

# WOOD SMOKE INFLUENCES ON ATMOSPHERIC CONCENTRATIONS OF PCDDs/PCDFs, PAHs AND NO<sub>2</sub>PAHs

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## Introduction

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). These data allowed for continued examination of the distribution and occurrences of PAHs, nitro-PAHs, oxygenated-PAHs, and PCDDs/PCDFs within the State of California. Further, these data served to augment the existing data base on population exposure to PCDDs/PCDFs and PAHs associated with wood smoke emissions in residential areas.

## Sampling Location, Duration and Methods

Samples were collected on five days between December 17, 1990 and January 3, 1991 at an existing ARB monitoring site situated in Fresno, California. The immediate vicinity of the station was characterized by single family homes and light commercial activities (3425 N. First Street, 205-B, Fresno, CA). 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. One field blank per day for each sorbent system (PCDDs/PCDFs and PAHs) and collocated samples were also collected.

## Analytical Methods

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). Nitro-PAHs/oxygenated-PAHs were measured by negative chemical ionization/gas chromatography/mass spectrometry (NCI/GC/MS). Mutagenicity testing was performed by The University of California at Riverside [1].

## Results and Discussion

### PCDDs/PCDFs

The highest concentrations are reported for the HxCDD, HpCDD and OCDD homolog groups. HxCDD values ranged from 1.7 to 7.7 pg/m<sup>3</sup>, the HpCDD values ranged from 5.2 to 21 pg/m<sup>3</sup>, and the OCDD values ranged from 9.2 to 32 pg/m<sup>3</sup>. A composite profile of PCDDs/PCDFs data is shown in Figure 1. Average concentrations for each of the C<sub>14</sub> – C<sub>18</sub> PCDDs/PCDFs homolog groups are reported in units of pg/m<sup>3</sup>. PCDDs/PCDFs data are compared to ambient concentration data representing selected US cities and rural and remote locations worldwide (See Table 1).

### PAHs

Measured concentrations for the PAH target parameters are considerably higher than ambient levels gathered during previous California monitoring programs and concentrations typically encountered in urban settings worldwide. The PAH concentrations measured at the Fresno site more closely approximate values observed at the Mammoth Lakes, California site as reported by Atkinson and Arey [5]. The latter site was impacted by wood-stove emissions during the field sampling program. Elevated concentrations of retene (1-methyl-7-isopropyl phenanthrene) were present in all of the Fresno samples analyzed. Retene concentrations ranged from 4.2 to 72 ng/m<sup>3</sup> with an average concentration of 18.7 ng/m<sup>3</sup>. Higher concentrations of retene were observed in nocturnal sampling periods than in diurnal sampling periods. Average retene concentrations of 32.4 ng/m<sup>3</sup> and 10 ng/m<sup>3</sup> were measured for nocturnal and diurnal periods, respectively. Elevated retene concentrations at nighttime suggest that the monitoring station was impacted by wood stove emissions [2].

### Mutagenicity Testing

The highest values are reported for the January 2-3 sampling period coincident with elevated PAH and PCDDs/PCDFs concentrations. There is no apparent trend in comparison of nocturnal and diurnal values, however. Mutagenic activity data for the diurnal samples are similar when values with activation (+S9) are compared to those without activation (-S9). These data suggest the presence of direct-acting mutagenicity.

### Nitro-PAH/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. The results of these analyses are provided in Table 2. All data are reported in units of  $\text{ng}/\text{m}^3$ . Nearly equivalent concentrations of four (4) oxygenated-PAHs were observed in nocturnal and diurnal composite samples. The highest concentrations were observed for 9-fluorenone ( $7.19 \text{ ng}/\text{m}^3$ ,  $6.32 \text{ ng}/\text{m}^3$ ) while the lowest concentrations were observed for pyrene, 3-4 dicarboxylic acid anhydride ( $0.42 \text{ ng}/\text{m}^3$ ,  $0.56 \text{ ng}/\text{m}^3$ ). The predominant nitro-PAH measured in the nocturnal sample was 9-nitrophenanthrene ( $0.43 \text{ ng}/\text{m}^3$ ) while 2-nitronaphthalene ( $0.55 \text{ ng}/\text{m}^3$ ) predominated in the diurnal sample. With the exception of 9-nitrophenanthrene, higher concentrations of the nitro-PAH were observed in the diurnal composite sample than were observed in the composite nocturnal sample. Elevated concentrations of 1-nitronaphthalene, 2-nitronaphthalene and 3-nitrobiphenyl in the Fresno diurnal sample (in contrast to the nocturnal composite) provide evidence for atmospheric photochemical reactions involving the respective parent PAH and OH radicals. Arey et al. report this to be a predominant reaction mechanism during daylight hours [4, 5, 7].

