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Polychlorinated Di-benzo-dioxins and Di-benzo-furans in Los Angeles Urban Runoff

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in Civil Engineering

by

Thomas Sheldon Fisher

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The thesis of Thomas Sheldon Fisher is approved.

Irwin M. Suffet

Thomas C. Harmon

Michael K. Stenstrom, Committee Chair

University of California, Los Angeles

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ABSTRACT OF THE THESIS

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by

Thomas Sheldon Fisher
Master of Science in Civil Engineering
University of California, Los Angeles
Professor Michael K. Stenstrom, Chair

Urban runoff, water that enters storm drainage systems, may contaminate surface water in areas since it is usually not treated. Los Angeles is such an area where much of the urban runoff is discharged into the coastal waters untreated. Urban runoff samples were collected during a one year period in the Santa Monica Bay watershed. They were collected during both dry and storm periods and analyzed for polychlorinated dioxins, polychlorinated furans, and polychlorinated naphthalenes. Polychlorinated dioxins, polychlorinated furans, and polychlorinated naphthalenes were found in nearly all of the samples collected. During storms polychlorinated dioxin and polychlorinated furan concentrations peaked. The congener and isomer profiles resemble environmental sinks more than typical urban sources.

I. Introduction

Urban runoff pollution is receiving increasing attention and the EPA is requiring national pollutant discharge elimination system (NPDES) permits for urban runoff. Research has evolved over the past decade, with investigators initially studying bulk parameters such as oil and grease (Sartor et al. 1974; Whipple et al. 1979; Asplund et al. 1982). More recent work has addressed specific compounds such as some of the more dangerous polynuclear aromatics (Eganhouse et al.1981; Hoffman et al.1984).

Polychlorinated di-benzo-dioxins and di-benzo-furans (dioxins and furans) are two classes of compounds that contain some of the most toxic chemical substances known. Some of these compounds are also regarded as potential human carcinogens, although this has yet to be proven. As such, their presence in the environment is of concern. As analytical methods and instrumentation continually improve, we are able to detect these compounds at lower and lower concentrations. With these improved detection limits, we find today that these compounds appear to be ubiquitous in the environment both in space and time (Crummett and Stehl 1973; Czuczwa and Hites 1985; Rappe et al. 1981; Ligon et al.1989; Schecter et al.1988). Though background environmental concentrations are commonly 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 (Buser et al.1978; Olie et al.1977; Stieglitz et al.1989). They also form as byproducts in organic reactions involved in the synthesis of chlorinated aromatic compounds (polychlorobiphenyls (PCBs), pentachlorophenol (PCP), etc.) (Rappe et al.1978), chlorine production, and pulp bleaching (Swansen 1988; Amendola et al.1989). Used motor oil contains 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 wastes 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 analyzing congener series concentration profiles it may be possible to determine sources. These concentration data may also aid health scientists in determining the potential health risks through contact recreation and ingestion of seafood. These results will form the beginnings of a database on dioxins and furans in urban runoff, which have rarely been measured. The second goal is to attempt to find correlations between the concentrations of polychlorinated naphthalenes (PCNs) and the concentrations of dioxins and furans. PCNs have the structure and activity relationships like those of dioxins and furans and PCBs, and may have human toxicity. We have observed that PCNs are generally 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.

II. Experimental Section

1. Materials

Acetone, hexane, methanol, methylene chloride, and toluene were high purity HPLC grade and pesticide residue grade solvents from Burdick and Jackson. 95% n-hexane was from EM-Sciences. Tetradecane (98+ % purity) and nonane (99+ % purity) were from Aldrich Chemical Co. Silica gel 60, 70-230 mesh was from Aldrich Chemical Co. and was column extracted with methanol and then dichloromethane. It was subsequently stored at 130 °C. High purity sulfuric acid was from EM Sciences. Acidic silica gel was made by taking the above mentioned silica gel and combining it with the above mentioned sulfuric acid and combining the two in a 40:60 (w/w) ratio followed by 30 minutes of mechanical shaking for homogenization. Woelm activity I neutral alumina and Woelm activity I basic alumina from ICN Chemicals was also stored at 130 °C. Reagent grade anhydrous sodium sulfate, 10-60 mesh, from Fisher Scientific was baked two hours at 550 °C in a muffle furnace and then stored at 130 °C. Nitrogen for the blow down apparatus was 99.999+ % and helium for the GC\MS was chromatographic grade (99.9999+%). The nitrogen was filtered through moisture and hydrocarbon traps. The helium was filtered through an oxygen trap.

The native chlorinated dioxin and native chlorinated furan standards as well as the $^{13}C_{12}$–labeled chlorinated dioxin and $^{13}C_{12}$–labeled chlorinated furan standards were purchased neat from Cambridge Isotope Laboratory (Woburn, MA). Stock solutions were made up into 50 µg/mL per compound native mixed standards and 50 µg/mL per compound the $^{13}C_{12}$–labeled mixed standards. These were mixed in different ratios in nonane to provide a four-point calibration curve. The calibration working solutions of were the $^{13}C_{12}$–labeled mixed standards were maintained at 25 µg/mL per compound except for octa-dioxin and octa-furan which were both at 50 µg/mL.

Rotary evaporators for solvent removal were Buchi RE-111A or equivalent equipped with water baths that could be maintained at 40 °C. Liquid nitrogen traps were placed between the rotary evaporators and mechanical vacuum pumps to trap solvents and to virtually eliminate backstreaming of hydrocarbons from the vacuum pumps to the samples. The nitrogen blow down apparatus was an N-Evap Analytical Evaporator, model 112 from Organomation Associates, Inc.

(Northborough, MA). Low pressure gas pressure regulators used to deliver the nitrogen to the blow down apparatus were 0-30 psig with stainless steel diaphragms from J&W Scientific (Rancho Cordova, CA).

Liquid measurements for dilutions on volumes of one mL or less were done with Hamilton glass and Teflon syringes. One mL, clear glass Reacti-vials from Pierce Chemical were used for storing the samples prior to GC/MS analysis. They were used because they allow for a sample to be concentrated down to a total volume of 10 µL or less from which 1 µL could be withdrawn for injection into the GC/MS. Such extreme concentration is necessary for this type of analysis. All glass vials used had Teflon lined caps. Glass fiber filter sheets were obtained from Nuclepore.

