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Polychlorinated Dibenzo-p-Dioxins and Dibenzofurans in Storm Water Outfalls Adjacent to Urban Areas and Petroleum Refineries in San Francisco Bay, California

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Abstract. Polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) were analyzed in storm water collected from 15 outfalls in San Francisco Bay, California, considered representative of areas located adjacent to petroleum refineries and mixed urban/commercial/residential land uses. Storm water sampling was conducted hourly over a 12-h period at two outfalls located near the city of Oakland and the suburban community of Benicia, which represent urban and mixed urban/light industrial land uses, respectively. Sampling was conducted hourly to determine temporal changes in the concentrations and distributions of PCDD/Fs during the first major rainstorm event of the 1995/96 winter season. In addition, storm water sampling was conducted in December 1995 and February/April 1996 at six publicly owned treatment work (POTW) outfalls located adjacent to developed, undeveloped, mixed residential/commercial, and industrial lands. Storm water sampling also was conducted at five outfalls located adjacent to petroleum refineries. The sampling results were used to examine changes in PCDD/F loadings to San Francisco Bay at the onset and midway through the winter rainy season and to characterize differences in PCDD/F concentrations, if any, between refinery and nonrefinery areas. The concentrations of tetra- through octa-chlorinated homologues and 2,3,7,8-substituted congeners were assayed in filtered storm water samples according to US EPA Method 1613A. Principal components analysis (PCA) was used as an exploratory technique to examine the similarities and differences in the distributions of PCDD/Fs in storm water from different outfalls. The sampling results showed few significant differences between storm water discharged from outfalls located in mixed urban/commercial/residential areas and outfalls located adjacent to petroleum refineries. The concentrations of 2,3,7,8-TCDD were below the analytical limits of detection in all storm water samples, with the exception of samples collected after the sixth hour of sampling at the Oakland outfall. Fingerprint patterns were generally dominated by the higher chlorinated PCDD/F congeners including OCDD, OCDF, and 1,2,3,4,6,7,8-HpCDD. Total TEQs were generally below US EPA ambient water quality criteria and aquatic ecotoxicology guideline values. The results of this study strongly suggest that discrete sampling of storm water outfalls is insufficient to characterize the concentrations and distributions of persistent hydrophobic contaminants such as PCDD/Fs. In addition to surface water runoff from the city of Oakland, other nonindustrialized urban locations may represent important sources of PCDD/Fs to San Francisco Bay.

Considerable attention has focused on whether storm water runoff is a significant source of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) and, in particular, 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) to the aquatic environment. Several studies have shown that, on a global scale, combustion-related processes, municipal and medical waste incinerators, and pentachlorophenol formulations are the largest contributors of PCDD/Fs to sediment and aquatic biota (Alcock and Jones 1996; US EPA 1996; Duarte-Davidson *et al.* 1997). The contributions from industrial manufacturing effluents and accidental releases have been shown to be limited, affecting primarily localized sediments and resident biota (Ehrlich *et al.* 1994; Shine *et al.* 1995; Long *et al.* 1996). More recently, the United States Environmental Protection Agency (US EPA) and others have identified nonpoint sources such as storm water runoff, publicly owned treatment works (POTWs), combined sewer outfalls (CSOs), and atmospheric deposition as potentially significant sources of these compounds (Alcock and Jones 1996; US EPA 1996).

There is limited information available on PCDD/Fs in storm water from which to infer temporal trends and relative contribu-

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tions to the aquatic environment. For example, 2,3,7,8-TCDD toxicity equivalents (TEQs) in urban runoff at the beginning and end of a rainstorm in Bayreuth, Germany, were 1 and 11 pg/L, which approaches the levels reported in local household wastewater and exceeds the 1 pg/L German water quality standard (Horstmann and McLachlan 1995). However, since storm water was only collected twice from a single location, namely at the beginning and the end of a rainstorm event, a temporal trend could not be ascertained from the data.

The relationship between sediment contamination and contributions from storm water discharged either directly through storm drains or indirectly through CSOs has been demonstrated in heavily urbanized waterways (Huntley *et al.* 1996; Fattore *et al.* 1997). For example, sediments located adjacent to CSO outfalls along the Passaic River in New Jersey, USA, have been shown to be contain elevated concentrations of PCDD/Fs and other persistent organochlorine contaminants (Huntley *et al.* 1996). The spatial distributions and fingerprint patterns suggest that CSOs are a significant source of PCDD/Fs and may affect the water and sediment quality of the Passaic River. In response to this and other evidence collected elsewhere in the United States, the US EPA has implemented a contaminated sediment management strategy that includes a nationwide inventory and evaluation of sediment chemistry and toxicity data (Long *et al.* 1996).

The San Francisco Bay estuary is a particularly sensitive ecosystem, both because of intense population pressures and the poor water exchange in many areas. It is the second largest estuary on the western coast of the United States, with a drainage basin of approximately 152 km by 103 km. The combination of fresh water originating from the Sacramento River and San Joaquin River and a narrow tidal outlet to the Pacific Ocean through the Golden Gate result in partially mixed estuarine conditions in the northern portion of the bay and relatively static lagoon-like conditions in the south. According to the 1995 U.S. census the approximately 6 million people that reside in the San Francisco Bay area is expected to reach 8 million by 2000. As a consequence, understanding the loading of contaminants, particularly persistent organic chemicals, to the San Francisco Bay is an important objective for managing and protecting this valuable resource.

There are relatively few studies on levels and sources of 2,3,7,8-TCDD and other PCDD/Fs to San Francisco Bay (Petreas *et al.* 1992; Long and Markel 1992; Petreas and Hayward 1994). San Francisco Bay was among the first estuaries included in the National Status and Trends (NS&T) Program implemented by the National Oceanic and Atmospheric Administration (NOAA) in 1981 (Long and Markel 1992). The few studies conducted over the past 10 years have focused on point sources of PCDD/F contamination as a result of specific industrial releases such as those from pulp and paper mills and wood treatment facilities (Petreas and Hayward 1994). Recent studies suggest some evidence of widespread polychlorinated biphenyl (PCB) contamination in San Francisco Bay, and extending into the San Joaquin delta (Jarman *et al.* 1999).

In this study, the concentrations of PCDD/Fs in storm water discharged to San Francisco Bay was investigated at 15 different outfalls located in areas adjacent to petroleum refineries and areas representative of mixed urban/commercial/residential land uses. Temporal changes in PCDD/F concentrations were determined in storm water collected hourly over a 12-h period during the first major rainstorm event of the 1995/96 winter season at two outfalls that drained areas considered representative of industrial and nonindustrial urban land uses. Storm water sampling was conducted 2 to 3 months apart at another 13 outfalls to examine changes in PCDD/F loadings to the bay at the onset and midway through the winter rainy season. Principal components analysis (PCA) was used as an exploratory statistical technique to examine temporal changes in the composition of PCDD/Fs in storm water, the similarities and differences in the distributions of PCDDs and PCDFs in storm water from different outfalls, and possible sources.

Materials and Methods

Collection of Storm Water

The locations of storm water outfalls are presented in Figure 1. In the first investigation, storm water samples were collected during the first rainstorm of the 1995/96 winter season from two outfalls located adjacent to the city of Oakland and the suburban community of Benicia. Eleven storm water samples were collected at the Oakland outfall. Ten samples were collected at the Benicia outfall. Storm water samples were collected from both outfalls simultaneously each hour over a 12-h period. Effluents were collected using a low-flow peristaltic pump with ¼-inch polyethylene tubing and a stainless steel wire-wrapped inlet with a ¹⁄₁₆-inch screen to restrict the intake of large suspended material. The intake was positioned in the outfall stream at a depth of approximately two-thirds the distance from the water surface. New polyethylene tubing was used for each hourly sampling event at both locations. Storm water samples were collected for 30 min into separate 15-L 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.

In the second investigation, 26 storm water samples were collected during rainstorm events in December 1995 and February/April 1996 from 13 outfalls located throughout San Francisco Bay. Storm water samples were collected from six outfalls located in areas considered representative of mixed residential, commercial, light and heavy industrial land uses and from seven outfalls located adjacent to active petroleum refineries. Two 1-L grab samples were collected at each outfall by submerging a glass bottle immediately beneath the water surface. Samples were stored on ice at 4°C until laboratory analysis.

