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DRY ACID DEPOSITION: MONITORING TECHNIQUE FOR NITRIC ACID AND PARTICULATE NITRATE - SIZE DISTRIBUTIONS OF ACIDIC PARTICLES

FINAL REPORT
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ABSTRACT

Testing in an environmental chamber and in ambient air at Claremont during the Nitrogen Species Methods Comparison Study showed that nitric acid is denuded with high efficiency by the internal surfaces of the Dichotomous sampler. Loss of ammonium nitrate by volatilization was prevented by using a Nylon filter following the usual Teflon membrane filter. The Dichotomous sampler was used at Claremont for 12 hr sampling of the major inorganic ions. Nitric acid concentrations were obtained from the AIHL cyclone - Dichotomous sampler combination, using the difference method. Good agreement was obtained with samplers employing conventional denuders.

Particle size distributions were obtained for the major inorganic ions, using the Berner nine stage cascade impactor. A denuder preceding the impactor removed nitric acid, and fluorocarbon grease on the Tedlar substrates prevented particle bounce. Volatile nitrate loss was shown to be less than 10%. Fine mode nitrate was associated with ammonium while coarse mode nitrate was associated with both ammonium and sodium. Detailed evidence was obtained for the production of coarse nitrate and hydrochloric acid by the reaction of nitric acid with sea salt. Sulfate was primarily in two submicron modes; hydrogen ion was associated with the smaller mode. Deposition velocities for nitrate and sulfate were measured with Tedlar surfaces and by washing the leaves and needles of potted plants.

I. INTRODUCTION

Major precursors of acidity in the atmosphere are sulfur oxide and nitrogen oxides from the combustion of fossil fuel. In California, nitrogen oxide emissions are about four times the sulfur oxide emissions (1). As a result, nitric acid and particulate nitrate are more important contributors to acid deposition in California than they are in the eastern U.S. Unfortunately, the sampling of these important nitrogen compounds poses technical difficulties which are still inadequately solved. There is a pressing need for a rigorous but practical sampling method which can be used for monitoring.

In the present work, a new monitoring technique for nitric acid and particulate nitrate is demonstrated, based on our previous finding (2) that the internal surfaces of a Dichotomous sampler efficiently denude nitric acid. A Dichotomous sampler with a modified filter holder samples particulate nitrate. A second sampling train consisting of the AIHL cyclone and filter pack samples nitric acid plus particulate nitrate, yielding nitric acid by the difference method. The new technique affords the possibility of sampling both the fine (< 2.5 μm) and coarse (2.5-10 μm) particulate fractions. This is important since deposition velocities increase with particle size. Moreover, at West Los Angeles we found that 51% of the particulate nitrate was in the coarse fraction, while at Tanbark Flats (in the mountains northeast of L.A.), 40% was in the coarse fraction (2).

The new method using the Dichotomous sampler was tested at the Nitrogen Species Methods Comparison Study at Claremont, CA, September 11-19, 1985. This afforded comparisons to results obtained by other investigators sampling in parallel with other techniques. In addition, we operated a Berner impactor in order to obtain the particle size distributions of the major acidic ions. There are almost no such data even though they are needed for the understanding of acidic aerosol formation, transport and deposition. The combined data from the Dichotomous sampler and Berner impactor were useful for testing the sampling techniques and for studying the aerosol at Claremont.

The field study at Claremont was also an opportunity to measure particle deposition velocities to surfaces, using methods we have previously developed (2). We exposed surrogate surfaces (Tedlar) and potted plants (L. ovalifolium, L. japonicum and P. coulteri).

Finally, the nitric acid denuding efficiency of the Dichotomous sampler was determined under controlled conditions in an environmental chamber. These tests were made on a sampler still dirty from the Claremont field sampling and on a clean sampler at various temperatures and relative humidities.

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II. A NEW METHOD FOR NITRIC ACID AND NITRATE AEROSOL MEASUREMENT USING THE DICHOTOMOUS SAMPLER

Nitric acid and particulate nitrate are inherently difficult to sample because of the propensity of nitric acid to deposit on surfaces and because of the volatility of ammonium nitrate (Spicer, et al., 1982; Appel, et al., 1984). The diffusion denuder sampling method is believed to be without significant artifactual error (Forrest, et al., 1982). Two identical filter sampling trains are operated in parallel, one preceded by a diffusion denuder to remove gaseous nitric acid. Particulate nitrate is obtained from the filter train with the denuder and nitric acid by the difference in the nitrate collected by the two sampling trains.

Conventional diffusion denuders consist of aerosol conducting tubes coated internally with a substance such as MgO which reacts with acid. The denuder is usually preceded by a cyclone to avoid loss of coarse particles in the denuder which would bias the difference (Russell and Cass, 1984). The parallel sampler for total nitrate is then also equipped with a cyclone. However, particulate nitrate occurs in both the fine and coarse modes. Moreover, a major mechanism for the formation of coarse (> 2.5 μm dia.) nitrate is the reaction of nitric acid with the surfaces of coarse particles (Harrison and Pio, 1983; Bruynseels and Van Grieken, 1985; Wolff, 1984). Coarse nitrate has a much higher deposition velocity than fine nitrate. This would normally require an additional sampler.

During previous sampling in the Los Angeles Air Basin, we observed that the fine particulate nitrate on the Teflon membrane filter of Dichotomous sampler correlated closely with that on a Teflon filter following a cyclone and a conventional acid denuder (John, et al., 1985). Thus, the internal, oxidized aluminum surfaces of the Dichotomous sampler apparently efficiently denuded nitric acid. This denuding action affords the basis of a new, simplified sampling method for particulate nitrate and nitric acid. Nitric acid can be obtained from the difference between a total nitrate sampler (nitric acid plus fine particulate nitrate) and the particulate nitrate from the fine fraction filter of the Dichotomous sampler. Besides eliminating the need for a separate

denuder, the Dichotomous sampler obtains the coarse particulate reaction. The Dichotomous sampler has been well-tested in the laboratory (John and Wall, 1983) and in the field (Rodes and Evans, 1985). Commercially available, it is already in widespread use.

An experiment to validate the new sampling method was conducted at the Nitrogen Species Methods Comparison Study at Claremont, CA, September 11-19, 1985. The results for nitric acid and particulate nitrate were compared to those obtained by two other groups operating conventional denuder difference samplers. Comparisons were also obtained to monitors based on different principles. The particle samples were analyzed for the major inorganic ions to demonstrate the capability of the method for aerosol characterization. Coupled with particle size distributions we obtained with a cascade impactor (Section III), these data revealed interesting details of atmospheric chemistry during the Claremont study.

Experimental

The Samplers

A manual, Sierra 244 Dichotomous Sampler equipped with the 10 μm Andersen SA-246B Inlet was operated at the standard flow rate of 16.7 L min^{-1} (1 m^3 hr^{-1}). The only modification was to the filter holders. A Nylon membrane filter (1 μm pore size Nylasorb, Gelman Sciences, Inc.) was added, following the usual Teflon membrane filter (2 μm pore size Teflon, Gelman Sciences, Inc.) (Figure 1). The purpose of the Nylon filter is to collect the nitric acid from the volatilization of ammonium nitrate on the Teflon prefilter. If the sole purpose were to sample nitrate, the Nylon filter alone would suffice; however, when one wishes to sample particulate sulfate, a Teflon filter is necessary, since Nylon filters collect sulfur dioxide to some extent. The 37 mm membrane filters were held in standard cassettes. Both the fine and coarse fraction filter holders were modified.

A second Dichotomous sampler was operated, identical to the first except that a denuder of anodized aluminum was inserted between the inlet and the virtual impaction stage (Figure 2). The purpose of the denuder was to determine if the standard Dichotomous sampler has sufficient aluminum

surface to completely denude the air stream. The denuder is annular, based on the design of Possanzini, et al., (1983) and has a theoretical denuding efficiency of 84%. The ends of the inner surface were tapered to minimize particle loss. Because the anodized aluminum surfaces were black, a sunshade of white PVC was placed over the denuder. The ends of the denuder were designed to mate with the Dichotomous sampler without modifications to the latter. This Dichotomous sampler was also equipped with the double filter holders. The legs of the stand were shortened so that the inlet was at the same height as that of the other Dichotomous sampler.

The total fine nitrate (nitric acid plus fine particulate nitrate) sampler is shown in Figure 3. A short, large diameter (4 cm) Pyrex inlet leads to the AIHL cyclone (John and Reischl, 1980) which is made of aluminum. The internal surfaces received three coats of Teflon by a standard commercial procedure developed by du Pont. The final two coats were PFA Teflon baked to form a smooth surface. B. Appel (private communication) tested a copy of this cyclone, using a nitric acid generator in an environmental chamber. The cyclone was still dirty from field sampling. In sampling 15 $\mu g/m^3$ of nitric acid for 2 hrs, the loss was found to be less than 5%. (Recent tests indicate that the cyclone has considerably higher losses when clean). A double 47 mm Nuclepore plastic filter holder was used; a loss of nitric acid in this filter holder of the order of 10% is possible (Appel, private communication).

The cyclone was operated at 24 L min^{-1} to obtain a 50% cutpoint of 2.5 μm. In order for the denuder difference method to be accurate, the cutoff curves of the cyclone and the Dichotomous sampler must match. Figure 4 shows that the curves match very closely indeed. The data points for the Dichotomous sampler are from John and Wall (1983) and Loo (private communication, reported in John and Wall, 1983). The solid line was fitted to the data by eye. The dashed curve for the AIHL cyclone is based on a large data set via a universal curve formalism (John and Reischl, 1980).

Sampling and Analysis

Before the field sampling, the Dichotomous samplers were washed with soap and water followed by an alcohol rinse. Then they were operated outdoors in Berkeley for two weeks in order to precondition the internal surfaces.

The samplers were located near the center of the platform at the Comparison Study in Claremont. Sampling periods were daytime (0800-2000) and nighttime (2000-0600), with the precise times synchronized to the Comparison Study periods. Flow rates were calibrated against dry test meters and audited with rotameters at the beginning and end of each period. Static and dynamic (sampler switched on an off) filter blanks were taken in the field. Upon removal from the sampler, the filters were immediately placed in airtight plastic Petri dishes, bagged and stored on dry ice until analysis.

