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Loss of Particle Nitrate from Teflon Sampling Filters:

Effects on Measured Gravimetric Mass

CALIFORNIA ENVIRONMENTAL PROTECTION AGENCY



**AIR RESOURCES BOARD
Research Division**

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Final Report

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Abstract

This report describes analysis of three data sets to evaluate the extent of mass loss on Teflon filters due to ammonium nitrate volatilization. The effect on measured mass is site-dependent, and depends on the meteorological conditions and the fraction of PM_{10} mass that consists of ammonium nitrate particles. There is no straightforward method to correct for the mass loss without measuring it.

The highest mass loss found in California in the CADMP network occurred during summer daytime in southern California, amounting to 30-50% of the gravimetric mass. At IMPROVE sites, the potential mass loss was consistent with the measured loss observed in the CADMP data.

The biased mass measurement implies that the Federal Reference Method sampler for fine particles may lead to control strategies that are biased toward sources of fugitive dust and other primary particle emission sources. This analysis also has implications for the speciation monitoring methods being considered by the EPA. Samples must be collected on nylon filters for nitrate analysis, and on Teflon and quartz filters for analysis of mass, elements, and carbon. It is not clear yet how the ammonium ion should be collected, but it is likely that ammonium is lost from Teflon filters just as nitrate is lost.

Finally, although there is loss of volatile nitrate from Teflon filters during sampling, the nitrate remaining after collection is quite stable. We found little, if any, loss of nitrate from Teflon filters after as much as two hours under vacuum and approximately one minute of PIXE analysis.

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Executive Summary

Background

A large body of evidence has accumulated in recent years that a significant fraction of particle nitrate can be volatilized from Teflon filters during sampling. In fact, this may occur during sampling on other filter media as well, but has not been as thoroughly investigated. Under some conditions, the volatilization losses can be large. Because particulate nitrate is a major component of PM_{10} in California, the loss may significantly affect the gravimetric mass measurement. Furthermore, because the nitrate particles are generally small (less than $2.5 \mu m$), the losses can also affect the measured size distribution. This means that the measured mass and particle size distribution can be significantly biased in current and planned reference sampling methods and in research studies that attempt to link mass, composition, and particle size to health and welfare effects. If nitrate concentrations are consistently under-reported while the concentrations of nonvolatile substances such as soil dust and sulfates are not, then control strategies would selectively emphasize sources of nonvolatile species, and may not effectively control ambient particle concentrations.

Methods

We analyzed data bases from the California Acid Deposition Monitoring Program (CADMP), the Southern California Air Quality Study (SCAQS), the Caltech Acid Gas and Aerosol Study, and the Interagency Monitoring of Protected Visual Environments (IMPROVE) program for this analysis. These data bases all measured nitrate using Teflon and nylon filters, so we could compare the nitrate on both filters to determine the amount lost from the Teflon.

The SCAQS data base was used to compare very different measurement techniques, including impactors and filtration methods. Comparability among these methods was used to verify denuder performance. However, the flow rates were higher, and the sampling times were shorter than in the FRM. The SCAQS data base also contained short-duration samples and hourly temperatures, so we could test a theoretical calculation of nitrate loss against measurements.

The Caltech sampler collected 24-hour samples, as in the FRM, but the flow rate, and hence the filter face velocity, was lower. The CADMP sampler used a flow rate that is comparable to the flow rate in the FRM. Both the CADMP and FRM samplers collect particles on 47mm Teflon filters, and the CADMP sample duration (12 hours) is closer to the FRM 24-hour duration than the shorter times in the southern California studies. We used the CADMP and Caltech data to examine seasonal and site-dependent effects on nitrate loss from Teflon filters.

The IMPROVE sampler collects $PM_{2.5}$ on three different filter substrates for speciated analysis. The Teflon filter face velocity was nearly 20 times that of the FRM sampler. We were not able to calculate actual nitrate losses from the IMPROVE data, but we calculated potential losses by assuming all the nitrate collected on the nylon filter could be volatilized from the Teflon filters.

Introduction

The United States Environmental Protection Agency has promulgated new National Ambient Air Quality Standards for particulate matter, including a new standard for fine particles ($PM_{2.5}$) and a reference method for measuring $PM_{2.5}$. The proposed new reference measurement method includes collection of the $2.5\mu m$ fraction ($PM_{2.5}$) on Teflon filters followed by gravimetric analysis for mass. This has sparked a great deal of debate on measurement methods and the validity of fine particle mass measurements.

A large body of evidence has accumulated in recent years that a significant fraction of particle nitrate can be volatilized from Teflon filters during sampling. In fact, this may occur during sampling on other filter media as well, but has not been as thoroughly investigated. Under some conditions, the volatilization losses can be large. Because particulate nitrate is a major component of PM_{10} in California, the loss may significantly affect the gravimetric mass measurement. Furthermore, because the nitrate particles are generally small (less than $2.5\mu m$), the losses could also affect the measured size distribution. The loss of the smaller nitrate particles could bias the measured size distribution toward larger particles in current and planned reference sampling methods and in research studies that attempt to link mass, composition, and particle size to health and welfare effects.

If nitrate concentrations are consistently under-reported while the concentrations of nonvolatile substances such as soil dust and sulfates are not, then control strategies would selectively emphasize sources of nonvolatile species. In other words, biases in control strategies are likely to follow biases in the reference method. The planned fine particle speciation monitoring network relies on the accurate and complete collection of particles so that the elemental and chemical components can be analyzed. If the measurement method biases the sample in any way, the speciated analysis can be misleading. We have identified several existing data sets, collected under funding by California and federal agencies, that could be used to quantify the nitrate loss effect on gravimetric mass. This report describes the results of our analyses of several of these data sets.

Objective

The objective of this study was to prepare a comprehensive review, based on existing data sets, that would

- (1) assess the magnitude of nitrate volatilization losses resulting from sampling on Teflon filters, and
- (2) quantify the corresponding bias in gravimetric mass determinations resulting from nitrate loss.

While nitrate volatilization artifacts have been discussed in various reports and journal articles over the years, there has never been a focused review of this artifact or how it affects gravimetric mass determinations. The objective of this work was to provide such a review using existing data sets.

Results

The loss of volatile nitrate from Teflon filters approached 100% during summer daytime conditions at sites in the South Coast Air Basin. The lower filter face velocity used in the Caltech network did not significantly reduce the loss of nitrate compared to the higher face velocity used in the SCAQS or CADMP networks. The effect on gravimetric mass depends on site and season, and varies with meteorology. The mass loss from Teflon filters can be as high as 20-30% of the actual mass (or 30-50% of the measured mass) in urban areas during the summer. If the ammonium ion volatilizes along with the nitrate ion, the total mass loss may be as high as 25-35% of the actual mass. At remote sites outside California, the potential mass loss also varies according to location and season. In summer, the potential mass loss is less than 5-10% at most sites. It is greatest at sites near southern California (28%), the San Francisco bay area (16%), and the Puget Sound area (11-28%). In winter, the potential mass loss is higher throughout the network, ranging as high as 30-50% at Washington, D.C., and in parts of the Southwest. Sites with particularly high potential for mass loss in winter include Sequoia, San Geronio, Point Reyes, and Pinnacles in California, Columbia River Gorge, WA, Lone Peak, UT, Badlands, SD, Boundary Waters, MN, Washington, D.C., and Upper Buffalo, AR.

Conclusions

The systematic bias in the EPA's reference method for sampling fine particles is likely to result in a bias in recommended control strategies. Control strategies developed from this biased data will tend to overemphasize controls on sources of fugitive dust and other primary particle emission sources, and underemphasize sources of NO_x and NH₃. Control strategies developed in this way may also be ineffective at reducing particulate matter concentrations as required by the Clean Air Act.

The loss of particulate nitrate from Teflon filters also has implications for the sampling methods being considered by the EPA for speciation monitoring. It is necessary to collect a sample on nylon filters for nitrate analysis. It is equally necessary to collect samples on Teflon and quartz filters for analysis of mass, elements, and carbon. It is not clear yet what is the best method for sampling ammonium ion. Furthermore, it does not matter whether samples collected on Teflon filters use a high or low filter face velocity. Samplers that use a face velocity as low as 3 cm/s experience nearly the same nitrate loss (nearly 100% during summer daytime) as samplers that use a face velocity of 21 cm/s.

Although there is loss of volatile nitrate from Teflon filters during sampling, the nitrate remaining after collection is quite stable. We found little, if any, loss of volatile nitrate from Teflon filters after as much as two hours under vacuum and approximately one minute of PIXE analysis.

Two of the data sets were collected using methods similar to the new Federal Reference Method (FRM). The CADMP sampler used a 20 liter per minute (lpm) flow rate that is comparable to the 16.7 lpm flow rate in the FRM. Both the CADMP and FRM samplers collect particles on 47mm Teflon filters. The CADMP sample duration (12 hours) is closer to the FRM 24-hour duration than the shorter times in the southern California studies. The 1985 Nitric Acid study also has data from 12-hour sample periods collected on Teflon-nylon filter packs operated in a dichotomous sampler, although the flow rates and filter sizes may differ.

The IMPROVE sampler collects $PM_{2.5}$ on three different filter substrates for speciated analysis. The first module collects particles at 22.8 lpm on 25mm Teflon filters for analysis of mass, elemental composition, and light absorption. At many sites, particularly in the western United States, the Teflon filter is masked to obtain a particle deposit with higher areal density. This increases the filter face velocity to nearly 20 times that of the FRM sampler. A second module collects $PM_{2.5}$ on 25mm nylon filters for analysis of ionic species, including nitrate. This module incorporates a carbonate-coated aluminum denuder to remove nitric acid prior to particle collection. A third module collects $PM_{2.5}$ on 25mm quartz filters for analysis of carbon. A fourth module collects PM_{10} on 25mm Teflon filters for gravimetric analysis of mass.

The database containing particulate air pollutant data and meteorological data collected at the Bakersfield - California Avenue site from November 19, 1994 through March 31, 1995 was examined, but was not used in this analysis. This database was found to be unusable for our study, as it did not collect particulate matter on a nylon filter downstream of a denuder. It only measured total inorganic nitrate on a Teflon/nylon filter pack. This measurement includes nitrate from nitric acid; there was no measurement of nitric acid or denuded particulate nitrate. Thus, there was no way to determine the extent of particulate nitrate loss from the Teflon filter.

Although there is no reference method *per se* for most of these data bases, denuded nylon filters have been found to accurately measure fine particulate nitrate. Hering et al. (1997) showed that particulate nitrate measured during SCAQS by a Berner impactor agrees to within 3% of measurements made in parallel by a denuded nylon filter. Lurmann et al. (1994) have shown that nylon filters may lose nitric acid for prolonged sampling, but such losses are less than 1% for 24-hr sampling. Comparisons from the 1985 Nitric Acid Comparison Study also provide verification of this method. The SCAQS sampler and the 1986 Caltech network sampler both used new MgO denuders to remove nitric acid. The CADMP and IMPROVE networks both used aluminum denuders, but they must be properly maintained when used in a high nitric acid environment. Fitz and Hering (1996) found a failure in the CADMP network after prolonged use in a high nitric acid environment, but such failures for MgO denuders have not been found. The IMPROVE data indicate that the carbonate-coated denuders maintain a high collection efficiency for HNO_3 for over 100 24-hour samples, even at sites with high SO_2 and HNO_3 .

The collection efficiency of a nitric acid denuder depends on the coating material, the diffusion length, and the residence time of the air stream in the denuder. It may also depend on the relative humidity, as there is evidence that nitric acid exists in the

Report structure

This report is structured around three reviews of available data. The first review focused on southern California, and examined the magnitude of nitrate volatilization and its implications for gravimetric fine mass measurement using data sets from the 1987 Southern California Air Quality Study (SCAQS) and the 1986 Caltech study. The second review extended to the rest of California using all available data from the California Acid Deposition Monitoring Network (CADMP). Finally, data from the Interagency Monitoring of Protected Visual Environments (IMPROVE) program were examined to estimate the possible magnitude of the nitrate volatilization loss nationwide

The next two sections of the report describe the data bases and analytical methods used. The results of the first review have been incorporated into a journal article for publication in the Journal of the Air & Waste Management Association. The complete article is included in Appendix A. This report summarizes the chief findings of the review paper, but does not include a detailed analysis. The second review using the CADMP data is not yet complete for publication, so the detailed analysis that will be in the review paper is included in the report.

Materials and Methods

We identified seven data sets that could potentially provide the information needed for this analysis. They were:

1. The Southern California Air Quality Study (SCAQS), 1987
2. Caltech Acid Gas and Aerosol Study in the South Coast Air Basin, 1986
3. Nitrogen Species Methods Comparison Study (NSMCS), 1985
4. The California Acid Deposition Monitoring Program (CADMP), 1988-present
5. Interagency Monitoring of Protected Visual Environments (IMPROVE), 1988-present
6. Special IMPROVE studies
7. Bakersfield PM_{2.5} Study, Winter 1994/95

Each of these data sets offered unique characteristics for examining the nitrate volatility issue. The SCAQS data base was used to compare very different measurement techniques, including impactors and filtration methods. Comparability among these methods was used to verify denuder performance. However, the flow rates were higher, and the sampling times were shorter than in the EPA reference method. The Caltech sampler collected 24-hour samples, as in the reference method, but the flow rate, and hence the filter face velocity, was lower. Five of the sampling sites used in the Caltech network are the same as for the Southern California Air Quality Study. These data provided a means to determine whether losses among these two samplers, with similar construction but differing sampling times and flow rates, were similar. Additionally, the Caltech sampler was used in the 1985 Nitric Acid Methods Comparison Study to collect both four to six hour samples and 22 hour samples which could be compared to determine the effect of sample duration on nitrate loss.

Table 1. Sample collection parameters for SCAQS, Caltech, CADMP, and IMPROVE networks

Database	Measurement	Flow Rate	Face Velocity
SCAQS	PM _{2.5} 47mm Teflon	20 lpm	21 cm/s
	PM _{2.5} 47mm denuded nylon	20 lpm	21 cm/s
	Berner impactor		N/A
Caltech	PM _{2.2} 47 mm Teflon/nylon	3 lpm	3 cm/s
	PM _{2.2} 47mm denuded nylon	3 lpm	3 cm/s
CADMP	PM _{2.5} 47mm Teflon/nylon	20 lpm	21 cm/s
	PM _{2.5} 47mm denuded nylon	20 lpm	21 cm/s
IMPROVE	PM _{2.5} 25mm Teflon **	22.8 lpm	100 and 175 cm/s
	PM _{2.5} 25mm denuded nylon	22.8 lpm	100 cm/s
Federal Reference Method	PM _{2.5} 47mm Teflon	16.7 lpm	~17.5 cm/s

** The IMPROVE Teflon filter is masked at most sites in the western United States. In this case the face velocity is 175 cm/s.

Table 1 summarizes the sample collection parameters for each of the databases examined in this report. Some researchers have suggested that low filter face velocity may reduce the volatilization of nitrate from Teflon filters. This was one reason the Caltech sampler used such a low flow rate to collect a sample.

CADMP Data validation

Examination of the CADMP data prior to analysis revealed a problem with internal consistency. The nitric acid measurement was made by the denuder difference method whereby one sampling train collected particles on a Teflon filter followed by a nylon filter to collect nitric acid. A separate sampling train collected particles on a nylon filter downstream of a nitric acid denuder. The Teflon filter nitrate is denoted NO325TF in the database, the non-denuded nylon filter nitrate collected downstream of the Teflon filter is denoted NO325NY, and the denuded nylon filter nitrate is denoted NO325DN. The data base initially provided for this analysis showed a difference in the method of calculating nitric acid before and after October 1, 1991. Prior to that date, the nitric acid was calculated by

$$HNO_3 = (NO_{325TF} + NO_{325DN} - NO_{325NY}) * \frac{63}{62} \quad (1)$$

The factor 63/62 accounts for the extra hydrogen atom in HNO₃, but the combination of the three nitrate measurements was incorrect. After October 1, 1991, the nitric acid in the data base was calculated by

atmosphere in a hydrated form. Hydrated nitric acid molecules have a lower diffusion coefficient than non-hydrated molecules. The denuder surface is usually an alkaline material such as MgO or Na₂CO₃, or may be untreated or anodized aluminum. The capacity of the denuder material is not fully understood. As described above, anodized aluminum denuders in Azusa have shown some evidence of saturation after several years of sampling, but IMPROVE data show no evidence of saturation by carbonate-coated aluminum denuders after one year of sampling. It is difficult to correct for a reduction in denuder efficiency, as it must be quantified to make the correction. For this study, only valid data, as reported in the data base, were used. The time period when the southern California sites were suspected of having saturated denuders was not included in this analysis.

Data description

Three measurements of fine particle nitrate were available from SCAQS data; a PM_{2.5} Teflon filter, a PM_{2.5} denuded nylon filter, and nitrate measurements from a Berner impactor. The Teflon filter was preceded by a Bendix 240 cyclone, while the nylon filter was preceded by an AIHL-design cyclone and a tubular MgO denuder. The face velocity on the 47 mm Teflon and nylon filters was 21 cm/s. Samples were collected for 4-6 hour periods several times each day, but only on days when nitric acid and ozone was forecast to be high. Data from both a summer field study and a fall field study were available.

For the Caltech data, samples were collected for 24 hours, beginning at midnight, every 6th day at nine sites around the South Coast Air Basin for one year. The sampler collected particles on Teflon filters at a face velocity of 3 cm/s (3 lpm through a 47mm filter) downstream of an AIHL-design cyclone operated at 24.8 lpm. This flow rate provided a 2.2 μm size cut. The sampler also collected particles on denuded and undenuded nylon filters at the same 3 cm/s face velocity downstream of the same AIHL cyclone. The denuder consisted of MgO-coated glass tubes.

CADMP measurements of nitrate are available from a PM_{2.5} Teflon filter, a PM_{2.5} nylon backup filter, and a PM_{2.5} denuded nylon filter. The filters collected particles downstream from a Teflon-coated Bendix 240 cyclone operated at 4 cfm (113 lpm) to give a 2.5 μm cut point, and the flow was split so that each 47mm filter collected particles at 20 lpm. This gave a face velocity of 21 cm/s. Samples were collected for two consecutive 12-hour periods every 6th day beginning at 6 p.m. The denuder consisted of an annular aluminum tube. These data were analyzed for the extent of nitrate loss on the Teflon filters.

The IMPROVE data set includes measurements of mass from a PM_{2.5} Teflon filter and nitrate from a PM_{2.5} denuded nylon filter. Both filters are 25mm diameter, but the Teflon filter at most sites is masked to produce a higher areal density of particles for x-ray fluorescence and PIXE analysis. The particles are collected through an AIHL-design cyclone at a flow rate of 22.8 lpm; this gives a particle size cut point of 2.5 μm. The face velocity on the nylon filter is 100 cm/s. For the Teflon filter, the face velocity ranges from 100-175 cm/s, depending on the mask used. Samples in the IMPROVE network are collected for 24 hours every Wednesday and Saturday beginning at midnight.

this is correct, the apparently incorrect calculation in Equation (1) turns out to give the correct result for nitric acid prior to October 1991. The nitric acid in the data base after that time would be low by 1.6%, as they do not include the factor of 63/62.

Subsequent examination of Air Resources Board files revealed that the most recent CADMP data were correctly entered in the data base. The NO325DN and NO325NY data in the preliminary data base provided for this analysis were corrected to match the Air Resources Board files. The correction consisted of swapping the NO325DN and NO325NY data prior to October 1, 1991 and correcting the nitric acid calculation after that time.

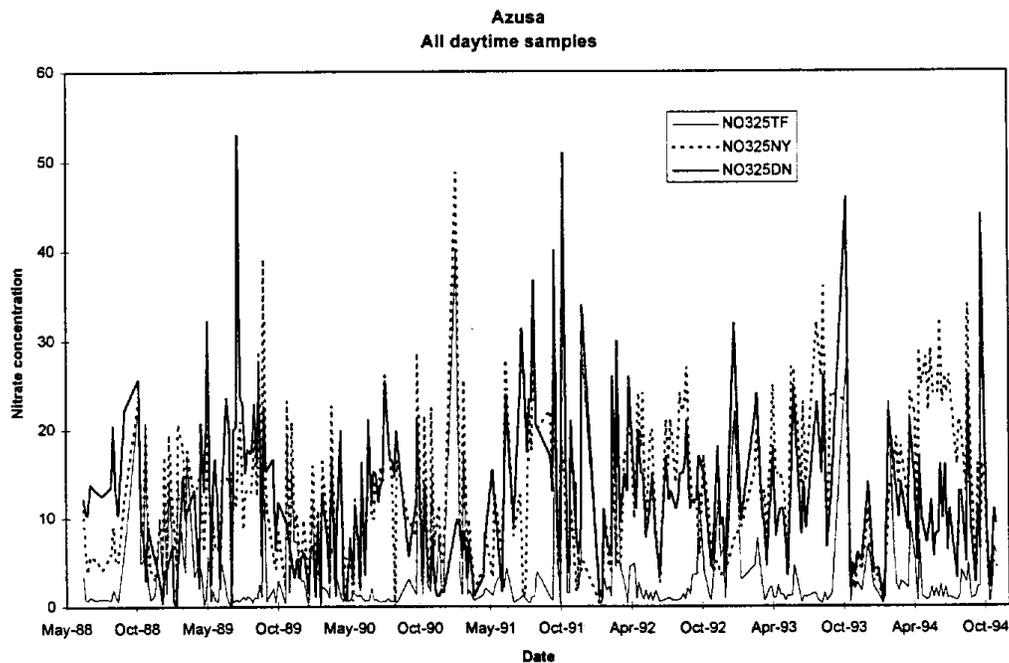


Figure 2. Nitrate data for CADMP daytime samples collected at Azusa

Results and Discussion

SCAQs and Caltech data

Figure 3 shows scatter plots of SCAQS summer nitrate measurements at Long Beach, central Los Angeles, Hawthorne, and Anaheim on denuded nylon filters vs. Teflon filters. These results are typical of summer measurements at other SCAQS sites. The denuded nylon filter collected more nitrate than the Teflon filter, especially during the daytime. The nighttime Teflon nitrate is closer to the nylon nitrate, although it is still lower. This suggests that nitrate is volatilized from the Teflon filter during the hot, dry daytime hours.

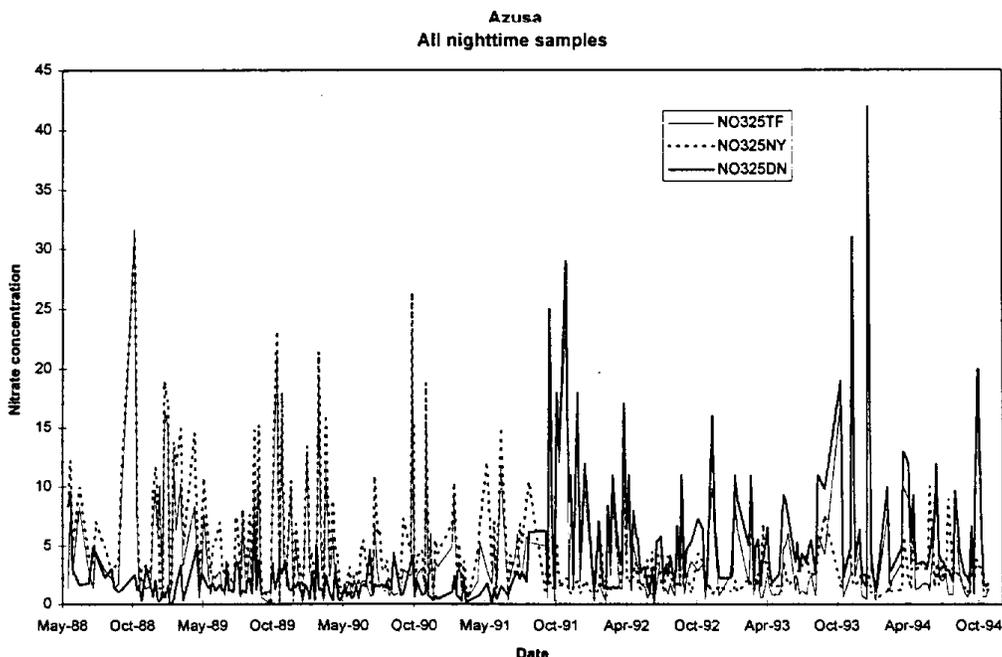


Figure 1. Nitrate data for CADMP nighttime samples collected at Azusa

$$HNO_3 = (NO_{325TF} + NO_{325NY} - NO_{325DN}). \quad (2)$$

This calculation uses the correct combination of the three nitrate measurements, but does not include the factor of 63/62 to account for the hydrogen in nitric acid.

Close examination of the data base revealed that the NO325TF data were consistent throughout, but the NO325NY and NO325DN data were not. Examination of the CADMP nighttime samples revealed that the two measurements were swapped in the data base beginning October 1, 1991. There is almost an order of magnitude difference between NO325DN and NO325NY at night, but they are very similar during the day.

Figure 1 shows the night time data for Azusa from May 1988 through December 1994, while Figure 2 shows the daytime data. Prior to October 1991, the nighttime data show NO325NY nitrate slightly higher than NO325TF nitrate, and with a high correlation. Both are much higher than the NO325DN nitrate. After October 1991, the nighttime data show the NO325DN nitrate slightly higher than the NO325TF nitrate, and with a high correlation. Both are much higher than the NO325NY nitrate. Note that the difference is not apparent in the daytime data. During the day, there is a large amount of nitric acid present, and much of the particulate nitrate volatilizes, so the NO325NY nitrate is large compared to the NO325TF nitrate. This masks the difference between the NO325NY and NO325DN nitrate measurements.