PCDD and PCDF Analyses

The cleanup, extraction, and quantification of PCDD and PCDF homologues and 2,3,7,8-substituted congeners in storm water was performed by Alta Analytical Laboratory (El Dorado Hills, CA) according to US EPA Method 1613A (US EPA 1988). Storm water samples were spiked with $^{13}C_{12}$-labeled PCDD/F internal standards and continuously extracted with benzene for 18 h 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 through an analyte enrichment procedure in

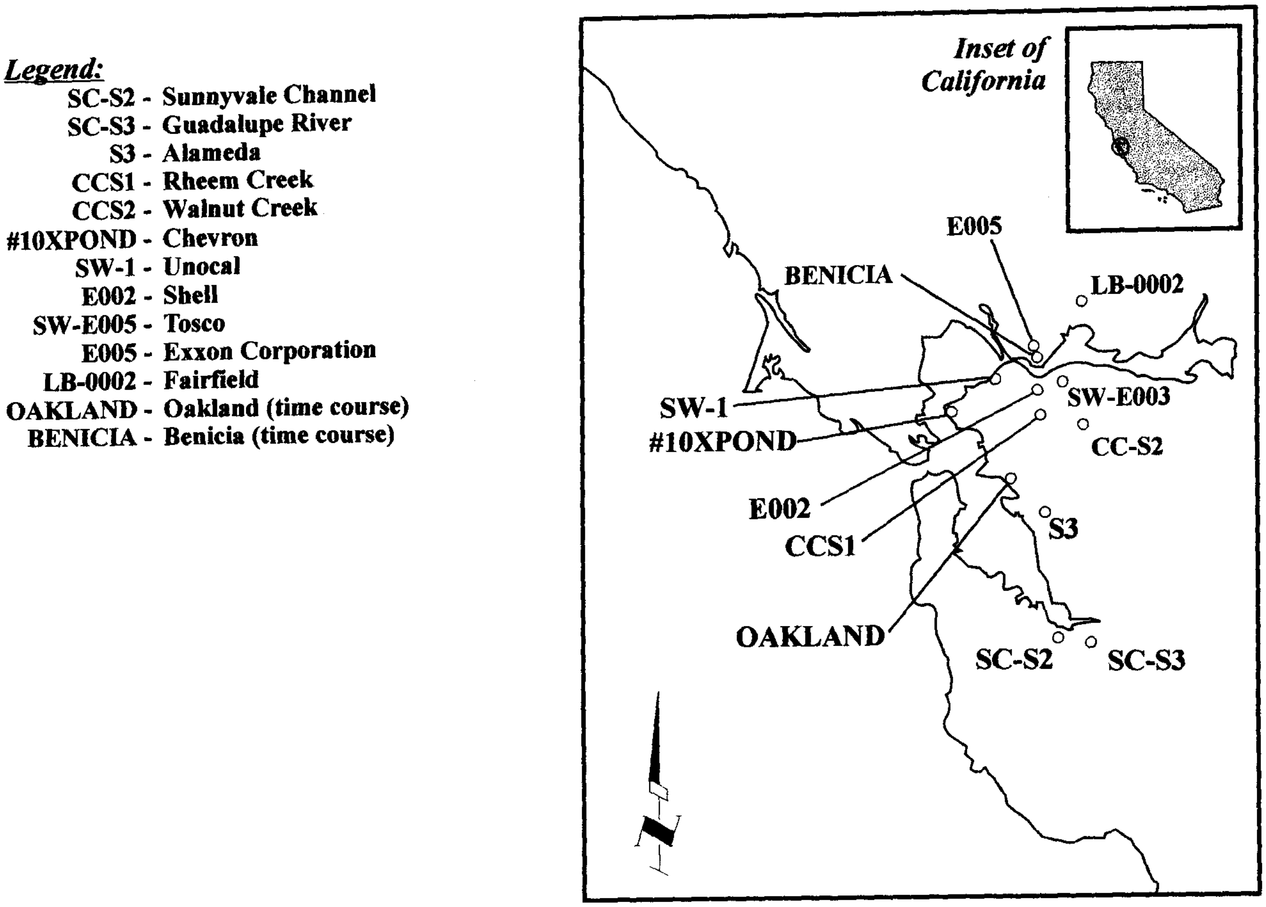

Fig. 1. Location and geographical grouping of storm water outfalls in San Francisco Bay, California

which sample extracts were dissolved in 100 ml of hexane and extracted with sodium hydroxide, concentrated sulfuric acid, and distilled water. The hexane extracts were concentrated to 1 ml and eluted with 60 ml hexane on a liquid chromatography column containing alternating layers of silica gel, concentrated sulfuric acid, and 33% 1 N sodium hydroxide on silica gel. Extracts were concentrated to 1 ml and fractionated on liquid chromatography columns containing 4 g activated alumina using methylene chloride/hexane. The fractions were concentrated to 1 ml and applied to the tops of chromatography columns containing 1 g of 5% AX-21 activated carbon on silica gel. Each column was eluted with cyclohexane/methylene chloride and cyclohexane/methanol/benzene in the forward direction and with benzene in the reverse direction. Each benzene fraction was collected, spiked with recovery standards, and concentrated to 20 ml.

The benzene extracts were assayed for 17 2,3,7,8-substituted PCDD/Fs by combined high-resolution gas chromatography/high-resolution mass spectrometry (HRGC/HRMS) using a Hewlett Packard Model 5890 GC and VG Model 70SE HRMS. The congener concentrations were acquired by selected ion-recovery monitoring of the groups of ion masses and quantified from relative response factors as described in US EPA Method 1613A (US EPA 1988). The method detection limits for 2,3,7,8-substituted congeners and homologue groups ranged between 0.29 and 1.4 pg/L. The lower method calibration limit was 1 ppq (parts per quadrillion). 2,3,7,8-TCDD toxic equivalents (TEQs) were calculated from the results using toxic equivalency factors (TEFs) recommended by an expert panel to the World Health Organization (WHO; Van den Berg *et al.* 1998).

Principal Components Analysis

The methods and mathematical basis for the use of PCA with multivariate data such as PCDD/Fs are provided elsewhere (Wold *et al.* 1987; Wenning and Erickson 1994; Akerfjord and Christophersen 1996). PCA was used in this study to determine if there were meaningful spatial and temporal differences in the concentrations of PCDD/Fs in storm water collected from different outfalls. Differences in the distributions of various PCDD/F congeners within or between outfalls may reflect variations in anthropogenic sources or environmental transport of these contaminants to San Francisco Bay. PCA was used to reduce the data from its original 17 congener by 15 sample matrix and project the results onto a three-dimensional space that preserves the maximum amount of variance described in the original data matrix.

The first three eigenvectors, or principal component axes, along which the data matrix showed the most variability were used for interpretation of the data. The first principal component axis retains the highest variance in the data set; subsequent principal component axes retain smaller portions of the total variance in the data set.

In the new three-dimensional space of PCA, storm water samples that have similar PCDD/F profiles are positioned close to each other on a PCA scores plot. Storm water samples with dissimilar PCDD/F profiles are positioned further apart from each other on the scores plot. The scores plot can provide a better indication of the similarities and differences between storm water samples than is possible from comparisons between individual variables. The relationships among the storm water variables (that is, the individual PCDD/F congeners)

Table 1. PCDD/Fs in storm water (n = 11) collected hourly from a single outfall located in Oakland, California, during the first rainstorm event of the winter 1995/96 season

