

# Spatial and Temporal Distribution of Atmospheric Nitric Acid and Particulate Nitrate Concentrations in the Los Angeles Area

Paul A. Solomon,<sup>†</sup> Lynn G. Salmon, Theresa Fall, and Glen R. Cass\*

Environmental Engineering Science Department and Environmental Quality Laboratory, California Institute of Technology, Pasadena, California 91125

■ A 1-year atmospheric measurement program was conducted throughout the South Coast Air Basin in the greater Los Angeles area during 1986 to determine the long-term average concentration patterns of gaseous  $\text{HNO}_3$  and aerosol nitrates. Upwind of the air basin at San Nicolas Island,  $\text{HNO}_3$  levels are very low, averaging  $0.3 \mu\text{g m}^{-3}$  (0.1 ppb) over the year 1986. Annual average  $\text{HNO}_3$  concentrations ranged from  $3.1 \mu\text{g m}^{-3}$  (1.2 ppb) near the Southern California coast to  $6.9 \mu\text{g m}^{-3}$  (2.7 ppb) at an inland site in the San Gabriel Mountains. At most monitoring stations, a majority of the inorganic nitrate ( $\text{HNO}_3$  plus its reaction product, aerosol nitrate) was in the aerosol phase. Conversion of  $\text{HNO}_3$  to aerosol nitrates was most pronounced at Rubidoux, near Riverside, CA, where on the average 94% of the inorganic nitrate was found in the aerosol phase, and where fine particle nitrate concentrations exceeded  $109 \mu\text{g m}^{-3}$  during the peak 24-h period examined.

## Introduction

Atmospheric oxides of nitrogen, including nitric acid vapor, are major contributors to the dry deposition flux of strong acids to the earth's surface in Southern California (1, 2). Nitric acid vapor also may react with ammonia to produce visibility-reducing fine aerosol nitrates and with sea salt or soil dust particles to produce coarse particle nitrates (3-11). While a number of short-term studies have been conducted in the Los Angeles area to measure ambient  $\text{HNO}_3$  levels (6, 12-17), data reported to date are for the summer season. No long-term record exists from which to examine seasonal trends and annual average values of gas-phase  $\text{HNO}_3$ .

This paper describes the results of a 1-year field experiment in which  $\text{HNO}_3$  plus fine and coarse particle nitrates were measured throughout the Los Angeles area. Measurements made in the urban area will be compared to observations at a remote background site on an offshore island and to data taken at a high elevation receptor site in the mountains downwind of the metropolitan area. Spatial and temporal trends in pollutant concentrations will be discussed in light of the transport patterns and atmospheric processes that govern the  $\text{HNO}_3$ /aerosol nitrate system.

## Experimental Section

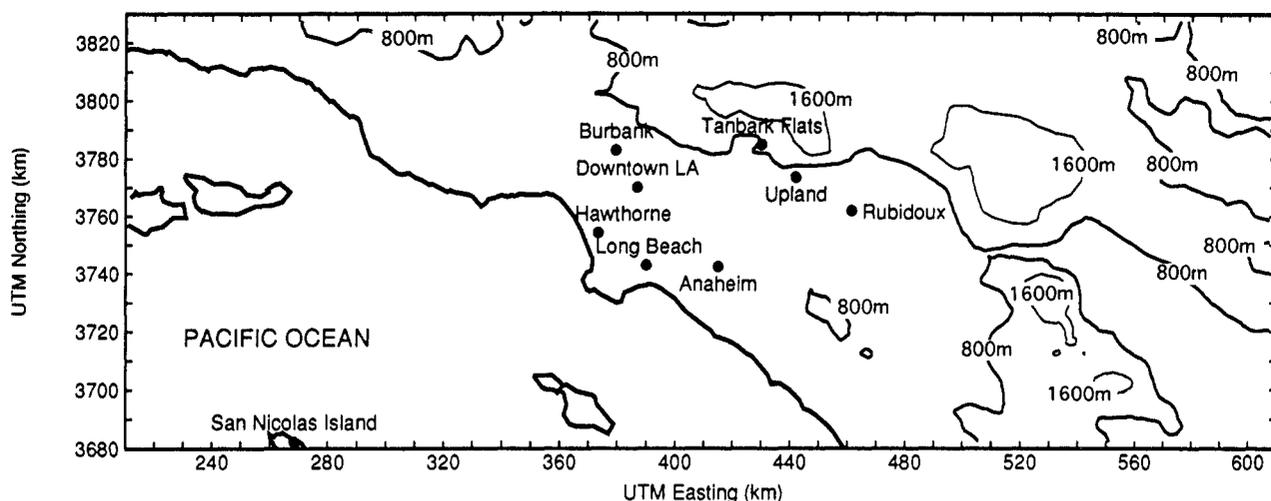
**Sampling Sites.** During calendar year 1986, a monitoring network designed to measure gas-phase  $\text{HNO}_3$  and atmospheric particulate matter was operated at nine sampling sites located throughout the South Coast Air Basin (SOCAB), which surrounds the Los Angeles area as shown in Figure 1. All sites except Tanbark Flats and San Nicolas Island were co-located with present South Coast Air Quality Management District (SCAQMD) continuous air-monitoring stations. A description of the SCAQMD sites is given by the U.S. Environmental Protection Agency (18, 19).

The Tanbark Flats site was located in the mountains north of San Dimas, in the Angeles National Forest, at an elevation of approximately 870 m. This site was chosen to determine the concentration of acidic pollutants present in the national forests to the north of Los Angeles, and because air quality modeling calculations suggest that nitric acid concentrations may be different at higher elevations than are observed near the ground within the urban area (20). The ninth site was located at the meteorological station on San Nicolas Island (SNI), approximately 140 km southwest of the Los Angeles coastline. This remote, off-shore location was chosen to determine background pollutant levels present in the marine environment upwind of Los Angeles. At four of the sites (Burbank, downtown Los Angeles, Long Beach, and Upland), the sampling systems were placed on the roofs of one- or two-story buildings. At the other sites the systems were placed with inlets 2-3 m above ground level. All sites except Tanbark Flats were below an elevation of 400 m above sea level.

**Sampler Design and Sample Collection.** The nitric acid, fine-particle nitrate, and total particle nitrate measurement system employed during this study is illustrated schematically in Figure 2. Nitric acid concentrations were determined by two methods: (1) the denuder difference method (DD) (6, 15, 16, 21-24) and (2) the tandem filter method (TF) (6, 15, 16, 24, 25).

