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Atmospheric Reactions Influence Seasonal PAH and Nitro-PAH Concentrations in the Los Angeles Basin

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Ambient measurements of polycyclic aromatic hydrocarbons (PAHs) and nitro-PAHs were carried out during August 2002 and January 2003 in Los Angeles, CA, a source site and in Riverside, CA, a downwind receptor site ∼90 km to the east of Los Angeles. Atmospheric concentrations of PAHs and nitro-PAHs are of interest because both of these compound classes include potent mutagens and carcinogens. To augment our current understanding of atmospheric formation of nitro-PAHs, four sampling periods were employed to study the diurnal variations of these compounds. The PAH concentrations were highest in Los Angeles during January, as a result of traffic input at this source site under tight wintertime atmospheric inversions. In contrast, nitro-PAH levels were highest in Riverside during August, as a result of enhanced summertime photochemistry. Hydroxyl radical-initiated reactions produced nitro-PAHs in both seasons, while in winter little evidence for nitrate radical chemistry was seen. For the August samples, nitrate radical-initiated formation of nitro-PAHs is suggested by nitro-PAH isomer profiles not only at the downwind location as anticipated, but also at the source site. In southern California, the contribution of atmospheric formation through gas-phase radical-initiated PAH reactions to the ambient burden of nitro-PAHs is dominant, with the semi-volatile nitro-PAHs being the most abundant and 2-nitrofluoranthene being the major particle-associated nitro-PAH.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous environmental pollutants released into the atmosphere during incomplete combustion of fossil fuels and biomass from natural and agricultural fires (*1*, *2*). In urban areas, vehicle emissions represent a major source of PAHs (*2*−*4*). Sources for the nitro-PAHs in ambient atmospheres include direct emissions from incomplete combustion processes (*5*) and atmospheric gas-phase formation from the parent PAHs by hydroxyl (OH) radical reactions during daytime and by nitrate (NO_3) radical reactions during evening and nighttime in the presence of NO_x (*6*−*8*). The nitro-PAH isomers present in direct emissions may be distinct from those resulting from atmospheric reactions, reflecting their differing formation

mechanisms. Incomplete combustion processes result in the formation of nitro-PAH isomers that are those formed by electrophilic nitration, for example, 1-nitropyrene (1NP) and 3-nitrofluoranthene (3NF) from the abundant 4-ring PAHs pyrene (Pyr) and fluoranthene (FL), respectively. In contrast, 2-nitrofluoranthene (2NF) and 2-nitropyrene (2NP) result from gas-phase OH radical reactions, postulated to proceed by initial radical attack to the position with the highest electron density, followed by NO_2 addition in the ortho position and loss of H_2O (*6*−*8*). A similar mechanism for the gas-phase NO_3 radical reaction with fluoranthene produces 2NF after loss of HNO_3. Ambient measurements (*9*−*18*) indicate that atmospheric formation is the dominant source of particle-associated nitro-PAHs, as shown by the elevated concentration of the atmospheric transformation product 2NF relative to that of 1NP, a marker of combustion, and primarily of diesel emissions.

The formation rate of the nitro-PAHs depends on the ambient PAH and OH radical and/or NO_3 radical concentrations, the rate constants for reaction of the parent PAHs with OH radicals and/or NO_3 radicals, and the nitro-PAH yields from these reactions. Hydroxyl radical concentrations of up to 5×10^6 molecule cm^{-3} have been reported for Los Angeles (in September 1993) (*19*). Since OH radicals are ubiquitous during daylight hours, and reactions with OH radicals generally result in lifetimes of hours for gas-phase PAHs (*6*−*8*), the atmospheric formation of nitro-PAHs from the OH radical reactions can be significant and a major contributor to ambient nitro-PAH levels.

Environmental chamber studies show generally higher nitro-PAH yields from the NO_3 radical-initiated reactions compared to the OH radical-initiated reactions (*6*−*8*). However, the presence of ambient conditions under which significant radical-initiated PAH reactions will occur are less predictable for NO_3 radicals than for OH radicals. The nitrate radical is formed by the reaction of NO_2 with O_3:

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \qquad (1)$$
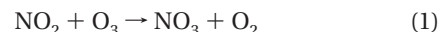
$$k_1(298 \text{ K}) = 3.2 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \ (20)$$

NO_3 radicals photolyze rapidly and therefore have generally been measured at considerable concentrations only approaching or after sunset in downwind receptor sites (*20*, *21*). Although daytime NO_3 reaction with phenol has been suggested (*22*), PAH reactions with NO_3 are significantly slower and daytime NO_3 chemistry is expected to be unimportant for the PAHs. Additionally, while the NO_3 radical photolyzes during the day, often both its daytime and nighttime concentrations are limited by the reaction of NO_3 with NO (*20*):

$$NO_3 + NO \rightarrow 2NO_2 \qquad (2)$$
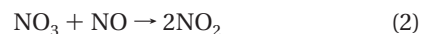
$$k_2(298 \text{ K}) = 2.6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

At ground level, the NO emitted from vehicles reacts to remove O_3, and therefore, when NO levels are significant, NO_3 radicals will not be present. It has recently been recognized, however, that an NO_3 gradient increasing with elevation may occur (*23*) and that significant NO_3 may be present at higher altitudes (*24*) even when none is present at ground level.

Nitro-PAHs are potent mutagens, and even if present at much lower concentrations than their parent compounds, they may have toxicological significance (*5*, *25*−*29*). Fur-

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thermore, since the position of the nitro-group influences the genotoxicity of the compound, isomer-specific identifications are essential.

Although extensive sampling has been carried out on the particle-associated nitro-PAHs, in particular on the nitropyrenes and nitrofluoranthenes (9–18), less emphasis has been put on the semi-volatile nitro-PAHs. In locations where the semi-volatile nitro-PAHs have been measured, including several studies carried out in the Los Angeles Air Basin (9, 10, 30) and in Houston, TX (31), and Rome, Italy (18), the semi-volatile nitro-PAHs such as nitronaphthalenes and methylnitronaphthalenes make up the majority of ambient nitro-PAHs. These semi-volatile nitro-PAHs are also mutagenic and have been reported by Gupta et al. (26) to contribute a significant portion of the total ambient air mutagenicity measured in a bacterial assay system. Ambient sampling has usually been carried out in 12-hr daytime and nighttime periods and only a few studies have employed shorter time periods, which would allow investigation of diurnal PAH and nitro-PAH patterns. In this work, samples were collected over 4 daily time intervals in 2 seasons at a source site in Los Angeles and a downwind receptor site in Riverside.

