

Atmospheric Concentrations of PCDDs/PCDFs, PAHs and NO₂-PAHs in Fresno, California During Winter Months

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Program Purpose and Objectives

A comprehensive program of field sampling and laboratory analyses was conducted in Fresno, California to determine ambient concentrations of a variety of semivolatile organic pollutants of regulatory significance to the California Air Resources Board (ARB)¹⁾. These data will assist the ARB in their continued examination of the distribution and occurrences of PAHs, nitro-PAHs, oxygenated-PAHs, and PCDDs/PCDFs within the State of California. Further, these data will serve to augment the existing data base on population exposure to PCDDs/PCDFs and PAHs. ARB has designated PCDDs/PCDFs as Toxic Air Contaminants (TAC) in accordance with AB 1807, while PAHs are currently under consideration for listing.

Sampling Location, Duration and Methods

Samples were collected on five days between December 17, 1990 and January 3, 1991 at the existing ARB monitoring site situated in Fresno, California. Two PS-1 air samplers (manufactured by General Metals Works) were outfitted with glass fiber filters and polyurethane foam (PUF) plugs for collection of PCDDs/PCDFs, and operated for a 24-hour period (approximately 0700 to 0700). Four PS-1 samplers, outfitted with PUF/XAD sorbent cartridges for collection of PAHs, operated for two sequential 12-hour periods (diurnal - 0700 to 1900; nocturnal - 1900 to 0700), concurrent with the PCDDs/PCDFs samplers. All sorbent cartridges were spiked in the laboratory prior to sampling with isotopically labeled compounds. In addition, one field blank per day for each sorbent system (PCDDs/PCDFs and PAHs) and collocated samples were also collected.

Analytical Methods

State-of-the-art analytical procedures were employed to determine atmospheric burdens of the toxicologically significant organics listed above. PAHs were measured by gas chromatography/mass spectrometry in the selected ion monitoring (SIM) mode, PCDDs/PCDFs were measured by high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS), and nitro-PAHs/oxygenated-PAHs were measured by negative chemical ionization/gas chromatography/mass spectrometry (NCI/GC/MS).

Results

PAHs. Table 1 provides results for each of eight field samples selected for PAHs analyses from the Fresno Field Program. All data are reported in units of ng/m^3 and represent field blank corrected values.

Nitro-PAH and Oxygenated-PAH. Two composite samples were selected to undergo analyses for nitro-PAHs and oxygenated-PAHs. Each composite included both the vapor phase and particulate portions of each sample selected. The results of these analyses are provided in Table 2. All data are reported in units of ng/m^3 .

PCDDs/PCDFs. A total of five samples were selected for analyses representing three daily sampling sessions. The days selected (December 17/18, 18/19 of 1990 and January 2/3 of 1991) were characterized by "worst-case" meteorological conditions for Fresno in wintertime. The five sample set includes two collocated pairs. Results for each of the nine 2,3,7,8-substituted PCDFs are plotted in Figure 1. All data for each of the three daily samples are reported in units of pg/m^3 and represent blank corrected values.

Conclusions

PAHs levels measured during the Fresno field program are indicative of wood combustion emissions. Elevated retene (a chemical marker for the combustion of coniferous woods) concentrations in concert with enhanced nocturnal PAHs concentrations suggest strong influences from residential wood burning². The PCDDs/PCDFs congener glass and isomer specific profiles are indicative of combustion source emissions³.

The predominant PAHs measured during the field campaign include naphthalene, 1-methylnaphthalene, 2-methylnaphthalene and biphenyl. Photochemical reactions involving these parent compounds and OH radicals during diurnal periods result in elevated concentrations of 1-nitronaphthalene, 2-nitronaphthalene and 3-nitrobiphenyl^{4,7}. Nearly equivalent concentrations of the four oxygenated-PAHs were observed in the Fresno samples. The highest concentrations were observed for 9-fluorenone, while the lowest concentrations were observed for pyrene and 3-4 dicarboxylic acid anhydride.