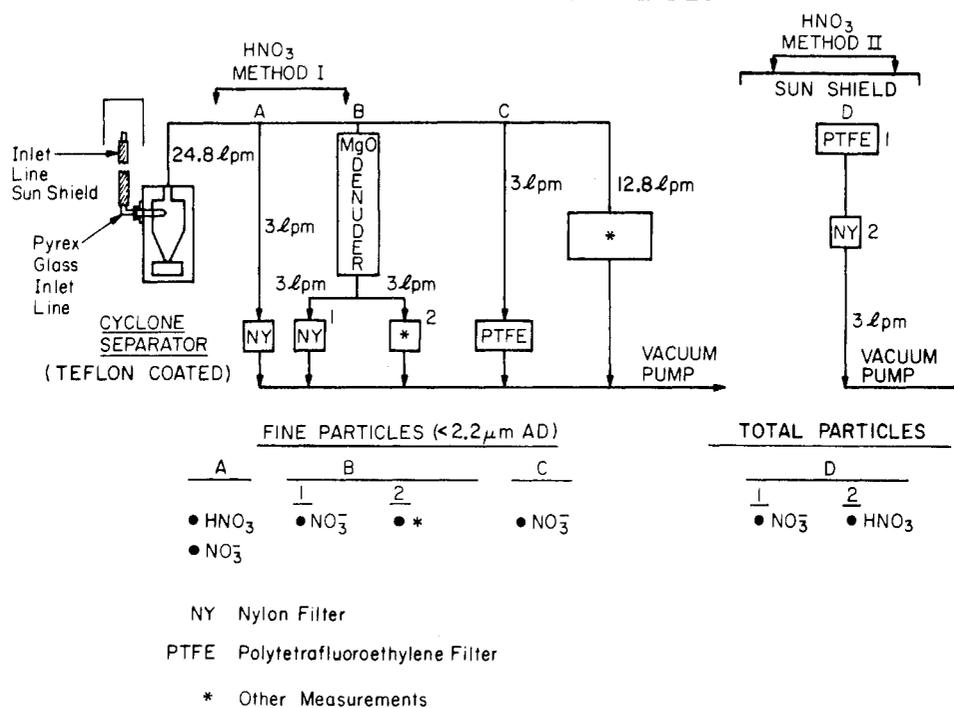
The denuder difference apparatus deployed during this study is illustrated at the left side of Figure 2, and its design has been described elsewhere (16). In this series of experiments, ambient air was drawn at a rate of  $24.8 \text{ L min}^{-1}$  through a Teflon-coated AIHL-design cyclone separator (26) and a 1-L Teflon-coated manifold. Coarse particles with aerodynamic diameter greater than  $2.2 \mu\text{m}$  were removed by the cyclone. The airflow then was divided between several parallel filter holders. One filter holder (sampling line A, Figure 2) held a nylon filter ( $1.0\text{-}\mu\text{m}$  pore size, 47-mm diameter; Membrana Corp. and Gelman Sciences) that acts as a sink for both fine-particle nitrate and nitric acid vapor. A second nylon filter (sampling line B1) was used as a backup filter beneath an MgO-coated diffusion denuder that was designed to remove gas-phase  $\text{HNO}_3$ . The denuder design was similar to that described by Forrest et al. (21), Stevens et al. (22), and Shaw et al. (23) except that 10 MgO-coated tubes 30 cm in length and 4 mm in interior diameter were used, and the denuder housing was made of Teflon plus shatter-resistant plastic instead of glass. Thus, nylon filter B1 collected only fine-particle nitrate. Nitric acid was determined by the difference between the nitrate ion concentration measured on these two nylon filters (A - B1). The denuder difference systems used were tested at the Nitrogen Species Methods Comparison Study conducted at Claremont, CA, where it was demonstrated that results for  $\text{HNO}_3$  obtained by these samplers are representative of denuder difference samplers as a class and that  $\text{HNO}_3$  concentrations measured by a pool of denuder difference samplers (including the present samplers) were comparable to  $\text{HNO}_3$  concentrations measured by Fourier transform

<sup>†</sup>Present address: Atmospheric and Radiation Sciences Group, Pacific Gas and Electric Co., San Ramon, CA 94583.



**Figure 1.** Los Angeles area monitoring network. All sites are at an elevation within 400 m of sea level except Tanbark Flats, which is at an elevation of 870 m in the San Gabriel Mountains.

### EXPERIMENTAL DESIGN



**Figure 2.** Sampler and sampling protocol.

infrared spectroscopy (FTIR) (15, 16).

In the tandem filter method (sampling line D, Figure 2), nitric acid was collected on a nylon backup filter (D2) after particles (including aerosol nitrate) were removed by the use of an open-face, inert poly(tetrafluoroethylene) (PTFE) prefilter (D1) (2.0-μm pore size, 47-mm diameter, Membrana Corp.). This method has been shown to produce HNO<sub>3</sub> measurements that are artificially high due to the decomposition of aerosol NH<sub>4</sub>NO<sub>3</sub> collected on the PTFE prefilter, which releases additional HNO<sub>3</sub> that is collected on the nylon backup filter (12, 15, 16, 25, 27, 28). A large Teflon-coated plate was positioned above the open face filter holders to protect them from particle sedimentation and from direct heating by the sun.

Aerosol nitrate concentrations were measured in several size ranges using the system just described. Fine-particle nitrate collected on nylon filter B1 (Figure 2), located below the diffusion denuder, provided a measure of fine-particle nitrate concentrations that did not suffer from major positive or negative artifact problems (15, 16, 26, 27,

28). In order to gauge the magnitude of the aerosol nitrate loss from Teflon filters, fine-particle nitrate concentrations also were measured from samples collected on a PTFE filter (sampling line C, Figure 2) located downstream of the cyclone separator. Total particulate nitrate concentrations (fine-particle nitrate plus coarse-particle nitrate) were determined from the nitrate ion collected on the open-face Teflon filter that preceded the nylon filter in the tandem filter sampler (filter D1, Figure 2). Total particulate nitrate concentrations reported here were corrected, to the extent possible, for the previously mentioned loss of aerosol nitrate from filter D1. It was assumed that volatilization losses from the PTFE filter (D1) were due mainly to decomposition of NH<sub>4</sub>NO<sub>3</sub>, which is found mostly in the fine particles (25, 27, 28). An estimate of fine-aerosol nitrate volatilization from PTFE filters was obtained during each sampling event based on the difference between fine-particle nitrate concentrations measured on filters B1 and C on that day at that site. That estimate of volatilized aerosol nitrate was then added to

**Table I. Summary of Field Blanks and Relative Analytical Precision for NO<sub>3</sub><sup>-</sup>**

filter location	filter type	analytical precision, <sup>c</sup> %	filter blank, <sup>d</sup> µg/filter (lot no., source)
cyclone-denuder system <sup>a</sup>	nylon	4.2	0.53 ± 0.17 (K07025E, Gelman Sciences) 1.57 ± 0.54 (84800, Gelman Sciences)
	PTFE (0.5 µm)	5.7	<0.6 (4215 and 2326, Membrana, Corp.)
tandem filter unit <sup>b</sup>	nylon	4.2	0.63 ± 0.33 (4222, Membrana Corp.) 2.38 ± 0.55 (84800, Gelman Sciences)
	PTFE (2.0 µm)	5.0	2.5 ± 0.8 (092, Membrana Corp.)

<sup>a</sup>Filters located following a 1-m acid-washed glass inlet line, a Teflon-coated cyclone separator and manifold, and/or a MgO diffusion denuder. <sup>b</sup>Open-face PTFE prefilter with the nylon filter located about 2.5 cm farther downstream. <sup>c</sup>Based on duplicate analysis of many split filters (*n* typically >50). <sup>d</sup>The detection limit was defined as two times the standard deviation of the filter blank when the filter blank was greater than the instrument detection limit for NO<sub>3</sub><sup>-</sup> of 0.6 µg/filter.

the total particle nitrate value measured on PTFE filter D1 on that day at that site to arrive at a corrected total particulate nitrate concentration. Coarse-particle nitrate concentrations were obtained by taking the difference between corrected total particulate nitrate concentrations and the fine-particle nitrate concentrations measured on the nylon filter located below the diffusion denuder in Figure 2.

