

**YIELDS AND REACTIONS OF INTERMEDIATE COMPOUNDS FORMED FROM
THE INITIAL ATMOSPHERIC REACTIONS OF SELECTED VOCs**

Final Report to California Air Resources Board Contract No. 96-306

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Abstract

This contract had three project elements dealing with aspects of the atmospheric chemistry of volatile or semi-volatile organic compounds.

Project Element No. 1 concerned the investigation of ambient NO_3 radical levels in the Los Angeles Air Basin during the 1997 Southern California Ozone Study (SCOS97-NARSTO), using the formation of nitronaphthalenes and methylnitronaphthalenes (MNNs) as a sensitive indicator of the presence of NO_3 radicals during nighttime. Naphthalene, 1- and 2-methylnaphthalene and biphenyl and their nitro-derivatives formed from atmospheric reactions: 1- and 2-nitronaphthalene, the 14 MNNs and 3-nitrobiphenyl were monitored in 12-hr daytime and 12-hr nighttime samples during the intensive sampling days of the SCOS97-NARSTO ozone study at three sites in the Los Angeles Air Basin, Azusa, Riverside and Banning. Evidence for the presence of NO_3 radicals is presented.

Project Element No. 2 involved the participation of Roger Atkinson in the Coordinating Research Council, Inc., Review Panel for the Atmospheric Chemistry of Hydrocarbons (RPACH). This data review panel was set up to carry out detailed reviews and evaluations of the literature data concerning the atmospheric chemistry of the various classes of VOCs of importance in photochemical air pollution, with this review and evaluation being concerned with the atmospheric chemistry of alkenes. This review and evaluation of alkene chemistry has been published by Oxford University Press, "The Mechanisms of Atmospheric Oxidation of the Alkenes", J. G. Calvert, R. Atkinson, J. A. Kerr, S. Madronich, G. K. Moortgat, T. J. Wallington, and G. Yarwood, 2000.

Project Element No. 3 was the preparation of two review chapters for the North American Research in Tropospheric Ozone (NARSTO) assessment document and included as part of this effort a sub-contract to Dr. Marcia C. Dodge. The two critical review papers dealt with the following topics: the current status of the kinetics, mechanisms and products of the atmospheric reactions of VOCs and NO_x (Roger Atkinson); and the "smog" chamber data-base and current programs in this area and the status of chemical mechanisms for air quality simulation models (Marcia C. Dodge). These NARSTO review papers have been published in a common volume in Atmospheric Environment, volume 34, issues 12-14, pp. 2063-2101 and pp. 2103-2130, respectively (2000).

Executive Summary

Background

In California's South Coast Air Basin vehicle traffic as well as other sources emit oxides of nitrogen and volatile organic compounds which undergo a complex series of photochemical reactions leading to products detrimental to human health including ozone, secondary particles and toxic species such as nitrated polycyclic aromatic hydrocarbons. This contract had three project elements dealing with aspects of the atmospheric chemistry of volatile or semi-volatile organic compounds.

Project Element No. 1 concerned the investigation of ambient NO_3 radical levels in the Los Angeles Air Basin during the 1997 Southern California Ozone Study (SCOS97-NARSTO), using the formation of nitronaphthalenes and methylnitronaphthalenes (MNNs) as a sensitive indicator of the presence of NO_3 radicals during nighttime.

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Methods Element No. 1

Naphthalene, 1- and 2-methylnaphthalene and biphenyl and their nitro-derivatives formed from atmospheric reactions: 1- and 2-nitronaphthalene, the 14 MNNs and 3-nitrobiphenyl were monitored in 12-hr daytime and 12-hr nighttime samples during the intensive sampling days of the SCOS97-NARSTO ozone study at three sites in the Los Angeles Air Basin, Azusa, Riverside and Banning. Tenax TA cartridges were used to sample the volatile polycyclic aromatic hydrocarbons (PAH) with analysis by thermal desorption gas chromatography/mass spectrometry (GC/MS) utilizing deuterated internal standards for quantification. Polyurethane foam plugs in modified high-volume samplers were used to sample the semi-volatile nitro-PAH. The samples were extracted in an organic solvent, fractionated by high performance liquid chromatography and analyzed by GC/MS.

Results Element No. 1

Ambient mixing ratios of naphthalene, 1- and 2-methylnaphthalene, biphenyl, 1- and 2-nitronaphthalene, 3-nitrobiphenyl and several methylnitronaphthalenes were measured at source and receptor sites in the Los Angeles Air Basin. Naphthalene was the most abundant volatile PAH, reaching concentrations of 1200 ng m^{-3} . The nitro-PAH were approximately two orders of magnitude lower in concentration than their precursor PAH, but clearly showed evidence that both OH radical-initiated and NO_3 radical-initiated nitro-PAH formation mechanisms were operating during the SCOS97-NARSTO intensive sampling days.

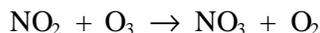
Conclusions Element No. 1

Monitoring two-ring PAH and their nitro-derivatives allowed ratios to be measured which served as markers for OH radical-initiated chemistry and nighttime NO₃ radical-initiated chemistry. Utilizing these ratios it was demonstrated that nitro-PAH were produced by NO₃ radical chemistry during the SCOS07-NARSTO ozone study, with downwind receptor sites showing more evidence for air masses processed by NO₃ radical chemistry.

**PROJECT ELEMENT NO. 1:
INVESTIGATION OF AMBIENT NO₃ RADICAL LEVELS IN THE LOS ANGELES
AIR BASIN DURING THE SCOS97 STUDY**

Introduction and Background

Nitrate (NO₃) radicals are formed from the gas-phase reaction of NO₂ with O₃.



Because of the rapid photolysis of the NO₃ radical, NO₃ radical concentrations are below the detection limit of present instruments during daytime, but can increase to detectable levels after sunset. While only a small database exists, nighttime NO₃ radical mixing ratios of up to 430 ppt have been measured in the Los Angeles air basin (Atkinson *et al.*, 1986). The maximum NO₃ radical concentration observed during an intercomparison of measurement methods for atmospheric nitrogenous species held in Claremont, CA, Sept. 11-19, 1985 was 70 ppt (Biermann *et al.*, 1988) and the maximum observed over 27 nights in July and August, 1990 during the San Joaquin Valley Air Quality study was 80 ppt (Smith *et al.*, 1995). Despite their variable and often low concentrations, NO₃ radicals can play an important role in atmospheric chemistry, by reacting with and removing reactive VOCs such as terpenes and phenols and as a sink for NO_x, either through reactions with reactive VOCs or through the equilibrium with N₂O₅,



followed by dry and/or wet deposition of N₂O₅. To date, NO₃ radicals have been identified and quantified by differential optical absorption spectroscopy (DOAS). This technique is limited to ground level measurements at one site per instrument. Because of the rapid reactions of NO with O₃ (the precursor to NO₃) and with NO₃ radicals, NO₃ radicals and NO cannot co-exist at appreciable levels and ground level NO₃ radical measurements may not be representative of elevated altitude airmasses. Indeed measurements made during the SCOS97 - NARSTO study of biogenic volatile organic compounds (BVOCs) at the elevated sites Pine Mountain (~1300 m) and Mount Baldy (~1200 m) suggested that nighttime NO₃ radical chemistry depleted isoprene and other reactive BVOCs at these elevated sites (Reissell and Arey, 2001). Because these elevated sites were isolated at night from the NO emissions in the valley by being located in a stable inversion layer, NO_x and O₃ transported from the valley during the afternoon formed NO₃ radicals at the elevated sites after sunset. In contrast, at Azusa, a heavily traffic impacted site at the base of the San Gabriel mountains, NO emissions into the shallow nocturnal boundary layer reacted with the O₃ formed during the afternoon and NO concentrations at Azusa built up during the night, precluding the formation of NO₃ radicals.

If unique product species or product profiles (i.e., characteristic ratios of specific products) from the atmospheric reaction of NO₃ with specific VOCs can be identified, these products can be monitored downwind of a source region and their concentrations used to indicate the levels of NO₃ radicals present in the air mass during its transport. The formation of nitrated polycyclic aromatic hydrocarbons (nitro-PAH) from the hydroxyl (OH) radical and NO₃ radical-initiated reactions of gas-phase PAH has been well documented (Atkinson and Arey, 1994; Arey, 1998). The postulated reaction mechanism involves the addition of the radical to the aromatic ring, followed by addition of NO₂ and the loss of water or nitric acid for the OH radical and NO₃ radical reactions, respectively (Sasaki *et al.*, 1997a). The OH radical-initiated and NO₃ radical-initiated reactions may form different relative abundances of the nitro-PAH products. In addition, the products from both radical reactions are often distinct from the nitro-PAH resulting from electrophilic PAH nitration and identified in diesel exhaust (Schuetzle, 1983) and other emission sources. Table 1 (adapted from Arey, 1998) lists for several abundant PAH, the specific nitro-PAH isomers formed by OH radical-initiated and NO₃ radical-initiated reactions, the available yield data, and for comparison, the nitro-PAH isomers formed by electrophilic nitration. The dominant atmospheric loss process for PAH is expected to be by reaction with the OH radical, but the significantly higher yield of nitro-PAH from the NO₃ radical reaction can make both radical-initiated reactions important contributors to the observed ambient nitro-PAH (Atkinson and Arey, 1994; Gupta *et al.*, 1996; Arey, 1998).

Fluoranthene and pyrene are four-ring PAH that are present in ambient atmospheres mainly in the gas-phase (Atkinson *et al.*, 1988; Coutant *et al.*, 1988; Arey *et al.*, 1989). The gas-phase OH and NO₃ radical-initiated reactions of these PAH form nitro-isomers distinct from the electrophilic nitration products found in direct emissions (see Table 1), and these nitro-isomers being less volatile than the parent fluoranthene and pyrene become particle-associated. We and others have identified the presence of 2-nitrofluoranthene and 2-nitropyrene in ambient particles as indicative of OH radical-initiated chemistry (see Figure 1A) and a high ratio of 2-nitrofluoranthene/2-nitropyrene as indicative of NO₃ radical-initiated formation of 2-nitrofluoranthene (see Figure 1B) [Atkinson *et al.*, 1988; Zielinska *et al.*, 1989; Ciccioli *et al.*, 1995; 1996; Arey, 1998; Dimashki *et al.*, 2000; Fielberg *et al.*, 2001]. 1-Nitropyrene, also observed in ambient particles, has been attributed to direct emissions from sources such as diesel exhaust (see Figure 1C), where the nitro-PAH identified have been the electrophilic nitration products of the PAH.