Experimental Section

Ambient Sampling Conditions. Ambient measurements were carried out in California during August 2002 and January 2003 in Los Angeles, an urban site, and Riverside, a downwind receptor site. The sampling site in Los Angeles was located on the roof of the Denney Research Center (a three story building) at the University of Southern California (USC). The site is heavily impacted by traffic due to its location on a busy city street (across from a parking structure) and approximately 3 km SW of the intersection of the 10 and 110 freeways. In Riverside, located approximately 90 km generally downwind of Los Angeles, samples were collected at an agricultural operations site on the University of California, Riverside (UCR) campus. Sampling was carried out over 5-day periods from August 12–16, 2002, and January 13–17, 2003, in Los Angeles and from August 26–30, 2002, and January 27–31, 2003, in Riverside. Samples were collected in four time periods per day (0700–1030, 1100–1430, 1500–1830 and 1900–0630, local time, PDT in August; PST in January) with fresh sampling media used for each collection. Samples of volatile PAHs were collected onto replicate Tenax-TA solid adsorbent cartridges at 200 cm^3 min^{-1} for the daytime samples and 100 cm^3 min^{-1} for the nighttime samples. A high-volume air sampler equipped with a Teflon-impregnated glass fiber (TIGF) filter (20 cm × 25 cm) and two polyurethane foam plugs (PUFs) in series beneath the filter and without a size-selective inlet was used to collect semi-volatile and particle-associated PAHs and nitro-PAHs at a flow rate of ~0.6 m^3 min^{-1}.

Hourly averaged air pollutant data (including CO, NO, NO$_2$, NO$_x$, and O$_3$) are available from the California Air Resources Board (CARB) (32) for the Los Angeles-North Main Street monitoring station (located <2 km from our sampling site at USC in Los Angeles) and the Riverside-Rubidoux monitoring station. The South Coast Air Quality Management District is the Operating Agency responsible for the measurements which use nondispersive infrared for CO, ultraviolet absorption for O$_3$, and chemiluminescent measurements for NO$_x$. On the basis of these gaseous pollutant data, the two August sampling periods were comparable to one another, as were the two January sampling periods. This is consistent with conclusions reached on the basis of temperatures and wind speeds by researchers sampling concurrently (33). The sampling days in August were characterized by moderate photochemical pollution, which followed the usual development pattern in that the O$_3$ concentrations reached at the downwind Riverside site were higher than those attained in Los Angeles. For the August 12–16 period when sampling was conducted in Los Angeles, the maxima values for the 1 h average O$_3$ concentrations were between 59 and 73 ppbv in Los Angeles and between 89 and 118 ppbv in Riverside. For the August 26–30, 2002, Riverside sampling period, the O$_3$ maxima were between 46 and 68 ppbv in Los Angeles and between 81 and 99 ppbv in Riverside. During the January 2003 sampling days, the O$_3$ in Los Angeles was suppressed (maxima from 7 to 29 ppbv) and even in Riverside did not exceed 41 ppbv.

The primary pollutants, CO and NO, were higher in the winter samples at both locations. During the August sampling days, the 1h CO maxima (ppmv) in Los Angeles and Riverside ranged from 0.6 to 2.7 and 0.7 to 2.7, respectively, while the corresponding maxima for January were 2.6–4.6 and 0.9–3.6. During the August sampling days, the highest NO levels were in the morning and NO became nondetectable (<1 ppbv) each night at both locations, but for varying lengths of time. In the winter, NO was always detected and increased during the night at both locations. With the exception of 2 days in Riverside, the 1h NO maxima during the January sampling days were >200 ppbv and reached as high as 461 ppbv in Los Angeles and 353 ppbv in Riverside. The measured hourly values of NO$_2$ varied from 9 to 121 ppbv, while the August maxima ranged from 28 to 92 ppbv and the January maxima from 38 to 121 ppbv.

Sample Analysis. Prior to analysis, the Tenax samples were spiked with naphthalene-d_8, 1-methylnaphthalene-d_{10}, biphenyl-d_{10}, acenaphthene-d_{10}, and acenaphthylene-d_8 to serve as internal standards. The Tenax samples were then thermally desorbed at 250 °C onto a DB-1701 column [0.25 mm i.d. × 60 m, 0.25 μm film thickness, (14% cyanopropylphenyl)methylpolysiloxane] held at 33 °C for 10 min and then temperature programmed to 280 °C at 10 °C min^{-1} and analyzed by electron impact (EI) gas chromatography–mass spectrometry with selective ion monitoring (GC/MS–SIM) (34). Each of the 8 Tenax samples per day was analyzed individually. The PUFs for each 5-day sampling period were composited according to time interval prior to analysis, as were the filters. Following spiking of the PUFs with 1-nitronaphthalene-d_7, phenanthrene-d_{10}, fluoranthene-d_{10}, and pyrene-d_{10} and the filters with 2-nitrofluoranthene-d_9, 1-nitropyrene-d_9, phenanthrene-d_{10}, fluoranthene-d_{10}, pyrene-d_{10}, and benzo[a]pyrene-d_{12} to serve as internal standards, PUFs and filters were Soxhlet extracted for 10 h in dichloromethane (DCM).

The extracted samples were concentrated to ~100 μL by rotary evaporation and fractionated by normal-phase high-performance liquid chromatography (HPLC) using a 5 μm, 25 cm × 10 mm semipreparative Regis Spherisorb S5W silica column (35). The collected PAH-containing fraction of the PUFs and filters was analyzed by GC/MS in positive ion/chemical ionization (PCI) and selective ion monitoring (SIM) mode and the collected nitro-PAH-containing fraction of the PUFs was analyzed by GC/MS in negative ion/chemical ionization (NCI) and SIM mode. For both analyses an HP-5MS column [0.25 mm i.d. x 30 m, 0.25 μm film thickness, (5% phenyl)methylpolysiloxane] was employed with a temperature program as follows: initial temperature at 40 °C, then temperature-programmed to 300 °C at 8 °C min^{-1}.

The fraction containing nitro-PAHs collected on the filters was analyzed by GC/MS-NCI/SIM on a DB-17 column. The sample was injected at 300 °C onto a DB-17 column [0.25 mm i.d. × 50 m, 0.25 μm film thickness, (50% phenyl)-methylpolysiloxane] held at 40 °C, then temperature-programmed to 200 °C at 20 °C min^{-1}, and then to 300 °C at 2 °C min^{-1}, which allowed separation of the MW 247 isomers (nitropyrenes and nitrofluoranthenes).

TABLE 1. Ambient Concentrations of PAHs (in ng m^{-3}) and Nitro-PAHs (in pg m^{-3}) Measured in Los Angeles and Riverside during August 2002 (all times PDT)[a]