Samples were collected over 24-h sampling periods from midnight to midnight every six days during the calendar year 1986. The first sample was collected on January 2 to coordinate this measurement network with the National Air Surveillance Network (NASN) high-volume sampling schedule. Filters were installed the day prior to, and removed the day after, sample collection. Flow rates were monitored before and after sampling with a rotameter which had been factory calibrated with an accuracy of 1% full scale. Rotameter calibration remained unchanged during the study. The flow rate checks were done to ensure that filter holders were not leaking and to determine that filter clogging had not occurred. As an additional precaution to help ensure the integrity of the samples after collection, the filters were stored in self-sealing, plastic Petri dishes, sealed with Teflon tape, and refrigerated until sample analysis.

Blank values and analytical precisions were determined for the measurements of nitrate ion on the nylon and PTFE filters employed in this study. Both filter types were obtained from two sources: Membrana Corporation, no longer in business, and Gelman Sciences, Inc. Three lots of each filter type also were employed throughout the year. From analysis of laboratory blanks, no difference between lots was observed for NO<sub>3</sub><sup>-</sup> measured on PTFE filter blanks; however, a considerable difference (almost 2 µg/filter) was observed between lots for NO<sub>3</sub><sup>-</sup> measured on nylon filter blanks. Dynamic field blanks were obtained during the year in an amount equal to one-tenth of the actual number of ambient samples taken, and results from the analysis of those field blank samples are given in Table I.

As can be seen in Table I, PTFE filters, which were better protected from the atmosphere (i.e., buried within the cyclone-denuder system, left side of Figure 2), had low filter blank values. In contrast, the open-face PTFE prefilter had a much higher dynamic blank value. This may have been due to wind-blown dust particles which settled on the filter during times when the filters were loaded onto the sampler but the sampler was not running. This was in spite of the fact that the open-face filters were protected from fallout by the sunshield shown in Figure

2. This observation reinforced our decision to install and remove the filters as close to the sampling event as possible on the days preceding and following sampling.

**Sample Analysis.** Nylon filters were leached by lightly shaking each of them in 20 mL of a CO<sub>3</sub><sup>2-</sup>/HCO<sub>3</sub><sup>-</sup> buffer (eluent for the ion chromatograph) for 3 h or more at 10 °C. Poly(tetrafluoroethylene) filters first were wetted with 0.2–0.25 mL of EtOH (100%), to reduce the hydrophobic nature of this material (29), and then leached in the same manner as the nylon filters. The leachate was analyzed by ion chromatography for nitrate ion. Concentrations were determined relative to standards of known concentrations prepared daily from more concentrated master standards. The standards were prepared new at least every 30 days from ACS analytical reagent-grade NaNO<sub>3</sub>.

Approximately 10% of the filters were cut in half, and each half was analyzed separately (i.e., a duplicate measurement to obtain the analytical precision of the measurement method). The coefficient of variation obtained for all nylon filters analyzed in this manner was about 4.2%, and for PTFE fine and total particle filters was 5.0 and 5.7%, respectively. The accuracy of our NO<sub>3</sub><sup>-</sup> measurements from nylon and PTFE filters was determined during a previous study (15, 16). In that study, the California Air Resources Board supplied blind spiked nylon and PTFE filters containing quantities of nitrate ion known only to the filter supplier. Results from that quality assurance study indicated an accuracy of better than ±10% for NO<sub>3</sub><sup>-</sup> determination over the concentration range tested, which corresponded to the equivalent of 2–46 µg m<sup>-3</sup> at the air flow rates used in the present study. The detection limit for NO<sub>3</sub><sup>-</sup> measured on the nylon filters employed in this study ranged from 0.3 to 1.1 µg/filter. This detection limit was based on 2 times the standard deviation of the average filter blanks and depended on the filter lot employed (see Table I). PTFE filter blanks ranged from less than the instrument detection limit for NO<sub>3</sub><sup>-</sup> (0.6 µg/filter), for PTFE filters located in the cyclone-denuder system, to 2.5 µg/filter for PTFE filters located in the open-face filter holders.

### Results

**Comparison of Nitric Acid and Aerosol Nitrate Measurement Methods.** Nitric acid was measured by the denuder difference method (DD; HNO<sub>3</sub> method I, Figure 2) and by the tandem filter method (TF; HNO<sub>3</sub> method II, Figure 2), both of which are described in the Experimental Section of this paper. Linear regression analysis was employed to compare these two techniques for the measurement of ambient HNO<sub>3</sub> concentrations.

The resulting regression equation, based on nearly all sampling periods, at all sites was  $TF = 1.48(DD) + 1.09 \mu\text{g m}^{-3}$ ;  $r = 0.932$ ;  $n = 514$ . This result indicated that, on the average, the tandem filter method yielded  $\text{HNO}_3$  concentrations that were greater than those obtained by the denuder difference method. Although there appeared to be a systematic error, the two methods were highly correlated, with a correlation coefficient ( $r$ ) of 0.932. These results were consistent with those obtained during the 1985 Claremont Nitrogen Species Methods Comparison Study (15, 16). In that field experiment, the exact methods and equipment employed in the present study were compared to measurements of ambient  $\text{HNO}_3$  concentrations made by Fourier transform infrared spectroscopy (FTIR). The conclusion from the 1985 Claremont study was that the denuder difference method yielded reasonably unbiased estimates of atmospheric  $\text{HNO}_3$ , while the tandem filter method overestimated atmospheric  $\text{HNO}_3$  concentrations. This positive  $\text{HNO}_3$  artifact, observed when using the tandem filter method, has been studied previously (25, 27, 28, 30) and is believed to be due to release of  $\text{HNO}_3$  from the decomposition of  $\text{NH}_4\text{NO}_3$  aerosol previously collected on the PTFE prefilter with the subsequent collection of that  $\text{HNO}_3$  on the nylon backup filter.

Fine-particle nitrate was measured in two ways: (1) by collection on a nylon filter located downstream of a cyclone separator that was followed by a diffusion denuder (the cyclone-denuder method, CD; see sampling line B1, Figure 2) and (2) by collection on a PTFE filter located downstream of a cyclone separator (the cyclone only method, CY; see sampling line C, Figure 2). Linear regression analysis also was used to compare these two methods for measuring ambient fine-particle nitrate concentrations (method CD versus CY). The resulting regression equation, based on nearly all sampling periods, at all sites was  $CY = 0.82(CD) - 1.98 \mu\text{g m}^{-3}$ ;  $r = 0.920$ ;  $n = 526$ . This result indicated that, on the average, the use of PTFE filters as a collection substrate leads to an underestimation of atmospheric fine-particle nitrate concentrations, again most probably due to vaporization of  $\text{NH}_4\text{NO}_3$  collected on the PTFE filter. Although there is a systematic difference, the results obtained by these two methods are highly correlated.