The time period after October 1991 shows the relationship we would expect to see between the three nitrate measurements. This implies that the data were entered into the data base incorrectly prior to October 1991, and the error was corrected afterwards. If

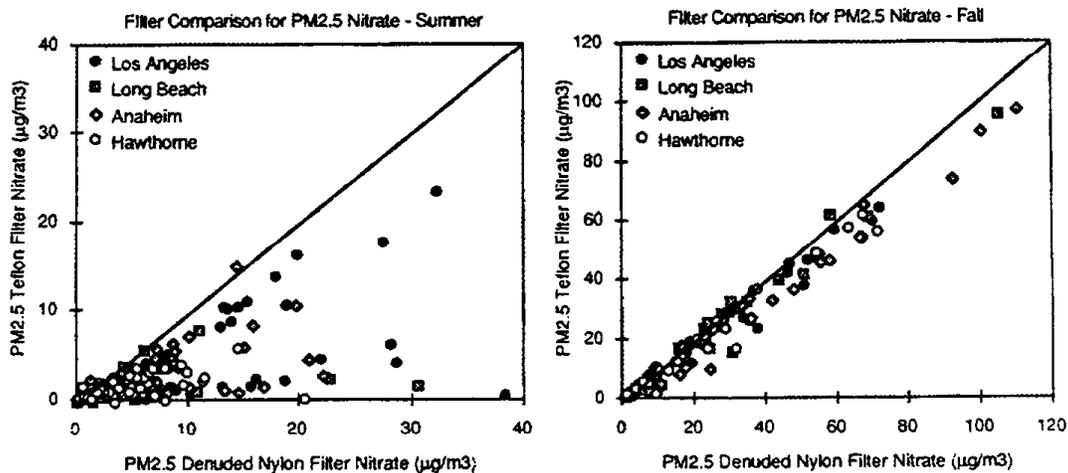


Figure 4. Denuded nylon nitrate vs. Teflon nitrate at Long Beach, Los Angeles, Hawthorne, and Anaheim for summer and fall during SCAQS.

The measured nitrate loss was examined using the theory of Zhang and McMurry (1987). Their model predicts the nitrate loss according to the mass that must be evaporated from the filter to achieve the saturation vapor pressure immediately downstream of the filter. The model requires the temperature and pressure downstream of the filter. Three scenarios were modeled. All assume no pressure drop in the sampling system. The first assumes 100% vapor depletion above the filter and no change in temperature at the filter. The second assumes no vapor depletion and a temperature increase at the filter of 5°C. The third assumes a 50% vapor depletion and a 3°C temperature rise at the filter. All three scenarios give equivalent results. Figure 5 compares the measured nitrate loss to the modeled loss under any of these scenarios.

Figure 4 shows the filter nitrate comparison for all four sites for summer and for fall. The nitrate loss from Teflon filters is greater in summer than in fall, in accord with the theory that nitrate is volatilized to a greater degree when temperatures are higher and humidity is lower. The nitrate loss from Teflon filters in fall was generally slight, while in summer it was as high as 100%.

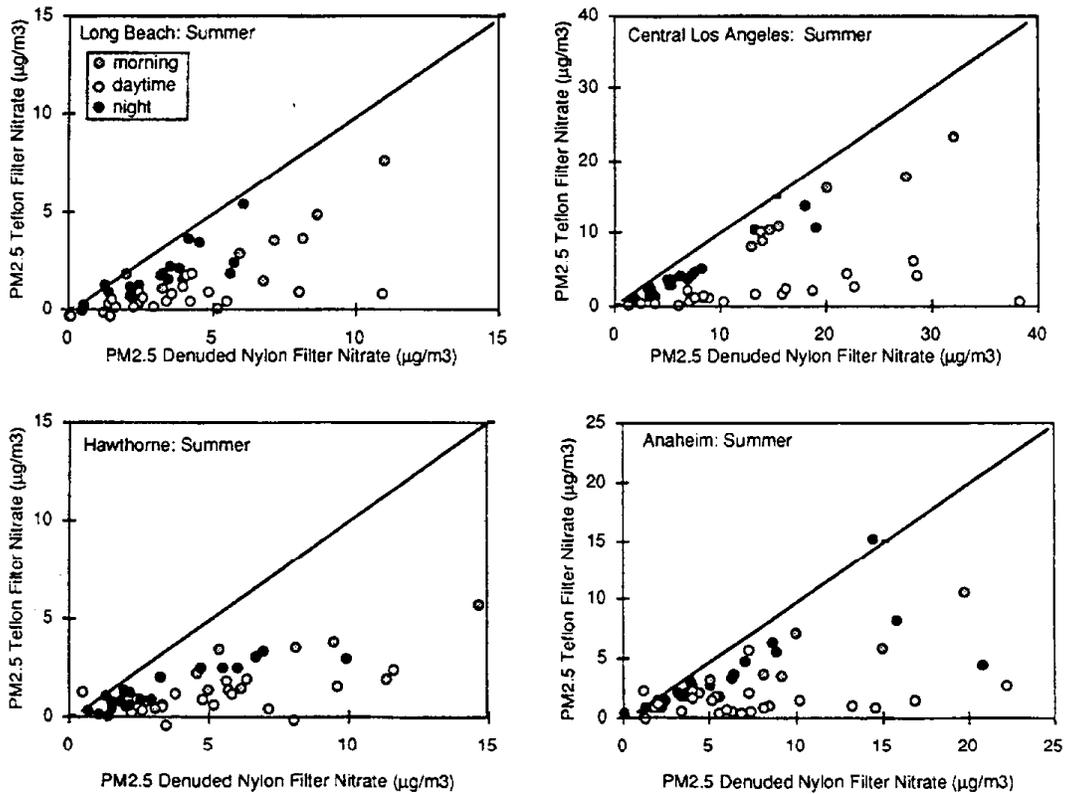


Figure 3. Denuded nylon nitrate vs. Teflon nitrate at Long Beach, Los Angeles, Hawthorne, and Anaheim during the summer SCAQS period.

CADMP data

The SCAQS and Caltech data were collected only in the South Coast Air Basin. The CADMP data base provides a more complete understanding of the effect of nitrate loss on gravimetric mass measurements throughout California. We examined the CADMP data by site, time of collection (daytime and nighttime), season, and species. Prior to analysis, we sorted the data to include only those time periods with valid data for all analytical measurements. The analyses conducted for this study are illustrated here for Azusa and Los Angeles. The results are summarized for all sites in tables, and a complete set of analysis plots for all sites is provided in Appendix B.

Figure 7 shows a scatter plot of nitrate data collected on Teflon and nylon filters at Los Angeles in the California Acid Deposition Monitoring Program. The same trend shown in Figure 3, i.e. higher volatilization of nitrate during the daytime hours and lower volatilization during the night, is evident in this plot. The regression line for the nighttime samples has a slope of 0.83, while the regression line for the daytime samples has a slope of 0.42. More nitrate is lost during the day than at night.

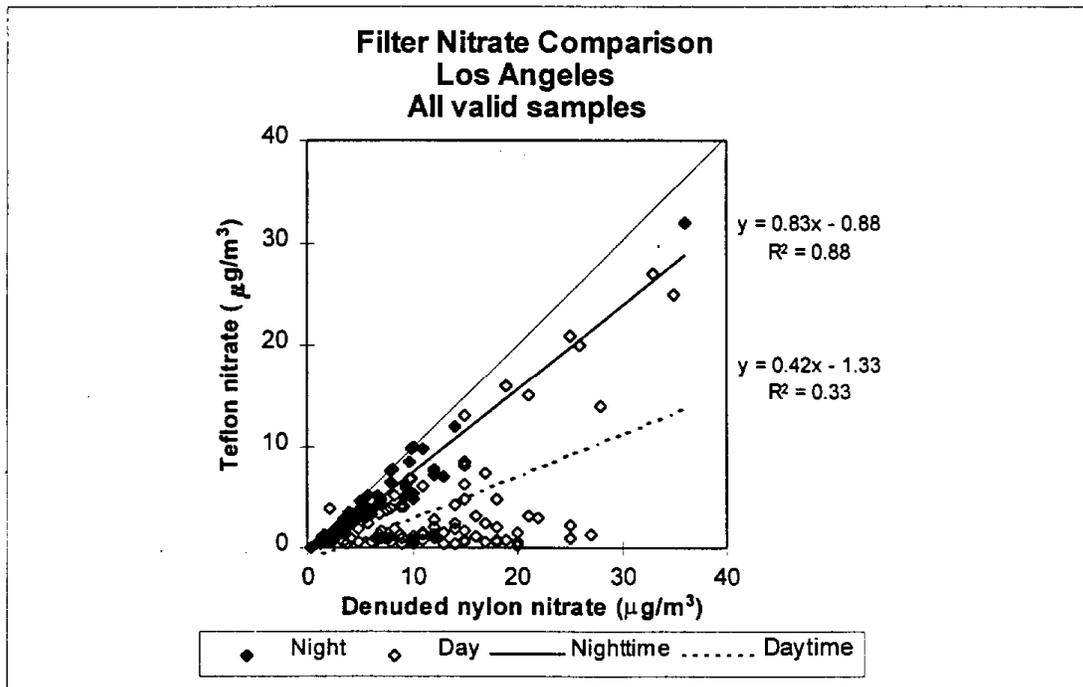


Figure 7. Nitrate collection by teflon and nylon filters in Los Angeles for CADMP

This result has implications for the sampling period of any monitoring network, including the national $\text{PM}_{2.5}$ mass and speciation networks. It is likely that, for samples with a start time of midnight, ammonium nitrate collected on Teflon filters will remain on the filters until the temperature increases and the humidity drops during the day. Most of the nitrate may then evaporate until the evening, when temperatures fall and humidity rises. Thus, a

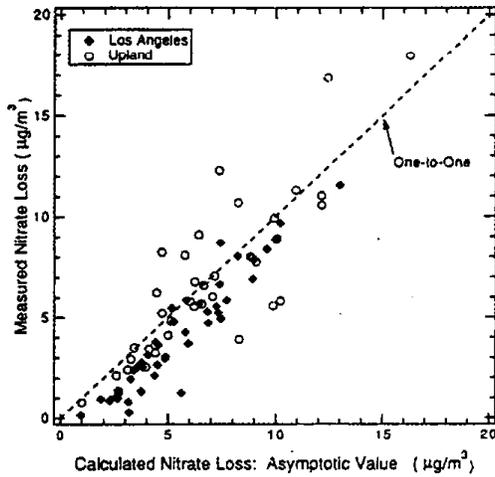


Figure 5. Comparison of measured nitrate loss to modeled loss using the theory of Zhang and McMurry.

Finally, the nitrate losses measured during SCAQS and in the Caltech data were examined to see if the difference in face velocity made a significant difference in the results. Figure 6 shows the fractional loss in mass as a function of measured mass for both data sets. There is a slightly lower fractional loss in the Caltech data compared to the SCAQS data, but the difference is not great. Despite the much lower face velocity on the Caltech filters (3 cm/s versus 21 cm/s for SCAQS), the nitrate losses were similar. This suggests that the lower face velocity used in the Caltech sampler did not significantly reduce the losses due to nitrate volatilization. Appendix D shows similar plots for the CADMP sites.

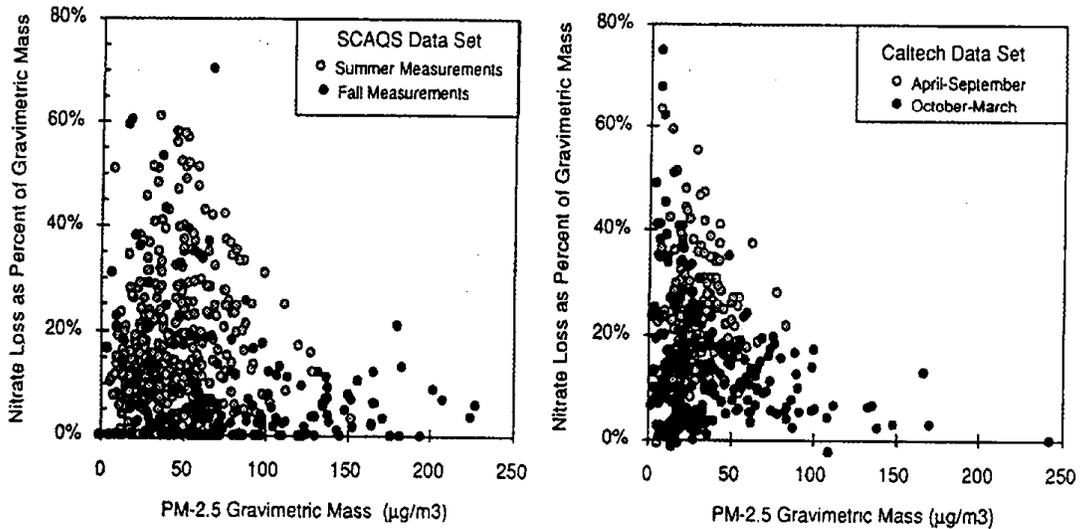


Figure 6. Fractional loss of mass as a function of measured mass for SCAQS and Caltech data sets

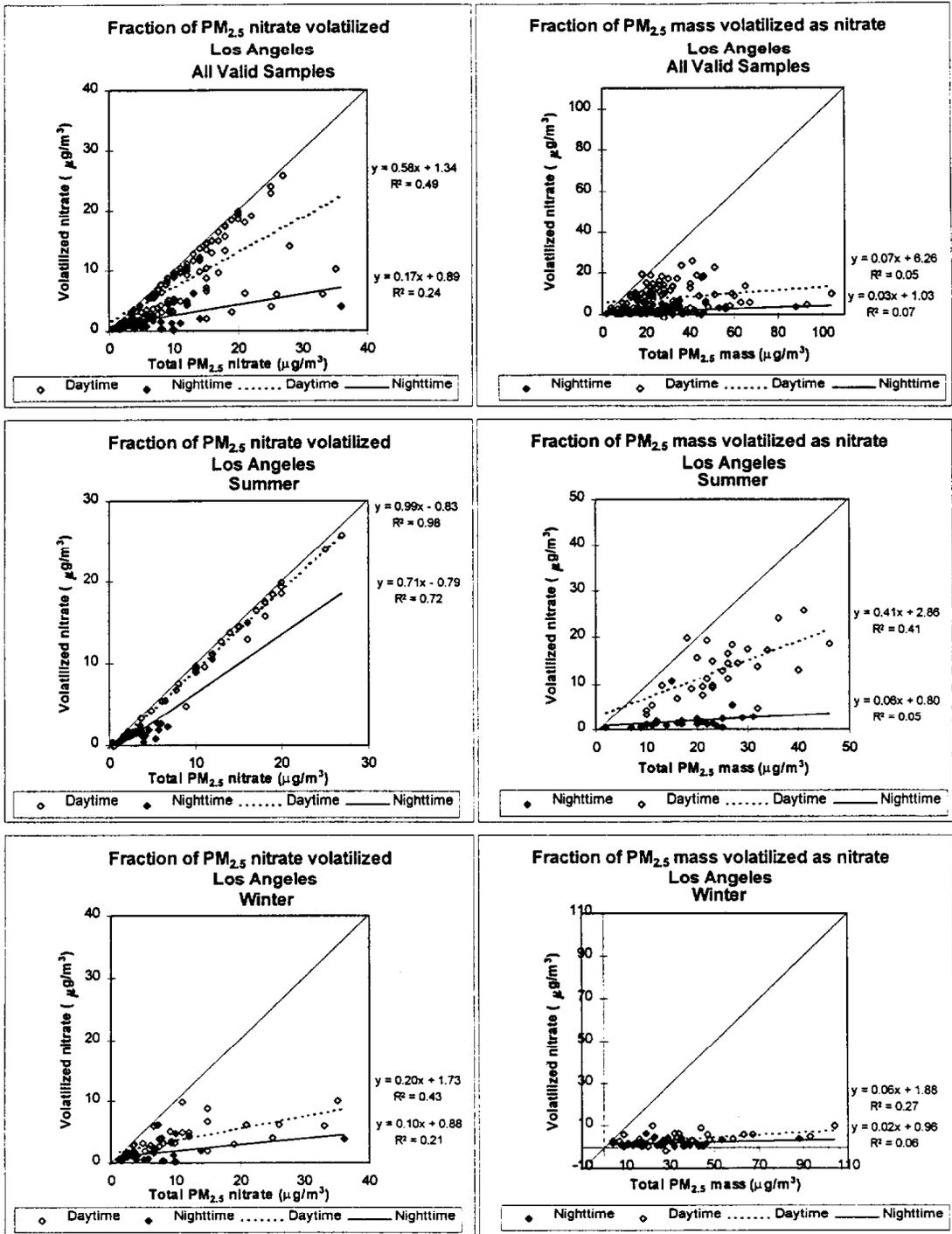


Figure 8. Nitrate measurements at Los Angeles

24-hour sample collected from midnight to midnight is likely to contain nitrate only for the last few hours of the sampling period. This would bias the speciation result and any source apportionment modeling that is performed on the data.

The top third of Figure 8 shows the volatilized nitrate compared to total nitrate and to measured PM_{2.5} mass for daytime and nighttime at Los Angeles. The volatilized nitrate is the difference between the nitrate collected on the denuded nylon filter and that collected on the Teflon filter. The total PM_{2.5} nitrate is the nitrate collected on the denuded nylon filter. The measured PM_{2.5} mass does not include the volatilized nitrate, as it was lost prior to weighing the filter. During the day, as much as 100% of the nitrate may be volatilized from the Teflon filter. On average over all valid samples, 58% of the nitrate evaporated from the Teflon filter during the daytime sampling period, and 17% evaporated during the nighttime sampling period. The fraction of PM_{2.5} mass lost to volatilized nitrate is calculated by

$$\text{Fraction of mass lost} = \frac{\text{Volatilized nitrate}}{\text{Measured mass} + \text{Volatilized nitrate}}$$

Note that the fraction of mass lost does not include the cation associated with the nitrate. Assuming the nitrate lost to volatilization is in the form of ammonium nitrate, and that the ammonium ion is also lost as ammonia gas, the fraction of PM_{2.5} mass lost to volatilized ammonium nitrate is calculated by

$$\text{Fraction of mass lost} = \frac{1.29 * \text{Volatilized nitrate}}{\text{Measured mass} + 1.29 * \text{Volatilized nitrate}}$$

Note that nitric acid and ammonia may react with very fine organic particles so that the ammonium nitrate is then associated with organic matter. It is unclear whether these particles would volatilize in the same manner as ammonium nitrate. It is also not clear whether the organic matter would volatilize with the ammonium nitrate or be left behind in particulate form. In either case, there are other possible artifacts that could affect loss of particle mass. There is some evidence that nylon filters could partially collect nitrogenous gases other than nitric acid from ambient air. If this is the case, the nylon filter nitrate would exhibit a positive artifact. The scatter plots of volatilized nitrate vs. PM_{2.5} nitrate might show data points above the one-to-one line. Although this is not the case, there could be a positive artifact on the nylon that would lead to an overestimate of the volatilized nitrate. More research on this possible effect is warranted.

For some daytime sampling periods, the volatilized nitrate was as high as the measured PM_{2.5} mass, although there is a lot of scatter in these data. Because the measured mass does not include this lost nitrate, as much as 50% of the actual PM_{2.5} mass evaporated before being measured. On average for all sampling periods, the volatilized nitrate at Los Angeles was approximately 7% of the measured mass during the day, and was 3% at night.

Table 2. Fraction of PM_{2.5} mass as nitrate and fraction of PM_{2.5} mass volatilized as nitrate by site, season, and time of day for CADMP measurements.

Site	Summer daytime	Summer nighttime	Winter daytime	Winter nighttime
Azusa	.37/.24	.37/.18	.46/.18	.36/.15
Bakersfield	-.02/-.02	.06/.04	.47/.19	.23/.10
Fremont	.19/.15	.27/.16	.45/.16	.31/.10
Gasquet	.05/.02	.09/.02	.01/.01	.00/.00
Los Angeles	.41/.29	.08/.06	.30/.06	.20/.02
Long Beach	.26/.20	.38/.19	.43/.17	.20/.07
Sacramento	-.05/-.05	.05/.03	.52/.21	.22/.09
Santa Barbara	.07/.04	.16/.08	.26/.15	.25/.06
Sequoia National Park	-.04/-.03	.03/.01	.42/.20	.24/.12
Yosemite National Park	.01/.01	.02/.00	.09/.06	.11/.04

*The numbers in this table represent the slope of the regression line between the appropriate variables. Negative numbers do not imply negative mass loss, but only that the relationship is not significantly different from zero. See the scatterplots in the appendix.

Table 3 shows the fraction of PM_{2.5} mass loss under the assumption that all the nitrate lost was in the form of ammonium nitrate, and that the ammonium ion was lost along with the nitrate ion. No data are available at this time to test this assumption, but there is no reason to suspect that the ammonium ion will be retained on the Teflon filter if the ammonium nitrate particle evaporates. In fact, there is reason to suspect that the ammonium ion will be lost, also. In that case, the winter nighttime period at Sacramento also shows a loss greater than 10% of the actual mass. The highest mass loss still occurs during the summer daytime at Los Angeles, but increases to 35% of the actual PM_{2.5} mass.

Table 4 shows the fraction of nitrate lost to volatilization for all CADMP sites for the same time periods as in Table 2 for mass. The highest fractional nitrate losses occur in the summer daytime at most sites, especially those where nitrate particles are produced via atmospheric chemistry. Exceptions are Gasquet and Santa Barbara, where the highest fractional losses occur in the winter daytime.

Figure 9 shows the measured and corrected PM_{2.5} mass, averaged by month, for Los Angeles. Similar plots for all CADMP sites are shown in Appendix C. Both the monthly mean and maximum measured mass are shown, along with the nitrate loss-corrected

The problem with annual averages is that they mask major seasonal differences in both concentrations and the fraction volatilized. In particular, the particulate mass and nitrate are both higher in the winter months. The middle third of Figure 8 shows the fraction of total nitrate volatilized and the effect of volatilized nitrate on measured $PM_{2.5}$ mass in Los Angeles for the summer months June-September. During these months, the volatilized nitrate during the daytime hours averaged 99% of the total nitrate and 41% of the measured mass. Thus, on average during the day from June through September 29% of the actual $PM_{2.5}$ mass was lost prior to measurement as the nitrate evaporated from the Teflon filter. During the nighttime hours, only 6% of the measured mass was lost to nitrate volatilization. In the cooler winter months of October through February (bottom third of Figure 8), the daytime loss of nitrate averaged only 6% of the $PM_{2.5}$ mass (20% of the nitrate) in Los Angeles, and the nighttime $PM_{2.5}$ mass loss was only 2% (10% of the nitrate).

The procedure described above for Los Angeles was repeated for all CADMP sites. Appendix B includes plots similar to Figure 8 for each CADMP site. Table 2 lists the fraction of $PM_{2.5}$ mass present as nitrate and the fraction of $PM_{2.5}$ mass lost to nitrate volatilization for each CADMP site by season and time of day. The first number in the table is the fraction of mass as nitrate, and the second is the fraction of mass lost to nitrate volatilization. There must be a significant fraction of the $PM_{2.5}$ mass as nitrate to show a significant loss due to volatilization, but there are times when the losses are not high even though there is significant nitrate present. In summer daytime, losses are high whenever nitrate is present in the particulate phase. In summer nighttime, losses are lower (relative to the amount of nitrate present) than in daytime, but can still be significant. In Fremont, for example, there is so much more nitrate present at night that the mass loss due to volatilization is slightly higher than in daytime. In winter daytime, mass loss is usually significant if nitrate is present. At Los Angeles, however, the winter daytime mass loss is low even though 30% of the mass is nitrate. At Bakersfield, Sacramento, Santa Barbara, and Sequoia National Park the mass loss in winter daytime exceeds that of summer daytime. At these sites, though, there is little nitrate in the particle phase during the summer and significant amounts in the winter. In winter nighttime, mass loss is low at most sites even though the nitrate is present at 20-30% of the particulate mass at most sites. At Azusa and Sequoia National Parks, the mass loss exceeds 10% of the mass even in winter nighttime.

Table 4. Fraction of nitrate mass lost to volatilization

Site	Summer daytime	Summer nighttime	Winter daytime	Winter nighttime
Azusa	.87	.59	.48	.47
Bakersfield	.95	.69	.49	.47
Fremont	.94	.71	.42	.35
Gasquet	.37	.23	.78	.68
Los Angeles	.99	.71	.20	.10
Long Beach	.96	.61	.46	.35
Sacramento	.96	.62	.52	.46
Santa Barbara	.57	.54	.69	.24
Sequoia National Park	.78	.40	.59	.54
Yosemite National Park	.94	.45	.68	.37

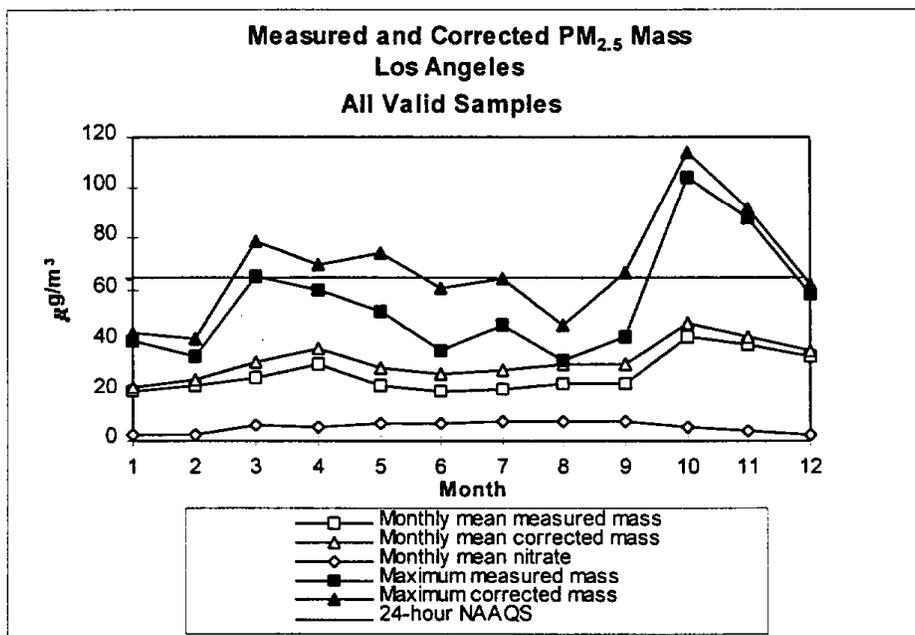


Figure 9. Annual plot of mass and nitrate concentrations for Los Angeles. The corrected mass accounts for observed nitrate losses due to ammonium nitrate volatilization.

mass. Note that the samples averaged for this plot represent two 12-hour samples every sixth day; from 6 a.m. to 6 p.m. and 6 p.m. to 6 a.m. The NAAQS is shown for comparison to the maximum measured mass. For Los Angeles, the difference between the average measured mass and the average corrected mass is greatest in the summer months. The corrected PM_{2.5} mass concentrations would increase the frequency of NAAQS violations compared to the measured PM_{2.5} mass.