2. Sample Collection

The 18 samples were collected from a total of 12 storm drains and runoff streams in the Santa Monica Bay drainage area over a one 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. Table 1 shows the names of the sampling stations and information about the stations at the time of sampling. Figure 1 is a map showing their locations. Table 2 gives the land use types for the drainage areas. Samples were collected from storm drain culverts with the aid of an 8 liter

Table 1. Sampling Station Names, Schedule and Weather Conditions

Sampling Date and Condition	**Sampling Station Name and Number**							
	Pico-Kenter **1**	7th St / Chataqua **2**	Centeinela Creek **3**	Ballona Creek **4**	Temiscal Creek **5**	Ashland Ave **6**	Market St **7**	Brooks Ave **8**
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(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
6/15/89 (Dry)	X	X	X	X				
9/17/89 (Wet)	X	X	X	X				

X denotes that sampling was performed. A blank indicates that no sampling occurred.

Names of the sampling stations and weather conditions at the time of sampling. The samples collected in May, 1989 were not all collected on one day. The various days are given above. All other sampling days and locations are given by "X".

Table 2: Land Use Distribution for the Various Sampling Stations

Distribution in Hectares

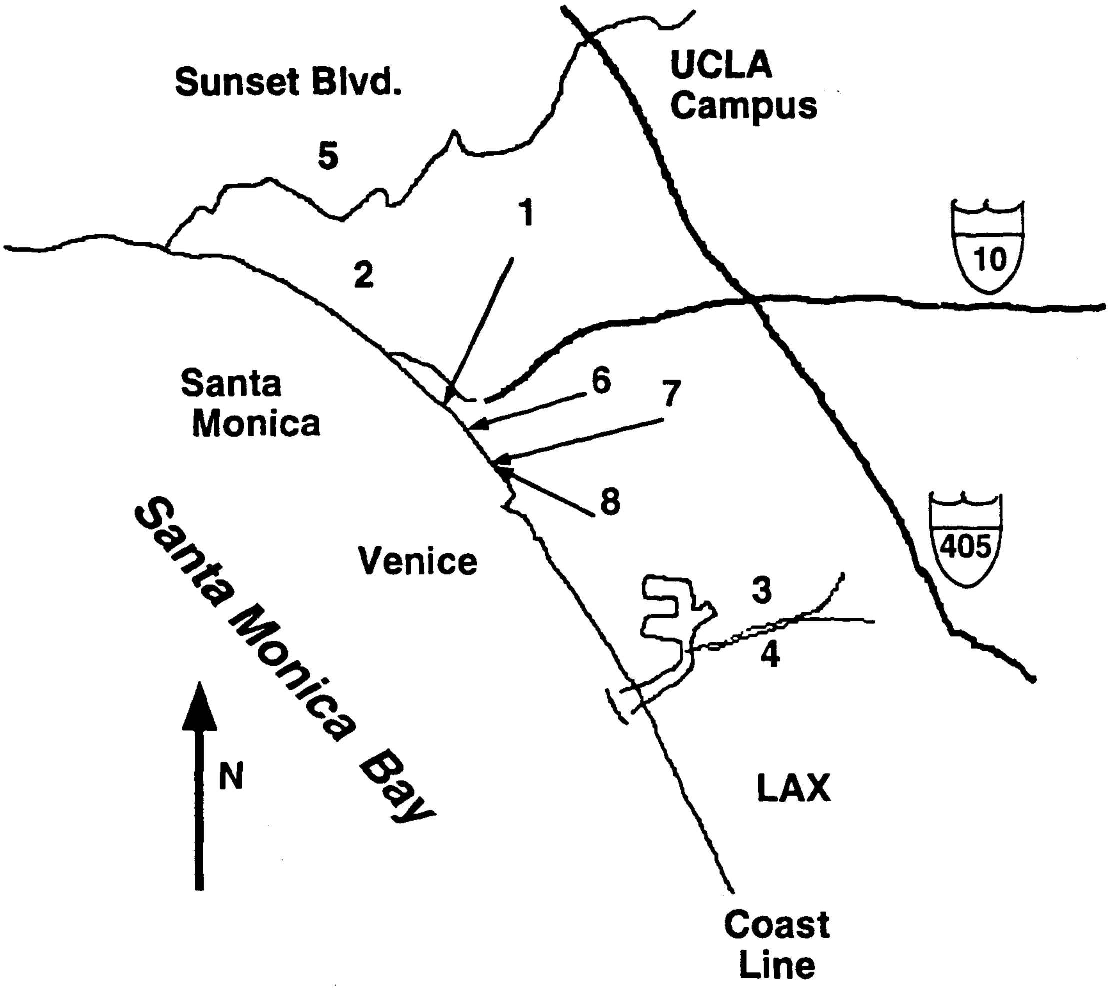
Category	**Station**							
	Pico-Kenter	7th St / Chataqua	Centeinella Creek	Ballona Creek	Temiscal Creek	Ashland Ave	Market St	Brooks Ave
Single Family	432055	1144449	112928338	112928338		4837288	3099722	3100197
Multi Family	396030	15567	48237158	48237158		1307597	1757869	1783107
Commercial	257876	23028	29542654	29542654		481359	742487	742563
Public	174094		9502827	9502827		284592	579242	579242
Light Industrial	202533		11616427	11616427		187584	253173	273372
Other	25067	12839	6224581	6224581		105372	1158323	1159679
Open	123101	2380679	40313052	40313052	1937500	4020474	10321995	10321995
Unknown	1716	914	1157448	1157448		10695	2111	2265
Total	1612472	3577476	259522485	259522485	1937500	11234961	17914922	17962420

Distribution as Percent of Total

Category	**Station**							
	Pico-Kenter	7th St / Chataqua	Centeinella Creek	Ballona Creek	Temiscal Creek	Ashland Ave	Market St	Brooks Ave
Single Family	27	32	44	44	0	43	17	17
Multi Family	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 (%)	100	100	100	100	100	100	100	100
Total (hectars)	161	358	25952	25952	194	1123	1791	1796

Land use types, as percentages, for some of the drainage basins in this study.

Figure 1: Sampling Sites



The greater Los Angeles area showing the various sampling locations used in this study. The numbers of the locations are given in Table 1.

polypropylene bucket. 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 bucket-full was discarded. The second and subsequent bucket-fulls were poured into pre-washed, one-gallon, 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.

