
Atmospheric concentrations of PAH, pesticides, and other semi-volatile organic compounds in the Los Angeles coastal region

Lisa D. Sabin, Kenneth C. Schiff, Jeong Hee Lim¹
and Keith D. Stolzenbach¹

ABSTRACT - Emissions of semi-volatile organic compounds into the atmosphere and subsequent deposition may contribute to the contamination observed in waterbodies throughout the Los Angeles region. However, few studies have evaluated the significance of atmospheric deposition of semi-volatile organic compounds, particularly in the Los Angeles air basin. The purpose of this study was to measure semi-volatile organic compounds in ambient air in the coastal Los Angeles basin to determine whether the atmosphere is a significant potential transport mechanism of these contaminants to local waterbodies. The target constituents included polynuclear aromatic hydrocarbons (PAHs), organophosphorus and organochlorine pesticides (diazinon, chlorpyrifos, malathion, toxaphene, DDT), and other chlorinated hydrocarbons (PCBs). Four seasonal measurements were made at each of six sites in proximity to waterbodies impacted by these organic compounds. Air concentrations were measured using a high-volume sampler equipped with a quartz fiber filter and a polyurethane foam plug, and analyzed using gas chromatography with mass spectrometry (GC-MS) detection. PAHs were detected in 96% of all samples, with concentrations ranging from 3 ng/m³ to 132 ng/m³. Ratios of individual PAH compounds indicated transportation-related processes, including gasoline and diesel combustion, were likely sources near the study sites. The detection of PAHs at all sites during all seasons indicates the potential for cross-media transport into waterbodies of concern. In contrast, infrequent detection and only low concentrations (< 1 ng/m³) of organophosphorus and organochlorine compounds were observed in this study, indicating chronically high atmospheric concentrations of these compounds are not a widespread problem in coastal Los Angeles.

INTRODUCTION

Recent studies suggest atmospheric deposition represents a significant portion of waterbody contaminant loading relative to other sources for nutrients, trace metals, and semi-volatile organic contaminants (Duce *et al.* 1991, Baker *et al.* 1994, Scudlark *et al.* 1994, Wu *et al.* 1994). Atmospheric deposition estimates accounted for 85% of PCB inputs to the Great Lakes region (Eisenreich *et al.* 1981). Similarly, atmospheric deposition was responsible for 20 kg/year to 400 kg/year of PAH compounds, 38 kg/year of PCB to the Chesapeake Bay (Leister and Baker 1994), and 2 tons/year of PAH to Galveston Bay, Texas (Park *et al.* 2001).

Atmospheric deposition of organic compounds in Southern California remains largely unmeasured despite the fact that the greater Los Angeles metropolitan area exhibits among the worst air quality in the nation (SCAQMD 2000). The poor air quality is partly a function of population (> 10 million), numerous industries, an extensive freeway system, and heavy traffic congestion, which culminate in high emissions of organic compounds to the atmosphere. In addition, 3.5 million pounds of pesticides were applied in Los Angeles County during 2001, including agricultural, commercial, and private uses (DPR 2002). Regardless of the large number of potential sources, ambient air concentrations of many semi-volatile petroleum and pesticide compounds in the Los Angeles region have not been well characterized.

Data on atmospheric concentrations and deposition of semi-volatile organic compounds may be limited in Southern California because the current monitoring system does not focus on ecological health.

¹Department of Civil and Environmental Engineering, University of California, Los Angeles, CA 90095

Instead, monitoring of air quality in the Los Angeles air basin is focused on smog and its precursors (NO_x , SO_x , etc.), and fine aerosols ($\text{PM}_{2.5}$) relative to human health. Of the limited monitoring for organic contaminants that does occur, the primary species are volatile compounds that are most easily inhaled. However, in aquatic environments, semi-volatile organic compounds are of greater concern. PAH, organophosphorus and organochlorine pesticides (diazinon, chlorpyrifos, malathion, toxaphene, DDT), and other chlorinated hydrocarbons (PCBs) can accumulate in sediments, resulting in toxicity and/or bioaccumulation in aquatic organisms. For example, PAHs have been observed in sediments at the mouths of urban watersheds throughout the Southern California region (Anderson and Gossett 1987, Zeng *et al.* 1997). Organophosphorus pesticides have been observed in runoff from urban watersheds and have been identified as the primary toxicant to the freshwater invertebrate *Ceriodaphnia dubia* (Schiff *et al.* 2002, Schiff and Sutula *in press*). Chlorinated pesticides and PCBs have been observed in the tissues of fish and invertebrates (Mearns *et al.* 1991, Schiff and Allen 2000).

The goal of this study was to measure semi-volatile organic compounds including organophosphorus and organochlorine pesticides, PCBs, and PAHs in ambient air within the coastal Los Angeles air basin. The primary objective was to determine whether these compounds were present in ambient air. For compounds with measurable concentrations in ambient air, the secondary objective was to characterize the concentrations using three methods: (1) assessment of atmospheric concentrations among coastal watersheds; (2) assessment of atmospheric concentrations among seasons; and (3) assessment of partitioning between aerosol and gas phases. For consistently detected compounds, atmospheric deposition may be a potential contributor to water quality problems identified in local waterbodies. This clearly has an impact on how environmental managers pursue potential cross-media transport of organic compounds in the Los Angeles coastal region. Ultimately, if these compounds are found in ambient air, then environmental managers (both air and water) may wish to identify specific sources of these compounds to air and measure deposition to nearby waterbodies or their surrounding watersheds. The information on the spatial and temporal patterns, as well as the partitioning of the constituents between aerosol and gas phases, will aid in focusing the addi-

tional management needs to the times and places of greatest importance.

METHODS

Approach

Measurements of atmospheric concentrations of semi-volatile organic compounds were made at six sampling sites in the Los Angeles coastal air basin (Table 1). Each site was sampled once in each of four seasons, corresponding approximately to the following schedule: summer (August-September); fall (November-December); winter (January-March); and spring (April-June). All samples were collected for 24 h to 48 h, and the total air volume collected per sample ranged from 345 m^3 to 750 m^3 . Sample volumes and flow rates were increased during the winter and spring seasons at selected sites to collect more mass. Atmospheric concentrations of organic compounds were compared among sites, among seasons, and then correlated to meteorological factors. Distributions between the gas and particle phases were described, as well as ratios between PAH compounds indicative of nearby sources.

