Aerosol Science and Technology

ISSN: 0278-6826 (Print) 1521-7388 (Online) Journal homepage: https://www.tandfonline.com/loi/uast20

Seasonal and Spatial Variation of Polycyclic Aromatic Hydrocarbons in Vapor-Phase and $PM_{2.5}$ in Southern California Urban and Rural Communities

Arantzazu Eiguren-Fernandez , Antonio H. Miguel , John R. Froines , Suresh Thurairatnam & Ed L. Avol

To cite this article: Arantzazu Eiguren-Fernandez , Antonio H. Miguel , John R. Froines , Suresh Thurairatnam & Ed L. Avol (2004) Seasonal and Spatial Variation of Polycyclic Aromatic Hydrocarbons in Vapor-Phase and $PM_{2.5}$ in Southern California Urban and Rural Communities, Aerosol Science and Technology, 38:5, 447-455, DOI: 10.1080/02786820490449511

To link to this article: https://doi.org/10.1080/02786820490449511

Aerosol Science and Technology, 38:447–455, 2004
Copyright © American Association for Aerosol Research
ISSN: 0278-6826 print / 1521-7388 online
DOI: 10.1080/02786820490449511

Seasonal and Spatial Variation of Polycyclic Aromatic Hydrocarbons in Vapor-Phase and PM$_{2.5}$ in Southern California Urban and Rural Communities

Arantzazu Eiguren-Fernandez,[1] Antonio H. Miguel,[1] John R. Froines,[1] Suresh Thurairatnam,[1] and Ed L. Avol[2]

[1] *Southern California Particle Center and Supersite, Institute of the Environment, University of California, Los Angeles, California*
[2] *Department of Preventive Medicine, USC Keck School of Medicine, Los Angeles, California*

Fifteen priority polycyclic aromatic hydrocarbons (PAHs) were measured in two rural communities (Atascadero and Lompoc) located several hundred km northwest of Los Angeles and in four urban communities 40–100 km downwind of Los Angeles (San Dimas, Upland, Mira Loma, and Riverside), during all seasons, from May 2001 to July 2002. PM$_{2.5}$ and vapor-phase PAHs were collected, on prebaked quartz fiber filters and PUF-XAD-4 resin, respectively, at 113 LPM, during 24 h periods, every eighth day, and quantified by HPLC-Fluorescence. At all sites vapor-phase PAHs contained >99.9% of the total PAH mass and were dominated by naphthalene (NAP), which varied from about 60 ng m^{-3} in Lompoc, a community with light traffic, to ∼580 ng m^{-3} in Riverside, a community traversed by ∼200,000 vehicles day^{-1}. During summer pollution episodes in urban sites, NAP concentrations reached 7–30 times annual averages. Except for summer episodes, concentrations of low MW PAHs showed small seasonal variations (∼2 times higher in winter). Similar concentrations of particle-phase PAHs were observed at all sites except for Lompoc. Benzo[*ghi*]perylene (BGP), a marker of gasoline exhaust emissions, showed the highest concentration among particle-phase PAHs, varying from 23.3 pg m^{-3} in Lompoc to 193 pg m^{-3} in Mira Loma. Benzo[*a*]pyrene and indeno[*1,2,3-cd*]pyrene, found exclusively in the particle phase, were much higher in urban sites (∼40–100 pg m^{-3}), than in Lompoc (∼12 pg m^{-3}). Winter particle-phase PAHs were 2 to 14 times higher than summer levels. Particle-phase PAHs were negatively correlated with mean air temperature in urban sites ($r = -0.50$ to -0.75), probably resulting from surface inversions occurring during winter. The data suggest that in Southern California vehicular exhaust emissions are a major contributor to particle-phase PAHs.

INTRODUCTION

While epidemiological evidence associating airborne particulate matter (PM) with adverse health effects in humans is extensive (Dockery et al. 1993; Schwartz et al. 1996; Schwartz and Neas 2000; Peters et al. 1999; Avol et al. 2001; Gauderman et al. 2000, 2002), fundamental uncertainties persist regarding specific identification of the precise physical and chemical properties of PM responsible for observed health associations. Based on presence and toxicity, a candidate component class of PM of potential importance is polycyclic aromatic hydrocarbons (PAHs). PAHs are of particular interest with respect to PM toxicity because a large fraction of their mass is found in fine particles, which is where a great deal of recent health research interest has focused (USEPA 2001). Recent studies in the Los Angeles basin have shown that PAHs are found mostly in the ultrafine mode (<0.18 um dp) near vehicular emission sources and in the accumulation mode (0.18–2.5 um dp) tens of km downwind of source emissions (Eiguren-Fernandez et al. 2003; Miguel et al. 2003). Similar results have been previously observed by Venkataraman and Friendlander (1994).

Research conducted over the last several decades have shown that several PAHs are toxic to living organisms. Studies have

---

Received 1 July 2003; accepted 23 February 2004.

The authors thank the school districts and schools participating in the Children's Health Study (California Air Resources Board Contract A033-186), for their cooperation, and for the use of facilities; Mahnaz Hakami for laboratory assistance; Barbara Zielinska for help with the sampling design; and Janet Arey, Roger Atkinson, James N. Pitts Jr., and Richard Kamens for helpful discussions and insights. Finally, we thank the reviewers for their very helpful suggestions. This research was supported by the Southern California Particle Center and Supersite (USEPA Grants #R827352-01-0 and CR-82805901). Additional investigator support (E. A. A. H. M., and A. E.-F.) was provided by a NIEHS Center Grant (SP30ES07048-02). Although the research described in this article has been funded wholly or in part by the United States Environmental Protection Agency, it has not been subjected to the Agency's required peer and policy review and therefore does not necessarily reflect the views of the Agency. No official endorsement should be inferred.

Address correspondence to Antonio H. Miguel, Southern California Particle Center and Supersite, Institute of the Environment, University of California, CHS 51.297, 650 Charles E. Young Drive South, Los Angeles, CA 90095-1772, USA. E-mail: ahmiguel@ucla.edu

revealed that heme oxygenase-1 (HO-1) expression, a sensitive marker for oxidative stress, and dithiothreitol (DTT) activity, a quantitative measure of in vitro reactive oxygen species formation, are directly correlated with the PAH and organic carbon content of ultrafine particles (Li et al. 2000, 2003). Recently, we reported that DTT activity is highly correlated with benzo[ghi]perylene, elemental carbon, and organic carbon contained in PM collected in several sites in the Los Angeles basin (Cho et al. 2003). Taken together, these results illustrate the importance of chemical composition and particle size distribution of airborne particles in understanding PM toxicity.

