Supporting Information

for

Formation of nitro-PAHs from the heterogeneous reaction of ambient particle-bound PAHs with $N_2O_5/NO_3/NO_2$

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Experimental Methods

Ambient Filter Sample Collection

Los Angeles Basin. Noted on Figure S1 are Los Angeles, Azusa, Riverside, and Banning, CA, four sites in the Los Angeles Air Basin where ambient filter samples were collected during a photochemical air pollution episode on August 22-23, 1997 as part of the Southern California Ozone Study-North American Research Strategy for Tropospheric Ozone (SCOS97-NARSTO) campaign. Samples were collected at an average flow rate of ~0.6 m^3 min^{-1} at time intervals of 0600-1200, 1200-1800, and 1800-0600 hr for Los Angeles and Azusa samples, and 0600-1800 and 1800-0600 hr for the Riverside and Banning sites. Filter samples were collected using high-volume (Hi-vol) sampling devices, each consisting of a Teflon-impregnated glass fiber (TIGF) filter (Pallflex T60A20, 8 in × 10 in) for collection of ambient particulate matter (PM) located upstream of two polyurethane foam (PUF) plugs in series for the collection of semi-volatile compounds. Filters were then stored at -20ºC until extraction and analysis in 2012. Volatile species, such as naphthalene, 1- and 2-methylnaphthalene, and biphenyl were sampled onto Tenax TA absorptive cartridges as previously described (Atkinson et al., 2001). Volatile PAHs collected on Tenax were analyzed in 1997 as soon as possible after sampling and are reported in Atkinson et al., 2001. Polyurethane foam (PUF) plugs collected during the same study were Soxhlet extracted with DCM, fractionated with high performance liquid chromatography (HPLC), and the nitro-PAH fraction (Fr. 4) analyzed by GC-MS as previously described (Atkinson et al., 2001). These PUF plug extracts were archived at -20 ºC until re-analysis of the nitro-PAH fraction for this study. Concentrations of semi-volatile nitro-PAHs collected on PUF plugs and reported (Atkinson et al., 2001), match well with the concentrations derived from re-analysis in 2012.

Riverside 2012: Particulate matter was collected on TIGF filters (Pallflex T60A20, 8 in × 10 in) at an average flow rate of ~0.6 m^3 min^{-1} for 12-hour intervals concurrently with two Hi-vol sampling apparatus located at the Air Pollution Research Center at the University of California, Riverside.

Beijing. Samples of particles with diameters <10 µm were collected at Peking University in Beijing, China from May 2009 to February 2010 and <2.5 µm from April 20-22, 2011 using a three-stage High Volume Cascade Impactor (Series 230, Tisch Environmental, Cleves, OH) equipped with quartz filters (no. 1851-865, Tisch Environmental, Cleves, OH; 8 in × 10 in) during 24-hour collection intervals at a flow rate of ~1.0 m^3 min^{-1} (Wang et al., 2009). Samples were stored frozen until shipment to the United States and then stored at -20 ºC until this study.

Table S1 gives a summary of the details of the sample collection for all the ambient filters used in chamber studies.

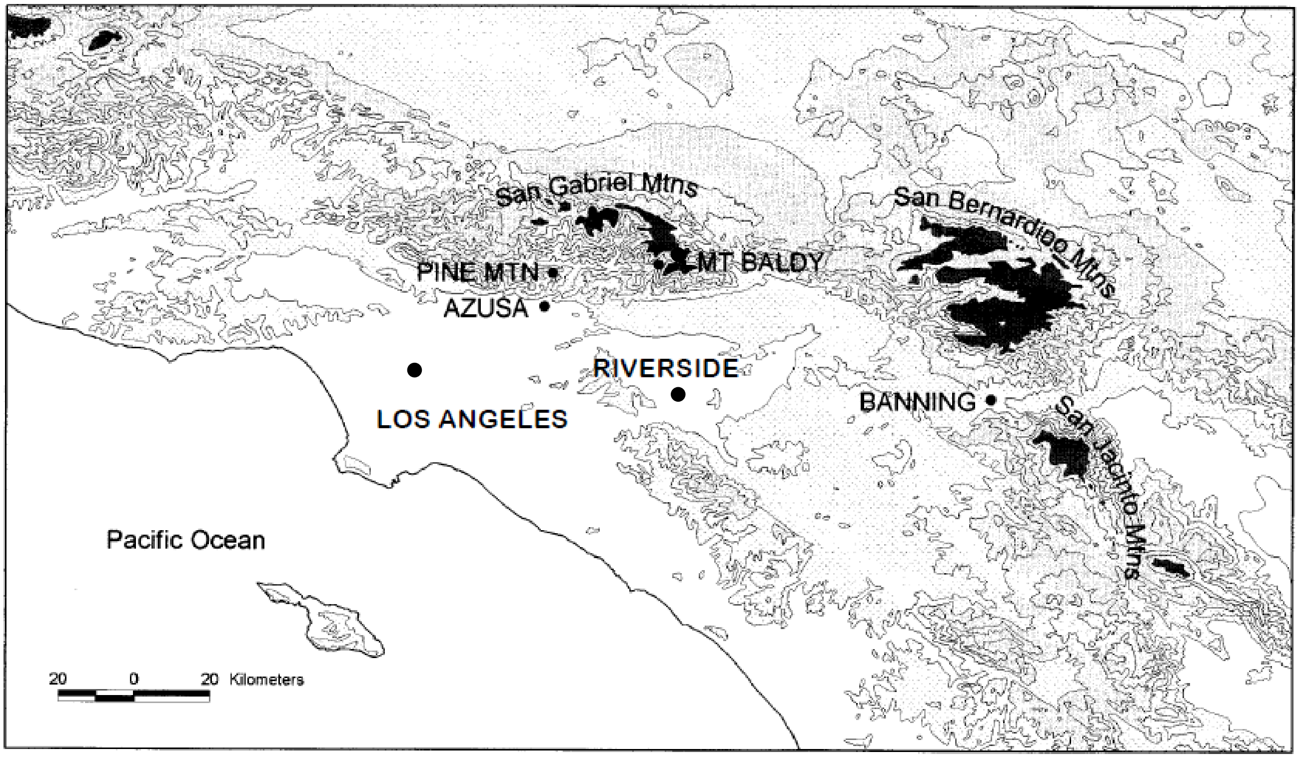

Figure S1. Map showing the four sites from the Southern California Ozone Study-North American Research Strategy for Tropospheric Ozone (SCOS97-NARSTO) campaign from which archived particulate matter (PM) filters were employed in this study. The sites were: Los Angeles, Azusa, Riverside, and Banning, CA. Half of each PM filter was analyzed for selected PAH and nitro-PAH and the remaining half was exposed to $N_2O_5/NO_3/NO_2$ in an environmental chamber prior to analysis.

Table S1. Sampling details for ambient samples used in chamber studies

Sample identification	Location	Date	Time	Total sample volume (m^3)[a]	Size selective inlet
Beijing 1[b]	Peking University[c]	May 2009-Feb 2010	24-hr.	1336	<10 µm
Beijing 2[b]	Peking University[c]	4/20/11-4/21/11	24-hr.	1401	<2.5 µm
Beijing 3[b]	Peking University[c]	4/21/11-4/22/11	24-hr.	1353	<2.5 µm
LA97-1	Central Los Angeles[d]	8/22/97	0600-1158	200	None
LA97-2	Central Los Angeles[d]	8/22/97	1202-1800	200	None
LA97-3	Central Los Angeles[d]	8/22/97-8/23/97	1803-0556	400	None
LA97-4	Central Los Angeles[d]	8/23/97	0602-1158	200	None
LA97-5	Central Los Angeles[d]	8/23/97	1202-1800	200	None
A97-13	Azusa[e]	8/22/97	0600-1200	200	None
A97-15	Azusa[e]	8/22/97	1203-1800	200	None
A97-16	Azusa[e]	8/22/97-8/23/97	1800-0600	400	None
A97-18	Azusa[e]	8/23/97	0603-1200	200	None
A97-20	Azusa[e]	8/23/97	1204-1800	200	None
R97-13	Riverside[f]	8/22/97	0600-1802	400	None
R97-14	Riverside[f]	8/22/97-8/23/97	1811-0600	400	None
R97-15	Riverside[f]	8/23/97	0614-1750	400	None
B97-14	Banning[g]	8/22/97	0605-1800	400	None
B97-15	Banning[g]	8/22/97-8/23/97	1814-0600	400	None
B97-17	Banning[g]	8/23/97	0607-1800	400	None
R2012 N1	Riverside[h]	5/10/12-5/11/12	1800-0600	446[i]	None
R2012 D1	Riverside[h]	5/11/12	0600-1800	446[i]	None
R2012 N2	Riverside[h]	5/11/12-5/12/12	1800-0600	446[i]	None

Sample identification	Location	Date	Time	Total sample volume (m^3)[a]	Size selective inlet
R2012 D2	Riverside[h]	5/12/12	0600-1800	446[i]	None
R2012 N3	Riverside[h]	5/12/12-5/13/12	1800-0600	446[i]	None
R2012 D3	Riverside[h]	5/13/12	0600-1800	446[i]	None
R2012 N4	Riverside[h]	5/13/12-5/14/12	1800-0600	446[i]	None
R2012 D4	Riverside[h]	5/14/12	0600-1800	446[i]	None
R97 MS	Riverside[f]	10/4/97	0555-1740	3200[j]	<20μm

[a] Total volume sampled using a high-volume (Hi-vol) sampling apparatus, unless noted otherwise.
[b] Each Hi-vol filter from Beijing, China was divided into six equal portions, allowing for three replicate exposed and unexposed measurements per filter sample.
[c] Sampling site located on the roof of the 7-story Geology Building, about 25 m above ground level.
[d] North Main Street monitoring station.
[e] Air Quality Management District monitoring station.
[f] University of California, Riverside Agricultural Operations Area.
[g] Banning Airport.
[h] University of California, Air Pollution Research Center.
[i] Reported volume represents the average volume sampled by two Hi-vols sampling simultaneously.
[j] Sampled using an ultra-high volume particulate sampler (Mega-sampler) containing four TIGF filters (each 16 in × 20 in).

Environmental Chamber Exposures

Ambient Particulate Matter and PAH-d_x Coated Filters. Experiments were performed at ~296 K and ~735 Torr of dry purified air in a ~7 m^3 collapsible Teflon chamber equipped with a Teflon-coated fan. The ambient filters were divided into equal portions to provide an unexposed control for each exposed filter portion, thus allowing the initial particle-bound PAH and nitro-PAH concentrations to be compared with those following exposure to $N_2O_5/NO_3/NO_2$ in the chamber (Figure S2). NO_3 radicals were generated in the dark from the thermal decomposition of N_2O_5 in the presence of NO_2. Initial concentrations of N_2O_5 and NO_2 (flushed into the chamber using N_2) were 0.42 - 0.48 ppmv and ~1 ppmv, respectively (1 ppmv = 2.4×10^{13} molecule cm^{-3} at 296 K and 735 Torr total pressure). The chamber was continually flushed at 100 L min^{-1} to avoid build-up of NO_2, resulting in a residence time of ~70 min for gaseous species in the chamber. N_2O_5 and NO_2 were introduced into the chamber at the above concentrations a total of 8 times (addition of N_2O_5 and NO_2 once per hour) during each experiment. Table S2 gives details of individual experiments, including experiments in which PAH-d_x coated filters were co-exposed with the ambient filters.

Deuterated PAH-Coated Filter Exposures. Mixtures of PY-d_{10}, FL-d_{10}, and TP-d_{12} in methanol were deposited onto clean TIGF filters (Pallflex T60A20, 8 in × 10 in), which were then dried in a clean atmosphere for ~30 min. In addition, separate filters coated with solutions of BaA-d_{12}, CHR-d_{12}, or BaP-d_{12} were exposed in two experiments. NO_3 radicals were generated as described above, with initial concentrations of N_2O_5 and NO_2: 0.21-0.48 ppmv and 0.5-1.0 ppmv, respectively. The number of additions of N_2O_5 and NO_2 varied among individual experiments with a maximum number of 8 additions during a single experiment (Table S2). After exposure, filters were removed from the chamber and stored at -20º C until further analysis. Several filters, coated and dried as described above, were stored unreacted at -20 ºC until analysis for observation of loss of deuterated PAHs during the deposition and drying processes. A polyurethane foam (PUF) plug was inserted into the chamber outflow vent for several experiments to allow monitoring of gas-phase deuterated PAHs and nitro-PAHs in the chamber.

Figure S2. Apparatus used for exposing filters to $N_2O_5/NO_3/NO_2$. Shown is a filter coated with deuterated PAH (that at the 5 o'clock position) and four filters on which ambient particles were collected.

Table S2. Experimental details for chamber exposures of ambient filter samples and filters with adsorbed deuterated PAH

Experiment No.	Date	Ambient filters	Deuterated filters	PUF in outflow[a]	N_2O_5/NO_2 additions[b]	Avg. N_2O_5 per addition[c]	Avg. NO_2 per addition[c]
2418	01/17/11	Beijing 1[d]	None	N	8	0.48 ppmv	1.0 ppmv
2419	01/20/11		FL-d_{10} / PY-d_{10} / TP-d_{12}	Y	2	0.47 ppmv	1.0 ppmv
2420	01/20/11		FL-d_{10} / PY-d_{10}/ TP-d_{12}	Y	2	0.46 ppmv	1.0 ppmv
2421	01/21/11		FL-d_{10} / PY-d_{10} / TP-d_{12}	Y	2	0.45 ppmv	1.0 ppmv
2422	01/21/11		FL-d_{10} / PY-d_{10} / TP-d_{12}	Y	2	0.47 ppmv	1.0 ppmv
2506	10/17/11		FL-d_{10}/PY-d_{10}/ TP-d_{12}, BaA-d_{12}, CHR-d_{12}, BaP-d_{12}	Y	2	0.45 ppmv	1.0 ppmv
2507	10/18/11		FL-d_{10} / PY-d_{10} / TP-d_{12}	Y	8	0.45 ppmv	1.0 ppmv
2508	10/19/11		FL-d_{10}/PY-d_{10}/ TP-d_{12}, BaA-d_{12}, CHR-d_{12}, BaP-d_{12}	N	1	0.21 ppmv	0.5 ppmv

Experiment No.	Date	Ambient filters	Deuterated filters	PUF in outflow[b]	N_2O_5/NO_2 additions[b]	Ave. N_2O_5 per addition[c]	Ave. NO_2 per addition[c]
2509	10/20/11	Los Angeles 1997, Azusa 1997	None	Y	8	0.42 ppmv	1.0 ppmv
2511	10/25/11	Beijing 2[d], Beijing 3[d], Riverside Megasampler 1997	None	N	8	0.42 ppmv	1.0 ppmv
2522	01/12/12	Riverside 1997, Banning 1997	FL-d_{10} / PY-d_{10} / TP-d_{12}	N	8	0.45 ppmv	1.0 ppmv
2529	05/15/12	Riverside 2012	FL-d_{10} /PY-d_{10}/ TP-d_{12}	Y	8	0.46 ppmv	1.0 ppmv
2530	05/16/12	Riverside 2012	FL-d_{10} / PY-d_{10}/ TP-d_{12}	Y	8	0.45 ppmv	1.0 ppmv

[a] Y = PUF plug present; N = PUF plug not present.

