high as 65 pg/liter) than in runoff from Benicia (as high as 14 pg/liter). TEQs in Oakland storm water also were significantly higher than TEQs calculated in any of the refinery or urban storm water samples collected during either the first or second sampling events. In addition, PCDD/F TEQs in storm water collected at the five outfalls located adjacent to refineries were significantly lower than the TEQs in storm water samples from urban locations collected during both the first and second sampling events.

The distinct temporal variability in the distributions of PCDD/Fs in the Oakland and Benicia outfalls[5] suggests that discrete sampling may be an inappropriate method for determining the concentrations of these compounds in storm water; although, it may provide some information on mass loading to San Francisco Bay. Time course studies appear to be an important consideration for gauging true environmental concentrations of PCDD/Fs during events that have a strong temporal bias.

The results of fingerprint pattern recognition using PCA suggest that it is possible, but difficult, to distinguish sources of PCDD/Fs among urban outfalls. Clearly, there are multiple sources of PCDD/Fs to San Francisco Bay. The results of this study also show that incremental contributions of petroleum refineries to PCDD/F loading to San Francisco Bay is indistinguishable from other non-refinery sources, and suggest that surface runoff from urban areas such as the city of Oakland may represent important sources of PCDD/Fs to the aquatic environment.

5. References

1. Clarke, A. N., M.M. Megehee, D.L. Lowe, J.H. Clarke. 1994. A Review of Polychlorinated Dibenzofurans and Polychlorinated Dibenzodioxins in Sediments in the United States and International Waterways. Haz. Waste Haz. Mat. 11(2): 253-275.
2. USEPA. 1994. Estimating Exposure to Dioxin-Like Compounds. Volume II: Properties, Sources, Occurrence, and Background Exposures. United States Environmental Protection Agency, Office of Research and Development, Washington, D.C. EPA/600/6-88/005Cb.
3. Huntley, S.L., T.J. Iannuzi, J.D. Avantaggio, H. Carlson-Lynch, C.W. Schmidt, B.L. Finley. 1996. Combined Sewer Overflows (CSOs) as Sources of Sediment Contamination in the Lower Passaic River, New Jersey. II. Polychlorinated Dibenzo-p-Dioxins, Polychlorinated Dibenzofurans, and Polychlorinated Biphenyls. Chemosphere. 34(2): 233-250.
4. Shear N.M., C.W. Schmidt, S.L. Huntley, D.W. Crawford, B.L. Finley. 1996. Evaluation of the Factors Relating Combined Sewer Overflows with Sediment Contamination of the Lower Passaic River. Mar Pollut Bull. 32(1): 288-304.
5. Paustenbach, D.J., Wenning, R.J., Mathur, D.B., Luksemburg, W. PCDD/PCDFs in Urban Stormwater Discharged to San Francisco Bay, California, USA. 16th Symposium on Dioxins and Related Compounds. Amsterdam, Netherlands, August 1996.
6. Regional Water Quality Control Board, San Francisco Bay Region. Survey of Storm Water Runoff for Dioxins in the San Francisco Bay Area. February 1997.
7. USEPA. 1988. Statement of Work for Dioxin Analyses. Multi-media, Multi-Concentrations. (Revision 8/88). United States Environmental Protection Agency. Washington D. C
8. Wenning R.J., D.J. Paustenbach, M.A.Harris, H.Bedbury. 1993: Principal components analysis of potentential sources of polychlorinated dibenzo-p-dioxins and dibenzofurans residues in surficial sediments from Newark Bay, New Jersey. Arch Environ Contam Toxicol 24, 271-289.

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Table 1. Data Summaries for PCDD/Fs in Storm Water Samples from Urban[a] and Petroleum Refinery Areas[b]