	Oakland Stormwater Outfall (pg/L)				
Congener	No. Positive Occurrences	Maximum Concentration	Minimum Concentration	Arthimetic Mean	Median
2,3,7,8-TCDD	4	2.7	ND	1.4	1.2
1,2,3,7,8-PeCDD	6	11	ND	5.1	5.1
1,2,3,4,7,8-HxCDD	7	21	ND	8.5	7.3
1,2,3,6,7,8-HxCDD	8	42	ND	18	16
1,2,3,7,8,9-HxCDD	8	40	ND	16	13
1,2,3,4,6,7,8-HpCDD	11	760	3.4	298	200
2,3,7,8-TCDF	6	8.6	ND	2.1	1
1,2,3,7,8-PeCDF	5	7.6	ND	2.2	1.2
2,3,4,7,8-PeCDF	7	39	ND	8.1	3.2
1,2,3,4,7,8-HxCDF	8	26	ND	6.6	4.1
1,2,3,6,7,8-HxCDF	8	47	ND	14	12
2,3,4,6,7,8-HxCDF	10	49	ND	13	7.1
1,2,3,7,8,9-HxCDF	5	5	ND	1.8	0.8
1,2,3,4,6,7,8-HpCDF	11	350	1.4	119	97
1,2,3,4,7,8,9-HpCDF	7	13	ND	5.4	3.8
Total TCDD	4	11	ND	4	1.3
Total PeCDD	6	31	ND	11	7
Total HxCDD	8	300	ND	119	89
Total HpCDD	11	1,500	6.5	557	360
Total OCDD	11	6,200	19	1,911	1,300
Total TCDF	7	250	ND	57	20
Total PeCDF	8	760	ND	161	77
Total HxCDF	10	870	ND	230	150
Total HpCDF	11	590	7.8	202	160
Total OCDF	11	500	4.2	180	100
Total PCDDs	—	7,562	27	2,602	1,807
Total PCDFs	—	2,970	15	831	576
Total TEQs	—	65	0.1	21	16

ND indicates a nondetect measurement using US EPA Method 1613A. Summary statistics include either the measured concentration or the laboratory detection limit for each sample. Toxic equivalents (TEQs) were calculated using WHO (Van den Berg *et al.* 1998) wildlife TEFs. Measurements below the detection limit were not included in the TEQ calculation. Total PCDDs and Total PCDFs were calculated as the sum of tetra- through octa-chlorinated homologues

and between the variables and the samples are provided in PCA by a variable loadings plot. As in the scores plot, variables positioned close to each other may be closely correlated in the storm water samples. In addition, the location of the variables on the variable loadings plot indicate their effect on the placement of storm water samples in the PCA scores plot. For example, a storm water sample with positive scores along the first and second principal component axes in the PCA scores plot is probably enriched with PCDD/Fs that have positive loadings along the first two axes in the variable loadings plot. In this manner, PCA provides a statistical basis for describing the similarities and differences in the composition of PCDD/Fs among different storm water samples.

For the purposes of calculating descriptive statistics (*e.g.*, mean and median concentrations) and PCA analysis, PCDD/F congener concentrations reported by the laboratory as below the detection limit were assumed to be present at the limit of detection (Wenning and Erickson 1994). Prior to PCA, the 2,3,7,8-substituted congener concentrations in each storm water sample were normalized to represent the fraction of the total concentration of the 17 2,3,7,8-substituted congeners. The normalized data were autoscaled in the PCA model such that all the variables had zero means and unit variance. The normalization procedures provided for equal weight to be given to each of the 17 congener variables and minimized domination of the loadings along the principal component axes by congeners with large variances. PCA modeling was conducted using Pirouette software (version 2.0, Infometrix Inc., Seattle, WA).

Results

Temporal Changes in PCDD/Fs in Oakland and Benicia Storm Water

A summary of PCDD/F concentrations in storm water samples collected hourly at the Oakland and Benicia outfalls are presented in Tables 1 and 2, respectively. 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 7,562 pg/L (arithmetic mean of 2,602 pg/L) and 15 to 2,970 pg/L (arithmetic mean of 831 pg/L), respectively. In Benicia storm water, ΣPCDD and ΣPCDF concentrations ranged from 11 to 2,798 pg/L (arithmetic mean of 480 pg/L) and 7 to 207 pg/L (arithmetic mean of 49 pg/L), respectively. The average TEQ level, using WHO

Table 2. PCDD/Fs in storm water (n = 10) collected hourly from a single outfall located in Benicia, California, during the first rainstorm event of the winter 1995/96 season

	Benicia Stormwater Outfall (pg/L)				
Congener	No. Positive Occurrences	Maximum Concentration	Minimum Concentration	Arthimetic Mean	Median
2,3,7,8-TCDD	0	1.5	ND	1	0.97
1,2,3,7,8-PeCDD	3	5.3	ND	2	1.4
1,2,3,4,7,8-HxCDD	3	9.4	ND	3	1.9
1,2,3,6,7,8-HxCDD	4	17	ND	4.6	1.8
1,2,3,7,8,9-HxCDD	4	19	ND	4.7	1.5
1,2,3,4,6,7,8-HpCDD	8	230	ND	50	6.4
2,3,7,8-TCDF	1	0.7	ND	0.6	0.56
1,2,3,7,8-PeCDF	2	1.8	ND	1.1	1.2
2,3,4,7,8-PeCDF	2	1.5	ND	1	0.98
1,2,3,4,7,8-HxCDF	3	2.8	ND	1.2	0.95
1,2,3,6,7,8-HxCDF	3	3.5	ND	1.3	0.97
2,3,4,6,7,8-HxCDF	4	3.4	ND	1.8	1.5
1,2,3,7,8,9-HxCDF	2	1.1	ND	0.9	0.92
1,2,3,4,6,7,8-HpCDF	5	52	ND	10	1.6
1,2,3,4,7,8,9-HpCDF	1	19	ND	2.9	1.2
Total TCDD	0	1.5	ND	1	0.97
Total PeCDD	3	16	ND	3.1	1.4
Total HxCDD	4	110	ND	24	2
Total HpCDD	8	770	ND	128	14
Total OCDD	10	1900	5.8	324	34
Total TCDF	1	3.3	ND	0.9	0.58
Total PeCDF	3	22	ND	4.5	1.4
Total HxCDF	4	52	ND	13	1.5
Total HpCDF	5	88	ND	16	3.2
Total OCDF	10	42	3	15	6.7
Total PCDDs	—	2798	11	480	51
Total PCDFs	—	207	7	49	17
Total TEQs	—	14	ND	3.5	0.11

ND indicates a nondetect measurement using US EPA Method 1613A. Summary statistics include either the measured concentration or the laboratory detection limit for each sample. Toxic equivalents (TEQs) were calculated using WHO (Van den Berg *et al.* 1998) wildlife TEFs. Measurements below the detection limit were not included in the TEQ calculation. Total PCDDs and Total PCDFs were calculated as the sum of tetra- through octa-chlorinated homologues

TEFs (Van den Berg *et al.* 1998), in Oakland storm water (21 pg/L; ranging between 0.1 and 65 pg/L) was nearly sevenfold higher than in Benicia storm water (3.5 pg/L; ranging between nondetect and 14 pg/l). Fewer 2,3,7,8-substituted congeners were detected in Benicia storm water than in Oakland storm water. Higher chlorinated homologues, particularly hepta- and octa-chlorinated PCDDs were predominant in storm water from both outfalls. 2,3,7,8-TCDD concentrations were below method detection limits in all Benicia storm water samples; 2,3,7,8-TCDD was measured in 4 of 11 Oakland storm water samples (ranging between 1.6 and 2.7 pg/L in 4 samples).

Temporal changes in PCDD/F concentrations as the rainstorm event progressed were evident in storm water collected during the later stages of sampling at both outfalls. Hourly changes in ΣPCDD, ΣPCDF, and 2,3,7,8-TCDD concentrations and TEQ levels in storm water from the Oakland and Benicia outfalls are presented in Figures 2 and 3, respectively. In Oakland storm water, PCDD/F concentrations increased 5 h after the start of the rainstorm, remained elevated after the sixth hour of sampling, and gradually declined after 9 h of sampling (Figure 2). In Benicia storm water, PCDD/F concentrations increased during the fourth and seventh hours of sampling and remained elevated after 8 h (Figure 3).