Vehicular PAH emissions have been estimated to contribute 35% of the total atmospheric burden in polluted and industrialized areas of the United States (Bjorseth and Ramdhal 1985), and much more in large cities such as Los Angeles. For example, in Pico Rivera, an urban community located downwind of central Los Angeles, Venkataraman and Friedlander (1994) calculated that more than 90 percent of five-ringed and larger PAHs (except for chrysene) originated from auto emissions.

Once in the atmosphere, partitioning of semivolatile PAHs will affect their atmospheric transformations as well as their dry and wet deposition during atmospheric transport. Extensive research (Pankow 1987, 1994; Kamens et al. 1988; Bidleman 1988; Wania et al. 1998; Dachs and Eisenreich 2000; Sofuoglu et al. 2001; Mader and Pankow 2001; Offenberg and Baker, 2002; Bae et al. 2002; Griffin et al. 2003 and references therein) show that partitioning is affected by several factors, including temperature, relative humidity, elemental and organic carbon content, and the PAH subcooled liquid vapor pressure. Thus, the atmospheric parameters that influence PAH gas-particle partitioning at a given site are expected to vary during the year, as meteorological and sunlight conditions change. Several studies have demonstrated the effects of these parameters on PAH partitioning (Bae et al. 2002; Gustafson and Dickhut 1997). Detailed studies of the seasonal and spatial variation of atmospheric levels of PAHs, in both vapor and particle phases, are needed in order to evaluate the effects of atmospheric transport and human exposure.

Our interest in atmospheric transport of vehicular emissions, coupled with an ongoing longitudinal investigation of the respiratory health development of schoolchildren (Gauderman et al. 2000, 2002), led us to undertake this study. This manuscript describes results from a yearlong investigation of the seasonal and spatial variation of fifteen USEPA priority PAHs in six communities located in urban and rural areas of Southern California.

EXPERIMENTAL

Sampling

Sampling was performed at six public school locations in a subset of communities participating in a multiyear chronic respiratory health study of Southern California schoolchildren (Peters et al. 1999) (see Figure 1). Communities were selected for health study participation on the basis of historical air quality data, comparable population demographics, a sufficient number of potential subjects attending public school, and the willingness of the local school district to participate. Four of the communities for which data are reported (San Dimas, Upland, Mira Loma, and Riverside) are located 40–100 km downwind and east of metropolitan Los Angeles. These "receptor" areas are

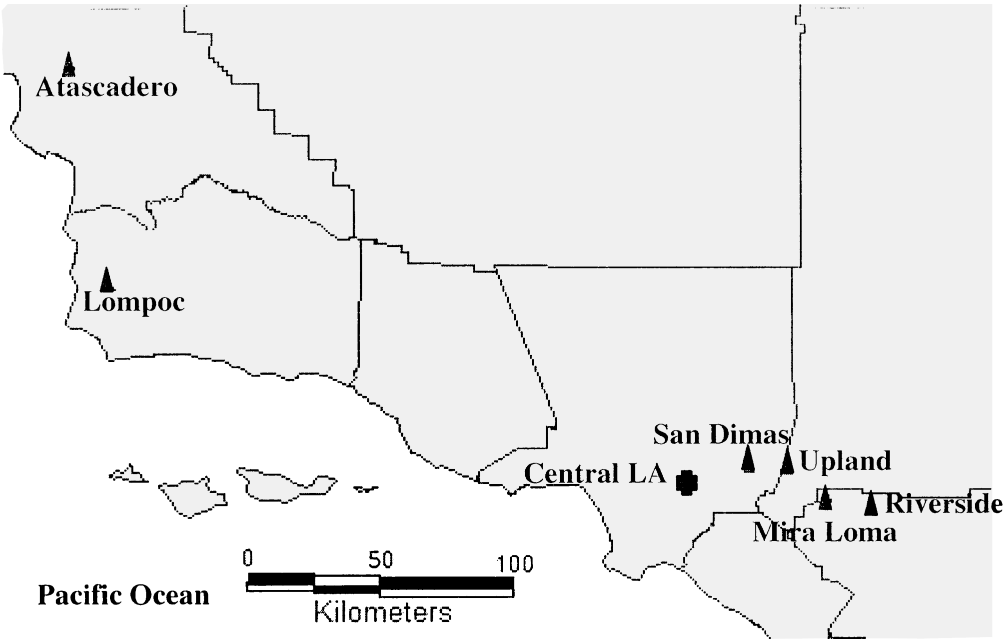

Figure 1. Sampling locations (code) in Southern California: Atascadero (ATS), Lompoc (LOM), San Dimas (SDS), Upland (UPL), Mira Loma (MRL), and Riverside (RIV).

influenced by upwind emissions enriched with secondary photochemical pollutants during transport. Ambient data from these reporting communities consistently rank among the highest reporting regional sites for ozone, PM_{10}, and $PM_{2.5}$ (Gauderman et al. 2000, 2002). The two remaining sampling sites (Lompoc and Atascadero) are communities located in counties several hundred km northwest of Los Angeles (Figure 1) in more rural regions.

At each sampling location, a Tisch Model 1202 sampler (Tisch, Cleves, OH) was deployed to obtain ambient samples. The unit contained a $PM_{2.5}$ cyclone inlet, a fall column chamber, a filter holder, a PUF-XAD-4 resin holder, an electronic controller, a mass flow meter, and a vacuum pump. This sampling train, described by Zielinska et al. (1998), is based on a hi-vol sampler arrangement reported by Zaranski et al. (1991). The sampling train used in the present study contained two quartz fiber filters (QFF; 10.4 cm diameter) and 10 g of XAD-4 resin "sandwiched" between two polyurethane foams (PUFs). XAD resins are known to have much higher collection efficiency for naphthalene than PUFs alone (Chuang et al. 1987; Zaranski et al. 1991). QFFs were baked for 16–20 h at 550°C prior to field use. In preparation for field use, PUFs were cleaned with distilled water and "compress-cleaned" using a mixture of hexane:methanol:methylene chloride (5:3:2 v/v) prior to matrix loading. The compress-cleaning procedure involved placing the PUFs in a beaker, submerging the PUFs in the cleaning mixture, and compressing the PUFs for 60 s. The compression was repeated three times, changing solvent each time. After cleaning, PUFs were dried in an oven until no solvent odor could be readily detected. XAD-4 resin was cleaned with triplicate rinses of water and methanol, using a Millipore filtering system. Cleaning was carried out in a Soxhlet system using methanol for 24 h, followed by methylene chloride for two 24 h periods. Once the XAD-4 was cleaned, it was placed in a vacuum oven at 40–50°C for 2–3 days until no odor was detected. Samplers were deployed on roofs of one-story buildings free of any local and immediate impediments to air flow. Field samples were collected every eighth day from midnight to midnight for 24 h periods at a 113 l pm flow rate. Sampled volume, measured by the sampler's mass flow meter, is corrected to 21.1°C and 1 atm. Prior to sampling, laboratory-prepared sampling matrices were stored in a conventional freezer, and their transport to and from the field was accomplished using a cooler containing frozen blue ice. Once the samples were collected and returned to the laboratory, they were placed in a freezer until extraction and analysis. Backup QFFs were used during the first weeks of each sampling period to estimate the extent of vapor-phase PAHs adsorbed on the top QFF for possible correction of the amount found in the particles deposited on the top QFF.

