PCDD/PCDFs In Urban Stormwater Discharged to San Francisco Bay, California USA

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1. Introduction

There has been little published work on sources of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs), and in particular 2,3,7,8-tetrachlorodibenzo-p-dioxins (2,3,7,8-TCDD), to San Francisco Bay California. The relationship between sediment contamination and chemical contributions from urban stormwater discharged either directly through storm drains or indirectly through combined sewer overflows has been demonstrated in other heavily urbanized waterways [1,2]. Although studies have shown, on a global scale, that the largest sources of PCDD/Fs in sediments and aquatic biota include several combustion-related processes, municipal waste and medical waste incinerators, pentachlorophenol formulations, and numerous industrial manufacturing chemical formulation processes [3]; urban runoff and stormwater should not be discounted as an important source.

This paper describes the results of PCDD/F analysis of stormwater collected from two outfalls that discharge to San Francisco Bay and represent sources of runoff from areas with different dominant land uses. The first stormwater outfall, located in the vicinity of the city of Oakland, discharges surface runoff from a major downtown metropolitan area. The second outfall, located in northern San Francisco Bay in the vicinity of the city of Benicia, discharges surface runoff from several industries, including a petroleum refinery. The distributions of homologues and 2,3,7,8-substituted congeners at both locations were analyzed to estimate PCDD/F loadings to San Francisco Bay and to characterize dioxin fingerprint patterns representative of each stormwater outfall.

2. Methods

Sampling. Water samples were collected simultaneously from Oakland and Benicia stormwater outfalls every hour during the first major rainstorm of the 1995/96 winter season. Effluents were collected using a low-flow peristaltic pump with 1/4 inch polyethylene tubing and a stainless steel wire-wrapped inlet with a 1/16 inch screen to restrict the intake of suspended particulates. The intake was positioned in the outfall stream at a depth of approximately 2/3 the distance from the water surface. New polyethylene tubing was used for each hourly sampling event at both locations. Stormwater samples were collected for 30 minutes into separate 5 gallon polyethylene containers. One equipment blank was collected for QA/QC purposes at each outfall by pumping clean laboratory-grade water through the peristaltic pump. Samples were stored on ice at 4°C until laboratory analysis.

PCDD/F Analyses. The cleanup, extraction, and quantification of PCDD/F homologues and 2,3,7,8-substituted congeners in stormwater by high resolution gas chromatography / mass spectrometry was performed by Alta Analytical Laboratory (El Dorado Hills, CA) according to USEPA Method 1613A [4]. The method detection limits for 2,3,7,8-substituted PCDD/F congeners and homologue groups ranged between 0.29 and 1.4 picograms per litre (pg/l). The lower method calibration limit for Method 1613A for these samples was 1 ppq (parts per quadrillion).

PCDD/F Pattern Recognition. The principal components analysis (PCA) technique used to characterize the relative distributions of PCDD/Fs in stormwater samples has been described elsewhere [5]. PCA modelling 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 PCDDs and PCDFs. PCDD/F concentrations below the detection limit were assumed to be present at the detection limit.

3. Results

PCDD/F Concentrations in Stormwater. A summary of the data for eleven samples from the Oakland stormwater outfall and ten samples from the Benicia outfall are presented in Tables 1 and 2, respectively. In general, the concentrations of 2,3,7,8-substituted congeners and PCDD/F homologue groups were higher in Oakland stormwater than in Benicia stormwater. The ∑PCDD and ∑PCDF concentrations in Oakland stormwater ranged from 27 to 7562 pg/litre (arithmetic mean of 2602 pg/litre) and 15 to 2970 pg/litre (arithmetic mean of 831 pg/litre), respectively. In Benicia stormwater, ∑PCDD and ∑PCDF concentrations ranged from 11 to 2798 pg/litre (arithmetic mean of 480 pg/litre) and 7 to 207 pg/litre (arithmetic mean of 49 pg/litre), respectively. The average TEQ level in Oakland stormwater (21 pg/litre; ranging between 0.1 and 65 pg/litre) was nearly seven-fold higher than in Benicia stormwater (3.5 pg/litre; ranging between ND and 14 pg/litre). Fewer 2,3,7,8-substituted congeners were detected in Benicia stormwater than in Oakland stormwater. Higher chlorinated homologues, particularly hepta- and octa- chlorinated PCDDs were predominant in both outfalls. 2,3,7,8-TCDD concentrations were below method detection limits (ranging from 0.65 to 1.5 pg/litre in all samples) in Benicia stormwater; 2,3,7,8-TCDD were measured in four of eleven Oakland stormwater samples (ranging between 1.6 and 2.7 pg/litre).