PCDD/Fs in Storm Water from Outfalls in Mixed Land Use and Refinery Areas

PCDD/F concentrations in storm water collected from outfalls located in mixed urban/rural areas and petroleum refineries during the December 1995 rainstorm event are presented in Table 3. ΣPCDD concentrations in storm water from outfalls in mixed urban/rural land use areas ranged from 140 pg/L (at Fairfield) to 2,222 pg/L (at Rheem Creek); ΣPCDF concentrations ranged from 24 pg/L (at Fairfield) to 482 pg/L (at Rheem Creek). In storm water collected during the same rainstorm from outfalls located adjacent to petroleum refineries, ΣPCDD concentrations ranged from 373 pg/L (at the Shell refinery outlet in Martinez) to 10,721 pg/L (near the Unocal refinery). A grassfire was reported in the area from where the storm water had been collected at the Unocal refinery shortly before sampling. The anomalously elevated PCDD concentrations at the Unocal refinery are unexplained, but may be attributable, in part, to this fire. ΣPCDF concentrations ranged from 59 pg/L (at the Shell refinery outlet in Martinez) to 2,450 pg/L (at the Shell refinery inlet in Martinez). 2,3,7,8-TCDD was not detected in storm water samples collected from any of the outfalls sampled

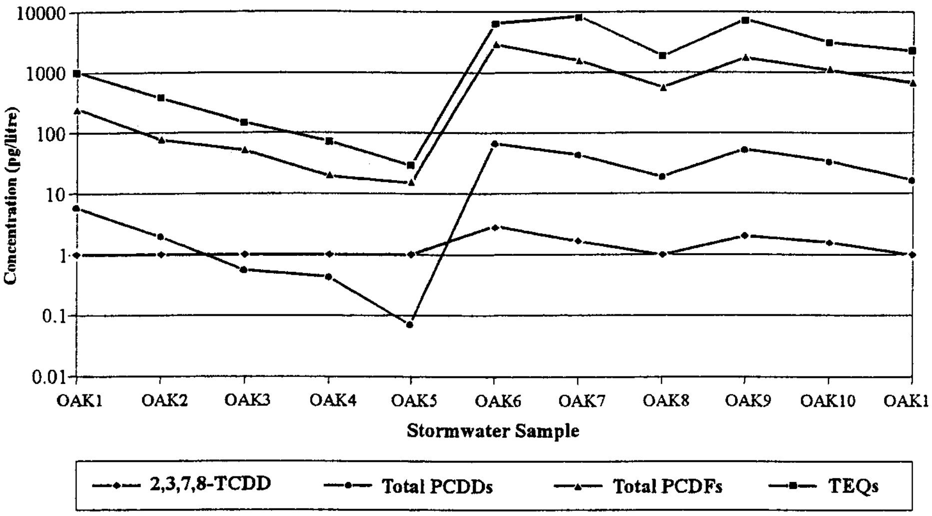

Fig. 2. Temporal changes in total PCDD/Fs and 2,3,7,8-TCDD concentrations and total TEQ levels in Oakland, CA, storm water

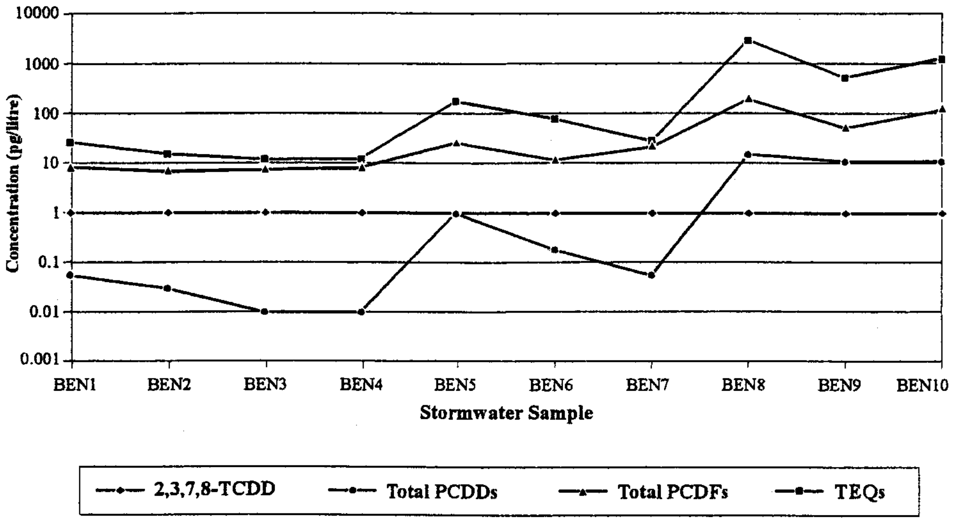

Fig. 3. Temporal changes in total PCDD/Fs and 2,3,7,8-TCDD concentrations and total TEQ levels in Benicia, CA, storm water

during the December 1995 rainstorm event. TEQ levels varied widely in storm water collected adjacent to petroleum refineries (between 5 and 72 pg/L, arithmetic average of 29 pg/L), but were generally higher than TEQ levels in storm water collected in mixed urban/rural land use areas (between 4 and 16 pg/L, arithmetic average of 11 pg/L).

PCDD/Fs in storm water were generally lower during the second round of sampling conducted in February/April 1996 than during the first round of sampling in December 1995. PCDD/F concentrations in storm water collected from outfalls located in mixed urban/rural areas and petroleum refineries during the February/April 1996 rainstorm event are presented in Table 4. ΣPCDD concentrations in storm water from outfalls located in mixed urban/rural land use areas ranged from 85 pg/L (at Fairfield) to 4,397 pg/L (at Alameda); ΣPCDF concentrations ranged from nondetect (at Fairfield) to 915 pg/L (at Alameda). In storm water collected during the same rainstorm from outfalls located adjacent to petroleum refineries, ΣPCDD concentrations ranged from nondetect (at the Shell refinery outlet in Martinez) to 15,521 pg/L (at the Shell refinery inlet in Martinez); ΣPCDF concentrations ranged from nondetect (at the Chevron refinery in Richmond and Shell refinery outlet in Martinez) to 3,070 pg/L (at the Shell refinery inlet in Martinez). 2,3,7,8-TCDD was not detected in storm water samples collected from any of the outfalls sampled during the December 1995 rainstorm event. TEQ levels varied widely in storm water. TEQ levels were generally higher in storm water from outfalls located near petroleum refineries (between 11 and 73 pg/L, arithmetic average of 22 pg/L) than in storm water from outfalls located in mixed urban/rural land use areas (between 8 and 30 pg/L, arithmetic average of 16 pg/L).

Principal Components Analysis

PCA modeling was used to examine temporal changes in the distributions of PCDD/Fs in storm water collected from the Oakland and Benicia outfalls. The three-dimensional principal components scores plot presented in Figure 4 was prepared using the congener data in Tables 1 and 2. The first three

Table 3. PCDD/Fs in storm water collected from outfalls located adjacent to mixed urban/rural areas and petroleum refineries during a rainstorm event in December 1995

	Mixed Urban/Rural Outfalls (pg/L)					Petroleum Refinery Outfalls (pg/L)					
Congener	Fairfield	Sunnyvale Channel	East Guadalupe River	CC Channel	Rheem Creek	Chevron, Richmond	Exxon, Benicia	Unocal, Rodeo	Shell (inlet), Martinez	Shell (outlet), Martinez	Tosco, Avon
2,3,7,8-TCDD	(0.9)	(0.9)	(1.1)	(1.0)	(1.8)	(1.4)	(1.4)	(3.7)	(3.2)	(1.2)	(1.0)
1,2,3,7,8-PeCDD	(1.3)	(2.5)	3.6	2.2	3.8	3.0	(3.1)	26	8.0	(1.3)	(2.0)
1,2,3,4,7,8-HxCDD	(1.5)	4.5	5.6	3.3	6.1	4.8	4.1	43	15	(3.0)	1.7
1,2,3,6,7,8-HxCDD	(1.7)	14	12	8.4	15	9.0	9.9	86	35	(3.3)	4.4
1,2,3,7,8,9-HxCDD	(1.6)	9.4	11	7.4	15	8.3	7.1	83	22	(3.0)	6.2
1,2,3,4,6,7,8-HpCDD	19	230	180	110	240	120	270	1,200	620	38	43
2,3,7,8-TCDF	(0.9)	1.2	2.4	(0.9)	(1.4)	(1.5)	(1.3)	(1.6)	(1.4)	(0.9)	(1.1)
1,2,3,7,8-PeCDF	(1.9)	1.8	2.5	(1.8)	(1.3)	(1.2)	(2.1)	3.8	(3.6)	(1.2)	(2.4)
2,3,4,7,8-PeCDF	(1.6)	3.2	8.5	(1.3)	3.3	2.0	2.4	7.7	61	(1.1)	(1.4)
1,2,3,4,7,8-HxCDF	(1.5)	3.8	5.4	1.9	4.0	3.7	2.4	14	(6.1)	(1.5)	(1.9)
1,2,3,6,7,8-HxCDF	(1.5)	5.3	5.1	2.1	4.2	2.8	2.3	16	20	(1.5)	(1.6)
2,3,4,6,7,8-HxCDF	2.9	6.4	9.2	5.0	7.1	5.1	9.7	21	35	3.0	3.5
1,2,3,7,8,9-HxCDF	(1.1)	(1.0)	(1.1)	(1.0)	(1.0)	(1.8)	(1.5)	3.5	(4.1)	(1.4)	1.8
1,2,3,4,6,7,8-HpCDF	4.7	46	54	31	69	36	30	300	150	8.1	9.3
1,2,3,4,7,8,9-HpCDF	(0.8)	2.4	4.2	(2.0)	4.3	3.2	2.7	16	(8.7)	(1.6)	(0.0)
Total TCDD	(0.9)	(0.9)	3.0	(1.0)	(1.8)	(1.4)	2.4	(3.7)	(3.2)	(1.2)	(2.5)
Total PeCDD	(1.3)	(2.5)	12	2.2	5.6	5.0	(3.1)	57	21	(1.3)	(2.0)
Total HxCDD	(3.2)	75	85	43	85	54	100	460	240	9.1	31
Total HpCDD	35	420	330	190	430	210	970	2,000	1,400	71	110
Total OCDD	100	1,700	1,100	750	1,700	760	2,500	8,200	4,800	290	270
Total TCDF	(0.9)	17	36	(1.2)	5.5	(1.5)	4.1	8.4	230	(0.9)	3.2
Total PeCDF	(1.9)	60	99	13	45	21	22	130	940	6.1	9.5
Total HxCDF	2.9	75	80	37	81	49	34	360	450	9.5	16
Total HpCDF	9.5	110	110	74	160	84	87	700	440	21.0	21
Total OCDF	8.4	88	92	60	190	65	82	590	390	22.0	19
Total PCDDs	140	2,198	1,530	986	2,222	1,030	3,576	10,721	6,464	373	416
Total PCDFs	24	350	417	185	482	221	229	1,788	2,450	59	69
Total TEQs	4	13	16	8.1	16	10	14	72	65	5	5.9