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Sampling Date	12-17-90	12-17-90	12-18-90	1-2-91	1-2-91	1-3-91	1-4-91	1-4-91
Period	nocturnal	diurnal	diurnal	diurnal	nocturnal	diurnal	diurnal	nocturnal
Spiking Status	spiked	unspiked	unspiked	spiked	spiked	spiked	spiked	spiked
Sample Volume (m ³)	181.2	151.6	183.2	184.4	186.7	179.0	196.7	184.2
Parameter	(ng/m ³)	(ng/m ³)	(ng/m ³)	(ng/m ³)	(ng/m ³)	(ng/m ³)	(ng/m ³)	(ng/m ³)
Naphthalene	1301	1357	520	464	587	947	240	148
2-Methylnaphthalene	882	856	326	298	455	670	198	113
1-Methylnaphthalene	391	362	141	135	209	296	86	52
Biphenyl	240	327	344	756	586	1114	216	166
Acenaphthylene	160	99	32	34	70	52	18	5.9
Acenaphthene	15	10	4.5	4.9	8.0	7.3	3.0	2.1
Fluorene	45	26	11	18	28	26	11	5.4
Phenanthrene	110	61	27	43	64	61	29	12
Anthracene	23	11	5.0	5.4	10	7.3	3.7	1.1
Fluoranthene	32	21	7.6	13	18	18	10	5.9
Pyrene	31	20	7.1	11	15	15	8.6	5.1
Retene	72	21	6.6	8.1	21	11	6.0	4.2
Benz(a)anthracene	13	7.3	2.1	2.5	5.0	3.0	1.1	0.39
Chrysene/Triphenylene	17	10	2.7	3.8	8.6	4.3	1.6	0.76
Benzo(b,j,k)fluoranthenes	25	18	3.5	6.0	11	7.3	2.7	1.4
Benz(e)pyrene	9.3	5.4	1.5	2.2	4.0	2.9	1.0	0.46
Benz(a)pyrene	12	6.6	2.0	2.7	5.9	3.1	1.0	0.31
Indeno(123,cd)pyrene	5.2	6.6	1.9	2.4	4.6	3.5	1.2	0.44
Dibenz(a,c/a,h)anthracene	1.7	1.3	0.3	0.4	0.91	0.56	0.10	0.11
Benzo(g,h,i)perylene	5.2	7.2	2.0	2.7	4.4	4.1	1.2	0.47
Coronene	13	11	2.6	3.1	5.9	5.6	1.6	0.49
Surrogate Recoveries (%)	%	%	%	%	%	%	%	%
Flourene, D10 (field surrog	75	NS	NS	70	84	84	91	68
2-Fluorobiphenyl (internal	78	72	48	60	56	84	78	47
Terphenyl, D14 (internal st	256	132	101	105	179	131	94	73

U = undetected at specified quantitation limit; E = exceeds calibration range

TABLE 1. Ambient Data Summary for PAHs in Fresno, California.

TABLE 2. Ambient Data Summary for Nitro-PAHs and Oxygenated PAHs in Fresno, California.

Parameter	Nocturnal (ng/m ³)	Diurnal (ng/m ³)	Parameter	Nocturnal (ng/m ³)	Diurnal (ng/m ³)
			8-Nitrofluoranthene	<0.014	<0.014
Fluoranthene	12.338	8.900	1-Nitropyrene	0.044	0.041
Benzo(a)pyrene	7.372	2.336	2-Nitropyrene	<0.014	<0.014
1-Nitronaphthalene	0.291	0.392	6-Nitrochrysene	0.022	<0.014
2-Nitronaphthalene	0.193	0.549	1,6-Dinitropyrene	<0.014	<0.014
3-Nitrobiphenyl	0.094	0.257	9-Fluorenone	7.191	6.318
9-Nitrophenanthrene	0.432	0.292	Naphthalene-1,8-dicarboxylic acid anhydride	4.786	4.792
9-Nitroanthracene	0.045	0.037	Benzo(a)anthracene-7,12-dione	1.020	0.514
2-Nitrofluoranthene	0.112	0.146	Pyrene-3,4-dicarboxylic acid anhydride	0.416	0.556
< = not detected below indicated detection limit. Sample volume: nocturnal: 367.9 m ³ ; diurnal: 363.4 m ³ .					

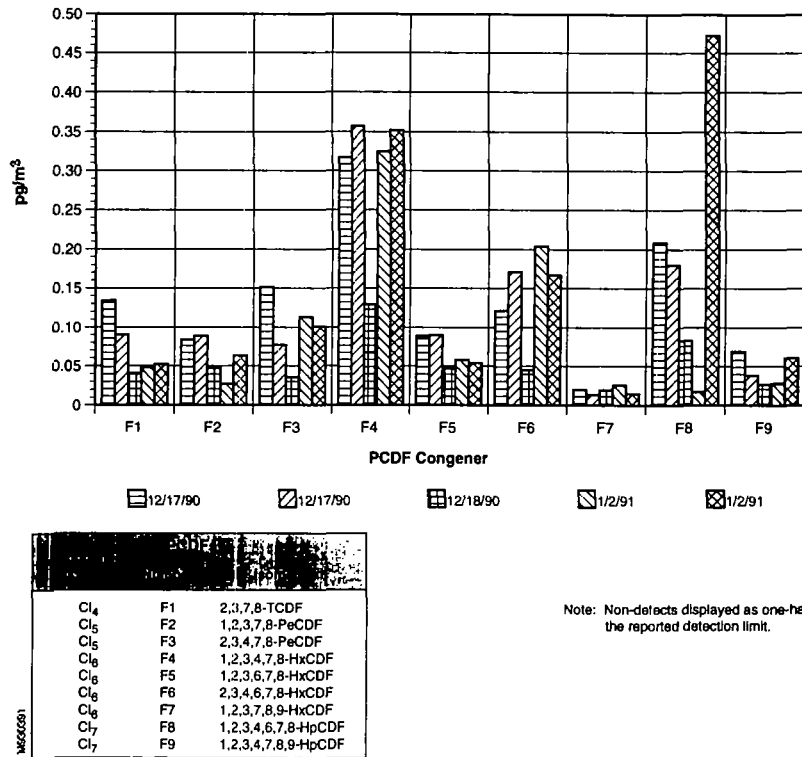


FIGURE 1
Fresno Ambient Profile for 2,3,7,8-PCDFs
(Session Specific)

DISCLAIMER

The statements and conclusions in this manuscript are those of the contractor and not necessarily those of the California Air Resources Board. The mention of commercial products, their source or their use in connection with material reported herein is not to be construed as either an actual or implied endorsement of such products.

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