Chemical Analysis

Details of the PAH quantification procedure are provided elsewhere (Eiguren-Fernandez and Miguel 2003). Briefly, QFFs were extracted by ultrasonication with 15 mL of methylene chloride. The extract was filtered and the volume reduced to ~5 mL; 1 mL was used for the analysis and the rest saved in a freezer. The entire extraction procedure was performed using amber glass vials under yellow light conditions. The PUF/XAD-4/PUF sandwiches were Soxhlet extracted using hexane (10% ethylether) for two periods of 8 h. Two milliliters of the extract were utilized to measure naphthalene, acenaphthene, and fluorene. The remaining extract was concentrated using rotary evaporation to determine PAHs with higher Molecular Weight (MW). Because quartz fibers have been shown to be susceptible to sampling artifacts of organic species (OC carbon), we sampled using quartz backup filters behind the regular quartz filter during the first weeks of the study. Our results showed that the target PAHs in the backup filters were below the LOD of the analytical method. One field matrix blank was extracted and analyzed for approximately every ten samples. PAH concentrations measured in blank filters and PUF/XAD/PUF blanks were subtracted from the concentrations found in the samples. In this study, we found that the PUF/XAD/PUF system collects a minimum of 93–97% of the lower MW PAHs, including naphthalene, phenanthrene, fluoranthene, and pyrene. All PAH and EC concentrations were corrected to 1 atm and 21.1°C. SRM 1649a was used to determine the analytical procedure precision (4.2%) and recovery efficiency (85%).

RESULTS AND DISCUSSION

Spatial Variation

Observed PAH concentrations varied from pg m^{-3} to ng m^{-3} levels for the higher and the lower molecular weight PAHs (see Table 1, which displays annualized concentrations; episodic outlier concentrations were not included in the annual means). For all target PAHs, the vapor phase contained $>99.9\%$ of the mass. Observed levels of vapor phase and total (particle+vapor) PAHs were similar. Total PAH concentrations among the different sites (with the exception of Lompoc) varied between ~260 and ~607 ng m^{-3}. The lowest PAH levels in both phases were found in Lompoc, a rural community with no major freeways. Similar PAH levels were observed in Atascadero, a community also considered a rural area (compared to urban Los Angeles), and in the urban sites. Naphthalene concentrations were by far the highest of all determined PAHs, contributing 91% of the measured total PAH mass. Typically, naphthalene levels were three orders of magnitude higher in concentration than most other PAHs. Several episodic days were observed during the sampling period when PAH levels (naphthalene to phenanthrene) were up to 10 times higher than typical observed concentrations. As an example, episode events were observed in May/June 2002, when measured levels of NAP were ~7 to 30 times higher than the average concentrations found. On May 8, vapor-phase NAP concentrations reached 6,336 ng m^{-3} in Riverside and 5,618 ng m^{-3} in San Dimas. Two days later, in Atascadero, a sample containing 2,309 ng m^{-3} NAP was observed. On June 30, NAP concentrations reached 4,290 ng m^{-3} in Mira Loma. Arey et al. (1989)

Table 1
PAH code, molecular weight, subcooled liquid vapor pressure (atm), and annual averages for vapor- and particle-phase concentrations (±SD) from May 2001 to July 2002

PAH	Code	MW	(log p_L°)^a	Atascadero	Lompoc	San Dimas	Upland	Mira Loma	Riverside
Particle-phase (pg m^{-3})									
Naphthalene	NAP	128	−3.53	1.82 ± 3.15	15.2 ± 20.3	7.21 ± 6.95	7.13 ± 12.3	4.85 ± 8.41	6.72 ± 11.6
Acenaphthene	ACE	154	−4.84	2.09 ± 3.61	2.56 ± 2.46	3.17 ± 5.49	0.39 ± 0.67	0.76 ± 1.31	1.32 ± 2.29
Fluorene	FLU	166	−5.18	5.91 ± 10.2	8.39 ± 11.2	9.85 ± 14.8	4.89 ± 4.55	2.35 ± 4.07	7.68 ± 10.2
Phenanthrene	PHE	178	−6.18	4.63 ± 6.83	1.46 ± 1.86	23.8 ± 14.7	32.6 ± 25.5	36.5 ± 29.0	27.3 ± 21.9
Anthracene	ANT	178	−6.23	0.16 ± 0.15	2.05 ± 2.62	3.18 ± 3.45	1.87 ± 1.85	2.77 ± 4.80	2.30 ± 2.60
Fluoranthene	FLT	202	−7.24	6.11 ± 13.7	4.51 ± 7.29	31.1 ± 41.7	40.8 ± 16.7	47.9 ± 70.2	24.3 ± 35.4
Pyrene	PYR	202	−7.48	17.3 ± 1.26	5.51 ± 5.60	48.0 ± 21.1	54.2 ± 11.2	69.5 ± 50.1	37.7 ± 21.3
Benz[a]anthracene	BAA	228	−8.49	24.2 ± 38.1	6.26 ± 8.19	29.8 ± 39.5	24.4 ± 23.3	41.2 ± 58.0	19.6 ± 27.4
Chrysene	CRY	228	−8.64	21.4 ± 25.8	7.98 ± 10.4	46.4 ± 40.6	39.5 ± 26.8	56.7 ± 66.7	32.0 ± 32.9
Benzo[*b*]fluoranthene	BBF	252	−9.63	64.8 ± 94.7	11.7 ± 15.3	79.0 ± 79.7	53.0 ± 36.0	99.1 ± 114	55.5 ± 60.4
Benzo[*k*]fluoranthene	BKF	252	−9.63	46.1 ± 68.4	5.80 ± 7.65	36.9 ± 36.0	22.7 ± 20.5	52.8 ± 53.5	26.8 ± 28.0
Benzo[*a*]pyrene	BAP	252	−10.0	88.1 ± 130	9.01 ± 11.9	76.2 ± 93.2	37.4 ± 42.9	99.9 ± 131	46.8 ± 54.2
Indeno[*1,2,3-cd*]pyrene	IND	276	−10.0	86.5 ± 129	12.3 ± 15.9	78.8 ± 91.9	49.1 ± 37.0	100 ± 105	52.4 ± 64.4
Dibenz[a,h]anthracene	DBA	278	−10.7	11.1 ± 18.4	2.09 ± 2.79	7.74 ± 10.4	5.67 ± 5.63	12.1 ± 13.8	5.54 ± 8.73
Benzo[*ghi*]perylene	BGP	276	−10.7	107 ± 128	23.3 ± 30.5	174 ± 147	94.3 ± 71.0	193 ± 187	112 ± 99.6
Vapor-phase (ng m^{-3})									
NAP				266 ± 171	58.5 ± 8.87	502 ± 404	207 ± 61.1	518 ± 436	575 ± 581
ACE				2.51 ± 2.18	2.16 ± 1.39	5.83 ± 2.39	10.6 ± 6.78	12.9 ± 3.55	4.58 ± 2.00
FLU				3.03 ± 2.37	4.04 ± 4.52	4.02 ± 3.79	21.4 ± 21.1	22.8 ± 20.7	5.45 ± 1.43
PHE				11.4 ± 3.43	7.32 ± 1.75	19.8 ± 8.07	17.8 ± 5.48	19.4 ± 7.69	18.5 ± 13.4
ANT				0.73 ± 0.29	0.13 ± 0.15	1.40 ± 1.07	0.36 ± 0.19	0.59 ± 0.40	1.10 ± 0.87
FLT				0.82 ± 2.14	^{b}	1.58 ± 0.48	0.04 ± 0.05	0.12 ± 0.02	1.14 ± 0.79
PYR				1.68 ± 0.44	^{b}	0.61 ± 0.56	0.32 ± 0.08	0.35 ± 0.14	0.79 ± 0.54
BAA				0.24 ± 0.12	^{b}	0.07 ± 0.10	0.03 ± 0.05	^{b}	0.07 ± 0.08
CRY				0.38 ± 0.18	^{b}	0.30 ± 0.35	0.12 ± 0.20	^{b}	0.26 ± 0.13
BBF				^{b}	^{b}	^{b}	^{b}	^{b}	^{b}
BKF				^{b}	^{b}	^{b}	^{b}	^{b}	^{b}
BAP				^{b}	^{b}	^{b}	^{b}	^{b}	^{b}
IND				^{b}	^{b}	^{b}	^{b}	^{b}	^{b}
DBA				^{b}	^{b}	^{b}	^{b}	^{b}	^{b}
BGP				^{b}	^{b}	^{b}	^{b}	^{b}	^{b}