The Teflon filters were extracted in distilled water on a rotating table for one hour. Repeated extractions showed that more than 99% efficiency was achieved. Nylon filters were extracted in a similar manner but in I.C. eluent (sodium bicarbonate solution). The solutions were analyzed on a Dionex ion chromatograph which was calibrated daily. Replicates, water blanks and filter blanks were analyzed. Most of the samples were well above the detection limit of 0.1 $\mu g\ m^{-3}$ for most ions; some samples needed dilution. The accuracy of the extraction and analysis can be estimated from results for spiked filters supplied by the Comparison Study. For Teflon filters having 25, 75 and 250 μg of nitrate, our results deviated from the reference value by 4%, 2% and -6%, respectively. For Nylon filters having 10, 70 and 200 μg nitrate, our results were 14%, 1% and -6%, respectively.

The uncertainty in the nitrate analysis, taking into account the magnitude of the actual filter loadings, averaged 3% for Teflon filters and 4% for Nylon filters. Another 1% variation was introduced by the filter extraction. The sampler flow rates were accurate to about 1% from comparison against AIHL and CARB flow standards. The change in flow rate from the beginning to the end of a sampling period averaged 2%.

The estimated overall error from combining the foregoing factors is 5% for particulate nitrate and 8% for nitric acid.

The nitrate on the Nylon afterfilter was added to that on the Teflon filter. Calculations of the concentrations obtained by the Dichotomous samplers were made with the usual formulae (Dzubay, et al., 1977), including the correction for the inclusion of 10% of the fine particles in the coarse fraction.

Strong acid concentrations were based on pH measurements on aliquots of the filter extracts. Strong acid concentrations obtained by Gran's titration on the same samples consistently yielded concentrations higher by as much as a factor of two, an impossibility since the pH includes a contribution from the partial dissociation of weak acids. These observations are in concordance with those of Keene and Galloway (1985), who showed that the presence of weak organic acids produces large errors in Gran's titration. Our acid concentrations based on pH are overestimates, depending on the amount of weak acid present and the pH.

Results

Comparison of the Dichotomous Sampler to Other Samplers

The fine particulate nitrate from the Dichotomous sampler is compared to that from the second Dichotomous sampler with the aluminum denuder in Figure 5. The correlation coefficient is 0.997, the slope of the regression line is 1.09 ± 0.02 and the intercept is -9 ± 3 nmoles m^{-3}. Since the second Dichotomous sampler with the denuder collected very slightly more than the standard Dichotomous sampler, we conclude that the standard Dichotomous sampler presents sufficient aluminum surface to the air stream to complete the denuding of nitric acid.

The second comparison is for fine particulate nitrate from the Dichotomous sampler to that from conventional MgO denuder sampling trains (Figure 6). B. Appel and Y. Tokiwa used AIHL cyclones identical to ours but the flow rate was 28 L min^{-1} (estimated cutpoint 2.2 μm). They used a single Nylon filter. J. Horrocks operated cyclones, machined from solid white Teflon to the AIHL cyclone dimensions, at 20 L min^{-1}

(estimated cutpoint 2.8 μm). He used Teflon-Nylon filter packs similar to ours. For the comparison, the shorter sampling periods used by the other groups were averaged over the appropriate periods. For the combined data, the correlation coefficient is 0.99, the slope of the regression line is 1.08 ± 0.03 and the intercept is -14 ± 4 nmoles m^{-3}. The small differences in cutpoints did not detectably affect the results. The excellent agreement between the samplers confirms that the Dichotomous sampler denudes nitric acid as efficiently as conventional MgO denuders. The 16 sampling periods spanned a wide range of atmospheric conditions and nitrate concentrations.

Nitric acid concentrations were derived from the difference between the nitrate from the AIHL cyclone and the Dichotomous sampler. In Figure 7, these are compared to nitric acid concentrations from the conventional MgO denuder difference method. The correlation coefficient is 0.94, the slope 1.10 ± 0.07 and the intercept 0.5 ± 11. The scatter of the data is increased over that for fine particulate nitrate, partly because of the subtractions, but mainly because all three total nitrate samplers are very similar. The scatter was about the same for any pairwise comparison of the three samplers. Since there is no statistically significant difference in the results for nitric acid, it is concluded that the AIHL cyclone-Dichotomous sampler difference method for nitric acid is equivalent to that of the conventional MgO denuder difference method.

By the end of the study, the Dichotomous sampler had been operated nearly a month, including the two weeks prior. It is not known how long the sampler can be operated before the denuding action might decrease; however, the large amount of aluminum surface suggests that this might be a considerable period of time.

In common with the conventional denuder difference methods, the AIHL cyclone-Dichotomous sampler difference method obtained nitric acid values higher than those from the laser diode spectrometers but only slightly higher (approx. 10%) than the limited data from the FTIR (Hering, 1986). There was possibly some positive interference from HONO; unfortunately, the HONO data from the various groups at Claremont did not agree well enough to permit an assessment.

Volatilization of Ammonium Nitrate

The fraction of fine particulate nitrate on the Nylon afterfilter, i.e., the fraction volatilized from the Teflon prefilter, is plotted as a time series in Figure 8. The two Dichotomous samplers agreed closely; the cyclone lost a lower fraction. In the Dichotomous samplers the denuded air stream would tend to cause volatilization of ammonium nitrate to restore the equilibrium. On the other hand, the cyclone had a 16% higher flow rate per unit area of filter. Absorption of some of the nitric acid on the cyclone prefilter would also increase the apparent volatilization since our calculation assumes all of the nitric acid to be on the afterfilter. The cyclone-Dichotomous sampler difference was not pronounced except during a few sampling periods. The diurnal variation shows that the dominant factors are the temperature and relative humidity. During the daytime, the fraction volatilized ranged up to over 90% and was even as high as over 60% at night. These data illustrate the necessity for the Nylon filters.

Ambient Concentrations of HNO_3, HCl and Particulate Ions

Data are presented below for ambient concentrations of gaseous nitric acid and hydrochloric acid obtained during the Claremont study by the AIHL cyclone-Dichotomous sampler difference method. Particulate ion concentrations are presented for both the fine (< 2.5 μm) and coarse (> 2.5 μm) fractions obtained by the Dichotomous samplers. Data from the second Dichotomous sampler with the aluminum denuder are included which show that there were no significant differences introduced by the denuder and that good precision was achieved during the sampling and analysis.

Conditions during the sampling period were conducive to observation of an interesting range of effects. It rained just prior to the study and began raining again on the last day of the study; the air was clean at the beginning and end, reaching moderate pollution levels during the middle of the period. During the first half of the study the daytime winds were predominately from inland, with weak sea breezes from the west at night. Over the second half of the study, the sea breeze predominated.

HNO_3: The time series in Figure 9 exhibits the typical diurnal pattern with very low concentrations at night. We have previously observed similar diurnal patterns at five California locations (John et al., 1985). The envelope of the concentrations shows the overall pollution trend discussed above.

NO_3^-: The fine nitrate shows a pattern (Figure 10) similar to that of nitric acid except that the nighttime concentrations are not as low, again typical. The coarse nitrate concentration peaks during the second half of the study, reaching levels comparable to the fine nitrate.

NH_4^+: Ammonium concentrations were corrected for volatilization losses of ammonium nitrate from the Teflon filter, based on the measured nitrate losses. If present, ammonium chloride could have contributed to the loss of ammonium; however the error would have been small since fine particulate chloride, when present, was much smaller in concentration than fine nitrate. The fine ammonium concentration (Figure 11) has a pattern very similar to that of fine nitrate, reflecting the predominance of ammonium nitrate in the Claremont atmosphere. Coarse ammonium showed a peak during the second half of the study as did coarse nitrate, but reached concentrations only about half as great; therefore, at least half of the coarse nitrate was not ammonium nitrate.

$SO_4^=$: Fine sulfate (Figure 12) reached highest concentrations during the second half of the study, consistent with transport from the sulfur sources to the west near the coast. Excellent agreement was obtained for the fine sulfate concentrations from the two Dichotomous samplers, the cyclone and that obtained by J. Horrocks. Coarse sulfate showed a diurnal pattern over the first half of the study, peaking at night when marine air was present. During the second half of the study, coarse sulfate varied smoothly over a peak, similar to coarse sodium (Figure 15). This suggests that coarse sulfate could have been produced by the reaction of sulfur dioxide with sea salt particles or droplets. The sulfate concentration is too high to be explained by the sulfur content of sea water. Unfortunately, conflicting sulfur dioxide data were obtained by various groups at Claremont, preventing its use for interpretation.

H^+ (Strong Acid): The strong acid concentrations are plotted in Figure 13. No correlation with the other ionic species is evident. Since no ammonia denuder was used, there is the possibility that some of the acid was neutralized during sampling; however, we believe it unlikely that this was significant. In previous sampling at five California locations including one with high ammonia concentrations (John, et al., 1985) we did not observe any significant difference in the strong acid obtained from parallel samplers, one with and one without an ammonia denuder. The ratio $[H^+]/[NH_4]$ averaged approximately 0.2, i.e., the aerosol is largely already neutralized in the atmosphere. The same conclusion was stated by Harrison and Pio (1983).

Cl^-: Fine and coarse chloride concentrations were about the same (Figure 14), with the highest concentrations occurring during the second half of the study, when westerly winds brought in marine air. It should be pointed out that our cascade impactor data show that the minimum between the accumulation and coarse modes occurred consistently below 2.5 μm, so that the "fine" fraction included some of the coarse mode. Even when this is subtracted, some fine chloride remains.

Na^+: Coarse sodium dominated over fine sodium (Figure 15). The nighttime peaking during the first half of the study and the overall peaking during the second half of the study are consistent with the marine air flow pattern. Coarse sodium concentrations are about double the coarse chloride concentrations; the chloride is believed to have been depleted from the sea salt as explained below.

K^+: No potassium ion was detected in any of the samples although it would have been seen in the cation chromatograms if the concentration had exceeded about 4 neq. m^{-3}.

Ion Balance: The sum of the cations from the fine fraction is plotted vs. the sum of the anions in Figure 16. The correlation coefficient is 0.97 and the slope of the regression line is 1.06. Therefore, a fairly good ion balance was achieved.

HCl: The ion results presented above suggest that the nitric acid reacted with sea salt particles to produce coarse nitrate particles by the reaction:

$$HNO_3 + NaCl \rightarrow NaNO_3 + HCl \qquad (1)$$

Detailed evidence for this reaction based on particle size distributions is presented in Section III. The present evidence includes:

(1) Coarse nitrate, coarse sodium and coarse chloride concentrations were highest during the second half of the study, a period of westerly winds.

(2) Coarse nitrate concentrations were much higher than coarse ammonium, requiring another cation.

(3) Coarse chloride was depleted relative to coarse sodium.