[b] Additions of N_2O_5 and NO_2 were performed approximately once every hour for experiments consisting of more than one addition, with the 1, 2, and 8 addition experiments corresponding to 0.25, 2.5, and 8 hr of exposure, respectively, of filters in the chamber.

[c] As noted in the section **NO_3/N_2O_5 Concentrations in Chamber Studies** (page S14), the estimated average NO_3 radical concentration was ~600 pptv (~1.4 × 10^{10} molecule cm^{-3}). Under our experimental conditions, 1 ppmv = 2.4 × 10^{13} molecule cm^{-3}.

[d] One filter was divided in six equal portions, providing 3 exposed replicates and 3 unexposed replicates.

Analytical Methods

Deuterated Filters. Each filter coated with deuterated PAHs (unexposed and exposed) was spiked with internal standards and Soxhlet extracted in dichloromethane (DCM). Extracts were then eluted through Si SPE columns with DCM and concentrated. All deuterated filter extracts were analyzed using GC-MS with EI ionization and selected ion monitoring (SIM) for both PAHs and nitro-PAHs.

Deuterated NPAHs. Each filter coated with deuterated PAHs (unexposed and exposed) was spiked with an internal standard of PY, TP, 1-NPY, and 2-NTP and Soxhlet extracted in DCM. Extracts were then eluted through Si SPE columns (Supelco Discovery DSC-Si, 6 mL, 1 g; conditioned with 20 mL DCM) with 40 mL DCM and concentrated. All deuterated filter extracts were analyzed with GC-MS (5973N MSD) with EI ionization and SIM for both PAHs and nitro-PAHs. Deuterated PAHs were quantified based on their molecular $[M]^+$ ion with an assumed 100% response and deuterated nitro-PAHs were quantified by summing the $[M]^+$, $[M\text{-}NO]^+$, $[M\text{-}NO_2]^+$, $[M\text{-}HNO_2]^+$ and $[M\text{-}CO\text{-}NO]^+$ ions, typically used to identify nitro-PAHs (Pitts et al., 1985a). Deuterated dinitrofluoranthenes (DNFLs) and dinitropyrenes (DNPYs) were tentatively identified by matching the retention times of 1,2-DNFL, 1,3-, 1,6-, and 1,8-DNPY, combined with reported retention indices of DNFLs (Ramdahl et al., 1986), and fragmentation patterns in EI mode (Ramdahl et al., 1988).

PUF Plug Analysis. Each PUF plug from the chamber outflow was Soxhlet extracted with DCM and eluted through a Si SPE column as described above. Extracts were then analyzed with GC-MS using NCI and EI ionization for nitro-PAHs and positive chemical ionization (PCI) and EI ionization for PAHs. Compound identifications were confirmed by retention times of authentic standards and deuterated nitro-PAH identifications were confirmed by observed EI fragmentation patterns.

SCOS97 and Riverside 2012. For each experiment, both unexposed and exposed ambient filter samples were spiked with an internal standard (PY-d_{10}, TP-d_{12}, and 1-NPY-d_9) and Soxhlet extracted separately with dichloromethane (DCM). Extracts were then concentrated and eluted through a silica (Si) solid-phase extraction column (SPE) (Supelco Discovery DSC-Si, 6 mL, 1 g, conditioned with 20 mL DCM) with 40 mL DCM. For Riverside filters sampled on May 10-14, 2012, the unexposed and exposed extracts consisted of composited filters from two co-located, simultaneously sampling, Hi-vol samplers. Ambient extracts were analyzed for PAHs with gas-chromatography mass-spectrometry (GC-MS, Agilent Technologies, 5973N MSD) with electron impact (EI) ionization in SIM mode, equipped with a 60 m DB-17 column (50% phenyl-substituted methylpolysiloxane, 0.25 mm inner diameter, 0.25 µm phase thickness, J&W Scientific, Inc). Ambient nitro-PAHs were identified with GC-MS (5975 MSD) using negative chemical ionization (NCI) with CH_4 as the reagent gas and a 60 m DB-17 column. Compound identifications were confirmed by retention times of authentic standards and quantities calculated based on NCI response factors of available authentic standards.

Beijing PM. Using the extraction method described previously (Wang et al., 2011), extracts from Beijing were analyzed for PAH and nitro-PAHs after spiking with perdeuterated PAH and nitro-PAH surrogates and then eluted through 20 g silica columns (Mega BE-SI, Agilent Technologies, New Castle, DE) with DCM. PAH analysis was performed using GC-MS (Agilent 6890 GC coupled with an Agilent 5973N MSD) in SIM mode using EI ionization. Nitro-PAHs were analyzed using GC-MS/NCI (using CH_4 as the reagent gas) with a programmed temperature vaporization (PTV) inlet (Gerstel, Germany), and both a DB-5MS (30 m × 0.25 mm I.D., 0.25 µm film thickness, J & W Scientific) and a DB-17MS (30 m × 0.25 mm I.D., 0.25 µm film thickness, J & W Scientific) as previously reported (Wang et al., 2011).

Chemicals

The chemicals used, along with their stated purities, were as follows: pyrene-d_{10} (98%), Cambridge Isotope Laboratories; fluoranthene-d_{10} (99.2%), MSD Isotopes; benz[a]anthracene-d_{12} (98%), KOR Isotopes; chrysene-d_{12} (99.7%), triphenylene-d_{12} (98.4%), benzo[a]pyrene-d_{12} (99.6%), benzo[b]fluoranthene-d_{12} (98.7%), 6-nitrochrysene-d_{11} (99.7%), CDN Isotopes; benzo[ghi]perylene-d_{12} (98%), Cambridge Isotope Laboratories; pyrene (≥99%), triphenylene (98%), Aldrich; 1-nitrotriphenylene, and 2-nitrotriphenylene, Hayashi Pure Chemicals. 1-nitropyrene-d_9 had been previously synthesized using N_2O_5 in CCl_4 solution (Zielinska et al., 1986). N_2O_5 was prepared and stored as previously described (Atkinson et al., 1990). NO_2 was prepared as needed by reacting NO with an excess of O_2. The NIST standard SRMs 1647c, 2265, and 1596 were used to identify PAHs, nitro-PAHs, and dinitro-PAHs and, for the nitro-PAHs, to calculate response factors for certain isomers. Methanol and dichloromethane (Optima grade), Fisher.

NO_3 Radical

NO_3/N_2O_5 Concentrations in Chamber Studies

The experiments were designed to mimic the possible exposure of PM to NO_3 radicals occurring during seven days of transport. Since NO_3 photolyzes rapidly (IUPAC, 2013), ambient exposures to NO_3 would occur during the night. For

$$N_2O_5 \rightarrow NO_2 + NO_3 \qquad (1)$$

$$NO_2 + NO_3 \rightarrow N_2O_5 \qquad (2)$$

then at the high pressure limit and 298K,

$$[NO_3] = k_1[N_2O_5]/k_2[NO_2] = 0.069[N_2O_5]/1.9 \times 10^{-12}[NO_2]$$

$$= 3.63 \times 10^{10}\ [N_2O_5]/[NO_2] \text{ with concentrations in molecule cm}^{-3}$$

with k_1 and k_2 being rate constants for reactions 1 and 2, respectively, and concentrations in molecule cm^{-3} (IUPAC, 2013).

For ambient PM exposure experiments, the 8 additions of 1 ppm NO_2 and 0.41-0.48 ppm N_2O_5, correspond to a total exposure of ~600 ppt of NO_3 for 9.75 hr. Since the concentrations would decrease with time between additions (every hour) due to wall loss and flush-out and the wall loss rate of N_2O_5 in a Teflon chamber in dry air has been measured to be ~0.3 hr^{-1} (Tuazon et al., 1983, Atkinson et al., 1986), the average NO_3 could be ~67% of the initial concentration, i.e., ~400 ppt. This is equivalent to 45 ppt (1×10^9 molecule cm^{-3}) for 12-hr nighttime periods for 7 days.

In the present study, the $[N_2O_5]/[NO_3]$ ratios in the chamber experiments were ~600, thus greatly exceeding the corresponding ratios in the ambient atmospheres. Therefore due to the high NO_2 concentrations employed, our chamber exposures had high potentials for heterogeneous N_2O_5 reactions. The concentrations of NO_2 (~1 ppmv) and N_2O_5 (~0.5 ppmv) are factors of ≥100 higher than observed in ambient atmospheres (Heintz et al., 1996; Stutz et al., 2004; Marley et al., 2007; Parrish et al., 2011). Thus, while the ambient PM was exposed to an NO_3 concentration reasonably appropriate for a week-long transport event, the NO_2 and N_2O_5 concentrations far exceed, by at least two orders of magnitude, those expected in ambient for the same time period.

NO_3/N_2O_5 Formation in Ambient Air

The nitrate radical is formed by the reaction of NO_2 with O_3.

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \qquad (1)$$

$$k_1(298K) = 3.5 \times 10^{-17}\ cm^3\ molecule^{-1}\ s^{-1}\ (IUPAC, 2013)$$

NO_3 radicals photolyze rapidly (IUPAC, 2013) and therefore have generally been measured at significant concentrations only approaching or after sunset. 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

$$NO_3 + NO \rightarrow 2NO_2 \qquad (2)$$

$$k_2(298K) = 2.6 \times 10^{-11}\ cm^3\ molecule^{-1}\ s^{-1}\ (IUPAC, 2013)$$

At ground level, NO emitted from vehicles will react to remove O_3 and, therefore, when traffic and 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 (Stutz et al., 2004) and that significant NO_3 may be present at higher altitudes (Reissell and Arey, 2001) even when none is present at ground level.

Results

Deuterated Nitro-PAH Formation

Filter-bound deuterated PAHs were exposed in the chamber to $N_2O_5/NO_3/NO_2$ for various exposure times (Table S2). For comparison of relative reactivity, experiments MTC 2506 and 2508 were exposures of FL-d_{10}, PY-d_{10}, TP-d_{12}, BaA-d_{12}, CHR-d_{12}, and BaP-d_{12}. Filters containing only FL-d_{10}, PY-d_{10}, and TP-d_{12} were exposed, along with ambient PM filters, to 8 additions of ~0.5 ppmv N_2O_5 with 1 ppmv NO_2, over an 8 hr period (Table S2). After 8 additions of N_2O_5, the majority of the FL-d_{10} and PY-d_{10} had chemically reacted or volatilized from the filter surface and approximately 25% of TP-d_{12} remained (Figure S3). A portion of each deuterated PAH was expected to volatilize during the process of drying each filter and during the extended reactions (thus accounting for the FL-d_{10} and PY-d_{10} observed on outflow PUF plugs). Based on control experiments, volatilization of FL-d_{10} and PY-d_{10} resulted in losses of 17-42% of the original deuterated PAH. Therefore, since total quantified PAH loss is calculated from the original amount of PAH-d_x coated onto the filter and the final PAH-d_x concentrations measured after exposure, the reported PAH-d_x loss is the sum of chemical degradation and desorption from the surface of the filter.

The formation of nitro-PAH-d_x during these reactions was measured to verify consistent experimental nitration conditions among different experiments exposing ambient PM. Figure S4 shows the increase in the amount of 1-, 3-, 7-, and 8-NFL-d_9, 1-NPY-d_9, and 1- and 2-NTP-d_{11} formed with exposure to increasing amounts of N_2O_5. As seen in Figure S4, replicates of 2 and 8 additions (n=4) of N_2O_5 and NO_2 gave reproducible amounts of deuterated nitro-products (MTC 2506 used a newly synthesized batch of N_2O_5 and is not included in Figure S4). The ratio of 1-NPY-d_9/ΣNFLs-d_9 decreased progressively in going from 1 to 2 to 8 additions of N_2O_5 and NO_2.

Under conditions of 1 addition of N_2O_5/NO_2 over 0.25 hr, 1-NPY-d_9 is the dominant isomer observed, followed by Σ(1-, 3-, 7-, and 8-NFL-d_9) and Σ(1- and 2-NTP-d_{11}) and this order is consistent with the study reported by Zimmermann et al. (2012) during a 3 min "active" exposure of filter-adsorbed PY-d_{10} FL-d_{10}, and TP-d_{12} to $N_2O_5/NO_3/NO_2$ (i.e., the chamber contents were pulled through the filter coated with the deuterated PAH). After 2 additions of N_2O_5, concentrations of PY are already quite low (see Figure S3) and the secondary reaction of 1-NPY-d_9 to form dinitropyrenes (DNPYs) is believed to be responsible for the relative decrease in 1-NPY-d_9/ΣNFLs-d_9 (see below).

The partial rate factors relative to nitrobenzene formation from nitration of benzene by HNO_3 in acetic acid at 0°C have been measured for a number of nitro-PAHs. The reported values from nitration of BaP, PY, CHR, FL and TP are: 6-NBaP (108,000); 1-NPY (17,000); 6-NCHR (3,500); 3-NFL (1,363); 8-NFL (846); 1-NTP (600); 2-NTP (600); 7-NFL (546) and 1-NFL (329) (Ruehle et al., 1985). As previously observed when comparing N_2O_5 nitrations of adsorbed PY and FL with those of filter adsorbed PAHs known to be more reactive toward solution-phase nitration (Pitts et al., 1985b), the more volatile PY and FL were more reactive than solution phase nitration would predict, perhaps suggesting that availability on the filter surface is important. Comparing nitration of the low volatility PAHs to one another (see Figure S5) the reactivity order that was observed is more similar to that in solution, namely, 7-NBaA-d_{11} > 6-NBaP-d_{11} > 6-NCHR-d_{11} > 2NTP ~ 1NTP > 12-NBaA-d_{11}.