compound	Los Angeles				Riverside				sampling media
	0700−1030	1100−1430	1500−1830	1900−0630	0700−1030	1100−1430	1500−1830	1900−0630	
PAHs (ng m^{-3})									
naphthalene	389	152	127	202	301	54.8	21.5	148	Tenax
2MN	166	48.2	49.3	86.7	113	12.4	6.4	51.1	Tenax
1MN	69.4	17.4	17.2	35.5	37.0	4.3	2.4	20.6	Tenax
2EN	4.8	1.5	1.7	2.3	3.0	0.8	0.5	1.6	Tenax
1EN	1.3	0.5	0.5	0.4	0.9			0.7	Tenax
2,6/2,7 DMN	8.9	1.8	2.0	4.6	3.4	0.7	0.5	2.7	Tenax
1,3/1,7 DMN	9.3	1.6	1.8	4.2	3.0	0.6	0.4	2.2	Tenax
1,6 DMN	5.0	1.0	1.1	2.7	1.9	0.4	0.3	1.8	Tenax
1,4 DMN	0.9	0.3	0.3	0.4	0.4			0.5	Tenax
1,5/2,3 DMN	2.2	0.5	0.6	1.2	0.9			0.7	Tenax
1,2 DMN	1.6	0.4	0.5	0.6	0.7	0.8		0.4	Tenax
biphenyl	8.2	3.5	2.4	2.1	6.1	3.6	2.7	2.3	Tenax
phenanthrene	14.9	11.6	8.2	5.7	10.5	8.2	7.7	5.3	PUF + filter
anthracene	0.5	0.3	0.3	0.03	0.3	0.1	0.1	0.1	PUF + filter
Σ(MePhe)	7.2	7.1	5.7	2.6	4.9	4.3	4.8	1.6	PUF + filter
fluoranthene	2.8	2.2	1.5	1.5	1.4	1.3	1.0	1.1	PUF + filter
pyrene	3.3	2.0	1.8	1.6	1.3	0.8	0.6	0.7	PUF + filter
NPAHs (pg m^{-3})									
1NN	237	243	112	152	190	201	142	354	PUF
2NN	258	243	90	99	308	273	140	237	PUF
2M4NN	10	8	4	10	15	5	9	34	PUF
1M4NN + 1M6NN	70	66	31	41	64	48	36	55	PUF
Σ(MNN)	244	237	108	164	227	167	215	283	PUF
Σ(DMNN + ENN)	128	98	49	106	107	61	38	139	PUF
3NBph	64	73	18	32	103	84	82	40	PUF
9NA	64	18	11	36	31	17	34	26	filter
NPhe	72	46	26	13	60	45	54	19	filter
2NF	131	63	16	41	252	72	30	262	filter
1NP	12	8	3	3	14	4	3	5	filter
2NP	4	1	0.2	1	7	2	0.3	3	filter

[a] Abbreviations: MN, methylnaphthalene; EN, ethylnaphthalene; DMN, dimethylnaphthalene; MePhe, methylphenanthrene; NN, nitronaphthalene; xMyNN, *x*-methyl-*y*-nitronaphthalene; MNN, methylnitronaphthalene; DMNN, dimethylnitronaphthalene; ENN, ethylnitronaphthalene; 3NBph, 3-nitrobiphenyl; 9NA, 9-nitroanthracene; NPhe, nitrophenanthrenes; 2NF, 2-nitrofluoranthene; 1NP, 1-nitropyrene; 2NP, 2-nitropyrene.

The PAHs and nitro-PAHs in the ambient samples were quantified on the basis of response factor solutions, which contained PAHs and nitro-PAHs and their corresponding deuterated species when available. The concentrations of the response factor solutions closest to the respective concentrations in the samples were utilized to determine the response factors relative to the appropriate deuterated internal standard. Naphthalene, naphthalene-d_8, 1- and 2-methylnaphthalene (MN), 1MN-d_{10}, biphenyl, biphenyl-d_{10}, 1- and 2-ethylnaphthalene (EN), and dimethylnaphthalenes (DMNs) were utilized to make the calibration solutions for the Tenax analysis. For 2MN and the ethyl- and dimethylnaphthalene isomers, the response factor was determined relative to 1MN-d_{10}.

For the PAHs collected by PUFs, a response factor solution of phenanthrene, 2-methylphenanthrene, phenanthrene-d_{10}, fluoranthene, fluoranthene-d_{10}, pyrene, and pyrene-d_{10} was used. Semi-volatile nitro-PAHs were quantified relative to a response factor solution containing 1- and 2-nitronaphthalene (NN), 2-methyl-1-nitronaphthalene (2M1NN), 1NN-d_7, and 2,−3, and 4-nitrobiphenyl (NBph). The response factors determined for 2M1NN were used for the quantification of all the ambient MNN and DMNN isomers.

The National Bureau of Standards Standard Reference Material 1587, with the addition of 1NP-d_9, was used to make a calibration solution for the quantification of 9-nitroanthracene, nitrophenanthrenes (assuming responses identical to 9-nitroanthracene), 3NF and 1NP. In addition one calibration solution containing 1NP, 1NP-d_9, and 2NF and one solution containing 2NF and 2NF-d_9 were used to determine response factors for 1NP and 2NF. A standard of 2NP was not available, but a nonquantitative mixture of all the NF and NP isomers was available (*36*). From injection of this mixture, it was apparent that the NCI response of 2NP was low compared to that of 1NP. A "correction factor" was applied to the 2NP NCI GC−MS quantification relative to 1NP-d_9 based on analysis of the mixture containing 1NP and 2NP by GC with a flame ionization detector (FID) and assuming that the GC-FID response of all the MW 247 isomers was equivalent.

Results and Discussion

Ambient measurements were carried out over 5-day periods in summer and winter both at a source site (Los Angeles) and a downwind receptor site (Riverside) in the Los Angeles Basin. The sampling times (given in local time) were chosen to emphasize direct emissions (early morning, 0700−1030, labeled "Morning" on figures), the period of highest expected photochemical activity (*19*) (1100−1430, "Day"), the period around sunset when NO$_3$ chemistry could begin (1500−1830, "Evening"), and an overnight sample (1900−0630, "Night").

Ambient PAH Concentrations. The measured ambient concentrations (in ng m^{-3}) of the PAHs collected on Tenax cartridges and PUFs + filters are given in Tables 1 and 2 for the summer and winter, respectively. The individual Tenax samples have been averaged to match the 16 composited PUF and 16 composited filter samples (2 sites × 2 seasons × 4 time intervals). Highest concentrations were observed for the volatile PAHs, with naphthalene and MNs being the most abundant PAHs. Phenanthrene was the most abundant PAH collected on PUFs and, at both Los Angeles and Riverside, fluoranthene and pyrene were present at con-

TABLE 2. Ambient Concentrations of PAHs (in ng m^{-3}) and Nitro-PAHs (in pg m^{-3}) Measured in Los Angeles and Riverside during January 2003 (all times PST)[a]

| compound	Los Angeles 0700−1030	1100−1430	1500−1830	1900−0630	Riverside 0700−1030	1100−1430	1500−1830	1900−0630	sampling media
				PAHs (ng m^{-3})					
naphthalene	1589	758	1211	1149	535	110	183	499	Tenax
2MN	728	310	587	621	287	50.5	79.8	240	Tenax
1MN	306	110	235	363	90.6	16.2	29.2	92.0	Tenax
2EN	30.2	11.3	22.5	36.5	14.6	3.9	7.8	12.7	Tenax
1EN	4.5	2.0	3.5	5.2	2.5	1.5	1.2	1.7	Tenax
2,6/2,7 DMN	40.3	13.5	33.1	59.2	18.0	4.4	7.9	17.7	Tenax
1,3/1,7 DMN	40.8	12.7	32.5	61.7	16.6	3.8	6.7	16.8	Tenax
1,6 DMN	19.4	6.7	15.6	30.5	9.4	2.3	4.0	9.5	Tenax
1,4 DMN	3.3	1.5	2.6	5.5	2.2	0.8	1.3	1.9	Tenax
1,5/2,3 DMN	9.6	3.6	8.7	16.4	4.9	1.4	2.7	5.1	Tenax
1,2 DMN	6.9	2.6	6.1	10.8	3.4	1.1	1.8	2.9	Tenax
biphenyl	22.9	15.0	14.5	21.4	10.5	5.4	5.6	10.9	Tenax
phenanthrene	17.3	15.1	18.0	15.4	13.5	7.2	12.8	10.5	PUF + filter
anthracene	1.6	0.5	1.2	1.3	0.7	0.1	0.3	0.6	PUF + filter
Σ(MePhe)	8.8	8.5	10.2	7.6	7.2	4.5	6.3	4.4	PUF + filter
fluoranthene	6.0	3.4	4.1	3.1	2.4	1.3	2.0	1.7	PUF + filter
pyrene	6.9	3.3	4.9	3.7	2.7	0.9	1.6	1.5	PUF + filter
				NPAHs (pg m^{-3})					
1NN	111	132	153	100	106	41	178	201	PUF
2NN	151	144	130	76	131	53	163	142	PUF
2M4NN	10	8	10	9	15	3	10	23	PUF
1M4NN + 1M6NN	35	48	56	30	30	19	56	45	PUF
Σ(MNN)	178	174	214	139	156	76	201	209	PUF
Σ(DMNN + ENN)	152	115	130	120	107	34	91	130	PUF
3NBph	138	138	48	26	80	62	86	49	PUF
9NA	12	13	44	20	11	9	50	21	filter
NPhe	20	44	52	10	16	27	65	15	filter
2NF	112	98	53	34	78	40	60	139	filter
1NP	38	13	12	21	19	8	9	13	filter
2NP	19	5	3	4	6	3	3	5	filter