HCl concentrations can be derived by the cyclone-Dichotomous sampler difference method, i.e., by subtracting the chloride on the filters of the Dichotomous sampler fine fraction from the chloride on the cyclone filters. Two assumptions are involved: that aluminum surfaces absorb hydrochloric acid and that Nylon filters are efficient collectors of hydrochloric acid. We have no prior knowledge of the retention of hydrochloric acid on aluminum; therefore, the present work constitutes a field test. On the second point, B. Appel (private communication) determined in the laboratory that Nylasorb filters collect hydrochloric acid with an efficiency of at least 88% at a loading of 100 μg. The efficiency would be expected to be the same or higher at the lower concentrations normally encountered in ambient air.

In Figure 17, the HCl concentrations derived from the cyclone-Dichotomous sampler difference are compared to those obtained by B. Appel with the MgO denuder difference technique. The correlation coefficient is 0.96; the intercept of the regression line is 0.8 ± 3.2, but the slope is 1.27 ± 0.12, which is just significantly different from one at the two sigma level. This result suggests that aluminum surfaces may be slightly less efficient collectors of HCl than MgO, although the limited

data cannot be regarded as conclusive. The cyclone-Dichotomous sampler method does show promise for hydrochloric acid monitoring.

The time series for HCl concentrations (Figure 18) shows that HCl was produced mainly during the second half of the study. The diurnal variation correlates with nitric acid. In Figure 19, the histogram shows that the sum of hydrochloric acid and coarse chloride is approximately equal to coarse sodium concentrations for daytime samples. The agreement is close, considering that the 2.5 μm cutpoint of the Dichotomous sampler excludes some the coarse mode (Section III). The peaking during the second half of the study is evident. These data are additional strong evidence for the reaction in Equation (1). The agreement of the HCl data from the two Dichotomous samplers (Figure 18) again shows that the addition of an aluminum denuder has no significant effect on the denuding efficiency.

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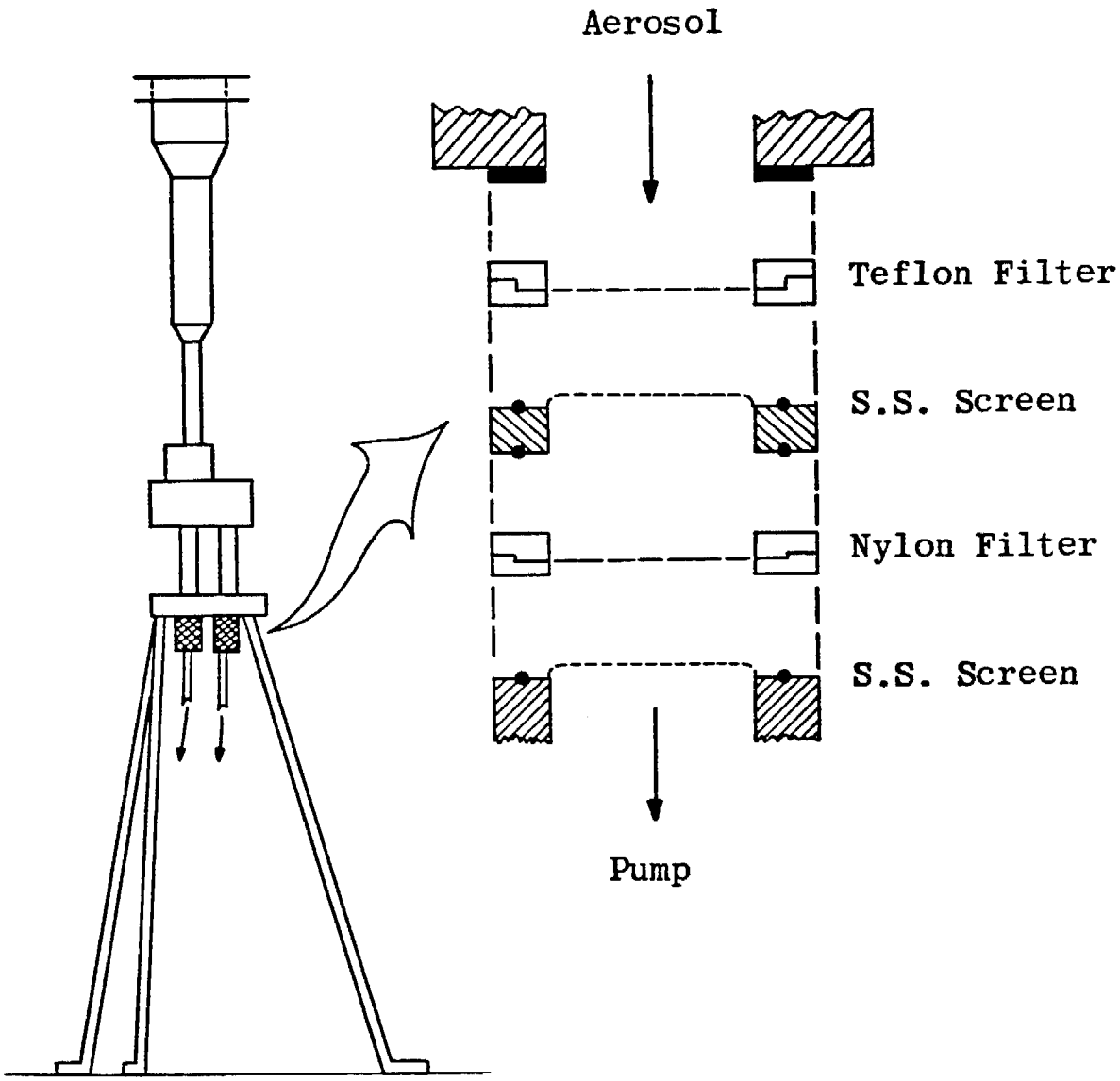

Figure 1.

Dichotomous sampler with filter holders modified to use a Teflon prefilter and a Nylon after filter.

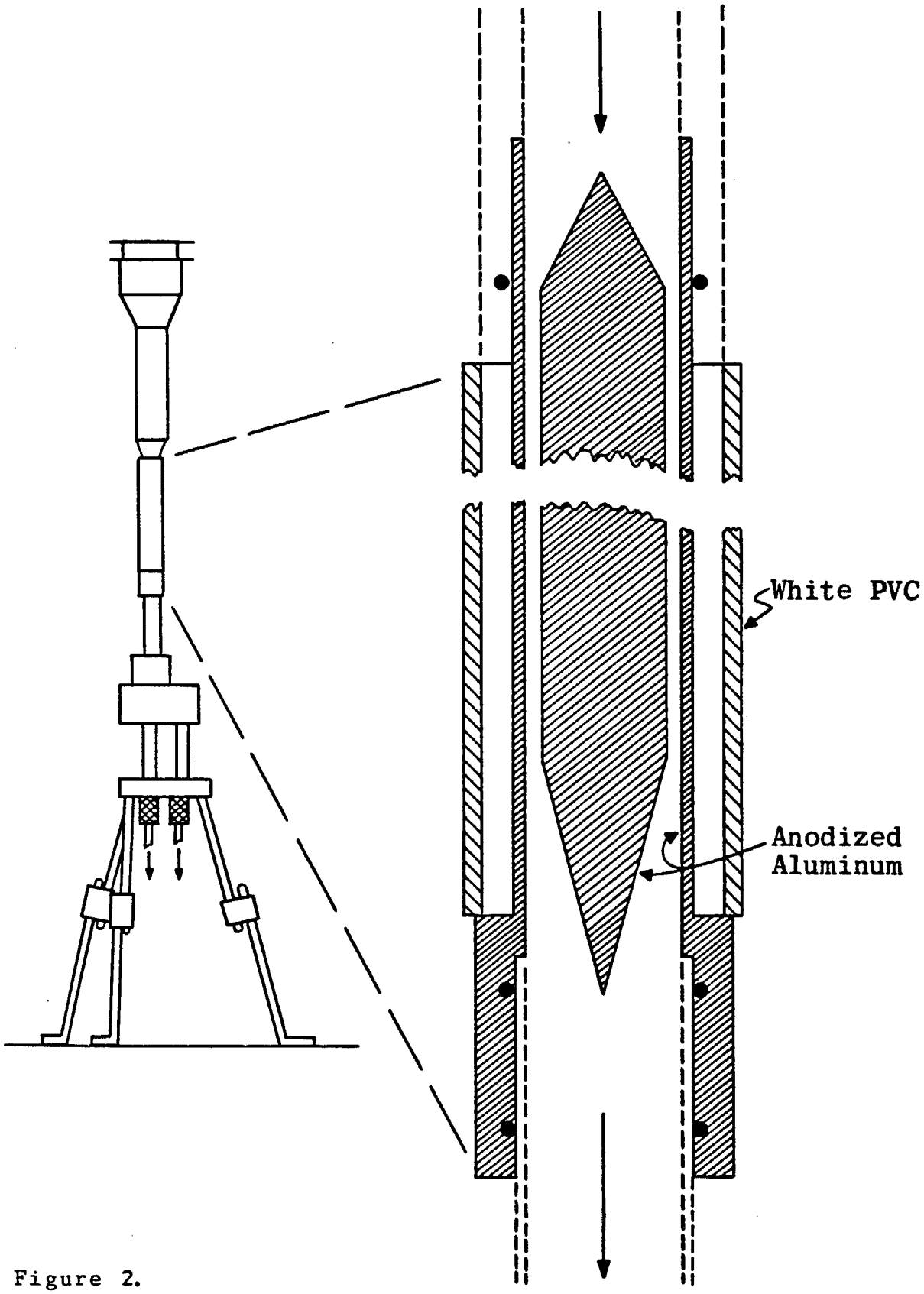

Figure 2.

Second Dichotomous sampler equipped with an annular denuder of anodized aluminum.