Among the two-ring PAH we have also identified nitro-PAH products (or nitro-PAH product ratios) which can serve as "markers" for both daytime OH radical-initiated reactions and for nighttime NO₃ radical-initiated reactions (Atkinson and Arey, 1994; Sasaki *et al.*, 1995, 1997a; Gupta *et al.*, 1996; Arey, 1998). In particular, the products of the 2-ring PAH, naphthalene, 1- and 2-methylnaphthalene and biphenyl, which are the most abundant PAH found in ambient air (Arey *et al.*, 1987; 1989) and are present totally in the gas-phase (Coutant *et al.*, 1988), are appropriate for examining OH radical-initiated versus NO₃ radical-initiated chemistry. The 2-ring nitro-PAH generally are significantly more abundant in ambient air than the nitrofluoranthenes and nitropyrenes, for example, in Glendora, CA in August 1986, the maximum values measured were (in ng/m³): 1-nitronaphthalene, 2.7 (day) and 5.7 (night); 2-nitronaphthalene, 2.6 (day) and 3.1 (night); 3-nitrobiphenyl, 1.2 (day) and 0.5 (night); 2-nitrofluoranthene, 0.3 (day) and 2.0 (night); 2-nitropyrene, 0.02 (day) and 0.05 (night); and 1-nitropyrene, 0.03 (day) and 0.04 (night) [Atkinson *et al.*, 1988; Arey *et al.*, 1989]. Because of the difficulty in collecting sufficient particles to analyze the nitrofluoranthenes and nitropyrenes and the fact that the precursor fluoranthene and pyrene will be distributed between

Table 1. Nitro-PAH isomers formed and their yields from the gas-phase reactions of selected PAH with OH radicals and NO₃ radicals (each in the presence of oxides of nitrogen) and the nitro-PAH formed by electrophilic nitration (adapted from Arey, 1998 and Sasaki *et al.*, 1997).

Parent PAH	Nitro-PAH Formed from		
	Gas-phase OH Radical-initiated Reaction (Yield)	Gas-phase NO ₃ Radical-initiated Reaction (Yield)	Electrophilic Nitration
Naphthalene	1-Nitronaphthalene (1.2%) 2-Nitronaphthalene (1.3%)	1-Nitronaphthalene (24%) 2-Nitronaphthalene (11%)	1-Nitronaphthalene > 2-Nitronaphthalene
1-Methylnaphthalene	1M5NN > 1M4NN ≥ 1M6NN ≥ 1M3NN ≥ 1M7NN ~ 1M2NN >> 1M8NN (Total Yield ~0.4%)	1M3NN > 1M5NN ≥ 1M4NN ≥ 1M8NN ~ 1M6NN > 1M7NN ≥ 1M2NN (Total Yield ~30%)	1M4NN > 1M2NN > 1M5NN > 1M8NN > 1M7NN ~ 1M3NN > 1M6NN
2-Methylnaphthalene	2M5NN > 2M6NN ~ 2M7NN ~ 2M4NN ~ 2M8NN >> 2M3NN > 2M1NN (Total Yield ~0.2%)	2M4NN > 2M1NN ~ 2M5NN ≥ 2M8NN ~ 2M3NN ~ 2M7NN ~ 2M6NN (Total Yield ~30%)	2M1NN >> 2M8NN > 2M4NN > 2M6NN > 2M5NN > 2M3NN > 2M7NN
Biphenyl	3-Nitrobiphenyl (5%)	No reaction observed	2-Nitrobiphenyl 4-Nitrobiphenyl
Fluoranthene	2-Nitrofluoranthene (~3%) 7-Nitrofluoranthene (~1%) 8-Nitrofluoranthene (~0.3%)	2-Nitrofluoranthene (~24%)	3-Nitrofluoranthene > 8-Nitrofluoranthene > 7-Nitrofluoranthene > 1-Nitrofluoranthene
Pyrene	2-Nitropyrene (~0.5%) 4-Nitropyrene (~0.06%)	4-Nitropyrene (~0.06%)	1-Nitropyrene

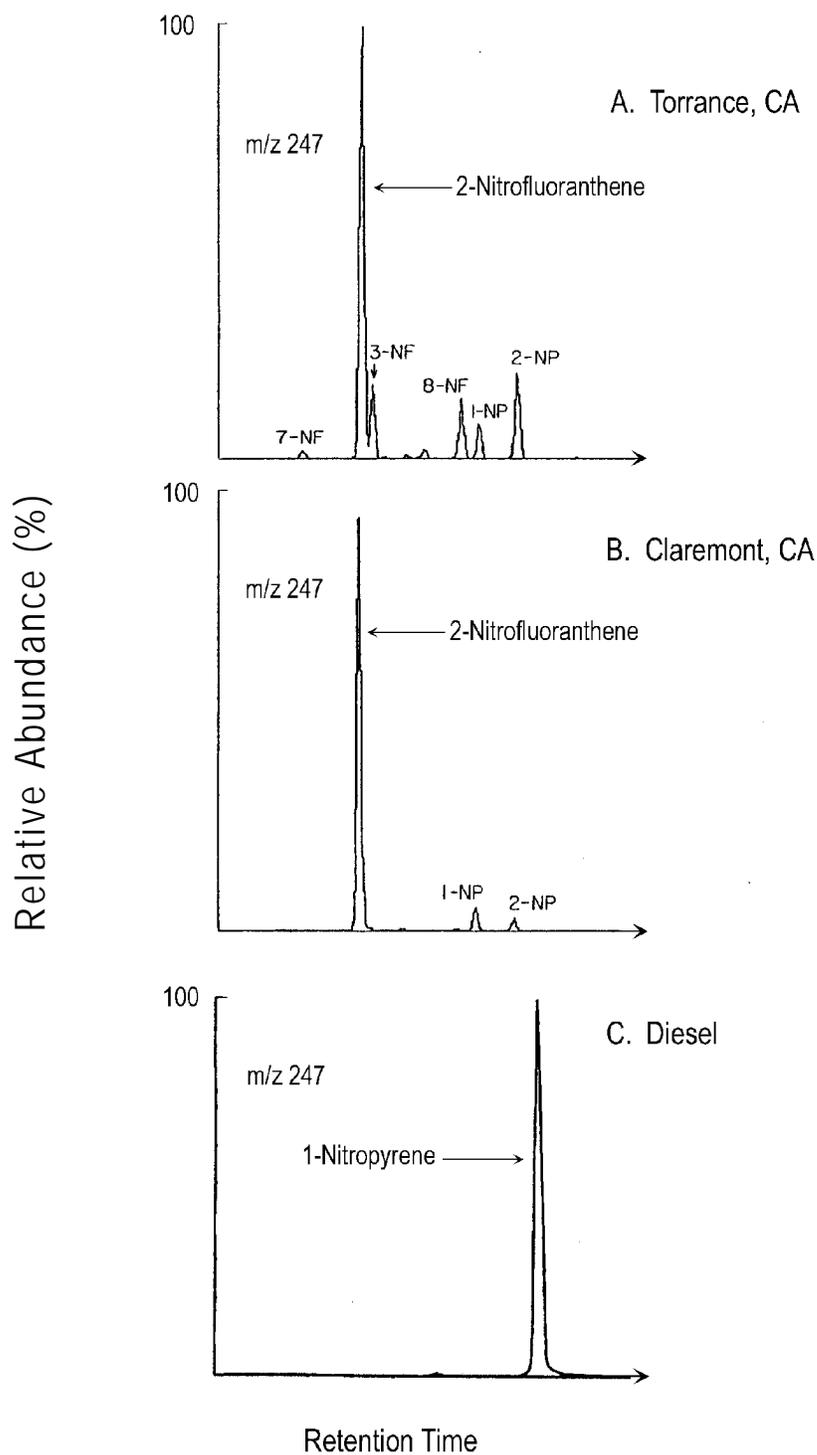
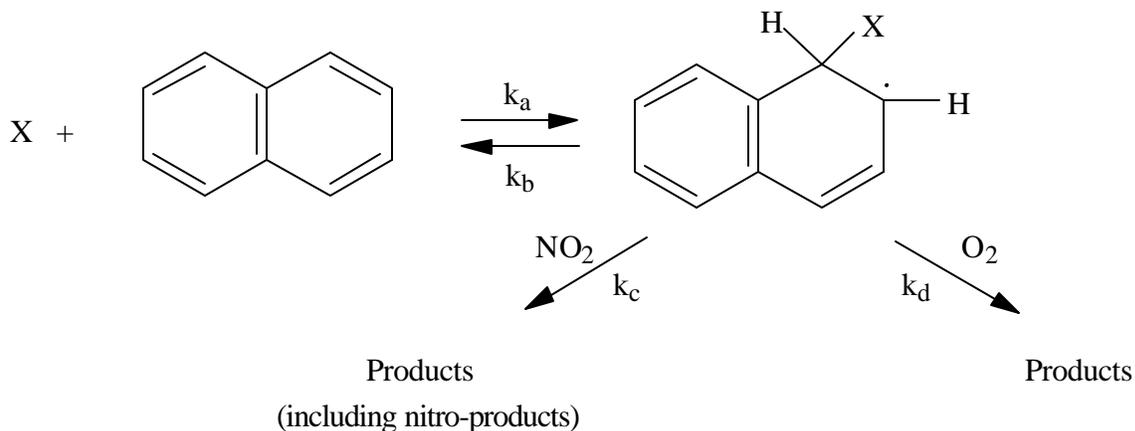


Figure 1. Mass chromatograms showing the molecular ion of the nitrofluoranthenes (NF) and nitropyrenes (NP) in (A) an ambient particle sample from Torrance, CA; (B) an ambient particle sample from Claremont, CA and (C) a diesel exhaust particle sample. Note that (C) was analyzed under different GC/MS conditions, resulting in a different retention time for 1-NP.

the gas-phase and the particles, the decision was made to concentrate on analysis of the 2-ring PAH and nitro-PAH in order to elucidate the chemistry occurring during the SCOS97-NARSTO study and to look in particular for NO_3 radical chemistry occurring during transport from the source site of Azusa to the downwind sites of Riverside and Banning

Based on ambient measurements of 1- and 2-nitronaphthalene (NN) and the 14 methylnitronaphthalenes (MNNs) in Redlands, CA, we have previously shown that NNs and MNNs formed from gas-phase atmospheric reactions of 2-ring PAH make important contributions to the gas-phase mutagenicity of ambient air samples assayed in a microsuspension bacterial system (Gupta, 1995; Gupta *et al.*, 1996). As noted above, the reactions leading to the formation of 1- and 2-nitronaphthalene (analogous reactions form the methylnitronaphthalenes from 1- and 2-methylnaphthalene) are:



where $\text{X} = \text{OH}$ or NO_3 . For the NO_3 radical reaction, the NO_3 -naphthalene or NO_3 -methylnaphthalene adduct either decomposes or reacts with NO_2 to form, in part, NNs or MNNs, respectively, and the rate of formation of these NNs and MNNs is given by $y k_a k_c [\text{NO}_3][\text{NO}_2][\text{PAH}]/k_b$, where y is the yield of the nitronaphthalene or methylnitro-naphthalene isomer (or sum of isomers) (Atkinson *et al.*, 1994). Hence NN and MNN formation depend on $\int [\text{NO}_3][\text{NO}_2] dt$. The values of y for 1-NN and 2-NN are 0.24 and 0.11, respectively, and y for the sum of the seven 1-methylnitronaphthalenes and the seven 2-methylnitronaphthalenes are ~ 0.3 each (Atkinson and Arey, 1994; Sasaki *et al.*, 1997a).