Seven deuterated dinitropyrenes (DNPYs) and dinitrofluoranthenes (DNFLs) were identified on filters following 2 and 8 additions of N_2O_5 (Figure S6), with 1,8-DNP-d_8 >1,6-DNP-d_8 >3,7-DNFL-d_8 >1,3-DNPY-d_8 identified as major isomers observed. As expected, the amounts of deuterated DNPYs increased with increasing exposure to N_2O_5. These secondary reactions and formation of deuterated dinitro-PAHs could affect isomer distributions observed from the 8 additions of N_2O_5 over 8 hr. For example, because of the secondary formation of 1,8-, 1,6-, and 1,3-DNPY-d_8, 1-NPY-d_9 was most likely originally formed in higher amounts than those measured at the end of the exposures.

The formation of 2-NFL by the reaction of FL with N_2O_5 (Zielinska et al., 1986) or with N_2O_4 (Squadrito et al., 1987; 1990) in CCl_4 solution at room temperature is interpreted as occurring by formation of a radical σ-complex followed by multiple addition-elimination pathways (Squadrito et al., 1990). This interpretation is supported by the fact that even at low extents of nitration, these reactions also produce unusual dinitrofluoranthenes, with substitution occurring in the same ring. Thus in aprotic CCl_4, N_2O_5 is not ionized and the NO_3-FL complex (with attachment of the NO_3 on position 3 of FL) adds NO_2 and then eliminates HNO_3 to form 2-NFL or adds another NO_3 followed by addition of NO_2 and loss of two HNO_3 molecules to give 1,2-DNFL. 1,2-DNFL was shown to be absent on the exposed filter by use of an authentic standard of this isomer, and the DNFLs present were identified as having NO_2 substitution on different rings, again suggesting that reaction of adsorbed FL was not an NO_3 radical reaction.

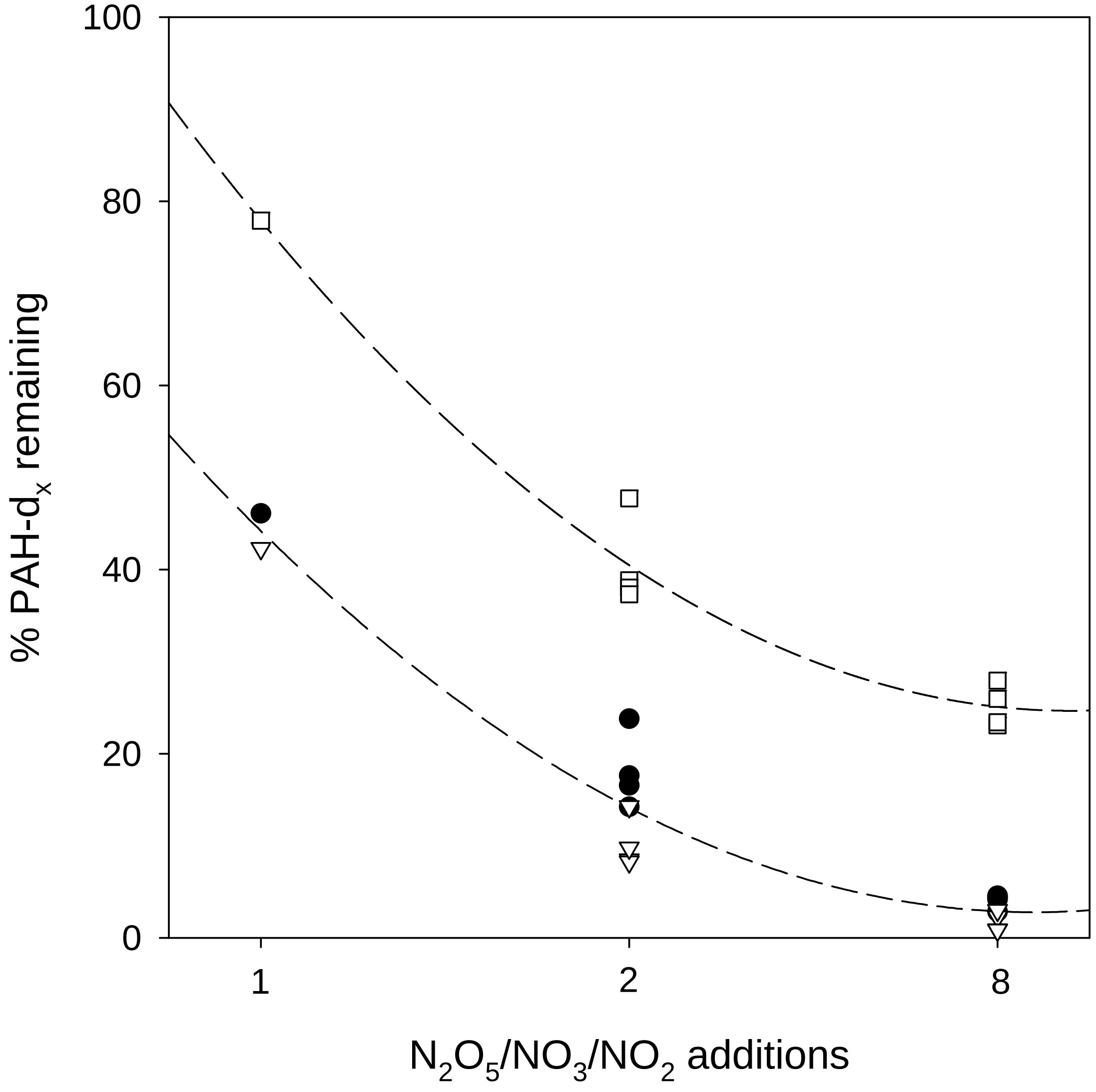

Figure S3. Decreases in deuterated FL-d_{10} (●), PY-d_{10} (▽), and TP-d_{12} (□) after 1, 2, and 8 additions of N_2O_5 and NO_2. Additions were performed once per hour for each type of experiment. The observed losses are the sum of chemical degradation and volatilization from the surface of the filter. Dashed lines are for illustrative purposes only.

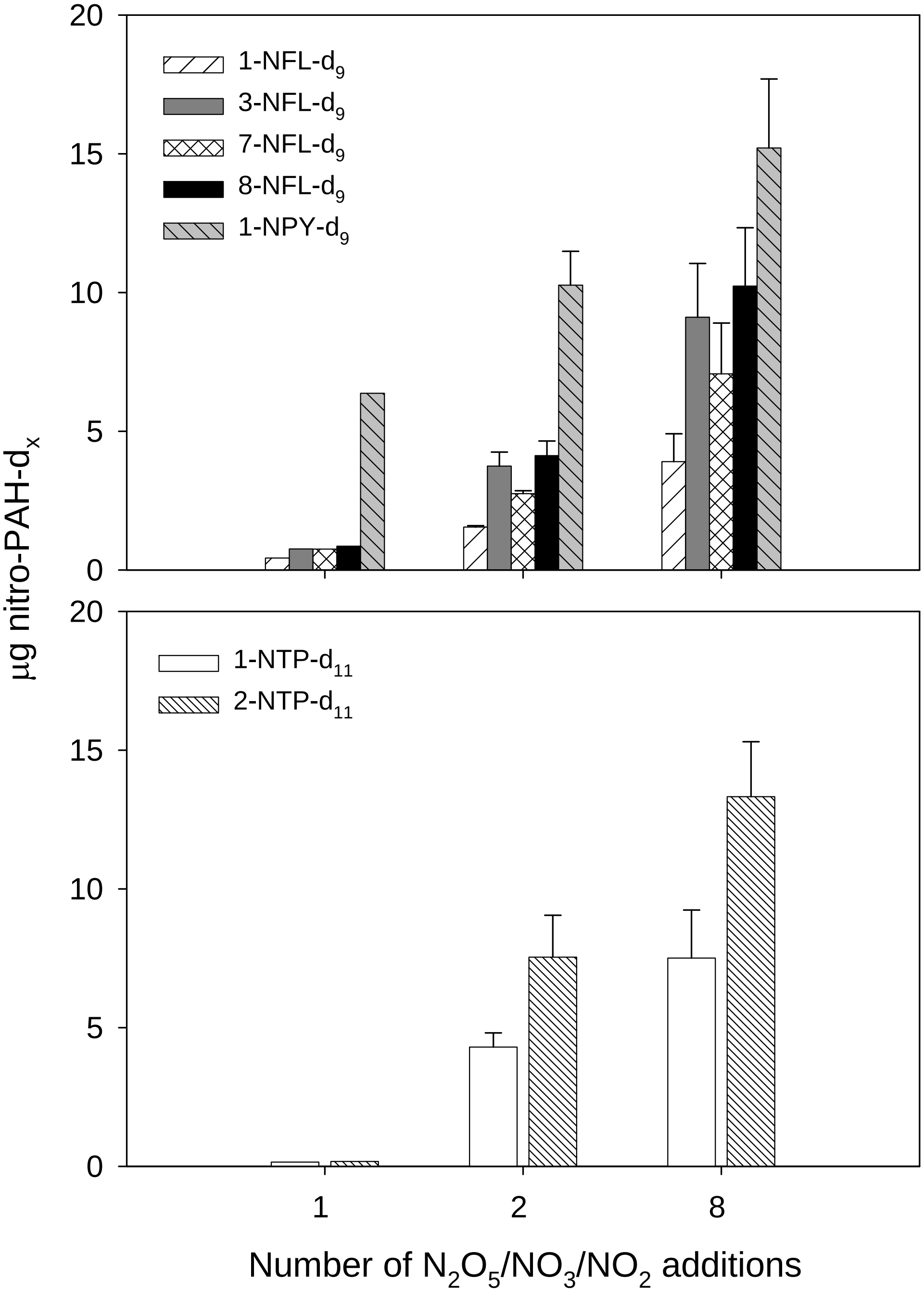

Figure S4. Deuterated NFLs, NPYs, and NTPs formed on the filters after 1, 2 , and 8 additions of N_2O_5 and NO_2, with additions performed once an hour. Error bars for shown for the 2 and 8 additions represent one standard deviation from the mean of replicate experiments (*n* = 4). No replicates were performed for the 1 addition of N_2O_5 and NO_2. Approximately 50 μg each of FL-d_{10}, PY-d_{10} and TP-d_{12} were added to each filter in methanol solution and then dried.

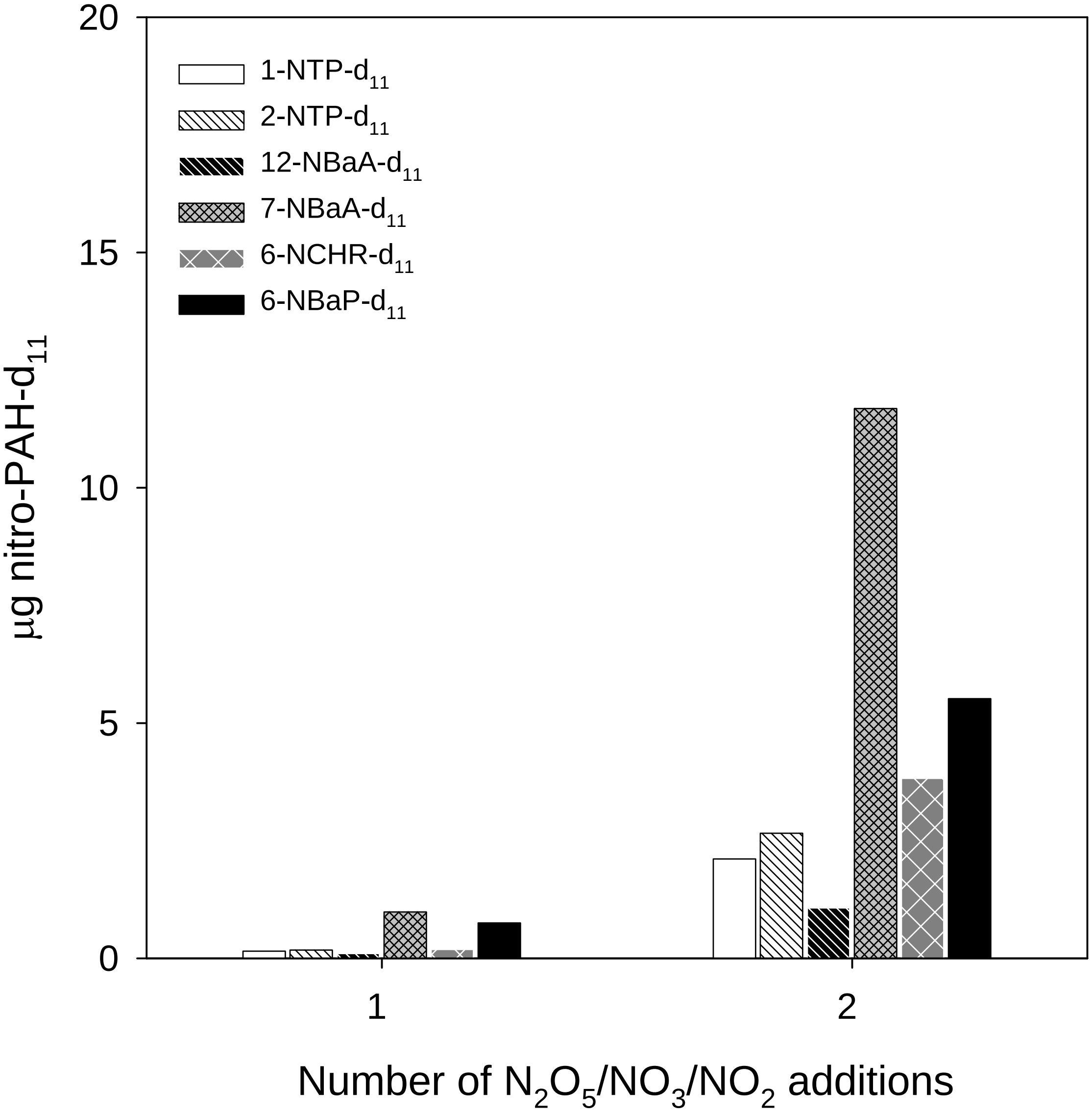

Figure S5. Deuterated NTPs, NBaAs, NCHR, and NBaP formed on the filters after 1 (MTC 2508) and 2 (MTC 2506) additions of N_2O_5 with additions performed once an hour (each experiment was performed only once). The amount of each deuterated PAH applied in methanol solution to the filters was approximately 50 µg. The amounts of 1-NPY-d_9 for the 1 and 2 additions shown here were 6.4 and 41.5 µg, respectively. The amounts of ΣNFLs-d_9 for the 1 and 2 additions shown here were 0.9 and 26.2 µg, respectively.