3. Sample Extraction

Preparation of samples continued only after all steps in the following described concentration and isolation procedures were shown not to contribute significant background of dioxins, furans, or PCNs. The one-gallon sample containers were allowed to warm to room temperature overnight before extraction. Two liters of the water samples were extracted for each GC/MS sample preparation. The samples were spiked with ten $^{13}C_{12}$ internal quantitation standards. The $^{13}C_{12}$ labeled standards used were: 2378-TCDD, 2378-TCDF, 23478-PeCDF, 12378-PeCDD, 123478-HxCDF, 123678-HxCDD, 1234678-HpCDF, 1234678-HpCDD, OCDF, and OCDD. The standards were dissolved in toluene at approximately 50 pg/µL except for octa-dioxin and octa-furan that were at 100 pg/µL. Two µL of the spiking solution were used in each two liter sample. They were extracted in two liter glass extraction funnels with Teflon stopcocks as two one-liter aliquots. Each one-liter aliquot was spiked with one µL of the spiking solution shortly before the extraction. One-liter aqueous sample aliquots were extracted with 1 x 90 mL and 2 x 60 mL dichloromethane. The organic layers from both one-liter sample aliquots were combined along with any emulsions formed during the extractions. The resultant dichloromethane solutions often contained a large amount of water. Granular sodium sulfate was added, with stirring, until the sodium sulfate no longer visibly clumped, to dry the dichloromethane solutions. The extracts were allowed to sit, with occasional swirling, for at least ten minutes before they were gravity-filtered through glass fiber filters (GFF) into 500 mL round bottomed flasks. Fifty µL of tetradecane were added to the solutions to avoid volatilization of the compounds of interest during evaporation. They were evaporated to near dryness under reduced pressure using a Buchi rotary evaporator. The samples were then transferred to 7 mL amber, glass vials using a minimum of 3 x 1 mL hexane washes. They were dried under a stream of clean, dry nitrogen to less than 1 mL liquid volume.

4. Sample Purification

One or two subsequent fractionations were necessary before injection into the GC/MS. The number of fractionations was dependent upon how much interfering chemical material was present in the original water samples. If they appeared too contaminated they were run through silica gel and 40% sulfuric acid on silica gel before alumina chromatography. These methods (Marklund et al.1986) are described below in more detail.

5. Alumina Separations

Two separation columns were prepared from disposable Pasteur pipettes by filling them in the following manner. Both columns had a small plug of clean glass wool inserted near the tips. A 0.5 cm layer of sodium sulfate was poured onto the glass wool. Column A was then filled with about 5 cm of Woelm basic activity I alumina, followed by 0.5 cm sodium sulfate. Column B was similarly filled with about 2.5 cm 40% sulfuric acid on silica gel, 0.5 cm sodium sulfate, 2.5 cm potassium silicate, and 0.5 cm sodium sulfate.

The columns were clamped vertically with the eluate from Column B dripping directly into column A. The columns were then washed with 10 mL hexane and the sample was transferred to the top of column B in 4 x 1 mL hexane. Column B was then discarded as soon as the hexane had eluted from it into column A. Column A was then eluted with 2 mL hexane that was collected as 'fraction 1' (very non-polar compounds). It was then eluted with 4 mL 1:1 dichloromethane:hexane that was collected as 'fraction 2' (PCNs, PCDDs, PCDFs).

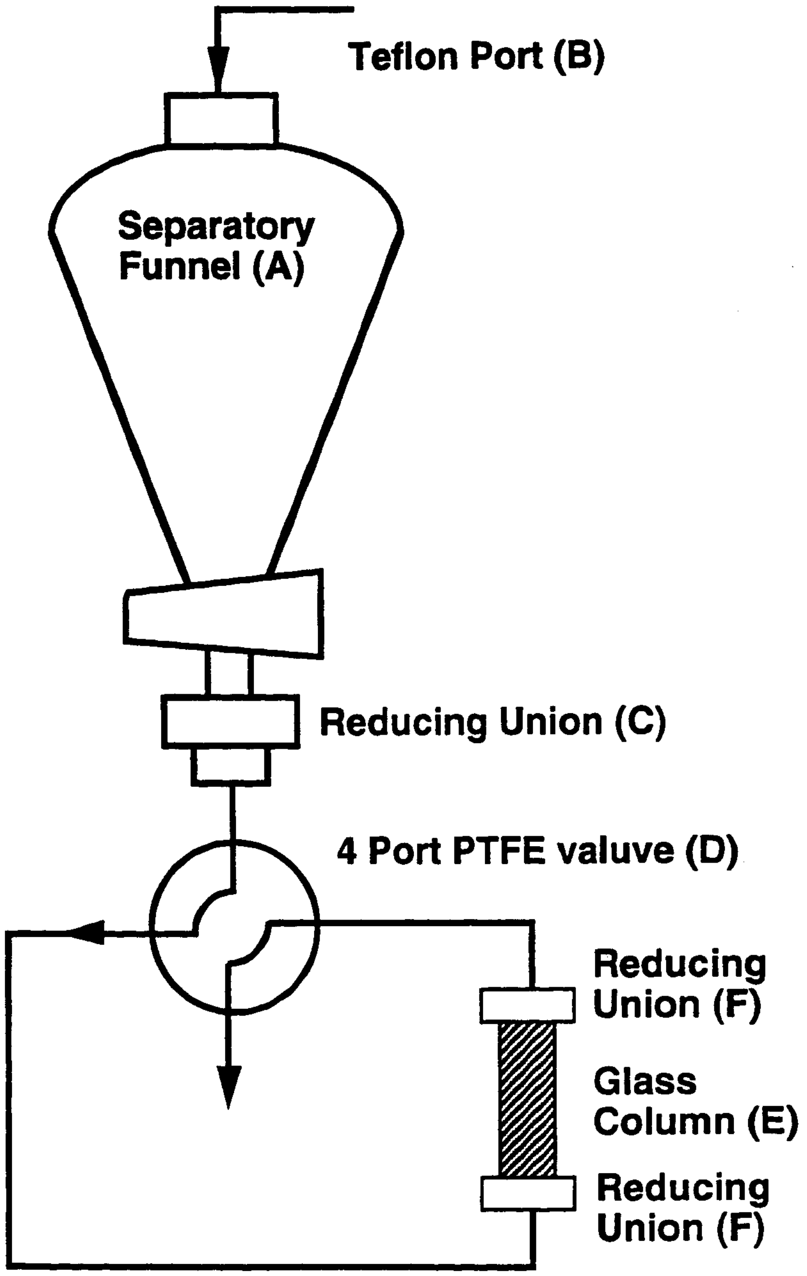
Fraction 2 was taken to near dryness under a stream of clean, dry nitrogen and transferred to a 1 mL conical vial with 3 x 0.3 mL dichloromethane. Ten µL tetradecane were added to the vial and was taken to near dryness (i.e., 10 µL tetradecane left) under a stream of clean, dry nitrogen.