We have carried out environmental chamber experiments to expose naphthalene and 1- and 2-methylnaphthalene to OH radicals (in the presence of NO_x) and, in separate experiments, to NO_3 radicals (Zielinska *et al.*, 1989; Gupta and Arey, unpublished data). Shown in Figure 2 (see also Table 1) is the MNN profile of daytime and nighttime samples collected in Redlands, CA in October, 1994 (Gupta *et al.*, 1996), together with the MNNs formed in the chamber OH radical- and NO_3 radical-initiated reactions (with the initial 1- and 2-methylnaphthalene ratio at 1:2, similar to ambient air measurements at Redlands) [Gupta and Arey, unpublished data]. As may be seen from the figure, the ambient daytime MNN profile at Redlands was similar to the OH radical reaction profile (in particular note the dominance of

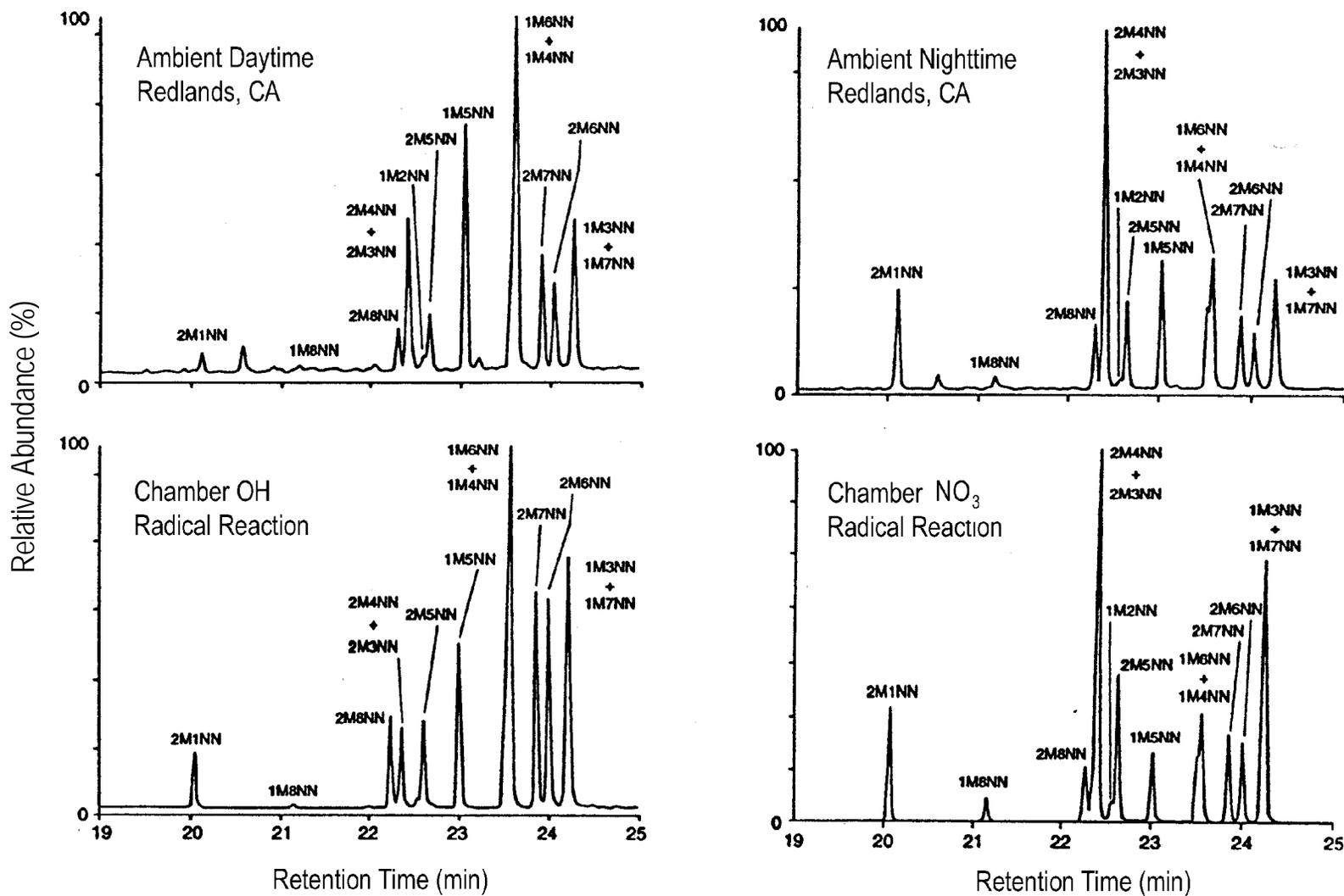


Figure 2. Mass chromatograms showing the molecular ion of the methylnitronaphthalenes ($xMyNN$) present in ambient samples collected in Redlands, CA and formed from environmental chamber reactions of 1- and 2-methylnaphthalene (in the 1:2 concentration ratio observed in ambient air) with OH radicals and NO₃ radicals in the presence of NO_x.

the 1M6NN + 1M4NN peak) and the nighttime Redlands profile was similar to the NO₃ radical reaction profile (note the dominance of the 2M4NN peak). The same was also the case for 1-NN and 2-NN, with the OH radical reaction and daytime Redlands 1-NN/2-NN concentration ratio both being ~1:1 and the NO₃ radical reaction and nighttime concentration ratio both being ~2:1. Because OH radicals are formed mainly from photolysis (e.g., photolysis of O₃) and are highly reactive, their nighttime concentrations are extremely low. Conversely, as noted above, the NO₃ radicals (formed from O₃ and NO₂) are present in significant levels only at night, because NO₃ photolyzes rapidly during the daytime.

It was previously postulated that the MNNs observed in Glendora, CA in August, 1986 during an intense photochemical air pollution episode were formed from the daytime OH radical-initiated reaction of gas-phase methylnaphthalenes (Zielinska *et al.* 1989b). In contrast to Redlands, at Glendora (Zielinska *et al.*, 1989b; Arey and Zielinska, 1989) the daytime and nighttime MNN profiles were very similar and little evidence for the occurrence of nighttime NO₃ radical chemistry was found, perhaps reflecting the fact that at Glendora, a more urban location, fresh emissions of NO would rapidly react with any NO₃ radicals formed. Presumably the MNNs measured during the nighttime at Glendora represented "carry-over" from the MNNs formed by daytime OH radical-initiated reactions. However, at Redlands further downwind in the South Coast Air Basin, the NN and MNN isomer distributions observed on October nights were consistent with the formation of NNs and MNNs from gas-phase NO₃ radical-initiated reactions of naphthalene (Atkinson and Arey, 1994) and the methylnaphthalenes (Zielinska *et al.*, 1989; Gupta, 1995; Gupta *et al.*, 1996). Additionally for one day/night sample pair at Redlands, the nighttime NN and MNN concentrations were nearly a factor of 10 higher than the daytime concentrations, convincing proof of a nighttime formation mechanism. It should be noted that 3-nitrobiphenyl, formed only from daytime OH radical-initiated reaction of biphenyl (see below) had similar daytime and nighttime concentrations, ruling out any possibility of meteorology or transport producing the elevated NN and MNN concentrations at night. Finally, based on their measured rate constants for reaction with the NO₃ radical, the resulting nitro-PAH yields (Atkinson and Arey, 1994) and the ≥300-fold higher concentrations of naphthalene and 1- and 2-methylnaphthalene than their nitrated derivatives (Gupta, 1995), this nighttime formation pathway for the NNs and MNNs at Redlands is plausible.

Biphenyl reacts with the OH radical forming an ~5% yield of 3-nitrobiphenyl (Atkinson and Arey, 1994; see Table 1). Because biphenyl does not react with the NO₃ radical, and direct emission sources would be expected to contain mainly 2- and 4-nitrobiphenyl, 3-nitrobiphenyl can be used as a marker for OH radical chemistry (Atkinson and Arey, 1994). Thus, we have identified a number of nitro-PAH, both gas-phase and particle-associated, which can serve as "markers" for OH radical reactions (1-NN/2-NN = 1, 1M6NN+1M4NN, 3-nitrobiphenyl, 2-nitropyrene) and NO₃ radical reactions (1-NN/2-NN = 2, 2M4NN, 2-nitrofluoranthene). Taking advantage of the higher abundances of the 2-ring PAH, we proposed to measure the volatile PAH naphthalene, 1- and 2-methylnaphthalene and biphenyl and, to serve as sensitive indicators of the presence of NO₃ radicals or OH radicals, their nitro-derivatives formed from atmospheric reactions: 1- and 2-nitronaphthalene, the 14 methylnitronaphthalenes and 3-nitrobiphenyl at source and receptor sites during SCOS97. Generally, twelve-hr daytime and nighttime samples were collected during the intensive sampling days of the SCOS97-NARSTO study, with simultaneous sampling occurring at "source" and "receptor" sites. The source site at Azusa was sampled during all six intensive sampling periods, as was the downwind receptor site of Riverside. The Banning site in the far eastern end of the air basin was sampled during 5 of the 6 intensive periods and the downtown source site at Los Angeles North Main Street was sampled during the August 22-23, 1997 sampling intensive.

In addition to our interest in nitro-PAH as markers of radical reactions occurring in an airmass, the formation of products from the gas-phase reactions of PAH, by both OH radical-initiated and NO₃ radical-initiated reactions, has important implications for potential health risks to populations downwind of urban areas. The PAH emitted from combustion sources such as vehicle exhaust are modified by these atmospheric radical reactions producing a large array of products, including, for example, dialdehydes and hydroxynitro-PAH, as well as nitro-PAH (Sasaki *et al.*, 1997a). Nitro-PAH are well known as potent bacterial mutagens (Tokiwa and Ohnishi, 1986; Rosenkranz, 1996; Gupta *et al.*, 1996; Enya *et al.*, 1997) and recent work has identified them as human cell mutagens as well (Busby *et al.*, 1994; Sasaki *et al.*, 1997b; 1999; Phousongphouang *et al.*, 2000). The health implications of other PAH reaction products are largely unknown at this time.