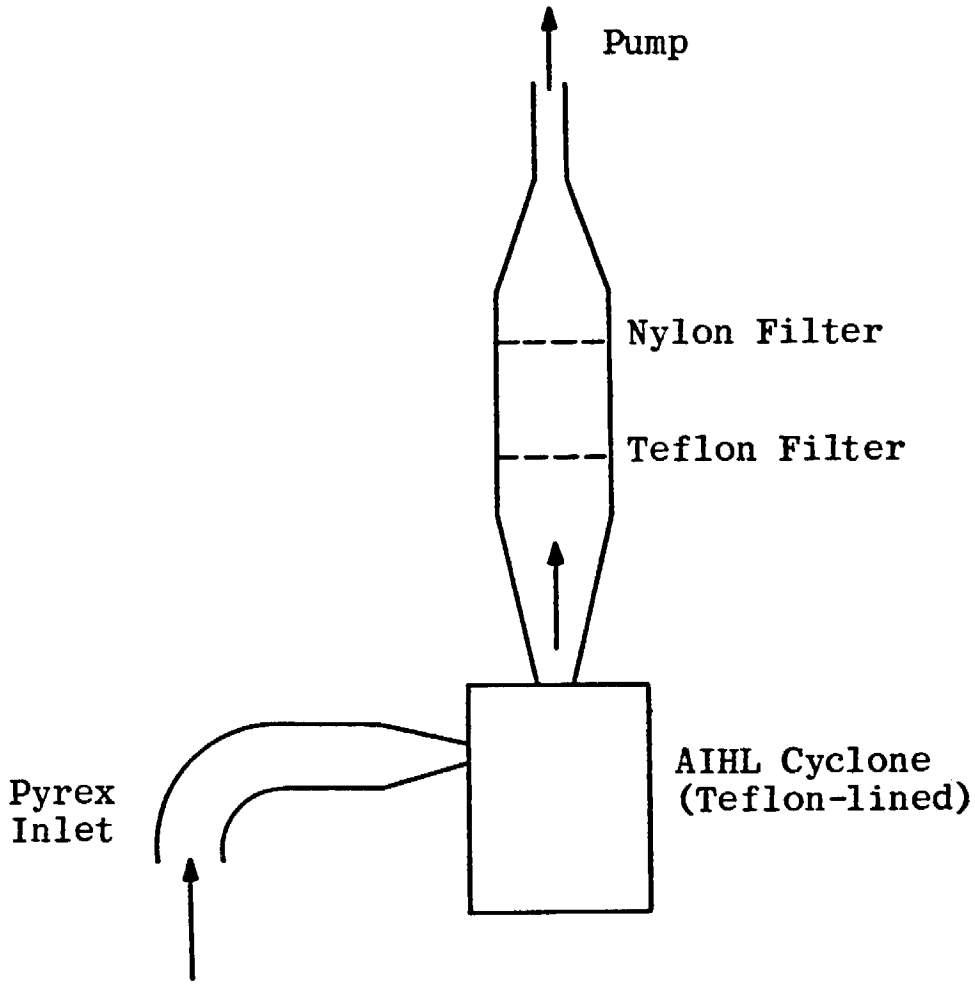

Figure 3. AIHL cyclone used for total fine nitrate sampling.

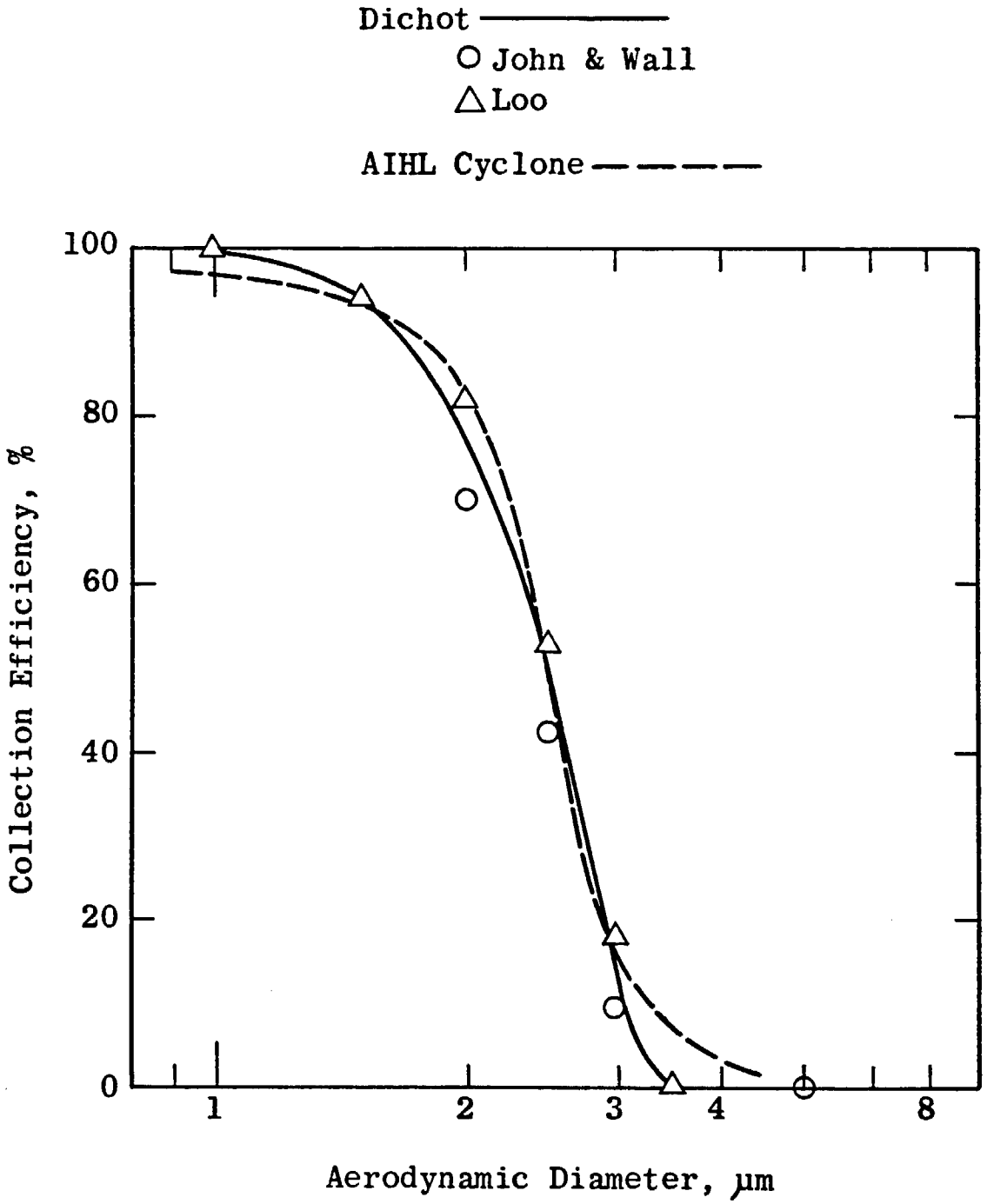

Figure 4.

Particulate collection efficiency curves showing the close match between the Dichotomous sampler and the AIHL cyclone.

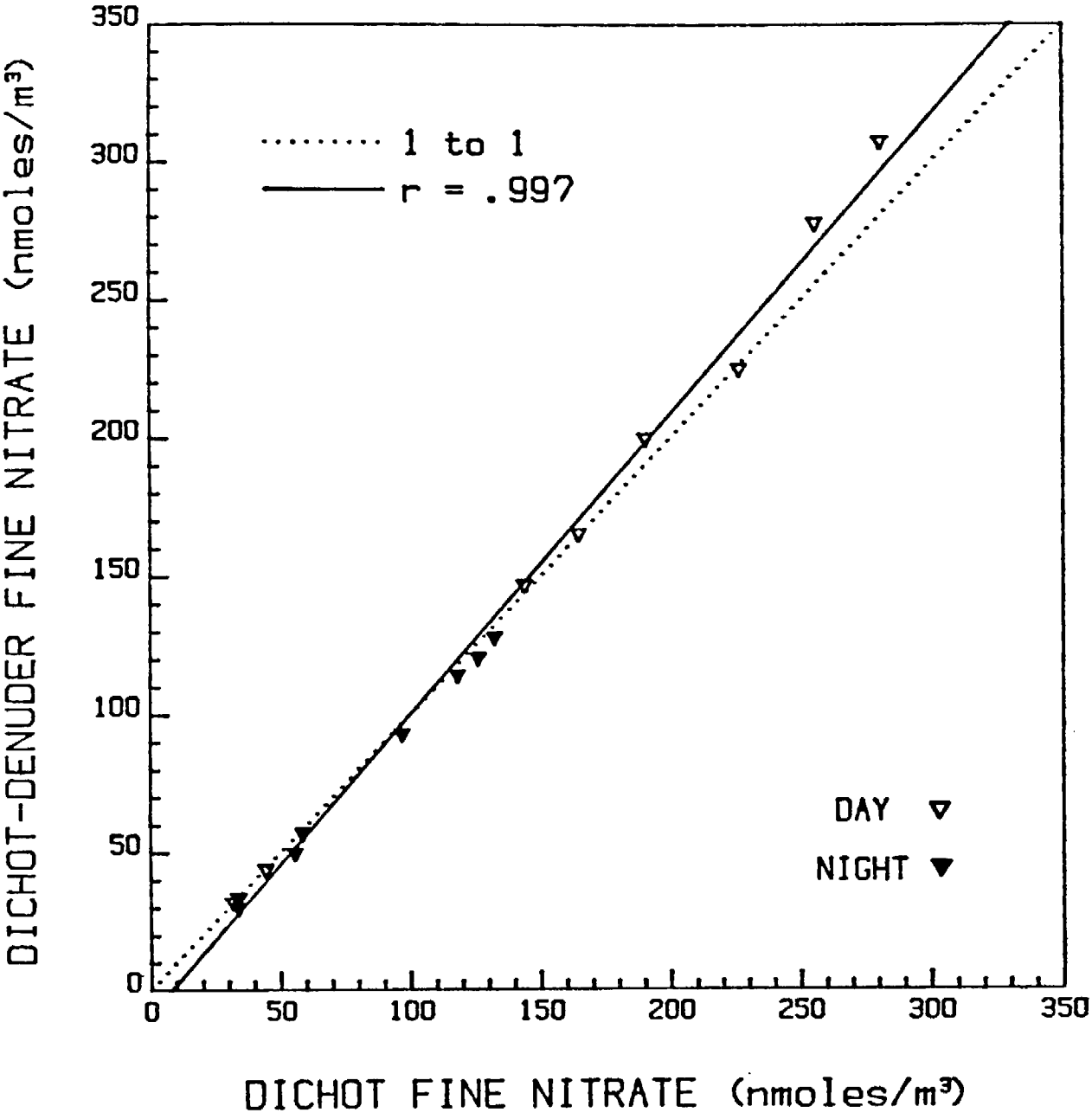

Figure 5.

Fine particulate nitrate collected by the second Dichotomous sampler with the aluminum denuder vs. that collected by the standard Dichotomous sampler.