6. Carbon Enrichment

Carbon columns were prepared by mixing 225 mg of celite with 25 mg Carbopak C 80/100 mesh or 25 mg of AX-21 carbon. This mixture was packed with gentle tamping into a 7.5 cm x 0.95 cm internal diameter (i.d.) heavy wall glass tube. Dead volume of either end of the column was filled with sodium sulfate followed by a small plug of glass wool. At both ends of the column were fitted 3/8 inch x 1/8 inch reducing unions that made a liquid tight seal with the glass by using 3/8 inch Teflon ferrules. The column was connected to a reservoir and a Hamilton four port four opposing valve with 1/8 inch heavy wall Teflon tubing (see Figure 2). The carbon column was sequentially conditioned with 20 mL toluene, 5 mL dichloromethane and 10 mL hexane.

Samples that contained high milligram amount of waxes and/or oils were taken up in 1:1 dichloromethane:hexane (3 x 1 mL were applied to the carbon column slowly with aid of N_2 gas pressure). Two mL of 50:50 hexane:dichloromethane were applied to the column and discarded. The dioxins, furans and PCNs were recovered

Figure 2: Concentration Apparatus



by passing 30 mL of warm (40 °C) toluene in the reverse direction. The flow was reversed by changing the position of the Hamilton four port four opposing valve. The toluene was evaporated and the residue was transferred to a Reacti-vial containing 10 µL tetradecane, with 3 x 0.5 mL dichloromethane and evaporated under nitrogen for GC/MS analysis.

7. GC/MS

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, CA, USA) fused silica capillary column (60 m x 0.25 mm i.d.) 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 °C - 260 °C at 20 °C per minute, 260 °C - 300 °C at 1 °C per minute. The injector was at 250 °C and the transfer line was at 260 °C.

The electron energy of the mass spectrometer source was 70 eV which was used to excite methane to ionize analytes. The mass spectrometer was operated in negative ion methane enhanced electron capture chemical ionization mode because the analysis of these samples required more sensitivity than was available to us using electron impact ionization with the available quadrapole instrument. The ions monitored for the various compounds are given in Table 3.

Table 3: Ions Monitored in Methane Enhanced Negative Chemical Ionization with Low Resolution Mass Spectrometry

Congener	Seconday	Quantitation	Isotope	Interferences	Primary	Seconday
	Ion *	Ion *	Ratio	(congener)	Ion *	Ion *
	M^-	$M^- +2$	$M^-/(M^- +2)$			
PeCDD	354	356	0.54-0.73			
$^{13}C_{12}$ PeCDD	366	368		HxPCB	360	358
HxCDD	388	390	0.44-0.6			
$^{13}C_{12}$ HxCDD	400	402				
HpCDD	422,387	424,389	0.37-0.53			
$^{13}C_{12}$ HpCDD	434,399	436,401				
OCDD	458,423	460,425	0.71-1.05	TeCN	264	262
$^{13}C_{12}$ OCDD	435,470	437,472		PeCN	300	298
TCDF	304	306	0.66-0.9	HxCN	334,300	332,298
$^{13}C_{12}$ TCDF	316	318		PeDFE	342	340
PeCDF	338	340	0.54-0.73	PeDFE	342	340
$^{13}C_{12}$ PeCDF	350	352		HxDFE	376	374
HxCDF	372	374	0.44-0.6	HpDFE	410	412
$^{13}C_{12}$ HxCDF	384	386		ODFE	446	444
HpCDF	408 $M^- +2$	410 $M^- +4$	0.89-1.02			
$^{13}C_{12}$ HpCDF	420	422				
OCDF	442	444	0.76-1.02			
$^{13}C_{12}$ OCDF	454 $M^- +2$	456 $M^- +4$				

* units are in mass to charge ratio (m/z)

See text for discussion

The disadvantage of running an instrument in this mode is that different isomers of chlorinated dioxins and chlorinated furans exhibit very different response factors. This is in contrast to the electron impact mode where most of the compounds give a linear response in relation to each other. An additional disadvantage is that 2,3,7,8-TCDD has a very low RRF in using this chemical ionization method. However, it is really the only choice available when you have a quadrapole instrument available and need high sensitivity. Typical relative response factors (RRF) for our system are given in Table 4. These data were obtained in 1992.

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 8000 resolution. This instrument in the electron impact mode had sensitivity similar to that which the quadrapole instrument had for it's most sensitive isomers in the chemical ionization mode. The GC/MS was fitted with a DB-5 column virtually identical to the one used in the quadrapole GC/MS. The temperature programming was also the same.

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

Table 4: Relative Response Factors

	RRF	RRF	RRF	RRF	RRF	MEAN	DEV	CV
1,2,3,4,7,8-HexaCDF	0.86	1.08	0.92	1.39	1.02	1.05	0.21	19.7
1,2,3,7,8-PentaCDF	0.84	1.18	1.05	1.31	1.15	1.11	0.18	16.1
1,2,3,4,7,8,9-HeptaCDF	0.97	1.09	0.79	1.22	1.13	1.04	0.17	16.1
2,3,4,7,8,9-HexaCDF	0.83	1.11	0.90	1.23	1.12	1.04	0.17	16.0
2,3,4,0,7,8-HexaCDF	0.86	1.22	0.88	1.04	1.06	1.01	0.15	15.2
1,2,3,7,8-PentaCDD	1.25	1.61	1.32	1.67	1.27	1.43	0.20	13.9
2,3,7,8-TetraCDF	0.60*	1.08	0.85	1.06	0.88	0.97	0.12	12.3
1,2,3,4,7,8-HexaCDD	1.04	1.32	1.04	1.27	1.05	1.14	0.14	12.2
1,2,3,4,6,7,8-HeptaCDD	n.d	1.81*	0.95	1.19	1.16	1.10	0.13	12.0
1,2,3,4,6,7,8-HeptaCDF	0.82	1.04	0.88	1.10	0.99	0.97	0.11	11.5
OCDF	0.90*	1.02	0.84	0.95	0.84	0.91	0.09	10.0
1,2,3,6,7,8-HexaCDD	1.42	1.40	1.42	1.74	1.55	1.51	0.15	9.7
1,2,3,7,8,9-HexaCDD	0.96*	0.88	0.84	0.86	1.04	0.91	0.09	9.7
2,3,4,7,8-PentaCDF	0.85	1.03	0.91	1.02	0.97	0.95	0.08	7.9
1,2,3,6,7,8-HexaCDF	0.89	0.97	0.97	1.10	1.01	0.99	0.08	7.6
OCDD	n.d	1.87*	0.84	0.80	0.78	0.81	0.03	4.2
Amt. 12C Tetra-hepta	0.5pg	1pg	10pg	40pg	250pg			
Amt. 12C OCCDD/OCDF	1pg	2pg	20pg	80pg	500pg		STD	

