DIOXINS AND FURANS URBAN RUNOFF

By Thomas S. Fisher,[1] Douglas G. Hayward,[2] Robert D. Stephens,[3] and Michael K. Stenstrom,[4] Fellow, ASCE

ABSTRACT: Urban runoff samples were collected in a 1-year period in the Santa Monica Bay watershed during both dry and storm periods and analyzed for polychlorinated dioxins, polychlorinated furans, and polychlorinated naphthalenes. Trace concentrations were found in nearly all of the samples collected. During storms polychlorinated dioxin and polychlorinated furan concentrations peaked. The congener and isomer profiles resemble profiles found in lake sediments and rainwater more than they resemble profiles found in urban sources such as dioxins from incinerators or dioxins in contaminated commercial products. Runoff from open land use had lower concentrations than runoff from developed land uses.

INTRODUCTION

Urban runoff pollution is receiving increasing attention and in response the U.S. Environmental Protection Agency is requiring national pollutant discharge elimination system permits. The permits often consider land use (e.g., residential, light commercial, etc.) as an indicator of pollution potential. Research has evolved over the past two decades, with investigators initially studying bulk parameters such as oil and grease (Sartor et al. 1974; Whipple and Hunter 1979; Asplund et al. 1982). More recent work has addressed specific compounds such as some of the more toxic polynuclear aromatics (Eganhouse et al. 1981; Hoffman et al. 1984; Pitt et al. 1995) and toxicity (Bay et al. 1996).

Polychlorinated dibenzodioxins and dibenzofurans (dioxins and furans) are two classes of compounds that contain some of the most toxic chemical substances known. Some of these compounds also are regarded as potential human carcinogens. In addition, these compounds may accumulate in the food chain. For these reasons, their presence in the environment is of concern. As analytical methods and instrumentation improve, we are able to detect these compounds at lower concentrations. With these improved detection limits, we find today that these compounds appear to be ubiquitous in the environment (Crummett and Stehl 1973; Rappe et al. 1981; Czuczwa and Hites 1985; Schecter et al. 1988; Ligon et al. 1989). Although background environmental concentrations commonly are thought to be harmless, the true risk of these contaminants is unknown.

Dioxins and furans form during combustion processes where organic carbon, chlorine, and metals are present (Olie et al. 1977; Buser et al. 1978; Stieglitz et al. 1989). Occasionally, they have been formed as unwanted byproducts in organic reactions involved in the synthesis of chlorinated aromatic compounds (polychlorobiphenyls, pentachlorophenol; Rappe et al. 1978), chlorine production, and pulp bleaching (Swansen 1988; Amendola et al. 1989). Used motor oil may contain some of these compounds (Marklund et al. 1990). Through atmospheric deposition of combustion aerosols and crankcase oil drippings, it is reasonable to expect urban runoff to contain dioxins and furans. Illegal dumping of waste into storm drains is another potential source.

The goals of this study are twofold. The first is to determine the concentrations of dioxins and furans in storm water runoff entering Santa Monica Bay. By comparing congener series concentration profiles it may be possible to suggest sources. These concentration data also may eventually aid in determining the potential health risks through contact recreation and ingestion of seafood. These results can form the beginnings of a database on dioxins and furans in urban runoff, which have been measured rarely. The second goal is to attempt to find correlations between the concentrations of polychlorinated naphthalenes (PCNs) and the concentrations of dioxins and furans. The PCNs have the structure and activity relationships like those of dioxins and furans and polychlorobiphenyls and may have human toxicity. We have observed that PCNs generally are present with dioxins and furans in environmental matrices and combustion residues. If this is true, it may be possible to correlate the presence or absence of dioxins and furans to PCNs, which are easier to detect and identify.

EXPERIMENTAL METHODS

Sample Collection

Eighteen storm water samples were collected from eight storm drains and runoff streams in the Santa Monica Bay drainage area over a 1-year period. Several cities and areas are included in this area, such as Los Angeles, Santa Monica, Venice, and Culver City. The samples were not filtered because we wanted to find total loading of dioxins and furans in the runoff samples. These drains typically flow year round, even though there is no rainfall during the summer. Table 1 shows the names of the sampling stations and information about the stations at the time of sampling. Fig. 1 is a map showing their locations. Table 2 gives the land-use types for the drainage areas. Land use data were extracted from the Southern California Association of Government's database (Wong et al. 1997).

Samples were collected from storm drain culverts with the aid of an 8-L polypropylene bucket. The bucket was solvent washed between sample collections and flushed with sample to further reduce any effects of sample carryover. When the samples were collected from a bridge to attain access to turbulent-flow areas, the bucket was lowered using a synthetic rope. The first bucketfull was discarded. The second and subsequent bucketfulls were poured into prewashed, 1-gal., narrow-neck, amber, glass bottles fitted with Teflon-lined screw caps. They were cooled with frozen ''Blue Ice'' packs in large plastic coolers, shipped overnight to the appropriate laboratory, and then stored at 4°C until they were extracted.

---

[1] Civ. and Envir. Engrg. Dept., Univ. of California, Los Angeles, 4173 Engineering I, Los Angeles, CA 90095-1593.

[2] USFDA, 200 C St. S.W., Washington, DC 20204; formerly, Haz. Mat. Lab., California Dept. of Toxic Substances Control, Room 515, 2151 Berkeley Way, Berkeley, CA 94704.