Nondetect measurement using US EPA Method 1613A are indicated in parentheses. Toxic equivalents (TEQs) were calculated using WHO (Van den Berg et al. 1998) TEQ factors for fish. Measurements below the detection limit were not included in the TEQ calculation. Total PCDDs and total PCDFs were calculated as the sum of tetra- through octa-chlorinated homologues

principal components explained 82%, 7%, and 4% of the original variance of the data set, respectively. PCA modeling indicated that the 2,3,7,8-substituted congener patterns in storm water samples changed significantly after 4 h of sampling at the Oakland (oak1–oak11) and the Benicia (ben1–ben10) outfalls (Figure 4). Four different 2,3,7,8-substituted congener patterns were evident in Oakland storm water samples after 11 h of sampling. Five different congener patterns were evident in Benicia storm water samples after 10 h of sampling.

The differences in the congener profiles observed in the PCA scores plot could be partially explained by the variable loadings plot presented in Figure 5. Hepta- and octa-chlorinated PCDD/F congeners were most responsible for the differences observed among Oakland and Benicia storm water samples (Figure 4). 1,2,3,4,7,8,9-HpCDF and OCDF were the most significant variables along the third principal component axis (Figure 5).

PCA was also used to examine the differences in the distributions of PCDD/Fs, if any, in storm water collected from outfalls located proximate to petroleum refineries and nonrefinery areas, and to identify changes in PCDD/F loadings to San Francisco Bay at the onset and midway through the winter rainy season. The three-dimensional PCA scores plot presented in Figure 6 was generated using the congener data presented in Tables 3 and 4. The first three principal components explained 79%, 9%, and 5% of the original variance in the data set, respectively. PCA indicated several different 2,3,7,8-substituted congener patterns in storm water samples collected in December 1995 and February/April 1996. Similar to storm water from Oakland and Benicia, the hepta- and octa-chorinated PCDD/F congeners were most responsible for the differences observed in the PCA scores plot (Figure 7).

Discussion

There are several important characteristics of the PCDD/F results in storm water collected during the December 1995 and February/April 1996 sampling events. With the exception of the Tosco and Shell outlet (samples collected in February/April 1996), PCDD/Fs in storm water collected from outfalls located adjacent to petroleum refineries were comparable to those found in outfalls located in mixed urban/rural areas (Tables 3 and 4). The concentrations of 1,2,3,4,6,7,8-HpCDD, 1,2,3,4,6,7,8-HpCDF, and OCDD were generally highest among the 2,3,7,8-substituted congeners measured in storm water from the 15 outfalls, including Oakland and Benicia. The presence of

Table 4. PCDD/Fs in storm water collected from outfalls located adjacent to mixed urban/rural areas and petroleum refineries during rainstorm events in February and April 1996

	Mixed Urban/Rural Outfalls (pg/L)						Petroleum Refinery Outfalls (pg/L)						
Congener	Fairfield	Sunnyvale Channel	East Guadalupe River	Alameda	CC Channel	Rheem Creek	Chevron, Richmond	Exxon, Benicia	Unocal, Rodeo	Shell (inlet), Martinez	Shell (outlet), Martinez	Tosco (inlet), Avon	Tosco (outlet), Avon
2,3,7,8-TCDD	(3.8)	(3.9)	(3.5)	(4.3)	(4.2)	(4.3)	(2.8)	(3.6)	(4.5)	(3.7)	(3.4)	(3.5)	(2.6)
1,2,3,7,8-PeCDD	(1.7)	(5.8)	(2.5)	7.7	(2.5)	(3.4)	(5.7)	(4.0)	(6.5)	(15)	(6.0)	(5.1)	(4.7)
1,2,3,4,7,8-HxCDD	(3.0)	(9.6)	(6.9)	13	3.8	5.5	(5.4)	(5.5)	(17)	(23)	(6.8)	(5.0)	(6.0)
1,2,3,6,7,8-HxCDD	(2.9)	(10)	8.5	28	9.3	13	(5.2)	(5.8)	(17)	54	(6.7)	5.2	(6.4)
1,2,3,7,8,9-HxCDD	(2.6)	(9.2)	7.6	24	6.6	11	(4.7)	(5.2)	(15)	29	(6.0)	(5.0)	(7.6)
1,2,3,4,6,7,8-HpCDD	7.9	61	130	460	120	220	(18)	39	140	1,300	(12)	97	26
2,3,7,8-TCDF	(1.5)	(2.7)	(2.8)	1.7	(3.4)	2.2	(1.5)	(3.6)	(2.7)	(3.5)	(1.2)	(3.0)	(2.6)
1,2,3,7,8-PeCDF	(2.0)	(4.4)	(3.3)	2.2	(1.5)	(2.3)	(3.4)	(3.2)	(5.2)	(8.0)	(3.4)	(3.6)	(4.0)
2,3,4,7,8-PeCDF	(2.0)	(4.2)	(3.3)	5.5	(2.3)	3.2	(3.7)	(2.7)	(4.7)	27	(3.7)	(2.6)	(2.9)
1,2,3,4,7,8-HxCDF	(1.5)	(8.4)	(2.4)	9.7	2.1	4.4	(2.4)	(3.4)	(4.6)	(7.9)	(2.4)	(5.2)	(3.8)
1,2,3,6,7,8-HxCDF	(1.4)	(8.1)	(2.2)	6.6	2.1	3.4	(2.3)	(3.3)	(4.4)	28	(2.3)	(5.0)	(3.7)
2,3,4,6,7,8-HxCDF	(2.7)	(7.3)	(3.8)	10	4.7	7.4	(2.5)	(3.6)	(3.9)	27	(2.4)	(5.5)	(4.0)
1,2,3,7,8,9-HxCDF	(1.6)	(7.8)	(2.6)	(3.4)	(1.8)	(2.4)	(2.2)	(3.9)	(3.0)	(10)	(2.3)	(6.7)	(4.4)
1,2,3,4,6,7,8-HpCDF	(1.9)	15	29	120	24	54	(4.5)	11	51	310	(3.3)	19	9.3
1,2,3,4,7,8,9-HpCDF	(1.2)	(2.7)	(2.0)	7.2	(1.9)	4.9	(4.0)	(2.2)	(7.2)	(20)	(4.2)	(5.4)	(3.9)
Total TCDD	(3.8)	(3.9)	(3.5)	(4.3)	(4.2)	(4.3)	(2.8)	(3.6)	(4.5)	(3.7)	(3.4)	(3.5)	(2.6)
Total PeCDD	(1.7)	(5.8)	(2.5)	13	(2.5)	(3.4)	(18)	(4.0)	(15)	(18)	(15)	(5.1)	(4.7)
Total HxCDD	(3.0)	(10)	48	160	54	81	(5.4)	(5.8)	(17)	390	(6.8)	26	(8.4)
Total HpCDD	16	110	230	820	220	400	(18)	75	250	3,100	(12)	250	41
Total OCDD	60	310	810	3,400	780	1,600	80	210	1,000	12,000	(20)	1,100	96
Total TCDF	(1.5)	(2.7)	(2.8)	22	(4.0)	12	(1.5)	(4.7)	(2.7)	120	(1.2)	(3.0)	(2.6)
Total PeCDF	(2.0)	(4.4)	16	63	14	41	(3.7)	(3.2)	13	520	(3.7)	(3.6)	(4.0)
Total HxCDF	(2.7)	(8.4)	34	180	41	83	(2.5)	(3.9)	28	530	(2.4)	(6.7)	(4.4)
Total HpCDF	(1.9)	15	29	350	68	150	(4.5)	27	180	970	(4.2)	64	20
Total OCDF	(5.8)	24	56	300	55	130	(7.8)	33	120	930	(13)	83	21
Total PCDDs	85	440	1,094	4,397	1,061	2,089	124	298	1,287	15,512	ND	1,385	153
Total PCDFs	ND	55	138	915	182	416	ND	72	344	3,070	ND	160	52
Total TEQs	7.6	17	13	30	12	17	11	11	20	73	12	14	11