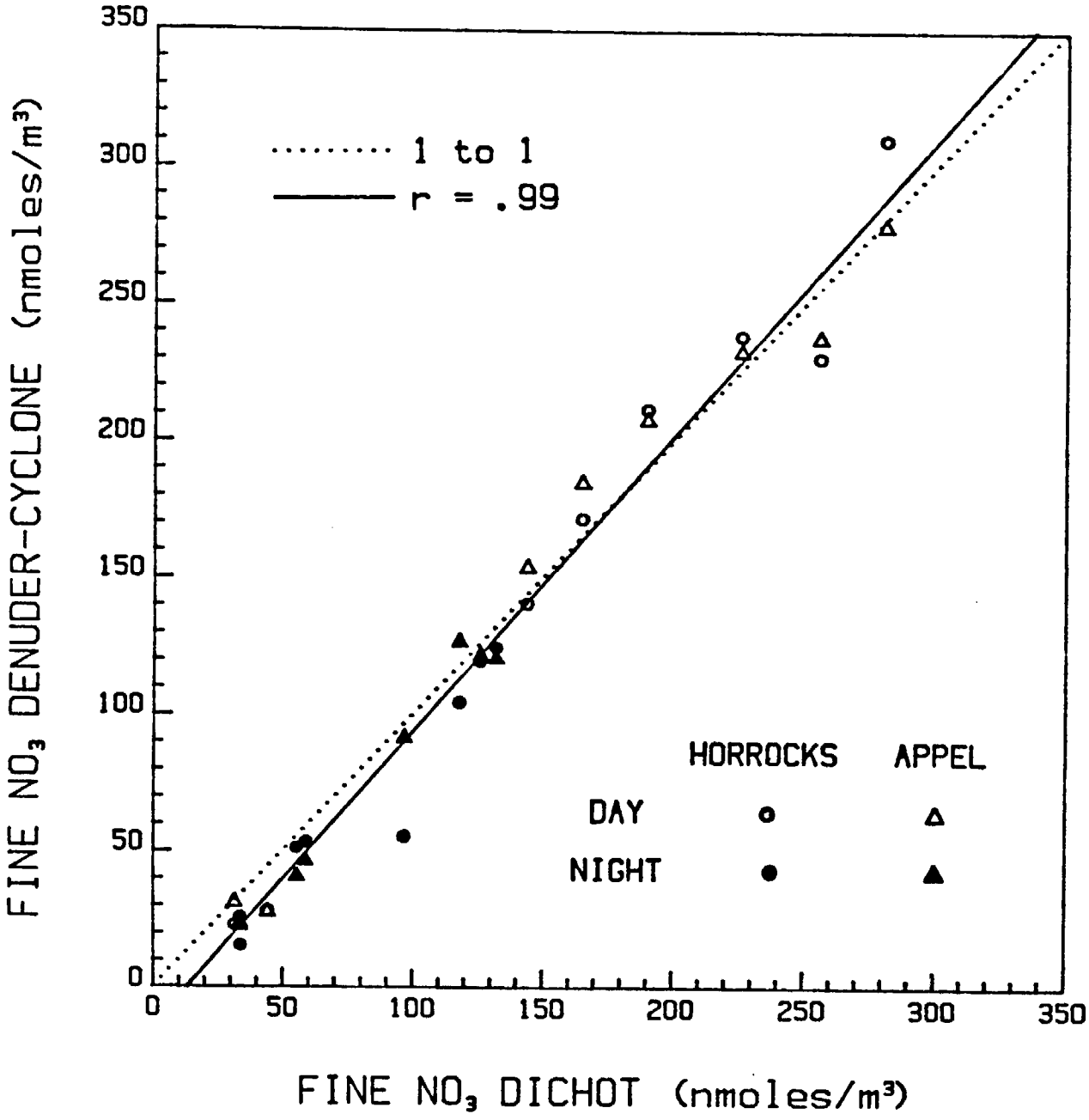

Figure 6.

Fine particulate nitrate collected by the conventional MgO denuder samplers vs. that collected by the Dichotomous sampler.

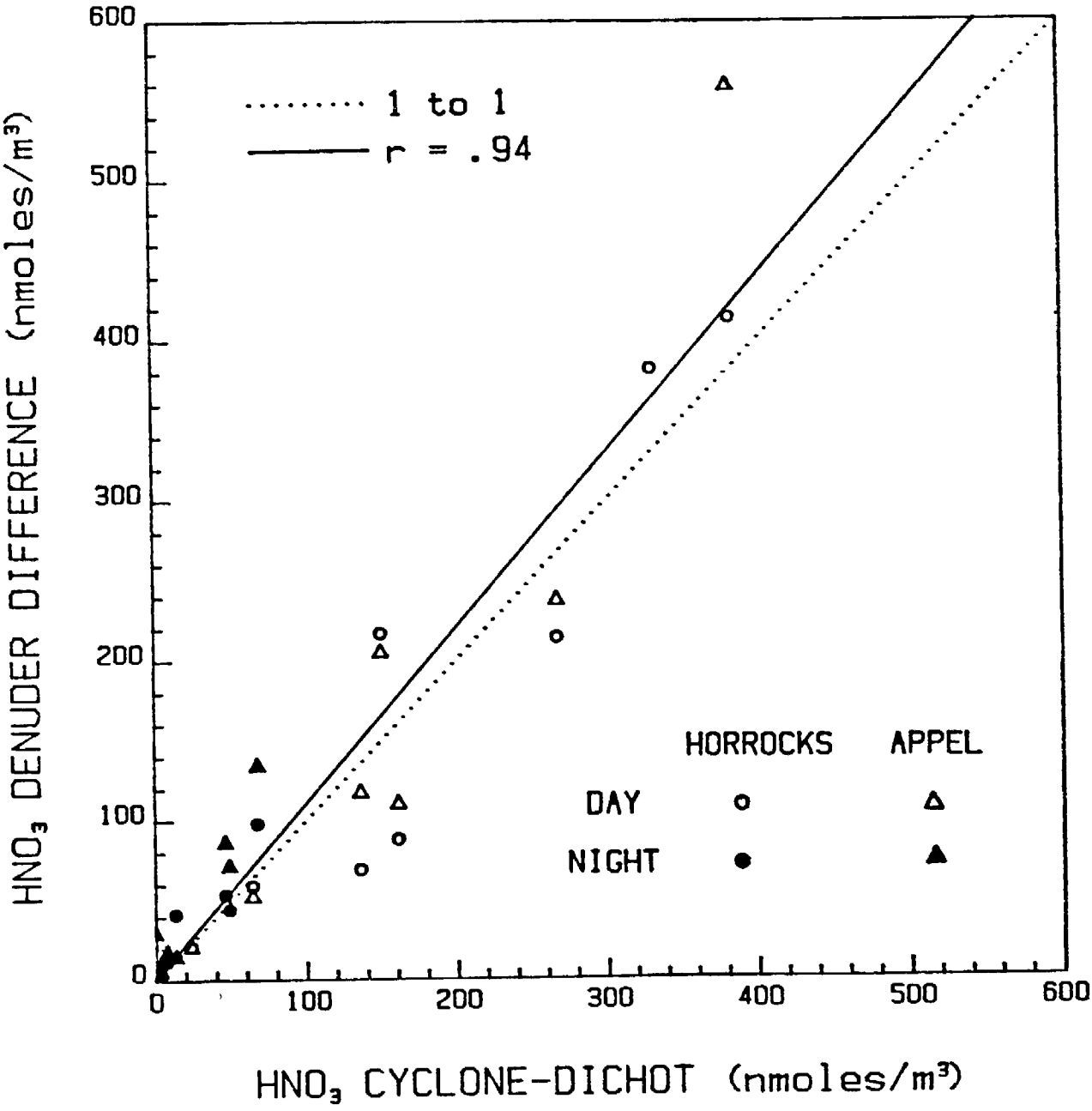

Figure 7.

Nitric acid concentrations determined by the MgO denuder difference method vs. that from the cyclone-Dichotomous sampler difference method.

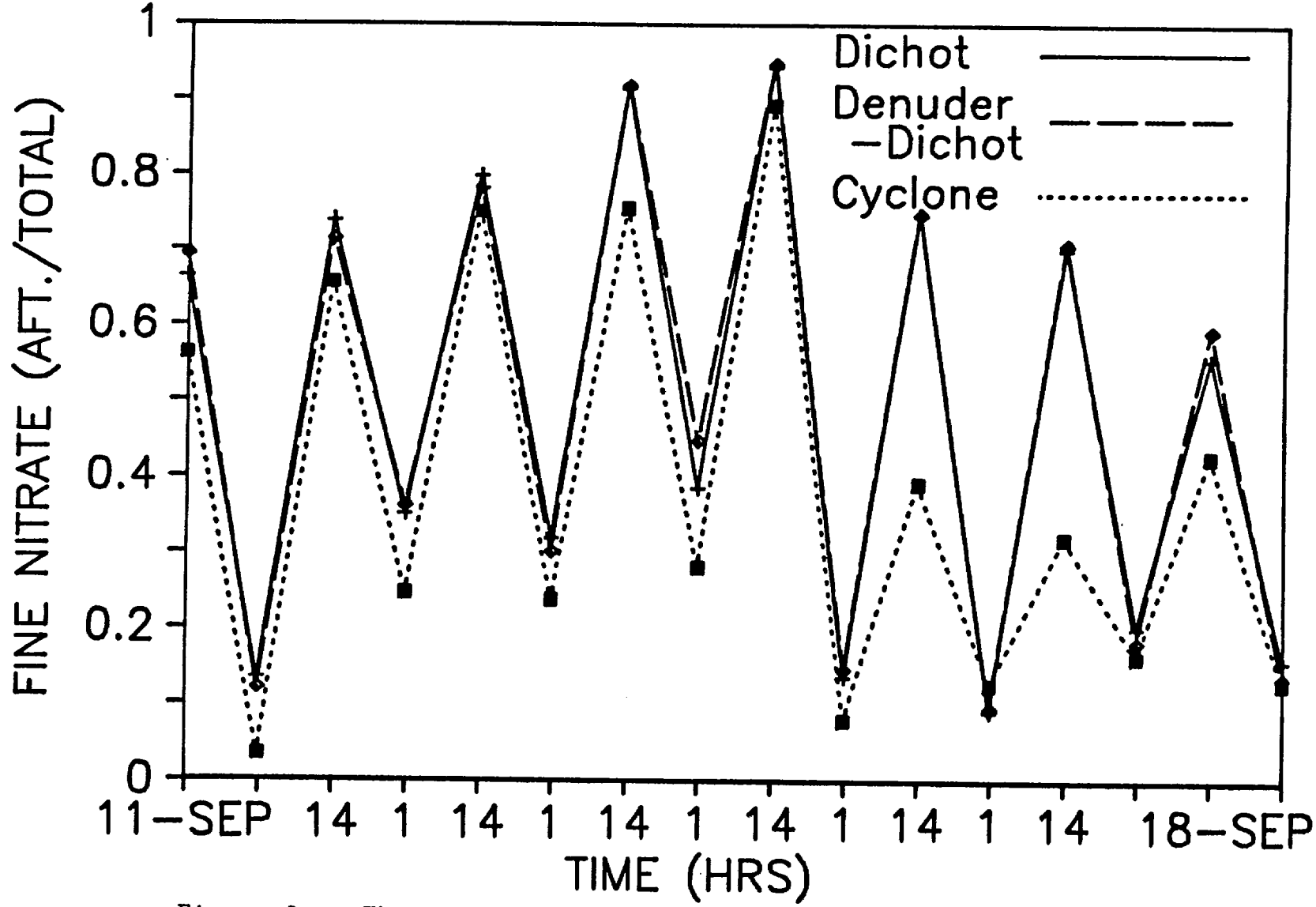

Figure 8. Time series for the fraction of fine particulate nitrate volatilized from the Teflon prefilters.