Fingerprint Patterns. PCA modelling indicated that the distributions of 2,3,7,8-substituted PCDD/Fs in stormwater from both outfalls were similar during the first six hours of sampling. A three dimensional principal components scores plot is presented in Figure 1. The first three principal components explained 89%, 6.5%, and 2 % of the original variance of the data set, respectively. Five unique 2,3,7,8-substituted congener distributions were evident in Oakland stormwater samples (oak6; oak7, oak9, oak10; oak8 and oak11) after 6 hours of sampling. Two different congener distributions were evident in Benicia stormwater samples (ben8; ben9 and ben10) after 8 hours of sampling. The congener distributions in stormwater samples collected in the first 6 - 8 hours were similar, with the exception of sample oak1. The variations among congener distributions could be partially explained by the principal components loading plot presented in Figure 2. Hepta- and octa- chlorinated PCDD congeners and tetra- and pent- chlorinated PCDF congeners were most responsible for the differences observed among Oakland and Benicia stormwater samples (Figure 1).

Temporal Changes in PCDD/F Discharges. Hourly changes in ∑PCDD, ∑PCDF and 2,3,7,8-substituted congener concentrations and TEQ levels in Oakland and Benicia stormwater samples are presented in Figures 3 and 4, respectively. In Oakland, PCDD/F concentrations increased five hours after the start of the rainstorm and remained elevated

after the sixth hour of sampling (Figure 3). In Benicia, PCDD/F concentrations increased during the fourth and seventh hours of sampling and remained elevated after eight hours (Figure 4).

4. Discussion

Despite large differences in land use at both outfall locations, few differences in the distributions of 2,3,7,8-substituted PCDD/F congeners were discerned in stormwater runoff collected in the first 6 hours of sampling during the first major rainfall of the winter season. TEQ levels were significantly higher in stormwater runoff from (as high as 65 pg/litre) Oakland than in runoff from Benicia (as high as 14 pg/litre). The fingerprint patterns in several samples closely resembled the patterns associated with municipal sewage sludge, municipal waste incineration, and some petroleum-based combustion sources.

Although some runoff discharged from the Benicia outfall may originate from a petroleum refinery, the levels of PCDD/Fs in stormwater were lower, on average, than the levels found in Oakland stormwater. Although there is some evidence to suggest that petroleum refineries may be a source of PCDD/Fs to the aquatic environment as a result of stack gas emissions and certain reforming catalyst regeneration processes [6,7], the concentrations of PCDD/Fs in Oakland stormwater were significantly higher than the levels found in Benicia. The results reported here suggest that surface runoff from urban non-industrialized areas such as the city of Oakland may represent important sources of PCDD/Fs to the aquatic environment.