Key: n.d. not detected * near detection limit, not included in the mean

An example of typical relative response factors fo methane enhanced negative ion negative chemical ionization with the quadrople MS (based on height)

Table 5. Dry Weather Sample Results

Compound	Station Numbers for the 5/88 Sample																Station Numbers for the 6/89 Sample							
	1		2		3		4		5		6		7		8		1		2		3		4	
	pg/L	DL	pg/L	DL	pg/L	DL	pg/L	DL	pg/L	DL	pg/L	DL	pg/L	DL	pg/L	DL	pg/L	DL	pg/L	DL	pg/L	DL	pg/L	DL
D 12378	-	1.3	-	1	-	1.9	-	1.5	-	2.1	-	1.5	-	7.6	-	1.3	-	1.6	-	0.86	-	-	-	0.83
D 123478	-	0.5	-	1.4	-	1.8	-	1.4	-	1.8	-	1.6	-	1.8	-	1.5	-	1.4	-	0.62	-	0.64	-	0.72
D 123678	-	0.6	-	1.6	-	2.1	-	1.6	-	2.1	-	1.9	-	2.2	-	1.7	-	1..6	-	0.71	-	0.73	-	0.82
D 123789	-	1.4	-	3.5	-	4.8	-	3.6	-	4.8	-	4.4	-	4.9	-	4	-	3.7	-	1.7	-	1.7	-	1.9
D 1234678	12	2.9	-	3	11	3	-	4.2	-	7.5	-	6.3	-	4.7	-	2.9	18	3.7	-	2.2	9.4	1.6	33	2
D 12346789	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
F 2378	-	0.7	-	1.4	-	0.8	-	1.1	-	0.6	-	-	-	0.6	-	0.6	-	3	-	2	-	-	-	-
F 12378	-	0.2	-	0.3	-	1.4	-	0.4	-	0.4	-	0.6	-	0.2	-	0.2	-	0.21	-	0.12	-	0.1	-	-
F 23478	-	0.2	-	0.2	-	0.7	-	0.5	-	0.4	-	0.3	-	0.2	-	0.2	-	0.22	-	0.12	0.25	0.1	0.42	0.1
F 123478	-	0.4	-	0.5	-	1.2	-	0.5	-	0.6	-	1.3	-	0.6	-	0.5	-	0.52	-	0.31	0.48	0.25	0.29	0.26
F 123678	-	0.5	-	0.4	-	1.1	-	0.4	-	0.5	-	0.8	-	2.2	-	0.5	-	0.51	-	0.3	-	0.24	-	0.25
F 234678	-	0.2	-	0.5	-	0.7	-	0.5	-	0.7	-	0.6	-	0.7	-	0.6	-	0.56	-	0.34	-	0.28	-	0.3
F 123789	-	0.5	-	1.3	-	1.8	-	1.3	-	1.8	-	1.6	-	1.8	-	1.5	-	1.3	-	0.77	-	0.62	-	0.64
F 1234678	1.7	0.6	-	1.3	3	1.5	-	1.4	-	1.6	4.1	1.8	-	2	-	1.4	2.3	1.4	-	0.85	1.6	0.64	4.7	0.67
F 1234789	-	0.8	-	1.8	-	3.6	-	2.9	-	3.5	-	3.8	-	4.2	-	3	-	2.9	-	1.7	-	1.3	-	1.4
F 12346789	6.1	2.9	-	4.5	-	7.4	-	6.4	-	11	7.1	3	-	11	-	8.4	-	2.9	-	3.6	-	3.1	-	3
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		-		-		-		-		-		-	
International Toxic Equivalency Factors (I-TEFs)*																								
	0.75		0.85		1.6+		1.3		1.3		1.2		1.1		1		1.6		0.72		1.3		1.2	
Polychlorinated Naphthalenes																								
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

Key: - indicates less than detection limit (DL); F indicates a furan; D indicates a dioxin.

* see Nato/ CCMS (1988a and 1988b).

Quantitative results of the samples collected during the dry seasons. Concentrations are given in picograms of analyte per liter of water collected (pg/L). See text for a discussion of the results.

Table 6. Wet Weather Sample Results

Compound	Station Numbers for the 11/88 Sample				Station Numbers for the 9/89 Sample							
	1		2		1		2		3		4	
	pg/L	DL	pg/L	DL	pg/L	DL	pg/L	DL	pg/L	DL	pg/L	DL
D 12378	-	1	-	1	-	10	-	1	-	2	-	0.9
D 123478	-	1	-	1	19	2	-	1	2.6	1	1.8	0.8
D 123678	8.9	1	-	1	59	2	-	1	8.7	1	7	1.1
D 123789	-	2	-	3	100	5	-	2	9.1	3	8	2.4
D 1234678	170	2	6.9	3	1100	2	4	2	180	2	140	3.3
D 12346789	1400	8	87	6	7700	3	35	2	1300	3	1000	5
F 2378	-	-	-	1	-	26	-	1	7.3	1	4.5	1
F 12378	-	-	-	0	8.6	1	-	0	-	0	-	0.7
F 23478	1.8	0	-	0	8.6	1	0	0	-	0	2.9	0.2
F 123478	4.1	0	-	0	21	1	-	0	5.9	0	3.4	0.4
F 123678	4.5	0	-	0	17	1	-	0	3.9	0	3.4	0.4
F 234678	3.1	0	-	0	12	1	-	0	8.9	0	3.6	0.4
F 123789	-	1	-	1	-	1	-	0	-	0	-	0.3
F 1234678	34	1	-	1	260	1	1	0	43	1	34	1.1
F 1234789	-	1	-	2	13	1	-	0	1.9	1	-	1.5
F 12346789	88	6	-	5	570	2	2	1	81	1	59	2.8
Congener Series Totals												
penta-D	-		-		-		-		-		-	
hexa-D	55		-		300		-		110		67	
hepta-D	360		21		2200		12		344		330	
octa-D	1400		87		7700		35		1300		1000	
tetra-F	-		1.1		-		-		79		33	
penta-F	58		-		17		0		57		25	
hexa-F	93		-		260		-		81		64	
hepta-F	100		-		600		2		93		76	
octa-F	88		-		570		2		81		59	
International Toxic Equivalency Factors (I-TEFs)*												
	6.5		0.8		53		1		8.9		8.1	
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

Key: - indicates less than detection limit (DL); F indicates a furan; D indicates a dioxin.
* see Nato/ CCMS (1988a and 1988b).