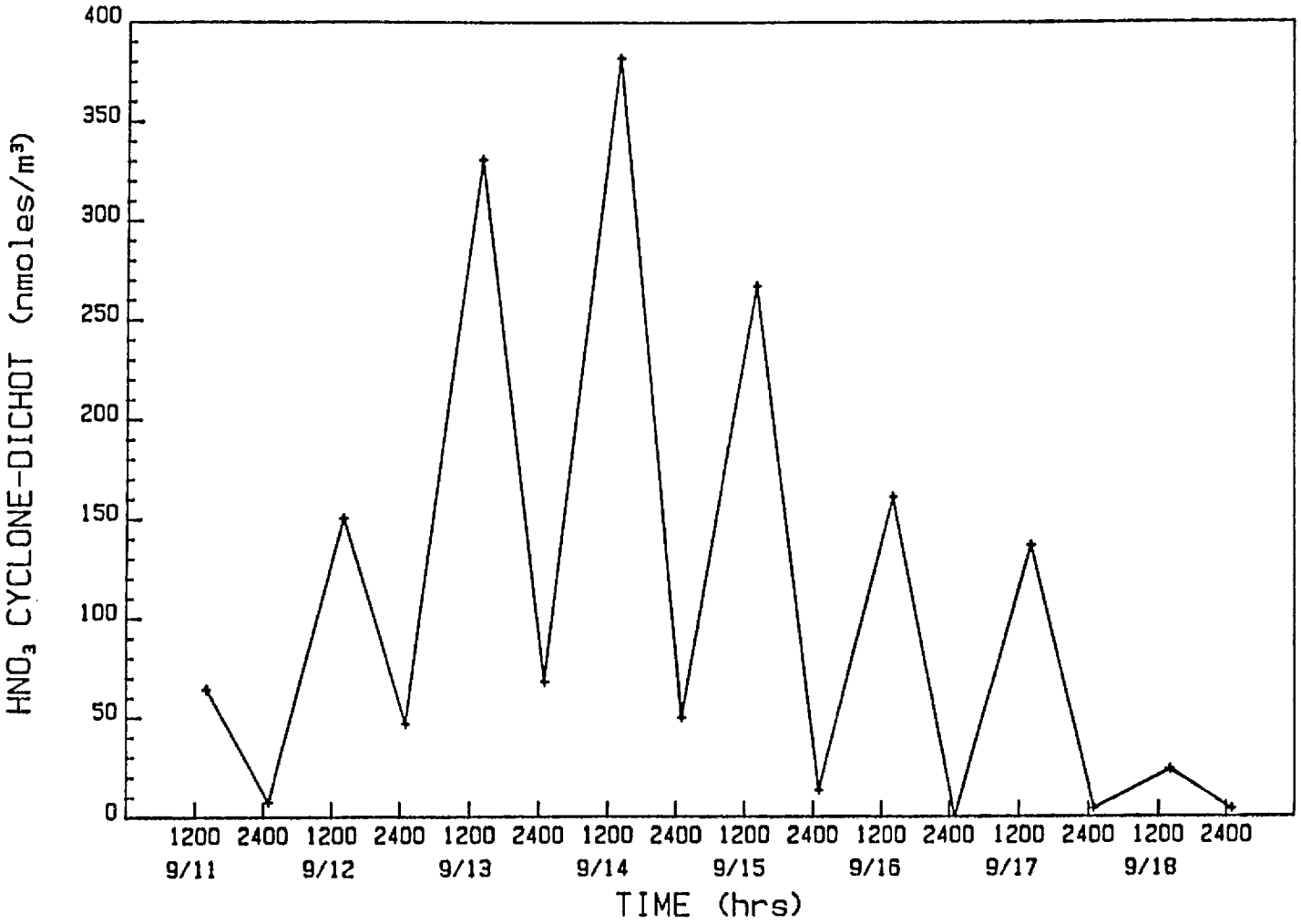

Figure 9. Time series of nitric acid concentrations at Claremont determined by the cyclone-Dichotomous sampler difference method.

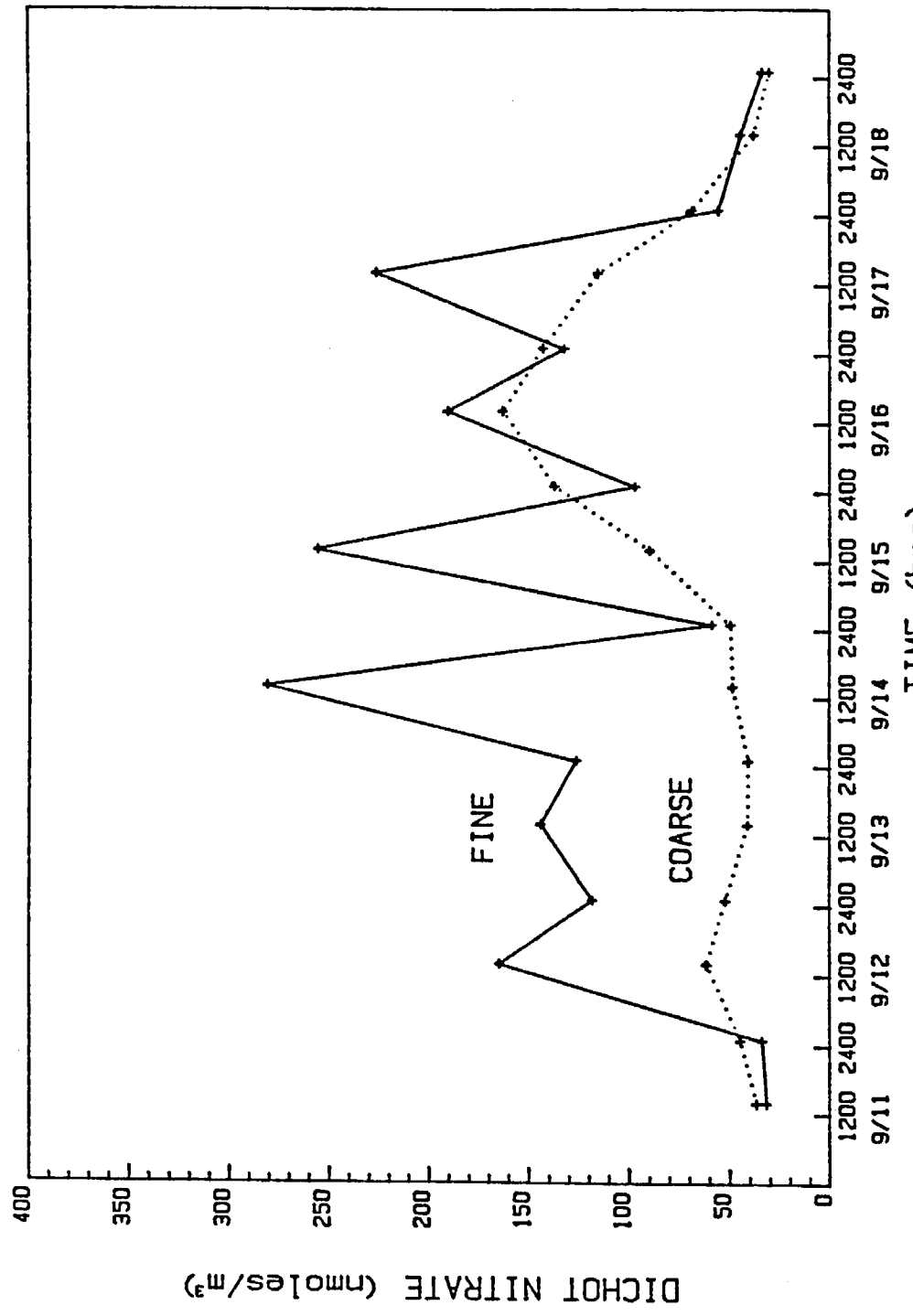

Figure 10. Fine and coarse nitrate concentrations vs. time at Claremont.