Table 3. Fraction of PM_{2.5} mass volatilized as ammonium nitrate by site, season, and time of day for CADMP measurements.

Site	Summer daytime	Summer nighttime	Winter daytime	Winter nighttime
Azusa	.29	.22	.22	.18
Bakersfield	-.03	.05	.23	.12
Fremont	.19	.20	.20	.12
Gasquet	.03	.03	.01	.00
Los Angeles	.35	.07	.07	.03
Long Beach	.24	.23	.21	.08
Sacramento	-.07	.04	.26	.11
Santa Barbara	.05	.10	.19	.07
Sequoia National Park	-.04	.01	.24	.14
Yosemite National Park	.01	.01	.07	.05

*See footnote to Table 2 regarding negative numbers.

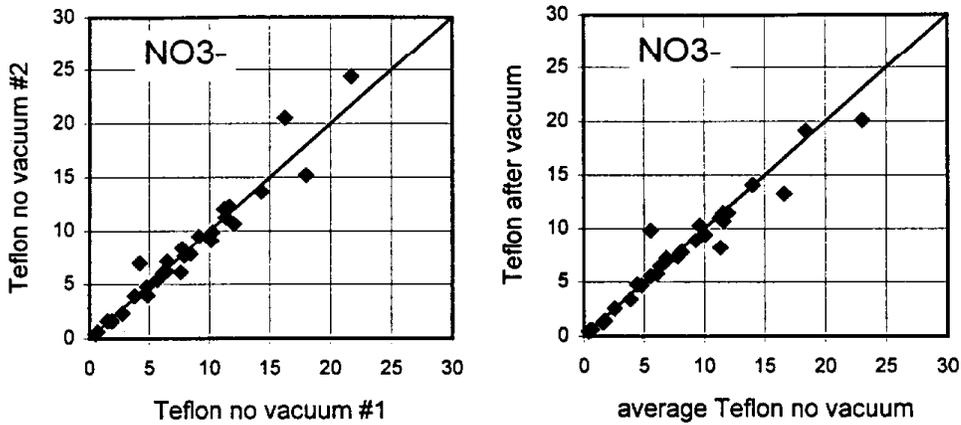


Figure 10. Comparison of nitrate concentrations in $\mu\text{g}/\text{m}^3$ collected on Teflon filters at Bakersfield between 1/22/97 and 3/19/97. The left plot compares the two samples that have not been subjected to vacuum between collection and analysis. The right plot compares the sample subjected to vacuum with the average of the two without vacuum.

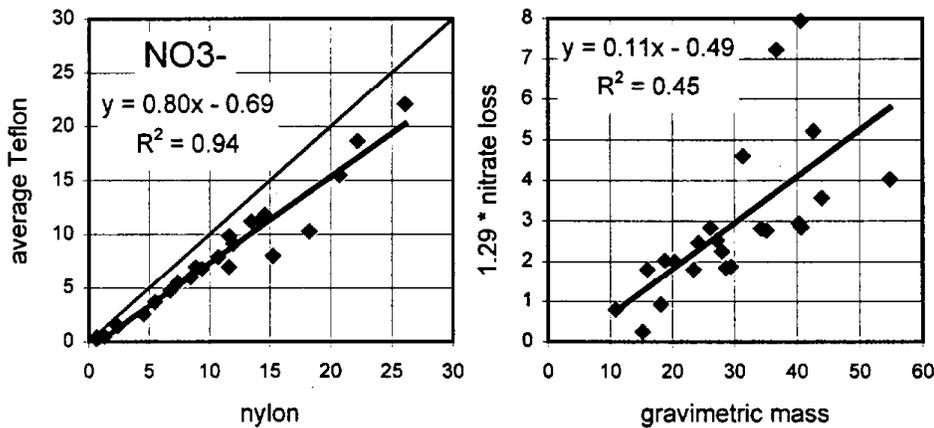


Figure 11. Comparison of nitrate concentrations and gravimetric mass in $\mu\text{g}/\text{m}^3$ collected on Teflon and nylon filters at Bakersfield between 1/22/97 and 2/12/79. The left plot compares the average from the three Teflon filters with that from the nylon filter. The right plot compares the lost nitrate (nylon minus Teflon), times 1.29 to account for the ammonium ion, with the measured gravimetric mass.

The right plot of Figure 11 compares the loss of nitrate, expressed as ammonium nitrate, with the measured gravimetric mass. The correlation is modest, with $r^2 = 0.45$. The slope of 0.11 (lost/measured) indicates that 10% of the ambient mass was lost during collection. The largest fractional loss from the ambient mass was 17%.

IMPROVE data

Bakersfield Field Test. As part of a comparison of the IMPROVE sampler with the new FRM sampler, a series of 23 PM_{2.5} samples were collected by the IMPROVE sampler on three Teflon filters and one nylon filter between January 22 and February 12, 1997. Seven additional samples were collected only on the Teflon filters, between March 11 and March 18. A carbonate-coated denuder was used in front of the nylon filter. All of the filters were analyzed for nitrate concentration using ion chromatography (IC) by Research Triangle Institute. Prior to the IC analysis one of the three Teflon filters for each set was placed in vacuum and analyzed for elemental composition by Particle Induced X-ray Emission (PIXE) using the Crocker Nuclear Laboratory cyclotron. It thus provides an additional test of whether additional nitrate is volatilized in vacuum. All filters were operated with face velocities of 100 cm/s.

Figure 10 compares the nitrate concentrations on the three Teflon filters for all 30 samples. The left plot compares the two filters that have not been subjected to vacuum between collection and IC analysis. The correlation coefficient (r^2) is 0.94. The slope of 1.04 ± 0.05 is not statistically different from unity. The ratio of means is 1.03. The average precision is 10%, which is slightly larger than predicted. The average relative precision is defined by:

$$P = \sqrt{\frac{2}{n} \sum_{i=1}^n \left(\frac{x_i - y_i}{x_i + y_i} \right)^2}$$

This demonstrates that the two measurements of nitrate on Teflon filters that were not exposed to vacuum are not statistically different. This is important in showing that the nitrate loss on Teflon is reproducible. That is, two identical samplers will yield the same nitrate loss.

The right plot of Figure 10 examines the question of whether additional nitrate is lost from the Teflon filter when the sample is placed in vacuum between collection and IC analysis. The nitrate values after exposure to vacuum are compared to the average of the values without exposure to vacuum. There is a small difference that is only marginally significant. The correlation coefficient (r^2) is 0.94. The slope is 0.90 ± 0.05 and the ratio of means is 0.97. The conclusion is that placing the filter in a vacuum before the IC analysis did not significantly remove any of the nitrate remaining on the filter after collection. Another way of stating the result is that that fraction of the nitrate that is volatile has already been removed during collection. Since it remains on the filter even in a vacuum, it will not be lost with normal handling. This suggests that the time between collection and analysis is not a major factor.

The left plot of Figure 11 compares the nitrate collected on Teflon filters with that collected on nylon filters. The nitrate values from all three Teflon filters are averaged. The slope is 0.80 ± 0.05 , representing a 20% loss of nitrate on the Teflon filters. The 20% loss is lower than the loss of 49% during the day and 47% during the night obtained for Bakersfield in winter using the CADMP sampler (Table 4).

These temporal plots for selected sites indicate that it is reasonable to examine the data in two seasons: summer and winter. Annual data is not appropriate because of seasonal variation of (1) the nitrate/mass ratio, and (2) the fraction of nitrate volatilized, based on the other California data.

Figure 15 shows the spatial distribution of the ratio of ammonium nitrate ($1.29 * \text{NO}_3$) to gravimetric mass for summer (June-August). All data collected between 1994 and 1997 are included; at some sites this includes only one summer. For most sites the ratio is below 5%, with values of 1% to 3% typical of the remote sites in the East. The ratio is much higher at sites near western cities. The maximum is 28% at San Geronio, east of the South Coast Basin, and at two sites in the Fraser Valley in British Columbia. It is 11% to 16% at other sites near San Francisco and Puget Sound.

Figure 16 shows the spatial distribution of the nitrate/mass ratio for winter (December-February). The ratios during winter are generally much larger than in summer and much less spatially uniform. The largest ratios, between 40% and 50%, are at San Geronio, Sequoia, and at Lone Peak, east of the Salt Lake City/Provo Basin. The ratios are above 25% at the two sites near San Francisco, the Columbia Gorge, Badlands, and Upper Buffalo. The ratios in Puget Sound are generally lower than in summer.

The summer and winter nitrate/gravimetric mass ratios for each site are listed in Table 5. The mean gravimetric mass concentrations are also given. The table is especially helpful in comparing summer and winter at each of the sites. The largest change is at Sequoia, with a summer ratio of 5% and a winter ratio of 47% and at Lone Peak, going from 5% to 40%. Badlands changes from 3% in summer to 26% in winter, while Boundary Waters goes from 2% to 24%.

IMPROVE Network. Figure 12 shows the locations of the IMPROVE sites where $PM_{2.5}$ nitrate was collected on a nylon filter following a carbonate denuder. $PM_{2.5}$ mass was measured from a Teflon filter. All samples were of 24-hour duration, starting at midnight.

The following analysis compares the nitrate collected on nylon filters with the gravimetric mass collected on Teflon filters. This ratio is the maximum loss possible, if all of the nitrate were to be volatilized. Figure 13 shows the temporal variation of the ratio of ammonium nitrate/gravimetric mass for 8 sites in California. At San Geronio, in the mountains east of the South Coast Basin, the ratio may be high at any time of the year. A very large seasonal dependence is seen at Sequoia and Yosemite, with low ratios during the summer and high during the winter. At Sequoia the increase begins in fall. At the other sites there is very little seasonal variation. At the four northernmost sites in California, nitrate rarely accounts for over 20% of the mass. The ratios are consistently higher at Pinnacles, south of the San Francisco region, but do not vary seasonally.

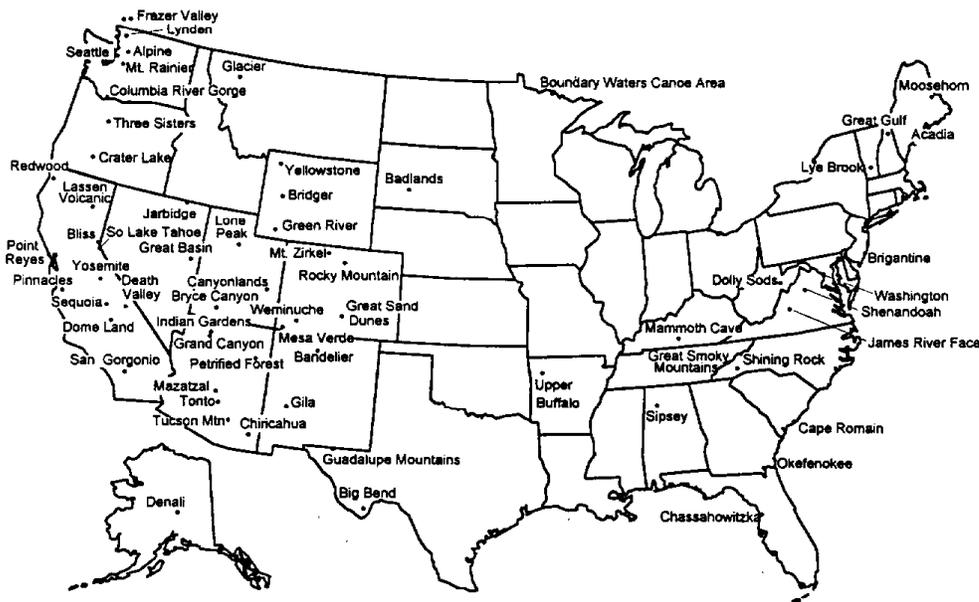


Figure 12. Sites in IMPROVE network measuring nitrate on nylon filter between 1993 and 1998.

Figure 14 shows the temporal variation of the ratio of ammonium nitrate/gravimetric mass for 14 IMPROVE sites outside California. At three sites in the Northwest, including Seattle, nitrate rarely accounts for over 20% of the mass. This is also true of most sites in the Eastern United States. The main exception is at the site in Washington DC, which can have relatively high contributions from nitrate in the fall and winter. In the southwestern United States, the nitrate ratio is generally low from the beginning of May

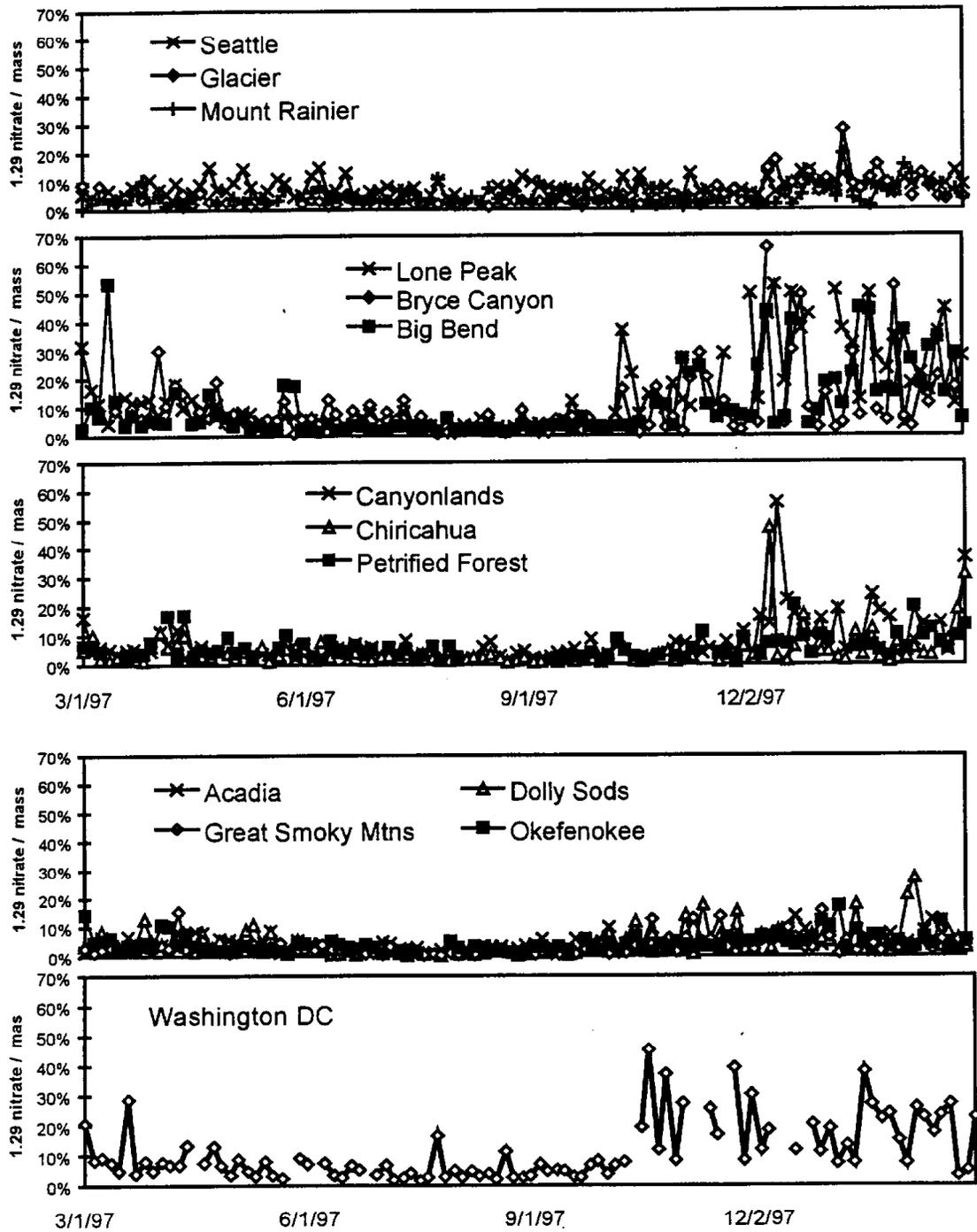


Figure 14. Time plots of the ratio of ammonium nitrate ($1.29 \cdot \text{NO}_3$) / gravimetric mass for 14 IMPROVE sites outside California.

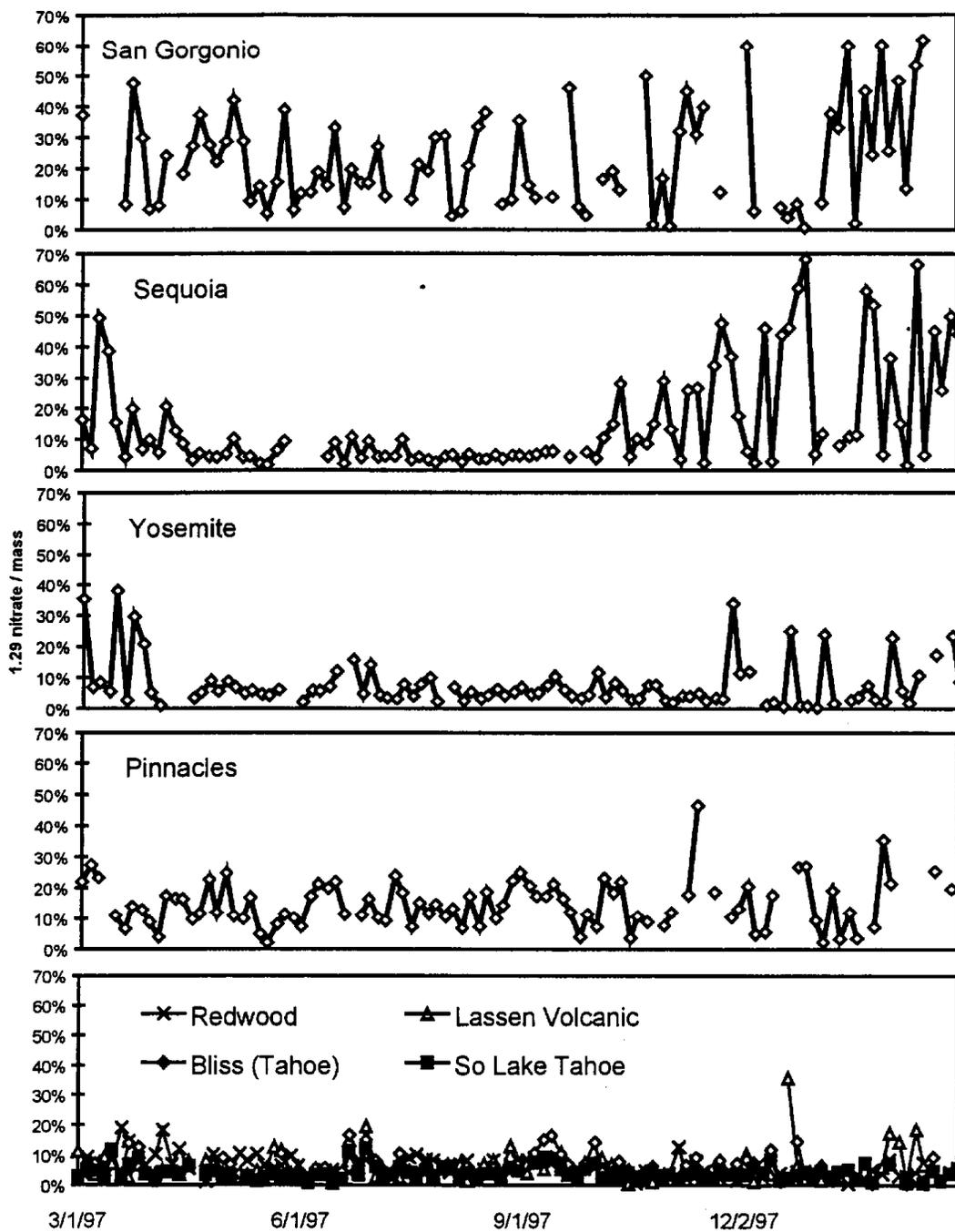


Figure 13. Time plots of the ratio of ammonium nitrate ($1.29 \cdot \text{NO}_3$) / gravimetric mass for 8 IMPROVE sites in California

Table 5. Ratio of mean ammonium nitrate (1.29*NO₃) measured on nylon to mean gravimetric mass measured on Teflon. IMPROVE sites summer (June-August) and winter (December-February) for samples collected between December 1994 and August 1997. The mean gravimetric mass is included for reference.

site	fraction		mass		site	fraction		mass	
	sum	win	sum	win		sum	win	sum	win
<u>California</u>					<u>Inland Southwest</u>				
Redwood	8%	7%	5.2	3.1	Canyonlands	4%	16%	4.5	2.1
Lassen Volcanic	5%	15%	4.3	1.2	Bryce Canyon	5%	15%	4.6	1.5
Bliss	6%	12%	4.3	2.1	Great Sand Dunes	3%	9%	4.2	1.9
So Lake Tahoe	4%	6%	7.1	11.8	Weminuche	3%	5%	3.9	1.7
Point Reyes	8%	34%	7.4	7.8	Mesa Verde	3%	7%	4.5	2.1
Yosemite	8%	16%	7.6	1.9	Indian Gardens	4%	6%	6.6	2.5
Pinnacles	16%	26%	5.9	4.0	Bandelier	3%	11%	4.5	2.5
Sequoia	5%	47%	18	6.2	Mazatzal	7%		4.7	
Dome Land	7%		9.8		Petrified Forest	4%	7%	5.1	2.6
San Geronio	28%	48%	10	4.0	Tonto	5%	10%	5.5	3.4
<u>Northwest Coast</u>					<u>Gila</u>				
Grand Canyon	5%	10%	4.3	1.8	Tucson Mountain	4%		5.7	
Frazer Valley BC	28%	13%	9.0	7.1	Chiricahua	3%	4%	5.7	2.7
Lynden	14%	18%	7.3	7.6	Guadalupe Mtns	4%	9%	7.0	3.9
Seattle	11%	6%	8.0	9.8	Big Bend	5%	5%	7.4	4.3
Alpine	7%	18%	5.2	2.5	<u>East</u>				
Mt Rainier	5%	3%	6.4	3.3	Moosehorn	3%	9%	8.1	5.5
Columbia East	6%	30%	6.2	6.6	Acadia	3%	9%	10.4	5.6
Columbia West	8%	13%	6.2	3.9	Great Gulf	1%		10.4	
Three Sisters	4%	8%	5.6	1.4	Brigantine	4%	19%	15.2	10.6
Crater Lake	3%	9%	4.5	1.5	Lye Brook	3%	15%	11.7	5.5
<u>Inland Northwest</u>					Washington DC				
Glacier	2%	12%	6.0	5.0	Dolly Sods	1%	12%	20.6	7.5
Yellowstone	3%	13%	5.0	1.5	James River Face	2%	10%	20.5	12.5
Bridger	4%	8%	3.8	1.1	Shenandoah	2%	17%	19.2	6.1
Jarbridge	2%	13%	5.1	1.7	Mammoth Cave	2%	13%	20.0	9.5
Green River		11%		3.0	Great Smoky Mtns	1%	9%	20.5	6.9
Mt Zirkel	4%	9%	3.8	1.4	Shining Rock	1%	7%	16.6	3.7
Rocky Mountain	6%	15%	5.0	1.5	Upper Buffalo	3%	27%	14.5	7.3
Lone Peak	5%	40%	6.8	4.6	Sipsey	2%	18%	17.4	9.3
Great Basin	4%	11%	4.3	1.6	Okefenokee	3%	7%	12.4	8.7
<u>North Central</u>					Cape Romain				
Badlands	3%	26%	5.7	3.8	Chassahowitzka	4%	7%	11.6	9.3
Boundary Waters	2%	24%	6.7	5.1	<u>Alaska</u>				
					Denali				
					1%	6%	3.3	1.4	

low as 3 cm/s experience nearly the same nitrate loss as samplers that use a face velocity of 21 cm/s. Moreover, the nitrate loss on samplers that use a face velocity of 21 cm/s is nearly 100% during summer daytime conditions. It is more important to collect a sample on nylon filters for nitrate analysis. It is equally important to collect additional samples on Teflon and quartz filters for analysis of mass, elements, and carbon. It is not clear yet how the ammonium ion should be collected, but it is likely that the best method would be to use an acidified filter preceded by an ammonia denuder. Field and laboratory testing is needed to confirm this.

Although there is loss of volatile nitrate from Teflon filters, the nitrate remaining after collection is quite stable. We found little, if any, loss of volatile nitrate from Teflon filters after as much as two hours under vacuum and approximately one minute of PIXE analysis.

Recommendations

The Federal Reference Method for fine particulate matter defines the measurement procedure for compliance with the National Ambient Air Quality Standard. The method requires collecting the particles on 47mm Teflon filters at a flow rate of 16.7 liters per minute. There will be a loss of mass from these filters as ammonium nitrate evaporates, especially during the daytime periods, but the method is prescribed and deviation is not allowed.