[a] See Table 1 for abbreviations.

centrations similar to one another. As noted on the tables, the concentrations of phenanthrene, anthracene, methylphenanthrenes, fluoranthene and pyrene given in Tables 1 and 2 are the sum of what was measured on the filters and on the PUFs. For phenanthrene the amount on the filters varied from 2% to 7% of the total and for fluoranthene and pyrene the amount on the filters ranged between 15 and 40% of the total.

In Los Angeles, sampling was carried out on a busy street close to the intersection of two major freeways, and therefore it is expected that the major source of PAHs was vehicular emissions. Consistent with a traffic source for the PAHs, their concentrations were higher in Los Angeles than downwind in Riverside. The relative abundance of the alkylnaphthalenes was similar to what has been found in diesel fuel, with 1,6-, 1,7-, 2,6 and 2,7-DMNs being the major DMN isomers identified both in diesel fuel (37, 38) and in our ambient air samples. At each time period, ambient concentrations of 2MN were 2−3-fold higher than ambient concentrations of 1MN. While this ratio is consistent with diesel emissions, where a 2MN:1MN ratio of 2 was observed (38, 39), and also with previous ambient measurements carried out in Glendora, CA in August 1986 (30), the relative contributions of gasoline and diesel emissions to the 2- to 4-ring PAH concentrations reported here is unknown.

On the basis of the 1997 CARB inventory, the mobile source contribution to CO in the Los Angeles air basin is estimated to be 97% (40), and CO may be viewed as a nonreactive tracer for vehicle emissions (41). Therefore, normalizing our PAH and nitro-PAH measurements to CO compensates for large differences in mixing heights that occur during a diurnal cycle, as well as for dilution during transport to Riverside. An inherent assumption in this normalization is that differences in the relative amounts of gasoline versus diesel traffic leads to only minor temporal or spatial variations in the ratios of emitted PAHs. Additionally, it should be recognized that a size-dependent physical removal of particles may affect ambient concentrations of the particle-associated species. As is clear from Tables 1 and 2 and Figure 1, observed PAH levels were higher during the winter, in particular for the volatile PAHs at the Los Angeles site. Although the morning PAH concentrations were a factor of 4 higher in the winter in Los Angeles, they were less than a factor of 2 higher when normalized to CO (see Figure 1), suggesting that differences in meteorology, and particularly lower morning mixing heights perhaps with surface inversions in January, contributed to the higher winter concentrations. While normalizing to CO removed much of the diurnal variation for the winter samples, the normalized summer samples show decreases in concentration for the Day and Evening samples at both sites, suggesting atmospheric reactions.

Hydroxyl Radical Reactions. The morning samples in Los Angeles are expected to be most strongly influenced by direct vehicle emissions, with the ratios of the various volatile PAHs creating a "traffic PAH profile" reflecting vehicle exhaust. The maximum OH radical concentration is expected to occur during the 1100−1430 sample (19). For the 2-ring PAHs listed in Table 1, calculated lifetimes due to gas-phase reaction with the OH radical for a radical concentration of 5×10^6 molecule cm^{-3} (as noted, this is a value reported by George et al. for Los Angeles (19)) vary from ~40 min for dimethylnaphthalenes (34) to 8 h for biphenyl (7, 8). Therefore, sufficient reaction could occur during the 1100−1430 sampling period to change the traffic PAH profile (i.e., with the most reactive PAHs decreasing the most). As may be seen from Figure 2, this is indeed the case. Figure 2 shows
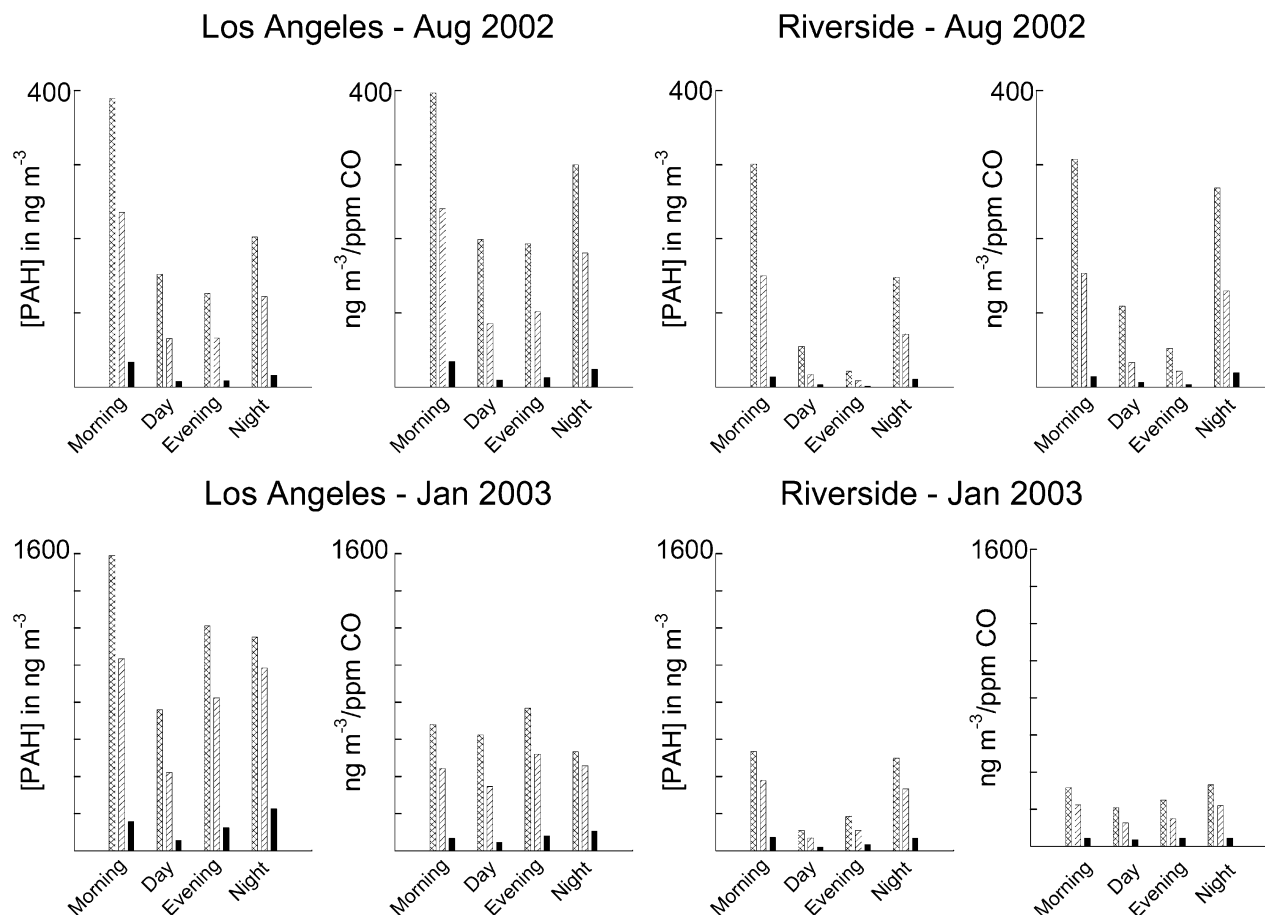
FIGURE 1. Diurnal and seasonal variations of ambient concentrations of naphthalene (bars with X's), MNs (hatched bars) and ENs/DMNs (■) observed in Los Angeles and Riverside. Ambient concentrations (ng m⁻³) and concentrations normalized to CO. The sampling times (PDT for August, PST for January) were as follows: morning, 0700−1030; day, 1100−1430; evening, 1500−1830; night, 1900−0630.
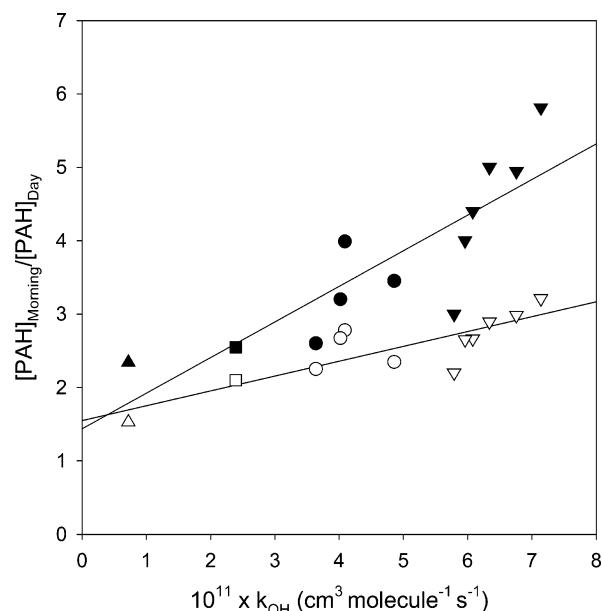