Relative Importance of Atmospheric Nitro-PAH Formation vs Direct Emissions

It is now generally recognized that when considering the nitrofluoranthenes and nitropyrenes (often the most abundant particle-associated nitro-PAH species in ambient atmospheres), atmospheric formation often dominates over direct emissions (Atkinson *et al.*, 1988; Zielinska *et al.*, 1989; Ciccioli *et al.*, 1995; 1996; Arey, 1998; Dimashki *et al.*, 2000; Fielberg *et al.*, 2001). As seen in Figure 1, the atmospherically formed 2-nitrofluoranthene (2-NF) is more abundant than 1-nitropyrene (1-NP) whose presence is attributed to direct emissions such as diesel exhaust.

Table 2 contains ambient data for selected PAH and their nitro-derivatives from a 12-hr daytime and a 12-hr nighttime sample collected in Glendora, CA on Aug. 13-14, 1986. For comparison, also shown are the results from analysis of diesel exhaust samples from a Cummins L10 engine running on a pre-1993 diesel fuel and on a reformulated diesel fuel (Truex *et al.*, 1998). Generally the relative abundance of the PAH present in ambient air is consistent with what is seen in the diesel exhaust, with the two-ring PAH more abundant (naphthalene the most abundant PAH, followed by 2-methylnaphthalene then 1-methylnaphthalene) than the 4-ring PAH, fluoranthene and pyrene. Only electrophilic nitration products of PAH were seen in the diesel exhaust and 1-nitropyrene was the most abundant nitro-PAH measured. Surprisingly, 2-nitronaphthalene was more abundant than 1-nitronaphthalene. No methylnitronaphthalenes were detected in the diesel exhaust, nor were any nitrobiphenyl isomers.

It may be concluded that for nitro-PAH formed solely by atmospheric radical-initiated reactions, i.e., 2-nitrofluoranthene, 2-nitropyrene and 3-nitrobiphenyl (see Table 1), their presence in ambient air can be attributed to in-situ atmospheric formation. In the recent diesel toxicity study (see Table 2), no methylnitronaphthalenes (MNNs) were seen and the only previously reported MNN identified in diesel exhaust was 2M1NN (Paputa-Peck *et al.*, 1983), the expected major electrophilic nitration product of 2-methylnaphthalene (Table 1). Therefore, the presence in ambient air of MNN isomers, in particular those isomers least likely to be formed by electrophilic nitration is indicative of the occurrence of atmospheric formation mechanisms. Furthermore, as shown in Figure 2, different MNN isomer distribution patterns are indicative of OH radical-initiated vs NO₃ radical-initiated formation mechanisms.

The judgement on whether the nitronaphthalenes in ambient air are atmospherically formed or present from direct emissions is made difficult because the radical-initiated reaction products include both isomers, and both 1- and 2-nitronaphthalene have been observed in diesel exhaust (Table 2). The highly elevated concentrations of nitronaphthalenes in comparison with 1-nitropyrene in the Glendora samples (Table 2) is strongly suggestive of atmospheric reactions forming the nitronaphthalenes, but direct emissions may have contributed to the NNs present. In addition, degradation of the NNs may influence the ratio of 1NN/2NN, for example, 1-nitronaphthalene has been reported to photolyze more rapidly than 2-nitronaphthalene (Fielberg *et al.*, 1999). Therefore, the nitronaphthalene data must be interpreted in conjunction with the MNN data and data for 3-nitrobiphenyl (an indicator of OH radical-initiated reactions).

Table 2. PAH and nitro-PAH measured in ambient air samples taken in Glendora, CA and in diesel exhaust samples.

Compound	Glendora (ng/m ³) ^a		Diesel Exhaust (µg/Bhp-hr) ^b	
	8/13/86 Daytime	8/13-14/86 Nighttime	pre-1993 Fuel	Reformulated Fuel
Naphthalene	2400	4800	1852	1500
1-Methylnaphthalene	160	390	1055	480
2-Methylnaphthalene	320	730	1617	899
Biphenyl	95	170	403	293
Fluoranthene	4.0	6.2	72	54
Pyrene	2.5	5.5	107	98
1-Nitronaphthalene	2.3	2.6	0.52	0.66
2-Nitronaphthalene	1.8	1.6	1.51	1.37
Methylnitronaphthalenes	Not quantified	Not quantified	None detected	None detected
3-Nitrobiphenyl	1.2	0.4	None detected	None detected
2-Nitrofluoranthene	0.2	0.5	None detected	None detected
1-Nitropyrene	0.03	0.04	1.95	1.64
2-Nitropyrene	0.02	0.05	None detected	None detected

^aAdapted from Arey *et al.* 1989 and Atkinson *et al.*, 1988.

^bMicrograms per Brake horse power hour (adapted from Truex *et al.*, 1998, Tables 31 and 35).

Experimental Methods

Ambient air sampling for selected PAH and nitro-PAH was conducted in Azusa, Banning, Central Los Angeles (LA North Main Street), and Riverside, CA during the SCOS97-NARSTO Intensive Sampling Periods in the summer and early autumn of 1997. Tenax TA cartridges were used to sample the volatile PAH and polyurethane foam (PUF) plugs in modified high-volume (Hi-vol) samplers were used to sample the semi-volatile nitro-PAH. To be able to detect differences in day/night atmospheric formation routes for the nitro-PAH, each 24-hr sampling period consisted of a 12-hr daytime and a 12-hr nighttime sample collection. The sampling began at 0600 hrs and at the end of the 12-hr sampling period the Hi-vol samplers were shut down for 10 minutes to accommodate a change of the sampling media.

PAH sampling on Tenax and analysis

The Tenax cartridges, sized to fit into the inlet of the gas chromatograph, were precleaned by heating overnight $>250\text{ }^{\circ}\text{C}$ with a constant flow of helium through the tubes. After conditioning and while still warm, the adsorbent tubes were capped with brass nuts, caps (Swagelock) and Teflon ferrules. The tubes were placed in cleaned glass jars which were sealed with a metal lid lined with Teflon film and were stored in a freezer prior to and after sampling. Two Tenax cartridges were placed in series, with analysis of the second tube serving to verify that no breakthrough occurred. At each site the Tenax sampling equipment consisted of a diaphragm pump (Thomas), a mass flow controller (Tylan General), and a mass flow control unit. The Tenax tubes were mounted at a height of 1.8 - 2.0 m (at Azusa the sampling equipment was located on the roof of the South Coast Air Quality Management District monitoring station) and the sampling was conducted at a flow rate of 100 mL min^{-1} .

Naphthalene, 1-methylnaphthalene (1MN), 2-methylnaphthalene (2MN) and biphenyl were identified and quantified by gas chromatography/mass spectrometry (GC/MS) using a Hewlett-Packard 5890 GC interfaced to a 5970 Mass Selective Detector. Deuterated internal standards in $2\text{ }\mu\text{L}$ of methanol were spiked on the Tenax cartridges in the following amounts (nanograms): naphthalene- d_8 (83.7), 1MN- d_{10} (20.9) and biphenyl- d_{10} (10.0). Each cartridge was thermally desorbed at $275\text{ }^{\circ}\text{C}$ onto the head of a 60 m DB-5MS capillary column (0.25 mm i.d.; $0.25\text{ }\mu\text{m}$ film thickness) equipped with a 1 meter DB-1701 pre-column with a $1\text{ }\mu\text{m}$ film thickness which allowed good focusing of the PAH with a column temperature of $30\text{ }^{\circ}\text{C}$ and a desorption time of 10 min.

By analyzing standard solutions of varying concentrations, response factors were calculated for the molecular ions of naphthalene (m/z 128), 1MN and 2MN (m/z 142), using the molecular ion of naphthalene- d_8 (m/z 136) and 1MN- d_{10} (m/z 164), respectively. For the molecular ion of biphenyl (m/z 154), the molecular ion of biphenyl- d_{10} (m/z 164) was used as an internal standard. These response factors were used for the GC/MS selected ion monitoring (GC/MS-SIM) quantification of the PAH. The deuterated internal standards eluted just prior to (not completely baseline resolved) the corresponding PAH.

Nitro-PAH sampling and analysis

Sampling for the semi-volatile two-ring nitro-PAH was conducted concurrently with the Tenax cartridge sampling. Two modified Hi-vol samplers with PUF plugs placed downstream from a filter in the modified sampling apparatus were located at each sampling site (with the exception of Intensive #3 when only one Hi-vol was available at the Riverside and LA North Main Street sites). The Hi-vol samplers were modified by the addition of a "New York Style" cylindrical aluminum cartridge for PUF adsorbent plugs used in sampling vapor-phase organic compounds. The samplers employed a standard 8 in. x 10 in. Teflon-impregnated glass fiber (TIGF) filter upstream of the PUF adsorbent and were operated at a relatively high flow rate of ~20 scfm (560 liters per minute). The aluminum cartridges were lined with glass sleeves, which contain the PUF adsorbent and were sealed with Teflon-jacketed gaskets. The samplers were housed in an anodized aluminum shelter and covered with an aluminum weather shield for outdoor service.

The TIGF filters (Pallflex T60A20) were precleaned by a 20-hour Soxhlet extraction with dichloromethane (DCM, Fisher Optima) followed by drying (60 °C, 3 hr) and a 20-hour Soxhlet extraction with methanol (Fisher Optima). The precut PUF plugs were obtained from S&W Plastics (Riverside, CA). Each sampling train consisted of a front PUF plug (3-in. dia. x 3.5-in. long) and a back PUF plug (3-in. dia. x 1-in. long). The purpose of the back plug was to check for breakthrough from the main front plug. The PUF plugs were pre-cleaned by extraction in a large Soxhlet apparatus, first with DCM (20 hr) followed by drying (60 °C, 3 hr) and then by Soxhlet extraction with methanol (20 hr) and drying. Prior to use the PUF plugs were wrapped in aluminum foil and placed in Ziploc bags inside glass canning jars and stored in the dark at -20 °C. After sampling the PUF plugs were returned to the freezer for storage until extraction.

The PUF plug samples were spiked with a deuterated internal standard solution of 1-nitronaphthalene- d_7 and 2-nitrofluorene- d_8 and then Soxhlet extracted for 16 hours with DCM. The extracts were prepared for GC/MS-SIM analysis of the semi-volatile nitro-PAH by fractionating the extract by high performance liquid chromatography (HPLC). The HPLC fractionation was performed on a Hewlett-Packard Model 1050VWD system equipped with a Spherisorb semi-preparative 5- μm Silica column and the fractions were collected by an ISCO Foxy 200 fraction collector. The mobile phase program employed, at a flow rate of 3 mL min^{-1} , was as follows: 100% n-hexane for 10 min, followed by a 5-minute linear gradient to 95% n-hexane and 5% DCM. The solvent was programmed over the next 25 minutes to 100% DCM where it was held for 10 min, then programmed to 100% acetonitrile over 10 min, held isocratic for an additional 10 min, and then programmed back to the initial conditions. The PAH fraction was collected from 10-19 min and the nitro-PAH fraction was collected from 24-37 min. Prior to GC/MS analysis, the HPLC fractions were concentrated by rotary evaporation under vacuum to 2 mL volume, and then by evaporation at atmospheric pressure and room temperature to 50 μL volume.