[3] Deputy Dir., Sci., Pollution Prevention and Technol. Program, California Dept. of Toxic Substances Control, Room 515, 2151 Berkeley Way, Berkeley, CA.

[4] Civ. and Envir. Engrg. Dept., Univ. of California, Los Angeles, 4173 Engineering I, Los Angeles, CA.

Note. Associate Editor: M. T. Suidan. Discussion open until July 1, 1999. To extend the closing date one month, a written request must be filed with the ASCE Manager of Journals. The manuscript for this paper was submitted for review and possible publication on October 1, 1997. This paper is part of the ***Journal of Environmental Engineering***, Vol. 125, No. 2, February, 1999. ©ASCE, ISSN 0733-9372/99/0002-0185–0191/$8.00 + $.50 per page. Paper No. 16714.

TABLE 1. Sampling Station Names, Schedule, and Weather Conditions

Date and condition (1)	Sampling Station Name and Number Pico-Kenter **1** (2)	7th St./Chataqua **2** (3)	Centeinela Creek **3** (4)	Ballona Creek **4** (5)	Temiscal Creek **5** (6)	Ashland Ave. **6** (7)	Market St. **7** (8)	Brooks Ave. **8** (9)
11/29/1988 (Wet)	X	X	—	—	—	—	—	—
5/23–5/26/89 (Dry)	5/26	5/25	5/26	5/26	5/23	5/26	5/26	5/26
(Dry)	X	X	X	X	—	—	—	—
9/17/89 (Wet)	X	X	X	X	—	—	—	—

Note: Boldface numbers refer to locations shown in Fig. 1; X denotes that sampling was performed; — indicates that no sampling occurred.

TABLE 2. Land Use Distribution for Various Sampling Stations as Percentages

Land-use category (1)	Station Pico-Kenter **1** (2)	7th St./Chataqua **2** (3)	Centeinela Creek **3** (4)	Ballona Creek **4** (5)	Temiscal Creek **5** (6)	Ashland Ave. **6** (7)	Market St. **7** (8)	Brooks Ave. **8** (9)
Single family	27	32	44	44	0	43	17	17
Multifamily	25	0	19	19	0	12	10	10
Commercial	16	1	11	11	0	4	4	4
Public	11	0	4	4	0	3	3	3
Light industrial	13	0	4	4	0	2	1	2
Other	2	0	2	2	0	1	6	6
Open	8	67	16	16	100	36	58	57
Unknown	0	0	0	0	0	0	0	0
Total area (hectars)	161	358	25,952	25,952	194	1,123	1,791	1,796

Note: Boldface numbers refer to locations shown in Fig. 1.

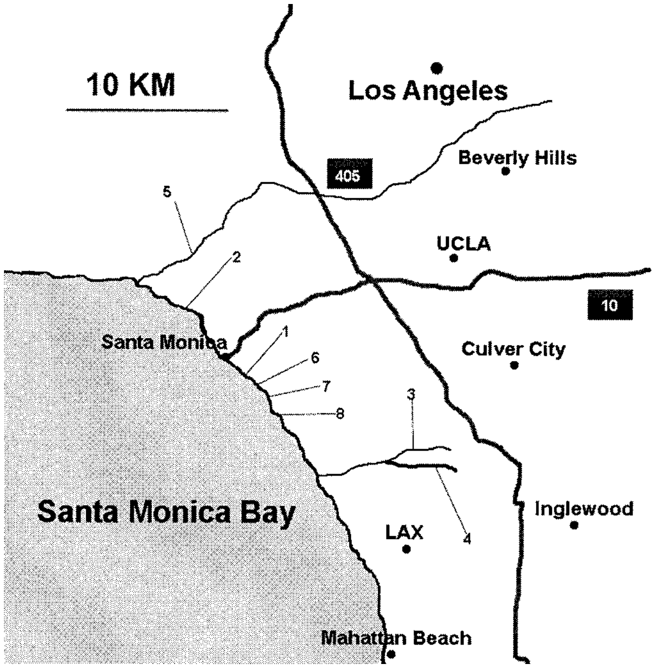

FIG. 1. Greater Los Angeles Area Showing Various Sampling Locations Used in This Study (Numbers of Locations Are Given in Table 1)

Analytical Methods

Fisher (1998) describes the sample preparation and analytical methods in greater detail. Two-liter samples were spiked with ^{13}C labeled standards in dichloromethane. In some cases it was necessary to purify the samples by passing them through silica gel, alumina, or carbon columns (Marklund et al. 1986). Gas chromatography/mass spectrometer (GC/MS) analyses were performed with a modified Finnigan MAT GC/MS (model number 4510B) with an INCOS data system fitted with a J & W Scientific (Rancho Cordova, Calif.) fused silica capillary column (60 m $\times$ 0.25 mm inside diameter) coated with a 0.25-μm layer of DB-5. The temperature program of the column oven used for GC/MS was 100°C injection, 100–260°C at 20°C/min, and 260–300°C at 1°C/min. The injector was at 250°C and the transfer line was 260°C. The mass spectrometer was operated in methane-enhanced electron-capture chemical ionization mode.

Confirmation of detected dioxins, furans, and PCNs was performed on a Finnigan MAT 90 high-resolution GC/MS, with a Finnigan MAT data system (PDP 11/73 running the Finnigan MAT Icis software package), in electron impact ionization mode at approximately 8,000 resolutions. The GC/MS was fitted with a DB-5 column virtually identical to the one used in the quadrupole GC/MS. The temperature programming also was the same.