Although this study has shown significant loss of nitrate from Teflon filters, Teflon filters have a number of desirable characteristics for collecting fine particles. They have a low pressure drop so the flow rate can be relatively high, they have a low initial mass which reduces uncertainty in gravimetric analysis, and they have a low blank for elemental analysis by x-ray fluorescence or PIXE analysis. If an accurate measure of mass is desired using a single sampler, it could be obtained using a nitric acid denuder followed by a filter pack of a Teflon filter followed by a nylon filter. The Teflon filter could be weighed directly, and the nylon filter could be analyzed for nitrate. The total mass is the sum of the gravimetric mass from the Teflon filter plus $1.29 \times \text{nitrate}$ from the nylon filter.

The utility of speciation monitoring for source identification and apportionment have been widely recognized. It is important to also recognize the benefits of complete particle speciation for quality assurance of gravimetric mass measurements. The procedure described above, or an equivalent one, is necessary to obtain the fine particle mass, but additional measurements of elemental content, inorganic ions, and organic content allow for quality assurance of the gravimetric mass, which otherwise has none. In particular, the sum of species should be relatively close to the gravimetric mass measurement (after adding the volatile nitrate to the gravimetric mass). Without such a quality assurance check, spurious mass measurements can go unnoticed.

Summary and Conclusions

The loss of volatile nitrate from Teflon filters during sampling can be a significant fraction of the total $PM_{2.5}$ mass. There is no straightforward way to correct for this loss without measuring it, nor is there a way to determine how much it affects the particle size distribution. The mass loss due to nitrate is greatest in southern California urban areas during the summer, and can be as high as 20-30% of the actual $PM_{2.5}$ mass (or 30-50% of the mass measured on Teflon filters). If the loss also includes the ammonium ion, it may be as high as 25-35% of the actual $PM_{2.5}$ mass. In Sacramento, Bakersfield, and Sequoia National Park the $PM_{2.5}$ mass loss is greatest during the winter, amounting to 15-20% if nitrate only is considered, or 15-25% if the loss includes the ammonium ion.

The potential mass loss identified in the IMPROVE data is consistent with that found in the CADMP data. In Bakersfield during the winter, the ammonium nitrate loss represents 10% of the measured $PM_{2.5}$ mass, comparable to the 10-19% mass loss measured in the CADMP program. At other IMPROVE sites in California, the potential mass loss is site-dependent. At northern California sites, the potential loss due to ammonium nitrate volatilization is generally less than 10%. At Sequoia and Yosemite National Parks, the potential loss is less than 10% in the late spring through early fall, and ranges up to 30-70% in the rest of the year. At San Geronio Wilderness there is a slight seasonal dependence, but the potential loss can range up to 30-60% at any time of year. At Pinnacles National Monument, there is also little seasonal dependence, with the potential loss ranging up to 20-30% throughout the year.

At IMPROVE sites outside California, the same pattern of site dependence is observed. At sites in the northwest and in the east (except Washington, D.C.), there is little seasonal dependence, and the potential mass loss due to ammonium nitrate volatilization is generally less than 10%. In Washington, D.C., and at some sites in the southwestern U.S., the potential mass loss is low (less than 10%) in late spring through early fall, and ranges up to 30-50% during the remainder of the year. At some other sites in the southwestern U.S., the potential mass loss remains less than 10% throughout the year, except for rare excursions up to 50-60% in late fall.

There is a significant implication of this loss to the EPA's reference method for sampling that relies on the use of Teflon filters for mass concentrations. The systematic bias in this sampling method is likely to result in a bias in recommended control strategies. If the measured mass is underrepresented by the nitrate in the atmosphere, other sources of particulate matter will be overrepresented. Control strategies developed from biased data will tend to overemphasize controls on nonvolatile species. More importantly, control strategies developed in this way may be ineffective at reducing particulate matter concentrations as required by the Clean Air Act. In particular, the control strategies are likely to be biased toward sources of fugitive dust and other primary particle emission sources, and less toward sources of NO_x and NH_3 .

This analysis also has implications for the sampling methods being considered by the EPA for speciation monitoring. It does not seem to matter whether samples collected on Teflon filters use a high or low filter face velocity. Samplers that use a face velocity as

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**The Magnitude of Bias in the Measurement of PM_{2.5} Arising from Volatilization of
Particulate Nitrate from Teflon Filters**

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Abstract

Because the Federal Reference Method for $PM_{2.5}$ specifies the collection of ambient particles on Teflon filters, we have examined the loss of a known volatile species, particulate nitrate, during sampling. Data are presented from two studies in southern California for which parallel samples were collected by different methods. Differences in collected nitrate are modeled using an evaporation model based on the work of Zhang and McMurry. The average nitrate obtained from sampling with Teflon filters was 28% lower on average than that measured by denuded nylon filters. In contrast, cascade impactor samples were within 5% of the denuded nylon filter on average. A simple model is presented that accounts for the particulate nitrate loss from Teflon filters either by scrubbing of nitric acid and ammonia in the sampler inlet or by heating of the filter substrate during sampling. The observed magnitude of the loss is explained by any of the following situations: (i) 100% nitric acid and ammonia vapor loss in the inlet, (ii) $5^{\circ}C$ heating of the filter substrate above ambient temperature during sampling, or (iii) a combination of these factors such as 50% vapor loss in the inlet and $3^{\circ}C$ heating of the filter.

measured by Teflon filters and by denuded nylon filters. The denuded nylon filter system is designed to provide an accurate measure of particulate nitrate, as described by Appel *et al.*¹. The denuder removes gaseous nitric acid by diffusion to a MgO-coated surface while allowing the particles to penetrate. The particles are then collected on a nylon filter which retains the nitrate because of its affinity for nitric acid.

The 1987 Southern California Air Quality Study (SCAQS) is of interest because it includes simultaneous measurements of particulate nitrate by different methods, including impactors as well as Teflon filters and denuded nylon filters. As such it provides an independent comparison to the denuded nylon filter method. However, samples collected during SCAQS were of short duration, 4 to 7 hours, and were retrieved immediately at the end of each collection period. Thus, the nitrate losses found here represent a lower limit for what would be expected for 24-hr sampling, with retrieval of the sample one or more days after collection.

The 1986 Caltech Study is of interest because the Caltech protocol more closely resembles that proposed for the national PM_{2.5} monitoring program. In the Caltech study samples were collected over a 24-period, commencing at midnight. Measurements were made at nine sites, every sixth day, throughout the year of 1986, with filter placement the day before and filter retrieval the day after sampling. Fine particulate nitrate concentrations were measured by using the denuded nylon filter method and by using a Teflon filter, such that the losses from the Teflon filter can be quantified. It provides an extensive data base representative of a variety of meteorological conditions.

In the discussion that follows, we first compare measurement methods through the SCAQS data set. Second, we examine losses for 24-hr sampling using the Caltech data set. Observed losses in the Caltech data set are discussed in terms of an evaporative model of Zhang and McMurry⁹⁻¹⁰. Those investigators applied their model to explain differences between impactor and filter sampling using the SCAQS data. In this work we extend their model to take into account changes due to temperature rise in the sampler.

SCAQS: Comparison of Filter and Impactor Measurements

The three systems used for the measurement of fine particulate nitrate in the SCAQS are: (1) a PM_{2.5} Teflon filter, (2) a PM_{2.5} denuded nylon filter and (3) a Berner impactor¹¹. Filter samples were collected with the SCAQS sampler¹² wherein the Teflon filter was preceded by a Sensidyne (Bendix 240) cyclone to remove particles above 2.5 μm and the

The Magnitude of Bias in the Measurement of PM_{2.5} Arising from Volatilization of Particulate Nitrate from Teflon Filters

Introduction

In July, 1997 the United States Environmental Protection Agency (EPA) promulgated a new ambient air quality standard for fine particles, or PM_{2.5}. The new regulation specifies a reference method for measuring PM_{2.5}. For regulatory purposes, PM_{2.5} is defined by this federal reference method. However, from a scientific point of view, PM_{2.5} is defined as the dry mass of airborne particles with diameters less than 2.5 μm aerodynamic diameter. The purpose of this paper is to evaluate one aspect of the extent by which these two definitions, the scientific and the regulatory, differ.

The federal reference method for PM_{2.5} is a gravimetric mass measurement of particles penetrating a specified size-selective, PM_{2.5} inlet. These particles are collected for 24 hours on a Teflon filter, which is then transported to a laboratory, equilibrated at room temperature and low relative humidity, and weighed. The sampling rate is 16.7 L/min through a 47 mm diameter filter.

Many studies have shown that particulate nitrates are easily volatilized during sampling with Teflon filters¹⁻⁶. The mechanism for this loss is the dissociation of collected particulate ammonium nitrate to form gas phase nitric acid and ammonia. How important is this loss to the determination of PM_{2.5} mass? Because many studies have shown that nitrates are a major component of fine particles in many regions of the western United States, we chose to examine this issue further.

The specific question addressed in this paper is the magnitude of the discrepancy between the scientific and regulatory definitions of PM_{2.5} due to the volatilization of particulate nitrate. We examine data from two field measurement programs in the Los Angeles Basin, the 1986 Caltech study⁷ and the 1987 Southern California Air Quality Study⁸. Both of these studies feature side-by-side comparison of particulate nitrate concentrations

than those from the Teflon filter. For the fall sampling period the agreement between the impactor and denuded nylon filter measurements is closer than for the summer, as reported by Hering et al.¹⁴. On average the particulate nitrate concentration measured using the impactor was lower than the denuded nylon filter value by just 2% for the fall measurements, and by 7% for the summertime measurements (with an overall difference of 5%). Correspondingly, the nitrate measured with the impactor is 21% higher than from the Teflon filter. However, we note that the mean sulfate concentration from the impactor was within 2% of that from the Teflon filter for both for summer and fall sampling. Thus, the collection on Teflon filters is in agreement with the impactor for a nonvolatile species, sulfate, but is lower than the impactor for a volatile species, nitrate.

Evaporative losses from filters and impactors have been modeled by Zhang and McMurry^{9,10}. In their 1992 paper they explicitly applied their model to the SCAQS data set presented here. They found that differences between nitrate collected by nylon and Teflon filters could be explained by their model, with greater losses during periods with warmer temperatures, when the thermodynamic equilibrium for ammonium nitrate favors larger vapor phase concentrations. Similarly, their model correctly predicted the lower evaporative losses observed for impactor sampling as compared to filter sampling.

This analysis of the SCAQS data set shows the following: (i) the lowest nitrate values from the Teflon filter relative to the nylon filter are found during the summer, and during the hottest periods of the day, and (ii) impactor-based fine particulate nitrate values are higher than those from the Teflon filter but close to the value from the denuded nylon filter while sulfate measurements made by Teflon filters and impactors agree. The differences between the particulate nitrate measured by Teflon filters and impactors has been explained by the higher evaporation from filters by the modeling of Zhang and McMurry¹⁰ and by the laboratory experiments of Wang and John¹⁵. Furthermore, the agreement between the denuded nylon filter and the impactor data argues against positive artifacts on the MgO-denuded nylon filters. Thus the difference between the particulate nitrate measured by denuded nylon filters and that measured by Teflon filters, i.e. the discrepancies shown in Figures 1 and 2, is attributed to volatilization of ammonium nitrate. For the remainder of the discussion of this paper we will refer to the difference between the nitrate collected on a denuded nylon filter nitrate and that collected by a Teflon filter as "volatilized nitrate" or "nitrate loss".

nylon filter samples were preceded by an AIHL-design cyclone¹³ to remove particles larger than 2.5 μm and a MgO tubular denuder⁷ to remove nitric acid. Measurement precision determined by collocated sampling was 6-7% for sulfate and nitrate¹². The Berner impactor provides particle collection in multiple particle size ranges from 0.05 to 10 μm aerodynamic diameter, and was operated with greased Tedlar substrates¹¹. The $\text{PM}_{2.5}$ ion concentrations were derived from the impactor size distribution measurements using the particle penetration efficiency curve for the AIHL cyclone, as described by Hering et al.¹⁴. In other words, the difference in the shape of the cyclone and impactor cutoffs was taken into account by using the complete impactor size distribution to calculate the mass that would penetrate through an AIHL cyclone. All samples were analyzed for nitrate by ion chromatography. The filter measurements were made at more sites than were the impactor measurements.

Scatter plots comparing the nitrate collected on Teflon filters to that collected on denuded nylon filters are given in Figure 1 for summer (June-September) and fall (October-December) SCAQS sampling periods. Teflon filter nitrate values are consistently lower than those from denuded nylon filters, although discrepancies are not as large for fall sampling periods as for the summer. Averaged over all samples the Teflon filter nitrate values were 28% lower than those from the denuded nylon filters. For summertime sampling the Teflon filter values were 61% lower on average. The mean difference in measured nitrate was 8 $\mu\text{g}/\text{m}^3$ for the summer and 7 $\mu\text{g}/\text{m}^3$ for the fall, with individual samples differing by as much as 54 $\mu\text{g}/\text{m}^3$.

Discrepancies between the two filter types depended on the time of day, as well as season. Figure 2 shows the same comparisons for summertime measurements at four sites, wherein data are segregated by the time of day that the samples were collected. Morning sampling refers to those samples collected between 0600 and 1000 PDT. Daytime samples were collected from 1000 to 1400, and from 1400 to 1800 PDT; nighttime samples were collected from 1800 to 0100, and 0100 to 0600. For seven of the eight sites in the Los Angeles area, the mean discrepancy between Teflon and denuded nylon filters for summer daytime samples was between 80% to 90% while those for nighttime sampling varied from 40% to 60%. Similar results are reported by John et al.⁴ who compared 12-hr Teflon filters to parallel denuded nylon filters and found that the Teflon values were 60% to 90% lower during the day and 10% to 50% lower at night.

Figure 3 shows that the summer particulate nitrate concentrations measured by the Berner impactor are much closer to the $\text{PM}_{2.5}$ nitrate values from the denuded nylon filter

times, their model predicts that the amount of nitrate lost is equal to the mass that must be evaporated from the filter to yield nitric acid and ammonia vapors at their saturation vapor pressures for the conditions immediately downstream of the filter. This volatilization process is driven by three factors: depletion of nitric acid and ammonia vapors ahead of the filter, increase in the filtration temperature above ambient; and the decrease in pressure downstream of the filter.

For the Teflon filters in the Caltech sampler we calculated an asymptotic value for the loss of nitrate corresponding to long sampling times for two scenarios. Scenario I assumes: (i) 100% vapor depletion above the filter, (ii) no elevation above ambient in the sampling temperature, and (iii) no pressure drop in the sampling system. Scenario II assumes: (i) partial vapor depletion above the filter (ii) elevation of filter temperature above ambient during sampling and (iii) no pressure drop. Scenario I is analogous to the worse-case situation modeled by Zhang and McMurry. Scenario II introduces the additional factor of sample heating. Losses can be driven by pressure drop across the filter¹⁶, but for these data the flow-induced pressure drop was measured to be less than 0.02 atmospheres. The corresponding 2% change in vapor pressure is small by comparison to the scenario assumptions of complete vapor depletion or temperature elevation, and thus was neglected in this analysis.

In our calculation the maximum loss of ammonium nitrate from the Teflon filter is taken to be the lesser of (i) the summation over time of the nitrate mass per unit air volume which brings the concentration of gas phase ammonia and nitric acid downstream of the filter back to equilibrium, or (ii) the airborne particulate nitrate concentration as measured by the denuded nylon filter. Because the variation in nitrate concentration over the 24-hour sampling period is unknown, we have ignored the induction time, described in the theory of Zhang and McMurry, which accounts for a lower loss rate at the beginning of the sample when the deposited nitrate is lower than the asymptotic evaporation rate. Instead, we simply do not allow the loss to exceed the particulate nitrate concentration as measured by the denuded nylon filter.

Calculations were done for two of the sites, downtown Los Angeles and Upland, for which the hourly temperature data are available during the year of the Caltech measurements. For each hour of the day the equilibrium dissociation constant for ammonium nitrate, K , was calculated from the temperature based on Mozurkewich¹⁷:

1986 Caltech Study

The data set from the Caltech Study consists of 526 samples collected at 9 sites in the Los Angeles Basin over the entire year of 1986, as reported by Solomon et al.⁷. All samples were 24 hours in duration, beginning at midnight, as proposed for the PM_{2.5} reference method. Particles were collected on Teflon filters at a face velocity of 5 cm/s (3 L/min on a 47 mm diameter filter) downstream of an AIHL cyclone. Denuded and undenuded nylon filters were collected downstream of the same cyclone. These were also 47 mm filters, operated at the same face velocity of 5 cm/s. As in the SCAQS sampler, the denuder consisted of parallel MgO coated glass tubes. The total flow through the cyclone was 24.8 L/min. The measurement precision for PM_{2.5} nitrate was 5%⁷

For the Caltech data set Solomon et al.⁷ compared the Teflon filter and denuded nylon filter values for fine particulate nitrate. They found that the Teflon filter nitrate (Tef) was linearly correlated with the denuded nylon filter (Ny) as follows: $Tef = 0.82 (Ny) - 1.98 \mu\text{g}/\text{m}^3$, with a correlation coefficient $R = 0.92$ ($N=526$). On average, for these nine sites over the entire year of 1986, the Teflon filter nitrate values were lower than the denuded nylon filters by $3.5 \mu\text{g}/\text{m}^3$.

The Caltech data from all nine sampling sites are composited in Figure 4, with distinction made between the fall-winter season (October through March) and the spring-summer season (April through September). As with the SCAQS data set, the largest percentage discrepancies are seen in the summer sampling period. However, the data show that the mass of particulate nitrate lost on a single day can be high at any point within the year. For the spring-summer months volatilized nitrate averaged $4 \mu\text{g}/\text{m}^3$ with a maximum single day loss of $18 \mu\text{g}/\text{m}^3$, for the fall-winter months the average loss was $3 \mu\text{g}/\text{m}^3$ with a maximum single day loss of $17 \mu\text{g}/\text{m}^3$.

The differences among sites can be seen in Figure 5 which shows a time series of the fraction of particulate nitrate lost. These data are for six sampling sites located within the Los Angeles Basin. This graph indicates a degree of correlation among sites, that is nitrate loss tends to be high (or low) at all sites on the same day. This suggests that a common variable, perhaps meteorological, may influence the extent of nitrate loss.

Comparison of Caltech Data to Theory

To better understand the nitrate loss, we examined the data using an asymptotic form of the evaporative model of Zhang and McMurry¹⁰. In the approximation of long sampling

Scenario II assumes partial depletion of vapor above the filter, and elevation of the filter temperature above ambient. With partial vapor depletion the amount of nitrate loss depends on the ratio of nitric acid to ammonia immediately above the filter as well as other factors. The calculation can be done for any known ratio, but this was not known. Thus we present the calculation for the simplest case, corresponding to equal molar concentrations of nitric acid and ammonia at the inlet of the filter. Including the effect of elevation of the filter temperature, the nitrate loss is given by:

$$\Delta\text{NO}_3^- = \frac{745.7}{T} \frac{1}{24} \sum_{i=1}^{24} [\sqrt{K_{\text{fltr},i}} - \gamma \sqrt{K_{\text{amb},i}}]$$

for Scenario II with sufficient NO_3^- (3)

Here γ is the fraction of vapor penetrating the inlet to the filter, and $K_{\text{fltr},i}$ is the dissociation constant evaluated at the filter temperature during hour i . If the molar concentration of ammonia ahead of the filter is greater than nitric acid, nitrate losses will be somewhat lower than predicted by this equation.

Heating of the filter can be important because the value of \sqrt{K} approximately doubles for every 5°C increase in temperature over the range from 0 to 40°C. By expressing the filter temperature as a fractional increase above the ambient temperature:

$$T_{\text{fltr},i} = T_{\text{amb},i} (1 + x) \quad (4)$$

the increase in the dissociation constant with temperature is approximated using a first order Taylor series expansion:

$$\begin{aligned} \sqrt{K_{\text{fltr},i}} &= \exp((12042/T - 3)x) \sqrt{K_{\text{amb},i}} \\ &= \kappa \sqrt{K_{\text{amb},i}} \end{aligned} \quad (5)$$

By comparison with $\sqrt{K_{\text{amb},i}}$ the value of κ varies slowly with temperature, and can be evaluated using the daily average temperature. For example, starting at 15°C, a 10°C temperature increase corresponds to a 3% increase in κ and a 370% increase in $\sqrt{K_{\text{amb}}}$.

$$\ln K = 118.87 - \frac{24084}{T} - 6.025 \ln T \quad (1)$$

where the units for K are nanobars², and T is in Kelvins. Equation (1) applies to a pure solid or saturated solution of ammonium nitrate, and as such represents an upper limit for the nitric acid and ammonia vapor concentrations in equilibrium with atmospheric aerosol. For the Caltech data set we compared the measured value of $K^{1/2}$ obtained from measured vapor nitric acid and ammonia concentrations to that calculated from ambient temperature using equation (1). We found that on average the measured and calculated values agreed to within $\pm 15\%$.

For Scenario I the nitrate loss ΔNO_3^- in $\mu\text{g}/\text{m}^3$ is obtained by converting the equilibrium partial pressure for nitric acid to a mass concentration, noting that the ammonia and nitric acid are formed in equal parts from the disassociation of the salt. For 24-hr sample collection at a constant flow rate, the nitrate loss is:

$$\begin{aligned} \Delta\text{NO}_3^- &= \frac{745.7}{T_R} \frac{1}{24} \sum_{i=1}^{24} \sqrt{K_{\text{amb},i}} && \text{when } \Delta\text{NO}_3^- < \text{NO}_3^- \\ &= \text{NO}_3^- \text{ otherwise} && \text{Scenario I} \quad (2) \end{aligned}$$

where:

ΔNO_3^- = nitrate loss in units of $\mu\text{g}/\text{m}^3$

$K_{\text{amb},i}$ = dissociation constant in nb² evaluated from equation (1) at the ambient temperature T_i measured during hour i .

T_R = reference temperature for the sampled air volume in Kelvins

The factor 745.7 results from the conversion of nitric acid concentrations measured in nanobars to nitrate concentrations measured in $\mu\text{g}/\text{m}^3$. Equation (2) calculates ΔNO_3^- by taking the average of the square root of the dissociation constant over each hour of the day. This is important because \sqrt{K} is a strongly nonlinear function of temperature, and its average value is not accurately predicted based on the average daily temperature. The loss is not allowed to be greater than NO_3^- , which is the particulate nitrate concentration measured by the denuded nylon filter.

for the period from mid-April to early June. Overall, the predictions corresponding to $\kappa\text{-}\gamma=1$ appear to provide a reasonable estimator of the nitrate loss for the Caltech data.

Implications for PM_{2.5} Mass

The loss of ammonium nitrate and other volatile species from Teflon filters reduces the particle mass measured gravimetrically. For the SCAQS and Caltech data sets we estimated the magnitude of the particle mass loss assuming that the volatile nitrate was ammonium nitrate, which yields a corresponding mass loss equal to 1.29 x nitrate lost. It is noted that the gravimetric mass was usually determined on Teflon filters collected in parallel to the Teflon filters assayed for nitrate. Because both were collected at the same temperature and face velocity, sampling losses should be equivalent. However, it was not determined whether there were additional losses for the gravimetrically assayed filters during the conditioning done prior to weighing.

The mass ammonium nitrate lost is expressed as a percentage of the gravimetric mass measurement in Figure 7. Since nitrate losses are driven by changes in equilibrium during sampling (either due to temperature increases, vapor depletion or filter pressure drops), these losses are not expected to correlate with the gravimetric mass. The data are presented in this format because of the regulatory interest in the accuracy of gravimetric mass determinations. We note that for individual samples the loss was as much as 60% of the gravimetric mass. As shown in Table 2, the results for the two studies are similar. The mean percentage loss, also shown in Table 2, was 17 % - 21 % for spring-summer measurements, and 9 % - 13 % for fall-winter. The mean mass loss varied from 4 $\mu\text{g}/\text{m}^3$ to 7 $\mu\text{g}/\text{m}^3$, or about 25%-50% of the proposed annual PM_{2.5} standard.

Discussion

The regulatory definition of PM_{2.5} mass is the gravimetric mass of particles collected on a Teflon filter by the Federal Reference Method (FRM) Sampler. This quantity will be lower than the dry mass of suspended particles below 2.5 μm aerodynamic diameter due to evaporation of ammonium nitrate and other volatile species during sampling.

What losses may be expected from the PM_{2.5} FRM? Our analysis shows that these losses will depend on: (i) the loss of nitric acid and ammonia vapors in the inlet, (ii) the heating of the filter above ambient and (iii) the ambient temperature.

(To within $\pm 7\%$ the value of κ can be approximated by $\kappa \approx \exp(37x)$ over the temperature range from 0 to 40°C.)

With this approximation equation (3) becomes:

$$\Delta \text{NO}_3^- = \left(\frac{745.7}{T} \right) (\kappa - \gamma) \frac{1}{24} \sum_{i=1}^{24} \sqrt{K_{\text{amb},i}}$$

for Scenario II with sufficient NO₃- (6)

This equation reduces to equation (2) for the conditions of Scenario I, namely no increase in the filter temperature above ambient ($x=0$ and $\kappa=1$) and with no vapor penetration through the inlet ($\gamma=0$).

Equation (6) gives a simple way to evaluate the combined effect of vapor depletion in the inlet of the sampler, given by $(1-\gamma)$, and the effect of an increase in the filter temperature above ambient, expressed through κ . Typical values of κ are given in Table 1. At an ambient temperature of 20°C (293K) an elevation of the filter temperature above ambient by 2.9°C corresponds to a value of $x=0.01$, and yields a value of $\kappa = 1.46$. For a 5.3°C increase in temperature, $\kappa=2$, in other words the value of the dissociation constant doubles.