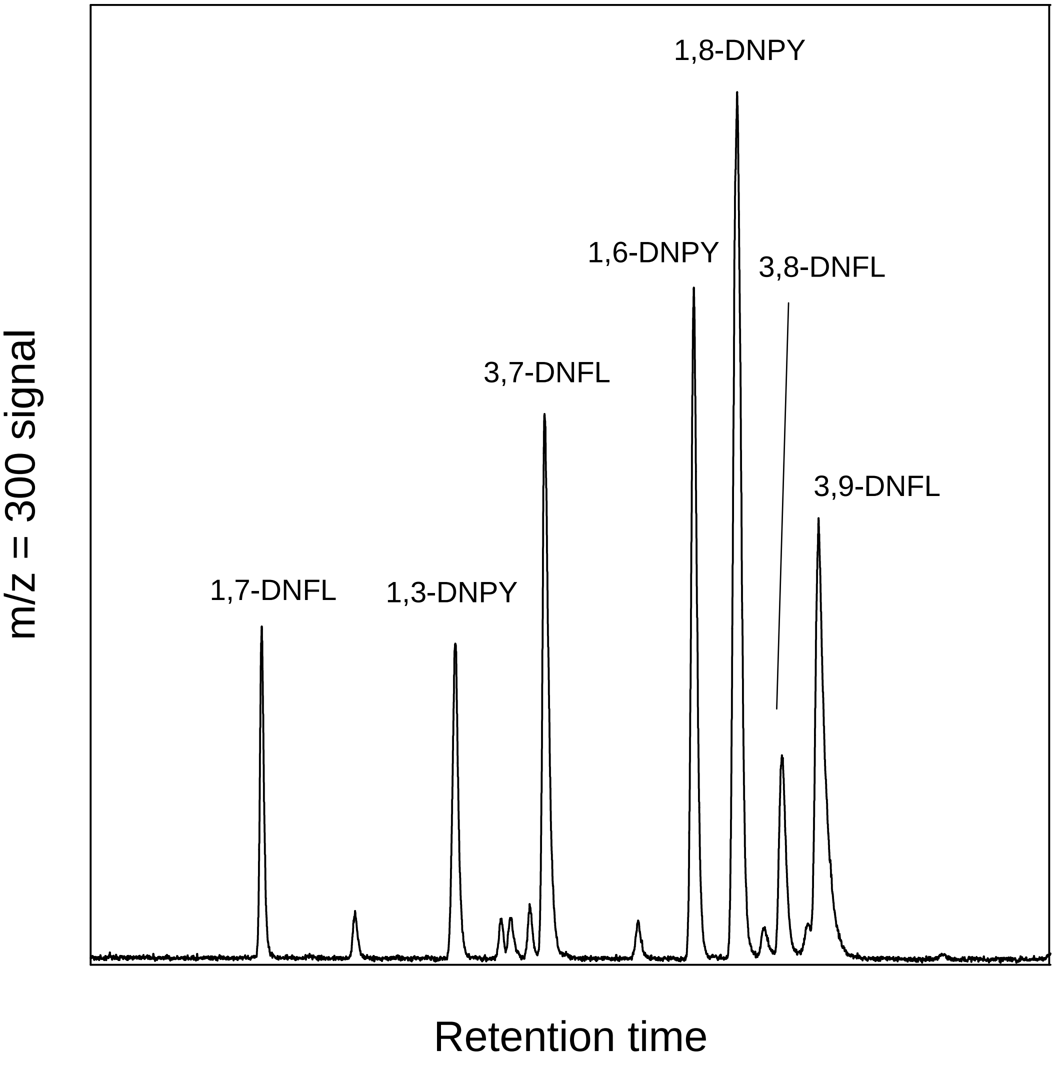

Figure S6. GC-MS/EI chromatogram with identifications of m/z 300 deuterated dinitropyrenes (DNPYs) and dinitrofluoranthenes (DNFLs) (from MTC 2421). Identification of 1,3-DNPY, 1,6-DNPY, and 1,8-DNPY (and exclusion of 1,2-DNFL, see text) were made by both retention time matching with standards and previous reported fragmentation patterns. Other isomers are tentative identifications based on previously reported EI fragmentation patterns (Ramdahl et al., 1986; 1988).

Ambient PM Results

The concentrations of selected PAH and nitro-PAH in ambient PM samples collected in Beijing, China, at four sites in southern California in August 1997 during the Southern California Ozone study (SCOS97), and in Riverside, CA (both in October 1997 as part of the SCOS97 study and May 2012) are given in Tables S3 and S4, respectively.

Ambient Particulate PAH Concentrations. PAHs are primary emissions resulting from incomplete combustion processes and Beijing is clearly highly impacted by direct emissions, with Beijing samples 1 and 2 having the highest concentrations of most PAHs (Table S3). Benzo[ghi]perylene (B(ghi)P) has been used as a marker of gasoline-powered vehicle activity, as it has the highest emission factor of the 16 priority PAHs in light-duty vehicle exhaust but is not detected in heavy-duty diesel exhaust (Marr et al., 1999; 2006). Reflecting the strong influence of vehicle traffic in the Southern California region, the top 6 B(ghi)P concentrations (all exceeding 1 ng m^{-3}) were observed for: a Los Angeles morning sample (LA97-1), followed by the Beijing samples (Beijing 1 and 2), the Los Angeles nighttime sample (LA97-3), the second Los Angeles daytime sample (LA97-5) and an Azusa morning sample (A97-13). The Riverside 2012 samples had the lowest B(ghi)P concentrations which probably reflects a cleaner vehicle fleet than in 1997. It should also be noted that the intensive sampling days of the SCOS97 study were chosen on the basis of meteorological predictions to be conducive to producing maximum pollution levels.

Ambient Nitro-PAH Concentrations. Initial ambient concentrations of particle-bound molecular weight (mw) 247 and 273 nitro-PAHs were measured at all sites and are reported in Table S4. While the 2-NFL/1-NPY ratios varied, 2-NFL was consistently the mw 247 nitro-PAH isomer observed in greatest abundance. Other isomers, such as 2-NPY, 4-NPY, 3-NFL and

8-NFL were identified and measured in most, but not all, samples. The mw 273 nitro-PAHs were present in lower concentrations relative to 2-NFL, and 7-NBaA was the most consistently measured mw 273 nitro-PAH in each sample (Table S4). Other isomers observed include 12-NBaA, 1- and 2-NTP, with 6-NCHR least frequently detected. Detectable concentrations of 6-NBaP were observed only in the particulate matter collected in Beijing, China, and one Azusa morning sample.

The highest 2-NFL concentration was observed in the Beijing 1 sample, followed by a Riverside nighttime sample (R97-14). The high 2-NFL/2-NPYratios in these samples suggest 2-NFL formation by NO_3 radical reaction (Zimmermann et al., 2012). Four samples exceeded 50 pg m^{-3} for 2-NPY: the two Los Angeles and two Azusa morning samples (LA97-1, LA97-4, A97-13, and A97-18). The low 2-NFL/2-NPY ratios in these samples indicate formation of 2-NFL and 2-NPY by OH radical-initiated reaction (Zimmermann et al., 2012).

Table S3. Ambient concentrations of particle-bound PAHs (pg m^{-3}) in Beijing, China and the Los Angeles air basin.[a] Note that depending upon the ambient temperature, a significant fraction of the FL and PY may be gas-phase and the PM concentrations given in the table, therefore, underestimate the actual ambient concentrations.

Site[b]	Time	**FL**	**PY**	**BaA**	**TP+CHR**	**B(b/k/j)F**	**BeP**	**BaP**	**PER**	**IP**	**B(ghi)P**	**D(a,h)A**
Beijing 1[c]	24-hr.	1431	990	594	827	4179[d]	1660	683	NM	1645	1663	273
Beijing 2[c]	24-hr.	2357	1581	762	959	3586[d]	1531	1147	NM	1576	1639	119
Beijing 3[c]	24-hr.	552	417	233	285	1596[d]	618	537	NM	677	697	44
LA97-1	0600-1158	549	601	411	1323	1345	893	470	98	679	1720	47
LA97-2	1202-1800	316	351	129	461	496	272	149	27	245	520	18
LA97-3	1803-0556	312	365	234	628	790	572	427	84	485	1516	20
LA97-4	0602-1158	507	473	274	680	966	510	335	62	533	1492	21
LA97-5	1202-1800	236	254	92	693	295	292	74	21	97	270	16
A97-13	0600-1200	902	927	420	959	1047	564	392	93	520	1382	36
A97-15	1203-1800	568	504	178	684	603	286	167	41	256	611	19
A97-16	1800-0600	236	266	136	398	585	359	220	51	315	905	26

Site[b]	Time	**FL**	**PY**	**BaA**	**TP+CHR**	**B(b/k/j)F**	**BeP**	**BaP**	**PER**	**IP**	**B(ghi)P**	**D(a,h)A**
A97-18	0603-1200	360	350	149	501	593	302	174	38	300	727	21
A97-20	1204-1800	266	247	74	316	306	142	89	22	114	249	17
R97-13	0600-1802	188	199	91	235	455	219	113	22	208	443	19
R97-14	1811-0600	243	272	100	299	316	187	94	20	132	361	15
R97-15	0614-1750	137	134	55	127	206	104	58	11	96	197	9.6
B97-14	0605-1800	94	109	32	87	95	61	26	5	47	148	4
B97-15	1814-0600	170	211	73	178	207	95	57	11	96	210	15
B97-17	0607-1800	89	128	50	127	168	66	68	13	73	94	12
R2012 N1	1800-0600	55	61	10	45.6	40	30	12	2	17	45	2
R2012 D1	0600-1800	70	84	14	122	51	55	17	4	20	59	2
R2012 N2	1800-0600	60	64	13	67	61	33	17	4	27	66	4
R2012 D2	0600-1800	78	82	17	130	62	59	21	4	25	67	4
R2012 N3	1800-0600	51	56	13	55	63	36	19	3	27	63	4

Site[b]	Time	**FL**	**PY**	**BaA**	**TP+CHR**	**B(b/k/j)F**	**BeP**	**BaP**	**PER**	**IP**	**B(ghi)P**	**D(a,h)A**
R2012 D3	0600-1800	52	58	6	111	39	46	14	2	15	41	2
R2012 N4	1800-0600	53	61	14	52	48	30	17	4	23	61	3
R2012 D4	0600-1800	90	107	23	146	72	64	22	6	28	85	3
R97 MS[e]	0555-1740	46	37	9	15	45[d]	33	8	NM	28	45	ND

[a] Abbreviations: FL = fluoranthene; PY = pyrene; BaA = benz[a]anthracene; TP+CHR = triphenylene + chrysene; B(b/k/j)F = benzo[b]fluoranthene + benzo[k]fluroanthene + benzo[j]fluoranthene; BeP = benzo[e]pyrene; BaP = benzo[a]pyrene; PER = perylene; IP = indeno[1,2,3-cd]pyrene; B(ghi)P = benzo[ghi]perylene; D(a,h)A = dibenz[a,h]anthracene; NM = not measured.

[b] Sampling information is described in Table S1.

[c] Reported values for Beijing samples are mean values of 3 replicate measurements.

[d] Reported value is equal to sum of benzo[b]fluoranthene and benzo[k]fluoranthene concentrations.

[e] Reported values for R97 MS are mean values of 9 replicate measurements.

Table S4. Ambient concentrations of mw 247 and 273 nitro-PAHs and 6-nitrobenzo[a]pyrene (mw 297) measured in Beijing, China and the Los Angeles air basin (pg m^{-3})[a,b]

Site[c]	Time	**2-NFL**	**3-NFL**	**4-NPY**	**8-NFL**	**1-NPY**	**2-NPY**	**12-NBaA**	**7-NBaA**	**1-NTP**	**6-NCHR**	**2-NTP**	**6-NBaP**
Beijing 1[d,e]	24-hr.	1158	4.0	ND	ND	22.1	4.4	ND	132	2.5	3.4	3.2	23.8
Beijing 2[d,e]	24-hr.	597	4.6	ND	ND	22.6	43.1	ND	105	2.6	0.7	1.9	26.3
Beijing 3[d,e]	24-hr.	143	4.7	ND	ND	10.0	35.8	ND	55.1	2.7	0.7	1.7	27.2
LA97-1	0600-1158	292	ND	17.7	11.2	27.0	68.7	18.2	20.6	ND	ND	ND	ND
LA97-2	1202-1800	149	ND	10.1	ND	10.4	ND	11.3	8.2	4.6	ND	9.2	ND
LA97-3	1803-0556	86.7	0.8	5.0	2.2	17.0	22.8	3.6	18.7	1.9	ND	ND	ND
LA97-4	0602-1158	304	ND	10.1	9.0	17.5	50.4	3.5	6.9	3.4	4.0	5.2	ND
LA97-5	1202-1800	79.6	ND	7.0	ND	8.9	41.8	5.7	13.2	4.3	ND	ND	ND
A97-13	0600-1200	197	ND	6.5	5.3	18.4	71.3	2.2	7.6	2.5	ND	2.9	4.2[f]
A97-15	1203-1800	210	ND	9.9	3.4	8.9	22.9	2.7	6.7	2.7	ND	7.7	ND
A97-16	1800-0600	301	ND	7.1	3.7	8.5	33.8	4.3	23.0	ND	ND	5.0	ND
A97-18	0603-1200	215	ND	5.8	4.5	12.10	64.8	1.7	7.7	1.5	ND	6.0	ND
A97-20	1204-1800	76.8	ND	12.4	ND	6.3	30.0	5.8	7.7	1.1	ND	ND	ND