For every dioxin and furan, detected or not, the background noise was evaluated for the given MID channel near the compound's retention time. The detection limit reported was four times the signal-to-noise ratio (as determined by the supplied software).

RESULTS AND DISCUSSION

Eighteen samples were analyzed in this study. The large amount of time necessary for each analysis limited the number of samples. Two samples collected in November 1988 during a storm were used to determine if we could obtain useful results from 2-L water samples. These first two samples were collected from sites with land uses associated with the greatest potential contamination of pollutants typically measured in urban runoff (e.g., oil and grease). Greater contamination is expected from sites with the greatest commercial and industrial development and the greatest motor vehicle activity (Stenstrom et al. 1984; Fam et al. 1987). The positive results from these two samples led us to try a larger number of sites during a dry month (May 1989) which were suspected to be at lower concentration. The Temescal Canyon sample was collected from a small stream in an uninhabited hilly area approximately 2 miles from the ocean. We believed this would be one of the cleanest background natural water samples we could find in the area. This proved to be true because no dioxins, furans, or PCNs were found in this sample. By comparison, OCDD was found in all the other samples in this study. Samples obtained during this month from three other locations were so low that it was decided to drop them from further consideration. In June 1989 the four most-contaminated sites in the first survey were sampled a second time during dry weather. These four locations were sampled again on September 17, 1989 during storm conditions.

Southern California had a severe drought during the 4 years before sampling for this study. We believe that dioxin and furan concentrations may be higher in our samples that might be found during normal rainfall years. We have noted buildup and washout trends with other pollutants such as oil and grease. Also, during droughts the winds tend to blow more toward the ocean and west side of the basin, which may result in higher concentrations of dioxins and furans in the coastal air mass (Hunt and Maisel 1992) and higher deposition on land.

The results from all of the samples are presented in Tables 3 and 4. These data were split into two tables representing those samples collected during a dry season (Table 3) and those samples collected during a storm (Table 4). Dioxin, furan, and chloronaphthalene congeners were detected in most samples. In the four winter storm samples that contained the highest dioxin and furan levels, PNCs were strongly suspected but could not be confirmed because of chemical interferences. These four samples contained milligram quantities of organic material, resembling waxes. Carbon chromatography (Fisher 1998) was required to remove the waxes. The resulting purified extract had a significantly lower recovery of tetra- and pentachlorinated dioxins, furans, and possibly tetra- and penta-naphthalene congeners and an elevated PCN background in the blanks. Additional purification significantly improved the recovery of tetradioxins and furans on all but one of the affected samples, but did not lower the elevated PCN background. Therefore, the interpretation of polychloronaphthalene levels in these samples is ambiguous. Two storm samples and four dry-season samples contained tetra- and/or pentachloronaphthalenes at levels comparable with that of the total dioxin and furan congeners. The highest levels of PCNs also were detected in one storm sample. However, information on PCN concentrations in the most polluted samples was lost.

Most samples contained OCDD, 1,2,3,4,6,7,8 and 1,2,3,4,6,7,9 HpCDD, whereas only some storm samples contained significant amounts of other congeners. Many samples also contained approximately equal amounts of 1,2,3,4,6,7,8 and 1,2,3,4,6,8,9 HpCDF, while containing very little or no 1,2,3,4,6,7,9 and 1,2,3,4,7,8,9 HpCDF. Detection of mainly OCDD and HpCDD was not method related because recoveries of the 10 labeled standards were similar, and OCDD and HpCDD have the lowest sensitivity in negative chemical ionization mode. Four dry-season samples contained only OCDD