Figure 6 compares the nitrate loss measured by the difference between the denuded nylon filter and the Teflon filter to the calculated maximum loss for the case of $\kappa-\gamma = 1$. This graph is applicable to several scenarios. It describes Scenario I, with the filter operated at ambient temperature ($\kappa=1$) and 100% vapor depletion before the filter (penetration= $\gamma=0$). It applies to Scenario II, with approximately 5°C heating of the filter above an ambient temperature of 10-20°C ($\kappa=2$), with no vapor depletion ($\gamma=1$). It also describes the combined effect of about 3°C heating of the filter ($\kappa=1.5$) with a 50% vapor depletion ($\gamma=0.5$). Note that the calculated value is an asymptotic loss that neglects the lower loss rate at the outset of sampling, and as such represents the maximum loss for $\kappa-\gamma=1$.

For much of the data, our analysis provides a reasonable estimate of the nitrate loss from the filters for 24-hr sampling. For downtown Los Angeles most of the data in Figure 6 are just below the 1:1 line, indicating that the measured loss is somewhat less than calculated. Some of the data from Upland show greater losses than predicted. Most of these points were

reported while the concentration of nonvolatile substances such as soil dust and sulfates are not, then control strategies would selectively emphasize sources of nonvolatile species. As such, the issue of measurement bias in an air quality standard could be very important from the perspective of the cost of inappropriate controls. Second, while it is possible to construct different samplers that agree with an accurate measure of fine particles (as demonstrated here in the comparison of nitrate data from cascade impactors and denuded nylon filters), it is nearly impossible to design alternative systems that will replicate a measurement bias under a variety of atmospheric conditions. Thus it is unlikely that monitoring networks will be able to take advantage of innovations in particle measurement technology that could provide automated, semi-continuous particle characterization methods if that characterization must match the results obtained by the PM_{2.5} Federal Reference Method Sampler.

Summary

Using two data sets from southern California, we have shown that the mean loss of ammonium nitrate in that locale from sampling with Teflon filters is in the range of 4 to 7 $\mu\text{g}/\text{m}^3$, or 9% to 21% of the gravimetric mass. These numbers are derived by comparison to side-by-side sampling with denuded nylon filters. We have further shown that the denuded nylon filters are in close agreement with impactor data for fine particulate nitrate, which argues for the accuracy of these two measurement methods.

The southern California data show that the discrepancy between the Teflon filters and denuded nylon filters are greatest during summer daytime samples, and also tend to be larger during warm summer months than during colder winter months. Further, we have found similar trends across sites in the Los Angeles Basin in the nitrate loss on a given day of sampling.

Both the magnitude and the variability in the nitrate losses can be accounted for through a simple model that takes into account the temperature dependence of the equilibrium dissociation constant for ammonium nitrate, coupled with a slight elevation of the sampling temperature above ambient or the loss of vapor nitric acid and ammonia in the sampling inlet. This model is based on the evaporative model of Zhang and McMurry, for which we have explicitly taken into account the increase in equilibrium vapor pressure with temperature.

We have used these results to estimate the potential ammonium nitrate loss that may be expected from the PM_{2.5} FRM, and predict losses somewhat higher than that observed for the Caltech Study. In regions where particulate nitrate is an important constituent of fine

First we examine nitric acid loss in the inlet. The FRM sampler uses a PM₁₀ inlet similar to that which has been used on the dichotomous sampler. John et al.⁴ showed that this inlet, when clean, is an effective denuder for nitric acid. For summertime measurements in Claremont, California they found that the anodized aluminum surface of the inlet tube effectively removed nearly 100% of the nitric acid. Penetration under moist wintertime conditions would certainly be no better. Thus, one expects that for the FRM sampler the nitric acid penetration is close to zero, or $\gamma=0$ in equation (6).

Next we examine heating of the sample. The FRM specifications require that the filter temperature be maintained within 5°C of ambient (Federal Register). In practice, filter temperatures are often 3°C above ambient (EPA docket). Although the filter chamber of the FRM sampler is ventilated, the sampled air can be elevated above ambient temperature due to solar heating of the inlet. From Table 1, the 3°C heating results in an increase in the equilibrium nitric acid concentration corresponding to a value of $\kappa = 1.5$.

Using equation (6) with $\kappa-\gamma = 1.5$, the potential nitrate loss can be calculated from the hourly ambient temperature data. By potential loss, we refer to the maximum loss if sufficient ammonium nitrate is present in the particle phase. Using the 1986 daily temperature profiles for Los Angeles and Upland, we calculated the potential ammonium nitrate loss for the PM_{2.5} FRM samplers assuming a value of $\kappa-\gamma = 1.5$. For days with an hourly maximum temperature above 25°C, the calculated potential mass loss is greater than 13 $\mu\text{g}/\text{m}^3$. Of course, the actual loss will be lower if the true fine particulate nitrate concentration is lower.

The implication of this work is that one can expect substantial mass loss, by comparison to the federal standard for PM_{2.5}, due to volatilization of ammonium nitrate during sampling in those areas of the country where ammonium nitrate is a significant contributor to the fine particle mass, and where ambient temperatures tend to be warm. The rate of loss is higher at higher ambient temperature, when measured nitrate concentrations tend to be lower. However, based on the data collected by Caltech the measured annual mean loss is on the order of 30% of the federal PM_{2.5} standard. For the FRM sampler, which has more efficient removal of nitric acid in its inlet, the sampling losses are predicted to be somewhat higher. Note that this analysis does not take into account additional loss that may occur in the storage and conditioning of samples prior to weighing.

There are many implications of a large systematic difference between the regulatory and scientific definitions of PM_{2.5}. First, if nitrate concentrations are consistently under-

About the authors

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Implications

Sampling losses on the order of 30% of the annual federal standard for $PM_{2.5}$ may be expected due to volatilization of ammonium nitrate in those areas of the country where nitrate is a significant contributor to the fine particle mass, and where ambient temperatures tend to be warm.

particles, these losses will significantly influence measured mass. Further, the systematic under reporting of nitrate could bias control strategies for PM_{2.5}.

Acknowledgments

We thank the California Air Resources Board for their support of this work. We thank Dr. Paul Solomon and Michael Chan for their diligent efforts in producing the data sets analyzed here, and the South Coast Air Quality Management District for providing the temperature data at their sites. We thank Dr. Mark Stolzenburg and Dr. Walter John for their helpful comments.

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Table 1. Typical values of κ , the factor by which the square root of the dissociation constant for ammonium nitrate increases with temperature

T_{amb} (°C)	$\Delta T = T_{fltr} - T_{amb}$ (°C)	$\kappa^1 = \frac{\sqrt{K_{fltr}}}{\sqrt{K_{amb}}}$
10	3.0	1.5
10	5.0	2.0
20	3.0	1.5
20	5.3	2.0
20	8.0	2.8

1 κ is defined by equation (5)

Table 2. Mass of ammonium nitrate lost from Teflon filters as percentage of the gravimetric mass.

Site	Mean Loss ($\mu\text{g}/\text{m}^3$)		Percent of Gravimetric Mass	
	summer	fall	summer	fall
<u>SCAQS Data Set (1987)</u>				
Anaheim	5.6	7.6	17 %	10 %
Burbank	10.1	9.5	21	12
Central LA	8.3	5.4	19	7
Hawthorne	4.4	4.8	14	9
Long Beach CC	4.2	5.2	15	12
Rubidoux	8.7	1.2	12	3
Azusa	8.0		16	
Claremont	9.0		20	
Average	7.3	5.6	17 %	9 %
<u>Caltech Data Set (1986)</u>				
Anaheim	3.4	5.5	20 %	15 %
Burbank	6.6	4.7	23	12
Central Los Angeles	5.9	4.7	19	10
Hawthorne	2.9	4.4	14	14
Long Beach	2.8	4.6	13	12
Rubidoux	9.6	2.4	24	13
Upland	9.2	4.6	33	15
Average	5.8	4.4	21 %	13 %

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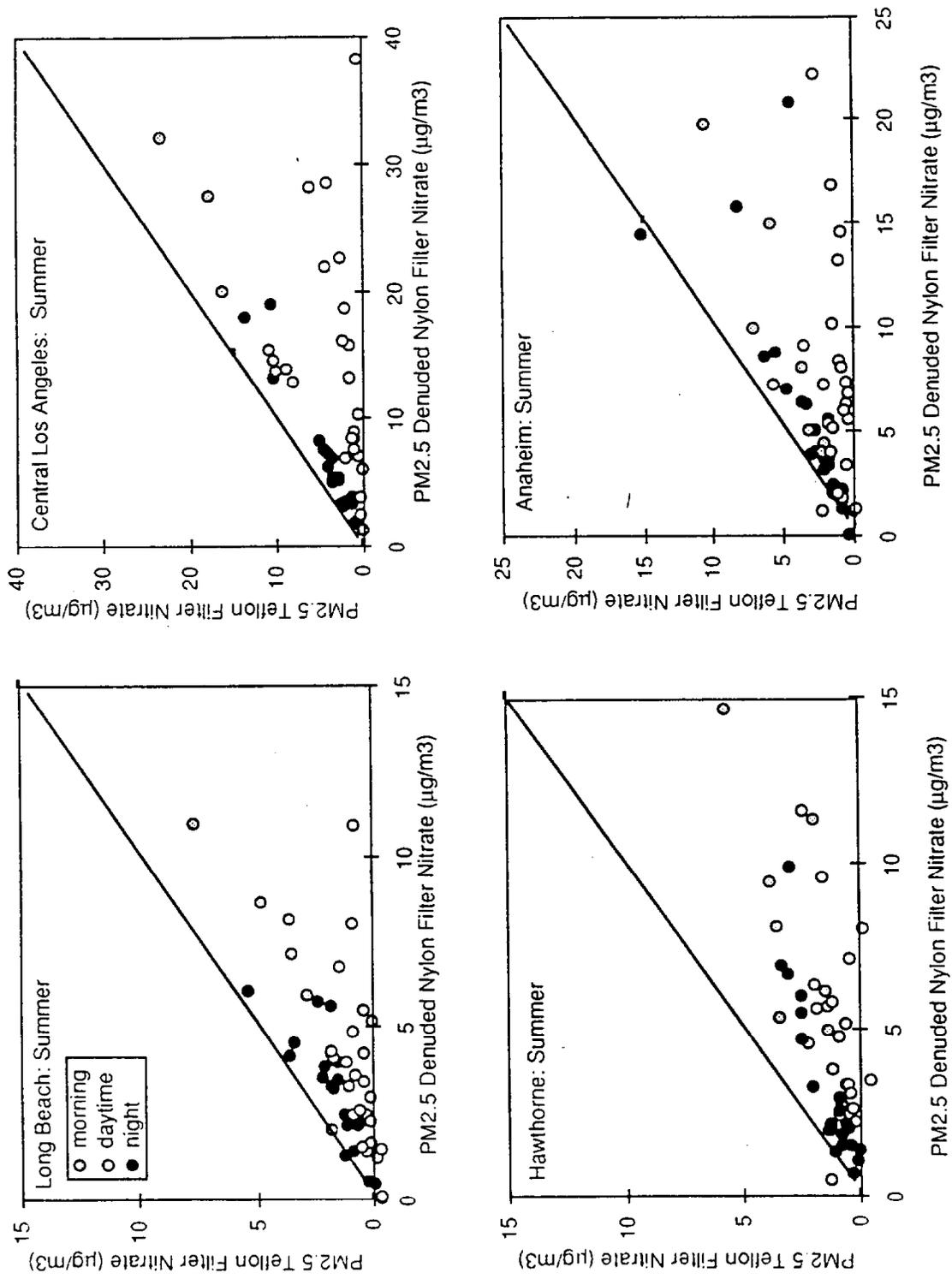


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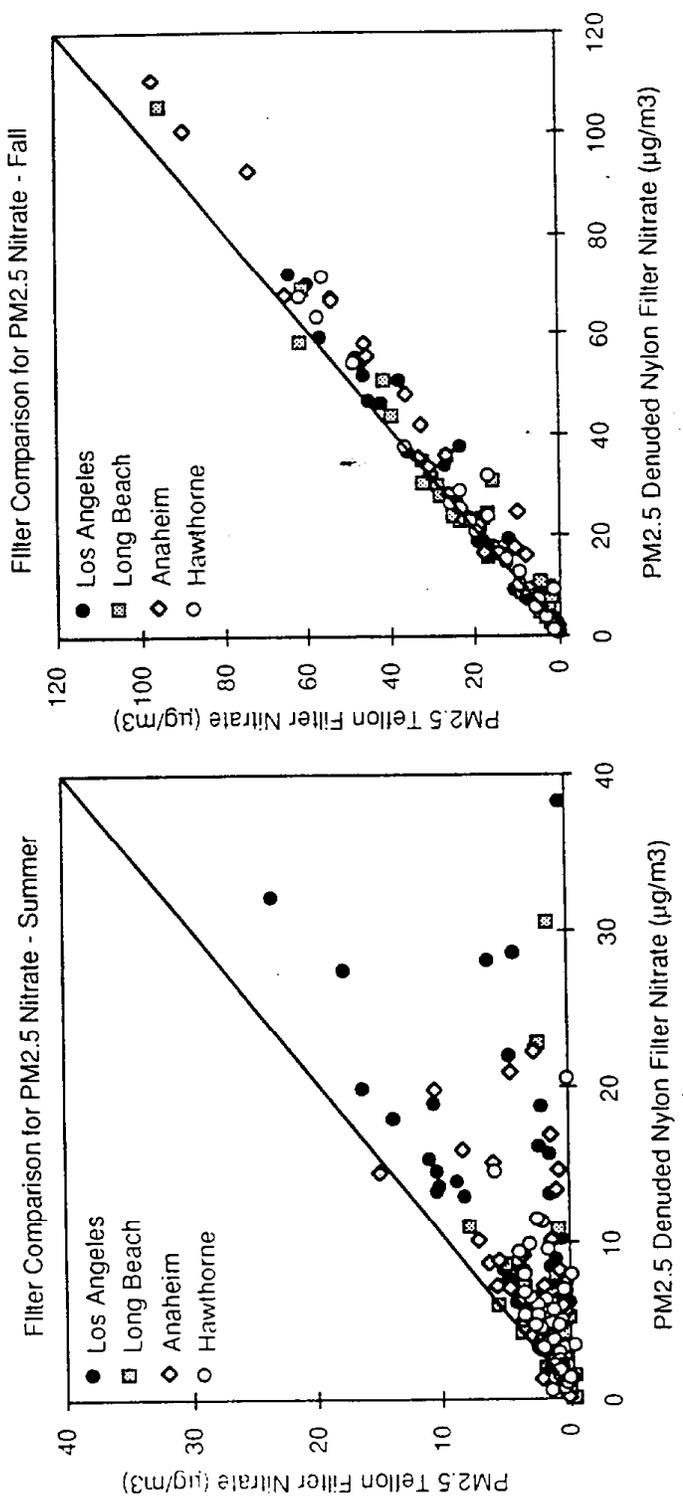


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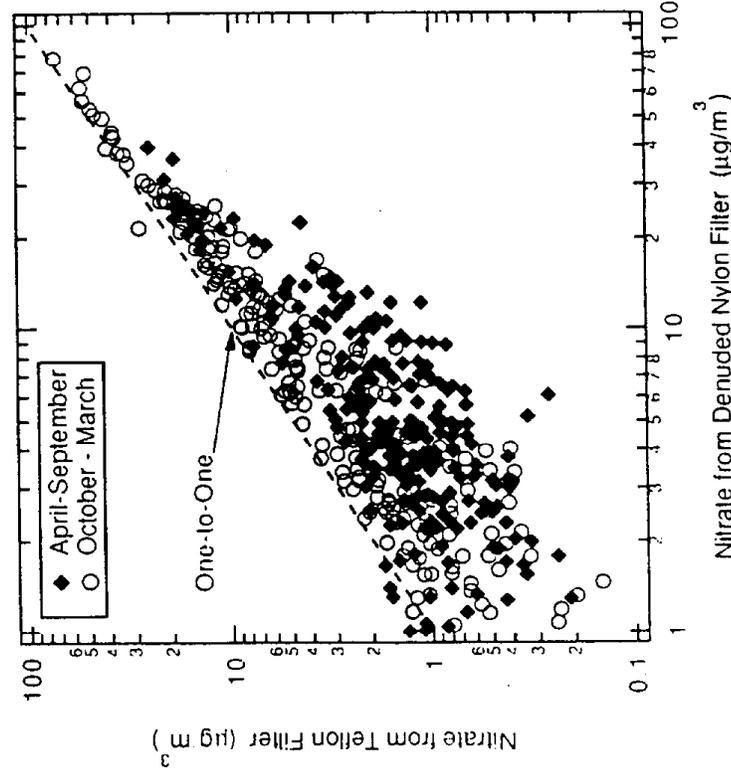
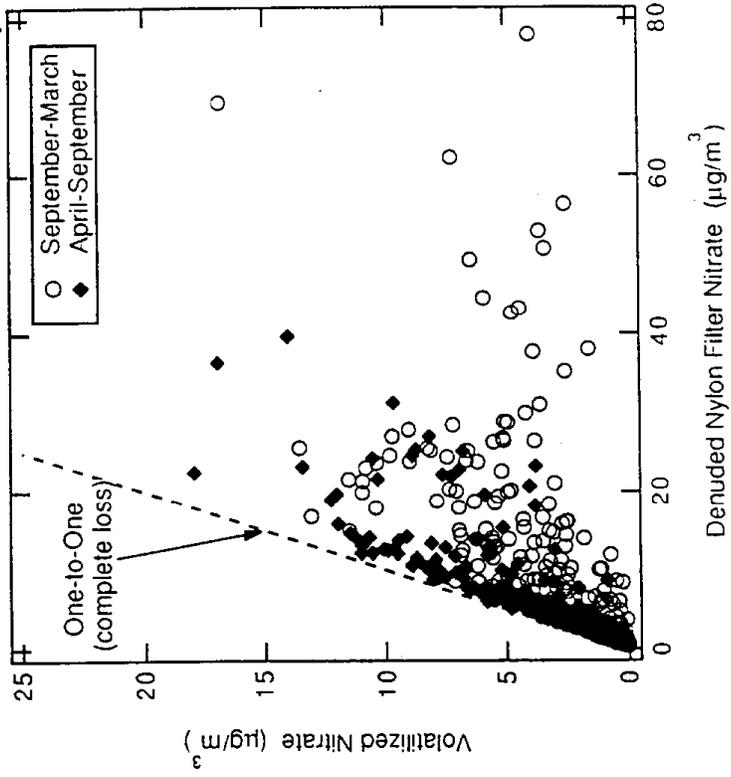


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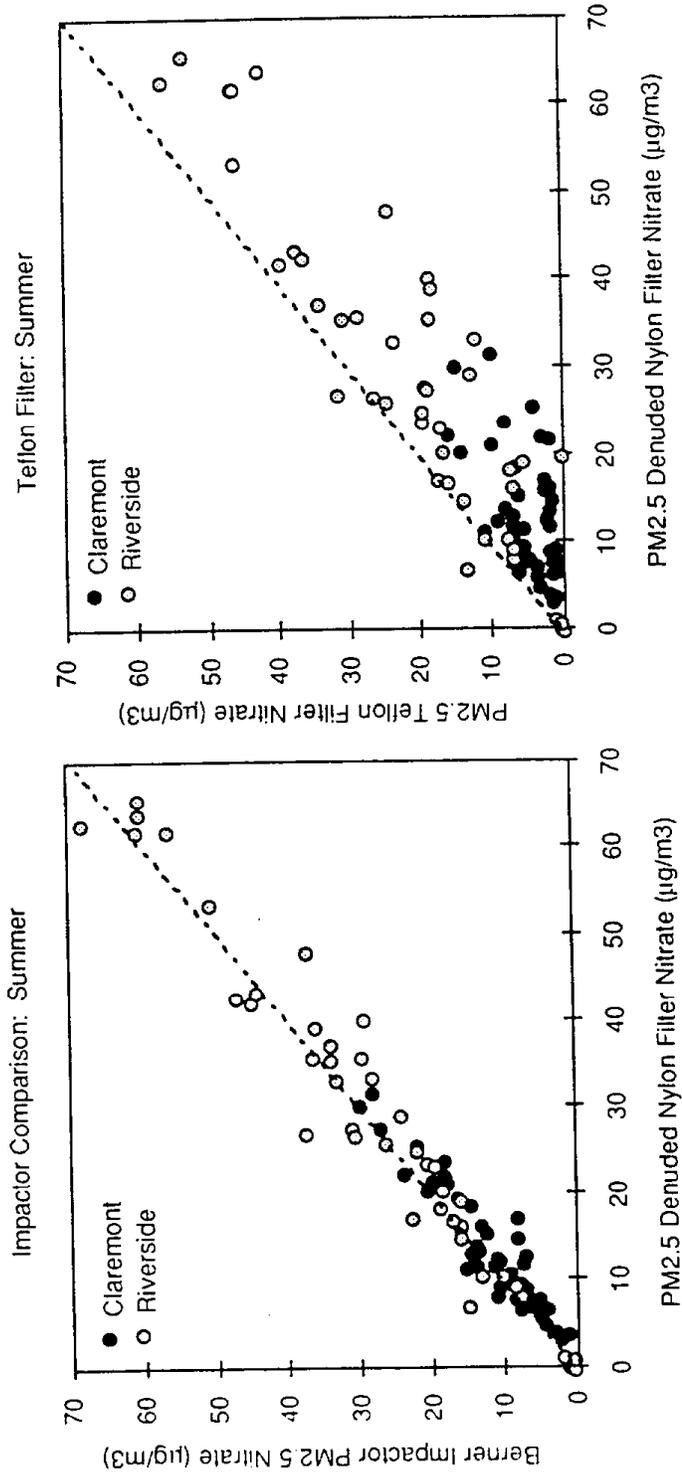


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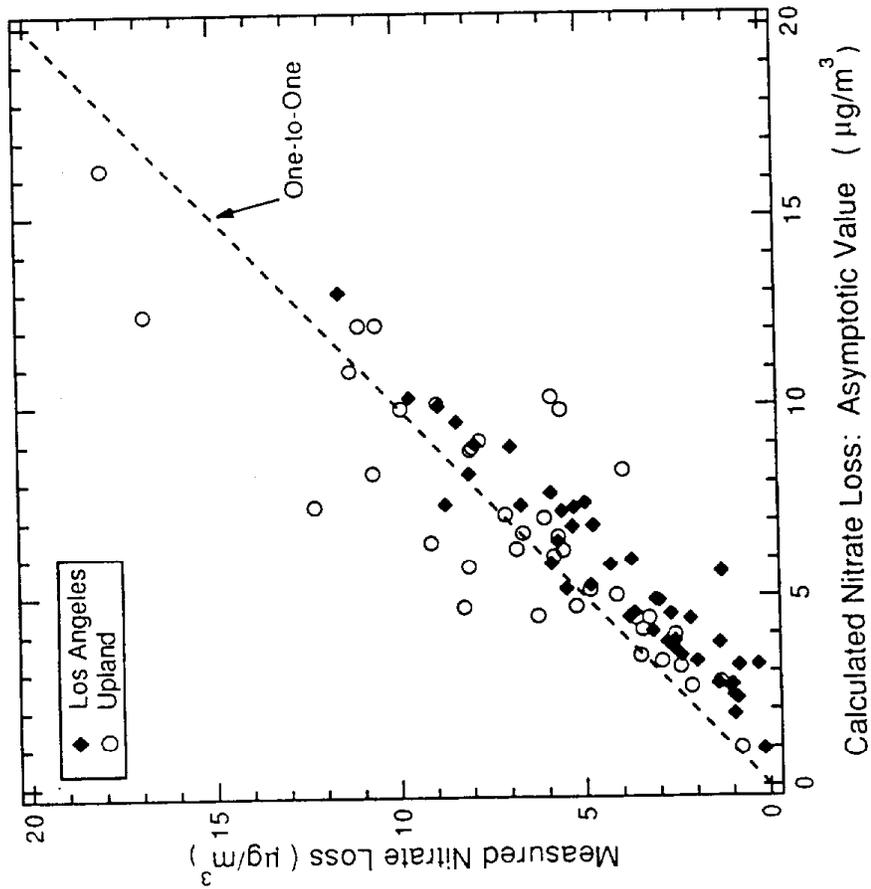