[a] atm at 25°C, data from several studies compiled in Calvert et al. (2002).

[b] < LOD: below limit of detection. Site locations and codes are shown in Figure 1.

observed naphthalene episode events in Glendora (~6 km west of San Dimas) during a moderately high photochemical air pollution period from August 12–21, 1986. They reported average daytime and nighttime naphthalene concentrations of 3,100 and 4,300 ng m^{-3}, respectively. Lower photochemical activity, wood burning (fire places, forest fires) and surface inverions may contribute to higher atmospheric levels of naphthalene during the winter. However, explanations for the observed summer episode events are not clear.

Particle-phase PAH concentrations were similar in all sites, with the exception of Lompoc, where very low concentrations were observed during all seasons. Benzo[ghi]perylene, a marker for gasoline exhaust emissions (Miguel et al. 1998; Marr et al. 1999), was the principal contributor to the total particle-phase PAH mass at all six sites, suggesting that vehicular exhaust emissions constitute a major source of particle-phase PAHs in the Los Angeles basin.

Seasonal Variation

The seasonal variability of PAH concentration and vapor–particle partitioning in the atmosphere have been reported for other cities, including Chicago, London, and Hong Kong (Cotham and Bidleman 1995; Gustafson and Dickhut 1997; Odabasi et al. 1999; Kendall et al. 2001; Lee et al. 2001). In those studies, significant differences were observed in both PAH concentrations and in vapor-particle partitioning. In order to evaluate the effect of season on the measured PAH levels, we grouped our results in three different seasons (hot—daily average above 22.9°C, warm, and cold—daily average below 13.7°C) based on the average temperature prevalent during the

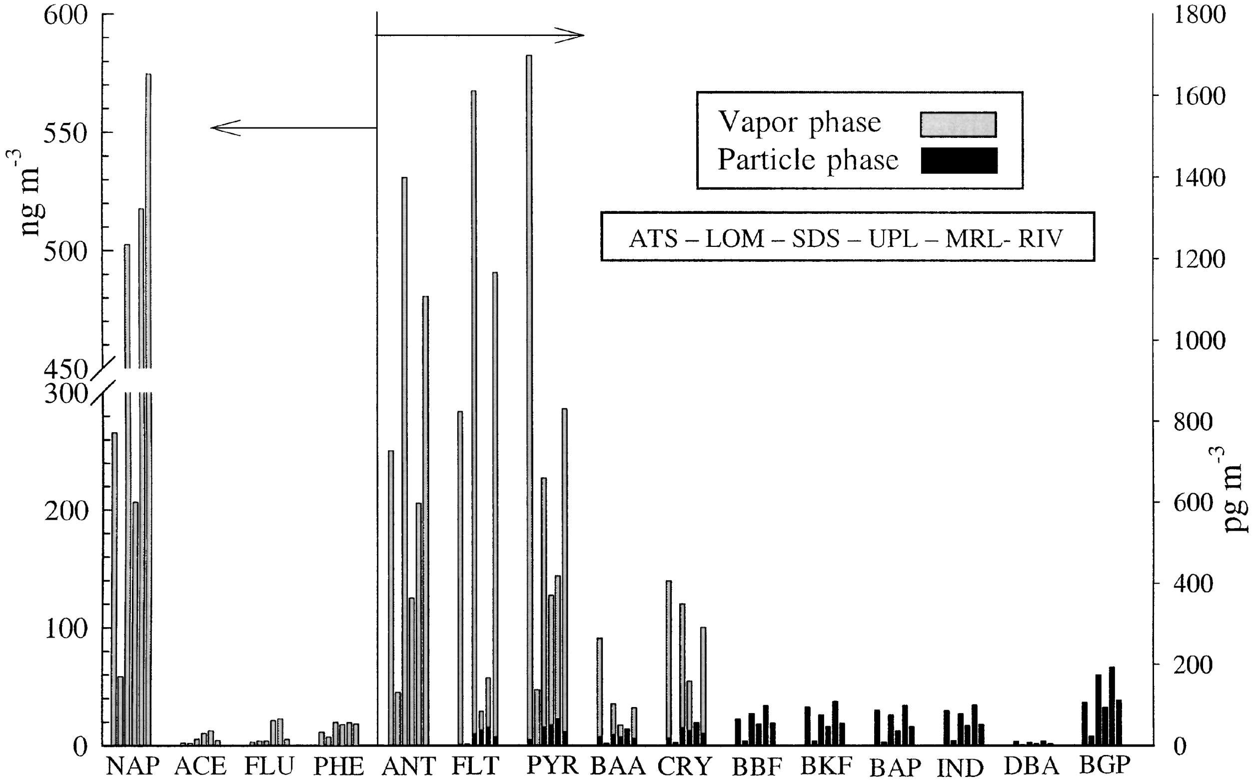

Figure 2. Annual averages for total PAH concentrations (vapor + particle phase) for individual species.