TABLE 3. Dry-Weather Sample Results

	STATION NUMBERS FOR 5/88 SAMPLE																STATION NUMBERS FOR 6/89 SAMPLE							
	1		2		3		4		5		6		7		8		1		2		3		4	
Compound (1)	pg/L (2)	DL (3)	pg/L (4)	DL (5)	pg/L (6)	DL (7)	pg/L (8)	DL (9)	pg/L (10)	DL (11)	pg/L (12)	DL (13)	pg/L (14)	DL (15)	pg/L (16)	DL (17)	pg/L (18)	DL (19)	pg/L (20)	DL (21)	pg/L (22)	DL (23)	pg/L (24)	DL (25)
D12378	—	1.3	—	1	—	2	—	2	—	2	—	2	—	8	—	1	—	1.6	—	0.9	—	—	—	0.8
D123478	—	0.5	—	1	—	2	—	1	—	2	—	2	—	2	—	2	—	1.4	—	0.6	—	0.6	—	0.7
D123678	—	0.6	—	2	—	2	—	2	—	2	—	2	—	2	—	2	—	1.6	—	0.7	—	0.7	—	0.8
D123789	—	1.4	—	4	—	5	—	4	—	5	—	4	—	5	—	4	—	3.7	—	1.7	—	1.7	—	1.9
D1234678	12	2.9	—	3	11	3	—	4	—	8	—	6	—	5	—	3	18	3.7	—	2.2	9.4	1.6	33	2
D12346789	79	20	32	8	69	30	54	11	—	18	59	12	43	18	45	23	280	3.8	57	4.8	26	4.1	140	4
F2378	—	0.7	—	1	—	1	—	1	—	1	—	—	—	1	—	1	—	3	—	2	—	—	—	—
F12378	—	0.2	—	0	—	1	—	0	—	0	—	1	—	0	—	0	—	0.2	—	0.1	—	0.1	—	—
F23478	—	0.2	—	0	—	1	—	1	—	0	—	0	—	0	—	0	—	0.2	—	0.1	0.3	0.1	0.4	0.1
F123478	—	0.4	—	1	—	1	—	1	—	1	—	1	—	1	—	1	—	0.5	—	0.3	0.5	0.3	0.3	0.3
F123678	—	0.5	—	0	—	1	—	0	—	1	—	1	—	2	—	1	—	0.5	—	0.3	—	0.2	—	0.3
F234678	—	0.2	—	1	—	1	—	1	—	1	—	1	—	1	—	1	—	0.6	—	0.3	—	0.3	—	0.3
F123789	—	0.5	—	1	—	2	—	1	—	2	—	2	—	2	—	2	—	1.3	—	0.8	—	0.6	—	0.6
F1234678	1.7	0.6	—	1	3	2	—	1	—	2	4.1	2	—	2	—	1	2.3	1.4	—	0.9	1.6	0.6	4.7	0.7
F1234789	—	0.8	—	2	—	4	—	3	—	4	—	4	—	4	—	3	—	2.9	—	1.7	—	1.3	—	1.4
F12346789	6.1	2.9	—	5	—	7	—	6	—	11	7.1	3	—	11	—	8	—	2.9	—	3.6	—	3.1	—	3
(*a*) Congener Series Totals																								
Penta-D	—		—		—		—		—		—		—		—		—		—		—		—	
Hexa-D	—		—		—		—		—		—		—		—		—		—		—		—	
Hepta-D	22		—		25		—		—		13		—		—		31		11		19		57	
Octa-D	79		32		69		54		—		59		43		45		280		57		26		140	
Tetra-F	—		—		—		—		—		—		—		—		—		2		—		2.2	
Penta-F	1.4		—		—		—		—		14		—		—		—		—		8.5		14	
Hexa-F	1.7		—		—		—		—		8.7		—		—		—		—		3.7		6.9	
Hepta-F	4.6		—		5.2		—		—		7		—		—		8.8		—		1.6		7.3	
Octa-F	6.1		—		—		—		—		7.1		—		—		—		—		—		—	
(*b*) International Toxic Equivalency Factors																								
	0.8		0.9		1.6+		1.3		1.3		1.2		1.1		1		1.6		0.7		1.3		1.2	
(*c*) Polychlorinated Naphthalenes[a]																								
Tetras	—	10	—	10	—	10	—	10	—	10	—	10	—	10	—	10	44	10	58	10	41	10	51	10
Pentas	—	10	92	10	91	10	41	10	—	10	—	10	—	10	—	10	93	10	220	10	210	10	210	10
Hexas	—	10	—	10	—	10	—	10	—	10	—	10	—	10	—	10	—	10	—	10	6.4	10	1.9	10
Unknown	—	10	8	10	7	10	—	10	—	10	—	10	—	10	—	10	7.6	10	19	10	27	10	23	10

Note: — indicates less than detection limit (DL); F indicates a furan; D indicates a dioxin. Concentrations in pg/L of water collected.

[a] See North Atlantic Treaty Organization, Committee on the Challenges of Modern Society (1988a,b).

TABLE 4. Wet-Weather Sample Results

	STATION NUMBERS for 11/88				STATION NUMBERS FOR 9/89 SAMPLE							
	1		2		1		2		3		4	
Compound (1)	pg/L (2)	DL (3)	pg/L (4)	DL (5)	pg/L (6)	DL (7)	pg/L (8)	DL (9)	pg/L (10)	DL (11)	pg/L (12)	DL (13)
D12378	—	1	—	1	—	10	—	1	—	2	—	0.9
D123478	—	1	—	1	19	2	—	1	2.6	1	1.8	0.8
D123678	8.9	1	—	1	59	2	—	1	8.7	1	7	1.1
D123789	—	2	—	3	100	5	—	2	9.1	3	8	2.4
D1234678	170	2	6.9	3	1,100	2	4	2	180	2	140	3.3
D12346789	1,400	8	87	6	7,700	3	35	2	1,300	3	1,000	5
F2378	—	—	—	1	—	26	—	1	7.3	1	4.5	1
F12378	—	—	—	0	8.6	1	—	0	—	0	—	0.7
F23478	1.8	0	—	0	8.6	1	0	0	—	0	2.9	0.2
F123478	4.1	0	—	0	21	1	—	0	5.9	0	3.4	0.4
F123678	4.5	0	—	0	17	1	—	0	3.9	0	3.4	0.4
F234678	3.1	0	—	0	12	1	—	0	8.9	0	3.6	0.4
F123789	—	1	—	1	—	1	—	0	—	0	—	0.3
F1234678	34	1	—	1	260	1	1	0	43	1	34	1.1
F1234789	—	1	—	2	13	1	—	0	1.9	1	—	1.5
F12346789	88	6	—	5	570	2	2	1	81	1	59	2.8
(*a*) Congener Series Totals												
Penta-D	—		—		—		—		—		—	
Hexa-D	55		—		300		—		110		67	
Hepta-D	360		21		2,200		12		344		330	
Octa-D	1,400		87		7,700		35		1,300		1,000	
Tetra-F	—		1.1		—		—		79		33	
Penta-F	58		—		17		0		57		25	
Hexa-F	93		—		260		—		81		65	
Hepta-F	100		—		600		2		93		76	
Octa-F	88		—		570		2		81		59	
(*b*) International Toxic Equivalency Factors[a]												
	6.5		0.8		53		1		8.9		8.1	
(*c*) Polychlorinated Naphthalenes												
Tetras	230	10	32	10	—	10	—	10	—	10	—	10
Pentas	510	10	100	10	—	10	—	10	—	10	—	10
Hexas	23	10	—	10	—	10	—	10	—	10	—	10
Unknown	61	10	8.4	10	—	10	—	10	—	10	—	10

Note: — indicates less than detection limit (DL); F indicates a furan; D indicates a dioxin. Concentrations in pg/L of water collected.