The nitro-PAH fraction was then analyzed by GC/MS-SIM with the system described above, except that a Hewlett-Packard 7673A Autosampler was utilized for sample injection in the splitless mode. For analysis of the nitro-PAH, the molecular ions and several characteristic fragment ions were monitored as follows: nitronaphthalenes (m/z 173, 127, 115), 1-nitro-naphthalene- d_7 (m/z 180, 134, 122), methylnitronaphthalenes (m/z 187, 170, 141, 139, 115) [Arey and Zielinska, 1989], and 3-nitrobiphenyl (m/z 199, 153, 152, 151). The methylnitronaphthalenes and 3-nitrobiphenyl were quantified on the basis of their molecular ion peaks relative to the m/z 180 molecular ion peak of 1-nitronaphthalene- d_7 . The nitronaphthalenes were quantified using the $[\text{M-NO}_2]^+$ fragment ion peak at m/z 127 and the corresponding deuterated fragment from the internal standard at m/z 134. The quantifications of 1- and 2-nitronaphthalene and 3-nitrobiphenyl were based on response factors calculated relative to 1-nitronaphthalene- d_7 from the analysis of standard solutions of varying concentrations. The methylnitronaphthalenes were quantified based on a response factor calculated for 2-methyl-1-nitronaphthalene, which may introduce a small bias depending upon the intensity of the molecular ion peak in the individual methylnitronaphthalene isomers.

Results

The ambient concentrations of the two-ring PAH: naphthalene (NAPH) 1-methylnaphthalene (1MN), 2-methylnaphthalene and biphenyl (BPh) and the semi-volatile two-ring nitro-PAH: 1-nitronaphthalene (1NN), 2-nitronaphthalene (2NN), 3-nitrobiphenyl (3NBPh) and the x-methyl-y-nitronaphthalenes (xMyNN) are given for the six sampling intensives in Tables 3-12, respectively. Note that not all of the 14 isomers of the MNNs were observed and quantified.

The PAH were collected quantitatively on the Tenax. Breakthrough of naphthalene, the most volatile of the PAH measured, was <1%. Some breakthrough of the nitronaphthalenes onto the backup PUF plug was observed, with the average % nitro-PAH on the backup PUF plug being 22% for 1NN, 20% for 2NN and 3% for 3NBPh. The values given in Tables 3-12 represent the sum of the nitro-PAH measured on the two PUF plugs.

Naphthalene was the most abundant PAH measured, with concentrations generally highest at the source sites of Azusa and LA North Main Street and lower concentrations in Riverside and Banning. The maximum naphthalene mixing ratio observed was nearly 1200 ng m⁻³ in a morning sample taken at LA North Main Street. At Azusa naphthalene reached 800 ng m⁻³ at night. Thus, the highest concentrations observed during this study were significantly less than those observed in Glendora in 1986 when the naphthalene reached 6000 ng m⁻³ (Arey *et al.*, 1989). As observed previously in Glendora, CA (Arey *et al.*, 1989) the ratio of 2MN/1MN was approximately two. The nitro-PAH were about two orders of magnitude lower in concentration than their precursor PAH.

Unlike previous studies (Atkinson *et al.*, 1988; Arey *et al.*, 1989), the measured 1-nitronaphthalene concentration was generally less than that of the 2-nitronaphthalene. It is not known whether this reflects differences in the emissions of the nitronaphthalenes, or perhaps lower formation rates than previously and, therefore, more influence of the more rapid photolysis of 1-nitronaphthalene vs 2-nitronaphthalene on the ambient ratio observed.

Table 3. PAH and nitro-PAH ambient concentrations (ng/m³) at Azusa, Riverside and Banning: Intensive #1; July 14, 1997

Intensive #1											
07/14/1997											
	BPh	3NBPh	NAPH	1NN	2NN						
Azusa											
07/14/97 (0600-1800)	196	0.23	a	0.20	0.34						
Riverside											
07/14/97 (0600-1800)	121	0.05	362	0.04	0.09						
Banning											
07/14/97 (0600-1800)	25	0.02	53	0.01	0.04						
	2MN	1MN	2M8NN	2M4+3NN	1M2NN	2M5NN	1M5NN	1M6+4NN	2M7NN	2M6NN	1M3+7NN
Azusa											
07/14/97 (0600-1800)	a	a	0.02	0.06	0.01	0.03	0.17	0.25	0.06	0.05	0.10
Riverside											
07/14/97 (0600-1800)	112	54	0.005	0.02	0.002	0.01	0.04	0.07	0.02	0.02	0.04
Banning											
07/14/97 (0600-1800)	23	13	0.004	0.01	0.002	0.004	0.01	0.03	0.01	0.01	0.01

^aNo data. problem with internal standard calibration.

Table. 4 PAH and nitro-PAH ambient concentrations (ng/m³) at Azusa, Riverside and Banning: Intensive #2; August 4-6, 1997

**Intensive #2
08/04-06/1997**

AZUSA	BPh	3NBPh	NAPH	1NN	2NN
8/4/97 (0600-1800)	78	0.17	450	0.11	0.21
8/4-5/97 (1800-0600)	65	0.06	820	0.30	0.39
8/5/97 (0600-1800)	84	0.16	482	0.11	0.18
8/5-6/97 (1800-0600)	45	0.04	837	0.18	0.26
8/6/97 (0600-1800)	82	0.12	494	0.06	0.12
RIVERSIDE	BPh	3NBPh	NAPH	1NN	2NN
8/4/97 (0600-1800)	18	0.09	183	0.11	0.34
8/4-5/97 (1800-0600)	15	0.02	364	0.21	0.23
8/5/97 (0600-1800)	28	0.10	357	0.10	0.23
8/5-6/97 (1800-0600)	18	0.02	429	0.14	0.17
8/6/97 (0600-1800)	27	0.05	336	0.02	0.04
BANNING	BPh	3NBPh	NAPH	1NN	2NN
8/4/97 (0600-1800)	a	0.01	a	0.01	0.02
8/4-5/97 (1800-0600)	12	0.02	151	0.15	0.14
8/5/97 (0600-1800)	27	b	55	b	b
8/5-6/97 (1800-0600)	14	0.02	175	0.05	0.07
8/6/97 (0600-1800)	6.4	0.004	19	0.003	0.004

^aTenax sample lost in wind dust.

^bSample lost.

Table 5. 1- and 2-Methylnaphthalene and methylnitronaphthalene concentrations (ng/m³) at Azusa, Riverside and Banning: Intensive #2; August 2-4, 1997

AZUSA	2MN	1MN	2M8NN	2M4+3NN	1M2NN	2M5NN	1M5NN	1M6+4NN	2M7NN	2M6NN	1M3+7NN
8/4/97 Day (0600-1800)	126	69	0.01	0.05	0.01	0.03	0.12	0.18	0.01	0.05	0.08
8/4-5/97 Night (1800-0600)	350	177	0.05	0.15	0.02	0.08	0.23	0.37	0.08	0.08	0.13
8/5/97 Day (0600-1800)	135	75	0.01	0.04	0.01	0.03	0.11	0.16	0.04	0.05	0.07
8/5-6/97 Night (1800-0600)	349	176	0.03	0.09	n.d.	0.01	0.17	0.25	0.06	0.06	0.10
8/6/97 Day (0600-1800)	144	84	0.01	0.03	n.d.	0.03	0.09	0.13	0.04	0.04	0.06
RIVERSIDE	2MN	1MN	2M8NN	2M4+3NN	1M2NN	2M5NN	1M5NN	1M6+4NN	2M7NN	2M6NN	1M3+7NN
8/4/97 Day (0600-1800)	45	24	0.02	0.06	0.01	0.02	0.11	0.21	0.07	0.06	0.11
8/4-5/97 Night (1800-0600)	136	69	0.03	0.13	0.01	0.05	0.17	0.22	0.06	0.05	0.08
8/5/97 Day (0600-1800)	92	47	0.01	0.03	n.d.	n.d.	0.10	0.15	0.05	0.04	0.07
8/5-6/97 Night (1800-0600)	162	82	0.03	0.09	0.01	0.04	0.13	0.18	0.03	0.04	0.06
8/6/97 Day (0600-1800)	85	45	0.01	0.01	0.002	0.006	0.02	0.04	0.02	0.02	0.03
BANNING	2MN	1MN	2M8NN	2M4+3NN	1M2NN	2M5NN	1M5NN	1M6+4NN	2M7NN	2M6NN	1M3+7NN
8/4/97 Day (0600-1800)	a	a	0.002	0.004	0.001	0.003	0.01	0.02	0.004	0.005	0.01
8/4-5/97 Night (1800-0600)	60	32	0.02	0.07	0.004	0.03	0.08	0.10	0.02	0.03	0.03
8/5/97 Day (0600-1800)	19	10	a	a	a	a	a	a	a	a	a
8/5-6/97 Night (1800-0600)	58	31	0.01	0.03	0.002	0.01	0.04	0.06	0.01	0.02	0.02
8/6/97 Day (0600-1800)	6.1	3.4	0.001	0.002	n.d.	n.d.	0.002	0.004	n.d.	0.002	n.d.