5. References

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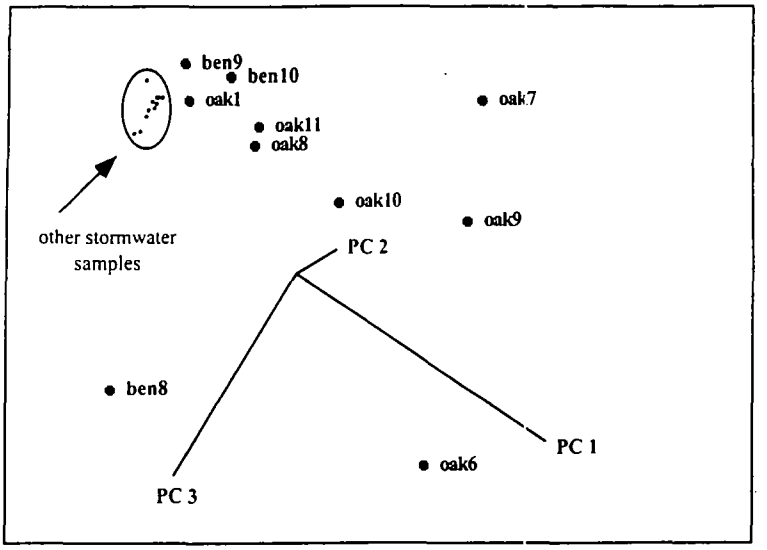

Fig. 1: Three dimensional principal components scores plot of normalized 2,3,7,8-substituted PCDD/Fs in urban stormwater samples collected hourly during the first major rainfall of the winter season from outfalls located in the cities of Oakland (oak) and Benicia (ben), California. Results indicate that the PCDD/F content in stormwater changed significantly 6 hrs (oak6 - oak11) and 8 hrs (ben8 - ben10) after collection of the first samples.

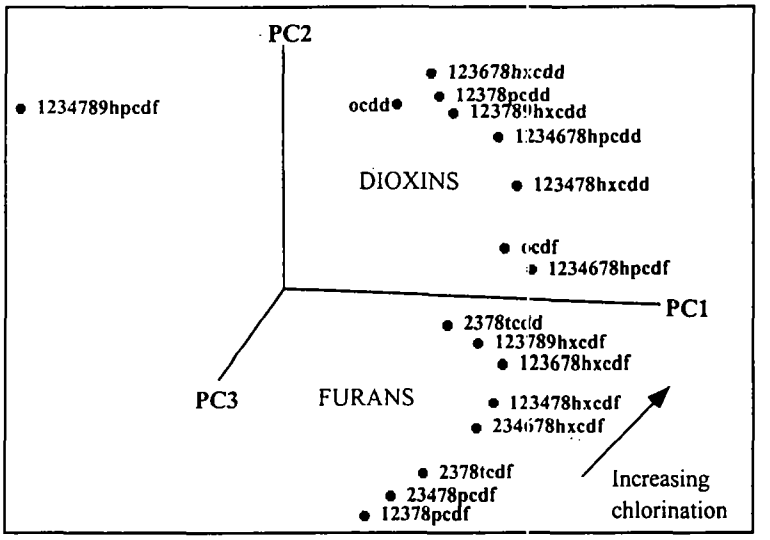

Fig. 2: The loadings plot for the first three principal components of normalized 2,3,7,8-substituted PCDD/Fs in urban stormwater samples. All congeners were positively correlated on principal component 1. With the exception of 2,3,7,8-TCDD, a clear separation of dioxins and furans and increasing chlorination of furan congeners was evident on principal component 2. 1,2,3,4,7,8,9-HpCDF and 2,3,7,8-TCDD were the most significant positively positioned variables on principal component 3.

Figure 3: Temporal Changes in Total PCDD/Fs and 2,3,7,8-TCDD Concentrations and Total TEQ Levels in Oakland, CA Stormwater