### Summary and Conclusions

PAHs levels measured during the Fresno field program are indicative of wood combustion. Elevated retene (a chemical signature for the combustion of coniferous woods) concentrations in concert with enhanced nocturnal PAH concentrations suggest strong influences from residential wood burning [2]. The PCDDs/PCDFs concentrations measured represent some of the highest levels reported in the open literature. The predominant PAHs measured during each of the three (3) field campaigns include naphthalene, 1-methyl naphthalene, 2-methyl naphthalene and biphenyl. Photochemical reactions involving these parent compounds and OH radicals during diurnal periods resulted in elevated concentrations of 1-nitronaphthalene, 2-nitronaphthalene and 3-nitrobiphenyl [4-7]. Mutagenic assay analyses of diurnal samples suggest the presence of direct acting mutagenicity. Conversely, results for nocturnal samples suggest a suppression of this direct-acting mutagenicity with +S9 activation. Nearly equivalent concentrations of four (4) oxygenated-PAHs were observed. The highest concentrations were observed for 9-fluorenone, while the lowest concentrations were observed for pyrene, 3-4 dicarboxylic acid anhydride.

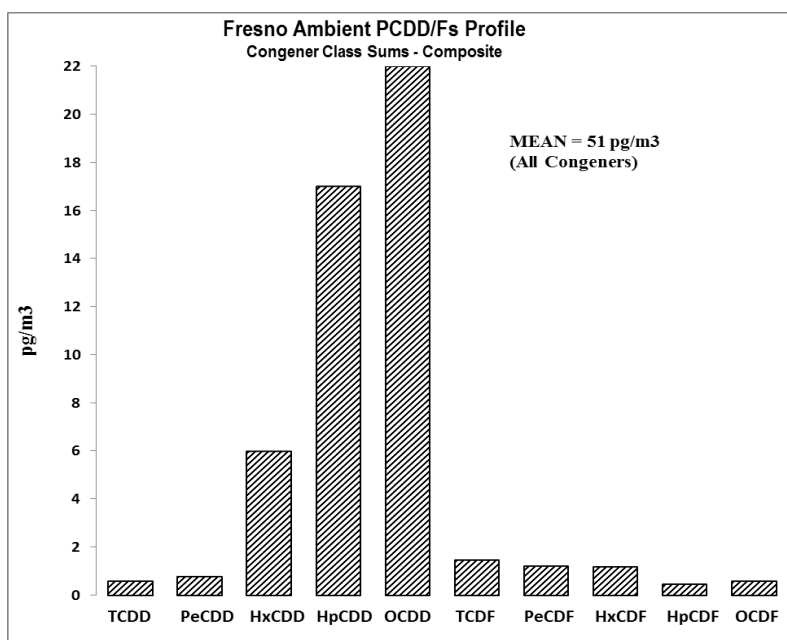


Figure 1.

Fresno Ambient Profile: C<sub>14</sub> – C<sub>18</sub> PCDDs/PCDFs Homologs (Composite of all Samples/Sessions)

Table 1. PCDDs/PCDFs Data Comparison Ambient Air US Cities, Global Rural and Remote Locations			
	Location	pg/m <sup>3</sup>	Reference
Urban US Cities	Hartford, CT	2.6	8
	Los Angeles, CA	7.4	3
	Phoenix, AZ	27	9
	Fresno, CA	51	1
	Bridgeport, CT	1.9	8
	Bloomington, IN	1.8	10
Rural Locations	TeWera, NZ	0.88	11
	Culverden, NZ	0.48	11
	Mohawk Mountain, CT (winter)	0.58	8
	Mohawk Mountain, CT (fall)	0.53	8
	Burlington, CT (winter)	0.68	8
	Burlington, CT (fall)	0.41	8
Remote Locations	Baring Head, NZ	0.14	11
	Nelson Lakes, NZ	0.04	11
	Bermuda (1993-1994)	0.11	12
	Bermuda (1996-1997)	0.04	12
	Barbados	0.02	12
PCDDs/PCDFs = Sum of Total PCDDs/PCDFs Tetra – Octa (Cl <sub>4</sub> – Cl <sub>8</sub> ) mass concentrations			

Table 2. Ambient Data Summary for Nitro-PAHs and Oxygenated PAHs in Fresno, California [1]					
Parameter	Nocturnal (ng/m <sup>3</sup> )	Diurnal (ng/m <sup>3</sup> )	Parameter	Nocturnal (ng/m <sup>3</sup> )	Diurnal (ng/m <sup>3</sup> )
			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
<b>&lt; = not detected below indicated detection limit.</b>					
<b>Sample volume: nocturnal 367.9 m<sup>3</sup>; diurnal 363.4 m<sup>3</sup>.</b>					

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