sampling campaign. NAP, ACE, FLU, PHE, and ANT were found mostly in the vapor phase while the semivolatile PAHs (FLT, PYR, BAA, and CRY), with subcooled liquid vapor pressure (at 25°C) log p_L^o between −7.24 and −8.64, were observed in both phases. PAHs with lower vapor pressures (BBF, BKF, BAP, IND, DBA, and BGP) were found predominantly in the particle phase (Figure 2). Low molecular weight PAHs displayed small variations in concentration during the three seasons, with slightly higher concentrations during the cold seasons (Figure 3) both in the urban and the rural communities. The cold/hot season concentration ratio for the volatile PAHs varied between 0.77 (Lompoc) and 5.7, with an average of 2.2 (Table 2). Particle-phase PAH concentrations increased significantly with decreasing ambient temperature (Figure 4), probably as a result of surface inversions, lower photochemical activity, and wood burning occurring in winter. In Riverside, the total particle-phase PAH concentration increased from 180 to 960 pg m^{-3} from the hot season to the cold season (Table 2). The ratios varied between 2.8 and 14, with an average of 7.4. The cold/hot season ratio increased with decreasing PAH vapor pressure. Among the six

Table 2

Cold and hot season averages for sum of PAH concentrations in the given phase and cold/hot seasons concentration ratios

	Particle phase (ng m^{-3})[a]			Vapor phase (ng m^{-3})[b]		
Site	Cold season	Hot season	Cold/hot ratio	Cold season	Hot season	Cold/hot ratio
Atascadero	1.22	0.12	10.2	228	98.9	2.30
Lompoc	0.28	0.02	14.0	86.8	113	0.77
San Dimas	1.36	0.30	4.53	406	212	1.92
Upland	0.76	0.27	2.81	240	87.1	2.76
Mira Loma	1.81	0.24	7.54	491	86.4	5.69
Riverside	0.96	0.18	5.33	324	217	1.49
Mean ratio			7.4			2.2

[a] PAHs measured on the filter.

[b] PAHs measured on the PUF/XAD-4/PUF.

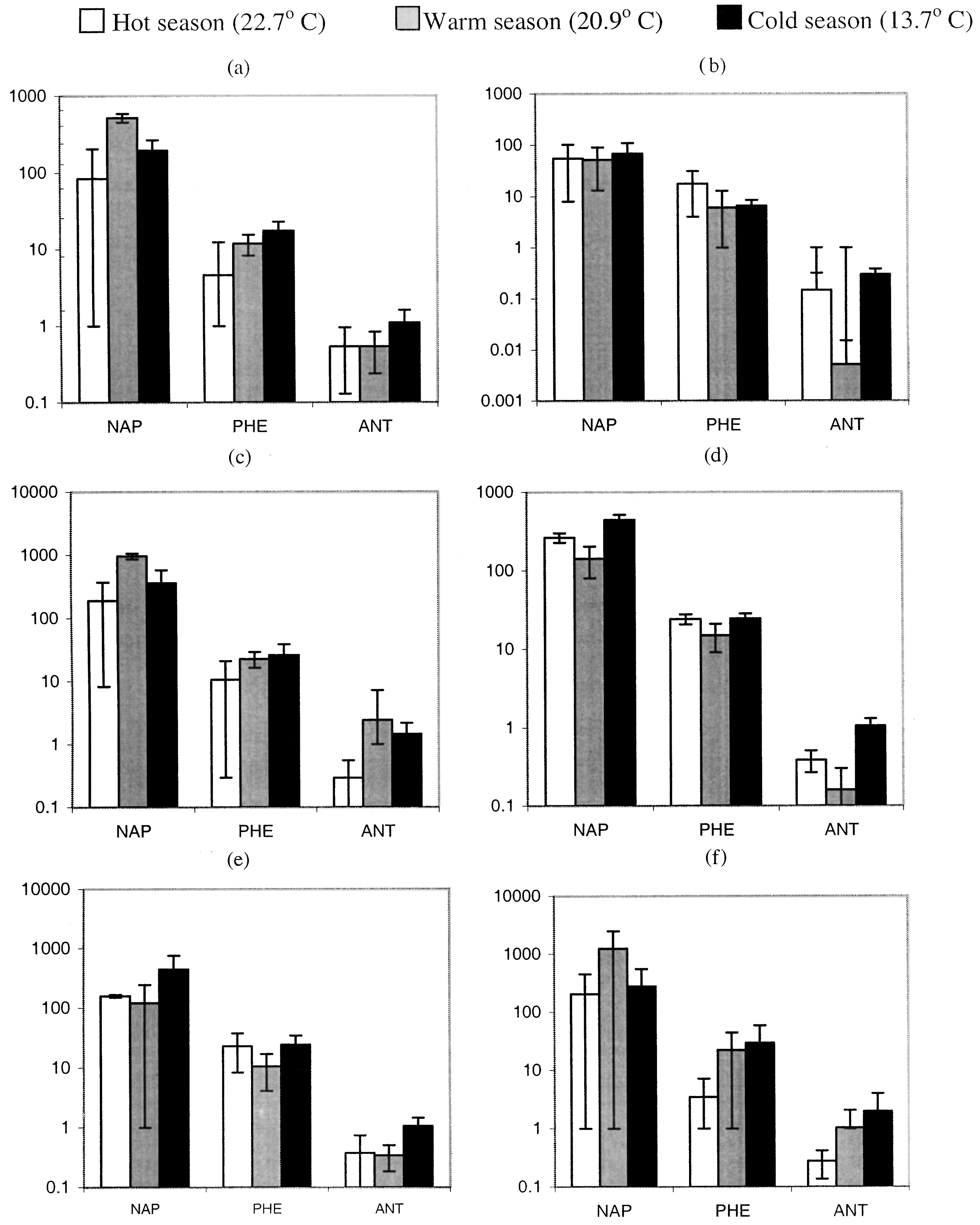

Figure 3. Seasonal concentration averages (ng m^{-3}) observed for vapor-phase PAHs at the six community sites. Error bars represent the standard deviations of the measurement: (a) Atascadero, (b) Lompoc, (c) San Dimas, (d) Upland, (e) Mira Loma, and (f) Riverside.