On an absolute basis, when comparing the denuder difference and the tandem filter methods for  $\text{HNO}_3$  measurement, the amount of nitrate observed as an increase in  $\text{HNO}_3$  due to aerosol nitrate loss from the PTFE prefilter D1 in Figure 2 was  $3.1 \mu\text{g m}^{-3}$  averaged over all samples taken. The loss of fine particle  $\text{NO}_3^-$  from the PTFE fine-particle filter (sampling line C, Figure 2) relative to fine-particle  $\text{NO}_3^-$  measured by the cyclone-denuder method (sampling line B1, Figure 2) was  $3.5 \mu\text{g m}^{-3}$  averaged over all samples taken. The smaller loss of particulate nitrate from the open-face PTFE filter (an average loss of  $3.1 \mu\text{g m}^{-3}$ ) relative to the PTFE filter behind the cyclone (an average loss of  $3.5 \mu\text{g m}^{-3}$ ) might have been due to the reaction of  $\text{HNO}_3$  with coarse-particle sea salt or soil-related particles which were collected on the open-face filter but which were largely removed by the cyclone separator and, thus, were present to a much lesser degree on the fine-particle PTFE filter.

The above observations suggest that the denuder difference method for  $\text{HNO}_3$  and the cyclone-denuder method for fine-particle nitrate determination are superior to the tandem filter method. That finding was consistent with the results of previous studies (15, 16, 25, 27, 28). Therefore, the analysis of Los Angeles air quality that follows was based on the denuder difference method results

for  $\text{HNO}_3$  and the cyclone-denuder method results for fine-particle nitrate. Total particulate nitrate concentrations collected on PTFE filters were corrected for nitrate aerosol volatilization to the extent possible by the method outlined earlier in this paper.

**Nitric Acid Concentrations.** Daily average nitric acid concentrations observed during 1986 are shown in time series in Figure 3. At San Nicolas Island, located in the prevailing upwind direction,  $\text{HNO}_3$  levels are very low, with an average  $\text{HNO}_3$  value of approximately  $0.3 \mu\text{g m}^{-3}$  (0.1 ppb). Peak single day events at San Nicolas Island are observed on rare occasions with  $\text{HNO}_3$  concentrations approaching  $5 \mu\text{g m}^{-3}$  (2 ppb).

Near the coastline at Hawthorne, nitric acid levels are typically less than  $5 \mu\text{g m}^{-3}$  (2 ppb) during most days of the year. The same is true at Long Beach although it is not shown in Figure 3. Periods of 24 h with  $\text{HNO}_3$  concentrations approaching  $10 \mu\text{g m}^{-3}$  (4 ppb) occur on isolated days during the winter, spring, and summer, but there is no pronounced summer seasonal peak in  $\text{HNO}_3$  concentrations near the coast.

Moving inland to Burbank, downtown Los Angeles, Upland, and Tanbark Flats, a summer seasonal peak in  $\text{HNO}_3$  levels is observed. Average 24-h  $\text{HNO}_3$  concentrations in the range  $15\text{--}20 \mu\text{g m}^{-3}$  (6–8 ppb) are seen on numerous occasions during the period June–September 1986. Although lower values prevail on average during the spring, fall, and winter seasons, Figure 3 shows that 24-h average  $\text{HNO}_3$  concentrations in the range  $10\text{--}15 \mu\text{g m}^{-3}$  (4–6 ppb) can be observed at these inland sites on isolated days during most seasons of the year.

Nitric acid concentrations measured at Rubidoux stand in direct contrast to the pattern of increasing nitric acid concentrations with increasing distance in the prevailing downwind direction (inland) over the urban area. Unlike the other sites in the eastern portion of the air basin,  $\text{HNO}_3$  levels at Rubidoux are very low during all seasons of the year, typically less than  $2 \mu\text{g m}^{-3}$  ( $\leq 1$  ppb).

Annual average and maximum 24-h average  $\text{HNO}_3$  concentrations are displayed in Figure 4. Annual average  $\text{HNO}_3$  levels at near-coastal sites are in the range  $3\text{--}4 \mu\text{g m}^{-3}$  (1.2–1.6 ppb) rising to  $6\text{--}7 \mu\text{g m}^{-3}$  (2.3–2.7 ppb) at inland locations like downtown Los Angeles, Burbank, Upland, and Tanbark Flats. Once again, Rubidoux shows the lowest annual average and the lowest maximum 24-h average  $\text{HNO}_3$  concentrations of any on-land monitoring site.

**Total Inorganic Nitrate Concentrations.** Annual average and maximum 24-h average total inorganic nitrate concentrations ( $\text{HNO}_3$  plus its further reaction product, aerosol nitrate) are shown in Figure 5. Annual average values range from a low of  $3 \mu\text{g m}^{-3}$  at San Nicolas Island to  $16\text{--}18 \mu\text{g m}^{-3}$  at near-coastal sites, to  $24 \mu\text{g m}^{-3}$  at Los Angeles and Burbank, rising to  $27\text{--}29 \mu\text{g m}^{-3}$  at the farthest inland urban sites, Upland and Rubidoux. Peak 24-h average inorganic nitrate concentrations follow a similar pattern, with the highest 24-h average value of  $139.5 \mu\text{g m}^{-3}$  measured at Rubidoux.

Subtraction of  $\text{HNO}_3$  concentrations (Figure 4) from total inorganic nitrate concentrations (Figure 5) shows that the majority of the inorganic nitrate is found in the aerosol phase at all sites except the high elevation mountainous site at Tanbark Flats. The spatial distribution of total particulate nitrate (fine- plus coarse-particle fractions) is shown in Figure 6. At Rubidoux, 94% of the annual average inorganic nitrate concentration was found in the aerosol phase. At the other urban sites, aerosol nitrates contribute from 72% (Burbank) to 82% (near the coast)