Sampling Sites

Sampling took place at six urban sites, each located near waterbodies with documented water quality impairments (Figure 1). These included three sites in the Los Angeles River watershed (LA1, LA2, and LA3); one in the Ballona Creek watershed (BC); one in the Dominguez Channel watershed (DC); and one in the lower Santa Ana River watershed (SA). Two sites, LA1 and LA2, were located at existing air monitoring stations operated by the South Coast Air Quality Management District (SCAQMD). Both BC and SA were located on rooftops near busy roadways, while LA3 was located within the grounds of a water reclamation facility, and DC was located on the grounds of a university. Site selection criteria incorporated the recommendations of the National Atmospheric Deposition Program (NADP 2000), which included: (1) areas generally representative of the region with minimal impact of local point or area sources; (2) areas a minimum distance of 100 m from major line sources; and (3) all objects or structures located a distance of at least twice their height from the sampling equipment.

Table 1. Summary of sampling effort and meteorological data.

Site Name	Sample Date	Season	Temperature ¹ (C)	Wind Speed ¹ (m/s)	Relative Humidity ¹
Los Angeles River 1 (LA1)	8/1/2002	Summer	20	1.6	77%
	11/21/2002	Fall	21	0.66	40%
	2/26/2003	Winter	14	3.1	68%
	5/21/2003	Spring	18	1.4	80%
Los Angeles River 2 (LA2)	8/28/2002	Summer	21	1.7	67%
	12/10/2002	Fall	14	1.9	68%
	3/5/2003	Winter	14	2.1	67%
	6/11/2003	Spring	17	2.0	77%
Los Angeles River 3 (LA3)	9/11/2002	Summer	24	1.0	53%
	11/26/2002	Fall	19	2.8	13%
	2/17/2003	Winter	14	0.61	66%
	5/7/2003	Spring	15	1.9	70%
Ballona Creek (BC)	9/18/2002	Summer	20	1.0	73%
	12/11/2002	Fall	14	0.89	59%
	2/5/2003	Winter	14	1.3	32%
	4/30/2003	Spring	15	1.6	68%
Dominguez Channel (DC)	9/24/2002	Summer	20	1.8	61%
	12/18/2002	Fall	11	1.0	63%
	3/12/2003	Winter	17	0.56	81%
	5/28/2003	Spring	21	0.50	73%
Santa Ana River (SA)	10/3/2002	Summer	18	0.88	51%
	12/5/2003	Fall	14	0.74	77%
	1/29/2003	Winter	15	1.0	77%
	5/14/2003	Spring	16	1.6	73%

¹24-h mean.

Field Activities and Instrumentation

Air samples were collected using a high-volume sampler (Anderson Instruments, Inc., Smyrna, GA) equipped with a quartz fiber filter, to collect particulate phase compounds, followed by a polyurethane foam (PUF) plug (7 cm long and 6 cm in diameter) held in a glass sleeve to collect vapor phase compounds. A sample flow rate of 0.25 m³/min was used over a period of 24 h. Sample flow rates and durations were increased in winter and spring to ensure adequate mass was collected. While samples of both the gas and particle phases were collected, these measurements were susceptible to partitioning artifacts (volatilization losses from particles on the filter and/or adsorption of gaseous compounds to the filter itself (Van Vaeck *et al.* 1984, Ligocki and Pankow 1989)). The data were not corrected for

these potential artifacts; however, artifacts were expected to be relatively small (Dickhut and Gustafson 1995, Park *et al.* 2001).

Meteorological data also were measured during each sampling event, including wind speed and direction, temperature, relative humidity, and barometric pressure, using a portable meteorological station (PortLog, Rain Wise, Inc., Bar Harbor, ME). The 24-h mean values were used to characterize meteorological conditions during each sampling event (Table 1).

Chemical Analysis

Prior to sampling, quartz fiber filters were wrapped in aluminum foil and baked at 425°C for 24 h, then stored in aluminum foil-lined petri dishes. PUF plugs were cleaned by extraction with acetone

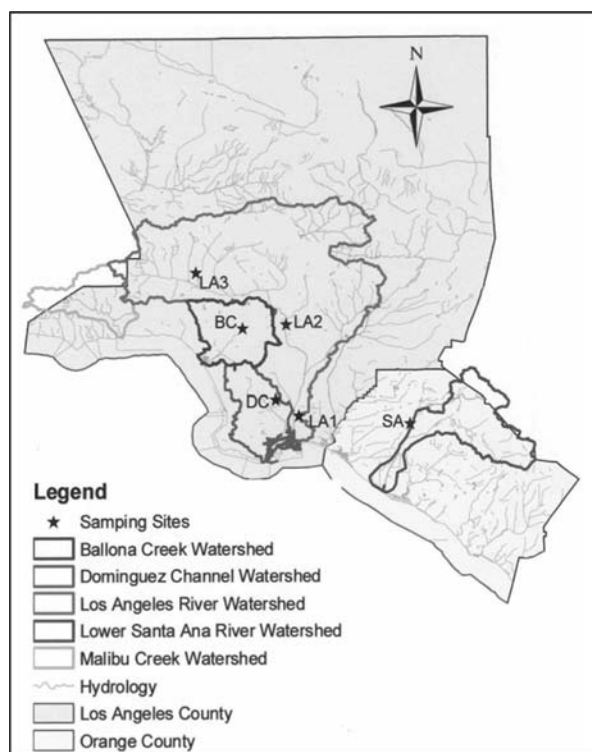


Figure 1. Map of sampling sites in the Los Angeles coastal air basin.

(24 h) followed by a 1:1 dichloromethane/hexane mixture (4 h), then stored in pre-cleaned glass jars with aluminum foil-lined lids. After sampling, the filter and PUF were returned to their original jars. All samples were maintained at 4°C during transport from the field to the laboratory and prior to being analyzed.