FIGURE 2. Plot of [PAH]$_{Morning}$/[PAH]$_{Day}$ concentration ratios vs OH radical reaction rate constant for biphenyl (▲, △), naphthalene (■, □), ENs and MNs (●, ○), and DMNs (▼, ▽) for the samples collected in Los Angeles during August 2002 (filled symbols) and January 2003 (open symbols). Shown are the least squares lines.

plots of the (average [PAH]$_{Morning}$/average [PAH]$_{Day}$) for nine individual PAHs and three pairs of coeluting DMNs plotted against their rate constants (*7, 34*) for reaction with the OH

radical. The linear correlations obtained indicate that OH radical reaction is influencing the ambient concentrations and the steeper slope of the summer data set compared to the winter data set suggests, as expected, higher OH radical concentrations in summer. Consistent with a significant effect on the Riverside samples of transport of PAHs from Los Angeles, a plot of the Riverside data similar to Figure 2 has more scatter and a slope close to zero.

The diurnal variations, as well as the winter/summer differences, were less pronounced for the semi-volatile PAHs compared to the naphthalenes and alkylnaphthalenes. This may reflect the fact that the semi-volatile PAHs, such as phenanthrene and especially fluoranthene and pyrene, have a temperature-dependent component which is particle-associated and unavailable for gas-phase radical-initiated reactions.

Ambient Nitro-PAH Concentrations. The measured ambient concentrations (in pg m⁻³) of the nitro-PAHs collected on PUFs and filters are shown in Tables 1 and 2 for the summer and winter, respectively. The gas-phase nitro-PAHs are the most abundant nitro-PAHs measured in ambient air. The nitronaphthalenes (NNs) and alkyl-nitronaphthalenes made up about 80% of the total nitro-PAHs measured. The most abundant isomers of the MW 223 nitrophenanthrenes/nitroanthracenes identified in our ambient samples were 9-nitroanthracene (9NA) and two isomers presumed to be nitrophenanthrenes, but lacking authentic standards these were not further identified. Four of the eight MW 247 isomers (nitropyrenes/nitrofluoranthenes) were identified in our samples. 2-Nitrofluoranthene (2NF) was by far the most abundant particle-associated nitro-PAH, and lower levels of 1-nitropyrene (1NP), 2-nitropyrene
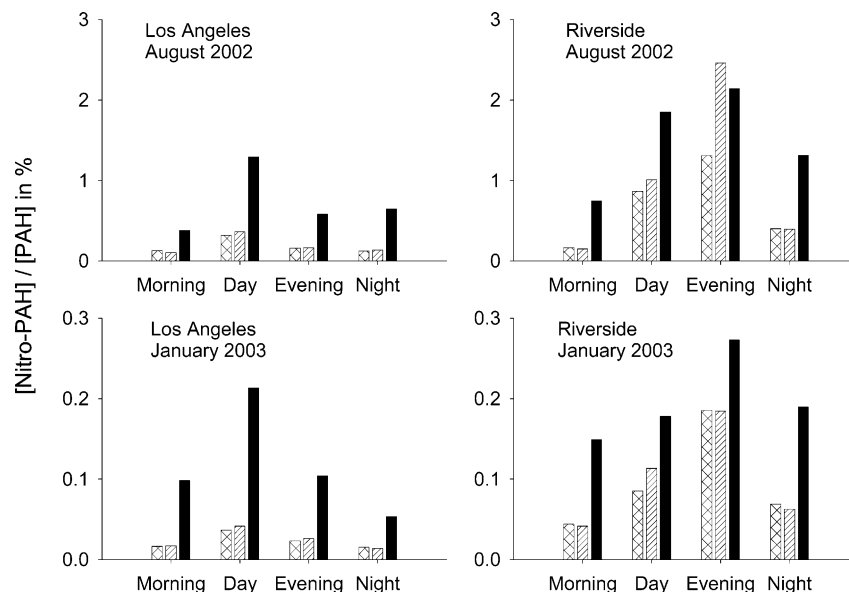
FIGURE 3. Diurnal, seasonal and spatial variations of the ratios of [NPAH]/[PAH] (in %) for NNs/Naph (bars with X's), MNNs/MNs (hatched bars) and (DMNNs + ENNs)/(DMNs + ENs) (■) for Los Angeles and Riverside. The sampling times are as listed in the caption to Figure 1.