Quantitative results of the samples collected during two storms. Concentrations are given in picograms of analyte per liter of water collected (pg/L). See text for a discussion of the results.

III. Results and Discussion

1. Sampling.

Eighteen samples were analyzed in this study. Considering the large amount of time necessary for each analysis, the sampling rationale was as follows. Two samples collected in November 1988 during a storm were used to determine if we could obtain useful results from two liter water samples. These first two samples were collected from sites with the greatest potential contamination of pollutants typically measured in urban runoff (e.g., oil and grease). The positive results from these two samples led us to try a large number of sites during a dry month (May 1989) which were suspected to be at lower concentrations. The Temescal Canyon sample was collected from a small stream in a largely uninhabited hilly area about two miles from the ocean. We believed this was one of the cleanest background natural water samples we could find in the area. This proved to be true as no dioxins, furans or PCNs were found in this sample. By comparison, OCDD was found in all the other samples in this study. Three of the other samples obtained during this month were so low that it was decided to drop the sampling locations from further consideration (see Table 1).

In June 1989 the four most contaminated sites were sampled a second time during dry weather. These four locations were sampled once again on September 17, 1989 during storm conditions.

2. Low Rainfall. Southern California had a severe drought during the four years before sampling for this study. The drought may have caused higher concentrations of the pollutants we measured in runoff water for two reasons. Frequent rains may scour contaminants from surfaces, eventually reducing their concentrations. A second reason relates to the local weather patterns. During hot, dry periods the typical on-shore breezes reverse themselves. The off-shore breezes move the more highly polluted air mass from the greater Los Angeles area towards the coast. This results in higher levels of dioxins and furans in the coastal air mass (Hunt and Maisel 1992). If these wind reversals were more frequent during 1988 and 1989, then our samples had a much greater contribution from air pollution than would be expected during non-drought periods.

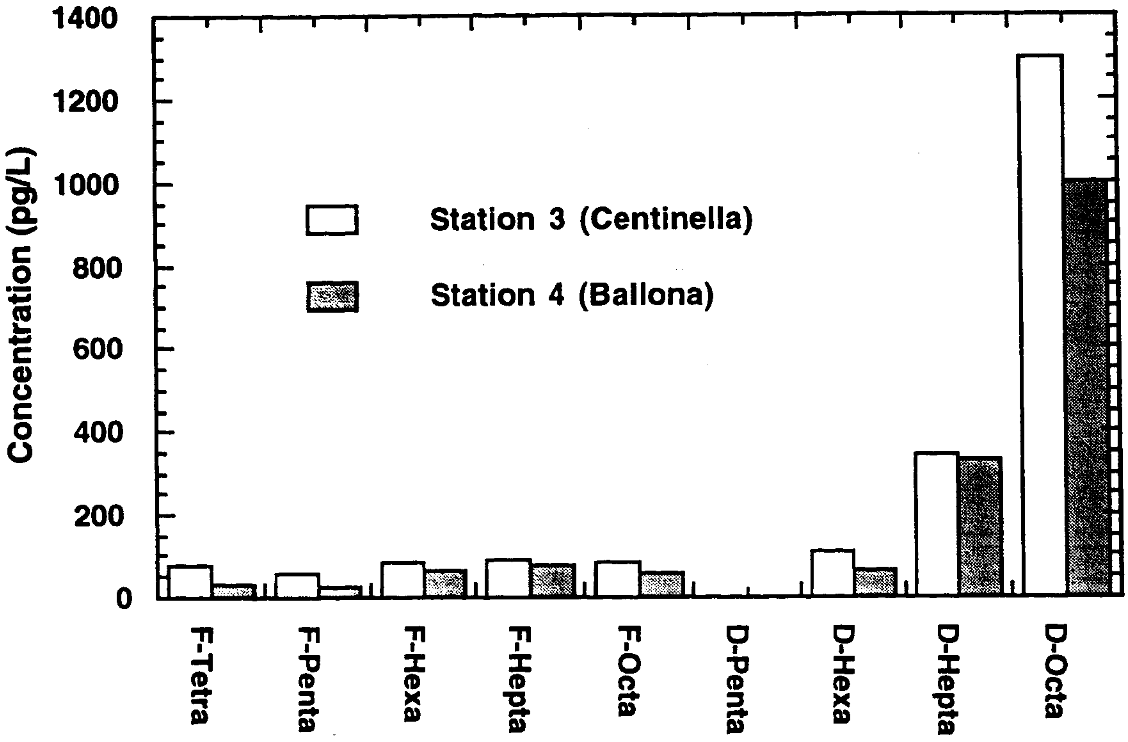
3. Data Interpretation. The results from all of the samples are presented in Tables 5 and 6. These data were split into two tables representing those samples collected during a dry season (Table 5) and those samples collected during a storm (Table 6). Dioxin, furan, and chloronaphthalene congeners were detected in most samples. In the four winter storm samples that contained the highest dioxin and furan levels, polychloronaphthalenes were strongly suspected but could not be confirmed for the reason given below. These four samples contained milligram quantities of material, possibly car waxes. Carbon chromatography (see Methods) was required to remove the waxes. The resulting purified extract had a significantly lower recovery of tetra and penta chlorinated dioxins, furans, and possibly tetra and penta naphthalene congeners and an elevated PCN background in the blanks. Additional purification significantly improved the recovery of tetra dioxins 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 was ambiguous. Two storm samples and four dry season samples contained tetra and/or pentachloronaphthalenes at levels comparable to that of the total dioxin and furan congeners. The highest levels of polychloronaphthalenes were also detected in one storm sample. However, most of the information on polychloronaphthalene levels 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, while 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 ten labeled standards were similar and OCDD and HpCDD have the lowest sensitivity in negative chemical ionization mode. Four dry season samples contained only OCDD 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 octa furan isomers, and hepta and octa dioxin isomers, and their relative concemtrations were quite similar to those reported by Czuczwa and Hites for sediments from Lake Huron (Czuczwa and Hites 1984).

Figure 3 shows congener series concentration profiles for two typical samples in our study for which we had the most complete data. They are very similar to congener series profiles found by Hites and co-workers (Hites 1990; Czuczwa and Hites 1986a; Czuczwa et al. 1985; Czuczwa et al.1984) in sediment samples collected from lakes at various locations in this country and in Switzerland. As well, these congener profiles are typical of those found in rainwater collected in Bloomington, IN (Hites 1990). We found similar profiles for both storm and dry conditions.