Site[c]	Time	**2-NFL**	**3-NFL**	**4-NPY**	**8-NFL**	**1-NPY**	**2-NPY**	**12-NBaA**	**7-NBaA**	**1-NTP**	**6-NCHR**	**2-NTP**	**6-NBaP**
R97-13	0600-1802	166	ND	6.1	2.9	6.8	21.0	3.2	7.0	2.6	1.8	3.5	ND
R97-14	1811-0600	638	ND	8.3	1.8	9.6	27.9	ND	11.7	3.4	3.5	2.9	ND
R97-15	0614-1750	142	ND	3.2	ND	3.7	11.5	ND	4.1	ND	ND	ND	ND
B97-14	0605-1800	37.6	ND	2.3	ND	3.1	ND	ND	2.6	0.8	0.6	1.9	ND
B97-15	1814-0600	201	ND	11.9	ND	7.8	7.0	27.7	12.4	4.0	ND	ND	ND
B97-17	0607-1800	28.0	0.2	1.6	2.2	1.3	1.6	ND	0.9	0.6	ND	1.5	ND
R2012 N1	1800-0600	11.0	ND	ND	ND	1.2	1.5	0.8	1.5	0.2	ND	ND	ND
R2012 D1	0600-1800	8.3	ND	0.8	ND	6.8	3.7	2.2	2.6	0.8	ND	ND	ND
R2012 N2	1800-0600	57.4	ND	2.7	ND	2.6	2.4	1.7	10.1	0.4	ND	ND	ND
R2012 D2	0600-1800	19.2	ND	1.2	ND	6.6	2.3	2.3	2.1	1.0	ND	ND	ND
R2012 N3	1800-0600	98.2	ND	1.2	ND	2.7	1.8	0.9	2.4	ND	ND	ND	ND
R2012 D3	0600-1800	8.3	ND	0.6	ND	3.2	1.0	3.8	1.1	0.5	ND	ND	ND
R2012 N4	1800-0600	75.6	ND	0.8	ND	1.5	1.2	1.1	1.3	ND	ND	ND	ND
R2012 D4	0600-1800	21.8	ND	0.7	ND	3.9	1.8	2.7	0.7	ND	ND	ND	ND
R97 MS[e]	0555-1740	37.9[g]	ND	ND	ND	2.1	ND	ND	ND	0.21	ND	ND	ND

[a] Abbreviations: NFL = nitrofluoranthene; NPY = nitropyrene; NBaA = nitrobenz[a]anthracene; NTP = nitrotriphenylene; NCHR = nitrochrysene; NBaP = nitrobenzo[a]pyrene; ND = not detected.

[b] All measurements were made on a DB-17 column unless otherwise specified.

[c] Sampling information is described in Table S1.

[d] Concentrations from each Beijing sample represent an average of 3 replicates.

[e] The mw 273 nitro-PAHs from Beijing samples and all isomers listed for the R97 MS sample were quantified on a DB-5MS column.

[f] Assumed response factor for 6-NBaP of 1.

[g] Quantified on a DB-5MS column as 2+3-NFL.

Ambient PM Exposed to $N_2O_5/NO_3/NO_2$

PAH Degradation. The relative degradation of select particle-bound PAHs upon exposure to $N_2O_5/NO_3/NO_2$ is expressed as: $[(\Delta[PAH]/[PAH]_0) \times 100]$, in which $\Delta[PAH]$ is the difference between the amounts on the unreacted and reacted filters and $[PAH]_0$ is the amount of PAH on the unreacted sample. Calculated degradation of these PAHs is given in Table S5. Degradation was observed for all reported particle-bound PAHs in Beijing PM, although the relative degradation of these PAHs differed among the three ambient Beijing samples. Results of paired *t*-test analyses of unreacted and reacted PAH concentrations (Table S5) show that statistical significance of PAH degradation is sample-dependent, with only pyrene (PY) changing significantly (*p*-value <0.05) for all three Beijing samples. PAHs that showed significant degradation in two out of the three Beijing samples included BaA, TP+CHR, B(b+k+j)F, BeP, BaP, IP, B(ghi)P. In contrast, exposure of R97 MS (consisting of 9 replicate measurements) did not result in the significant degradation of any of the measured PAHs (Table S5). Variable PAH degradation was also observed for PM collected during SCOS97 and in Riverside in 2012, with no loss detected for several PAHs in these samples. Therefore, considering the large losses of deuterated PAHs in the chamber exposures (Figure S3), it is clear that some fraction of the PAH present in ambient particles is unavailable for reaction.

Loss of BaP was observed in all but one of the samples exposed, while no loss of BeP was observed for several samples. As noted in the manuscript, BeP is considered a relatively unreactive PAH, while BaP is considered reactive. Our data are consistent with these findings as shown in Table S6, where the BaP/BeP ratios of the unexposed PM were higher than the corresponding ratio for the exposed PM for 78% of the samples. Therefore, as discussed below, to compare relative amounts of atmospheric processing in samples from various sites and times, we have chosen to ratio the PAHs and their atmospheric reaction products to the initial BeP concentration as a way of normalizing the ambient samples for the strength of direct emissions and meteorological differences such as inversion heights.

Nitro-PAH Formation and Loss. For the majority of samples, 1-NPY was formed in the greatest amounts (Table S7). Other isomers consistently formed, but to lesser extents, included 3-NFL, 8-NFL, and 6-NCHR (Figure 2 and Figure S7). Formation of nitro-PAHs such as 12- and 7-NBaA and 1- and 2-NTP was less consistent, but was observed in > 60% of the samples studied (Figure S7). Results of paired *t*-test analyses of unreacted and reacted nitro-PAH concentrations (Table S7) showed statistically significant formation of 1-NPY, 7-NBaA, 6-NCHR, 2-NTP, and 6-NBaP in all three Beijing samples and the 6-NBaP formation in these samples exceeded that of 1-NPY. Formation of 3-NFL and 1-NTP was statistically significant for two of the three Beijing samples. Thus the nitro-isomers formed in the exposed ambient PM were the same isomers observed from the PAH-d_x coated on filters. Formation of these isomers in our ambient PM exposures is not only consistent with these deuterated filter studies, but also with earlier studies of heterogeneous formation of nitro-PAHs from reactions of filter-bound PY, FL, BaA, and BaP (Pitts et al., 1985b).

In contrast, 2-NFL and 4-NPY, nitro-PAHs formed from gas-phase reaction of FL and PY with NO_3 radicals, respectively, were not enhanced by exposure to $N_2O_5/NO_3/NO_2$, but rather were degraded in 70% of samples. Formation in the Beijing samples of 2-NPY, which has been shown to result from the OH radical-initiated reaction of gas-phase PY (Atkinson et al., 1990), was not statistically significant (Table S7). In fact, the changes for both 2-NFL and 2-NPY in the Beijing samples were shown to be statistically insignificant, as were those for nitro-PAHs measured in the R97 MS sample. These results, as well as the results of the FL-d_{10} and PY-d_{10} exposures discussed above, call into question a recent report of heterogeneous formation of 2-NFL and 2-NPY during ambient PM exposures (Ringuet et al., 2012).

Table S5. Percent change ($\Delta[PAH]/[PAH]_0$) in particle-bound PAHs after exposure to 8 additions of N_2O_5[a, b]. Numbers that are underlined in bold represent significant changes using the paired *t*-test ($p < 0.05$)

Site[c]	Time	**FL**	**PY**	**BaA**	**TP+CHR**	**B(b/k/j)F**	**BeP**	**BaP**	**PER**	**IP**	**B(ghi)P**	**D(a,h)A**
Beijing 1[d]	24-hr.	**-20**[e]	**-25**[e]	**-29**[e]	**-7.3**[e]	**-7.2**[e,g]	**-10**[e]	**-35**[e]	NM	**-8.3**[e]	**-16**[e]	-7.2[f]
Beijing 2[d]	24-hr.	-1.9[f]	**-25**[e]	-18[f]	-7.2[f]	-6.7[f,g]	-6.2[f]	-25[f]	NM	-1.7[f]	-7.8[f]	NLD
Beijing 3[d]	24-hr.	-3.7[f]	**-42**[e]	**-32**[e]	**-11**[e]	**-14**[e,g]	**-15**[e]	**-35**[e]	NM	**-14**[e]	**-18**[e]	**-14**[e]
LA97-1	0600-1158	-4.7	-13	-7.9	-14	NLD	-2.5	-25	-36	NLD	NLD	NLD
LA97-2	1202-1800	-17	-23	-16	-9.8	NLD	-4.9	-17	NLD	-3.4	-11	NLD
LA97-3	1803-0556	-14	-37	-29	-24	-6.5	-14	-50	-58	-8.5	-14	NLD
LA97-4	0602-1158	-24	-28	-37	-24	-11	-13	-32	-28	-13	-18	-16
LA97-5	1202-1800	-25	-28	-23	-35	-6.3	-24	-2.9	-4.2	-0.6	-3.7	NLD
A97-13	0600-1200	-13	-20	-10	-0.4	-1.0	-1.9	-32	-36	-1.6	-7.5	-4.3
A97-15	1203-1800	-11	-16	-18	-5.9	NLD	NLD	-21	-23	NLD	-3.0	NLD
A97-16	1800-0600	-0.6	-8.3	-0.9	NLD	NLD	NLD	-18	-12	NLD	NLD	NLD
A97-18	0603-1200	-2.6	-4.1	NLD	NLD	NLD	NLD	-7.8	NLD	NLD	NLD	-5.0
A97-20	1204-1800	-4.6	-3.8	-13	-9.6	NLD	NLD	NLD	-6.6	NLD	-4.5	NLD
R97-13	0600-1802	-7.4	-14	-5.3	-9.0	-4.2	-9.8	-23	-18	NLD	-6.9	-1.1
R97-14	1811-0600	-19	-28	-26	-22	-13	-17	-19	-42	-3.7	-10	NLD

Site[e]	Time	**FL**	**PY**	**BaA**	**TP+CHR**	**B(b/k/j)F**	**BeP**	**BaP**	**PER**	**IP**	**B(ghi)P**	**D(a,h)A**
R97-15	0614-1750	-2.7	NLD	NLD	NLD	NLD	NLD	NLD	-3.6	NLD	NLD	NLD
B97-14	0605-1800	-26	-35	-17	-9.0	NLD	-7.6	-29	-3.1	-2.0	-17	NLD
B97-15	1814-0600	-19	-22	-22	-11	-3.0	NLD	-19	-33	-5.6	-1.5	-13
B97-17	0607-1800	-23	-32	-15	-16	-9.9	-16	-28	-34	-10	-16	-7.1
R2012 N1	1800-0600	-9.2	-23	-13	NLD	NLD	NLD	-11	-24	NLD	NLD	NLD
R2012 D1	0600-1800	-5.4	-16	-26	-35	-11	-48	-24	-30	-8.7	-7.8	NLD
R2012 N2	1800-0600	-11	-13	-11	NLD	-5.4	NLD	-30	-32	-8.5	-6.9	-10
R2012 D2	0600-1800	-16	-19	-7.8	-36	-5.3	-30	-12	-5.1	NLD	NLD	NLD
R2012 N3	1800-0600	-19	NLD	-29	NLD	-5.6	-4.1	-23	-5.8	-4.7	-1.3	-8.5
R2012 D3	0600-1800	-27	-32	NLD	-52	-9.5	-47	-32	-43	-2.0	-4.4	-5.0
R2012 N4	1800-0600	-5.3	-19	-24	-7.0	NLD	-5.0	-38	-31	-9.0	-7.9	-3.5
R2012 D4	0600-1800	-15	-27	-25	-36	-13	-34	-21	-42	-11	-6.7	-14
R97 MS[h]	0555-1740	NLD	-4.0[f]	-37[f]	-1.6[f]	-6.5[f,g]	-2.8[f]	-6.0[f]	NM	-3.9[f]	NLD	NLD

[a] Abbreviations: FL = fluoranthene; PY = pyrene; BaA = benz[a]anthracene; TP+CHR = triphenylene + chrysene; B(b/k/j)F = benzo[b]fluoranthene + benzo[k]fluroanthene + benzo[j]fluoranthene; BeP = benzo[e]pyrene; BaP = benzo[a]pyrene; PER = perylene; IP = indeno[1,2,3-cd]pyrene; B(ghi)P = benzo[ghi]perylene; D(a,h)A = dibenz[a,h]anthracene; NM = not measured; NLD = no loss detected.

[b] Negative signs denote losses upon exposure to N_2O_5/NO_3/NO_2.

[c] Sampling information is described in Table S1.

[d] Reported values for Beijing samples are an average of 3 replicate measurements.

[e] Denotes a p-value <0.05 for the paired t-test suggesting a significant change in concentration due to exposure to $N_2O_5/NO_3/NO_2$.

[f] Denotes a p-value >0.05 for the paired t-test suggesting no significant difference in concentration due to exposure to $N_2O_5/NO_3/NO_2$.

[g] Changes calculated by finding the difference in the sums of benzo[b]fluoranthene and benzo[k]fluoranthene concentrations.

[h] Reported values for RMS are averages of 9 replicate measurements.

Table S6. Ratios of particulate BaP/BeP[a]

Site[b]	Time	BaP/BeP unexposed[c]	BaP/BeP exposed[d]
Beijing 1[e]	24-hr.	0.41	0.24
Beijing 2[e]	24-hr.	0.75	0.60
Beijing 3[e]	24-hr.	0.86	0.50
LA97-1	0600-1158	0.53	0.41
LA97-2	1202-1800	0.55	0.48
LA97-3	1803-0556	0.75	0.44
LA97-4	0602-1158	0.66	0.51
LA97-5	1202-1800	0.25	0.33
A97-13	0600-1200	0.69	0.48
A97-15	1203-1800	0.59	0.45
A97-16	1800-0600	0.61	0.43
A97-18	0603-1200	0.58	0.45
A97-20	1204-1800	0.63	0.65
R97-13	0600-1802	0.52	0.44
R97-14	1811-0600	0.50	0.49
R97-15	0614-1750	0.56	0.54
B97-14	0605-1800	0.42	0.32
B97-15	1814-0600	0.61	0.43
B97-17	0607-1800	1.03	0.88

Site [b]	Time	BaP/BeP unexposed[c]	BaP/BeP exposed[d]
R2012 N1	1800-0600	0.54	0.43
R2012 D1	0600-1800	0.31	0.45
R2012 N2	1800-0600	0.53	0.37
R2012 D2	0600-1800	0.35	0.44
R2012 N3	1800-0600	0.52	0.41
R2012 D3	0600-1800	0.30	0.39
R2012 N4	1800-0600	0.56	0.37
R2012 D4	0600-1800	0.34	0.41
R97 MS	0555-1740	f	f

[a] Abbreviations: BaP = benzo[a]pyrene; BeP = benzo[e]pyrene.
[b] Sampling information is described in Table S1.
[c] Initial ratios of BaP/BeP observed from ambient particulate matter .
[d] Ratios of BaP/BeP after filters samples were exposed to 8 additions of N_2O_5 and NO_2. Additions were performed once per hour.
[e] Reported Beijing ratios are each the mean value of 3 replicate measurements.
[f] Of nine replicates, only one contained measureable BaP concentrations.