(2NP) and small amounts of 8-nitrofluoranthene (8NF) were also observed.

Unlike the PAHs, where higher levels were observed during the winter and in Los Angeles, nitro-PAH concentrations were in general higher during the summer and in Riverside (see Tables 1 and 2). This is compelling evidence that the presence of these nitro-PAHs is due to atmospheric formation rather than direct emissions.

Nitro-PAH Formation from OH Radical Reaction. Whereas nitro-PAH concentrations are highest for NNs followed by MNNs and DMNNs + ENNs (Tables 1 and 2), as shown in Figure 3, an inverse trend is observed for the ratios of nitro-PAH/PAH. These nitro-PAH/ PAH formation ratios were higher in the summer than in winter by a factor of ~10, highlighting the increased chemistry occurring during summertime. In Los Angeles the high [nitro-PAH]/[PAH] ratio during 1100−1430 h (Day on figures) is attributed to nitro-PAH formation from the OH radical-initiated reactions and the higher ratios obtained for the alkylated naphthalenes relative to [1 + 2NN]/[naphthalene] (see Figure 3) are likely due to the enhanced reactivity toward OH radical reaction resulting from the addition of one or two methyl groups to the naphthalene ring (34, 42), but may also reflect higher nitro-PAH formation yields. In Riverside, the highest [nitro-PAH]/[PAH] ratios were observed in the evening indicating transport of an aged, reacted air mass from Los Angeles in addition to on-site OH and/or NO_3 radical chemistry.

In each of the PUF samples 1- and 2NN, 13 of the 14 methylnitronaphthalene (MNN) isomers (2M3NN was not identified), 3-nitrobiphenyl (3NBph), and, as recently reported for the first time (43), dimethylnitronaphthalenes (DMNNs) and possibly ethylnitronaphthalenes (ENNs) were present. In Los Angeles in summer the highest concentrations of these semi-volatile nitro-PAHs were observed during the two daytime samples and the highest ratio of nitro-PAH/ PAH was observed for the 1100−1430 sample in both summer and winter (see Figure 3, Day). The profiles of the specific MNN and DMNN/ENN isomers in the Los Angeles samples were compared to those formed from a PAH-containing fraction of diesel fuel volatilized and reacted with the OH radical in the presence of NO_x (43), and the isomer profiles were similar, consistent with OH radical-initiated formation modified by rapid photolysis of certain isomers (43−45).

Seasonal differences in nitro-PAH concentrations and differences between nitro-PAHs formed only by OH radical-initiated reactions (3-nitrobiphenyl and 2-nitropyrene (6−8)) and those formed both by OH and NO_3 radical-initiated reactions are seen in Figure 4, which shows the nitro-PAH concentrations normalized to CO. 3-Nitrobiphenyl formation (3NBph/Bph) shows the same Day period high in Los Angeles shown in Figure 3 for NNs, MNNs and DMNNs/ENNs and this Day high is also seen, although not as obviously, in the ratios to CO for 3NBph, NNs, and MNNs (Figure 4). Although the lifetime of biphenyl is long relative to that of the DMNs, the 5% yield of 3-NBph from the OH radical reaction (6−8) results in relatively high 3-NBph concentrations. In contrast to the semi-volatile nitro-PAHs, the ratios for the particle-associated nitro-PAH, 2NP and 2NF, did not show the same Day period maxima in Los Angeles. However, like the semi-volatile nitro-PAHs, the highest ratios of 2NF/CO (and for 2NP/CO the 2nd and 3rd highest ratios) were in the summer Riverside samples, consistent with OH radical-initiated formation of 2NP, and OH and NO_3 (discussed further below) radical-initiated formation of 2NF.

Nitro-PAH Formation from NO_3 Radical Reaction. As seen from Figure 4, those nitro-PAHs formed only by OH radical-initiated reactions, i.e., 3NBph and 2NP, showed less variation in their summer vs winter ratios to CO than those nitro-PAHs formed by both OH and NO_3 radical-initiated reactions, i.e., 1NN, 2NN, MNNs, DMNNs, and 2NF (6−8), suggesting that summertime NO_3 radical chemistry contributed to the ambient concentrations of the latter. For example, comparing the Riverside summer maxima to the Riverside winter maxima (both normalized to CO), the summer values were factors of 2.3, 1.9, 2.0, and 5.2 greater for the NNs, MNNs, DMNNS + ENNs, and 2NF, respectively. In contrast, the corresponding factors for summer over winter in Riverside were 1.7 and 1.5 for 3NBph and 2NP, respectively. Additionally, while the ratios of the nitro-PAH/PAH shown in Figure 3 for the nitronaphthalenes and alkylnitronaphthalenes are an order of magnitude higher in the summer than in the winter (note *y*-axes on figure), the corresponding summer versus winter difference for 3-NBPh/Bph is only approximately a factor of 2.

In contrast to Los Angeles where the semi-volatile nitro-PAH/PAH and nitro-PAH/CO ratios peaked during the 1100−
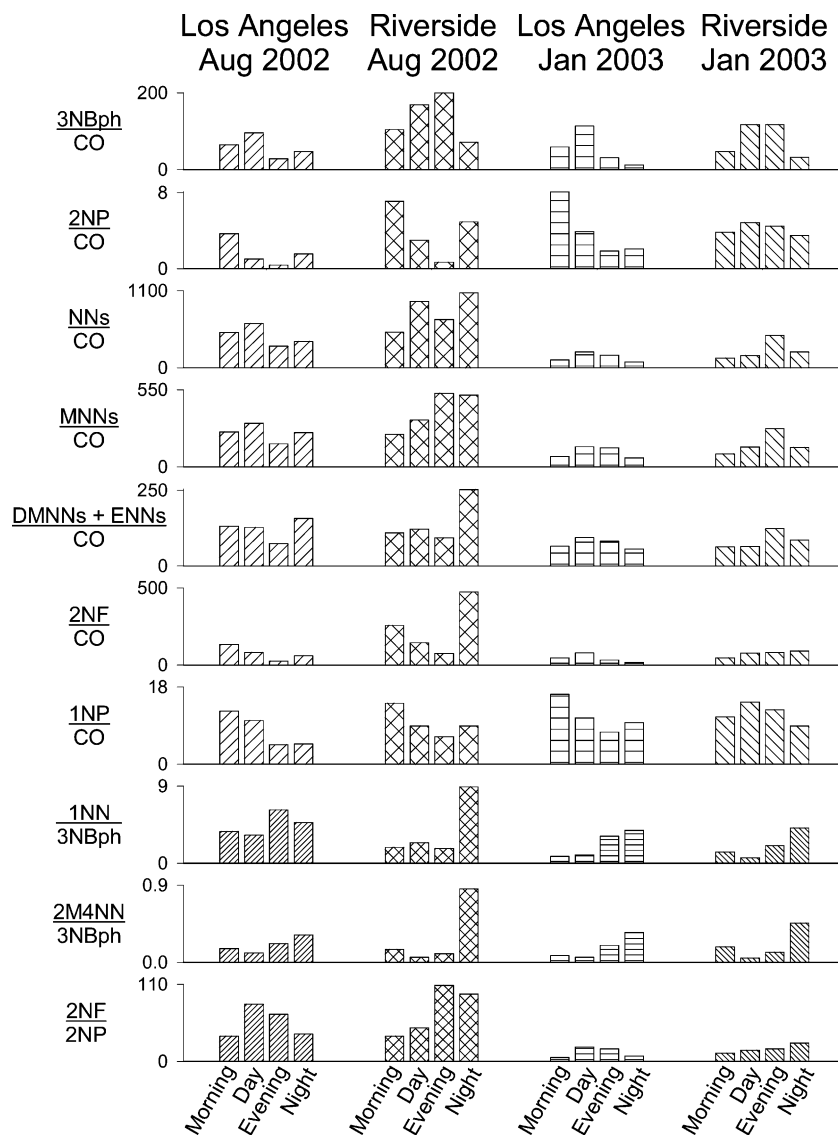
FIGURE 4. Ratios of [Nitro-PAHs]/[CO] in units of pg m⁻³/ppm for semi-volatile and particle-associated nitro-PAHs for samples collected in Los Angeles and Riverside and ratios of nitro-PAH pairs with different possible formation mechanisms. The sampling times are as listed in the caption to Figure 1.