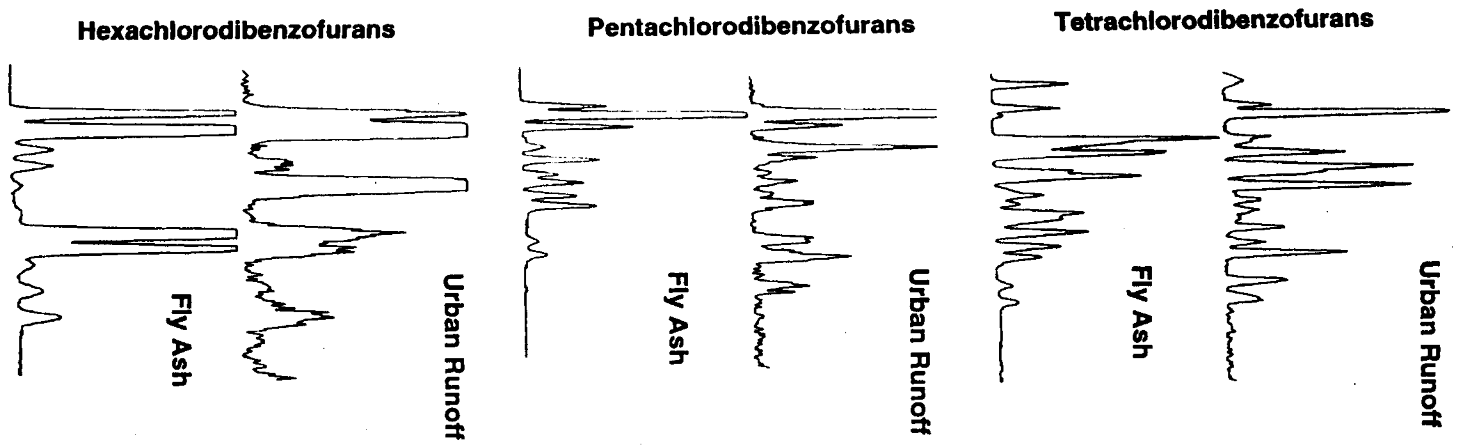
Figure 4 shows some of the high resolution electron impact mass chromatograms of isomer profiles for Centinella Creek contrasted with a typical fly ash profile. Most of the reconstructed ion chromatogram (RIC) peaks observed in fly ash are also observed in the sample. Some isomers are missing or greatly reduced in all congener groups. The relative intensities of peaks are quite different in some cases as well. In the pentafurans the 2,3,4,7,9 isomer is nearly absent, while the

Figure 3: Typical Congener Series Concentration Profiles



Congener series profiles of two storm samples. These profiles show sums of all of the isomers in the various congener series for the dioxins and furans. For example, "F7" refers to the sum of the concentrations of all furans with seven chlorines substituted in place of hydrogens on it.

Figure 4: High Resolution Isomer Profiles

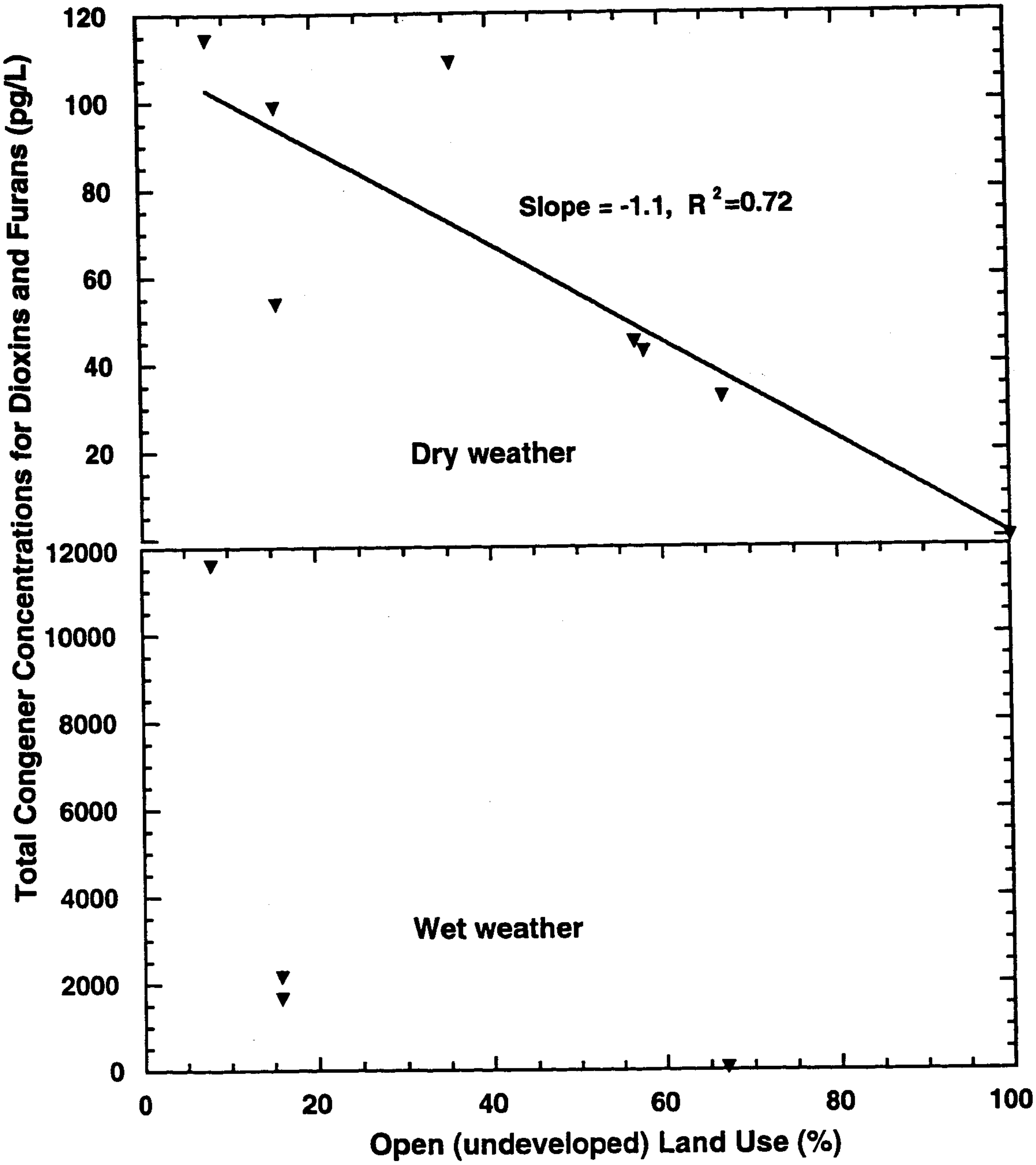


High resolution GC/MS mass chromatograms of one of our samples compared to a fly ash extract from a West German incinerator. Fly ash is used because it contains virtually all of the isomers of dioxins and furans. B, D, and F are from the fly ash while A, C, and E are from our sample. The tetrachlorodibenzofurans traces are of m/z 306. The pentachlorodibenzofurans traces are of m/z 340. The hexachlorodibenzofurans traces are of m/z 374. This data was digitized and smoothed with Un-plot-it^{TM}.