Filter and PUF samples were extracted three times following EPA Compendium Method TO-14 using dichloromethane instead of hexane/ether (U.S. EPA 1999). The extracts were combined and condensed using a roto-evaporator, then cleaned up with Alumina/Silica Gel prior to analysis with gas chromatography-mass spectroscopy (GC-MS). A Hewlett Packard 6890/5972 GC-MS was used in the full-scan mode, equipped with a J&W DB-5 capillary column (60m x 0.25mm x 0.25µm). The oven temperature was programmed to increase from 100°C to 295°C at 2.5°C/minute.

Each sample was quantified for 24 PAH compounds (summed for total PAH), a number of pesticides including chlorpyrifos, diazinon, malathion, toxaphene, DDT isomers, and metabolites (summed for total DDT), as well as other chlorinated hydrocarbons including 47 PCB compounds (summed for total PCB) (Table 2).

A blank quartz fiber filter and PUF plug also were prepared in the same manner as the samples and taken to the field sites during each sampling event. These field blanks were analyzed with the samples to account for contamination in the preparation and transportation of sample media. Laboratory blanks were analyzed with each batch of 15 or less samples. No blank samples exceeded the detection limit for any of the organophosphorus or organochlorine compounds. However, both filter and PUF field blanks contained levels of PAH above detection limits and all samples were corrected for blank levels. The samples were all spiked with a mixture of surrogate analytes (chlorinated hydrocarbons and PAHs) and analyzed along with field samples to estimate recovery efficiency. Recoveries ranged from 42% to 154% for chlorinated hydrocarbons and from 34% to 129% for PAH. Sample concentrations were not recovery corrected.

Data Analysis

Data analysis for this study proceeded through three steps. First, the potential extent of contamination was examined by assessing the frequency of detection of PAHs in the air (including both vapor and particulate phases) during each sampling event, and the spatial and temporal differences in air concentrations among sites, seasons, and meteorological variables. Differences among sites and seasons were determined using analysis of variance (ANOVA) (Rao 1998). In an attempt to explain differences between sampling events, atmospheric concentrations were correlated with several meteorological variables including mean daily wind speed, mean daily temperature, and mean daily relative humidity. Second, the relative distribution of individual PAH compounds was evaluated. This was refined by assessing the differences in relative abundance within the gas and particle phases independently. Third, selected ratios of PAH compounds were calculated to provide information about important sources. A ratio of benzo[g,h,i]perylene to benze[e]pyrene (BGHIP/BEP) closer to 2.0 indicates traffic influence, while ratios closer to 0.8 indicate non-traffic sources (Nielsen 1996). A ratio of benzo[g,h,i]perylene to indeno[1,2,3-cd]pyrene (BGHIP/IP) closer to 1.1 indicates diesel-powered vehicles while ratios greater than 3.5 indicates gasoline-powered vehicles (Benner *et al.* 1989, Li and Kamens 1993). The ratio of alkylated PAHs to parent homologues and photolabile PAHs to stable homologues has been used to distinguish between petroleum and combustion

Table 2. Target organic compounds and instrument detection limits (IDL).

	IDL (ng/sample)
Pesticides	
Chlorpyrifos	0.02
Diazinon	0.02
Malathion	0.02
Toxaphene	0.02
Total DDT:	
2,4-DDD	0.02
2,4-DDE	0.02
2,4-DDT	0.02
4,4-DDD	0.02
4,4-DDE	0.02
4,4-DDT	0.02
Polycyclic Aromatic Hydrocarbons (PAHs)	
Acenaphthene (ACE)	0.02
Acenaphthylene (AC)	0.02
Anthracene (AN)	0.02
Benz[a]anthracene (BAA)	0.02
Benzo[a]pyrene (BAP)	0.02
Benzo[b]fluoranthene (BBF)	0.02
Benzo[e]pyrene (BEP)	0.02
Benzo[g,h,i]perylene (BGHIP)	0.02
Benzo[k]fluoranthene (BKF)	0.02
Biphenyl (BI)	0.02
Chrysene (CHR)	0.02
Dibenz[a,h]anthracene (DBAHA)	0.02
2,6-Dimethylnaphthalene (DMN)	0.02
Fluoranthene (FL)	0.02
Fluorene (F)	0.02
Indeno[1,2,3-c,d]pyrene (INP)	0.02
1-Methylnaphthalene (1MN)	0.02
2-Methylnaphthalene (2MN)	0.02
1-Methylphenanthrene (MP)	0.02
Naphthalene (NA)	0.02
Perylene (PER)	0.02
Phenanthrene (PH)	0.02
Pyrene (PY)	0.02
2,3,5-Trimethylnaphthalene (TMN)	0.02
Polychlorinated Biphenyls (PCB)	
PCB 018; PCB028; PCB031; PCB033; PCB037; PCB044; PCB049; PCB052; PCB066; PCB070; PCB074; PCB077; PCB081; PCB087; PCB095; PCB097; PCB099; PCB101; PCB105; PCB110; PCB110; PCB114; PCB118; PCB119; PCB123; PCB126; PCB128; PCB138; PCB141; PCB149; PCB151; PCB153	0.02

sources, and to evaluate the aging of ambient PAH aerosol (Simo *et al.* 1997, Park *et al.* 2001). The process of frequency of detection, and comparison among sites and seasons was then repeated for organophosphorus and chlorinated pesticides and PCB.

RESULTS

Polynuclear Aromatic Hydrocarbons

Frequency and magnitude of total PAH concentrations in ambient air

PAHs in both the gas and particle phases were detected at all sites and in all seasons. Total PAH concentrations ranged over four orders of magnitude, from 3 ng/m³ to 132 ng/m³, among all sampling events (Table 3). The highest single sample event concentration of total PAHs was measured at DC during the fall, which was two orders of magnitude greater than the lowest single sample event concentration, measured at LA3 during the spring.