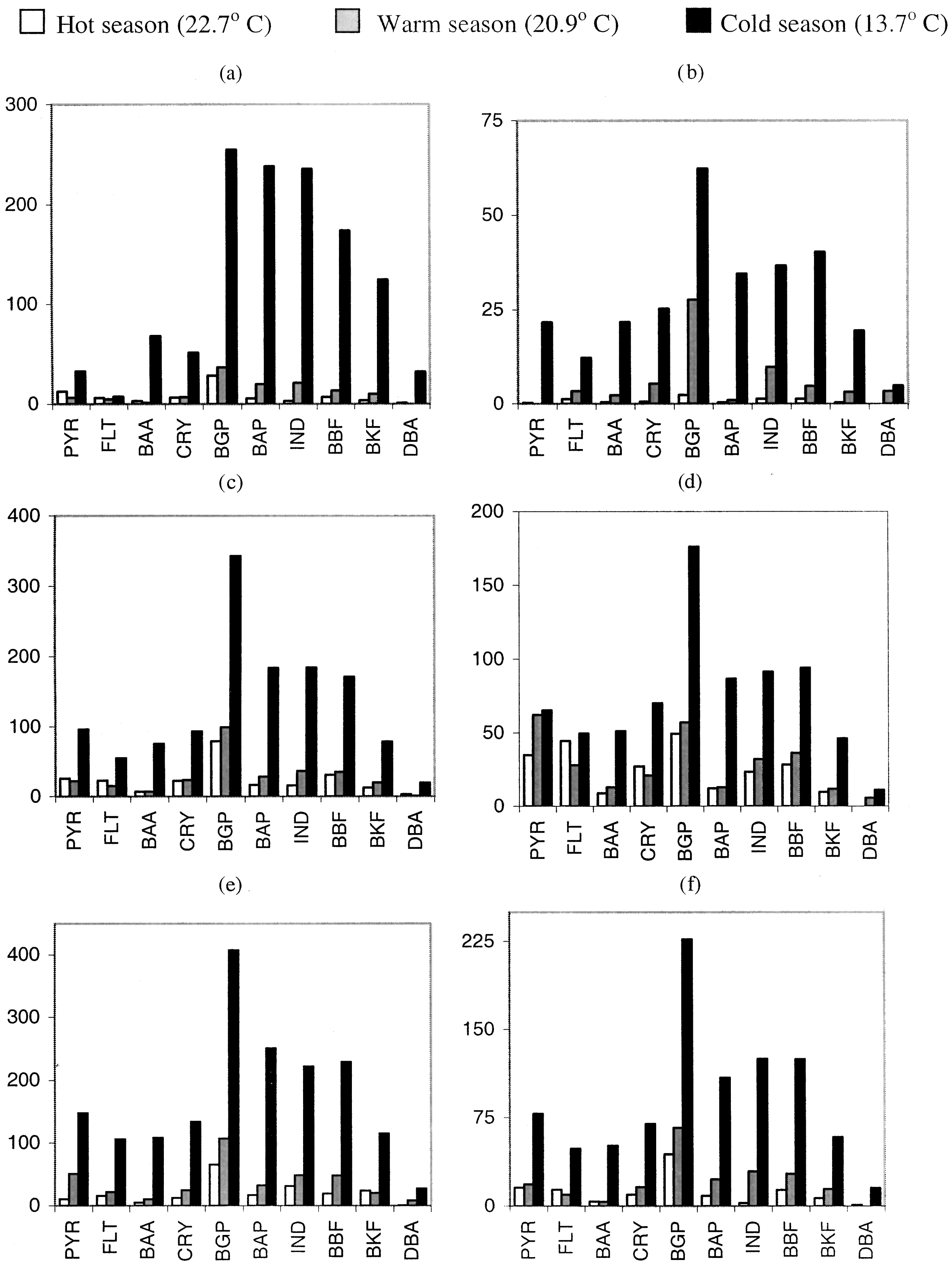

Figure 4. Seasonal concentration averages (pg m^{-3}) observed for particle-phase PAHs at the six community sites: (a) Atascadero, (b) Lompoc, (c) San Dimas, (d) Upland, (e) Mira Loma, and (f) Riverside.

Table 3

Pearson correlation coefficients between mean ambient temperature and annual concentration of representantive PAHs in the six study communities

	Particle phase						Vapor phase		
Community\PAH	BGP	BAP	IND	BKF	BBF	DBA	NAP	PHE	ANT
Atascadero	−0.64	−0.60	−0.67	−0.66	−0.65	−0.64	−0.03	−0.56	−0.40
Lompoc	−0.33	−0.42	−0.46	−0.42	−0.47	−0.26	−0.29	0.12	−0.48
San Dimas	−0.64	−0.74	−0.77	−0.75	−0.70	−0.67	−0.43	−0.20	−0.43
Upland	−0.57	−0.58	−0.59	−0.60	−0.54	−0.55	−0.16	0.17	−0.38
Mira Loma	−0.57	−0.64	−0.60	−0.65	−0.65	−0.59	0.00	−0.37	−0.70
Riverside	−0.48	−0.58	−0.60	−0.54	−0.55	−0.52	0.02	−0.27	−0.33

sites, a cold/hot season ratio of 14 was found for particle-phase PAHs in rural Lompoc, the community with the lowest PAH levels. A number of factors may be responsible for observed increases in particle-phase PAH concentrations during the cold season, including lower ambient temperatures, inversion layer height, and slower photochemistry: PAHs adsorbed on particulate organic matter, or on glass and Teflon-impregnated glass fiber filters, are susceptible to ozone degradation (Pitts et al. 1986). In addition, different sources may have contributed significant emissions, e.g., wood combustion in fireplaces and home heaters, during the winter months. The effect of a lower inversion layer on the PAH concentration is expected to be similar for both the vapor phase and the fine-particle PAHs. Compared with other cities, such as Chicago, and the northeastern U.S., ambient temperatures in southern California do not vary widely during the different seasons (we observed a temperature change of ∼9°C between the hot and cold season).

Correlations Between Measured PAH Levels and Ambient Temperature

To investigate the importance of temperature and how it affects ambient PAH concentration, we evaluated the correlation between ambient temperature and PAH concentration. The resulting Pearson correlation coefficients (r) are shown in Table 3 for the more representative PAHs. Correlation coefficients were mostly negative; concentrations increased as temperature decreased. PAHs found mostly in the vapor phase showed a significantly smaller temperature effect than particle-phase PAHs. Compounds that are found mostly in the vapor phase have low vapor/particle partition coefficients (Pankow and Bidleman 1991) and it is therefore expected that their vapor/particle distribution will be less affected by temperature. Values were generally lower in Lompoc, but similar for the other communities, and in agreement with other studies (Sofuoglu et al. 2001; Gigliotti et al. 2000).