[a] See North Atlantic Treaty Organization, Committee on the Challenges of Modern Society (1988a,b).

among the dioxins and furans. It is noteworthy that chloronaphthalenes were detected in two of the samples containing detectable levels of only OCDD among all of the dioxins and furans. The congeners, hexa through octafuran isomers, and hepta- and octadioxin isomers, and the ratios of their concentrations were quite similar to those reported by Czuczwa and Hites (1984) for sediments from Lake Huron.

Fig. 2 shows congener series concentration profiles for two typical samples, which had the most complete data. They are very similar to congener series profiles found by Hites and coworkers (Czuczwa et al. 1984, 1985; Czuczwa and Hites 1986a; Hites 1990) in sediment samples collected from lakes at various locations in this country and in Switzerland. These congener profiles also are typical of those found in rainwater collected in Bloomington, Ind. (Hites 1990). We found similar profiles for both storm and dry conditions.

Fig. 3 shows some of the high-resolution electron impact mass chromatograms of isomer profiles for Centinela Creek contrasted with a typical fly ash profile. Most of the reconstructed ion chromatogram peaks observed in fly ash also are observed in the sample. Our profiles are very similar to profiles of air particulates, fly ash, and car exhaust (Rappe et al. 1989). The 1,3,4,6,7,9 and 1,2,3,4,7,9 hexafurans are missing and the 1,2,3,4,7,8, 1,2,3,6,7,8, and 2,3,4,6,7,8 congeners are attenuated greatly, whereas the 1,2,4,6,8,9 congener is much higher than in the fly ash. Among the hexadioxin isomers the 1,2,3,4,6,8, 1,2,3,4,6,9, and 1,2,3,4,6,7 congeners are missing. If these isomers had been present at the same relative amounts as in the fly ash, they should have been above our detection limits. They either were never in the sources or had been degraded.

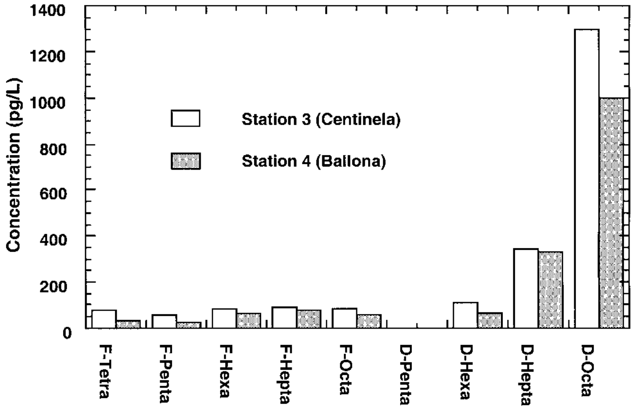

FIG. 2. Congener Series Profiles of Wet-Weather Samples from Ballona and Centennial Creeks; These Profiles Show Sums of All of Isomers in Various Congener Series for Dioxins and Furans (e.g., F7 Refers to Sum of Concentrations of All Furans with Seven Chlorines)

Fig. 4 shows the relationship between the total concentration of dioxin and furan cogeners for each sample location plotted versus open land use. The negative correlation suggests a relationship between development and its associated activities,

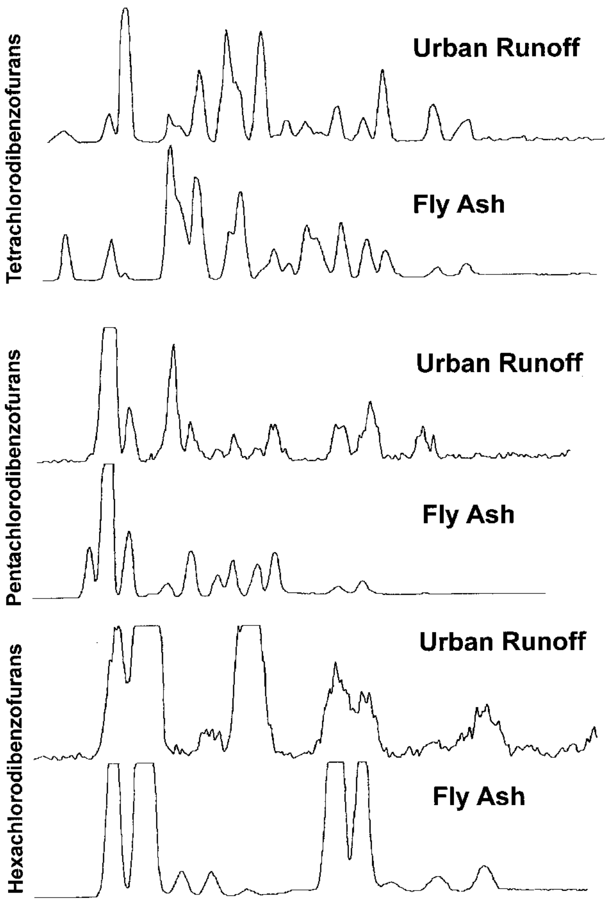

FIG. 3. High-Resolution GC/MS Mass Chromatograms of One of Our Samples Compared with Fly Ash Extract from West German Incinerator; Fly Ash Is Used Because It Contains Virtually All of the Isomers of Dioxins and Furans