1430 samples, in Riverside in the summer the NNs, MNNs, and DMNNs normalized to CO (see Figure 4) were highest in the overnight samples and the formation ratios of nitro-PAH/PAH peaked in the Evening samples (see Figure 3). The isomer profiles of the MNNs provide confirmation of NO_3 radical-initiated formation of nitro-PAHs. In the nighttime Riverside sample (Figure 5, bottom mass chromatogram), 2M4NN, 2M1NN, and 1M3NN were elevated relative to 1M5NN and 1M4NN + 1M6NN when compared with the other samples. The most abundant MNN isomers in all our samples were 1M5NN and 1M6NN + 1M4NN, consistent with OH radical chamber reactions of MNs (reacted in a 2:1 ratio of 2MN:1MN, reflecting ambient levels), where highest yields from the OH reactions were measured for 1M5NN, 1M4NN, 1M6NN, 2M5NN, 2M6NN, and 2M7NN (*7, 43, 46*). As noted above, the MNN profiles in the daytime samples (top and center in Figure 5) match the profile of chamber OH radical reactions (*7, 43, 46*), except that the isomers that photolyze rapidly, in particular 2M1NN, are lower in the ambient samples. 2M4NN has been reported to be the major isomer formed from the NO_3 radical reactions of 2MN, followed by 2M1NN (*7, 46*) and 1M3NN has been reported to be the major isomer formed from 1MN (*7, 46*). Thus, the elevated levels of 2M4NN, 2M1NN, and 1M3NN in the

nighttime Riverside summer sample (bottom mass chromatogram in Figure 5) indicate the occurrence of NO_3 radical formation. The highest ratios of 1NN/2NN were observed in the nighttime Los Angeles and Riverside samples. Since the ratio of 1NN/2NN is ~1 for the OH radical-initiated reaction of naphthalene and ~2 for the NO_3 radical-initiated reaction (*47*), this nighttime increase is consistent with NO_3 chemistry occurring, but it should be noted that 1NN also photolyzes more rapidly than 2NN (*44, 45*).

Since 3NBph is formed only by OH radical reaction, while 1NN is formed by both OH and NO_3 radical reactions of naphthalene and 2M4NN is formed by both OH and NO_3 radical reactions of 2MN, the ratios 1NN/3NBph and 2M4NN/3NBph should increase if NO_3 chemistry occurs. The high values of both ratios observed in the summer, Riverside, nighttime samples (see Figure 4) are consistent with the altered MNN profile noted above, and with our previous reports of NO_3 radical-initiated formation of NNs and MNNs at downwind sites in the Los Angeles air basin (*26, 48*).

As noted, 2NF is formed by both OH and NO_3 radical reactions, while 2NP is only formed by the OH radical-initiated reaction (*6−8*). From environmental chamber studies (*49*) in which the products of the rate constants (*k*) for the OH radical-initiated reactions with gas-phase FL and
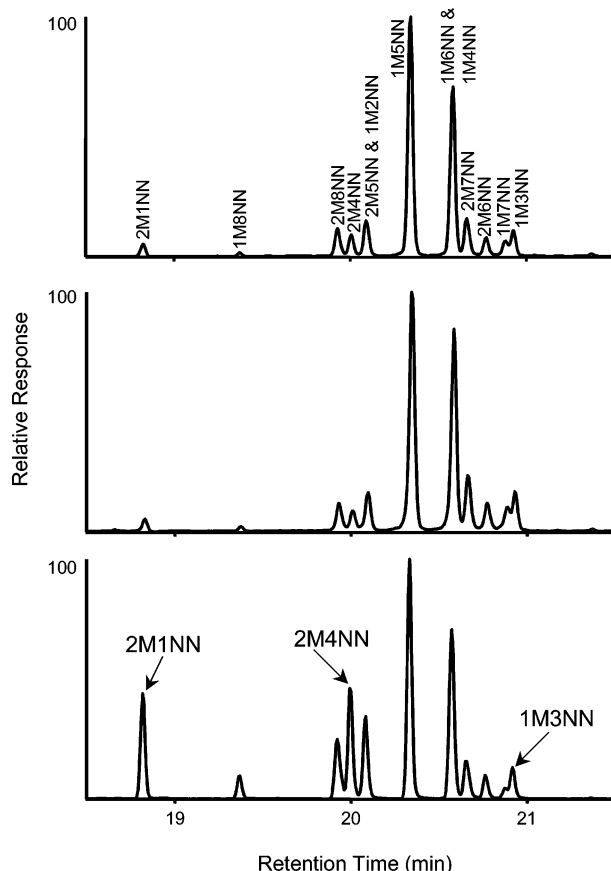
FIGURE 5. Mass chromatograms for the methylnitronaphthalenes (*m/z* 187) observed by GC/MS NCI-SIM analysis of composite air samples collected during August 2002: top, 1100–1430 h (Day) samples collected in Los Angeles; center, 1100–1430 h samples collected in Riverside; bottom, 1900–0630 h (Night) samples collected in Riverside.

Pyr and the nitro-PAH yields (Y) were measured (i.e., $k_{FL}Y_{2NF}$ and $k_{Pyr}Y_{2NP}$), the ratio determined for 2NF/2NP was ∼6. Because FL and Pyr are isomers and are generally present in ambient air in nearly equal concentrations (see Tables 1 and 2), their gas-phase concentrations should also be similar, and if only OH radical chemistry is considered, the 2NF/2NP formation ratio should be similar to the chamber value of ∼6. If NO₃ chemistry occurs in an airmass, the 2NF/2NP ratio will increase.

Widely varying ratios of 2NF/2NP in ambient air have been observed, and varying criteria are used to distinguish the presence of 2NF formed by NO₃ chemistry (*9–11, 13, 15–18*). Values of 2NF/2NP of 10 or less have most often been observed, while we have reported values as high as 200 for Claremont, CA (*11*). Although higher O₃ maxima were reached in Riverside, during the August sampling the NO became nondetectable each night at both sampling locations. Furthermore, O₃ and NO₂ were present at sunset, and therefore, NO₃ formation was expected to occur. In contrast, in the winter at Los Angeles no photochemical production of O₃ occurred and in Riverside the maximum calculated NO₃ from equations (1) and (2) was <1pptv, recognizing that this calculation assumes that steady-state conditions apply.