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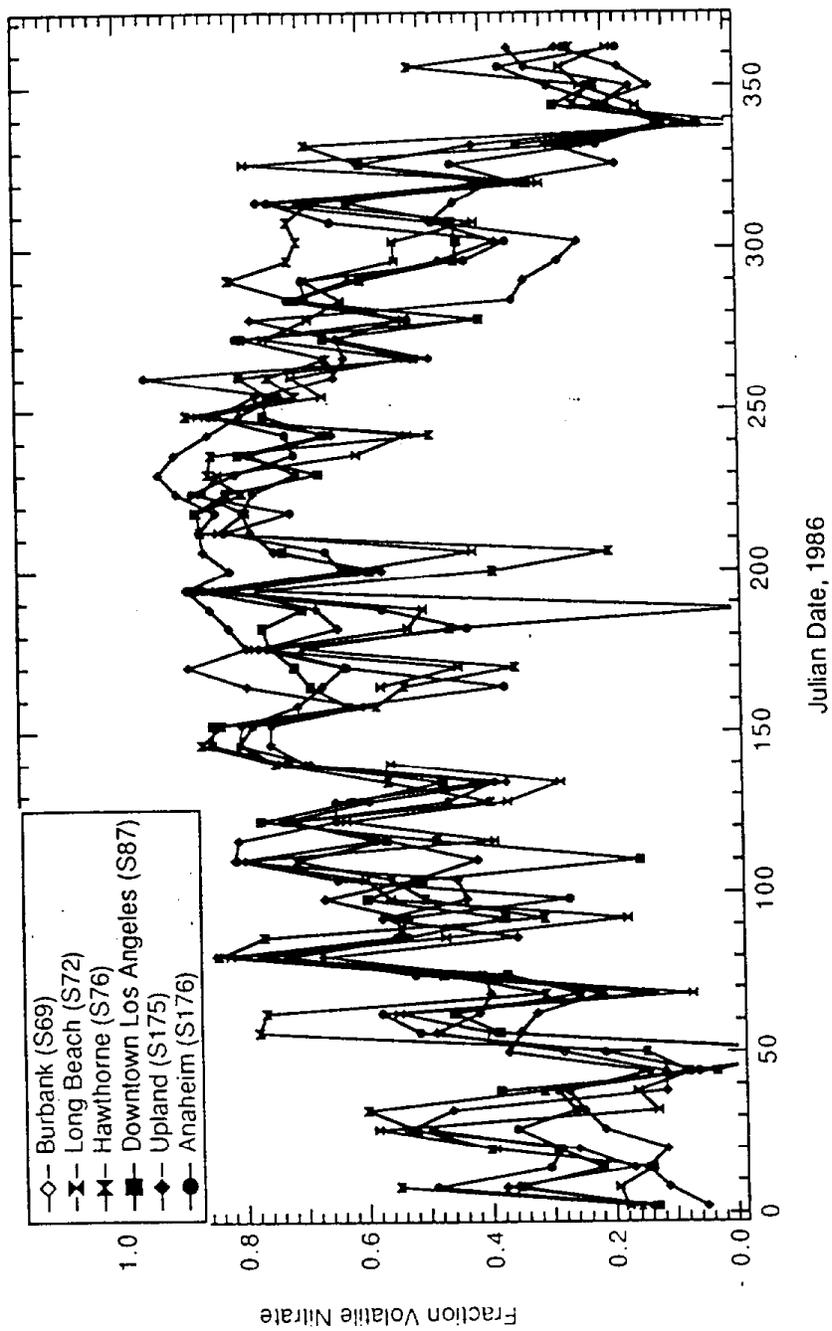


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Appendix B

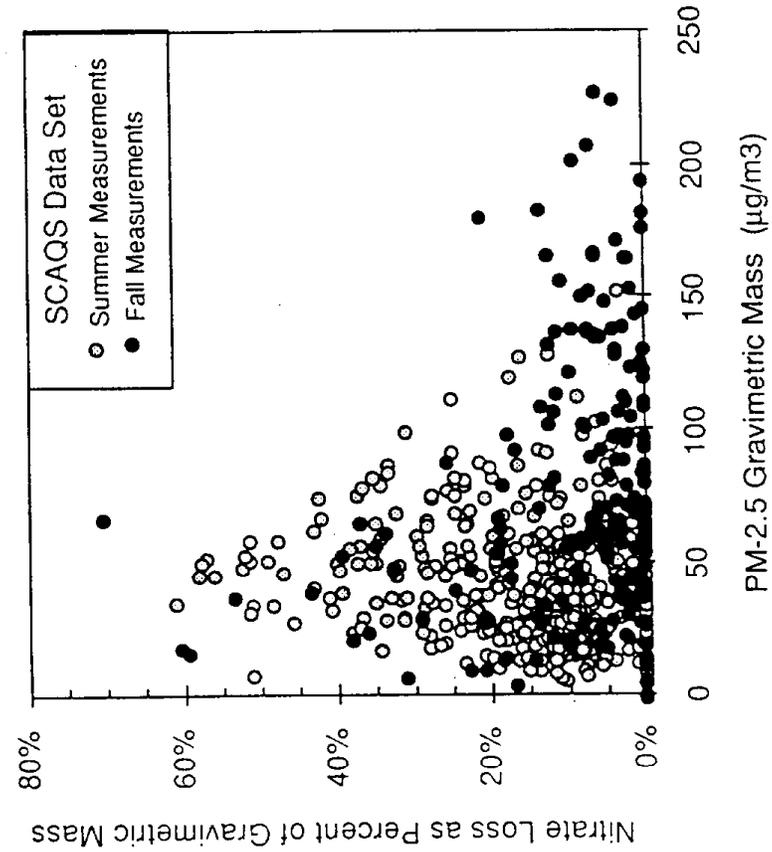
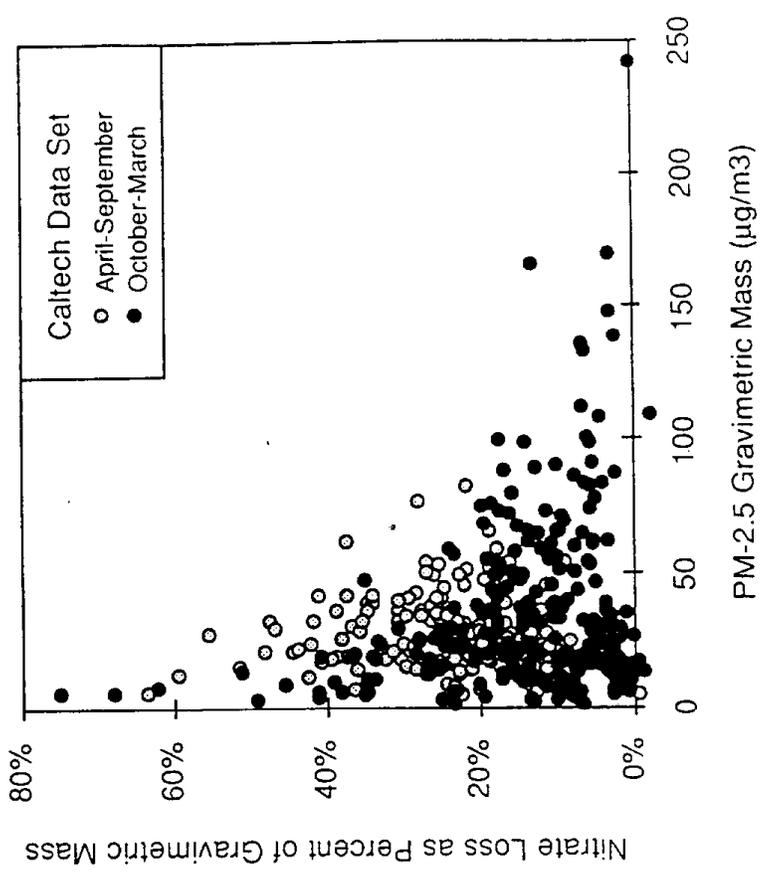


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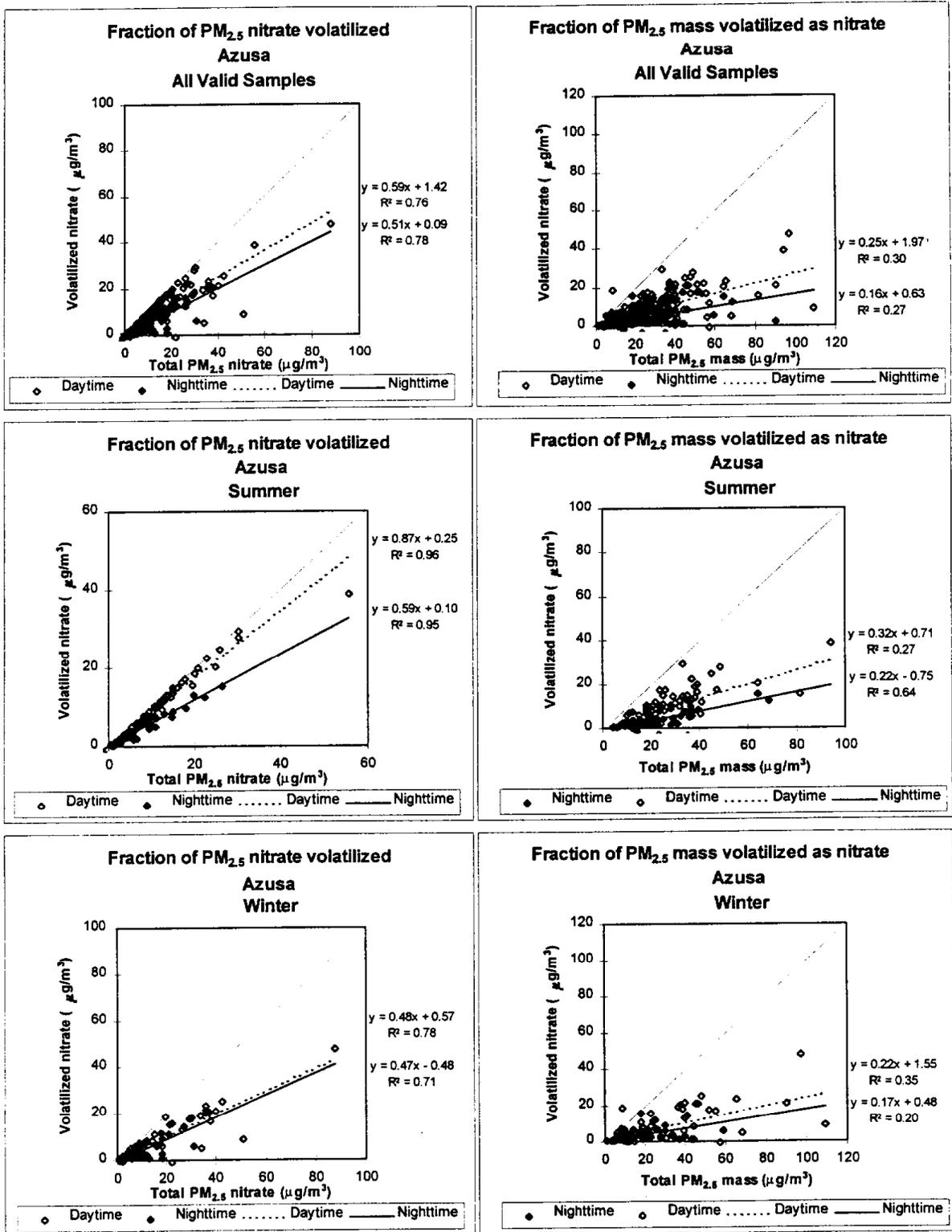