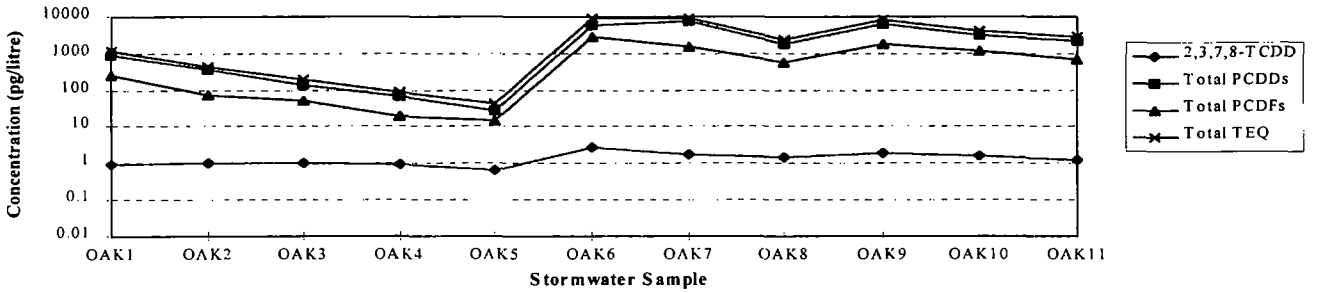

Figure 4: Temporal Changes in Total PCDD/Fs and 2,3,7,8-TCDD Concentrations and Total TEQ Levels in Benecia, CA Stormwater

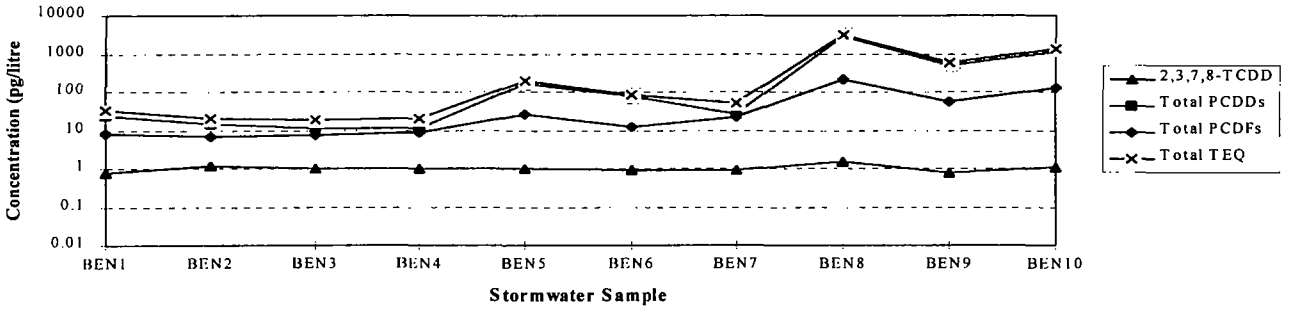

Table 1. PCDDs and PCDFs in stormwater runoff collected from a single outfall in Oakland California during the first major rainfall of the Winter 1995/96 season.

	Oakland Stormwater Outfall (pg/L)					
Congener	N	No. Positive	Maximum	Minimum	Arith. Mean	Median
2,3,7,8-TCDD	11	4	2.7	ND	1.4	1.2
1,2,3,7,8-PeCDD	11	6	11	ND	5.1	5.1
1,2,3,4,7,8-HxCDD	11	7	21	ND	8.5	7.3
1,2,3,6,7,8-HxCDD	11	8	42	ND	18	16
1,2,3,7,8,9-HxCDD	11	8	40	ND	16	13
1,2,3,4,6,7,8-HpCD	11	11	760	3.4	298	200
2,3,7,8-TCDF	11	6	8.6	ND	2.1	1
1,2,3,7,8-PeCDF	11	5	7.6	ND	2.2	1.2
2,3,4,7,8-PeCDF	11	7	39	ND	8.1	3.2
1,2,3,4,7,8-HxCDF	11	8	26	ND	6.6	4.1
1,2,3,6,7,8-HxCDF	11	8	47	ND	14	12
2,3,4,6,7,8-HxCDF	11	10	49	ND	13	7.1
1,2,3,7,8,9-HxCDF	11	5	5	ND	1.8	0.84
1,2,3,4,6,7,8-HpCD	11	11	350	1.4	119	97
1,2,3,4,7,8,9-HpCD	11	7	13	ND	5.4	3.8
Total TCDD	11	4	11	ND	4.0	1.3
Total PeCDD	11	6	31	ND	11	7
Total HxCDD	11	8	300	ND	119	89
Total HpCDD	11	11	1500	6.5	557	360
Total OCDD	11	11	6200	19	1911	1300
Total TCDF	11	7	250	ND	57	20
Total PeCDF	11	8	760	ND	161	77
Total HxCDF	11	10	870	ND	230	150
Total HpCDF	11	11	590	7.8	202	160
Total OCDF	11	11	500	4.2	180	100
PCDDs	-	-	7562	27	2602	1807
PCDFs	-	-	2970	15	831	576
TEQ PCDD/F	-	-	65	0.07	21	16