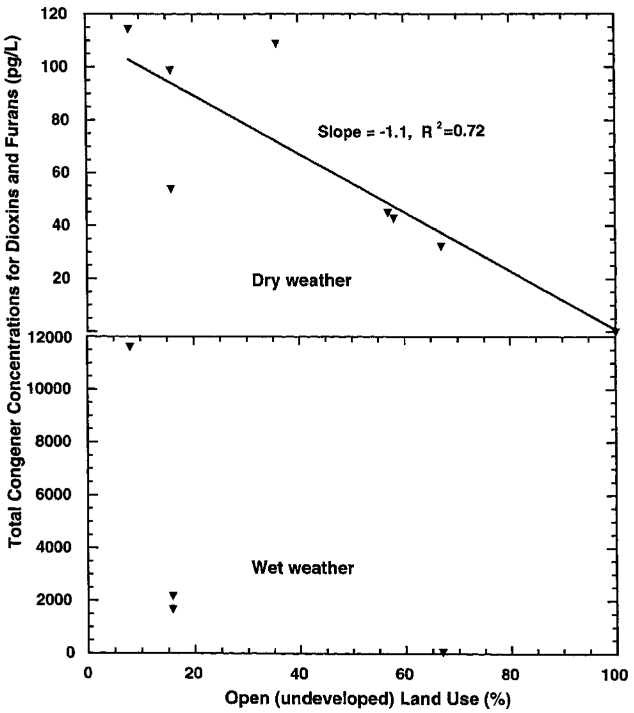

FIG. 4. Total Dioxin and Furan Congener Concentrations for Wet- and Dry-Weather Samples as Function of Open Land Area.

such as vehicle activity and combustion and dioxin and furan cogener concentrations. The correlation exists for both the dry-weather (Fig. 4, top) and the wet-weather (Fig. 4, bottom) conditions. Conventional pollutants show similar trends (Wong et al. 1997).

Known airborne sources of dioxins and furans, such as incinerators, show markedly different congener series profiles than those we observed. They have higher concentrations (relative to octadioxin) of all the dioxins and furans with at least four chlorine atoms per molecule. Some of the congener series from selected sources had concentrations as high as, or even higher than, octadioxin itself (Czuczwa and Hites 1986b). The particulate portions of ambient samples collected in and near large cities also typically show congener concentration profiles more similar to those of incinerators than those from lake bed sediments and our urban runoff samples (Broman et al. 1989; Hites 1990; Hunt and Maisel 1992). The general conclusion we draw from our data is the same as that of several previous authors. We are observing weathered patterns of congener series profiles (Hites 1990). Our observations are in contrast to unweathered or source congener series profiles such as those in extracts from typical sources such as incinerators.

The focus of our study was the dioxin and furan levels in runoff water, which raises another possibility. We observed high concentrations of dioxins and furans well into storms, after rain scrubbing of the air should have been complete, which suggest that air scrubbing is not the most important source. Urban activities that involve the handling of chemicals contaminated with dioxins and furans, and are not emitted into air, could have contributed to the dioxin and furan load in our samples. For example, heavy use of pentachlorophenol for wood preservation may have been responsible for the amounts of certain hepta- and octachlorodioxin and hepta- and octachlorofuran isomers in our runoff samples. These sources could have contributed significantly to our observed levels and congener profiles and may explain differences between our isomer profile and that of fly ash. This possibility is difficult to evaluate without a more comprehensive inventory of urban sources.

If we assume that the sources for our samples were deposited on the ground from typical urban air contamination or if the ground sources have similar congener and isomer profiles to airborne sources, then the weathering process becomes important. How do the congener series shift greatly toward octadioxins and heptafurans, and why or how are certain isomers within a congener series destroyed? Dioxins and furans bound to particle surfaces are emitted from sources and rapidly come to equilibrium on entry into the atmosphere. Gas phase dioxins and furans then are available to destructive processes such as photolysis (Podoll et al. 1986; Fiedler et al. 1990; Atkinson 1991) and hydroxide radical attack (Atkinson 1991). Particle-bound dioxins and furans generally are not considered open to such destructive pathways because they can be shielded from sunlight or protected from the gas phase. In addition, contaminants we measured, whether originating from airborne deposition or ground sources, could have been adsorbed to particles for long periods of time (up to 6 months) before being washed into the runoff. This opens the possibility that destructive pathways other than photolysis and hydroxide radical attack could be important. These paths may explain the congener and isomer profiles we observed as well. Microbial degradation or biogenesis of these compounds is possible (Bumpus et al. 1985; Oberg and Rappe 1992).

CONCLUSIONS

The following conclusions are made:

1. Dioxins, furans, and PCNs can be detected in urban runoff from the Santa Monica Bay watershed.
2. Dioxins, furans, and PCNs were detected well into

storms, which suggests that falling rain is not the only source. Wash-off from land sources must be occurring. Air sampling during storms should be performed to confirm this conclusion.