The highest site mean concentration of total PAH was observed at DC (48 ng/m³) and was a factor of five greater than the lowest site mean concentration observed at LA3 (9 ng/m³). However, ANOVA analysis showed no significant differences between sites based on total PAH concentrations ($p=0.64$). The highest season mean concentration was observed in fall (65 ng/m³) and was a factor of five greater than the lowest season mean concentration observed in spring (13 ng/m³). Based on ANOVA analysis, differences between seasons were significant ($p=0.01$); post hoc testing indicated that fall was significantly greater than spring or summer. No significant correlations were found between atmospheric concentrations of total PAH and meteorological parameters including temperature, wind speed, or relative humidity ($r^2 < 0.15$).

Individual PAH distributions

The distributions of individual PAHs were not homogeneous (Figure 2). Phenanthrene had the highest concentration of the 24 PAH compounds quantified averaging 11 ng/m³. Only three other PAHs averaged ≥ 2 ng/m³ including naphthalene, 2-methyl naphthalene, and fluorene. Fifteen of the remaining 20 PAH compounds averaged < 1 ng/m³. The relative distribution of PAHs was similar between seasons (data not shown). Phenanthrene was the single most abundant PAH compound during summer, fall, winter, and spring.

The majority of the PAH mass was observed in the gas phase, averaging 95% of the total PAH mass during this study (Figure 3). The distribution of PAH between gas and particle phases varied by compound, and was strongly dependent upon molecular weight (Figure 4). There was a general trend of decreasing mass in the gas phase with increasing molecular weight. Low molecular weight com-

Table 3. Concentrations of total PAH by site and by season.^{1,2}

		Mean	Standard Deviation	Minimum	Maximum
Site	LA1	35	35	15	87
	LA2	40	27	16	78
	LA3	9	9	ND	21
	BC	33	23	14	65
	DC	48	56	16	132
	SA	30	22	4	57
Season	Summer	20	12	ND	33
	Fall	65	45	11	132
	Winter	32	18	18	65
	Spring	13	9	3	27
Annual Mean		32.6	31.0	ND	132.4

¹Total PAH concentrations=the sum of the vapor and particle phases.

²ND=not detected in either the vapor or particle phase.

pounds (MW <230) dominated the gas phase with phenanthrene, methylphenanthrene, naphthalene, methylated naphthalenes, fluorene, acenaphthalene, fluoranthene, and pyrene comprising approximately 85% of the mass of gas phase PAHs. Phenanthrene represented roughly half of all gas phase PAHs. In reverse of gas phase PAH, there was a general trend of increasing mass of high molecular weight compounds (MW>230) in the particle phase. Pyrene and benzo[g,h,i]perylene were the major contributors to the particle phase.

PAH Ratios

With several exceptions, ratios of individual PAHs collected during this study suggest that much of the PAHs were derived from traffic sources, predominantly from gasoline-powered vehicles (Table 4). Two-thirds of the BGHIP/BEP ratios measured in this study were similar to the estimated traffic ratio of 2.0. The remaining one-third were similar to the non-traffic ratios of 0.8. The highest BGHIP/BEP ratio of 4.58, observed at DC during the fall, suggested additional contributions of PAH from other sources during this sampling event. During sampling events when IP was detected, the ratios of BGHIP/IP were typically between 2 and 4, indicative of gasoline vehicles. One exception was during the fall sampling at DC, in which the ratio of BGHIP/IP was approximately 50, more than 12 times the gasoline vehicle source signature of approximately 3.5-3.8. As with the high BGHIP/BEP ratio during this same sampling event, there was an additional source

of BGHIP other than typical vehicle emissions relative to other PAH in the ambient air. Finally, ratios of (BAA+BAP)/(CHR+BEP) indicated that the majority of our sites were influenced by near-source traffic aerosols. The MP/PH ratios, however, were typically closer to the aged urban aerosol signature, suggesting that sources other than fresh traffic emissions may also have contributed to the overall ambient PAH concentration.

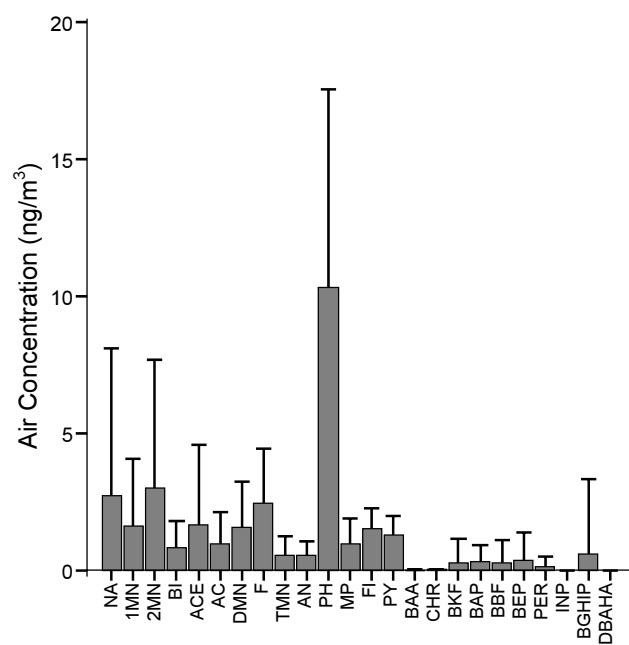


Figure 2. Mean PAH concentrations (gas + particle phases). Error bars represent the standard deviation.

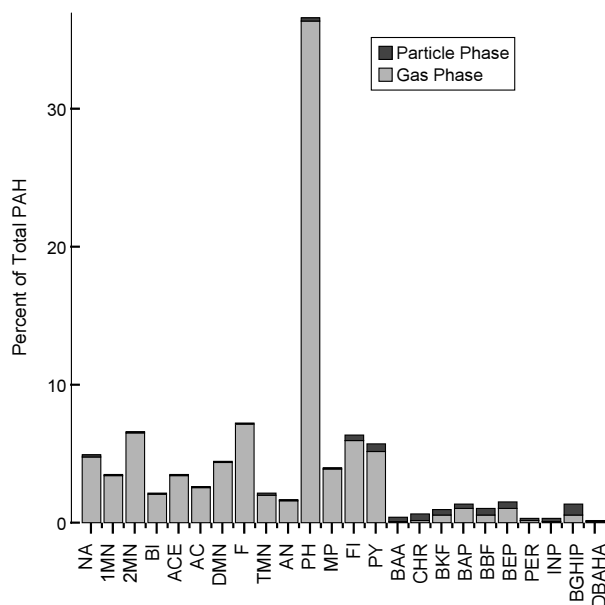


Figure 3. Mean percent contribution to the total PAH mass (gas + particle phases).