SUMMARY AND CONCLUSIONS

Ambient PAH concentrations were measured over a one-year sampling period for six Southern California communities, including both rural upwind and metropolitan downwind sites from Los Angeles. Observed vapor- and fine-particle–phase PAHs showed significant seasonal differences in the rural and the urban communities studied. The highest seasonal difference was observed for particle-phase PAHs, which increased with decreasing ambient temperature. Rural site PAH levels were significantly lower than communities located downwind from Los Angeles. At all sites, PAH mass was dominated by the vapor phase with more than 99.9% of mass. Total PAH levels were dominated by naphthalene, which was typically 1000s of times higher in concentration than other measured PAHs. Occasional episodic events were captured with elevated PAH levels, but the explanation for these elevated occurrences will require further investigation. PAH concentrations correlated well with their subcooled liquid vapor pressure. We conclude that exhaust emissions from motor vehicles play an important role in observed particle-phase PAH levels.

REFERENCES

Arey, J., Atkinson, R., Zielinska, B., and McElroy, P. A. (1989). Diurnal Concentrations of Volatile Polycyclic Aromatic Hydrocarbons and Nitroarenes During a Photochemical Air Pollution Episode in Glendora, California, *Environ. Sci. Technol.* 23:321–327.

Avol, E. L., Gauderman, W. J., Tan, S. M., London, S., and Peters, J. M. (2001). Respiratory Effects of Relocating to Areas of Differing Air Pollution Levels, *Am. Rev. Rep. Crit. Care. Med.* 164:2067–2072.

Bae, S. Y., Yi, S. M., and Kim, Y. P. (2002). Temporal and Spatial Variations of the Particle Size Distribution of PAHs and Their Dry Deposition Fluxes in Korea, *Atmos. Environ.* 34:5491–5500.

Bidleman, T. F. (1988). Atmospheric Processes—Wet and Dry Deposition of Organic Compounds Are Controlled by Their Vapor Particle Partitioning, *Environ. Sci. Technol.* 22:361–367.

Bjorseth, A., and Ramdhal, T. (1985). Emission sources and recent progress in analytical chemistry, In Handbook of Polycyclic Aromatic Hydrocarbons, edited by A. Bjorseth and T. Ramdhal. Marcel Decker, New York, Vol. 2, pp. 1–25.

Calvert, J. G, Atkinson, R., Becker, K. H., Kamens, R. M., Seinfeld, J. H., Wallington, T. J., and Yarwood, G. (2002). *The Mechanisms of Atmospheric Oxidation of Aromatic Hydrocarbons*, Oxford University Press, New York, p. 348.

Chuang, J. C., Hannan, S. W., and Wilson, N. K. (1987). Field Comparison of Polyurethane Foam and XAD-2 Resin for Air Sampling for Polynuclear Aromatic Hydrocarbons, *Environ. Sci. Technol.* 21:798–804.

Cho, A. K., Schmitz, D. A., Kumagai, Y., Sioutas, C., Misra, C., Singh, M., Miguel, A. H., Eiguren-Fernandez, A., and Froines, J. R. (2003). Redox Activity of Airborne Particulate Matter (PM) at Different Sites in the Los Angeles Basin, Submitted for publication.

Cotham, W. E., and Bidleman, T. F. (1995). Polycyclic Aromatic Hydrocarbons and Polychlorinated-Biphenyls in Air at an Urban and Rural Site near Lake Michigan, *Environ. Sci. Technol.* 29:2782–2789.

Dachs, J., and Eisenreich, S. (2000). Adsorption onto Aerosol Soot Carbon Dominates Gas-Particle Partitioning of Polycyclic Aromatic Hydrocarbons, *Environ. Sci. Technol.* 34:3690–3697.

Dockery, D. W., Pope, C. A., Xu, X. P., Spengler, J. D., Ware, J. H., Fay, M. E., Ferris, B. G., and Speizer, F. E. (1993). An Association Between Air-Pollution And Mortality In 6 United-States Cities, *N. Engl. J. Med.* 329:1753–1759.

Eiguren-Fernandez, A., and Miguel, A. H. (2003). Determination of Semivolatile and Particulate Polycyclic Aromatic Hydrocarbons in SRM 1649a and $PM_{2.5}$ Samples by HPLC-Fluorescence, *Polycyclic Aromatic Compounds* 23:193–205.

Eiguren-Fernandez, A., Miguel, A. H., Jaques, P., and Sioutas, C. (2003). Evaluation of a Denuder-MOUDI-PUF Sampling System to Measure the Size Distribution of Semivolatile Polycyclic Aromatic Hydrocarbons in the Atmosphere, *Aerosol Sci. Technol.* 37:201–209.

Gauderman, W. J., Gilliland, G. F., Vora, H., Avol, E., Stram, D., McConnell, R., Thomas, D., Lurmann, F., Margolis, H. G., Rappaport, E. B., Berhane, K., and Peters, J. M. (2002). Association Between Air Pollution and Lung Function Growth in Southern California Children—Results from a Second Cohort, *Am. J. Resp. Crit. Care Med.* 166:76–84.

Gauderman, W. J., McConnell, R., Gilliland, F., London, S., Thomas, D., Avol, E., Vora, H., Berhane, K., Rappaport, E. B., Lurmann, F., Margolis, H. G., and Peters, J. M. (2000). Association Between Air Pollution and Lung Function Growth in Southern California Children, *Am. J. Resp. Crit. Care Med.* 162:1383–1390.

Gigliotti, C. L., Dachs, J., Nelson, E. D., Brunciak, P. A., and Eisenreich, S. J. (2000). Polycyclic Aromatic Hydrocarbons in the New Jersey Costal Atmosphere, *Environ. Sci. Technol.* 34:3547–3554.

Griffin, R. J., Nguyen, K., Dabdub, D., and Seinfeld J.H. (2003). A Coupled Hydrophobic-Hydrophilic Model for Predicting Secondary Organic Aerosol Formation, *J. Atmos. Chem.* 44:171–190.

Gustafson, K. E., and Dickhut, R. M. (1997). Particle/Gas Concentrations and Distributions of PAHs in the Atmosphere of Southern Chesapeake Bay, *Environ. Sci. Technol.* 31:140–147.

Kamens, R. M., Guo, Z., Fulcher, J. N., and Bell, D. A. (1988). The Influence of Humidity, Sunlight, and Temperature on the Daytime Decay of Polyaromatic Hydrocarbons on Atmospheric Soot Particles, *Environ. Sci. Technol.* 22:103–108.