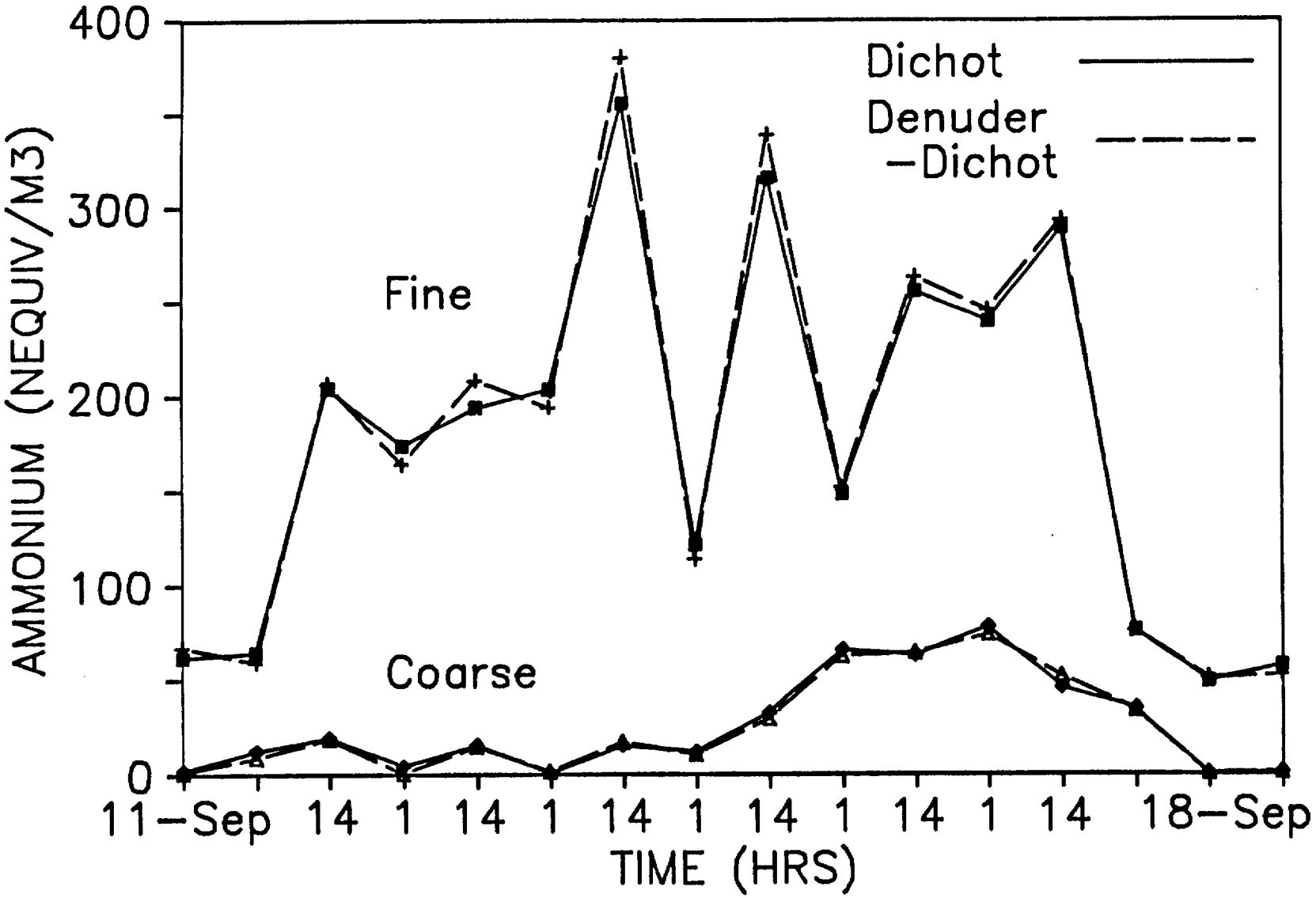

Figure 11. Fine and coarse ammonium concentrations from the Dichotomous sampler and the second one with the aluminum denuder.

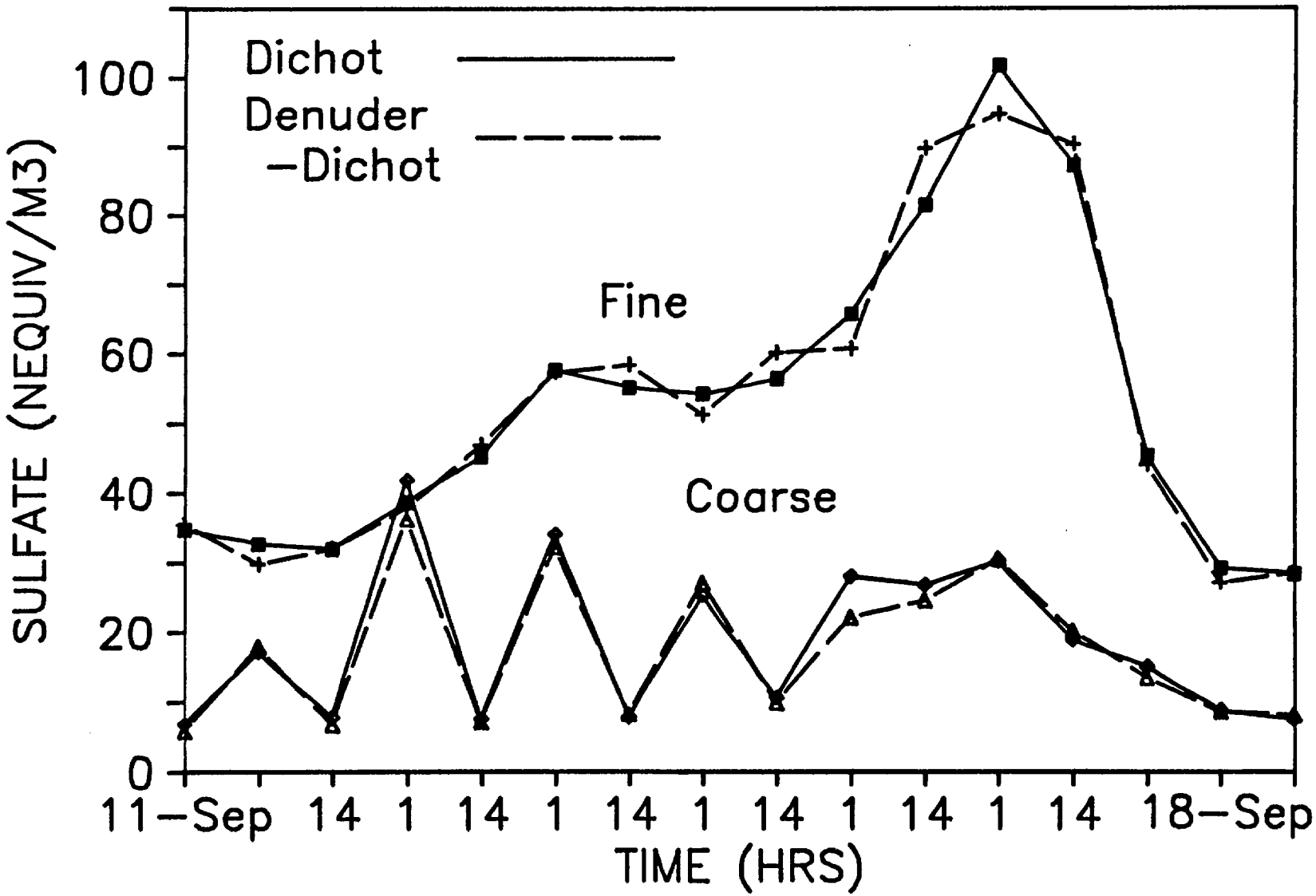

Figure 12. Fine and coarse sulfate concentrations.

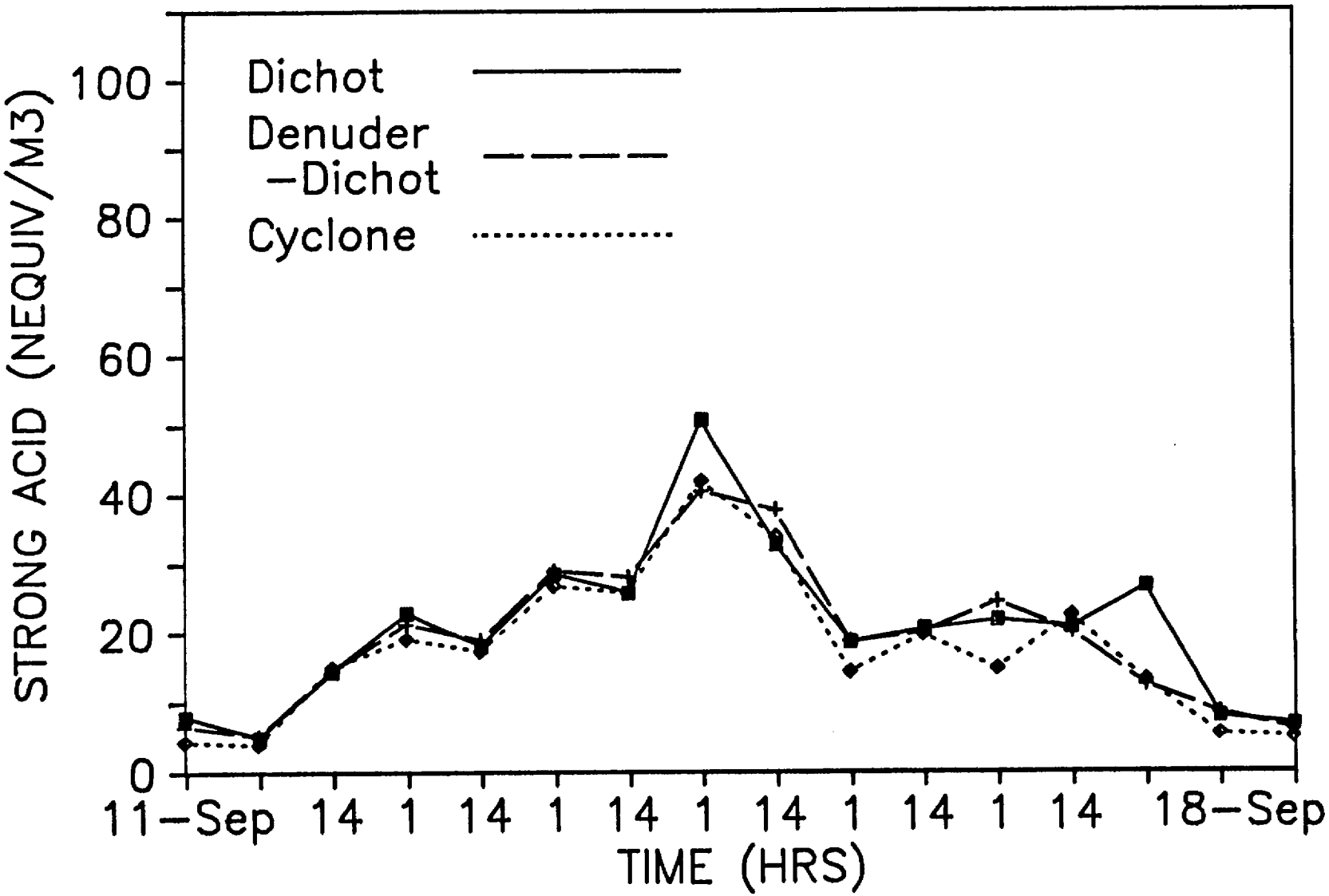

Figure 13. Strong particulate acid concentrations.