Nondetect measurement using US EPA Method 1613A are indicated in parentheses. Toxic equivalents (TEQs) were calculated using WHO (Van de Berg et al. 1998) TEQ factors for fish. Measurements below the detection limit were not included in the TEQ calculation. Total PCDDs and total PCDFs were calculated as the sum of tetra- through octa-chlorinated homologues

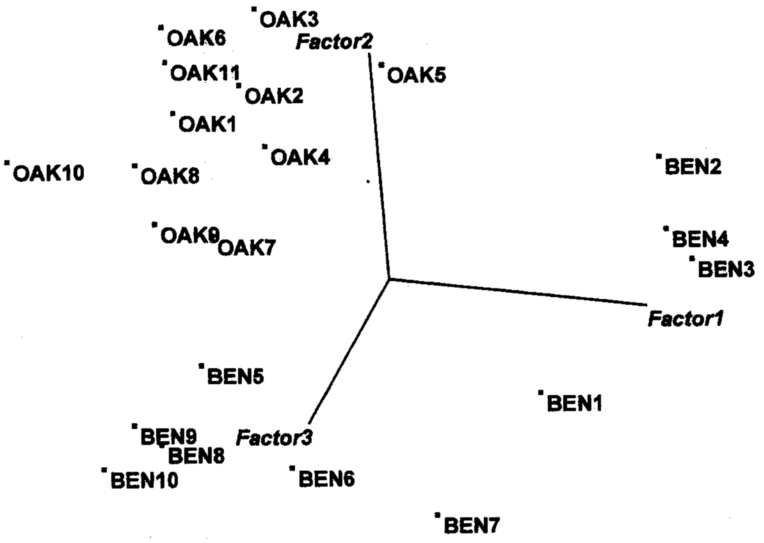

Fig. 4. Three-dimensional principal components scores plot of normalized 2,3,7,8-substituted PCDD/Fs in urban storm water samples collected hourly during the first major rainfall of the winter season from outfalls located in the cities of Oakland (oak) and Benicia (ben), California

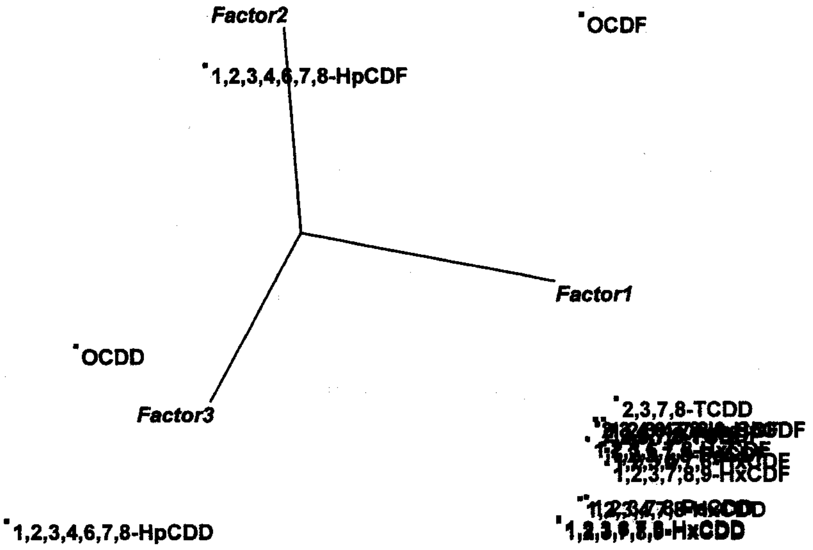

Fig. 5. The loadings plot for the first three principal components scores plot shown in Figure 4

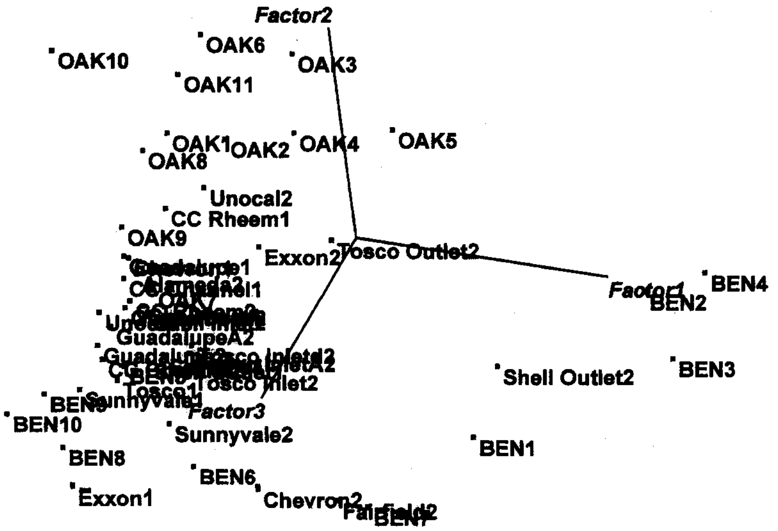

Fig. 6. Three-dimensional principal components scores plot of normalized 2,3,7,8-substituted PCDD/Fs in storm water samples collected in December 1995 and February/April 1996 from outfalls in San Francisco Bay located adjacent to petroleum refineries and in areas representing mixed urban/commercial/rural land uses

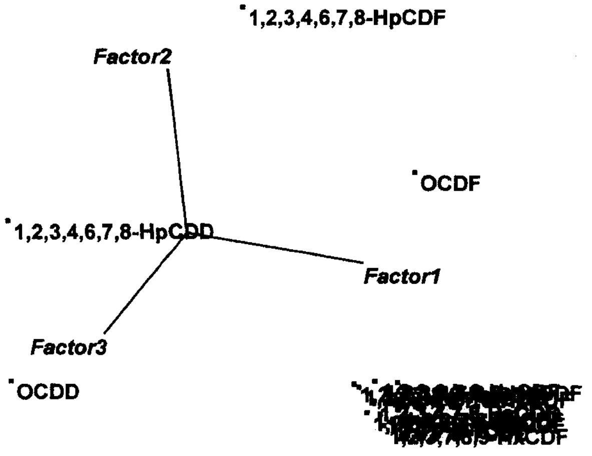

Fig. 7. The loadings plot for the first three principal components scores plot shown in Figure 6

these three congeners at elevated concentrations contribute significantly to the total TEQs in storm water. With the exception of Oakland storm water collected after the fifth hour of sampling (Table 1), 2,3,7,8-TCDD was not measured in storm water samples. 2,3,7,8-TCDF was detected in some mixed urban/rural outfalls such as Oakland, Alameda, Rheem Creek, Sunnyvale, and East Guadalupe River. 2,3,7,8-TCDF was not measured in storm water collected from outfalls located near petroleum refineries.