Figure B-1. Nitrate measurements at Azusa

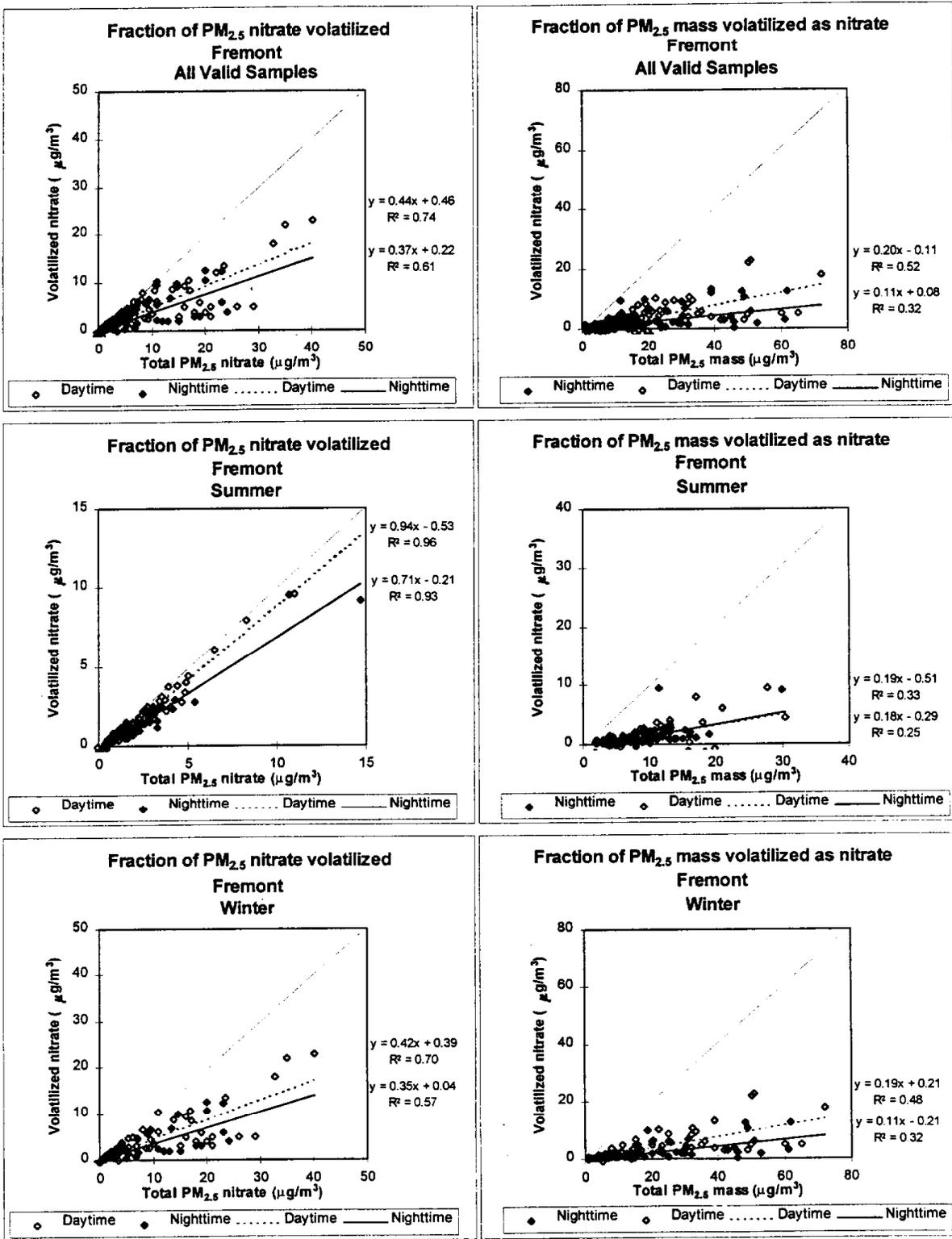


Figure B-3. Nitrate measurements at Fremont

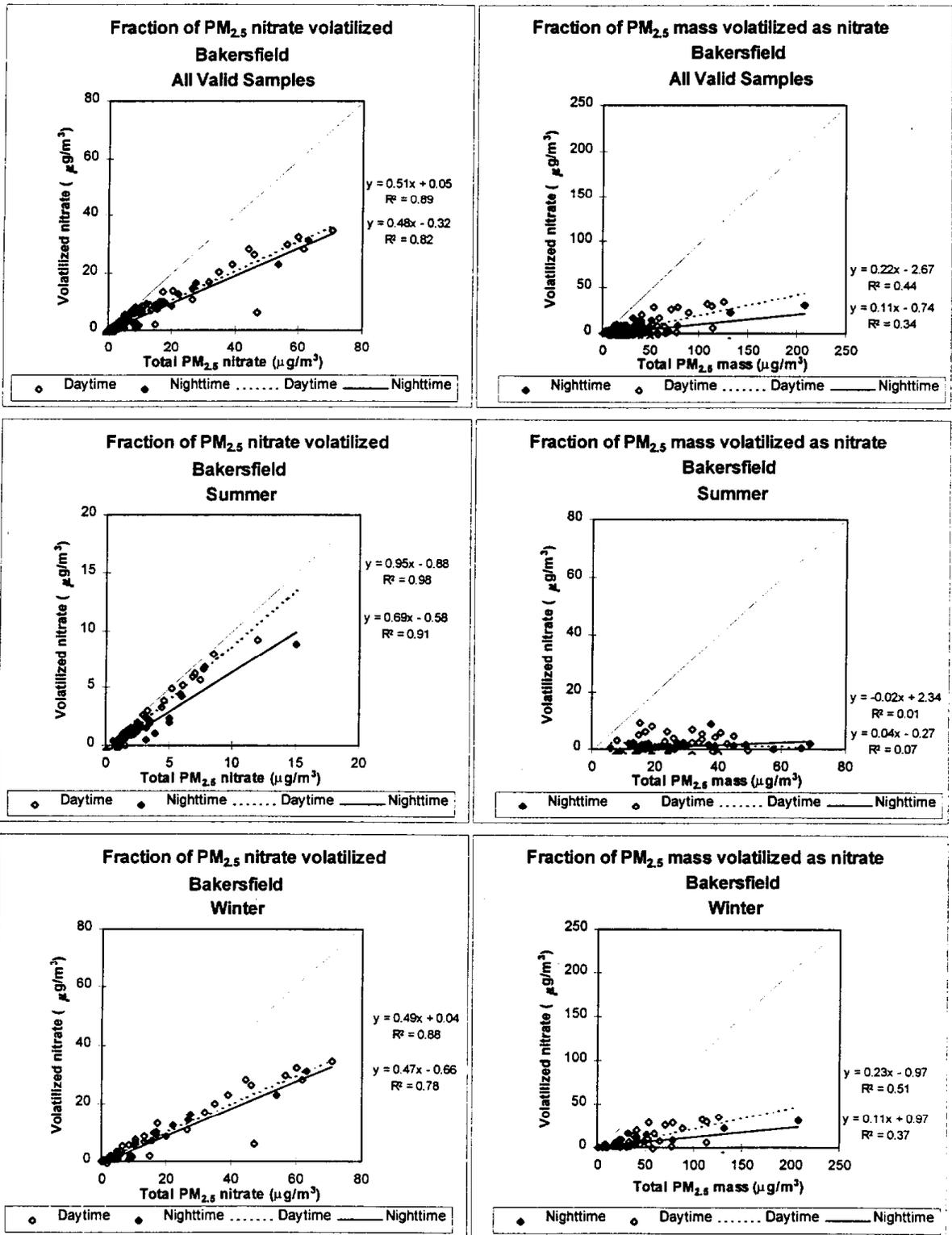


Figure B-2. Nitrate measurements at Bakersfield

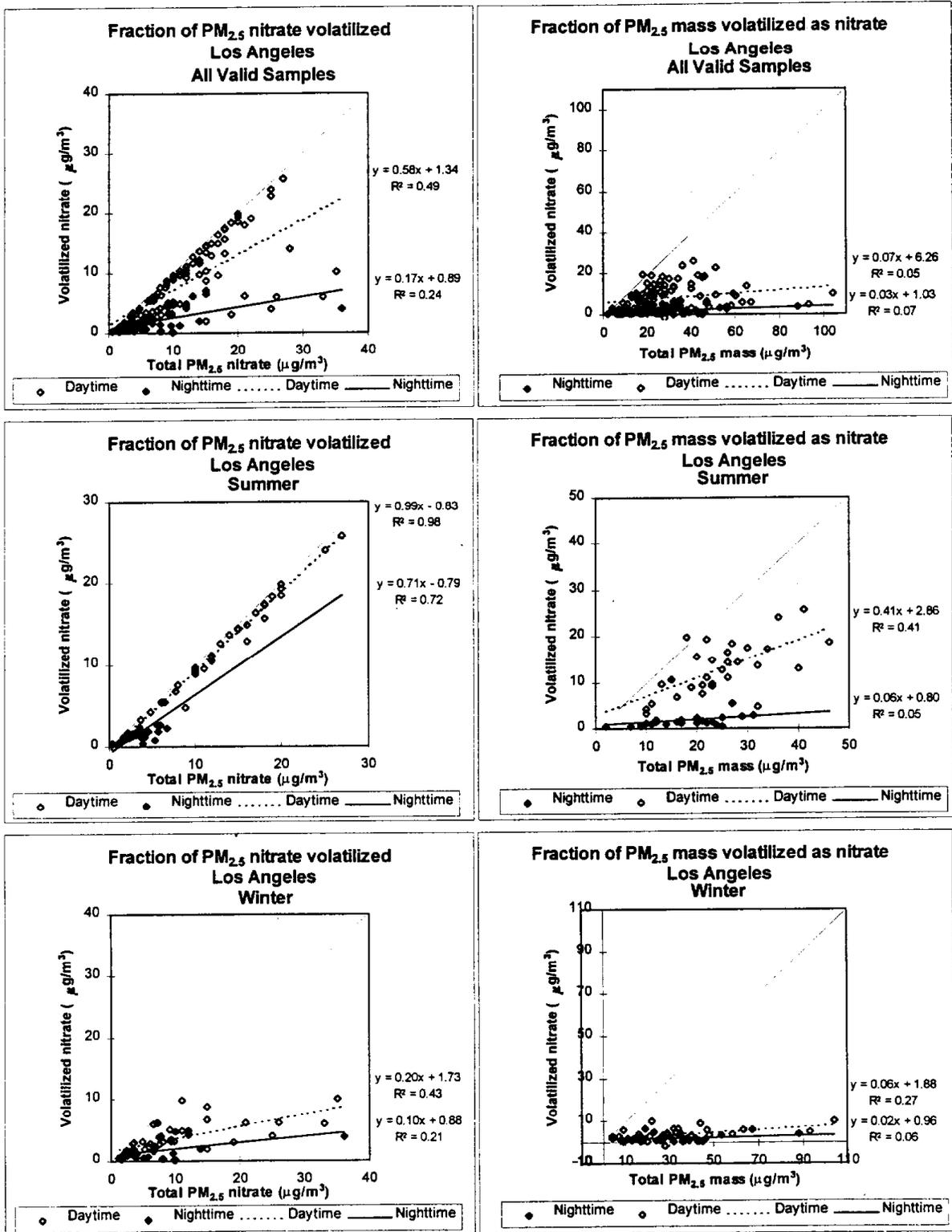


Figure B-5. Nitrate measurements at Los Angeles

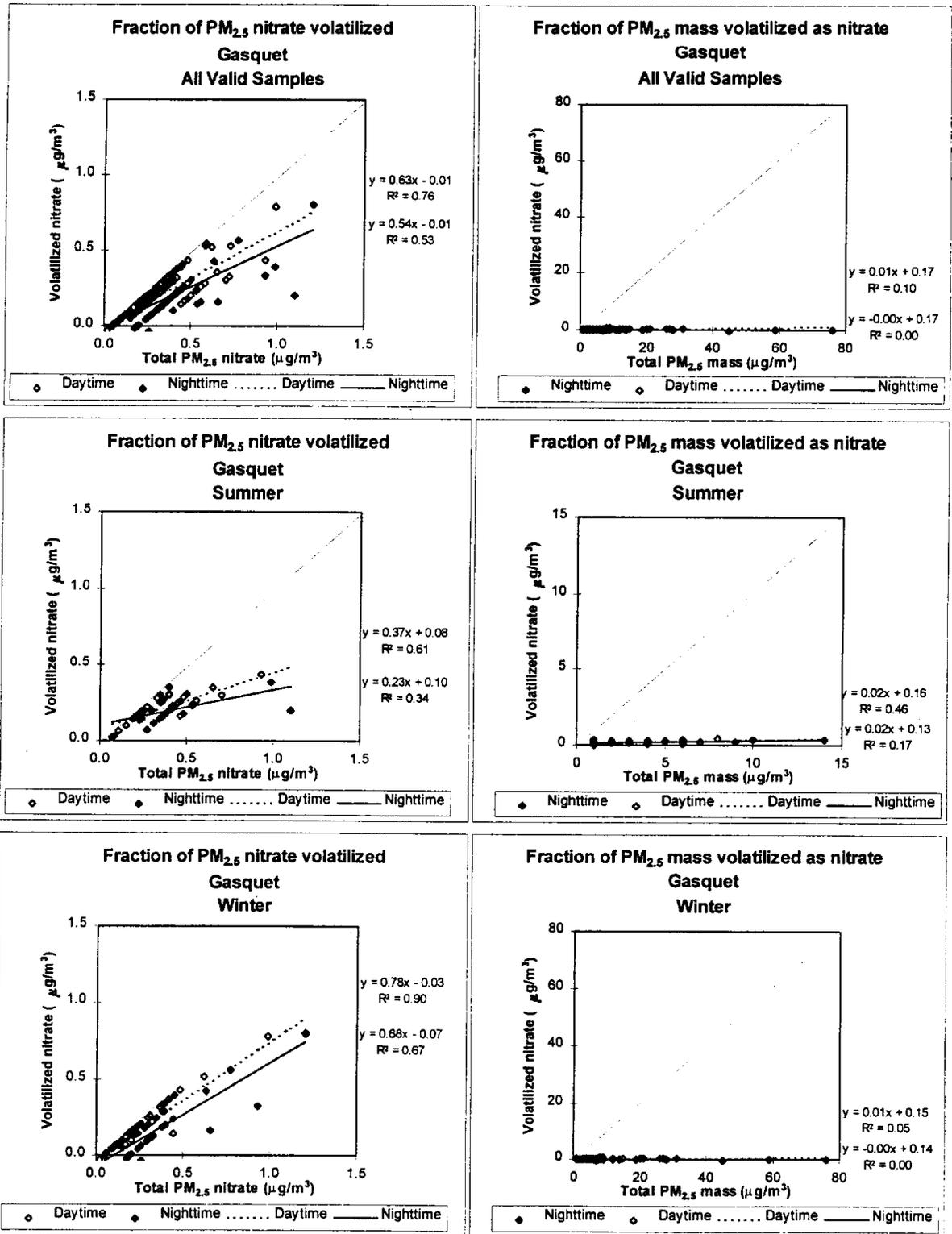


Figure B-4. Nitrate measurements at Gasquet

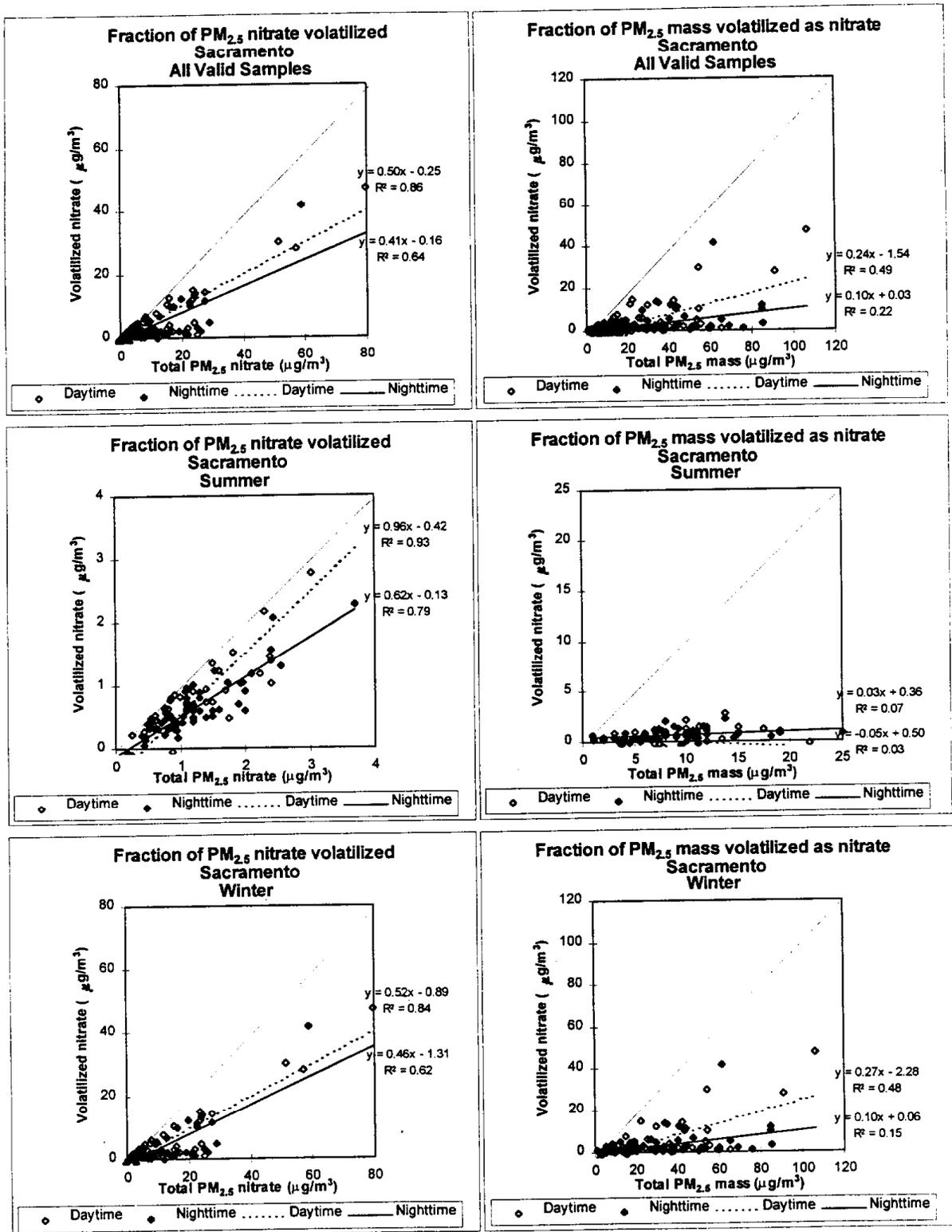


Figure B-7. Nitrate measurements at Sacramento

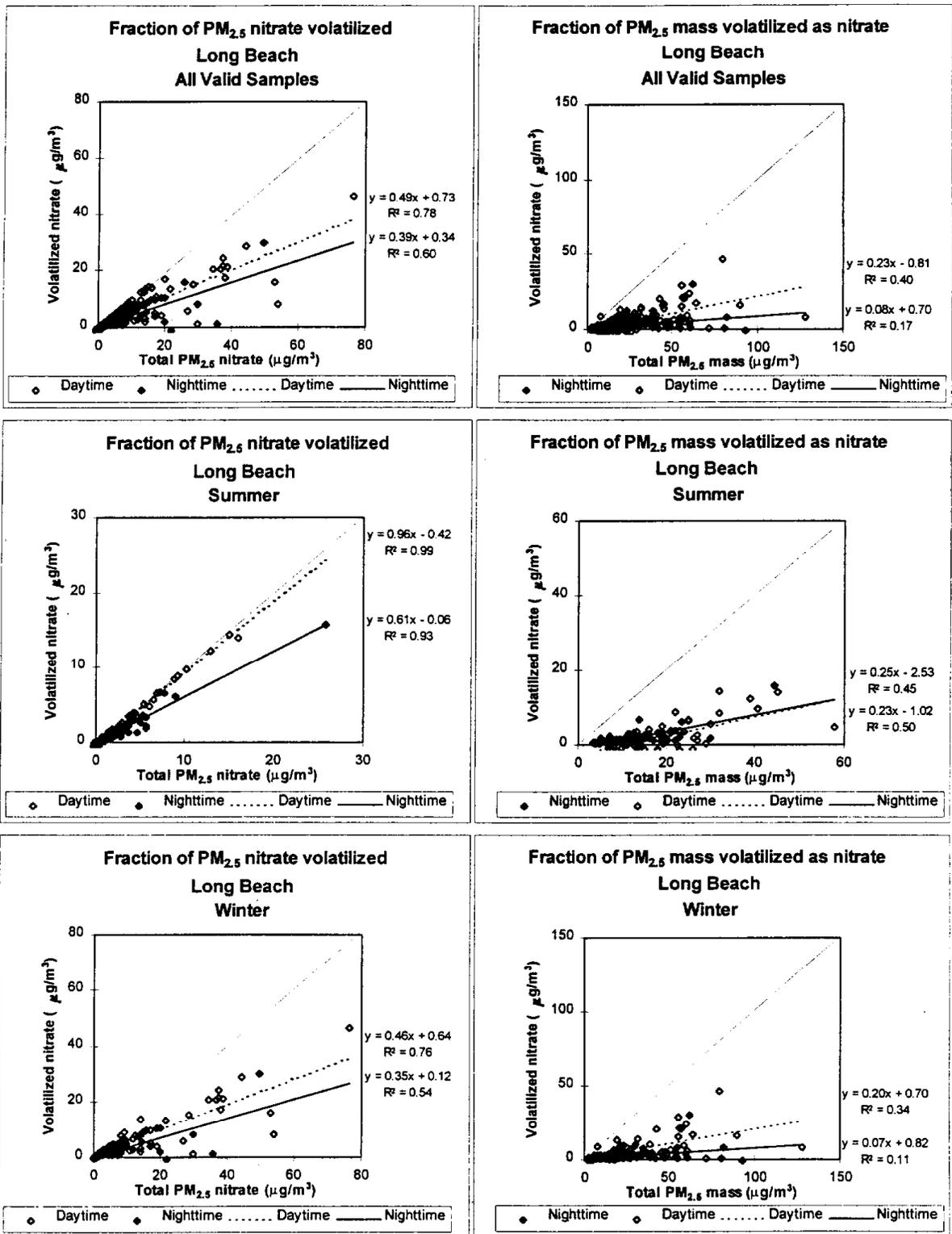


Figure B-6. Nitrate measurements at Long Beach

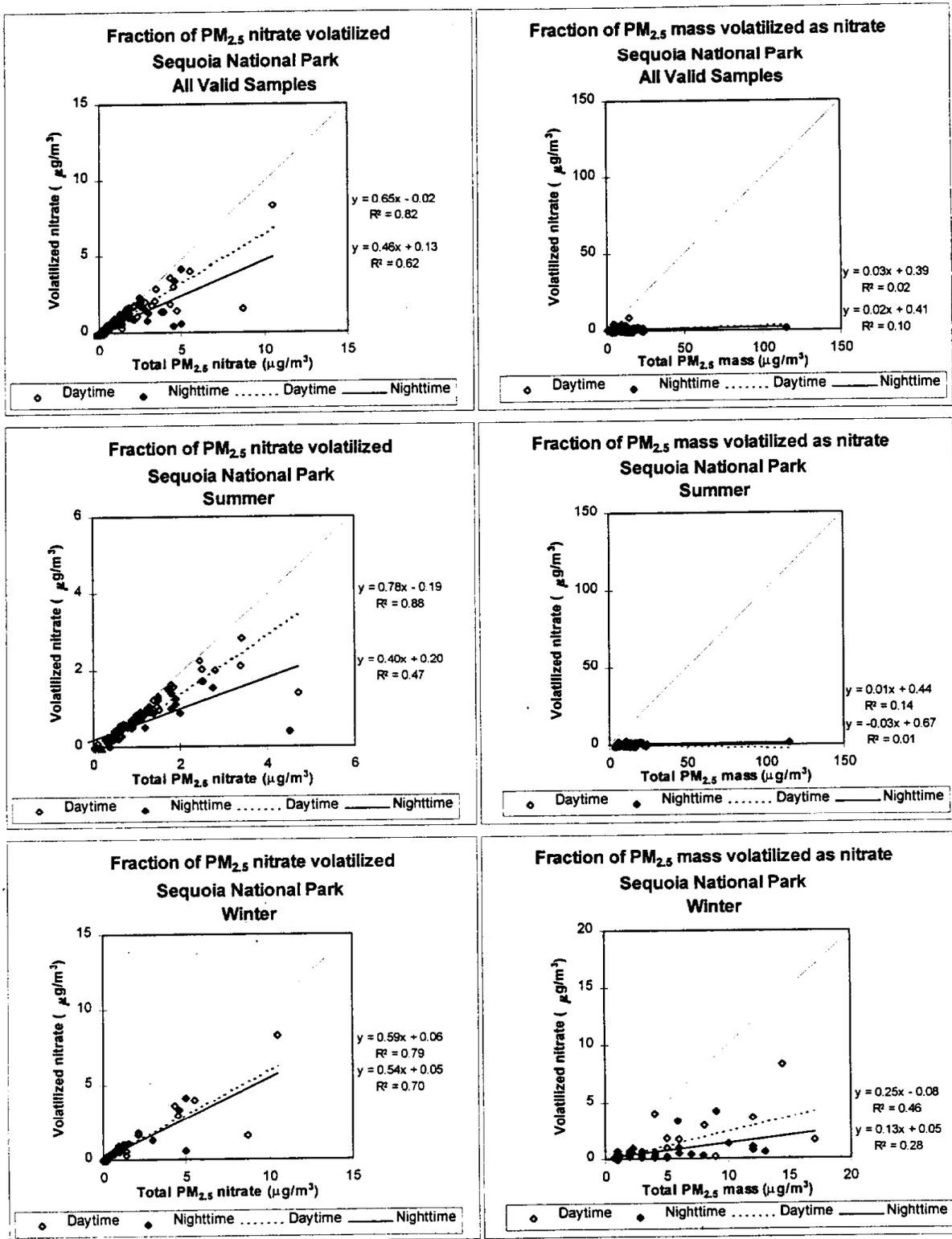


Figure B-9. Nitrate measurements at Sequoia National Park

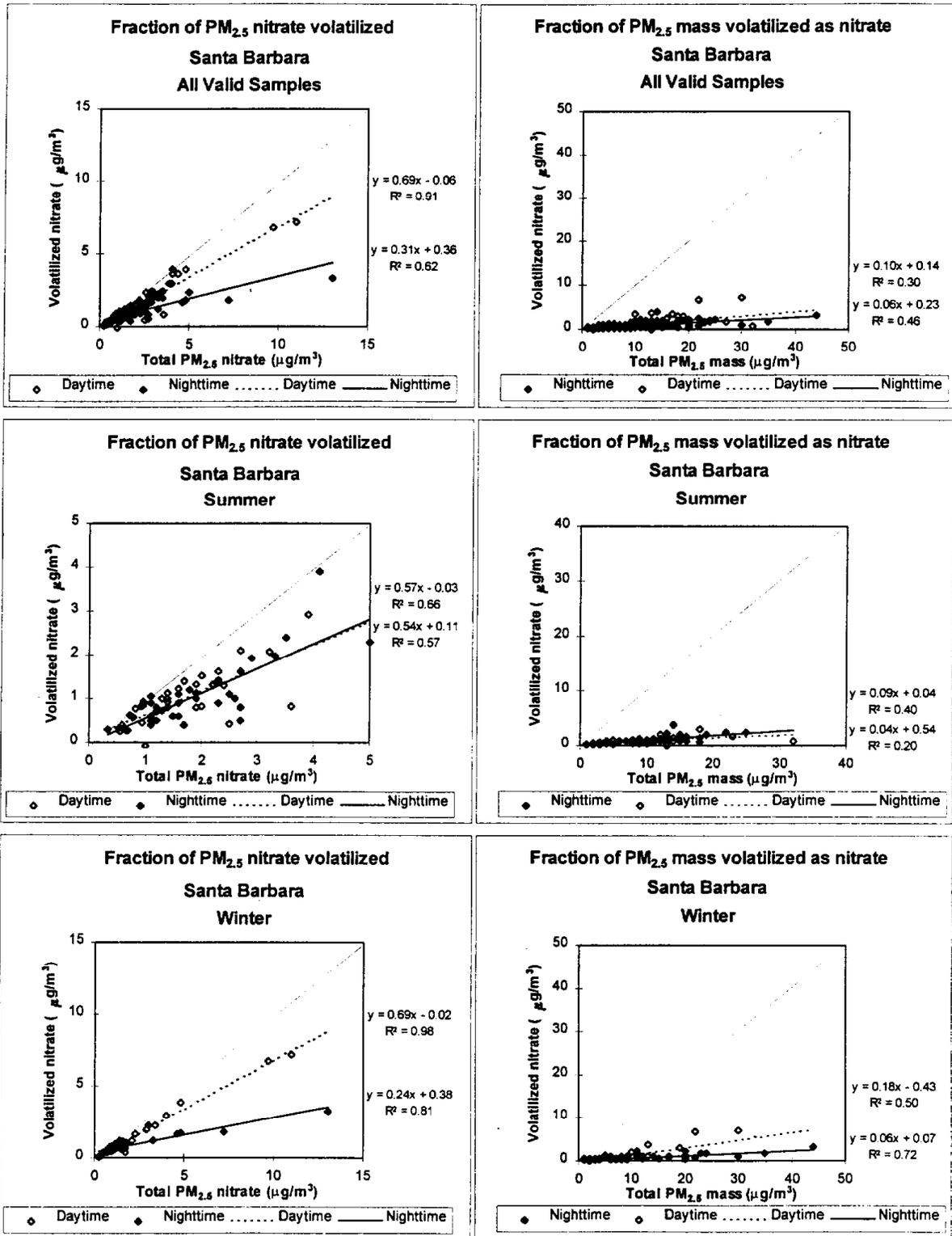


Figure B-8. Nitrate measurements at Santa Barbara

Appendix C

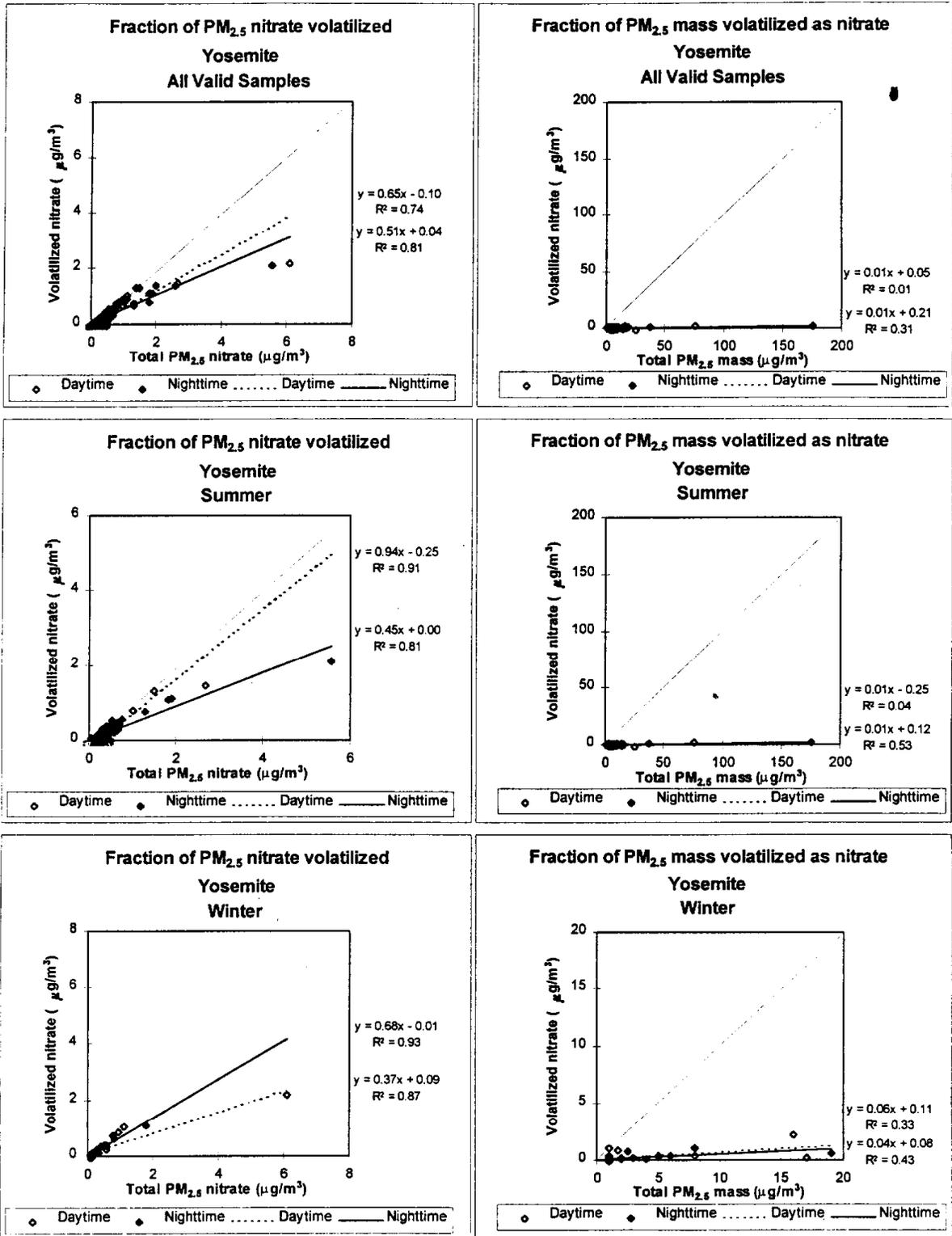


Figure B-10. Nitrate measurements at Yosemite

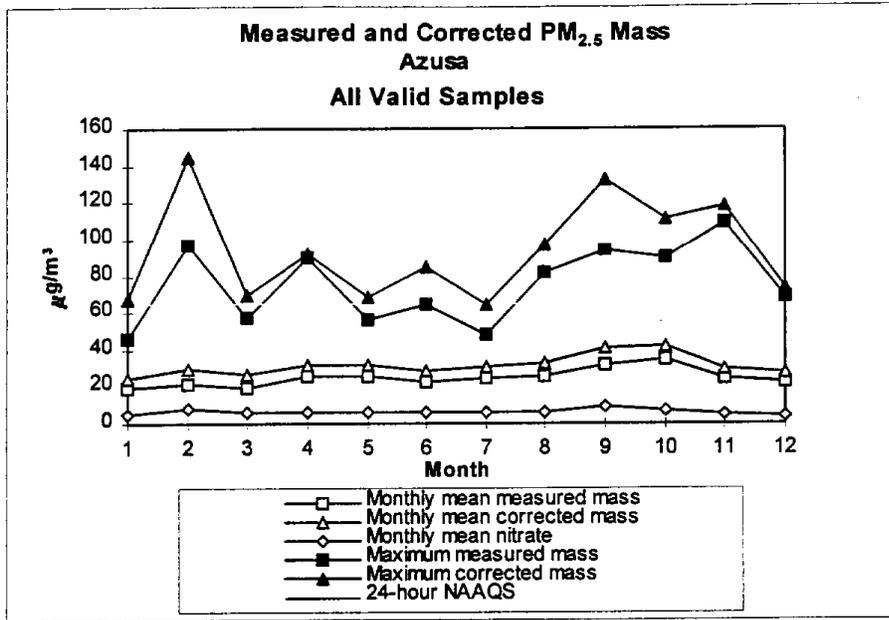


Figure C-1. Monthly average nitrate measurements at Azusa

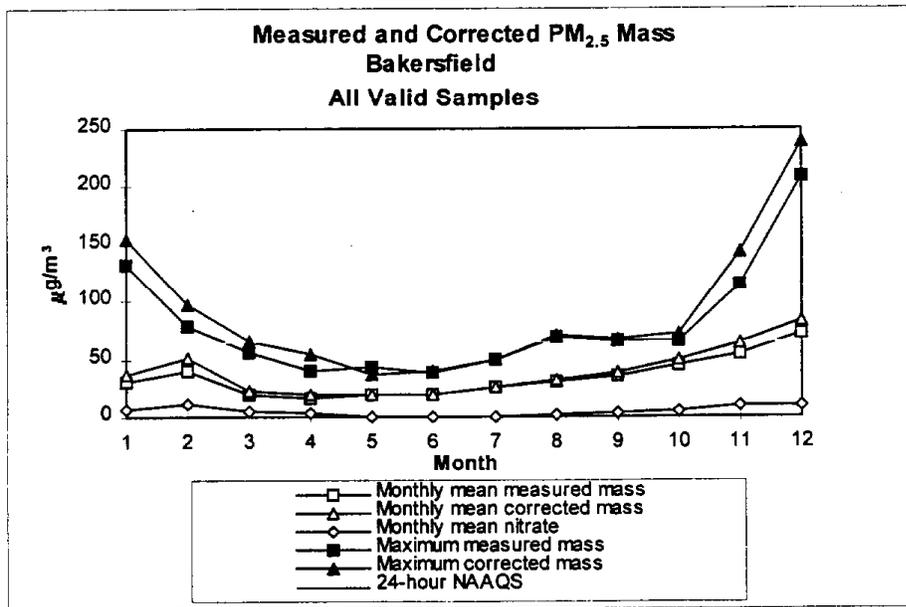


Figure C-2. Monthly average nitrate measurements at Bakersfield

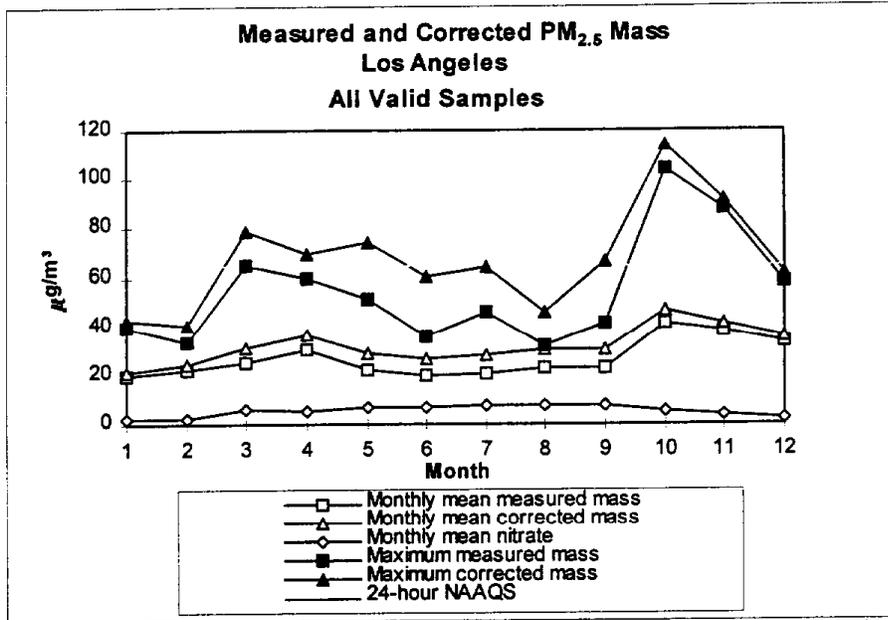
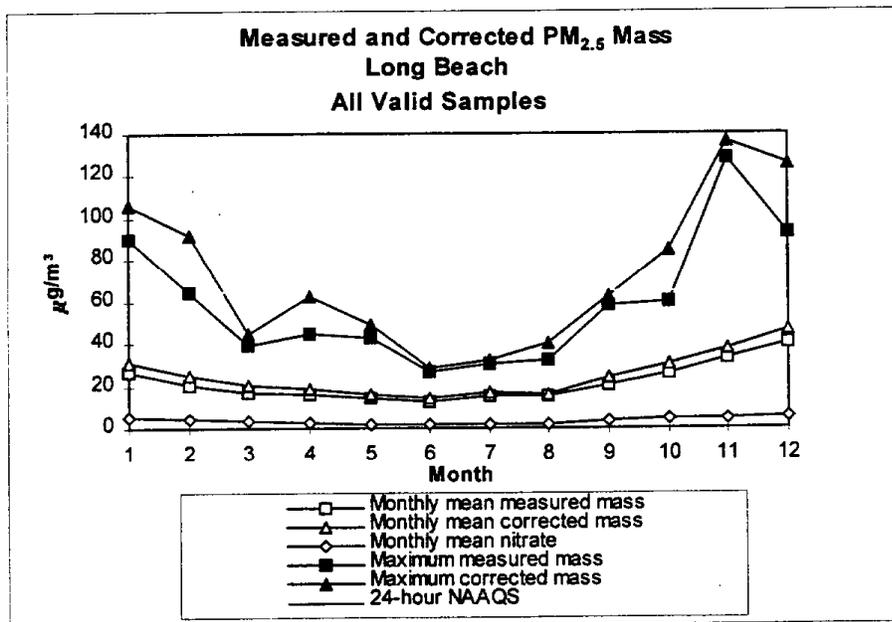