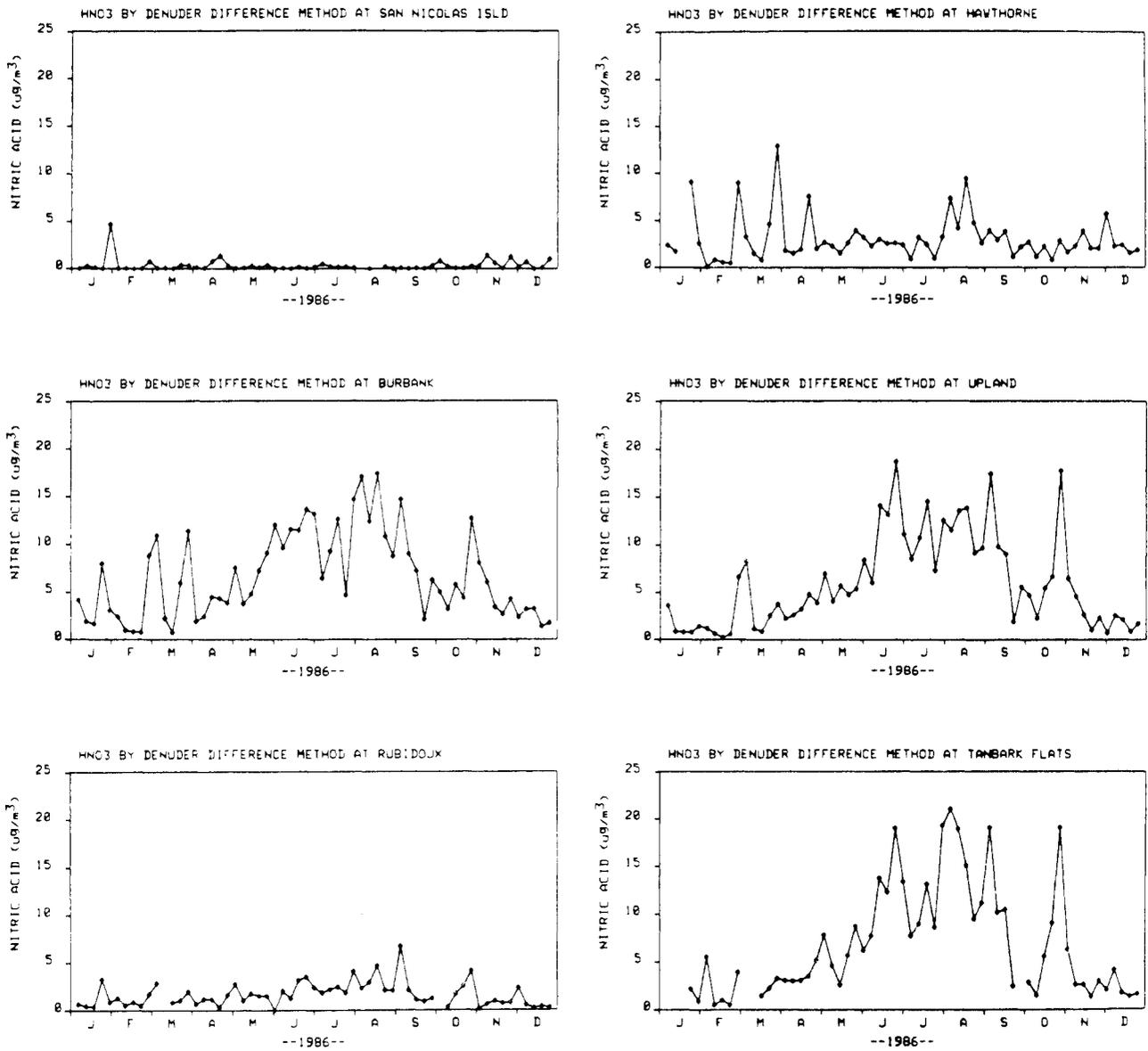


Figure 3. Daily  $\text{HNO}_3$  concentrations at selected sites in the Los Angeles area.  $\text{HNO}_3$  was measured by the denuder difference method.

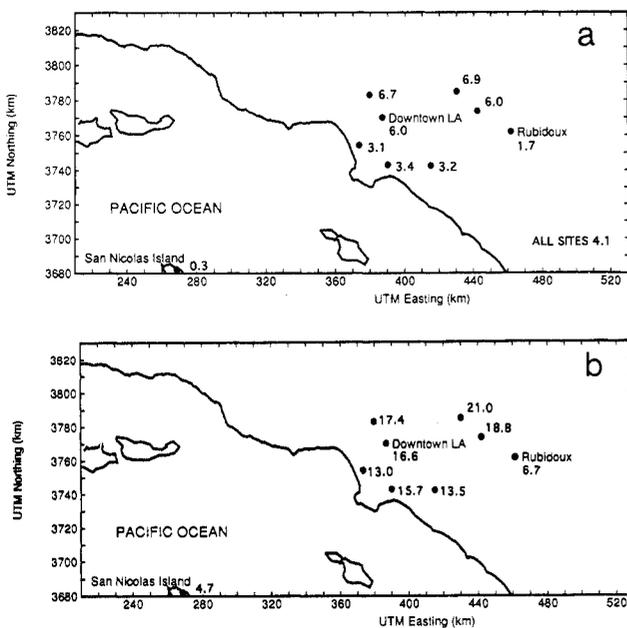


Figure 4.  $\text{HNO}_3$  concentrations ( $\mu\text{g m}^{-3}$ ) observed in the Los Angeles area, 1986.  $\text{HNO}_3$  was measured by the denuder difference method. (a) Annual averages. (b) Maximum 24-h average.

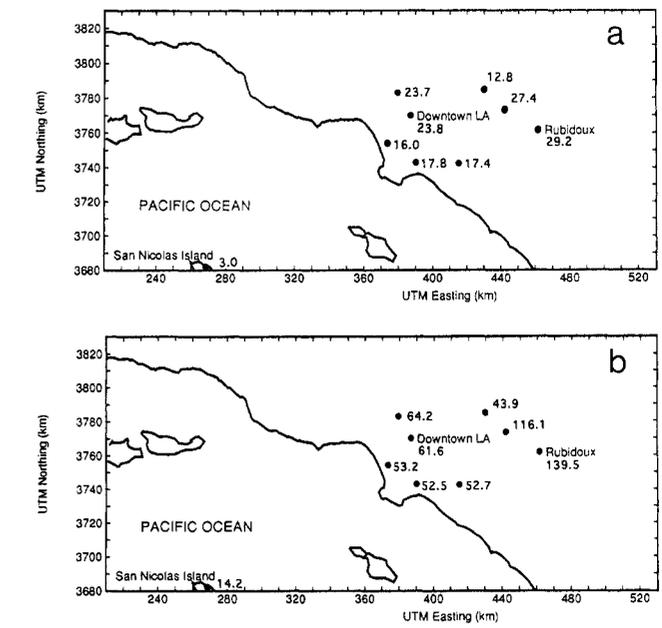
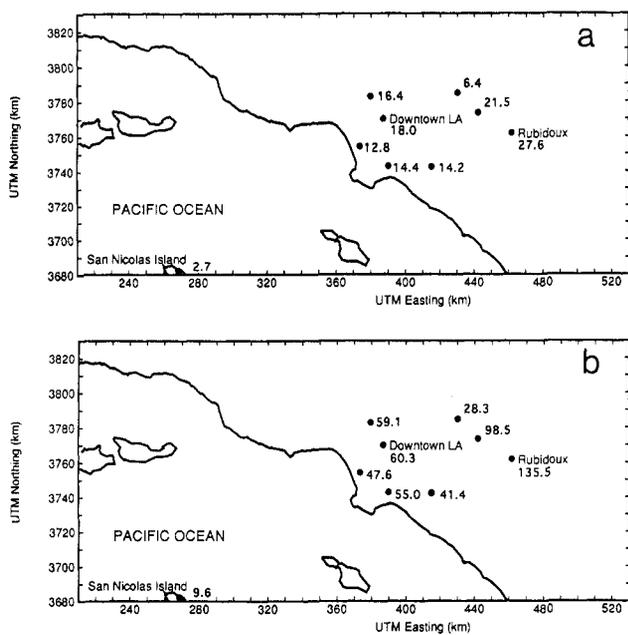


Figure 5. Total inorganic nitrate (i.e., sum of gas-phase  $\text{HNO}_3$  plus aerosol nitrate) observed in the Los Angeles area, 1986. (a) Annual averages. (b) Maximum 24-h average.