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Table S7. Change in selected ambient particle-bound nitro-PAHs (Δ ng = reacted – unreacted) upon exposure to $N_2O_5/NO_3/NO_2$[a, b]. Numbers that are underlined in bold represent significant changes using the paired *t*-test ($p < 0.05$)

Site	Time	**2-NFL**	**3-NFL**	**4-NPY**	**8-NFL**	**1-NPY**	**2-NPY**	**12-NBaA**	**7-NBaA**	**1-NTP**	**6-NCHR**	**2-NTP**	**6-NBaP**
Beijing 1[c]	24-hr.	-27[e]	**14**[d]	NM	NM	**83**[d]	1.6[e]	NM	**19**[d]	**3.2**[d]	**24**[d]	**5.2**[d]	**86**[d]
Beijing 2[c]	24-hr.	1.7[e]	5.7[e]	NM	NM	**67**[d]	0.7[e]	NM	**10**[d]	**0.5**[d]	**6.7**[d]	**1.0**[d]	**185**[d]
Beijing 3[c]	24-hr.	-0.3[e]	**5.7**[d]	NM	NM	**61**[d]	2.3[e]	NM	**20**[d]	1.2[e]	**11**[d]	**1.2**[d]	**165**[d]
LA97-1	0600-1158	-3.9	0.3	-0.3	0.4	4.4	0.4	0.5	1.3	6.8	3.7	5.5	ND
LA97-2	1202-1800	-0.1	0.3	-0.5	1.0	3.1	ND	-0.4	0.1	0.2	0.4	-0.1	ND
LA97-3	1803-0556	-5.2	0.7	-0.3	1.1	14	-1.4	0.5	1.1	1.7	1.9	2.2	3.0
LA97-4	0602-1158	-6.6	0.7	-0.6	1.0	4.3	-0.4	0.2	0.6	0.1	0.3	0.1	2.8
LA97-5	1202-1800	-0.1	0.0	0.1	0.6	1.7	-1.2	0.4	1.4	7.0	4.2	7.5	ND
A97-13	0600-1200	-2.5	0.8	0.0	1.5	8.9	0.8	0.2	0.9	0.1	0.6	0.6	-4.2
A97-15	1203-1800	-4.2	0.4	-0.1	0.9	3.9	-0.7	0.0	0.4	0.1	0.5	0.0	ND
A97-16	1800-0600	-4.2	0.4	-0.1	0.9	6.0	2.0	0.0	1.3	0.7	0.9	0.3	ND
A97-18	0603-1200	-5.0	0.4	0.2	0.8	3.5	0.0	0.5	1.5	0.4	0.8	0.8	ND
A97-20	1204-1800	-0.2	0.3	-0.7	0.6	1.3	-1.7	-0.3	-0.2	0.2	0.3	0.6	ND
R97-13	0600-1802	-2.1	0.3	-0.4	0.4	2.1	0.1	0.0	0.0	0.0	0.2	0.1	ND
R97-14	1811-0600	-17	0.5	-0.5	0.7	3.8	-0.4	0.8	-1.0	-0.3	-0.2	-0.3	ND
R97-15	0614-1750	-3.8	0.4	-0.1	0.8	1.3	1.3	0.0	-0.3	0.3	0.0	0.0	ND
B97-14	0605-1800	-3.1	0.5	-0.2	0.6	2.7	ND	0.7	-0.3	0.0	0.0	-0.2	ND

Site	Time	**2-NFL**	**3-NFL**	**4-NPY**	**8-NFL**	**1-NPY**	**2-NPY**	**12-NBaA**	**7-NBaA**	**1-NTP**	**6-NCHR**	**2-NTP**	**6-NBaP**
B97-15	1814-0600	-0.6	0.0	-1.2	0.0	0.4	-0.4	-4.4	-1.0	-0.2	0.0	0.0	ND
B97-17	0607-1800	-0.6	0.3	-0.1	0.1	1.9	0.0	0.1	0.0	0.0	0.3	0.0	ND
R2012 N1	1800-0600	0.3	0.3	0.0	0.3	8.9	-0.7	2.1	0.1	0.0	0.3	0.1	ND
R2012 D1	0600-1800	-0.3	0.4	0.0	0.4	2.1	-0.3	-0.3	0.2	0.5	2.2	2.6	ND
R2012 N2	1800-0600	-6.9	0.0	-0.6	0.2	1.8	-0.4	-0.2	-3.2	0.1	0.3	0.0	ND
R2012 D2	0600-1800	-0.9	0.4	-0.5	0.0	0.1	-1.0	-0.4	0.7	0.8	2.7	3.8	ND
R2012 N3	1800-0600	-13	0.0	0.3	0.0	1.0	0.2	1.0	1.4	0.0	0.0	0.0	ND
R2012 D3	0600-1800	-1.7	0.3	0.0	0.6	0.8	0.6	-0.1	1.1	0.8	3.5	3.2	ND
R2012 N4	1800-0600	-2.9	0.1	0.0	0.0	2.7	-0.5	0.0	0.1	0.0	0.0	0.0	ND
R2012 D4	0600-1800	-1.2	0.3	-0.1	0.0	0.6	-0.8	-0.4	0.6	0.7	3.0	2.3	ND
R97 MS[f]	0555-1740	-0.3[e]	ND	ND	ND	-0.01[e]	ND	ND	ND	ND	ND	ND	ND

[a] Abbreviations: NFL = nitrofluoranthene; NPY = nitropyrene; NBaA = nitrobenz[a]anthracene; NTP = nitrotriphenylene; NCHR = nitrochrysene; NBaP = nitrobenzo[a]pyrene; NM = not measured; ND= not detected.

[b] Negative signs denote loss in concentration upon exposure to $N_2O_5/NO_3/NO_2$.

[c] Mean change calculated from three replicate sets of measurements.

[d] Denotes a *p*-value <0.05 for the paired *t*-test suggesting a significant change in concentration due to exposure to $N_2O_5/NO_3/NO_2$.

[e] Denotes a *p*-value >0.05 for the paired *t*-test suggesting no significant difference in concentration due to exposure to $N_2O_5/NO_3/NO_2$.

[f] Mean change calculated from nine replicate sets of measurements.

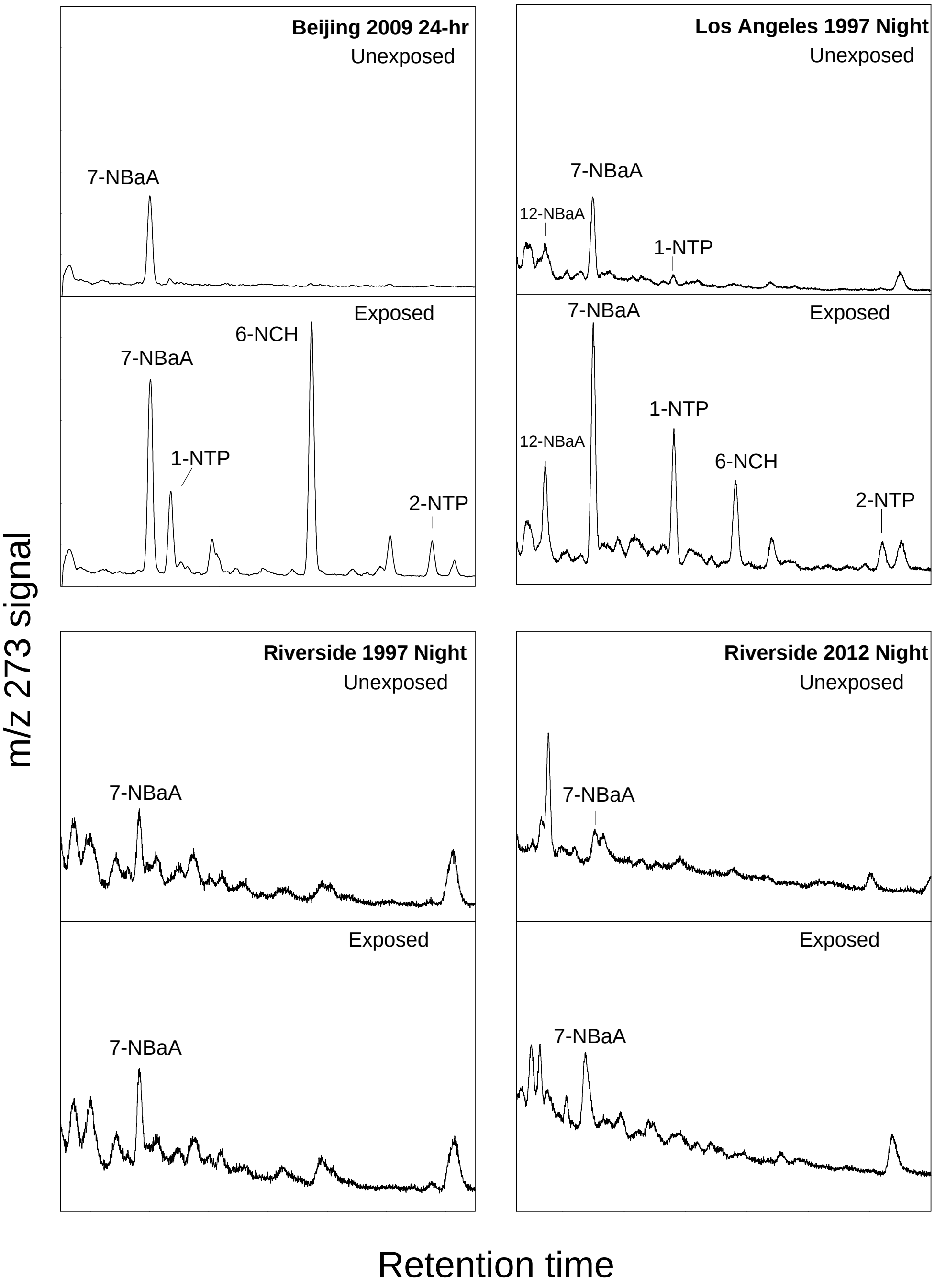

Figure S7. GC-MS/NCI chromatograms of m/z 273 for unexposed and exposed (to $N_2O_5/NO_3/NO_2$) particulate matter collected in Beijing 2009 (top left), Los Angeles 1997 night (top right), Riverside 1997 night (bottom left), and Riverside 2012 night (bottom right) to N_2O_5. The unexposed and exposed chromatograms for each site are shown on the same scale relative to one another.

Table S8. Ratios of ambient 2-NFL/1-NPY, 2-NFL/BeP, Reactivity toward nitration[a], 2-NFL/2-NPY and 1-NPY/BeP for ambient particulate samples collected in Beijing, China and the Los Angeles air basin (1997 and 2012)[b]

Site	Time	2-NFL/1-NPY	2-NFL/BeP	Reactivity	2-NFL/2-NPY	1-NPY/BeP
Beijing 1[c]	24-hr.	52.9	0.70	37.58	173.9[d]	0.013
Beijing 2[c]	24-hr.	26.4	0.39	18.12	13.9	0.015
Beijing 3[c]	24-hr.	14.4	0.23	65.40	4.0	0.016
LA97-1	0600-1158	10.8	0.33	7.36	4.2	0.030
LA97-2	1202-1800	14.3	0.55	8.70	ND	0.038
LA97-3	1803-0556	5.1	0.15	19.76	3.8	0.030
LA97-4	0602-1158	17.4	0.60	9.17	6.0	0.034
LA97-5	1202-1800	9.0	0.27	6.55	1.9	0.030
A97-13	0600-1200	10.7	0.35	9.59	2.8	0.033
A97-15	1203-1800	23.7	0.73	7.70	9.2	0.031
A97-16	1800-0600	35.3	0.84	11.32	8.9	0.024
A97-18	0603-1200	17.7	0.71	10.01	3.3	0.040
A97-20	1204-1800	12.1	0.54	5.35	2.6	0.045
R97-13	0600-1802	24.3	0.76	5.40	7.9	0.031
R97-14	1811-0600	66.7	3.40	6.99	22.8	0.051
R97-15	0614-1750	38.5	1.36	4.89	12.3	0.035
B97-14	0605-1800	12.3	0.61	12.60	ND	0.050
B97-15	1814-0600	25.8	2.12	1.05	28.7	0.082
B97-17	0607-1800	21.4	0.42	7.33	17.9	0.020
R2012 N1	1800-0600	9.5	0.48	32.67	7.3	0.051
R2012 D1	0600-1800	1.2	0.15	5.67	2.2	0.124
R2012 N2	1800-0600	22.0	1.75	6.14	23.8	0.079

Site	Time	2-NFL/1-NPY	2-NFL/BeP	Reactivity	2-NFL/2-NPY	1-NPY/BeP
R2012 D2	0600-1800	2.9	0.32	0.36	8.5	0.112
R2012 N3	1800-0600	36.8	2.73	3.93	54.9	0.074
R2012 D3	0600-1800	2.6	0.18	3.24	7.9	0.070
R2012 N4	1800-0600	50.4	2.52	9.96	61.0	0.050
R2012 D4	0600-1800	5.6	0.34	1.27	11.8	0.061
R97 MS[e]	0555-1740	19.2	1.17	0.50	ND	0.066

[a] Reactivity toward nitration is expressed by: reactivity = $(\Delta[\text{1-NPY}]/[\text{PY}]_0) \times 100$ where Δ[1-NPY] is the change (exposed filter - unexposed filter) in 1-NPY and $[\text{PY}]_0$ is the original amount of PY measured on each unexposed filter.

[b] Ratios for unexposed ambient samples. Abbreviations: NFL = nitrofluoranthene; NPY = nitropyrene; BeP = benzo[e]pyrene; ND = 2-NPY not detected.

[c] Values are reported as the mean of three replicate measurements.

[d] Mean value calculated from only 2 of 3 replicates due to a possible outlier or measurement error.

[e] Values are reported as the mean of nine replicate measurements.