Pesticides and Chlorinated Organic Compounds

Pesticides and PCBs were detected infrequently in this study. Chlorpyrifos, diazinon, and total DDT were detected in 4%, 8%, and 12% of the samples, respectively. Malathion, toxaphene, and total PCB were not detected in any samples. Total air concentrations of organophosphorus and chlorinated pesticides varied one order of magnitude over the course of this study among all sites (Table 5). Air concentrations ranged from non-detectable (ND) - 0.64 ng/m³ for chlorpyrifos; ND - 0.71 ng/m³ for diazinon; and ND - 0.56 ng/m³ for total DDT. Chlorpyrifos was detected at only one site (DC), while diazinon was detected at two sites (DC and SA). Both chlorpyrifos and diazinon were found only during the summer sampling period. However, the mean concentration of diazinon at SA was twice the concentration measured at DC. Total DDT also was detected at two sites (LA2 and LA3), with similar mean concentrations at each site. Total DDT was detected during both the summer and winter sampling events, but the mean winter concentration was a factor of nearly ten less than the mean summer concentration. Finally, all constituents were detected primarily in the gas phase. For instance, chlorpyrifos was detected only in the gas phase, while diazinon and total DDT were detected 69% and 55% respectively, in the gas phase.

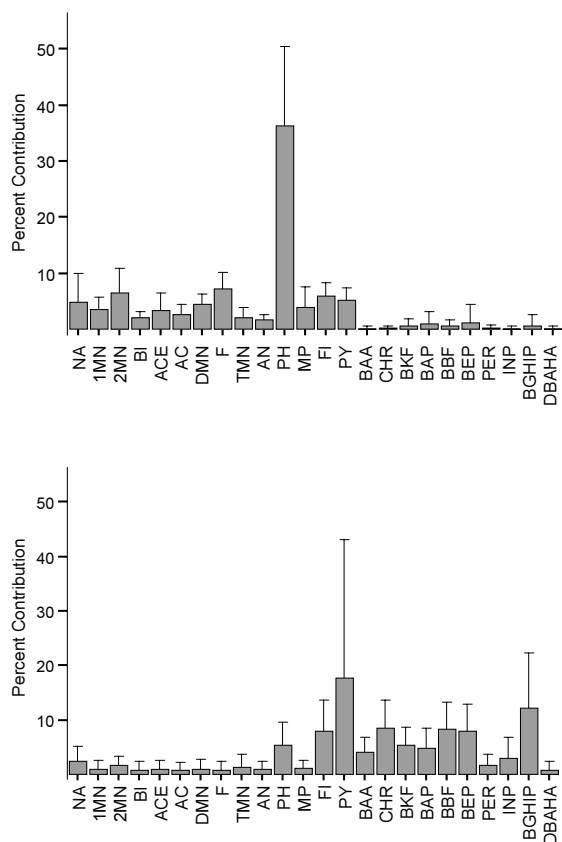


Figure 4. Percent contribution of individual PAH compounds to (A) the total gas phase and (B) the total particle phase.

DISCUSSION

Atmospheric concentrations of total PAH were detected routinely over the course of this study and were measured at every site and in every season. Temporal differences in PAH air concentrations were observed during this study, while spatial differences were not. Seasonal differences in air concentrations of PAH have been observed by others (Leister and Baker 1994, Gardner *et al.* 1995, Gustafson and Dickhut 1997), largely due to changes in meteorological conditions. Compared to the previous studies, though, the seasonal differences observed in the coastal Los Angeles air basin were moderate. There was no correlation with temperature, wind speed, or humidity. The moderated seasonality signature of PAH air concentrations is a result of the temperate climate of the region (small range in temperature, wind speed, and humidity) and the lack of emissions from coal-fired power plants used for heating during cooler months. The lack of spatial differences, how-

Table 4. PAH ratios and source signatures.

Site	Season	BGHIP	BGHIP	BAA+BAP	MP
		BEP	IP	CHR+BEP	PH
LA1	Summer				0.11
	Fall	2.13	3.02	0.82	0.11
	Winter	3.03	3.03	0.42	0.14
	Spring	0.22		0.07	0.47
LA2	Summer			3.15	0.06
	Fall	0.48		0.63	0.06
	Winter	2.83	1.90	0.84	0.07
	Spring				0.08
LA3	Summer				
	Fall	1.94	2.23	0.74	0.07
	Winter	1.95		0.51	0.08
	Spring				0.12
BC	Summer	0.95			0.09
	Fall	1.05		2.37	0.06
	Winter	3.32	4.30	0.84	0.09
	Spring				0.08
DC	Summer	1.04		0.40	0.08
	Fall	4.58	50.38	0.66	0.09
	Winter	0.87		0.35	0.09
	Spring			0.42	0.06
SA	Summer				0.07
	Fall	2.00	2.62	0.79	0.06
	Winter	3.89		0.39	0.09
	Spring				0.12
Source Signatures	Traffic ^{1,2}	2.0		0.3-1.0	0.3-1.0
	Non-Traffic ¹	0.8			
	Aged Urban Aerosol ²			0.2-0.4	0.1
	Diesel ^{3,4}		1.1-1.2		4.5
	Gasoline ^{3,4}		3.5-3.8		0.6

¹PAH acronyms are defined in Table 2.

²Nielson 1996.

³Simo *et al.* 1997.

⁴Li and Kamens 1993.

⁵Benner *et al.* 1989.

ever, is more likely a reflection of small sample size combined with large sample-to-sample variability.