1,3,4,6,9, and 1,2,4,7,9 congeners are much greater than in the fly ash. 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 greatly attenuated, while 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 detected. In addition, our exclusive use of chromatography on a 60 meter DB-5 capillary column was not sufficient to separate many of the isomers, therefore more isomers could be missing that we never detected. They either were never in the sources or had been degraded. Rappe, et al., (Rappe et al.1989) report that the isomer profiles of air particulate, fly ash and car exhaust are essentially the same. If our congener groups contained most, if not all, of the isomers present in the actual, as yet undetermined, sources, then degradation only could have occurred if all isomers in a congener group had degraded at the same rate. This could be possible if vapor pressures were similar and, if activation free energies were small relative to the available energy for activation from UV light.

Figure 5 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, such as vehicle activity and combustion, and dioxin and furan cogener

Figure 5: Compound Concentration Versus Open Land Use



Total dioxin and furan congener concentrations for wet and dry weather samples as a function of open land area.

concentrations. The correlation exists for both the dry weather (Figure 5, top) and wet weather (Figure 5, bottom) conditions.

4. Sources and Fates. Known airborne sources of dioxins and furans, such as incinerators, show markedly different congener series profiles than those we observed. They had higher relative (to octadioxin) concentrations 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 1986a). The particulate portion 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 (Hunt and Maisel 1992; Hites 1990; Broman et al.1989).

The general conclusion we draw from our data is the same as that of several previous authors, i.e., that we are observing weathered patterns of congener series profiles (Hites 1990). The unweathered, or source, congener series profiles are those exhibited by extracts from typical sources such as incinerators.

One problem with this approach is that there has recently been a report of large discrepancies in the mass balance of all known sources of dioxins and furans to the total amount of fallout found for dioxins and furans (Oeberg and Rappe 1992). The findings have been that the source fluxes of dioxins and furans found near large cities account for less than 2-4% of the atmospheric fallout fluxes. One interpretation of this observation is that we do not yet known the major sources and therefore cannot say what the predominant source congener series should be (Oeberg and Rappe 1992).

It is also possible that source profiles have been adequately investigated and that differences in mass balance are due to systematic measuring errors. Other possibilities include that there are many small sources, such as hospital incinerators, which are ignored in mass balance studies but which have similar congener series concentration profiles. In any case, we believe the mass balance 'problem' is not a problem in large city air basins because the congener series profiles in air samples at large cities closely mimic that of known sources such as municipal incinerators and automobile exhaust (Hunt and Maisel 1992; Hites 1990; Rappe et al.1989; Czuczwa and Hites 1986b).

The focus of our study was the dioxin and furan levels in runoff water, which raises another possibility. Urban activities that involve the handling of chemicals contaminated with dioxins and furans, and were 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 could be 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, and/or the ground sources have similar congener and isomer profiles to airborne sources, the question then arises about the weathering process, i.e., how the congener series become shifted greatly towards octa-dioxins and hepta-furans and how certain isomers within a congener series are destroyed while others are not. Dioxins and furans bound to particle surfaces are emitted from sources and rapidly come to equilibrium upon entry into the atmosphere. Gas phase dioxins and furans are then available to destructive processes such as photolysis (Podoll et al.1986; Atkinson 1991; Fiedler and Hutzinger 1990) and hydroxide radical attack (Atkinson 1991). Particle bound dioxins and furans are generally not considered open to such destructive pathways because they are, to a large degree, bound to the interior of particles. In addition, contaminants we measured, whether originating from airborne deposition or ground sources, were on surfaces and soil for long periods of time (up to 6 months) before being washed into the runoff. This opens the possibility that other destructive pathways could be more important than photolysis and hydroxide radical scavenging in air. 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 et al.1991).

The most poorly understood process involved in the destruction of particulate bound dioxins and furans before ground or water deposition is the equilibrium between gas phase and particulate bound dioxins and furans. Vapor pressures of dioxins and furans have been determined (Podoll et al.1986; Atkinson 1991; Eitzer and Hites 1988; Eitzer and Hites 1986) but these parameters can only be used to predict equilibria from the *surface* of particulates that have no strong binding sites. This is clearly not the case in actual samples where the dioxins and furans condense together with some of the particulate material, trapping some of the dioxins and furans inside the particulates. As the destructive pathways of gas phase dioxins and furans become still better understood, we believe the lack of understanding of the equilibria between gas phase and particulate bound dioxins and furans will become the last major stumbling block to predicting rates of destruction of dioxins and furans in the atmosphere (and therefore in sediments).

In any case, the trend of destruction of dioxins and furans in the atmosphere is clear. As they go into the gas phase, they are transformed into non-dioxins and non-furans by photolysis and/or hydroxide radical scavenging. This reduces their concentrations in the gas phase and so more of the same compounds equilibrate out of the particulate bound reservoirs. No matter what the overall rate, those congeners with higher vapor pressures will equilibrate faster into the gas phase and therefore more of the higher vapor pressure isomers will be transformed into non-dioxin and furan compounds. This process must account for much of the difference in congener series profiles between weathered samples and those from sources. We believe that the heat induced rearrangements suggested by Wilson (Wilson 1986) are of small importance because of the similarity between source congener profiles and congener profiles observed in large city air (Hunt and Maisel 1992).

IV. Conclusions

1. Not enough reliable data were collected to allow a statistical correlation, or lack thereof, between PCN concentrations and dioxin/furan concentrations to be obtained.

2. Dioxins, furans, and PCNs can be detected in urban runoff from the Santa Monica basin.

3. The bulk of the material from the samples probably came from material already deposited on ground as opposed to material suspended in the air because we observed high levels of these pollutants several hours into the storms.

4. The concentrations of dioxins, furans, and PCNs observed were much higher during storms. 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.

5. There were significant differences between both congener and isomer profiles found in our samples and those found in urban air or in typical incineration ash.

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 the urban runoff.

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