^aSample lost. n.d. = not detected

Table 6. PAH and nitro-PAH ambient concentrations (ng/m³) at Azusa, LA N. Main, Riverside and Banning: Intensive #3; August 22-23, 1997

**Intensive #3
08/22-23/1997**

AZUSA	BPh	3NBPh	NAPH	1NN	2NN
08/22/97 (0600-1200)	36	0.24	672	0.33	0.35
08/22/97 (1200-1800)	40	0.84	326	1.25	1.24
08/22-23/97 (1800-0600)	45	0.24	767	0.83	0.88
08/23/97 (0600-1200)	36	0.35	600	0.49	0.74
08/23/97 (1200-1800)	15	0.18	118	0.33	0.39
LA N. MAIN	BPh	3NBPh	NAPH	1NN	2NN
08/22/97 (0600-1200)	142	1.02	1165	0.35	0.35
08/22/97 (1200-1800)	60	0.54	463	0.57	0.56
08/22-23/97 (1800-0600)	148	0.16	985	0.34	0.28
08/23/97 (0600-1200)	78	0.34	868	0.32	0.35
08/23/97 (1200-1800)	30	0.19	270	0.55	0.52
RIVERSIDE	BPh	3NBPh	NAPH	1NN	2NN
08/22/97 (0600-1800)	25	0.16	373	0.20	0.25
08/22-23/97 (1800-0600)	24	0.11	486	0.41	0.39
08/23/97 (0600-1800)	27	0.19	251	0.12	0.35
BANNING	BPh	3NBPh	NAPH	1NN	2NN
08/22/97 (0600-1800)	20	0.04	70	0.03	0.10
08/22-23/97 (1800-0600)	18	0.05	199	0.48	0.53
08/23/97 (0600-1800)	15	0.03	31	0.03	0.06

Table 7. 1- and 2-Methylnaphthalene and methylnitronaphthalene concentrations (ng/m³) at Azusa, LA N. Main, Riverside and Banning: Intensive #3; August 22-23, 1997

AZUSA	2MN	1MN	2M8NN	2M4+3NN	1M2NN	2M5NN	1M5NN	1M6+4NN	2M7NN	2M6NN	1M3+7NN
08/22/97 (0600-1200)	230	125	n.d.	0.05	n.d.	n.d.	0.14	0.26	0.09	0.05	0.12
08/22/97 (1200-1800)	97	54	0.09	0.20	n.d.	n.d.	0.48	0.69	0.15	0.13	0.26
08/22-23/97 (1800-0600)	325	170	0.12	0.29	n.d.	n.d.	0.52	0.81	0.18	0.16	0.27
08/23/97 (0600-1200)	185	99	n.d.	0.09	n.d.	n.d.	0.24	0.42	0.11	0.09	0.19
08/23/97 (1200-1800)	25	14	n.d.	0.03	n.d.	n.d.	0.13	0.19	0.04	0.03	0.09
LA N. MAIN	2MN	1MN	2M8NN	2M4+3NN	1M2NN	2M5NN	1M5NN	1M6+4NN	2M7NN	2M6NN	1M3+7NN
08/22/97 (0600-1200)	371	196	n.d.	n.d.	n.d.	n.d.	0.12	0.20	n.d.	n.d.	0.11
08/22/97 (1200-1800)	143	73	n.d.	0.1	n.d.	n.d.	0.29	0.41	0.09	n.d.	0.16
08/22-23/97 (1800-0600)	386	193	0.05	0.08	n.d.	n.d.	0.16	0.24	0.07	0.05	0.08
08/23/97 (0600-1200)	279	145	n.d.	n.d.	n.d.	n.d.	0.13	0.21	n.d.	n.d.	n.d.
08/23/97 (1200-1800)	71	37	n.d.	n.d.	n.d.	n.d.	0.23	0.31	n.d.	n.d.	n.d.

n.d. = not detected

Table 7. 1- and 2-Methylnaphthalene and methylnitronaphthalene concentrations (ng/m³) at Azusa, LA N. Main, Riverside and Banning: Intensive #3; August 22-23, 1997 (continued)

RIVERSIDE	2MN	1MN	2M8NN	2M4+3NN	1M2NN	2M5NN	1M5NN	1M6+4NN	2M7NN	2M6NN	1M3+7NN
08/22/97 (0600-1800)	104	55	0.005	0.01	n.d.	0.006	0.09	0.15	0.01	0.01	0.02
08/22-23/97 (1800-0600)	162	83	0.06	0.24	n.d.	0.01	0.17	0.24	0.08	0.07	0.13
08/23/97 (0600-1800)	56	29	n.d.	0.06	n.d.	0.01	0.09	0.19	0.08	0.07	0.12
BANNING	2MN	1MN	2M8NN	2M4+3NN	1M2NN	2M5NN	1M5NN	1M6+4NN	2M7NN	2M6NN	1M3+7NN
08/22/97 (0600-1800)	25	13	n.d.	0.02	n.d.	n.d.	0.02	0.06	0.02	0.03	0.04
08/22-23/97 (1800-0600)	60	33	0.05	0.30	n.d.	n.d.	0.13	0.21	0.09	0.07	0.12
08/23/97 (0600-1800)	11	6	0.01	0.03	n.d.	0.01	0.02	0.05	0.01	0.01	0.03

n.d. = not detected

Table 8. PAH and nitro-PAH ambient concentrations (ng/m³) at Azusa Riverside and Banning: Intensive #4; September 4-6, 1997

Intensive #4					
09/04-06/1997					
AZUSA	BPh	3NBPh	NAPH	1NN	2NN
09/04/97 (0600-1800) ^a	34	0.10	387	0.07	0.12
09/04-05/97 (1800-0600) ^b	26	0.03	544	0.11	0.16
09/05/97 (0600-1800)	30	0.09	412	0.08	0.17
09/05-06/97 (1800-0600)	84	0.05	643	0.17	0.21
09/06/97 (0600-1800)	55	0.15	372	0.08	0.17
RIVERSIDE	BPh	3NBPh	NAPH	1NN	2NN
09/04-05/97 (1800-0600)	14	0.03	315	0.20	0.23
09/05/97 (0600-1800)	22	0.04	225	0.03	0.08
09/05-06/97 (1800-0600)	16	0.02	400	0.16	0.19
09/06/97 (0600-1800)	22	0.05	261	0.01	0.04
BANNING	BPh	3NBPh	NAPH	1NN	2NN
09/05/97 (0600-1800)	8.5	0.01	49	0.01	0.03
09/05-06/97 (1800-0600)	9.6	0.01	150	0.09	0.10
09/06/97 (0600-1800)	4.7	0.01	32	0.02	0.03

^aThe Tenax sample from which the PAH were quantified was collected from 0600-2000 hr.

^bThe Tenax sample from which the PAH were quantified was collected from 2000-0600 hr.

Table 9. 1- and 2-Methylnaphthalene and methylnitronaphthalene concentrations (ng/m³) at Azusa, Riverside and Banning: Intensive #4; September 4-6, 1997

AZUSA	2MN	1MN	2M8NN	2M4+3NN	1M2NN	2M5NN	1M5NN	1M6+4NN	2M7NN	2M6NN	1M3+7NN
09/04/97 (0600-1800) ^a	132	69	0.01	0.02	0.004	0.01	0.07	0.10	0.01	0.03	0.04
09/04-05/97 (1800-0600) ^b	232	120	0.03	0.07	0.01	0.04	0.13	0.23	0.03	0.05	0.08
09/05/97 (0600-1800)	117	63	0.01	0.04	0.006	0.02	0.10	0.16	0.04	0.04	0.07
09/05-06/97 (1800-0600)	264	131	0.03	0.07	0.02	0.03	0.14	0.20	0.05	0.05	0.06
09/06/97 (0600-1800)	113	61	0.01	0.03	0.006	0.02	0.09	0.13	0.04	0.03	0.05
RIVERSIDE	2MN	1MN	2M8NN	2M4+3NN	1M2NN	2M5NN	1M5NN	1M6+4NN	2M7NN	2M6NN	1M3+7NN
09/04-05/97 (1800-0600)	116	59	0.04	0.14	0.01	0.06	0.16	0.21	0.06	0.06	0.08
09/05/97 (0600-1800)	63	33	0.01	0.02	0.003	0.01	0.04	0.06	0.02	0.02	0.03
09/05-06/97 (1800-0600)	155	77	0.02	0.06	0.01	0.03	0.12	0.19	0.04	0.03	0.06
09/06/97 (0600-1800)	65	34	0.003	0.01	n.d.	0.01	0.02	0.04	0.02	0.01	0.02
BANNING	2MN	1MN	2M8NN	2M4+3NN	1M2NN	2M5NN	1M5NN	1M6+4NN	2M7NN	2M6NN	1M3+7NN
09/05/97 (0600-1800)	19	11	0.004	0.01	0.001	0.006	0.02	0.03	0.01	0.01	0.01
09/05-06/97 (1800-0600)	63	34	0.01	0.06	0.003	0.02	0.05	0.07	0.02	0.02	0.03
09/06/97 (0600-1800)	14	8	0.003	0.01	0.001	0.004	0.01	0.02	0.01	0.01	0.01

^aThe Tenax sample from which the PAH were quantified was collected from 0600-2000 hr. n.d. = not detected.

^bThe Tenax sample from which the PAH were quantified was collected from 2000-0600 hr.

Table 10: PAH and nitro-PAH ambient concentrations (ng/m³) at Azusa and Riverside: Intensive #5; September 28-29, 1997

**Intensive #5
09/28-29/1997**

AZUSA	BPh	3NBPh	NAPH	1NN	2NN							
09/28/97 (0600-1800)	24	0.08	272	0.10	0.18							
09/28-29/97 (1800-0600)	20	0.04	420	0.17	0.24							
09/29/97 (0600-1800)	30	0.08	476	0.09	0.17							
RIVERSIDE	BPh	3NBPh	NAPH	1NN	2NN							
09/28-29/97 (1800-0600)	13	0.02	283	0.17	0.20							
09/29/97 (0600-1800)	15	0.04	213	0.03	0.08							
AZUSA	2MN	1MN	2M8NN	2M4+3NN	1M2NN	2M5NN	1M5NN	1M6+4NN	2M7NN	2M6NN	1M3+7NN	
09/28/97 (0600-1800)	80	41	0.01	0.04	0.006	0.02	0.10	0.16	0.05	0.04	0.07	
09/28-29/97 (1800-0600)	174	87	0.04	0.12	0.02	0.06	0.17	0.26	0.08	0.06	0.11	
09/29/97 (0600-1800)	152	79	0.02	0.05	0.01	0.03	0.12	0.19	0.06	0.05	0.08	
RIVERSIDE	2MN	1MN	2M8NN	2M4+3NN	1M2NN	2M5NN	1M5NN	1M6+4NN	2M7NN	2M6NN	1M3+7NN	
09/28-29/97 (1800-0600)	114	55	0.03	0.13	0.01	0.04	0.12	0.15	0.05	0.04	0.06	
09/29/97 (0600-1800)	62	31	0.01	0.02	0.01	0.02	0.05	0.09	0.03	0.03	0.04	

Table 11. PAH and nitro-PAH ambient concentrations (ng/m³) at Azusa, Riverside and Banning: Intensive #6; October 3-4, 1997

Intensive #6					
10/03-04/1997					
AZUSA	BPh	3NBPh	NAPH	1NN	2NN
10/03/97 (0600-1800)	33	0.07	255	0.08	0.12
10/03-04/97 (1800-0600)	40	0.04	460	0.15	0.19
10/04/97 (0600-1800)	27	0.10	259	0.07	0.14
RIVERSIDE	BPh	3NBPh	NAPH	1NN	2NN
10/03/97 (0600-1800)	15	0.03	133	0.05	0.11
10/03-04/97 (1800-0600)	8.0	0.02	222	0.13	0.15
10/04/97 (0600-1800)	18	0.06	163	0.05	0.13
BANNING	BPh	3NBPh	NAPH	1NN	2NN
10/03/97 (0600-1800)	8.7	0.01	96	0.02	0.05
10/03-04/97 (1800-0600)	18	0.01	201	0.12	0.11
10/04/97 (0600-1800)	7.7	0.03	105	0.03	0.06