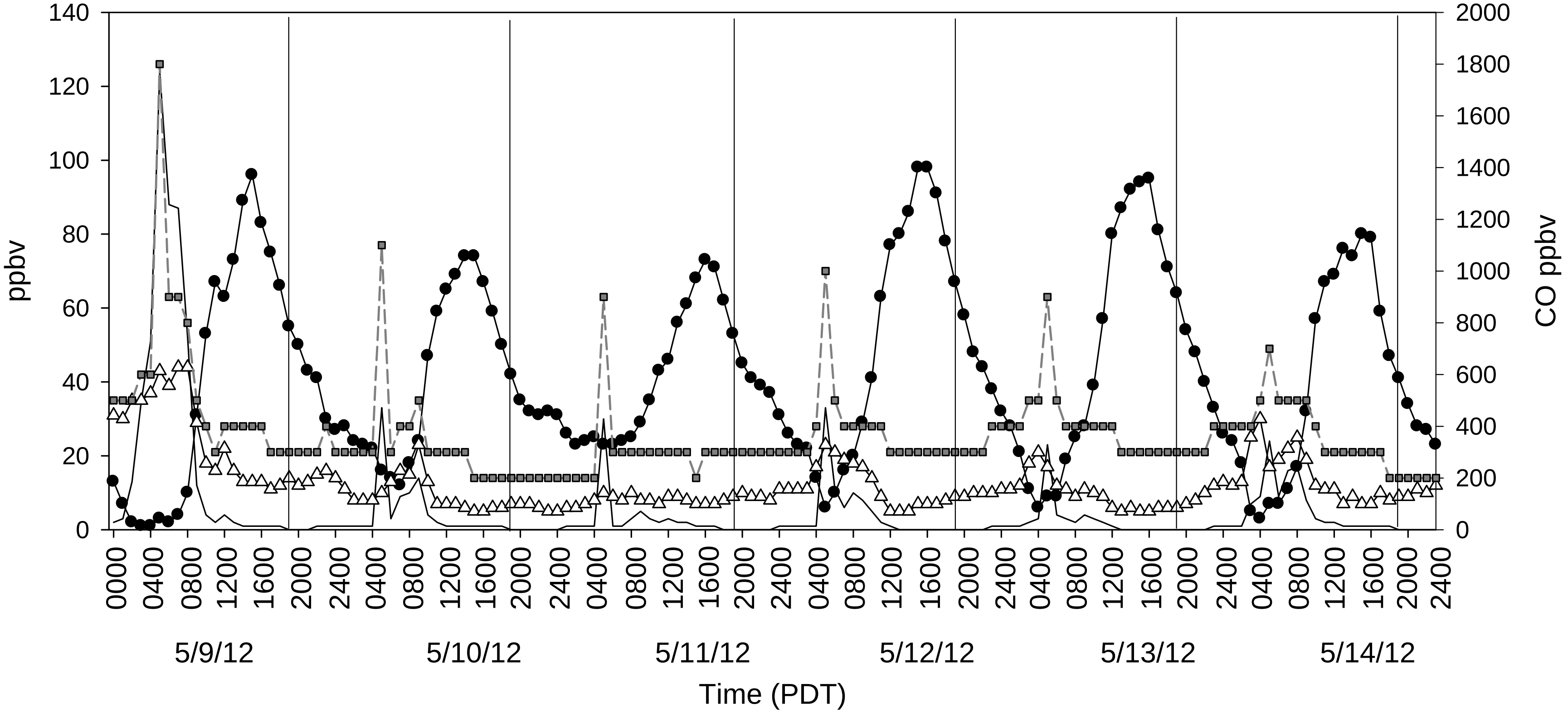

Figure S8. Hourly co-pollutant data for Riverside 2012 sampling. Vertical lines represent the approximate times of sunset during sampling (19:45). Sampling periods began on May 10, 2012 from 1800-0600 and continued at 12-hr intervals until May 14, 2012 from 0600-1800. ●, Hourly average O_3 measurements; △, hourly average NO_2 measurements; ─, hourly average NO; --■--, hourly average CO (refer to right-hand axis). Data from California Air Resources Board.

SCOS97

Figure S9 shows the co-pollutant data for August 22-23, 1997 (the 3rd Intensive sampling of the SCOS97campaign) taken from the California Air Resources Board (CARB) website (http://www.arb.ca.gov). Sampling was started at 0600 hr on August 22 and ended at 1800 hr on August 23.

Figures S10, S11 and S12 utilize the filter-adsorbed PAH and nitro-PAH data from Tables S3 and S4, the naphthalene and 3-nitrobiphenyl data reported in Atkinson et al., 2001 (available from the CARB website) and methylnitronaphthalene and dimethylnitronaphthalene data from re-analysis of the PUF plug extracts archived from 1997.

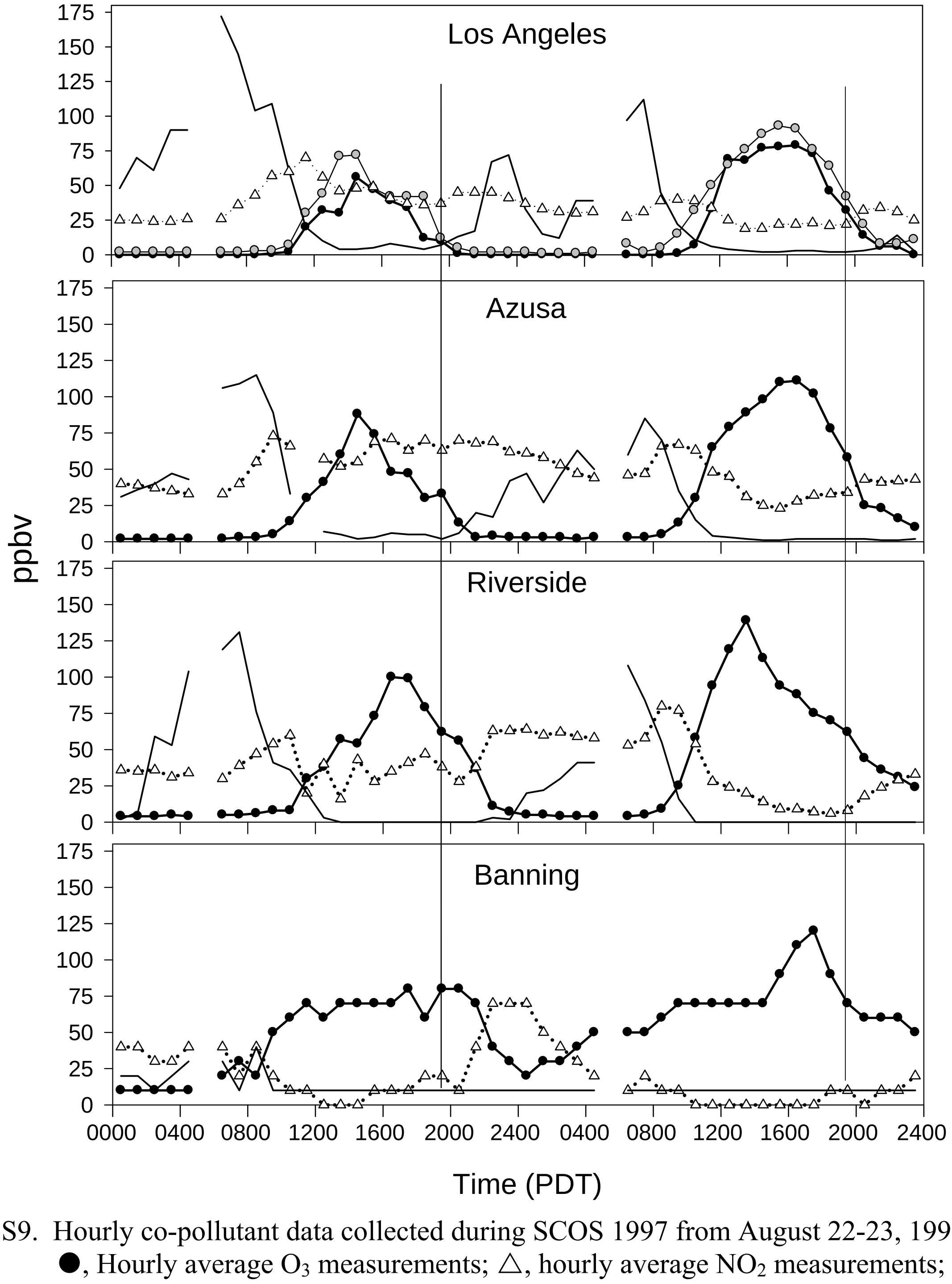

Figure S9. Hourly co-pollutant data collected during SCOS 1997 from August 22-23, 1997. ●, Hourly average O_3 measurements; △, hourly average NO_2 measurements; —, hourly average NO. NO and NO_2 data for the Los Angeles North Main sampling site were unavailable, so the data shown is from the nearby Pico Rivera (PR) site along with O_3 data from both the Los Angeles site (●) and the PR site (●). Solid vertical lines represent the approximate time of sunset during the sampling period (19:31). Sampling periods in Los Angeles and Azusa ran from 0600-1200, 1200-1800 and 1800-0600 hr while sampling periods in Riverside and Banning ran from 0600-1800 and 1800-0600 hr.

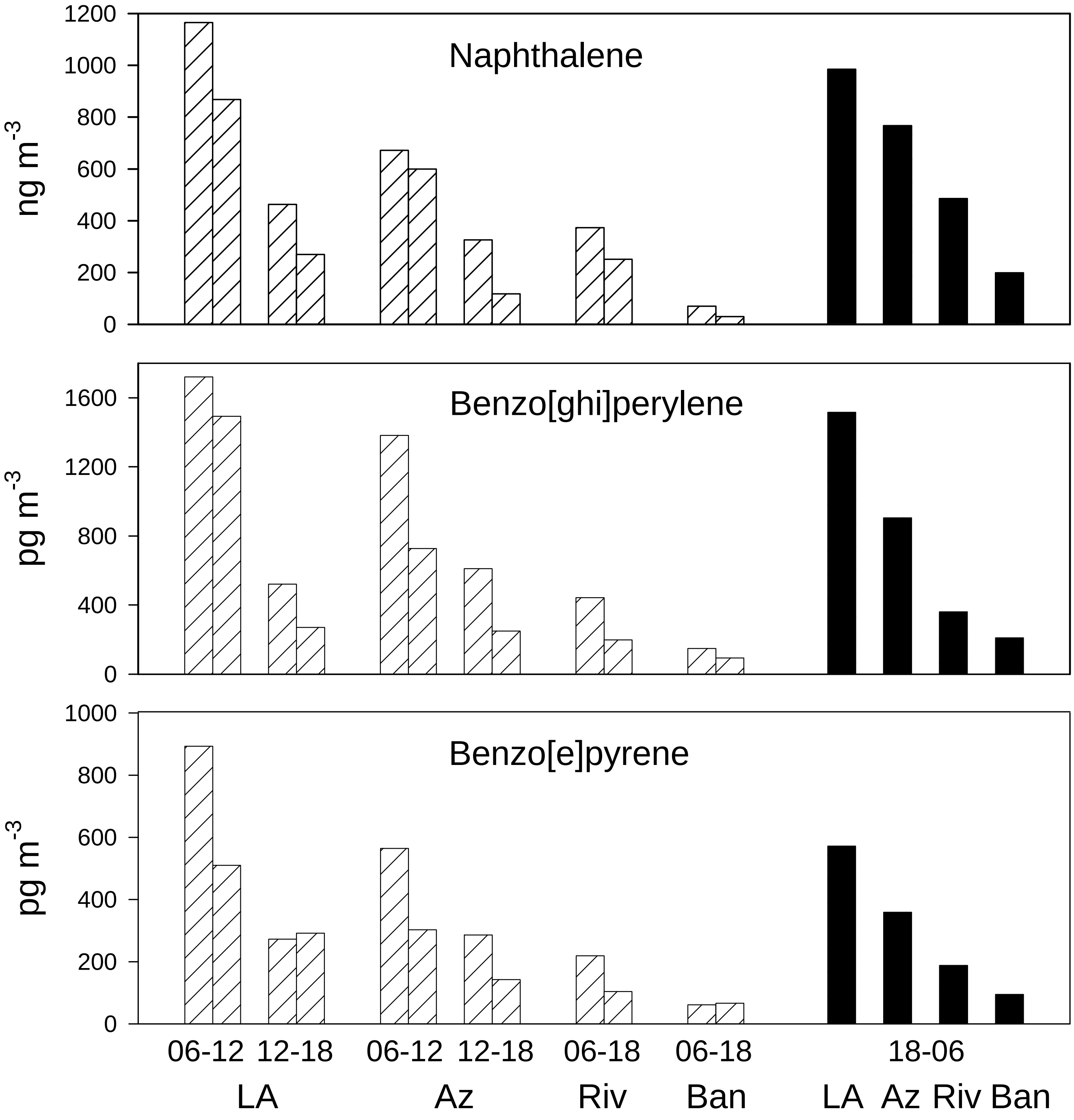

Figure S10. Ambient concentrations of naphthalene, benzo[ghi]perylene, and benzo[e]pyrene measured at sites during the SCOS97 campaign. The naphthalene concentrations are reported from gas-phase samples collected on Tenax-TA adsorbent (Atkinson et al., 2001); note the ng m^{-3} scale for naphthalene. Patterned data bars, ▨, represent daytime samples while filled data bars, ■, represent 12-hr nighttime samples; LA = Los Angeles; Az = Azusa; Riv = Riverside; Ban = Banning.