If the winter nitro-PAHs in the present study were formed largely or solely by OH radical-initiated reactions, the average of the eight 2NF/2NP winter values of 16 ± 7 can be taken as indicative of OH radical-initiated chemistry. Note that because we did not have a quantitative 2NP standard (see Experimental Section), there may be some systematic error in the ratio we are reporting here. The highest ratios of 2NF/

2NP were observed in the summer in the Riverside evening (1500–1830; 2NF/2NP = 109) and nighttime (1900–0630; 2NF/2NP = 96) samples. Moreover, the ratios for all of the summertime samples were >35, suggesting that NO₃ radical-initiated reactions contributed to 2NF formation during August at both the Los Angeles site and the downwind Riverside location. Because of the continuous input of NO from traffic, the finding of significant NO₃ chemistry occurring in Los Angeles was initially somewhat unexpected, but as noted in the Introduction, the presence of NO₃ aloft has recently been reported (*23, 24*).

Directly Emitted Nitro-PAHs. The photochemically formed nitro-PAHs showed seasonal and spatial variations, with the highest nitro-PAH/CO ratios generally observed in the summer samples at the downwind inland site. The range in the ratio of 1NP/CO was significantly less than that for 2NP/CO or 2NF/CO (see Figure 4), consistent with a direct emission vehicle traffic source for 1NP. Its concentration increased in the winter as a result of lower mixing heights and was not diminished by the reduced photochemistry in January.

As noted, observations similar to this study of the dominance by 2NF of the particle-associated nitro-PAHs have been made at other locations in the United States (*9–12, 17*), Europe (*13–16, 18*), and sites worldwide (*13*). Recently, 1NP/2NF ratios > 1 were observed in some samples collected in Copenhagen (*16*). Additionally, very high 1NP concentrations (up to 42 ng m⁻³) have been measured in an underground Estonian oil shale mine contaminated by diesel exhaust (*50*), and 1NP/2NF ratios > 1 have also been observed in roadway tunnels (*51*). These data suggest that 1NP concentrations are controlled by emissions from vehicles, in particular from diesel engines, and are influenced primarily by atmospheric dilution.

Fate of Nitro-PAHs. The major loss process for gas-phase nitro-PAHs is photolysis (*44, 45*) and the specific isomer strongly influences the photolysis rate (*44, 45*). For example, measurements of the photolysis rate of the NNs and of 11 of the 14 MNNs resulted in calculated lifetimes ranging from 6 min (for 1M8NN) to 177 min (for 2NN) [calculated for an NO₂ photolysis rate, J_{NO2}, of 0.312 min⁻¹] (*45*). On the basis of modeling 2NF, 1NP, and 2NP decay on diesel soot or wood smoke particles in an outdoor chamber, Kamens and co-workers concluded there was little difference in the rate of photooxidation in sunlight based on structure, but they found faster decay on wood smoke particles than on diesel soot particles (*52*). The lifetime they determined for photolysis of 2NF on diesel soot [J_{NO2} of 0.312 min⁻¹] was 126 min (*52*). Radical chain reactions initiated by reactive carbonyl compounds have been suggested to control the degradation of nitro-PAHs on aerosol particles, and it was proposed that degradation may be faster on aged organic aerosols than freshly emitted aerosols (*53*). These laboratory studies indicate that the nature of the particles is an important determinant of photolysis rates of particle-associated nitro-PAHs, making extrapolations to ambient conditions uncertain. Also, 2NF has been found at remote locations worldwide, suggesting a long atmospheric lifetime (*13*).

Evidence for the occurrence of NO₃ radical reactions, based on nitro-PAH formation, is most apparent from the 2NF/2NP ratios, which suggested a contribution from NO₃ reaction to the 2NF concentration for all of the Los Angeles and Riverside summer samples. The ratios of 2M4NN/3NBph and 1NN/3NBph, as well as the profile of the MNN isomers (Figure 5), only identified the nighttime, Riverside, August sample as obviously influenced by NO₃ radical chemistry (see Figure 4). In the Los Angeles air basin, nighttime elevated polluted layers are known to occur (*54–56*). If NO₃ radical chemistry occurred in an elevated layer isolated from ground level NO emissions, 2NF, NNs, MNNs, and DMNNs would

be expected to be formed and when the morning convective boundary layer exceeded the height of the nocturnal boundary layer they would be mixed downward. The contribution of nitro-PAHs formed by nighttime NO_3 radical reaction to samples collected during the day will depend on how much of the nitro-PAH was formed by NO_3 reaction and its rate of loss due to photolysis. The impact of the NO_3 radical-formed nitro-PAH on the daytime profile will depend on the magnitude of formation from the OH radical reaction. The high 2NF/2NP ratio in all the summer samples suggests that there is indeed a "carry-over" contribution (or in the case of Riverside a "transported" contribution) to daytime 2NF from nighttime NO_3 radical-initiated 2NF formation. As seen in Figures 3 and 4, the semi-volatile 2-ring nitro-PAHs maximized in Los Angeles during the 1100−1430 Day period, while 2NF was higher in the morning than Day samples, suggesting that the rate of OH radical-initiated formation of the 2-ring nitro-PAHs is faster than for 2NF (this is consistent with a lower ratio of $[FL]_{Morning}/[FL]_{Day}$ than for the 2-ring PAHs shown in Figure 2) and/or there was a higher relative contribution (i.e., for NO_3 vs OH radical formation) to 2NF than occurred for the semi-volatile nitro-PAHs.

In addition to an OH radical concentration profile which follows light intensity (19), there can also be a morning spike in OH radical concentration due to early morning photolysis of HONO which built up overnight (57, 58). If this occurred, 2NF, 2NP, 3NBph, NNs, MNNs, and DMNNs would be formed. The presence of enhanced 2NF and 2NP in certain morning samples, and especially of 2NP in the winter in Los Angeles (Figure 4) could be due to HONO photolysis, but the lack of corresponding maxima in 3NBph and other 2-ring nitro-PAHs is difficult to explain. It should be noted that the present samples were not collected with a size-fractionated inlet. Nitro-PAH analyses of size-resolved particles, sampling of nitro-PAHs with greater time resolution and/or at elevated sites, as well as additional laboratory studies of nitro-PAH formation and photolysis could improve our understanding of the apparent differences in behavior seen in this study between the semi-volatile and particle-associated nitro-PAHs.

Clearly, in southern California and many other localities, atmospheric 2NF formation dominates over direct emissions of nitro-PAHs such as 1NP. Despite their rapid photolysis, in southern California and other areas where vehicle emissions of 2-ring PAHs and high levels of photochemical oxidants occur, semi-volatile nitro-PAHs achieve concentrations higher than those of particle-associated nitro-PAHs. Further investigations of ambient nitro-PAHs are needed, in part because formation of short-lived 2-ring nitro-PAHs may "cycle" gas-phase PAHs onto other compound classes, including quinones (59, 60), which may also have important toxicological implications (61, 62).

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