**Figure 6.** Total particulate nitrate (fine-particle plus coarse-particle nitrate) observed in the Los Angeles area, 1986. (a) Annual average. (b) Maximum 24-h average.

**Table II.** Annual and Peak 24-h Average Fine-<sup>a</sup> and Coarse-Particle<sup>b</sup> Nitrate Concentrations ( $\mu\text{g m}^{-3}$ ) Observed at Each Site

site	annual av $\text{NO}_3^-$		max 24-h av $\text{NO}_3^-$	
	fine particle	coarse particle	fine particle	coarse particle
metropolitan area				
Burbank	9.5	7.4	50.8	17.1
downtown LA	9.7	8.0	56.3	18.6
Hawthorne	6.2	6.3	39.4	18.3
Long Beach	7.6	7.0	42.7	15.5
Anaheim	8.6	5.9	37.7	14.4
Rubidoux	18.2	9.0	109.0	38.2
Upland	13.3	8.1	78.0	29.1
inland, high elevation				
Tanbark Flats	4.0	2.1	25.2	7.8
background				
San Nicolas Island	1.1	1.7	6.7	5.4

<sup>a</sup> Fine particles are particles in sizes of less than  $2.2 \mu\text{m}$  aerodynamic diameter. <sup>b</sup> Coarse particles are particles in sizes of greater than  $2.2 \mu\text{m}$  aerodynamic diameter.

of the total inorganic nitrate concentrations observed. At Tanbark Flats, 46% of the inorganic nitrate was in the aerosol phase. Clearly aerosol nitrate formation is a major sink for atmospheric  $\text{HNO}_3$ .

**Fine- and Coarse-Particle Nitrate Concentrations.** Annual average and maximum 24-h average fine- and coarse-particle nitrate concentrations observed at each sampling station are presented in Table II. Annual average fine-particle nitrate concentrations within the Los Angeles metropolitan area ranged from  $6.2 \mu\text{g m}^{-3}$  along the coast to  $18.2 \mu\text{g m}^{-3}$  inland at Rubidoux. Coarse-particle nitrate concentrations ranged from  $5.9 \mu\text{g m}^{-3}$  at Anaheim to  $9.0 \mu\text{g m}^{-3}$  at Rubidoux over the 1986 annual averaging period.

The importance of the contribution of fine-particle nitrate during periods of peak 24-h average nitrate concentrations is clearly seen in Table II. The highest 24-h average fine-particle nitrate concentration observed in the SOCAB was  $109.0 \mu\text{g m}^{-3}$  at Rubidoux. Other peak day fine-particle nitrate values, within the Los Angeles metropolitan area, ranged from  $37.7$  to  $78.0 \mu\text{g m}^{-3}$ . Maximum 24-h coarse-particle nitrate values exhibited a much smaller

range from  $14.4$  to  $38.2 \mu\text{g m}^{-3}$  within the metropolitan area, including Rubidoux. These high aerosol nitrate concentrations are of particular importance for the Los Angeles area because they affect compliance with the 24-h average federal ( $150 \mu\text{g m}^{-3}$ ) (31), and existing State of California ( $50 \mu\text{g m}^{-3}$ ) (32),  $\text{PM}_{10}$  standards. The highest fine-particle  $\text{NO}_3^-$  concentration observed during this study represents 73% of the allowable 24-h average federal  $\text{PM}_{10}$  standard and more than 2 times the State of California 24-h average  $\text{PM}_{10}$  standard.

### Discussion

Nitric acid and aerosol nitrate concentration patterns in the Los Angeles area have been examined previously by means of short-term photochemical air quality models that are capable of explaining the observed concentration patterns on a cause and effect basis (20, 33-35). The findings of the present long-term monitoring study are consistent with these prior air quality model predictions. These modeling results (see Figure 3 of ref 35) indicate that the highest  $\text{NO}_2$  concentrations accumulate near the coast in the western portion of the air basin overnight and during the early morning hours. As the day proceeds, NO and  $\text{NO}_2$  typically are advected eastward across the air basin;  $\text{NO}_2$  is oxidized to form nitric acid, and high nitric acid concentrations are predicted to occur in the middle portion of the air basin (e.g., at Burbank and Upland in the present study). As this nitric acid-laden air mass passes over the Chino dairy area (just to the west of Rubidoux), very large amounts of ammonia are injected into the atmosphere from livestock waste decomposition and from other agricultural activities. Ammonia measurements made at the same time as the present study show a 1986 annual average  $\text{NH}_3$  concentration of  $30 \mu\text{g m}^{-3}$  downwind of Chino at Rubidoux. This is approximately 10 times higher than the  $\text{NH}_3$  concentrations measured at upwind sites in the western portion of the air basin during 1986 (36). The available nitric acid reacts to form large amounts of ammonium nitrate aerosol, resulting in the extremely high aerosol nitrate concentrations and the low  $\text{HNO}_3$  levels measured farther downwind at Rubidoux. The modeling study of Russell et al. (35) predicts that Rubidoux should have the highest aerosol nitrate concentrations and the lowest  $\text{HNO}_3$  concentrations of any routine monitoring site in the air basin during 1982 summertime conditions. The present monitoring study shows that this was a year-round condition at Rubidoux during the year 1986.

Monthly average time series graphs of  $\text{HNO}_3$ , fine- and coarse-particle nitrate, and total inorganic nitrate at Hawthorne, Downtown Los Angeles, and Upland are illustrated in Figure 7. As seen in Figure 7, inorganic nitrate production almost always is in great excess of the amount of  $\text{HNO}_3$  in the atmosphere, with average fine-particle nitrate concentrations in winter often higher than in the summer. These results suggest that the pronounced summertime peak in  $\text{HNO}_3$  observed at inland sites is apparently due to factors governing the partition of inorganic nitrate between the gas and aerosol phases in addition to the expected increase in production of inorganic nitrate during the summer as compared to the winter. Based on thermodynamic considerations, it is predicted that atmospheric  $\text{HNO}_3$  and  $\text{NH}_3$  often are in equilibrium with  $\text{NH}_4\text{NO}_3$  aerosol and that the equilibrium dissociation constant for  $\text{NH}_4\text{NO}_3$  often governs the concentration product of  $\text{HNO}_3$  times  $\text{NH}_3$  in the atmosphere and the partition of inorganic nitrate between the gas and aerosol phases (3-5, 33). The  $\text{NH}_3$ - $\text{HNO}_3$ - $\text{NH}_4\text{NO}_3$  equilibrium condition is very sensitive to temperature, with greatly increased ambient  $\text{HNO}_3$  concentrations predicted to be