3. The concentrations of dioxins, furans, and PCNs observed were much higher during storms as compared with dry-weather flow. Combined with the higher flow rates resulting from storms, this implies there is much higher mass loading of these pollutants into the bay during storms.
4. There were qualitative differences between both congener and isomer profiles found in our samples and those found in urban air or in typical incineration ash.
5. Not enough reliable data were collected to allow a statistical correlation, or lack thereof, between PCN concentrations and dioxin and furan concentrations to be obtained. However, the data suggest a possible relationship between dioxin and furan concentration.
6. We believe these results reflect isomer and/or isomer-specific degradation processes occurring during transport and the time these pollutants spent on the ground before entering urban runoff.
7. Total dioxin, furan, and PCN concentrations were correlated positively with commercial and urbanized land use. This further supports storm water control strategies that are based on land use.

ACKNOWLEDGMENTS

The writers thank Robert Cheng for help in collecting samples and Lynn Goldman for many lively discussions and suggestions during the writing of this paper. The writers thank the California Department of Health Services, the California Public Health Foundation, and the University of California at Los Angeles for financial support. The first writer was employed by the California Department of Health Services when this study was conducted.

APPENDIX. REFERENCES

Amendola, G., et al. (1989). ''The occurrence and fate of PCDDs and PCDFs in five bleached kraft pulp and paper mills.'' *Chemosphere*, 18(1-6), 1181–1188.

Asplund, K., Mar, B. W., and Ferguson, J. F. (1982). ''Total suspended solids in highway runoff in Washington State.'' *J. Envir. Engrg. Div.*, ASCE, 108, 391–404.

Atkinson, R. (1991). ''Atmospheric lifetimes of dibenzo-*p*-dioxins and dibenzofurans.'' *Sci. Total Envir.*, Amsterdam, 104(1), 17–33.

Bay, S. M., Greenstein, D. J., Lau, D. J., Stenstrom, S.-L., and Kelley, M. K. (1996). ''Toxicity of dry weather flow from the Santa Monica Bay watershed.'' *Bull. of Southern California Acad. Sci.*, 95, 33–45.

Broman, D., Naf, C., Zebuhr, Y., and Lexen, K. (1989). ''The composition, distribution and flux of PCDDs and PCDFs in settling particulate matter (SPM)–a sediment trap study in the northern Baltic.'' *Chemosphere*, 19(1-6), 445–450.

Bumpus, J. A., Tien, M., Wright, D., and Aust, S. D. (1985). ''Oxidation of persistent environmental pollutants by a white rot fungus.'' *Science*, 228, 1434–1436.

Buser, H. R., Bosshardt, H.-P, Rappe, C., and Lindahl, R. (1978). ''Identification of polychlorinated dibenzofuran isomers in fly ash and PCB pyrolyses.'' *Chemosphere*, 7(5), 419–429.

Crummett, W. B., and Stehl, R. H. (1973). ''Determination of chlorinated dibenzo-*p*-dioxins and dibenzofurans in various materials.'' *Envir. Health Perspective*, 5, 15–25.

Czuczwa, J. M., and Hites, R. A. (1984). ''Environmental fate of combustion-generated polychlorinated dioxins and furans.'' *Envir. Sci. and Technol.*, 18(6), 444–450.

Czuczwa, J. M., and Hites, R. A. (1985). ''Historical record of polychlorinated dioxins and furans in Lake Huron sediments.'' *Chlorinated dioxins and dibenzofurans in the total environment II*, L. H. Keith, C. Rappe, and G. Choudhary, eds., Butterworth's, Boston, 59–63.

Czuczwa, J. M., and Hites, R. A. (1986a). ''Sources and fate of PCDD and PCDF.'' *Chemosphere*, 15(9-12), 1417–1420.

Czuczwa, J. M., and Hites, R. A. (1986b). ''Airborne dioxins and dibenzofurans: Sources and fates.'' *Envir. Sci. and Technol.*, 20(2), 195–200.

Czuczwa, J. M., NcVeety, B. D., and Hites, R. A. (1984). ''Polychlorinated dibenzo-*p*-dioxins and dibenzofurans in sediments from Siskiwit Lake, Isle Royale.'' *Science*, 226, 568–569.

Czuczwa, J. M., Niessen, F., and Hites, R. A. (1985). ''Historical record of polychlorinated dibenzo-*p*-dioxins and dibenzofurans in Swiss lake sediments.'' *Chemosphere*, 14(9), 1175–1179.

Eganhouse, R. P., Simoneit, B. R. T., and Kaplan, I. R. (1981). ''Extractable organic matter in urban stormwater runoff. 2. Molecular characterization.'' *Envir. Sci. and Technol.*, 15, 315–326.

Fam, S., Stenstrom, M. K., and Silverman, G. (1987). ''Hydrocarbons in urban runoff.'' *J. Envir. Engrg.*, ASCE, 113(5), 1032–1046.

Fiedler, H., Hutzinger, O., and Timms, C. W. (1990). ''Dioxins: Sources of environmental load and human exposure.'' *Toxicological and Envir. Chem.*, 29(3), 157–234.

Fisher, T. S. (1998). ''Dioxins, furans, and polychlorinated furans in urban runoff,'' MS thesis, Department of Civil and Environmental Engineering, University of California, Los Angeles.