The range of total PAH concentrations measured in ambient air of the Los Angeles air basin during the present study was similar to the concentrations measured in Los Angeles by others, as well as measurements in other urban areas such as Chicago, Illinois; Corpus Christi and Houston, Texas; and Elizabeth, New Jersey (Table 6). The similarities in total PAH concentrations, we suspect, are a reflection of the similarities in urban sources of combusted fossil fuels. Other investigators have used the ratios of selected PAH compounds to identify the source contribution to ambient concentrations (Benner *et al.* 1989, Li and Kamens 1993, Nielsen 1996, Simo *et al.* 1997). In this study, the dominance of parent compounds and low parent/methylated homologue ratios provides evidence that combustion sources

dominated (Park *et al.* 2001). Moreover, ratios of individual PAH compounds indicated that traffic, including gasoline and diesel combustion, were likely sources to our study sites. We assume these types of mobile sources are ubiquitous to most congested urban environments in the U.S.; hence, similar distributions and concentrations of PAH are to be expected.

In contrast to PAHs, detectable concentrations of many pesticides and PCBs were not consistently observed. Chlorpyrifos, diazinon, and DDT were detected infrequently, while malathion, toxaphene, and PCB were not detected in any sample. The range of atmospheric concentrations of organophosphorus pesticides in Los Angeles measured during this study were comparable to urban regions along the Mississippi River, as well as in Minnesota and Corpus Christi, Texas. When examining only urban

Table 5. Mean concentrations and standard deviations of semi-volatile organic compounds by site and season.^{1,2}

		Concentration (ng/m ³)					
		Chlorpyrifos	Diazinon	Malathion	Toxaphene	tDDT	tPCB
Site	LA1	ND	ND	ND	ND	ND	ND
	LA2	ND	ND	ND	ND	0.16 ± 0.26	ND
	LA3	ND	ND	ND	ND	0.14 ± 0.28	ND
	BC	ND	ND	ND	ND	ND	ND
	DC	0.16 ± 0.32	0.18 ± 0.35	ND	ND	ND	ND
	SA	ND	0.08 ± 0.16	ND	ND	ND	ND
Season	Summer	0.11 ± 0.26	0.17 ± 0.29	ND	ND	0.18 ± 0.28	ND
	Fall	ND	ND	ND	ND	ND	ND
	Winter	ND	ND	ND	ND	0.02 ± 0.04	ND
	Spring	ND	ND	ND	ND	ND	ND

¹ND = Not detected.

²Zero used for all non-detectable values when calculating statistics.

Table 6. Air concentrations of organic compounds across the United States.

Sample Location	Year	Air Concentrations (ng/m ³)						
		Chlorpyrifos	Diazinon	Malathion	Toxaphene	Total DDT	Total PCB	Total PAH
Los Angeles, CA (this study)	2002-2003	ND - 0.64	ND - 0.71	ND	ND	ND - 0.56	ND	3 - 132
Sierra Nevada Mountain Range, CA ¹	1996	0.05 - 17.5	0.07 - 0.24	0.15 - 0.4				
Sacramento, CA ²	1996-1997	0.03 - 26.8 ^a	0.01 - 112 ^a	0.23 - 3.77 ^a				
California's Central Valley ³	1990-1991	0.57 - 6.5	0.004 - 3					
Mississippi River Area ⁴	1994	0.29 ^b	0.08 ^b	0.23 ^b				
Minnesota ⁵		0.07 ^c	ND	0.09 ^c				
Arizona ⁶		ND - 22.5 ^d	ND - 131 ^d					
Corpus Christi, TX ⁷	1998-1999	0.03 ^c				ND - 0.003	0.034 ^c	2.2 - 57
Chesapeake Bay ⁸	1993	0.002 - 0.1						
Chesapeake Bay ⁹	1990-1991						0.21	
Alabama ¹⁰	1996-1997				0.008 - 0.61	0.25 - 91		
Great Lakes Region ¹¹	1996-1997				0.007			
Concord, CA ¹²	2000						0.17 - 0.32	5.7 - 56
Chicago, IL ¹³	1994						0.27 - 14	27 - 430
Los Angeles, CA ¹⁴	1999-2000							4.2 - 62
Houston, TX ¹⁴	1999-2001							10 - 160
Elizabeth, NJ ¹⁴	1999-2002							12 - 110

¹LeNoir *et al.* 1999

²Majewski and Baston 2002

³Zabik and Seiber 1993

⁴Majewski *et al.* 1998

⁵Clayton *et al.* 2003

⁶Gordon *et al.* 1999

⁷Park *et al.* 2002

⁸McConnell *et al.* 1997

⁹Leister *et al.* 1994

¹⁰Jantunen *et al.* 2000

¹¹Cortes *et al.* 1998

¹²Tsai *et al.* 2002

¹³Simcik *et al.* 1997

¹⁴Naumova *et al.* 2002

^aDetection frequencies reported for these results are 12-49%, 10-47%, and 0 - 11% for chlorpyrifos, diazinon, and malathion, respectively.

^bMedian air concentration reported.

^cMean air concentration reported.

^dDetection frequencies reported were 10% and 21% for chlorpyrifos and diazinon, respectively.

areas in California, however, air concentrations of organophosphorus pesticides in Los Angeles were at the low end of the range. The differences in air concentrations between coastal Los Angeles and other California locations are likely a combination of the pesticide sources and the timing of the measurements. In other studies, urban sites were impacted, at least in part, by adjacent agricultural use

(Majewski and Baston 2002, LeNoir *et al.* 1999, McConnell *et al.* 1997). A second explanation of reduced organophosphorus pesticide concentrations during this study is the recent reductions in urban applications. In 2001, DPR reported a 21% drop in organophosphorus pesticide use in California compared to the previous year (DRP 2002). In addition, the manufacture and sale of products containing

chlorpyrifos and diazinon for residential use is being phased out beginning in 2001 (U.S. EPA 2000 a,b).