Figure C-5. Monthly average nitrate measurements at Los Angeles



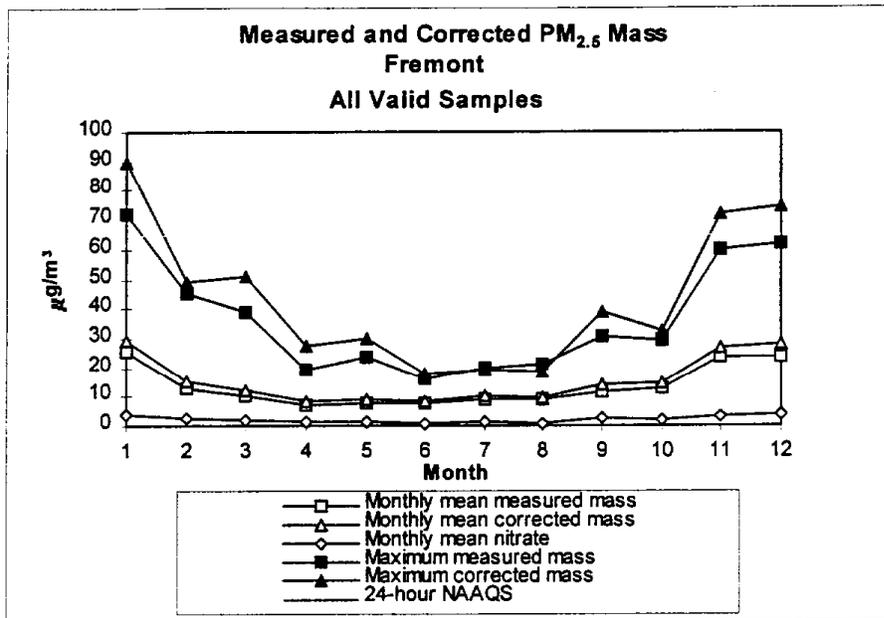


Figure C-3. Monthly average nitrate measurements at Fremont

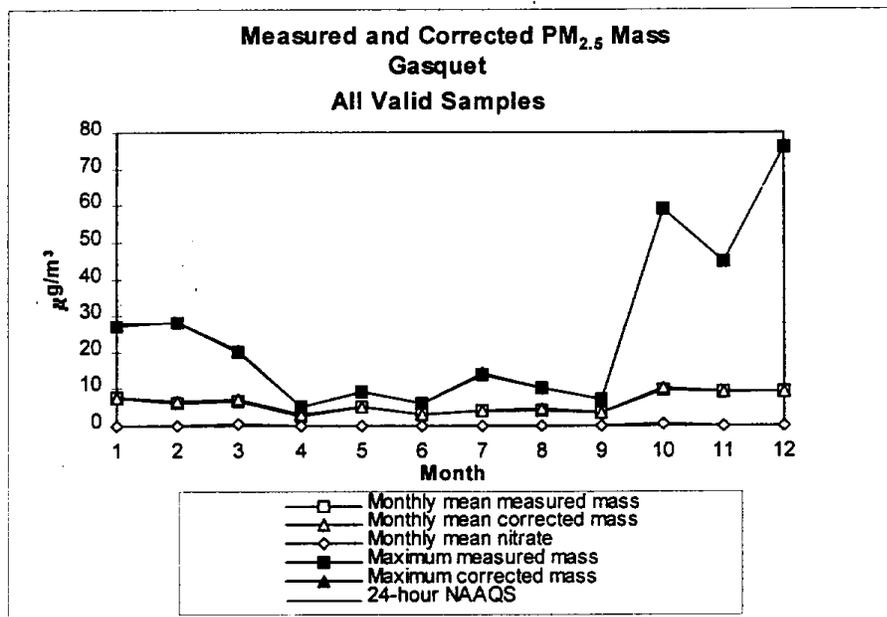


Figure C-4. Monthly average nitrate measurements at Gasquet

Figure C-8. Monthly average nitrate measurements at Santa Barbara

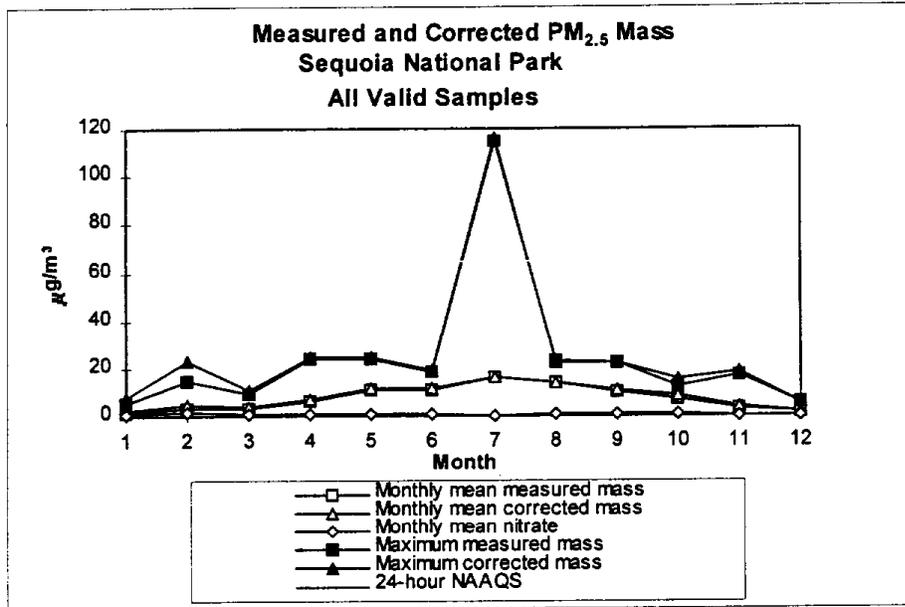


Figure C-9. Monthly average nitrate measurements at Sequoia National Park

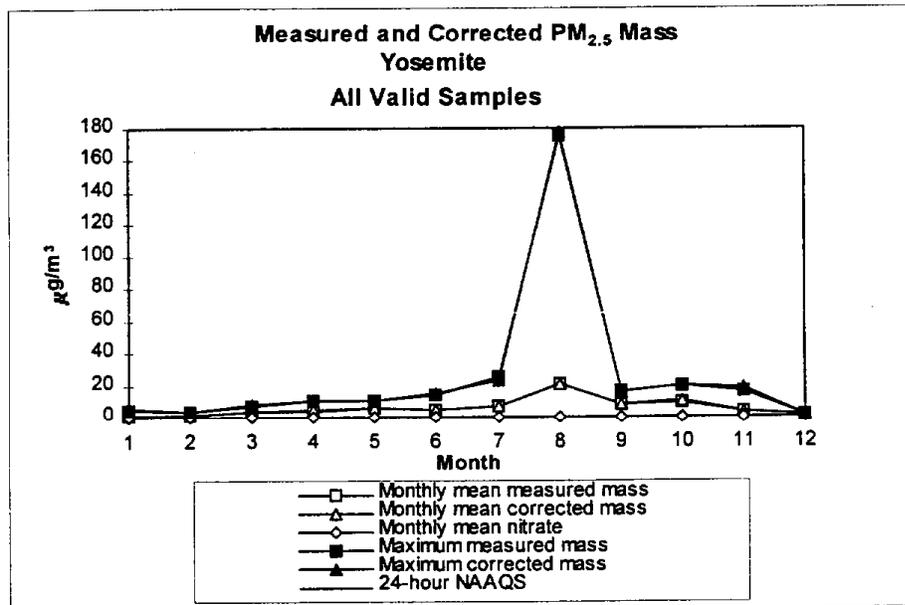


Figure C-6. Monthly average nitrate measurements at Long Beach

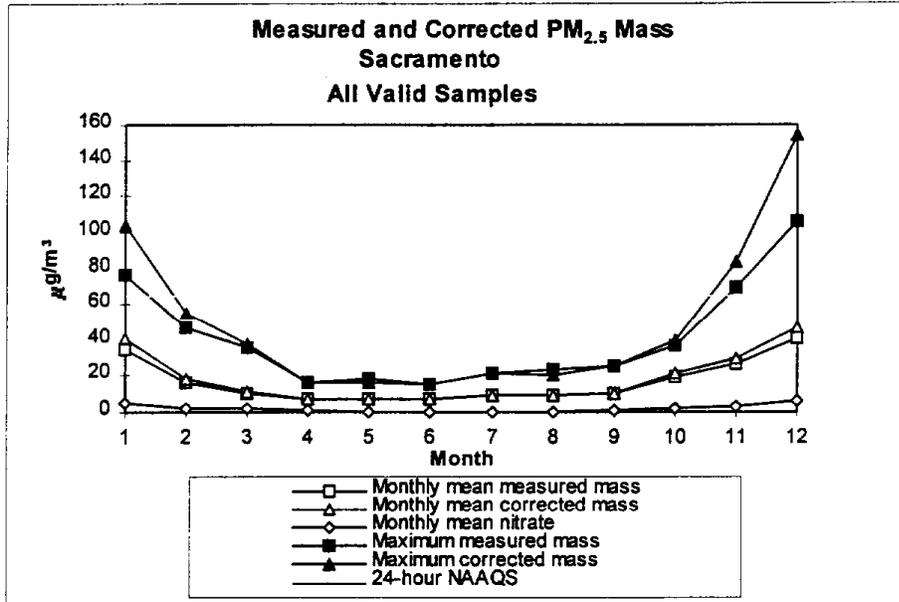
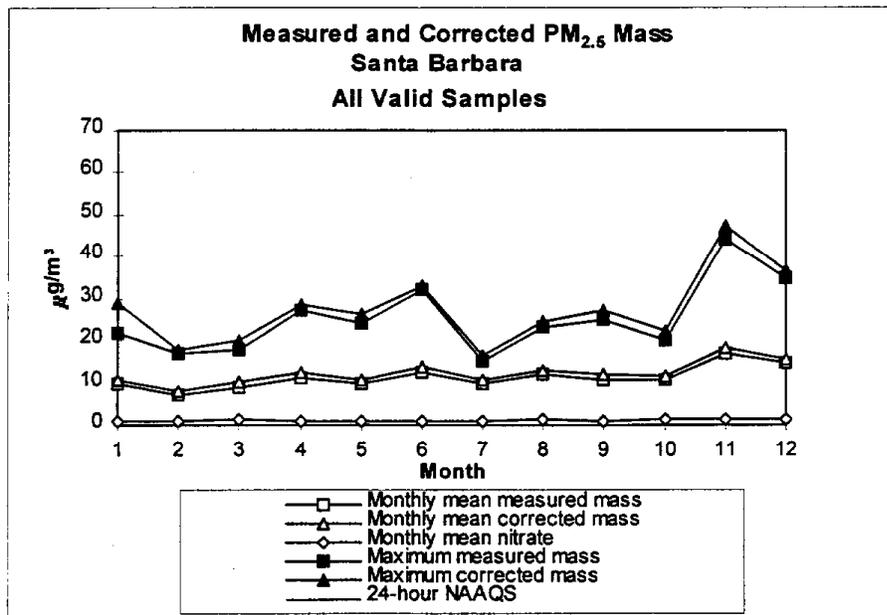


Figure C-7. Monthly average nitrate measurements at Sacramento



Appendix D

Figure C-10. Monthly average nitrate measurements at Yosemite

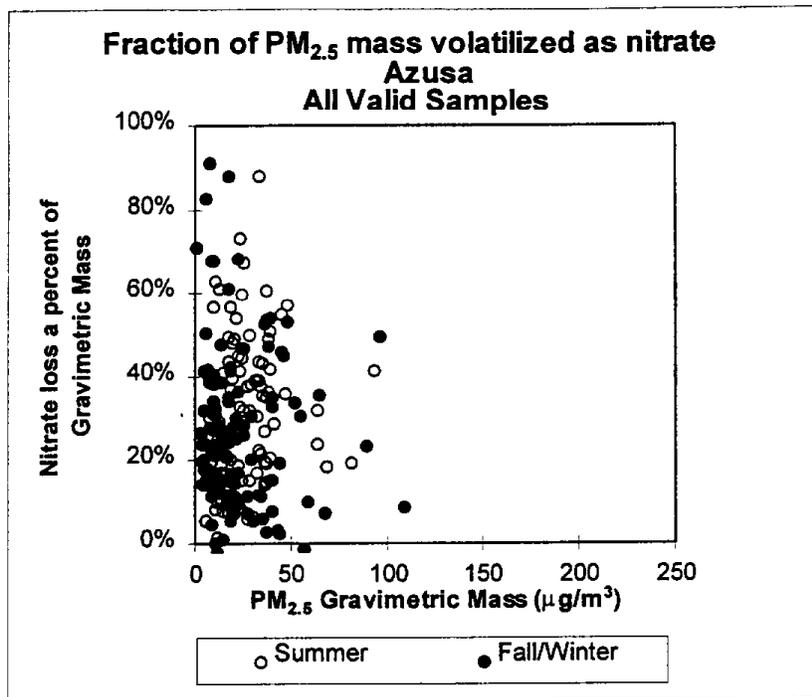


Figure D-1. Mass of nitrate volatilized from Teflon filters as a percent of the measured PM_{2.5} gravimetric mass for Azusa

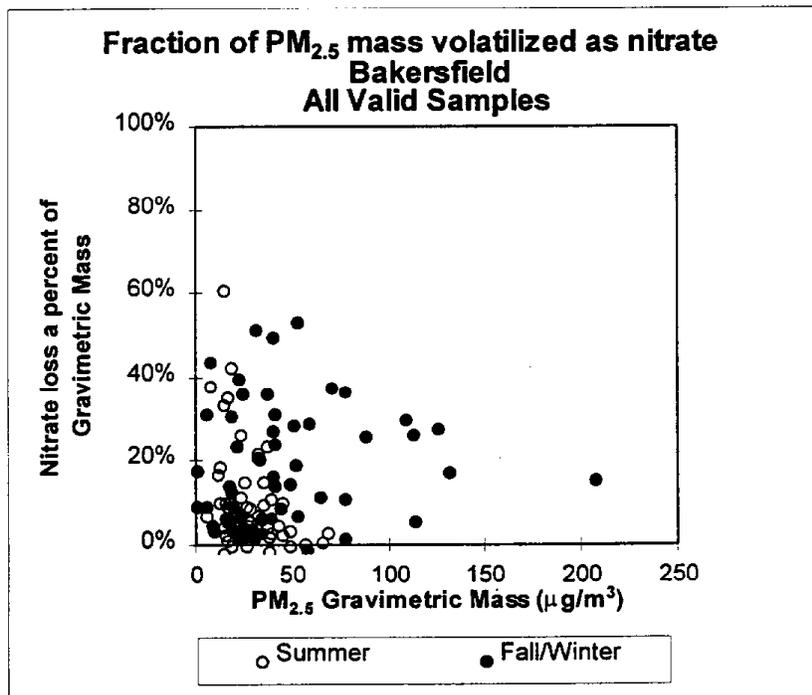


Figure D-2. Mass of nitrate volatilized from Teflon filters as a percent of the measured PM_{2.5} gravimetric mass for Bakersfield

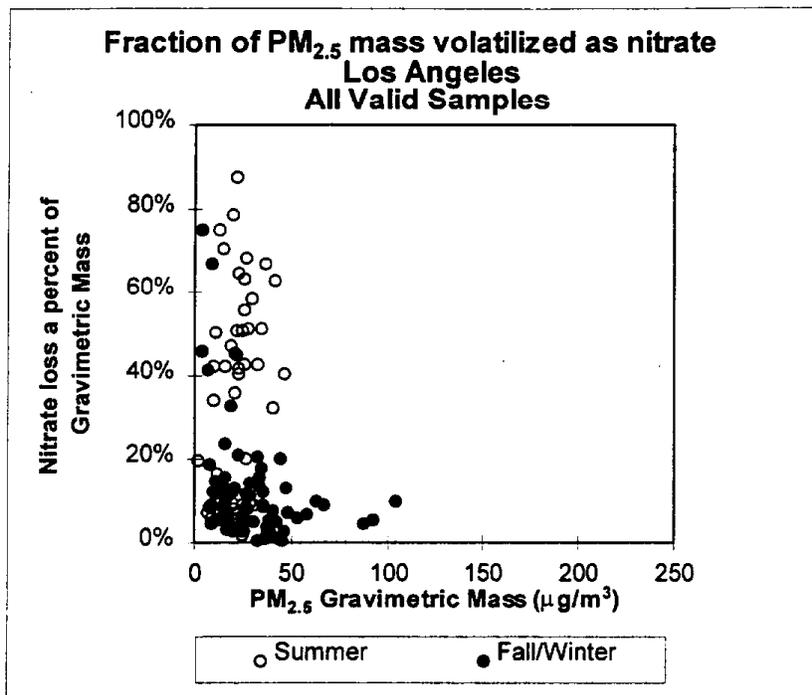


Figure D-5. Mass of nitrate volatilized from Teflon filters as a percent of the measured PM_{2.5} gravimetric mass for Los Angeles

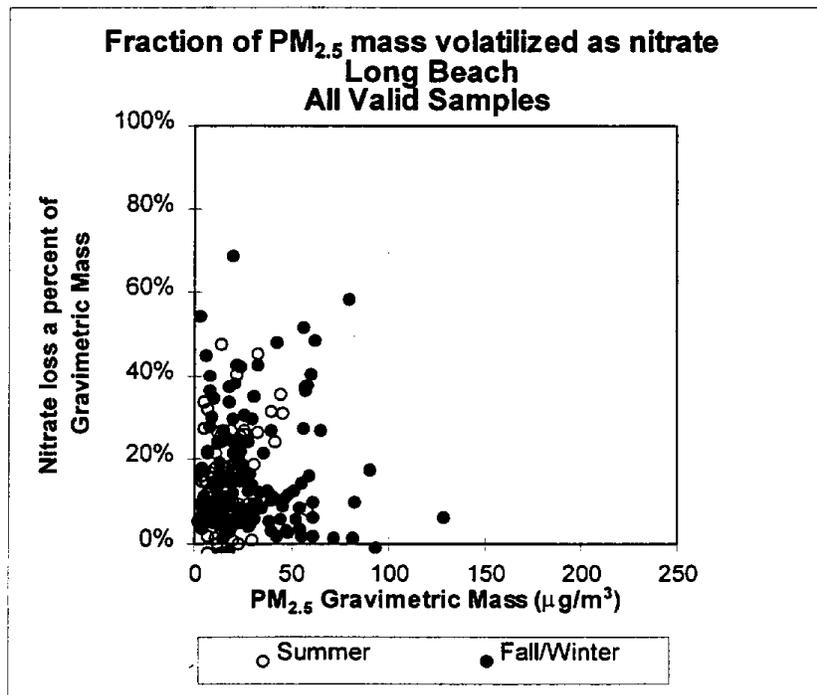


Figure D-6. Mass of nitrate volatilized from Teflon filters as a percent of the measured PM_{2.5} gravimetric mass for Long Beach

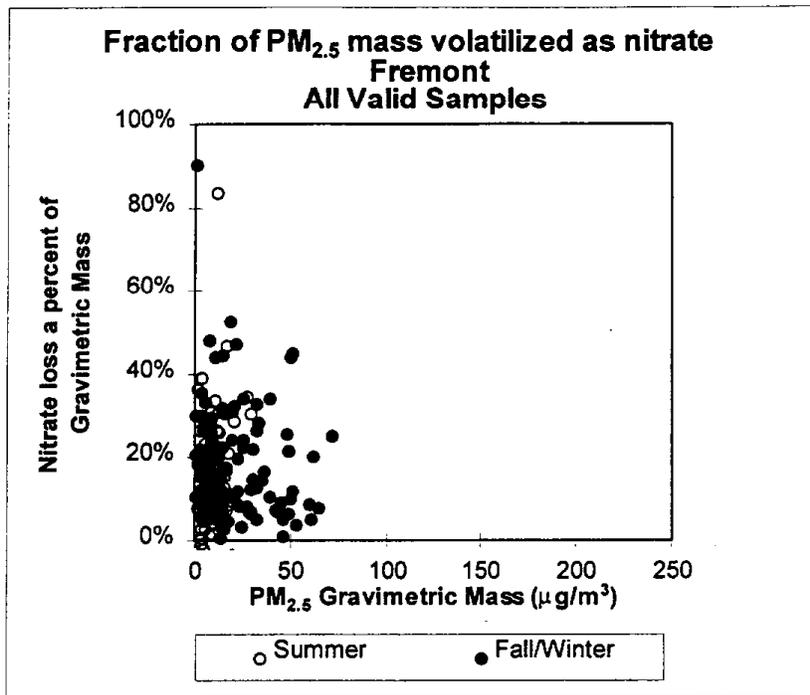


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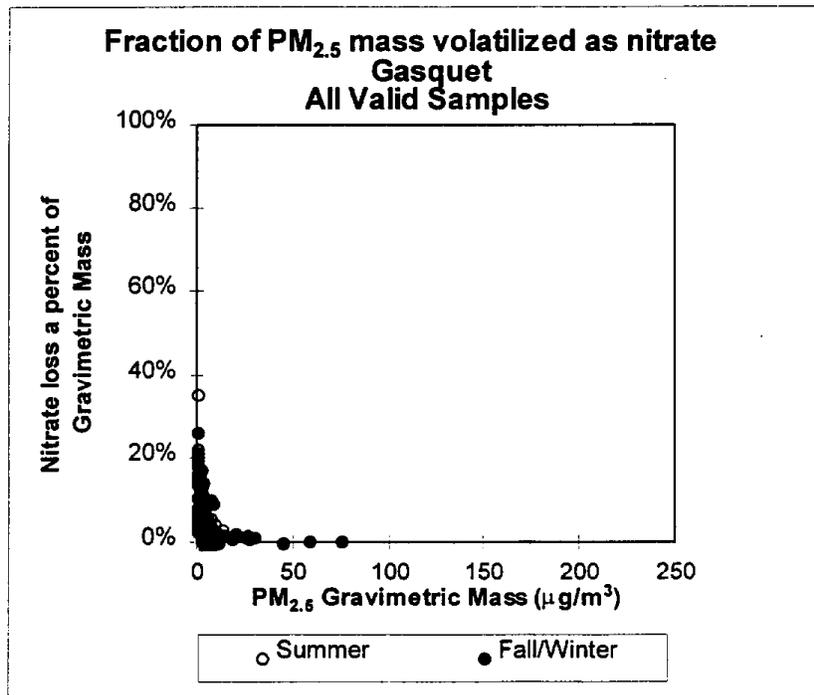


Figure D-4. Mass of nitrate volatilized from Teflon filters as a percent of the measured PM_{2.5} gravimetric mass for Gasquet

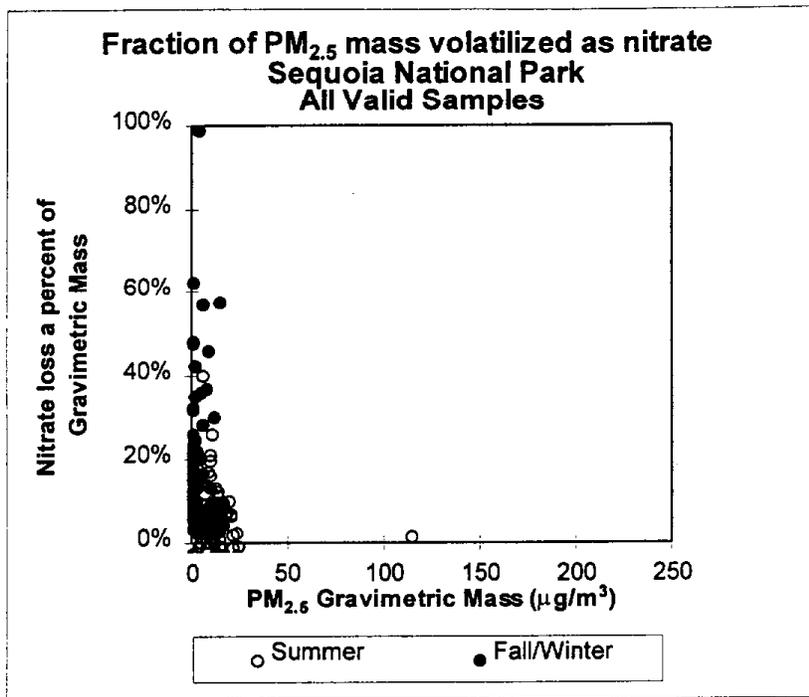


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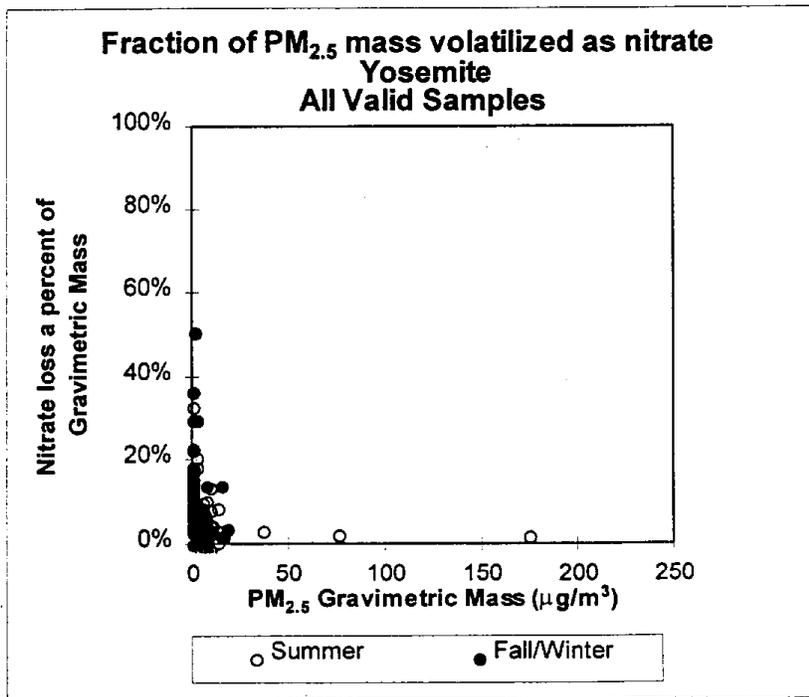


Figure D-10. Mass of nitrate volatilized from Teflon filters as a percent of the measured PM_{2.5} gravimetric mass for Yosemite