Another feature shown in Tables 3 and 4 is a more than a tenfold difference in the concentrations of PCDD/Fs in storm water discharged from the outlet and inlet outfalls located at the Shell refinery in Martinez. Storm water discharged from the Shell inlet outfall is collected in a holding pond prior to discharge through the Shell outlet outfall into San Francisco Bay. Comparable reductions in PCDD/F concentrations are evident between the inlet and outlet outfalls at the Tosco refinery located in Avon (Table 4).

The lowest concentrations of PCDD/Fs in storm water were measured in outfalls located in Benicia and Fairfield, where the predominant land uses are residential and light commercial. The highest PCDD/F concentrations measured at the eighth, ninth, and tenth hours of sampling at the Benicia outfall (Table 2) were lower than the concentrations measured at other outfalls, with the exception of both Fairfield outfall samplings and the CC Channel outfall in December 1995. The highest PCDD/F concentrations in storm water occurred, as expected, in outfalls located in urban and moderate to heavily commercialized areas such as Oakland, Sunnyvale, East Guadalupe, and Alameda. The concentrations of PCDD/Fs in storm water collected during the first 5 h of sampling at the Oakland outfall (Table 1) and first 7 h at the Benicia outfall (Table 2) were comparable or lower than the concentrations measured at other mixed urban/rural outfalls.

The TEQ levels calculated in storm water from outfalls located in mixed urban/rural areas (as high as 65 pg/L in Oakland, and averaging between 15–25 pg/L elsewhere) and near petroleum refineries (as high as 72 pg/L at the Unocal refinery, and averaging between 10–15 pg/L at other refineries) approach the range associated with adverse effects to some aquatic biota. However, at locations where settling ponds are used, there is likely to be considerable reductions in the TEQ levels in storm water between the inlet to the settling ponds and the outlet to San Francisco Bay. It is also important to recognize that the possibility for adverse effects to some aquatic biota is not related only to the TEQ levels in storm water, but also to the volume of contaminants discharged from the outfall. It is reasonable to assume that an outfall discharging a large volume of storm water with a low TEQ level would, in terms of mass loading, contribute more to the total mass of TEQs released to San Francisco Bay than an outfall with the opposite characteristics.

TEQs are typically used to express the toxicity of a complex mixture of PCDD/F congeners in terms of an equivalent concentration of 2,3,7,8-TCDD. In the United States and elsewhere, regulatory limits for the protection of public health and wildlife are typically promulgated either on the basis of 2,3,7,8-TCDD or total dioxin TEQs. A review of the aquatic ecotoxicology literature on dioxins indicates an adverse response level for rainbow trout fry, the most sensitive aquatic receptor, in the range of 0.011–0.038 ng 2,3,7,8-TCDD L^{-1} (Grimwood and Dobbs 1996; Boening 1998). Using this range, a mean value of 0.02 ng/L may be an acceptable aquatic guideline value in water (Comber *et al.* 1996). At present, the US EPA ambient water quality guideline value for 2,3,7,8-TCDD is 0.0013 pg/L (US EPA 1984), which has been associated with a fish body burden of 25 pg/g that is acceptable for protection of public health (Boyer *et al.* 1991; Boening 1998). It is important to note, however, that a range of values have been associated with toxic tissue levels in some fish and benthic species, and some of these values overlap with reported tissue levels that result in no toxic effects. This overlap can be attributed to species variability and uncertainties regarding the mechanism for toxicity in aquatic biota (Barber *et al.* 1998). Bioconcentration from water to biota is another source of uncertainty when associating PCDD/F concentrations in storm water with acceptable aquatic guideline values for the protection of fish.

The results of the temporal analysis reported in this study are consistent with those reported elsewhere (Huntley *et al.* 1996; Shear *et al.* 1996). The temporal variability in the concentrations of PCDD/Fs and the distributions of 2,3,7,8-substituted congeners in storm water collected from outfalls located near Oakland and Benicia suggests that discrete sampling is inappropriate for characterizing the concentrations of these contaminants in storm water. The results of discrete sampling for PCDD/Fs in storm water would appear to be highly dependent on the time of sampling after the last rainstorm event. Periodic sampling within a 12- to 24-h period would appear to be a more appropriate method for characterizing nonpoint sources of PCDD/Fs and other persistent chemicals to the aquatic environment.

It has been reported that petroleum refineries may be a source of PCDD/Fs to the aquatic environment as a result of discharges associated with certain reforming catalyst regeneration processes (Thompson *et al.* 1990; Beard *et al.* 1993; US EPA 1994, 1996). The available data summarized in Table 5 indicate that ΣPCDD and ΣPCDF concentrations in some catalyst regenera-

Table 5. PCDD/Fs in caustic wash waters from catalytic regeneration processes used at some petroleum refineries

Congener	Caustic Wash Water (ppt)	Caustic Wash Water (ppt)	Continuous Regenerator Stack Gas, No Scrubber (ng/m^3)	Wash Water from Scrubber, Periodic/Cyclic Regenerator (ppg)	Wash Water from Scrubber, Periodic/Cyclic Regenerator (ppg)
Total TCDD	(0.2)	(0.2)	1.6	44	110
Total PeCDD	11	(0.2)	3.4	15	90
Total HxCDD	101	1.5	1.9	(17)	160
Total HpCDD	277	14	1.2	(20)	64
Total OCDD	274	35	0.8	(22)	56
Total TCDF	489	80	46	150	660
Total PeCDF	1336	435	120	40	330
Total HxCDF	4547	2621	31	20	260
Total HpCDF	6600	4742	12	10	160
Total OCDF	3548	2415	1.7	23	93

Caustic wash water data are from Huang and Buekens (1995). Continuous and periodic/cyclic regenerator data are mean of seven samples from Thompson *et al.* (1990). Nondetect measurements reported by the authors are indicated in parentheses

tion caustic wash waters may be as high as 650 ppt (parts per trillion) and 16,500 ppt, respectively (Thompson *et al.* 1990). However, according to Thompson *et al.* (1990), the catalyst regeneration process used by some petroleum refineries is a closed manufacturing system that does not involve the release of process fluids to the environment. Using PCA to compare PCDD/F data provided in Thompson *et al.* (1990) with sampling results for storm water collected adjacent to petroleum refineries as part of this study indicates no apparent similarities between catalyst regeneration fluids and storm water discharged to San Francisco Bay.

Not surprisingly, PCA comparisons between PCDD/F distributions in storm water and various nonpoint sources suggest that combustion-type sources are likely sources of PCDD/Fs in storm water discharged to San Francisco Bay. The fingerprint patterns in storm water from several mixed urban/rural and petroleum refinery outfalls were similar to those typically associated with different combustion and incineration processes.

In addition, the distributions of PCDD/Fs in storm water collected as part of this study are similar to those in storm water and combined sewer overflow discharges in other urban environments. PCA reveals several similarities in the PCDD/F congener profiles in data provided by Wenning *et al.* (1992) and Horstmann and McLachlan (1995). The occurrence of higher chlorinated congeners, comparable TEQ levels, and low concentrations of 2,3,7,8-TCDD are also evident in storm water and combined sewer overflow discharges in other urban and heavily industrialized waterways and bays.

It is widely known that PCDD/F are ubiquitous in ambient air (Alcock and Jones 1996; Duarte-Davidson *et al.* 1997). Atmospheric deposition has been identified as the predominant source of PCDD/Fs in post-1940 dated soils and vegetation and in sediments from relatively remote water bodies (Alcock and Jones 1996). Global background concentrations in surface soil are estimated at between 5 and 10 pg/kg (Alcock and Jones 1996). Recent studies in the United States and the United Kingdom indicate that background levels are higher in industrialized countries (US EPA 1996; Duarte-Davidson *et al.* 1997). The more abundant hepta- and octa-chlorinated PCDD/Fs measured in ambient air are bound primarily to aerosols or adsorbed to particulate, which could settle on soil and become entrained in surface water runoff during storm events. Several studies conducted in the United States, Germany, and the United Kingdom indicate that air emissions from municipal solid waste incinerators and coal or fossil fuel combustion are the predominant sources of PCDD/Fs to the environment (Alcock and Jones 1996; US EPA 1996; Duarte-Davidson *et al.* 1997). Releases from the combustion of diesel and leaded fuels have also been reported to be significant sources in coastal urban environments, particularly where automobile and shipping traffic increased with post–World War II economic expansion (Buchert and Ballschmitter 1986).