The major conclusion regarding the lack of organochlorine and organophosphorus compounds in regional air samples from the coastal Los Angeles air basin is limited by a relatively small sample size and a relatively high detection limit. Our limited number of sampling sites and small sample size (n=24) may be insufficient to characterize precisely all spatial and temporal variability in air concentrations across the entire Los Angeles coastal region over a one-year period. However, we are confident the recurring non-detectable results indicate chronically high atmospheric concentrations of these compounds is not a widespread problem in this region. Moreover, while the detection limit for organochlorine and organophosphorus compounds in this study was marginally greater than studies conducted by others (Leister and Baker 1994, Tsai *et al.* 2002), we are confident this was not an issue for two primary reasons. First, increasing sample volumes by increasing the flow rate and sampling duration during the winter and spring seasons did not increase the detection frequency for the organochlorine or organophosphorus compounds. Second, the bias of our higher detection limit was assessed by recalculating the mean concentrations for each of our target compounds, setting each of the non-detectable results equal to the detection limit. This recalculation resulted in virtually no change in mean concentrations. For example, air concentrations at DC, our site with the highest diazinon levels, increased marginally from 0.18 ng/m³ to 0.19 ng/m³. Similarly, the concentration of diazinon during the summer season for all sites combined increased from 0.17 ng/m³ to 0.18 ng/m³.

Site-specific issues within the region may still exist for organophosphorus and organochlorine compounds, particularly where there is a known source. The atmospheric concentrations and subsequent deposition and transport to a nearby waterbody of concern may require a localized investigation. Where PAHs are problematic, additional research estimating deposition is a reasonable next step to ascertain the atmospheric contribution of PAHs to specific waterbodies.

LITERATURE CITED

Anderson, J.W. and R.W. Gossett. 1987. Polynuclear aromatic hydrocarbon contamination in sediments from coastal waters of southern California. SCCWRP Technical

Report No. 199. Southern California Coastal Water Research Project, Westminster, CA.

Baker, J.E., D.L. Poster, C.A. Clark, T.M. Church, J.R. Scudlark, J.M. Ondov, R.M. Dickgut and G. Cutter. 1994. Loadings of atmospheric trace elements and organic contaminants to the Chesapeake Bay. pp. 171-194. *in*: J.E. Baker (ed.), Atmospheric Deposition of Contaminants to the Great Lakes and Coastal Waters. SETAC Press. Pensacola, FL.

Benner, B.A. Jr., G.E. Gordon and S.A. Wise. 1989. Mobile sources of atmospheric polycyclic aromatic hydrocarbons: A roadway tunnel study. *Environmental Science and Technology* 23: 1269-1278.

California Department of Pesticide Regulation (DPR). 2002. <http://www.cdpr.ca.gov/docs/pressrls/october16.htm>

Clayton, C.A., E.D. Pellizzari, R.W. Whitmore, J.J. Quackenboss, J. Adgate and K. Sefton. 2003. Distributions, associations, and partial aggregate exposure of pesticides and polynuclear aromatic hydrocarbons in the Minnesota Children's Pesticide Exposure Study (MNCPEs). *Journal of Exposure Analysis and Environmental Epidemiology* 13: 100.

Cortes, D.R., E. Basu, C.W. Sweet, D.A. Brice and R.M. Hoff. 1998. Temporal trends in gas-phase concentrations of chlorinated pesticides measured at the shores of the Great Lakes. *Environmental Science and Technology* 32: 1920.

Dachs, J., T.R. Glenn IV, C.L. Gigliotti, P. Brunciak, L.A. Totten, E.D. Nelson, T.P. Franz and S.J. Eisenreich. 2002. Processes driving the short-term variability of polycyclic aromatic hydrocarbons in the Baltimore and northern Chesapeake Bay atmosphere, USA. *Atmospheric Environment* 36: 2281-2295.

Dickhut, R.M. and K.E. Gustafson. 1995. Atmospheric inputs of selected polycyclic aromatic hydrocarbons and polychlorinated biphenyls to Southern Chesapeake Bay. *Marine Pollution Bulletin* 30: 385-396.

Duce, R.A., P.S. Merrill, E.L. Atlas, P. Buat-Menard, B.B. Hicks, J.M. Miller, J.M. Prospero, R. Arimoto, T. Church, M. Ellis, J.N. Galloway, L. Hanson, T.D. Jickells, A.H. Knap, K.H. Reinhardt, B. Schneider, A. Soudine, J.J. Tokos, S. Tsunogai, R. Wollast and M. Zhou. 1991. The atmospheric input of trace species to the world ocean. *Global Biogeochemical Cycles* 5: 193.

Eisenreich, S.J., B.B. Looney, and J.D. Thornton. 1981. Airborne organic contaminants in the Great Lakes ecosystem. *Environmental Science and Technology* 15: 30-38.