Table 12. 1- and 2-Methylnaphthalene and methylnitronaphthalene concentrations (ng/m³) at Azusa, Riverside and Banning: Intensive #6; October 3-4, 1997

AZUSA	2MN	1MN	2M8NN	2M4+3NN	1M2NN	2M5NN	1M5NN	1M6+4NN	2M7NN	2M6NN	1M3+7NN
10/03/97 (0600-1800)	78	41	0.01	0.03	0.004	0.01	0.07	0.10	0.03	0.02	0.04
10/03-04/97 (1800-0600)	175	86	0.03	0.09	0.01	0.04	0.12	0.17	0.05	0.04	0.07
10/04/97 (0600-1800)	68	36	0.01	0.03	0.003	0.01	0.07	0.11	0.03	0.03	0.05
RIVERSIDE	2MN	1MN	2M8NN	2M4+3NN	1M2NN	2M5NN	1M5NN	1M6+4NN	2M7NN	2M6NN	1M3+7NN
10/03/97 (0600-1800)	36	19	0.01	0.02	0.003	0.01	0.05	0.08	0.02	0.02	0.03
10/03-04/97 (1800-0600)	88	43	0.02	0.07	0.01	0.03	0.10	0.14	0.04	0.03	0.05
10/04/97 (0600-1800)	41	21	0.01	0.02	n.d.	0.01	0.05	0.10	0.02	0.02	0.04
BANNING	2MN	1MN	2M8NN	2M4+3NN	1M2NN	2M5NN	1M5NN	1M6+4NN	2M7NN	2M6NN	1M3+7NN
10/03/97 (0600-1800)	30	15	0.003	0.01	0.001	0.005	0.02	0.04	0.01	0.01	0.01
10/03-04/97 (1800-0600)	72	36	0.02	0.05	0.004	0.02	0.06	0.08	0.03	0.02	0.03
10/04/97 (0600-1800)	31	16	0.01	0.02	0.003	0.006	0.02	0.04	0.01	0.01	0.03

n.d. = not detected

Discussion

As noted in the Introduction certain nitro-PAH and nitro-PAH ratios can be utilized as "markers" for OH radical and NO₃ radical chemistry. Tables 13-15 give marker ratios for the 12-hr daytime and 12-hr nighttime samples collected during Intensives #2, #4, #5 and #6 at Azusa, Riverside and Banning, respectively. (Because only a single daytime sample was collected in July, the data from Intensive #1 is not discussed further.) Table 16 gives marker ratios for Intensive #3, during which 6-hr morning and 6-hr afternoon samples were collected at Azusa and LA North Main Street.

As seen from Table 1 the only source of 3-nitrobiphenyl in the atmosphere is expected to be its formation from OH radical-initiated reaction of gas-phase biphenyl. As noted, biphenyl reacts only with the OH radical (*i.e.*, photolysis, reaction with O₃, and reaction with NO₃ are all expected to be insignificant loss processes for gas-phase biphenyl) and forms an ~5% yield of 3-nitrobiphenyl. There are no known emission sources of 3-nitrobiphenyl, which is not an expected electrophilic nitration product of biphenyl. Thus the formation of 3-nitrobiphenyl is an indicator that OH radical chemistry has occurred.

At heavily traffic-impacted source sites such as Azusa and LA North Main Street, biphenyl emissions will be fairly constant throughout the day and night with some enhanced emissions during peak traffic times. The biphenyl mixing ratios will vary, largely under the control of meteorology (Lu and Turco, 1994; 1995; 1996). For example, the increased mixing heights generally present during the afternoons in the South Coast Air Basin will result in lower afternoon mixing ratios, while emissions of biphenyl into the shallow marine layer which forms at night will produce higher nighttime biphenyl mixing ratios. The ratio of 3NBPh/BPh is an indicator of OH radical chemistry and because of varying dilution (mixing heights) is a better indicator than the 3-nitrobiphenyl concentration alone. Since 3-nitrobiphenyl is being produced during the daytime, higher 3NBPh/BPh ratios would be expected during the day, reflecting OH radical chemistry. This ratio is indeed consistently higher during the day with the average 3NBPh/BPh ratios at Azusa being 0.26% daytime and 0.11% nighttime (Table 13) and at Riverside: 0.29% daytime and 0.15% nighttime (Table 14). Banning is a downwind receptor site and the mixing ratios of the PAH and nitro-PAH measured at Banning are clearly influenced by dilution during transport as well as by chemical formation and destruction reactions (*i.e.*, more uncertainty exists in a ratio of lower ambient concentrations), however, the highest value measured for the 3NBPh/BPh ratio at Banning, 0.34%, was a daytime value (Table 15). Isolating the afternoon hours when the OH radical concentration is expected to peak (note that solar noon would be 1300 hrs. PDT), a value of the ratio of 3NBPh/BPh as high as 2.1% was observed at Azusa for the 1200-1800 hr. sample on August 22, 1997 (Table 16)

2-Nitronaphthalene is produced both by the OH radical-initiated reaction of naphthalene (yield ~1%) and from the nighttime NO₃ radical-initiated reaction (yield 11%). If nighttime NO₃ radical reaction is producing 2-NN, the ratio of the 2-NN formation (2NN/NAPH) to the 3NBPh formation (3NBPh/BPh) would increase (the ratio is labeled "NN formation" on the tables). An additional marker for NO₃ radical chemistry is the ratio of 1M6NN (more correctly 1M6NN + 1M4NN, since they co-elute in our analyses) to 2M4NN (the co-eluting 2M3NN is very minor). As may be seen from Figure 1, in the chamber NO₃

Table 13. Ratios indicative of OH radical vs NO₃ radical nitro-PAH formation mechanisms at Azusa

Sampling Dates & Times	% Reaction 3NBPh/BPh x 100		% Reaction 2NN/NAPH x 100		"NN formation" (2NN/NAPH)/(3NBPh/BPh)		"NO ₃ /OH" 2M4NN/1M6NN	
	Day	Night	Day	Night	Day	Night	Day	Night
8/4/97 (0600-1800)	0.22		0.05		0.21		0.28	
8/4-5/97 (1800-0600)		0.10		0.05		0.48		0.41
8/5/97 (0600-1800)	0.19		0.04		0.20		0.25	
8/5-6/97 (1800-0600)		0.08		0.03		0.40		0.36
8/6/97 (0600-1800)	0.15		0.02		0.17		0.23	
09/04/97 (0600-1800)	0.29		0.03		0.11		0.20	
09/04-05/97 (1800-0600)		0.11		0.03		0.26		0.30
09/05/97 (0600-1800)	0.30		0.04		0.14		0.25	
09/05-06/97 (1800-0600)		0.06		0.03		0.54		0.35
09/06/97 (0600-1800)	0.26		0.05		0.17		0.23	
09/28/97 (0600-1800)	0.33		0.07		0.20		0.23	
09/28-29/97 (1800-0600)		0.20		0.06		0.29		0.46
09/29/97 (0600-1800)	0.27		0.04		0.14		0.26	
10/03/97 (0600-1800)	0.21		0.05		0.22		0.30	
10/03-04/97 (1800-0600)		0.09		0.04		0.46		0.53
10/04/97 (0600-1800)	0.37		0.05		0.15		0.23	
Average	0.26	0.11	0.04	0.04	0.17	0.40	0.25	0.40

Table 14. Ratios indicative of OH radical vs NO₃ radical nitro-PAH formation mechanisms at Riverside

Sampling Dates & Times	% Reaction 3NBPh/BPh x 100		% Reaction 2NN/NAPH x 100		"NN formation" (2NN/NAPH)/(3NBPh/BPh)		"NO ₃ /OH" 2M4NN/1M6NN	
	Day	Night	Day	Night	Day	Night	Day	Night
8/4/97 (0600-1800)	0.52		0.19		0.36		0.29	
8/4-5/97 (1800-0600)		0.14		0.06		0.44		0.59
8/5/97 (0600-1800)	0.35		0.07		0.19		0.18	
8/5-6/97 (1800-0600)		0.12		0.04		0.32		0.50
8/6/97 (0600-1800)	0.18		0.01		0.07		0.24	
09/04-05/97 (1800-0600)		0.18		0.07		0.40		0.67
09/05/97 (0600-1800)	0.18		0.03		0.19		0.29	
09/05-06/97 (1800-0600)		0.10		0.05		0.47		0.30
09/06/97 (0600-1800)	0.23		0.02		0.07		0.18	
09/28-29/97 (1800-0600)		0.16		0.07		0.44		0.88
09/29/97 (0600-1800)	0.28		0.04		0.14		0.21	
10/03/97 (0600-1800)	0.19		0.08		0.43		0.27	
10/03-04/97 (1800-0600)		0.20		0.07		0.34		0.50
10/04/97 (0600-1800)	0.36		0.08		0.22		0.16	
Average	0.29	0.15	0.06	0.06	0.21	0.40	0.23	0.57

Table 15. Ratios indicative of OH radical vs NO₃ radical nitro-PAH formation mechanisms at Banning

Sampling Dates & Times	% Reaction 3NBPh/BPh x 100		% Reaction 2NN/NAPH x 100		"NN formation" (2NN/NAPH)/(3NBPh/BPh)		"NO ₃ /OH" 2M4NN/1M6NN	
	Day	Night	Day	Night	Day	Night	Day	Night
8/4-5/97 (1800-0600)		0.18		0.09		0.52		0.76
8/5-6/97 (1800-0600)		0.13		0.04		0.31		0.48
8/6/97 (0600-1800)	0.06		0.02		0.34		0.53	
09/05/97 (0600-1800)	0.10		0.06		0.62		0.28	
09/05-06/97 (1800-0600)		0.09		0.07		0.78		0.86
09/06/97 (0600-1800)	0.21		0.09		0.44		0.67	
10/03/97 (0600-1800)	0.16		0.05		0.33		0.20	
10/03-04/97 (1800-0600)		0.08		0.05		0.65		0.60
10/04/97 (0600-1800)	0.34		0.06		0.17		0.54	
Average	0.17	0.12	0.06	0.06	0.38	0.56	0.44	0.67

Table 16. Ratios indicative of OH radical vs NO₃ radical nitro-PAH formation mechanisms during Intensive #3: August 22-23, 1997