Hites, R. A. (1990). ''Environmental behavior of chlorinated dioxins and furans.'' *Acc. Chem. Res.*, 23(6), 194–201.

Hoffman, E. J., Mills, G. L., Latimer, J. S., and Quinn, J. G. (1984). ''Urban runoff as a source of polycyclic aromatic hydrocarbons to coastal waters.'' *Envir. Sci. and Technol.*, 18, 580–587.

Hunt, G. T., and Maisel, B. E. (1992). ''Atmospheric concentrations of PCDDs/PCDFs in Southern California.'' *J. Air Waste Mgmt. Assoc.*, 42(5), 672–680.

Ligon Jr., W. V., Dorn, S. B., and May, R. J. (1989). ''Chlorodibenzofuran and chlorodibenzo-*p*-dioxin levels in Chilean mummies dated to about 2,800 years before the present.'' *Envir. Sci. and Technol.*, 23(10), 1286–1290.

Marklund, S., et al. (1986). ''Determination of PCDDs and PCDFs in incineration samples and pyrolytic products.'' *Chlorinated dioxins and dibenzofurans in perspective*, C. Rappe, G. Choudhary, and L. H. Keith, eds., Lewis, Chelsea, Mich., 79–82.

Marklund, S., et al. (1990). ''Emissions of PCDDs and PCDFs in gasoline and diesel fueled cars.'' *Chemosphere*, 20(5), 553–561.

North Atlantic Treaty Organization, Committee on the Challenges of Modern Society (NATO/CCMS). (1988a). ''Pilot study on international information exchange on dioxins and related compounds.'' *International Toxicity Equivalency Factor (I-TEF) Method of Risk Assessment for Complex Mixtures of Dioxins and Related Compounds, Rep. No 176*, NATO, Brussels.

North Atlantic Treaty Organization, Committee on the Challenges of Modern Society (NATO/CCMS). (1988b). ''Pilot study on international information exchange on dioxins and related compounds.'' *Scientific basis for the Development of International Toxicity Equivalency Factor (I-TEF) Method of Risk Assessment for Complex Mixtures of Dioxins and Related Compounds, Rep. No. 178*, NATO, Brussels.

Oberg, L. G., and Rappe, C. (1992). ''Biochemical formation of PCDD/Fs from chlorophenols.'' *Chemosphere*, 25(1-2), 49–52.

Olie, K., Vermeulen, P. L., and Hutzinger, O. (1977). ''Chlorodibenzo-*p*-dioxins and chlorodibenzofurans are trace components of fly ash and flue gas of some municipal incinerators in the Netherlands.'' *Chemosphere*, 6(8), 455–459.

Pitt, R., Field, R., Lalor, M., and Brown, M. (1995). ''Urban stormwater toxic pollutants: assessment, sources and treatability.'' *Water Envir. Res.*, 67(3), 260–274.

Podoll, R. T., Jaber, H. M., and Mill, T. (1986). ''Tetrachlorodibenzodioxin: Rates of volatilization and photolysis in the environment.'' *Envir. Sci. and Technol.*, 20(5), 490–492.

Rappe, C., Buser, H. R., Stalling, D. L., Smith, L. M., and Dougherty, R. C. (1981). ''Identification of polychlorinated dibenzofurans in environmental samples.'' *Nature*, 292, 524–526.

Rappe, C., Gara, A., and Buser, H. R. (1978). ''Identification of polychlorinated dibenzofurans (PCDFs) in commercial chlorophenol formulations.'' *Chemosphere*, 7(12), 981–991.

Rappe, C., Marklund, S., Kjeller, L.-O., and Lindskog, A. (1989). ''Long-range transport of PCDDs and PCDFs on airborne particles.'' *Chemosphere*, 18(1-6), 1283–1290.

Sartor, J. D., Boyd, G. B., and Agardy, F. J. (1974). ''Water pollution aspects of street surface contaminants.'' *J. Water Pollution Control Fed.*, 46, 458–467.

Schecter, A., Dekin, A., Weerasinghe, N. C. A., Arghestani, S., and Gross, M. L. (1988). ''Sources of dioxins in the environment: A study of PCDDs and PCDFs in ancient, frozen Eskimo tissue.'' *Chemosphere*, 17(4), 627–631.

Stenstrom, M. K., Silverman, G. S., and Bursztynsky, T. A. (1984). ''Oil and grease in urban stormwaters.'' *J. Envir. Engrg.*, ASCE, 110(1), 58–72.

Stieglitz, L., Zwick, G., Beck, J., Roth, W., and Vogg, H. (1989). ''On the de-nova synthesis of PCDD/PCDF on fly ash of municipal waste incinerators.'' *Chemosphere*, 18(1-6), 1219–1226.

Swansen, S. E. (1988). ''Dioxins in the beach plant: a study of the occurrence and formation of polychlorinated dibenzofurans and polychlorinated dibenzo-p-dioxins in the chlorine bleaching of wood pulp,'' PhD dissertation, Institute of Environmental Chemistry, University of Umea, Umea, Sweden.

Whipple, J. A., and Hunter, J. V. (1979). ''Petroleum hydrocarbons in urban runoff.'' *Water Resour. Bull*., 15, 1096–1105.

Wong, K., Strecker, E. W., and Stenstrom, M. K. (1997). ''A Geographic Information System to estimate stormwater pollutant mass loadings.'' *J. Envir. Engrg*., ASCE, 123(8), 737–745.