- Franz, T.P., S.J. Eisenreich and T.M. Holsen. 1998. Dry deposition of particulate polychlorinated biphenyls and polycyclic aromatic hydrocarbons to Lake Michigan. *Environmental Science and Technology* 32: 3681-3688.
- Gardner, B., C.N. Hewitt and K.C. Jones. 1995. PAHs in air adjacent to two inland water bodies. *Environmental Science and Technology* 29: 2405-2413.
- Gordon, S.M., P.J. Callahan, M.G. Nishioka, M.C. Brinkman, M.K. O'Rourke, M.D. Lebowitz and D.J. Moschandreas. 1999. Residential environmental measurements in the National Human Exposure Assessment Survey (NHEXAS) pilot study in Arizona: Preliminary results for pesticides and VOCs. *Journal of Exposure Analysis and Environmental Epidemiology* 9: 456.
- Gustafson, K.E. and R.M. Dickhut. 1997. Particle/gas concentrations and distributions of PAHs in the atmosphere of Southern Chesapeake Bay. *Environmental Science and Technology* 31: 140-147.
- Jantunen, L.M., T.F. Bidleman, T. Harner and W.J. Parkhurst. 2000. Toxaphene, chlordane, and other organochlorine pesticides in Alabama air. *Environmental Science and Technology* 34: 5097.
- Leister, D.L. and J.E. Baker. 1994. Atmospheric deposition of organic contaminants to the Chesapeake Bay. *Atmospheric Environment* 28: 1499.
- LeNoir, J.S., L.L. McConnell, G.M. Fellers, T.M. Cahill and J.N. Seiber. 1999. Summertime transport of current-use pesticides from California's Central Valley to the Sierra Nevada Mountain Range, USA. *Environmental Toxicology and Chemistry* 18: 2715.
- Li, C.K. and R.S. Kamens. 1993. The use of polycyclic aromatic hydrocarbons as source signatures in receptor modeling. *Atmospheric Environment* 27: 523-532.
- Ligocki, M.P. and J.F. Pankow. 1989. Measurements of the gas/particle distributions of atmospheric organic compounds. *Environmental Science and Technology* 23: 75-83.
- Lu, R., R.P. Turco, K.D. Stolzenbach, S.K. Freidlander, C. Xiong, K. Schiff, L. Tiefenthaler and G. Wang. 2003. Dry deposition of airborne trace metals on the Los Angeles Basin and adjacent coastal waters. *Journal of Geophysical Research* 108: 4074.
- Majewski, M.S., W.T. Foreman, D.A. Goolsby and N. Nakagaki. 1998. Airborne pesticide residues along the Mississippi River. *Environmental Science and Technology* 32: 3689.
- Majewski, M.S. and D.S. Baston. 2002. Atmospheric transport of pesticides in the Sacramento, California, Metropolitan area, 1996 – 1997. U.S. Geological Survey, Water Resources Investigations Report 02-4100.
- McConnell, L.L., E. Nelson, C.P. Rice, J.E. Baker, W.E. Johnson, J.A. Harman and K. Bialek. 1997. *Environmental Science and Technology* 31: 1390.
- Mearns, A.M., G. Matta, D. Shigenaka, M. MacDonald, H. Buchman, J. Harris, G. Golas and G. Lauenstein. 1991. Contaminant trends in the Southern California Bight: Inventory and assessment. NOAA Technical Memorandum NOS ORCA 62. National Oceanic and Atmospheric Administration, National Ocean Service. Seattle, WA.
- NADP (National Atmospheric Deposition Program). 2000. Instruction Manual NADP/NTN Site Selection and Installation.
- Naumova, Y.Y., S.J. Eisenreich, B.J. Turpin, C.P. Weisel, M.T. Morandi, S.D. Colome, L.A. Totten, T.H. Stock, A.M. Winer, S. Alimokhtari, J. Kwon, D. Shendell, J. Jones, S. Maberti and S.J. Wall. 2002. Polycyclic aromatic hydrocarbons in the indoor and outdoor air of three cities in the U.S. *Environmental Science and Technology* 36: 2552.
- Nielsen, T. 1996. Traffic contribution of polycyclic aromatic hydrocarbons in the center of a large city. *Atmospheric Environment* 30: 3481-3490.
- Park, J-S, T.L. Wade and S.T. Sweet. 2002. Atmospheric deposition of PAHs, PCBs, and organochlorine pesticides to Corpus Christi Bay, Texas. *Atmospheric Environment* 36: 1707.
- Scudlark, J.R., K.M. Conko and T.M. Church. 1994. Atmospheric wet deposition of trace elements to Chesapeake Bay: CBAD study year 1 results. *Atmospheric Environment* 28: 1487.
- Schiff, K. and M. J. Allen. 2000. Chlorinated hydrocarbons in livers of flatfishes from the southern California Bight. *Environmental Toxicology and Chemistry* 19: 1559-1565
- Schiff, K., S. Bay and C. Stransky. 2002. Characterization of stormwater toxicants from an urban watershed to freshwater and marine organisms. *Urban Water* 4: 215-227
- Schiff, K. and M. Sutula. Organophosphorus Pesticides in Stormwater Runoff from Southern California (USA) Accepted for publication in *Environmental Toxicology and Chemistry*.

Simcik, M.F., H. Zhang, S.J. Eisenreich, and T.P. Franz. 1997. Urban contamination of the Chicago/coastal Lake Michigan atmosphere by PCBs and PAHs during AEO-LOS. *Environmental Science and Technology* 31: 2141.

Simo, R., J.O. Grimalt, and J. Albaiges. 1997. Loss of unburned-fuel hydrocarbons from combustion aerosols during atmospheric transport. *Environmental Science and Technology* 31: 2697-2700.

SCAQMD (South Coast Air Quality Management District). 2000 Air Quality Report. <http://www.aqmd.gov>.

Tsai, P., R. Hoenicke and D. Yee. 2002. Atmospheric concentrations and fluxes of organic compounds in the Northern San Francisco Estuary. *Environmental Science and Technology* 36: 4741.

U.S. EPA (United States Environmental Protection Agency). 1999. Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Second Edition. Document EPA/625/R-96/010b.

U.S. EPA (United States Environmental Protection Agency). 2000a. www.epa.gov/pesticides/op/chlorpyrifos.htm.

U.S. EPA (United States Environmental Protection Agency). 2000b. www.epa.gov/pesticides/op/diazinon.htm.

Van Vaeck, L., K. Van Cauwenbergh, J. Janssens. 1984. The gas-particle distribution of organic aerosol constituents – measurements of the volatilization artifact in hi-vol. Cascade impactor sampling. *Atmospheric Environment* 18: 417-430.

Wu, Z.Y., M. Han, Z.C. Lin, and J.M. Ondov. 1994. Chesapeake Bay atmospheric deposition study, year 1: sources and dry deposition of selected elements in aerosol particles. *Atmospheric Environment* 28: 1471.

Zabik, J.M. and J.N. Seiber. 1993. Atmospheric transport of organophosphate pesticides from California's Central Valley to the Sierra Nevada Mountains. *Journal of Environmental Quality* 22: 80.

Zeng, E.Y. and C.L. Vista. 1997. Organic pollutants in the coastal environment off San Diego, California. I. source identification and assessment by compositional indices of polycyclic aromatic hydrocarbons. *Environmental Toxicology and Chemistry* 16: 179-188.

ACKNOWLEDGEMENTS

We would like to acknowledge the assistance of T. Parsons, T. Mack, B. Moore, M. Guardi, and D. Vosooghi who provided access to their facilities for our sampling. We wish to acknowledge the valuable contributions from L. Tiefenthaler and D. Tsukada. This project was funded in part by the California Department of Pesticide Regulation.