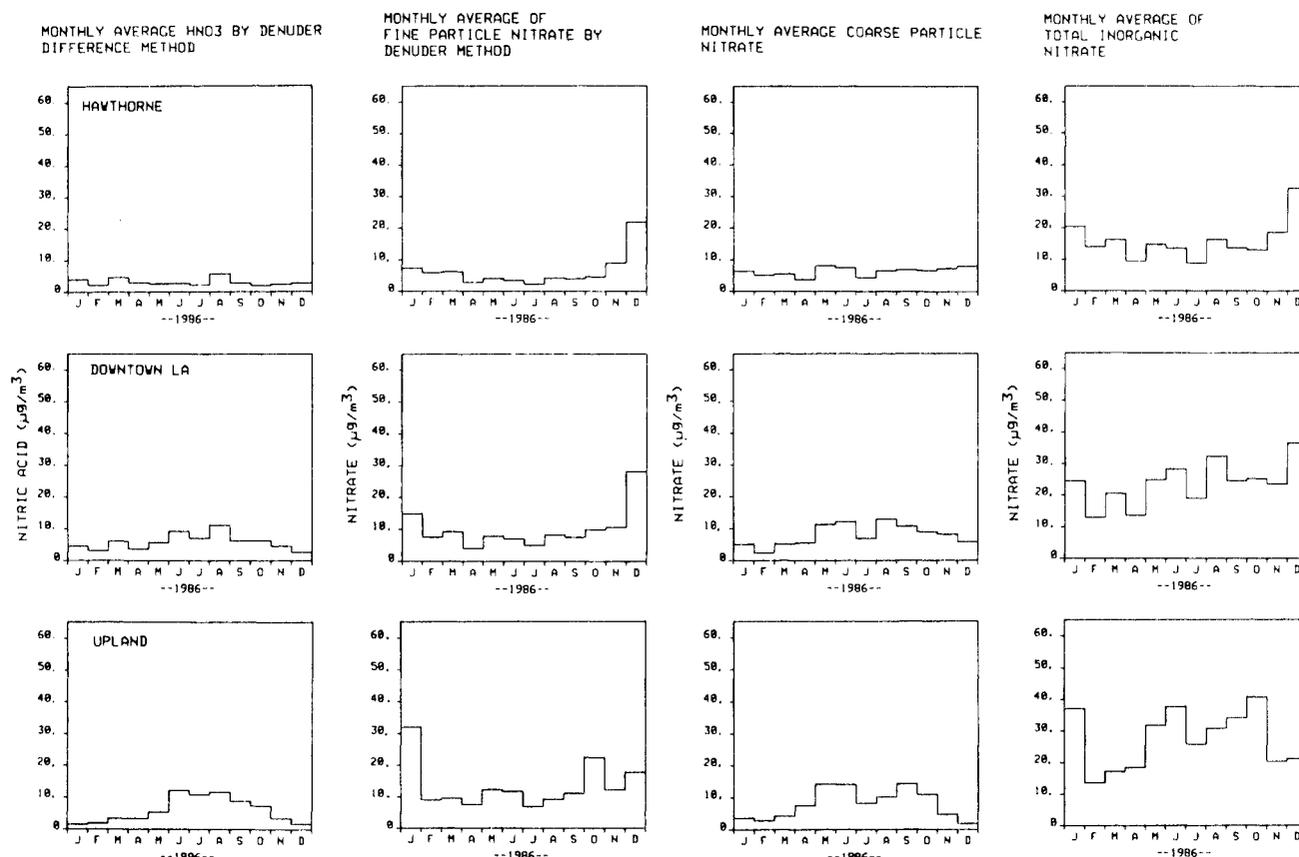


Figure 7. Monthly average  $\text{HNO}_3$ , fine-particle nitrate, coarse-particle nitrate, and total inorganic nitrate at Hawthorne, downtown Los Angeles, and Upland.

in the gas phase at higher ambient temperatures (3–5, 33). Aerosol  $\text{NH}_4\text{NO}_3$  formation also is sensitive to the absolute magnitude of the concurrently observed  $\text{NH}_3$  concentrations, and measured  $\text{NH}_3$  concentrations at most of the monitoring sites studied here are lowest during the summer months (36). Therefore, it is likely that the broad summer seasonal  $\text{HNO}_3$  peak observed at inland low elevation monitoring sites (e.g., Burbank, Upland) results from the higher summer temperatures and lower summer  $\text{NH}_3$  concentrations that shift the  $\text{NH}_4\text{NO}_3$ – $\text{HNO}_3$ – $\text{NH}_3$  equilibrium toward the gas phase. Conversely, the increased fine-particle nitrate levels observed at most sites during the winter most likely result from the lower winter temperatures and higher winter  $\text{NH}_3$  levels which shift the  $\text{NH}_4\text{NO}_3$ – $\text{HNO}_3$ – $\text{NH}_3$  equilibrium toward the aerosol phase. Nearer to the coast, seasonal temperature extremes are moderated by the presence of the ocean,  $\text{NH}_3$  concentrations are lower (36), and there is little seasonal pattern in the  $\text{HNO}_3$  concentrations.

Coarse-particle nitrate concentrations during 1986 were found to be comparable in many cases to the fine-particle nitrate concentrations observed (see Table II and Figure 7). Chemical analyses of samples collected in the Los Angeles area and elsewhere (7, 8, 11, 37, 38) have shown that the coarse-particle nitrates are largely composed of the nonvolatile reaction products of  $\text{HNO}_3$  with sea salt or soil dust, while the fine-particle nitrates consist largely of  $\text{NH}_4\text{NO}_3$  which may dissociate to release  $\text{HNO}_3$  and  $\text{NH}_3$ . Coarse-particle nitrate formation has been examined via photochemical modeling calculations (34) in which nitric acid transport to the surface of the sea salt or soil dust particle is the governing factor limiting coarse-particle nitrate formation. As seen in Figure 7, coarse-particle nitrate concentrations display approximately the same seasonal variation as  $\text{HNO}_3$  concentrations, with a flat

seasonal distribution near the coast and a summer seasonal peak at inland sites such as Burbank and Upland. This is consistent with the pattern expected if coarse-particle nitrate formation is limited by  $\text{HNO}_3$  diffusion to an existing coarse-particle surface that acts as an irreversible sink for  $\text{HNO}_3$ ; coarse-particle nitrate formation is driven by the availability of  $\text{HNO}_3$  in the gas phase. Coarse-nitrate concentrations also may be affected by sedimentation losses of large particles, particularly in winter months when resultant wind speeds are slow and retention times for air masses in the Los Angeles airshed increase.

The highest  $\text{HNO}_3$  levels observed in this air basin in 1986 occurred at the high elevation monitoring site at Tanbark Flats, while total inorganic nitrate concentrations at that site are much lower than at the nearest monitoring stations on the populated valleys below. The most likely explanation for this increased  $\text{HNO}_3$  concentration at high elevation in the presence of lower total inorganic nitrate concentrations is that aerosol nitrate formation has been suppressed. Previous modeling studies have shown that ammonia concentrations should be much higher at low elevations at night and in the early morning hours than at higher elevations (33). This is because  $\text{NH}_3$  is released principally from ground-level sources located on the floor of the air basin. Nitrogen oxides emissions may be produced by both ground-level sources and elevated sources. Hence, there is the possibility that the ratio of  $\text{NO}_x$  to  $\text{NH}_3$  may vary with elevation in the atmosphere. Ambient  $\text{NH}_3$  measurements made concurrently with the present study show that annual average  $\text{NH}_3$  concentrations at Tanbark Flats are very low (only  $0.6 \mu\text{g m}^{-3}$ ), compared to  $2.1$ – $4.4 \mu\text{g m}^{-3}$  at most other urban sites and  $30 \mu\text{g m}^{-3}$  at Rubidoux. The high  $\text{HNO}_3$  concentrations observed at Tanbark Flats when compared to the other sites are consistent with suppression of  $\text{NH}_4\text{NO}_3$  formation due to the near absence

of available ammonia in the gas phase.