Note #1: ND indicates a non-detect measurement using USEPA Method 1613A.
Note #2: Summary statistics include either the measured concentration or the laboratory detection limit for each sample.
Note #3: Toxic equivalents (TEQs) were calculated using USEPA TEQ factors (1989)[$]. Measurements below the detection limit were not included in the calculation.
Note #4: PCDDs and PCDFs are expressed as the sum of the tetra- through octa-chlorinated homologues

Table 2. PCDDs and PCDFs in stormwater runoff collected from a single outfall in Benicia California during the first major rainfall of the Winter 1995/96 season.

	Benicia Stormwater Outfall (pg/L)					
Congener	N	No. Positive	Maximum	Minimum	Arith. Mean	Median
2,3,7,8-TCDD	10	0	1.5	ND	1.0	0.97
1,2,3,7,8-PeCDD	10	3	5.3	ND	2.0	1.4
1,2,3,4,7,8-HxCDD	10	3	9.4	ND	3.0	1.9
1,2,3,6,7,8-HxCDD	10	4	17	ND	4.6	1.8
1,2,3,7,8,9-HxCDD	10	4	19	ND	4.7	1.5
1,2,3,4,6,7,8-HpCD	10	8	230	ND	50	6.4
2,3,7,8-TCDF	10	1	0.69	ND	0.6	0.56
1,2,3,7,8-PeCDF	10	2	1.8	ND	1.1	1.2
2,3,4,7,8-PeCDF	10	2	1.5	ND	1.0	0.98
1,2,3,4,7,8-HxCDF	10	3	2.8	ND	1.2	0.95
1,2,3,6,7,8-HxCDF	10	3	3.5	ND	1.3	0.97
2,3,4,6,7,8-HxCDF	10	4	3.4	ND	1.8	1.5
1,2,3,7,8,9-HxCDF	10	2	1.1	ND	0.9	0.92
1,2,3,4,6,7,8-HpCD	10	5	52	ND	10	1.6
1,2,3,4,7,8,9-HpCD	10	1	19	ND	2.9	1.2
Total TCDD	10	0	1.5	ND	1.0	0.97
Total PeCDD	10	3	16	ND	3.1	1.4
Total HxCDD	10	4	110	ND	24	2.0
Total HpCDD	10	8	770	ND	128	14
Total OCDD	10	10	1900	5.8	324	34
Total TCDF	10	1	3.3	ND	0.9	0.58
Total PeCDF	10	3	22	ND	4.5	1.4
Total HxCDF	10	4	52	ND	13	1.5
Total HpCDF	10	5	88	ND	16	3.2
Total OCDF	10	10	42	3	15	6.7
PCDDs	-	-	2798	11	480	51
PCDFs	-	-	207	7	49	17
TEQ PCDD/F	-	-	14	ND	3.5	0.11

Note #1: ND indicates a non-detect measurement using USEPA Method 1613A.
Note #2: Summary statistics include either the measured concentration or the laboratory detection limit for each sample.
Note #3: Toxic equivalents (TEQs) were calculated using USEPA TEQ factors (1989)[$]. Measurements below the detection limit were not included in the calculation.
Note #4: PCDDs and PCDFs are expressed as the sum of the tetra- through octa-chlorinated homologues