	% Reaction 3NBPh/BPh x 100			% Reaction 2NN/NAPH x 100			"NN formation" (2NN/NAPH)/(3NBPh/BPh)		
	Morning	Afternoon	Night	Morning	Afternoon	Night	Morning	Afternoon	Night
AZUSA									
08/22/97 (0600-1200)	0.66			0.05			0.08		
08/22/97 (1200-1800)		2.11			0.38			0.18	
08/22-23/97 (1800-0600)			0.53			0.11			0.21
08/23/97 (0600-1200)	1.00			0.12			0.12		
08/23/97 (1200-1800)		1.21			0.33			0.28	
LA N. MAIN									
08/22/97 (0600-1200)	0.72			0.03			0.04		
08/22/97 (1200-1800)		0.92			0.12			0.13	
08/22-23/97 (1800-0600)			0.11			0.03			0.27
08/23/97 (0600-1200)	0.44			0.04			0.09		
08/23/97 (1200-1800)		0.63			0.19			0.31	

	% Reaction 3NBPh/BPh x 100		% Reaction 2NN/NAPH x 100		"NN formation" (2NN/NAPH)/(3NBPh/BPh)				
	Day	Night	Day	Night	Day	Night			
RIVERSIDE									
08/22/97 (0600-1800)	0.63		0.07		0.11				
08/22-23/97 (1800-0600)		0.47		0.08		0.17			
08/23/97 (0600-1800)	0.71		0.14		0.20				
BANNING									
08/22/97 (0600-1800)	0.18		0.14		0.78				
08/22-23/97 (1800-0600)		0.26		0.27		1.02			
08/23/97 (0600-1800)	0.21		0.21		1.00				

radical reaction of 2MN and 1MN (with the MNs present in the same ratio as in ambient air), 2M4NN is the major product formed and the 2M4NN peak is several-fold greater than the 1M6NN peak. In contrast, in the OH radical reaction of 2MN and 1MN, the product peak corresponding to 1M6NN + 1M4NN is the largest (and several-fold higher than 2M4NN). Thus the ratio 2M4NN/1M6NN should be a sensitive marker for NO₃ radical chemistry (the ratio is labeled "NO₃/OH" on the tables). Since the NO₃ radical reactions occur only at night, the nighttime ratio "NO₃/OH" should increase if the air mass has been exposed to NO₃ radicals. This ratio was indeed higher at night and increased as the sampling site was further downwind of central Los Angeles. The average "NO₃/OH" ratios were: at Azusa: 0.25 daytime and 0.40 nighttime (Table 13); at Riverside: 0.23 daytime and 0.57 nighttime (Table 14); and at Banning: 0.44 daytime and 0.67 nighttime (Table 15). Consistent with NO₃ radical reactions also producing 2NN, the highest values of "NO₃/OH" generally correspond with high values for the ratio "NN formation" as well. Thus the ambient nitro-PAH profiles observed during the SCOS97-NARSTO study indicate that NO₃ radicals were present.

**PROJECT ELEMENT NO. 2:
CRC DATA REVIEW PANEL FOR ATMOSPHERIC CHEMISTRY OF VOCs**

Dr. Roger Atkinson was an invited member of this data review panel, with the focus of the first review concerning the atmospheric chemistry of alkenes (a subsequent review has dealt with aromatic hydrocarbons). The panel was comprised of seven scientists (Drs. J. G. Calvert, R. Atkinson, J. A. Kerr, S. Madronich, G. K. Moortgat, T. J. Wallington, and G. Yarwood), with each of the panel members being initially responsible for specific aspects of the atmospheric chemistry of alkenes and selected reaction products. Dr. Atkinson's primary responsibility was to review and evaluate the kinetics of the gas-phase reactions of alkenes with OH radicals, NO₃ radicals, O₃, O(³P) atoms and NO₂, and the kinetics of the reactions of selected first-generation products with OH radicals, NO₃ radicals and O₃. Because the reactions of alkenes with O(³P) atoms and NO₂ are of minor importance in the atmosphere (but may be important under certain conditions in laboratory experiments), the kinetics of these reactions were not dealt with at the same level of detail as for the OH radical, NO₃ radical and O₃ reactions with alkenes and selected first-generation products.

The review of the atmospheric chemistry of alkenes was successfully completed, and this review has been published by Oxford University Press ("The Mechanisms of Atmospheric Oxidation of the Alkenes", by J. G. Calvert, R. Atkinson, J. A. Kerr, S. Madronich, G. K. Moortgat, T. J. Wallington, and G. Yarwood, pp. 552, 2000). The title page and table of contents of the published book are attached in Appendix A.

**PROJECT ELEMENT NO. 3:
CRITICAL REVIEW PAPERS ON ATMOSPHERIC CHEMISTRY AND CHEMICAL KINETIC
MECHANISMS FOR
THE 1998 NARSTO OZONE ASSESSMENT**

Dr. Roger Atkinson and Dr. Marcia C. Dodge were invited to prepare critical review chapters on the atmospheric chemistry of VOCs and NO_x (Roger Atkinson) and the current status of chemical mechanism development and “smog chamber“ facilities and data-base (Marcia C. Dodge). After an initial NARSTO meeting in Denver, CO, in October 1996, draft chapters were prepared by Drs. Atkinson and Dodge and presentations concerning the chapter contents made by Drs. Atkinson and Dodge at the 1997 NARSTO Science Symposium in West Palm Beach, FL, in November 1997. Completed chapters were submitted for internal review by NARSTO scientists in early 1998, and revised manuscripts were submitted in mid-1998 for publication in a special issue of *Atmospheric Environment*. This special issue of *Atmospheric Environment* (Special Issue: The NARSTO Ozone Assessment – Critical Reviews) was published in 2000 (volume 34, Nos. 12-14), and the reviews of Drs. Atkinson (“Atmospheric Chemistry of VOCs and NO_x”, *Atmos. Environ.*, **34**, 2063-2101, 2000) and Dodge (“Chemical Oxidant Mechanisms for Air Quality Modeling: Critical Review”, *Atmos. Environ.*, **34**, 2103-2130, 2000) are attached in Appendix B and Appendix C, respectively. The review of Dr. Atkinson was the second most-requested article from *Atmospheric Environment* during the time-period March-September 2000 from the ScienceDirect web site, with 608 requests.

Summary and Conclusions

This contract had three project elements dealing with aspects of the atmospheric chemistry of volatile or semi-volatile organic compounds.

Investigation of Ambient NO₃ Radical Levels in the Los Angeles Air Basin During the SCOS97-NARSTO Study

Ambient mixing ratios of naphthalene, 1- and 2-methylnaphthalene, biphenyl, 1- and 2-nitronaphthalene, 3-nitrobiphenyl and several methylnitronaphthalenes were measured at source and receptor sites in the Los Angeles Air Basin. Naphthalene was the most abundant volatile PAH, reaching concentrations of 1200 ng m⁻³. The nitro-PAH were approximately two orders of magnitude lower in concentration than their precursor PAH, but clearly showed evidence that both OH radical-initiated and NO₃ radical-initiated nitro-PAH formation mechanisms were operating during the SCOS97-NARSTO intensive sampling days.

Monitoring two-ring PAH and their nitro-derivatives allowed ratios to be measured which served as markers for OH radical-initiated chemistry and nighttime NO₃ radical-initiated chemistry. Utilizing these ratios it was demonstrated that nitro-PAH were produced by NO₃ radical chemistry during the SCOS07-NARSTO ozone study, with downwind receptor sites showing more evidence for air masses processed by NO₃ radical chemistry.

CRC Data Review Panel for Atmospheric Chemistry of VOCs

Roger Atkinson participated in the Coordinating Research Council, Inc., Review Panel for the Atmospheric Chemistry of Hydrocarbons (RPACH). This data review panel was set up to carry out detailed reviews and evaluations of the literature data concerning the atmospheric chemistry of the various classes of VOCs of importance in photochemical air pollution, with this review and evaluation being concerned with the atmospheric chemistry of alkenes. This review and evaluation of alkene chemistry has been published by Oxford University Press, "The Mechanisms of Atmospheric Oxidation of the Alkenes", J. G. Calvert, R. Atkinson, J. A. Kerr, S. Madronich, G. K. Moortgat, T. J. Wallington, and G. Yarwood, 2000.

Critical Review Papers on Atmospheric Chemistry and Chemical Kinetic Mechanisms for the 1998 NARSTO Ozone Assessment

Two review chapters for the North American Research in Tropospheric Ozone (NARSTO) assessment document were prepared. The two critical review papers dealt with the following topics: the current status of the kinetics, mechanisms and products of the atmospheric reactions of VOCs and NO_x (Roger Atkinson); and the "smog" chamber data-base and current programs in this area and the status of chemical mechanisms for air quality simulation models (Marcia C. Dodge, sub-contractor). These NARSTO review papers have been published in a common volume in Atmospheric Environment, volume 34, issues 12-14, pp. 2063-2101 and pp. 2103-2130, respectively (2000).

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Glossary and Abbreviations for PAH and nitro-PAH

GC/MS	Gas chromatography-mass spectrometry
HPLC	High Performance Liquid Chromatography
k_a	Rate constant for reaction pathway A
MNNs	Methylnitronaphthalenes
nitro-PAH	Nitrated polycyclic aromatic hydrocarbons
nm	Nanometer (10^{-9} m)
NNs	Nitronaphthalenes
NO_2	Nitrogen dioxide
NO	Nitric oxide
NO_x	Oxides of nitrogen
NO_3 radical	Nitrate radical
N_2O_5	Dinitrogen pentaoxide
O_2	Molecular oxygen
O_3	Ozone
OH	Hydroxyl radical
PAH	Polycyclic Aromatic Hydrocarbons

Abbreviations for PAH and nitro-PAH

1-NN	1-nitronaphthalene
2-NN	2-nitronaphthalene
1M2NN	1-methyl-2-nitronaphthalene
1M3NN	1-methyl-3-nitronaphthalene
1M4NN	1-methyl-4-nitronaphthalene
1M5NN	1-methyl-5-nitronaphthalene
1M6NN	1-methyl-6-nitronaphthalene
1M7NN	1-methyl-7-nitronaphthalene
1M8NN	1-methyl-8-nitronaphthalene
2M1NN	2-methyl-1-nitronaphthalene
2M3NN	2-methyl-3-nitronaphthalene
2M4NN	2-methyl-4-nitronaphthalene
2M5NN	2-methyl-5-nitronaphthalene
2M6NN	2-methyl-6-nitronaphthalene
2M7NN	2-methyl-7-nitronaphthalene
2M8NN	2-methyl-8-nitronaphthalene
3NBPh	3-nitrobiphenyl
2NF	2-nitrofluoranthene
1NP	1-nitropyrene
2NP	2-nitropyrene
NAPH	naphthalene
BPh	biphenyl
1MN	1-methylnaphthalene
2MN	2-methylnaphthalene
FL	fluoranthene
PY	pyrene