#### Acknowledgments

Air monitoring sites were provided through the cooperation of the South Coast Air Quality Management District, the U.S. Forest Service, and the U.S. Navy. Special thanks are given to Jay Rosenthal, Carl Otten, Grady-Jim Roberts, and Lloyd Willet for their assistance in transporting samples and operating the samplers at San Nicolas Island. Betsy Andrews, Sandra Blumhorst, David Cole, Nancy Drehwing, Doug Gray, Mike Jones, Philip Lin, Havey Liu, and Frank Vasquez of the California Institute of Technology assisted with the field experiments, laboratory analyses, and database management aspects of the project.

Registry No. HNO<sub>3</sub>, 7697-37-2.

#### Literature Cited

- (1) Liljestr nd, H. M. Ph.D. Thesis, California Institute of Technology, 1980.
- (2) McRae, G. J.; Russell, A. G. In *Deposition Both Wet and Dry*; Hicks, B. B., Ed.; Acid Precipitation Series; Butterworth: Boston, 1984; Vol. 4, Chapter 9, pp 153-193.
- (3) Stelson, A. W.; Friedlander, S. K.; Seinfeld, J. H. *Atmos. Environ.* 1979, 13, 369-371.
- (4) Stelson, A. W.; Seinfeld, J. H. *Atmos. Environ.* 1982, 16, 983-992.
- (5) Hildemann, L. M.; Russell, A. G.; Cass, G. R. *Atmos. Environ.* 1984, 18, 1737-1750.
- (6) Spicer, C. W. In *Advances in Environmental Science and Technology*; Pitts, J. N., Metcalf, R. L., Eds.; Wiley: New York, 1977; Vol. 7, pp 163-261.
- (7) Mamane, Y.; Mehler, M. *Atmos. Environ.* 1987, 21, 1989-1994.
- (8) Wolff, G. T. *Atmos. Environ.* 1984, 18, 977-981.
- (9) Cronn, D. R.; Charlson, R. J.; Knights, R. L.; Crittenden, A. L.; Appel, B. R. *Atmos. Environ.* 1977, 11, 929-937.
- (10) Savoie, D. L.; Prospero, J. M. *Geophys. Res. Lett.* 1982, 9, 1207-1210.
- (11) Kadowaki, S. *Atmos. Environ.* 1977, 11, 671-675.
- (12) Spicer, C. W.; Howes, J. E.; Bishop, T. A.; Arnold, L. H.; Stevens, R. K. *Atmos. Environ.* 1982, 16, 1487-1500.
- (13) Grosjean, D. *Environ. Sci. Technol.* 1983, 17, 13-19.
- (14) Russell, A. G.; Cass, G. R. *Atmos. Environ.* 1984, 18, 1815-1827.
- (15) Hering, S. V.; Lawson, D. R.; et al. *Atmos. Environ.* 1988, 22, 1519-1539.
- (16) Solomon, P. A.; Larson, S. M.; Fall, T.; Cass, G. R. *Atmos. Environ.* 1988, 22, 1587-1594.
- (17) Schetter, R. E.; Stedman, D. H.; West, D. H. *J. Air. Pollut. Control Assoc.* 1983, 33, 212-214.
- (18) *Directory of Air Quality Monitoring Sites—1972*; EPA-450/2-73-006; U.S. Environmental Protection Agency, U.S. Government Printing Office: Research Triangle Park, NC, 1973.
- (19) *Directory of Air Quality Monitoring Sites Active in 1977*; EPA-450/2-78-048; U.S. Environmental Protection Agency, U.S. Government Printing Office: Research Triangle Park, NC, 1978.
- (20) Russell, A. G.; McRae, G. J.; Cass, G. R. *Atmos. Environ.* 1985, 19, 893-903.
- (21) Forrest, J.; Spandau, D. J.; Tanner, R. L.; Newman, L. *Atmos. Environ.* 1982, 16, 1473-1485.
- (22) Stevens, R. K.; Dzubay, T. G.; Russwurm, G. M.; Rickel, D. *Atmos. Environ.* 1978, 12, 55-58.
- (23) Shaw, R. W.; Stevens, R. K.; Bowermaster, J.; Tesch, J. W.; Tew, E. *Atmos. Environ.* 1982, 16, 845-853.
- (24) Stevens, R. K., Ed. *Current Methods to Measure Atmospheric Nitric Acid and Nitrate Artifacts*; EPA-600/2-79-051; U.S. Environmental Protection Agency, U.S. Government Printing Office: Research Triangle Park, NC, 1979.
- (25) Appel, B. R.; Wall, S. M.; Tokiwa, T.; Haik, M. *Atmos. Environ.* 1980, 14, 549-554.
- (26) John, W.; Reischl, G. *J. Air Pollut. Control Assoc.* 1980, 30, 872-876.
- (27) Appel, B. R.; Tokiwa, Y.; Haik, M. *Atmos. Environ.* 1981, 15, 283-289.
- (28) Forrest, J.; Tanner, R. L.; Spandau, D. J.; D'Ottavio, T.; Newman, L. *Atmos. Environ.* 1980, 14, 137-144.
- (29) Derrick, M. R.; Moyers, J. L. *Anal. Lett.* 1981, 14, 1637-1652.
- (30) Harker, A. B.; Richards, L. W.; Clark, W. E. *Atmos. Environ.* 1977, 11, 87-91.
- (31) U.S. Environmental Protection Agency. National Ambient Air Quality Standards for Particulate Matter; Final Rules, 40 CFR Parts 50-53 and 58. *Fed. Reg.* 1987, 52 (126), 24633.
- (32) State of California Air Resources Board. Suspended Particulate Matter Standards, California Administrative Code, Title 17, Section 70200. *ARB Reg.* 1987, 87 (7) 812.
- (33) Russell, A. G.; McRae, G. J.; Cass, G. R. *Atmos. Environ.* 1983, 17, 949-964.
- (34) Russell, A. G.; Cass, G. R. *Atmos. Environ.* 1986, 20, 2011-2025.
- (35) Russell, A. G.; McCue, K. F.; Cass, G. R. *Environ. Sci. Technol.* 1988, 22, 263-271.
- (36) Solomon, P. A.; Fall, T.; Salmon, L.; Cass, G. R.; et al. Acquisition of acid vapor and aerosol concentration data for use in dry deposition studies in the South Coast Air Basin Report 25; Environmental Quality Laboratory, California Institute of Technology; Pasadena, CA, 1988.
- (37) Wall, S. M.; John, W.; Ondo, J. L. *Atmos. Environ.* 1988, 22, 1649-1656.
- (38) Eldering, A.; Solomon, P. A.; Salmon, L. G.; Fall, T.; Cass, G. R. *Atmos. Environ.* 1991, 25A, 2091-2102.

Received for review April 3, 1992. Accepted April 6, 1992. This work was supported by the California Air Resources Board under agreement A4-144-32.