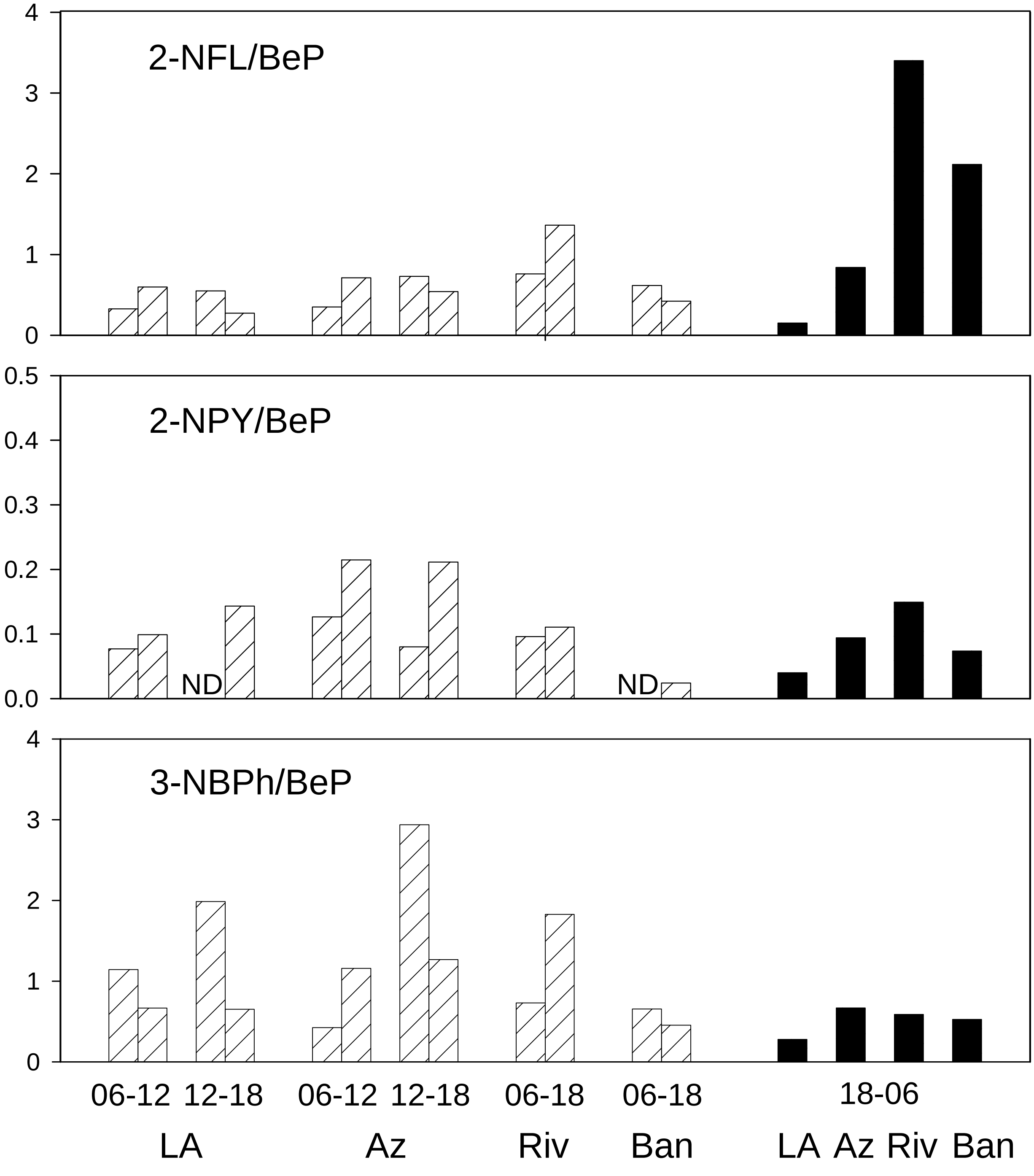

Figure S11. Ratios of 2-nitrofluoranthene/benzo[e]pyrene (2-NFL/BeP) (top), 2-nitropyrene/benzo[e]pyrene (2-NPY/BeP) (middle) and 3-nitrobiphenyl/benzo[e]pyrene (3-NBPh/BeP) (bottom) measured during the SCOS97 study. Patterned data bars, ▨, represent daytime samples while filled data bars, ■, represent 12-hr nighttime samples; LA = Los Angeles; Az = Azusa; Riv = Riverside; Ban = Banning; ND = not determined.

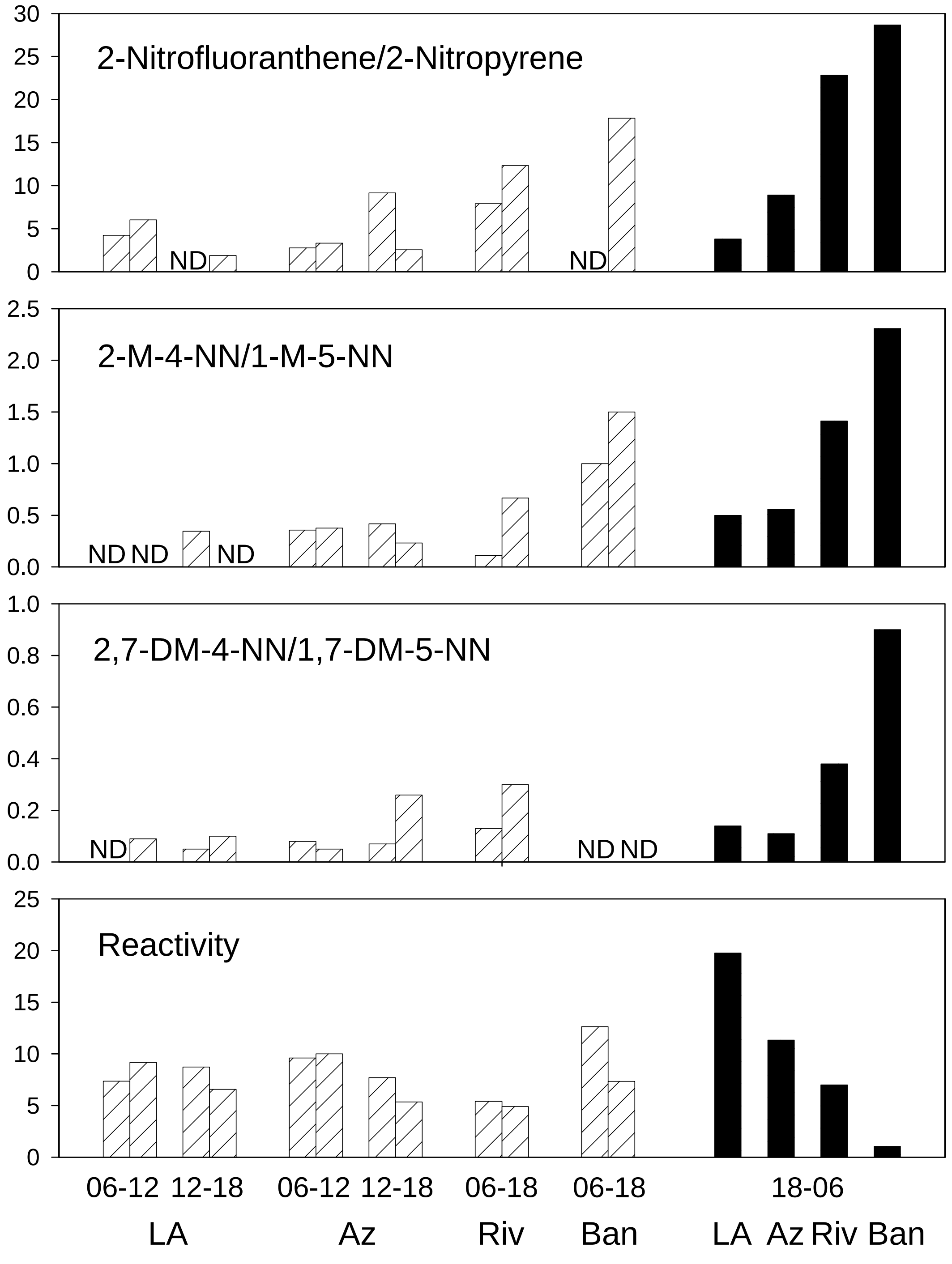

Figure S12. Ratios of 2-nitrofluoranthene/2-nitropyrene (top), 2-methyl-4-nitronaphthalene/1-methyl-5-nitronaphthalene [2-M-4-NN/1-M-5-NN] (second panel), 2,7-dimethyl-4-nitronaphthalene/1,7-dimethyl-5-nitronaphthalene [2,7-DM-4-NN/1,7-DM-5-NN] (third panel), and reactivity of ambient particles towards nitration (bottom) for the SCOS97 study. Patterned data bars, ▨, represent daytime samples while filled data bars, ■, represent 12-hr nighttime samples; LA = Los Angeles; Az = Azusa; Riv = Riverside; Ban = Banning; ND = not determined.

Table S9. Ratios of 1-NPY/BeP calculated for ambient samples with and without exposure to $N_2O_5/NO_3/NO_2$

Site[b]	Time	1-NPY/BeP unexposed[c]	1-NPY/BeP exposed[d]
Beijing 1[e]	24-hr.	0.013	0.33
Beijing 2[e]	24-hr.	0.015	0.22
Beijing 3[e]	24-hr.	0.016	0.60
LA97-1	0600-1158	0.030	0.082
LA97-2	1202-1800	0.038	0.16
LA97-3	1803-0556	0.030	0.18
LA97-4	0602-1158	0.034	0.14
LA97-5	1202-1800	0.030	0.12
A97-13	0600-1200	0.033	0.19
A97-15	1203-1800	0.031	0.16
A97-16	1800-0600	0.024	0.092
A97-18	0603-1200	0.040	0.13
A97-20	1204-1800	0.045	0.13
R97-13	0600-1802	0.031	.089
R97-14	1811-0600	0.051	0.19
R97-15	0614-1750	0.035	0.092
B97-14	0605-1800	0.050	0.290
B97-15	1814-0600	0.082	0.093

Site[b]	Time	1-NPY/BeP unexposed[c]	1-NPY/BeP exposed[d]
B97-17	0607-1800	0.020	0.19
R2012 N1	1800-0600	0.051	0.84
R2012 D1	0600-1800	0.124	0.40
R2012 N2	1800-0600	0.079	0.20
R2012 D2	0600-1800	0.112	0.17
R2012 N3	1800-0600	0.074	0.14
R2012 D3	0600-1800	0.070	0.17
R2012 N4	1800-0600	0.050	0.27
R2012 D4	0600-1800	0.061	0.12
R97 MS[f]	0555-1740	0.066	0.065

[a] Abbreviations: 1-NPY = 1-nitropyrene; BeP = benzo[e]pyrene.
[b] Sampling information is described in Table S1.
[c] Initial ratios of 1-NPY/BeP observed from ambient particulate matter .
[d] Ratios of 1-NPY/BeP after filters samples were exposed to 8 additions of N_2O_5 and NO_2. Additions were performed once per hour.
[e] Reported Beijing ratios are each the mean value of 3 replicate measurements.
[f] Reported R97 MS ratios are each the mean value of 9 replicate measurements.

Mechanistic Implications

Gas-phase versus Heterogeneous Formation of Nitro-PAHs. The atmospheric gas-phase NO_3 radical-initiated reactions of PAHs are postulated to proceed by initial addition of NO_3 radicals to the position of highest electron density, followed by *ortho* or *para* addition of NO_2, and subsequent loss of HNO_3 (Arey, 1988; Atkinson and Arey, 2007; Wang et al., 2010). Theoretical studies have shown this mechanism to be the most energetically favorable for naphthalene when compared with direct attack by N_2O_5 or NO_2 because of high free energy barriers for the latter reactions (36 kcal mol^{-1} and 25-28 kcal mol^{-1} for N_2O_5 and NO_2, respectively) (Ghigo et al., 2006). Thus, in the case of the gas-phase reaction of FL with NO_3 radicals, the initial addition of NO_3 is expected to proceed at the most electron-dense 3-carbon position (Arey, 1998), followed by *ortho* addition of NO_2 at the 2-carbon position, with the loss of HNO_3 resulting in 2-NFL. This mechanism could also apply to the gas-phase PY + OH reaction, in which OH adds initially to the electron dense 1-carbon (Ruehle et al., 1985) followed by addition of NO_2 at the 2-carbon position and loss of H_2O to form 2-NPY (this has also been observed to occur in the PY + NO_3 reaction at very high NO_2 concentrations (Atkinson et al., 1990)). It should be noted that a significant energy barrier exists to the elimination of H_2O during these reactions (Ghigo et al, 2006), and so it is possible that nitro-PAH formation occurs through decomposition of the chemically-activated intermediate.

If a similar step-wise mechanism is suggested to occur for the heterogeneous reaction of FL or PY with NO_3 and NO_2 to form nitrofluoranthenes and nitropyrenes (Gross and Bertram 2008; Kwamena and Abbatt, 2008; Zhang et al., 2011), then the expected isomers would be 2-NFL or 4-NPY. In contrast, previous studies of heterogeneous nitration of PY and FL via $N_2O_5/NO_3/NO_2$ formed 1-NPY as the dominant isomer, followed by 3-NFL, 8-NFL, 7-NFL, and 1-NFL in differing relative amounts (Zimmermann et al., 2012; Pitts et al., 1985a). Thus, isomer distributions of NFLs and NPYs appear to provide a qualitative way of assessing gas-phase *versus* heterogeneous formation of nitro-PAHs in chamber or flow-tube systems.

Recent measurements of low uptake coefficients for N_2O_5 onto PAH surfaces relative to that of NO_3 radicals (Gross and Bertram, 2008) suggest that N_2O_5 is not the agent of nitration for heterogeneous reactions of PAHs. Although Mak et al. (2007) coupled the measurement of these uptake coefficients to the formation of oxygen- and nitrogen-containing functional groups by Fourier transform infrared spectroscopy (FTIR) and Kwamena and Abbatt (2008) identified nitro-PAHs as products from these reactions, no studies, to the authors knowledge, have investigated the unique isomer distribution of NFL or NPY products in combination with uptake coefficient measurements. Such studies would be very helpful in further elucidating the mechanism of PAH nitration via the heterogeneous reaction with $N_2O_5/NO_3/NO_2$.

Furthermore, the relatively low reactivity toward nitration of all the ambient PM samples collected during the daytime, including samples with high PAH concentrations, suggest that ambient particulate PAHs are rapidly deactivated (or become unavailable) toward nitration in the atmosphere. The two Los Angeles morning samples (0600-1200) and the nighttime sample (1800-0600) had high and similar B(ghi)P and BeP concentrations and the particle-associated PY concentrations were comparable, with the morning samples having somewhat higher PY than the nighttime sample (Table S3). However, three-fold greater formation of 1-NPY resulted from exposing the nighttime sample in comparison with the morning samples (Table S7). The resulting higher calculated reactivity toward nitration for the nighttime sample suggests that daytime OH radical chemistry (perhaps by a mechanism of secondary VOC products depositing on the particles) rapidly decreased the particle-associated PAH reactivity toward nitration. This again illustrates the potential difficulties in extrapolating from laboratory results to ambient atmospheres.

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