Congener	Urban-1st storm event[c]					Urban-2nd Storm Event[d]					Refinery-1st Storm Event[c]					Refinery-2nd Storm Event[d]				
	N	No. Positive[e]	Max[f]	Min[g]	Mean[h]	N	No. Positive[e]	Max[f]	Min[g]	Mean[h]	N	No. Positive[e]	Max[f]	Min[g]	Mean[h]	N	No. Positive[e]	Max[f]	Min[g]	Mean[h]
2,3,7,8-TCDD	5	0	-	-	-	6	0	-	-	-	5	0	-	-	-	5	0	-	-	-
1,2,3,7,8-PeCDD	5	3	4	ND	2	6	1	8	ND	1	5	2	3	ND	1	5	0	-	-	-
1,2,3,4,7,8-HxCDD	5	4	6	ND	4	6	3	13	ND	4	5	4	5	ND	3	5	0	-	-	-
1,2,3,6,7,8-HxCDD	5	4	15	ND	10	6	4	28	ND	10	5	4	10	ND	6	5	0	-	-	-
1,2,3,7,8,9-HxCDD	5	4	15	ND	9	6	4	24	ND	8	5	4	8	ND	5	5	0	-	-	-
1,2,3,4,6,7,8-HpCDD	5	5	240	19	156	6	6	460	8	166	5	5	270	38	118	5	3	140	ND	41
OCDD	5	5	1700	100	1070	6	6	3400	60	1160	5	5	2500	270	954	5	4	1000	ND	277
2,3,7,8-TCDF	5	2	2	ND	1	6	2	2	ND	1	5	0	-	-	-	5	0	-	-	-
1,2,3,7,8-PeCDF	5	2	3	ND	1	6	1	2	ND	0.4	5	0	-	-	-	5	0	-	-	-
2,3,4,7,8-PeCDF	5	3	9	ND	3	6	2	6	ND	1	5	3	2	ND	1	5	0	-	-	-
1,2,3,4,7,8-HxCDF	5	4	5	ND	3	6	3	10	ND	3	5	3	4	ND	2	5	0	-	-	-
1,2,3,6,7,8-HxCDF	5	4	5	ND	3	6	3	7	ND	2	5	3	3	ND	1	5	0	-	-	-
2,3,4,6,7,8-HxCDF	5	5	9	3	6	6	3	10	ND	4	5	5	10	2	5	5	0	-	-	-
1,2,3,7,8,9-HxCDF	5	0	-	-	-	6	0	-	-	-	5	2	2	ND	0.5	5	0	-	-	-
1,2,3,4,6,7,8-HpCDF	5	5	69	5	41	6	5	120	ND	40	5	5	36	8	21	5	3	51	ND	14
1,2,3,4,7,8,9-HpCDF	5	3	4	ND	2	6	2	7	ND	2	5	3	3	ND	1	5	0	-	-	-
OCDF	5	5	190	8	88	6	5	300	ND	95	5	5	82	19	47	5	3	120	ND	35

Table 2. Data Summaries for PCDD/Fs in Storm Water Samples from Oakland and Benicia, California

Congener	Oakland					Benicia				
	N	No. Positive[e]	Max[f]	Min[g]	Mean[h]	N	No. Positive[e]	Max[f]	Min[g]	Mean[h]
2,3,7,8-TCDD	11	4	2.7	ND	0.7	10	0	-	-	-
1,2,3,7,8-PeCDD	11	6	11	ND	4.6	10	3	5.3	ND	1.2
1,2,3,4,7,8-HxCDD	11	7	21	ND	7.9	10	3	9.4	ND	1.9
1,2,3,6,7,8-HxCDD	11	8	42	ND	17	10	4	17	ND	3.7
1,2,3,7,8,9-HxCDD	11	8	40	ND	15	10	4	19	ND	3.9
1,2,3,4,6,7,8-HpCDD	11	11	760	3.4	298	10	8	230	ND	49
OCDD	11	11	6200	19	1911	10	10	1900	5.8	324
2,3,7,8-TCDF	11	6	8.6	ND	1.9	10	1	0.6	ND	0.1
1,2,3,7,8-PeCDF	11	5	7.6	ND	1.7	10	2	0.9	ND	0.2
2,3,4,7,8-PeCDF	11	7	39	ND	7.8	10	2	1.4	ND	0.3
1,2,3,4,7,8-HxCDF	11	8	26	ND	6.4	10	3	2.8	ND	0.6
1,2,3,6,7,8-HxCDF	11	8	47	ND	13	10	3	3.5	ND	0.7
2,3,4,6,7,8-HxCDF	11	10	49	ND	13	10	4	3.4	ND	1.1
1,2,3,7,8,9-HxCDF	11	5	5	ND	1.4	10	2	1.0	ND	0.2
1,2,3,4,6,7,8-HpCDF	11	11	350	1.4	119	10	5	52	ND	9.8
1,2,3,4,7,8,9-HpCDF	11	7	13	ND	5.1	10	1	19	ND	1.9
OCDF	11	11	500	4.2	180	10	10	42	ND	13

Notes for Tables 1 and 2:

a. Urban- Consist of runoff from a mixture of developed, undeveloped, residential commercial and industrial land including: Sunnyvale East Channel, Guadalupe River, Castro Valley Creek, Rheem Creek, Walnut Creek and Laurel Creek.
b. Refinery- Consist of outfalls draining areas in and around petroleum refineries including: Shell Martinez, Exxon Benicia, Unocal Rodeo, Tosco Avon and Chevron Richmond.
c. 1st Storm Event- samples collected in December 1995
d. 2nd Storm Event- samples collected between February and April 1996.
e. No. Positive- Number of samples above detection limit
f. Max- Maximum detected concentration for outfall or outfall group
g. Min- Minimum detected concentration for outfall or outfall group
h. Mean- Arithmetic mean concentration for outfall or outfall group
i. ND- Not Detected