Summary

In this study, PCDD/Fs were measured in storm water collected from 15 different outfalls in San Francisco Bay located in areas adjacent to petroleum refineries and in areas representative of mixed urban/commercial/residential land uses. Temporal information was collected at two outfalls by sampling hourly over a 12-h period during the first major rainstorm event of the 1995/96 winter season. Storm water sampling was conducted 2 to 3 months apart at other locations to evaluate changes in PCDD/F loadings to the bay at the onset and midway through the winter rainy season. PCA was used as an exploratory statistical technique to examine the similarities and differences in the distributions of PCDD/Fs in storm water from the different outfalls.

The sampling results showed few significant differences between storm water discharged from outfalls located in mixed urban/commercial/residential areas and outfalls located adjacent to petroleum refineries. The concentrations of 2,3,7,8-TCDD were below the analytical limits of detection in all storm water samples, with the exception of samples collected after the sixth hour of sampling at the Oakland outfall. PCDD/F profiles were generally dominated by the hepta- and octa-chlorinated congeners. Total TEQ levels were generally below US EPA ambient water quality criteria and aquatic ecotoxicology guideline values. The results of this study strongly suggest that discrete sampling of storm water outfalls is insufficient to characterize the concentrations and distributions of persistent contaminants in storm water. In addition to the contributions of PCDD/Fs from storm water outfalls located in urban areas, contributions from nonindustrialized areas should not be discounted as significant sources of these chemicals to the aquatic environment.

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References

Akerfjord M-A, Christopherson N (1996) Assessing mixing models within a common framework. Environ Sci Technol 30(7):2105–2112

Alcock RE, Jones KC (1996) Dioxins in the environment: a review of trend data. Environ Sci Technol 30(11):3133–3143

Barber TJ, Chappie DJ, Duda DJ, Fuchsman PC, Finley BL (1998) Using a spiked sediment bioassay to establish a no-effect concentration for dioxin exposure to the amphipod [*Ampelisca abdita*]. Environ Toxicol Chem 17:420–439

Beard A, Nalkwadi KP, Karasek FW (1993) Formation of polychlorinated dibenzofurans by chlorination and *de novo* reactions with $FeCl_3$ in petroleum refining processes. Environ Sci Technol 27:1505–1511

Boening D (1998) Toxicity of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin to several ecological receptor groups. Ecotoxicol Environ Saf 39:155–175

Boyer IJ, Kokoski CJ, Bolger PM (1991) Acceptable concentrations of TCDD in Great Lakes fish consumed by recreational fishermen and the general public. J Toxicol Environ Health 33:93–101

Buchert H, Ballschmitter K (1986) Polychlorodibenzofurans (PCDF) and -dioxins (PCDD) as part of the general pollution in environmental samples of urban areas. Chemosphere 15:1923–1926

Comber SDW, Dobbs AJ, Lewis S (1996) Guideline values for sediments contaminated with dioxins and furans. Ecotoxicol Environ Safety 35:102–108

Duarte-Davidson R, Stewart A, Alcock RE, Cousins IT, Jones KC (1997) Exploring the balance between sources, deposition, and the environmental burden of PCDD/Fs in the U.K. environment: an aid to identifying uncertainties and research needs. Environ Sci Technol 31(1):1–10

Ehrlich R, Wenning RJ, Johnson GW, Su SH, Paustenbach DJ (1994) A mixing model for polychlorinated dibenzo-p-dioxins and dibenzofurans in surface sediments from Newark Bay, New Jersey using polytopic vector analysis. Arch Environ Contam Toxicol 27:486–500

Fattore E, Benfenati E, Mariani G, Fanelli R, Evers EHG (1997) Patterns and sources of polychlorinated dibenzo-p-dioxins and dibenzofurans in sediments from the Venice Lagoon, Italy. Environ Sci Technol 31(6):1777–1784

Grimwood MJ, Dobbs AJ (1996) A review of the aquatic ecotoxicology of polychlorinated dibenzo-p-dioxins and dibenzofurans. Environ Toxicol Water Qual 10:57–75

Horstmann M, Kaune A, McLachlan MS, Reissenger M, Huntziger O (1992) Temporal variability of PCDD/F concentrations in sewage sludge. Chemosphere 25(7–10):1463–1468

Horstmann M, McLachlan MS (1995) Concentrations of polychlorinated-p-dioxins (PCDD) and dibenzofurans (PCDF) in urban runoff and household wastewaters. Chemosphere 31(3):2887–2896

H. Huang, A. Buekens (1995) On the mechanisms of dioxin formation in combustion processes. Chemosphere 31(9):4099–4117

Huntley SL, Iannuzi TJ, Avantaggio JD, Carlson-Lynch H, Schmidt CW, Finley BL (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

Jarman WM, Johnson GW, Bacon CE, Davis JA, Risebrough RW, Ramer R (1999) Levels and patterns of polychlorinated biphenyls in water collected from the San Francisco Bay and estuary, 1993–95. J Anal Chem (in press)

Long ER, Markel R (1992) An evaluation of the extent and magnitude of biological effects associated with chemical contaminants in San Francisco Bay, California. NOAA Technical Memorandum NOS ORCA 64; National Oceanic and Atmospheric Administration, Seattle, WA

Long ER, Robertson A, Wolfe DA, Hameedi J, Sloane GM (1996) Estimates of the spatial extent of sediment toxicity in major U.S. estuaries. Environ Sci Technol 30(12):3585–3592

Petreas MX, Wiesmuller T, Palmer FH, Winkler JJ, Stevens RD (1992) Aquatic life as biomonitors of dioxin/furan and coplanar polychlorinated biphenyl contamination in the Sacramento–San Joaquin River Delta. Chemosphere 25(4):621–631

Petreas MX, Hayward D (1994) Aquatic life as biomonitors of dioxin/furan and coplanar polychlorinated biphenyl contamination in the San Joaquin River in the vicinity of Stockton. Report Prepared for the State Water Resources Control Board, California

Shear NM, Schmidt CW, Huntley SL, Crawford DW, Finley BL (1996) Evaluation of the factors relating combined sewer overflows with sediment contamination of the Lower Passaic River. Mar Pollut Bull 32(1):288–304

Shine JP, Ika RV, Ford TE (1995) Multivariate statistical examination of spatial and temporal patterns of heavy metal contamination in New Bedford Harbor marine sediments. Environ Sci Technol 29(7):1781–1788

Thompson TS, Clement RE, Thornton N, Luyt J (1990) Formation and emission of PCDD/PCDFs in the petroleum refining industry. Chemosphere 20(10–12):1525–1532

US EPA (1984) Ambient water quality criteria for 2,3,7,8-tetrachlorodibenzo-p-dioxin. Office of Water, Regulations, and Standards, Washington, DC

US EPA (1988) Statement of work for dioxin analyses. Multimedia, multiconcentrations, revision 8/88. Washington, DC

US EPA (1994) Estimating exposure to dioxin-like compounds, volume 2: properties, sources, occurrence, and background exposures. Office of Research and Development, Washington, DC

US EPA (1996) Formation mechanisms and sources of dioxin. Office of Research and Development, Washington, DC

Van den Berg M, Birnbaum L, Bosveld ATC, Brunstrom B, Cook P, Freely M, Giesey J-P, Hanberg A, Hasegawa R, Kennedy SW, Kubiak T, Larsen JC, van Leeuwen FXR, Liem AKD, Nolt C, Peterson RE, Poellinger L, Safe S, Schrenk D, Tillitt D, Tysklind M, Younes M, Waern F, Zacharewski T (1998) Toxic equivalency factors (TEFs) for PCBs, PCDDs, PCDFs for humans and wildlife. Environ Health Perspect 106:775–792

Wenning RJ, Harris MA, Ungs ML, Paustenbach DJ, Bedbury H (1992) Chemometric comparisons of polychlorinated dibenzo-p-dioxins and dibenzofurans in surficial sediments from Newark Bay, New Jersey and other industrialized waterways. Arch Environ Contam Toxicol 22:397–413

Wenning RJ, Erickson GA (1994) Interpretation and analysis of complex environmental data using chemometric methods. Trends Anal Chem 13(10):446–457

Wold S, Esbensen K, Gelati P (1987) Principal components analysis. Chemo Int Lab Systems 2:37–47