Kendall, M., Hamilton, R. S., Watt, J., and Williams, I. D. (2001). Characterization of Selected Speciated Organic Compounds Associated with Particulate Matter in London, *Atmos. Environ.* 35:2483–2495.

Lee, S. C., Ho, K. F., Chan, L. Y., Zielinska, B., and Chow, J. C. (2001). Polycyclic Aromatic Hydrocarbons (PAHs) and Carbonyl Compounds in Urban Atmosphere of Hong Kong, *Atmos. Environ.* 35:5949–5960.

Li, N., Sioutas, C., Cho, A., Schmitz, D., Misra, C., Sempf, J., Wang, M. Y., Oberley, T., Froines, J., and Nel, A. (2003). Ultrafine Particulate Pollutants Induce Oxidative Stress and Mitochondrial Damage, *Environ. Health Persp.* 111:455–460.

Li, N., Venkatesan M. I., Miguel, A., Kaplan, R., Gujuluva, C., Alam, J., and Nel, A. (2000). Induction of Heme Oxygenase-1 Expression in Macrophages by Diesel Exhaust Particle Chemicals and Quinone Via the Antioxidant-Responsive Element, *J. Immunol.* 165:3393–3401.

Mader, B. T., and Pankow, J. F. (2001). Gas/Solid Partitioning of Semivolatile Organic Compounds (SOCs) to Air Filters. 2. Partitioning of Polychlorinated Dibenzodioxins, Polychlorinated Dibenzofurans, and Polycyclic Aromatic Hydrocarbons to Quartz Fiber Filters, *Atmos. Environ.* 35:1217–1223.

Marr, L. C., Kirchstetter, T. W., Harley, R. A., Miguel, A. H., Hering, S. V., and Hammond, S. K. (1999). Characterization of Polycyclic Aromatic Hydrocarbons in Motor Vehicle Fuels and Exhaust Emissions, *Environ. Sci. Technol.* 33:3091–3099.

Miguel, A. H., Eiguren-Fernandez, A., Jaques, P. A., Froines, F. R., Grant, W. L., Mayo, P. R., and Sioutas, C. (2003). Seasonal Variation of the Particle Size Distribution of Polycyclic Aromatic Hydrocarbons and of Major Aerosol Species in Claremont, California, *Atmos. Environ.* In press.

Miguel, A. H., Kirchstetter, T.W., Harley, R. A., and Hering, S. V. (1998). On-road emissions of particulate polycyclic aromatic hydrocarbons and black carbon from gasoline and diesel vehicles, *Environ. Sci. Technol.* 32:450–455.

Odabasi, M., Vardar, N., Sofuoglu, A., Tasdemir, Y., and Holsen, T. M. (1999). Polycyclic Aromatic Hydrocarbons (PAHs) in Chicago Air, *Sci. Total Environ.* 227:57–67.

Offenberg, J. H., and Baker, J. E. (2002). The Influence of Aerosol Size and Organic Carbon Content on Gas/Particle Partitioning of Polycyclic Aromatic Hydrocarbons (PAHs), *Atmos. Environ.* 36:1205–1220.

Pankow, J. F. (1987). Review and Comparative Analysis of the Theories on Partitioning Between the Gas and Aerosol Particulate Phases in the Atmosphere, *Atmosp. Environ.* 21:2275–2283.

Pankow, J. F. (1994). An Adsorption Model of the Gas/Aerosol Partitioning Involved in the Formation of Secondary Organic Aerosol, *Atmos. Environ.* 28:189–193.

Pankow, J. F., and Bidleman, T. F. (1991). Effects of Temperature, *TSP* and Per Cent Non-exchangeable Material in Determining the Gas-Particle Partitioning of Organic Compounds, *Atmos. Environ.* 25A:2241–2249.

Peters, J. M., Avol, E. L., Navidi, W., London, S. J., Gauderman, W. J., Lurmann, F., Linn, W., Margolis, H., Rappaport, E., Gong, H. Jr., and Thomas, D. (1999). A Study of Twelve Southern California Communities with Differing Levels and Types of Air Pollution. I. Prevalence of Respiratory Morbidity, *Am. J. Respir. Crit. Care Med.* 159:760–767.

Pitts, Jr., J. N., Paur, H.-R., Zielinska, B., Arey, J., Winer, A.M., Ramdahl, T., and Mejia, V. (1986). Factors Influencing the Reactivity of Polycyclic Aromatic Hydrocarbons Adsorbed on Filters and Ambient POM with Ozone, *Chemosphere* 15:675–685.

Schwartz, J., Spix, C., Touloumi, G., Bacharova, L., Barumamdzadeh, T., leTertre, A., Piekarksi, T., deLeon, A. P., Ponka, A., Rossi, G., Saez, M., and Schouten, J. P. (1996). Methodological Issues in Studies of Air Pollution and Daily Counts of Deaths or Hospital Admissions, *J. Epidemiol. Commun.* H 50: (Suppl. 1) S3–S11.

Schwartz, J., and Neas, L. M. (2000). Fine Particles are More Strongly Associated Than Coarse Particles with Acute Respiratory Health Effects in Schoolchildren, *Epidemiology* 11:6–10 .

Sofuoglu, A., Odabasi, M., Tasdemir, Y., Khalili, N. R., and Holsen, T. M. (2001). Temperature Dependence of Gas-Phase Polycyclic Aromatic Hydrocarbon and Organochlorine Pesticide Concentrations in Chicago Air, *Atmos. Environ.* 35:6503–6510.

United States Environmental Protection Agency (USEPA). (2001). *Air Quality Criteria for Particulate Matter, Second External Review Draft (EPA600/P-99-002aB).* United States Environmental Protection Agency Office of Research and Development.

Venkataraman, C., and Friedlander, S. K. (1994). Source Resolution of Fine Particulate Polycyclic Aromatic-Hydrocarbons Using a Receptor Model Modified for Reactivity, *J. Air Waste Manag. Assoc.* 44:1103–1108.

Wania, F., Haugen, J. E., Lei, Y. D., and Mackay, D. (1998). Temperature Dependence of Atmospheric Concentrations of Semivolatile Organic Compounds, *Environ. Sci. Technol.* 32:1013–1021.

Zaranski, M. T., Patton, G. W., McConnell, L. L., Bidleman, T. F., and Mulik, J. D. (1991). Collection of Nonpolar Organic Compounds from Ambient Air Using Polyurethane Foam-Granular Adsorbent Sandwich Cartridges, *Anal. Chem.* 63:1228–1232.

Zielinska, B., Fujita, E., Sagebiel, J., Harshfield, G., Uberna, E., Hayes, T., and Keene, F. (1998). Arizona Hazardous Air Pollutants Monitoring Program, *J. Air Waste Manag. Assoc.* 48:1038–1050.