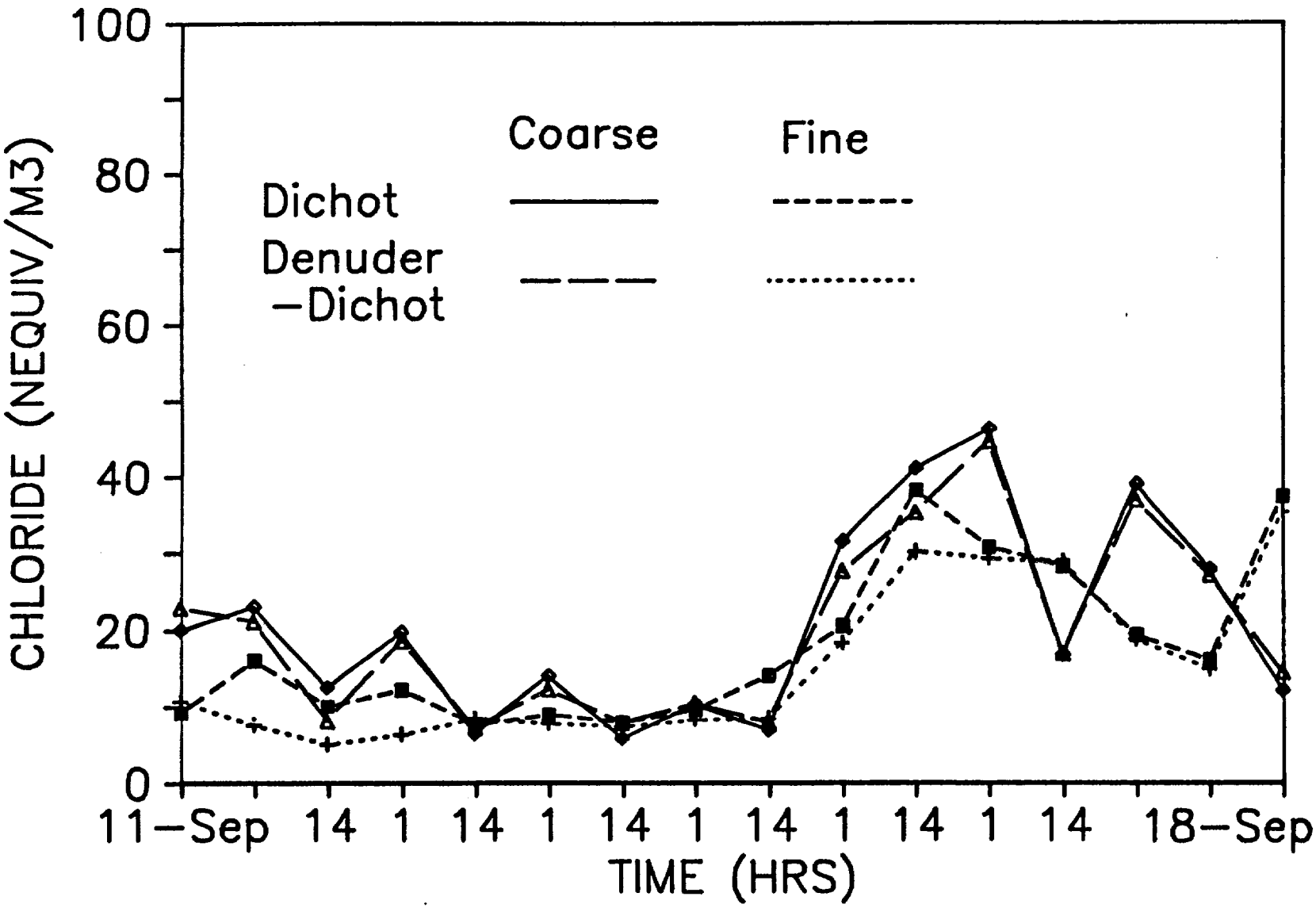

Figure 14. Fine and coarse chloride concentrations.

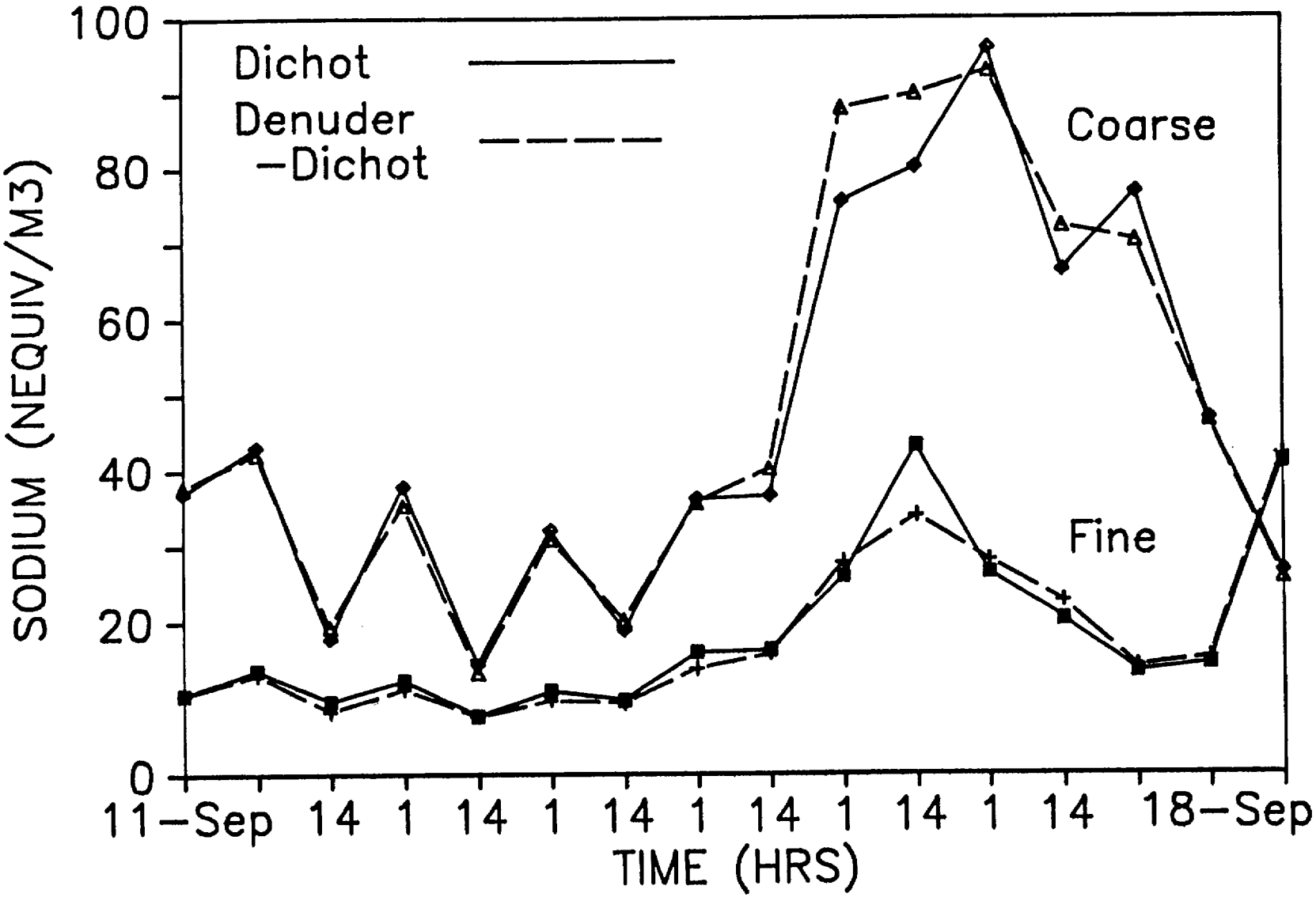

Figure 15. Fine and coarse sodium concentrations.

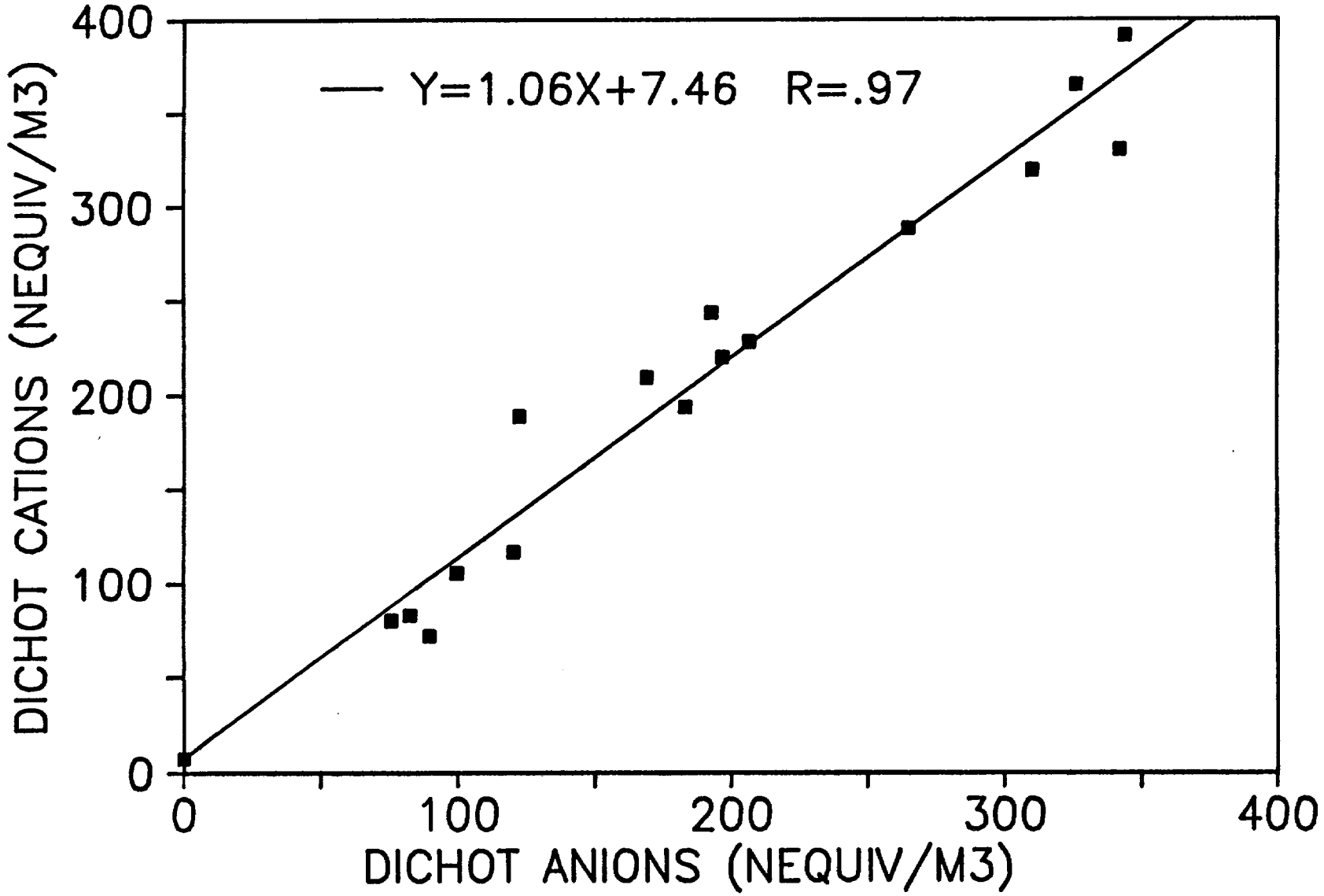

Figure 16. Total cations vs. total anions for the fine fractions of the Dichotomous sampler.

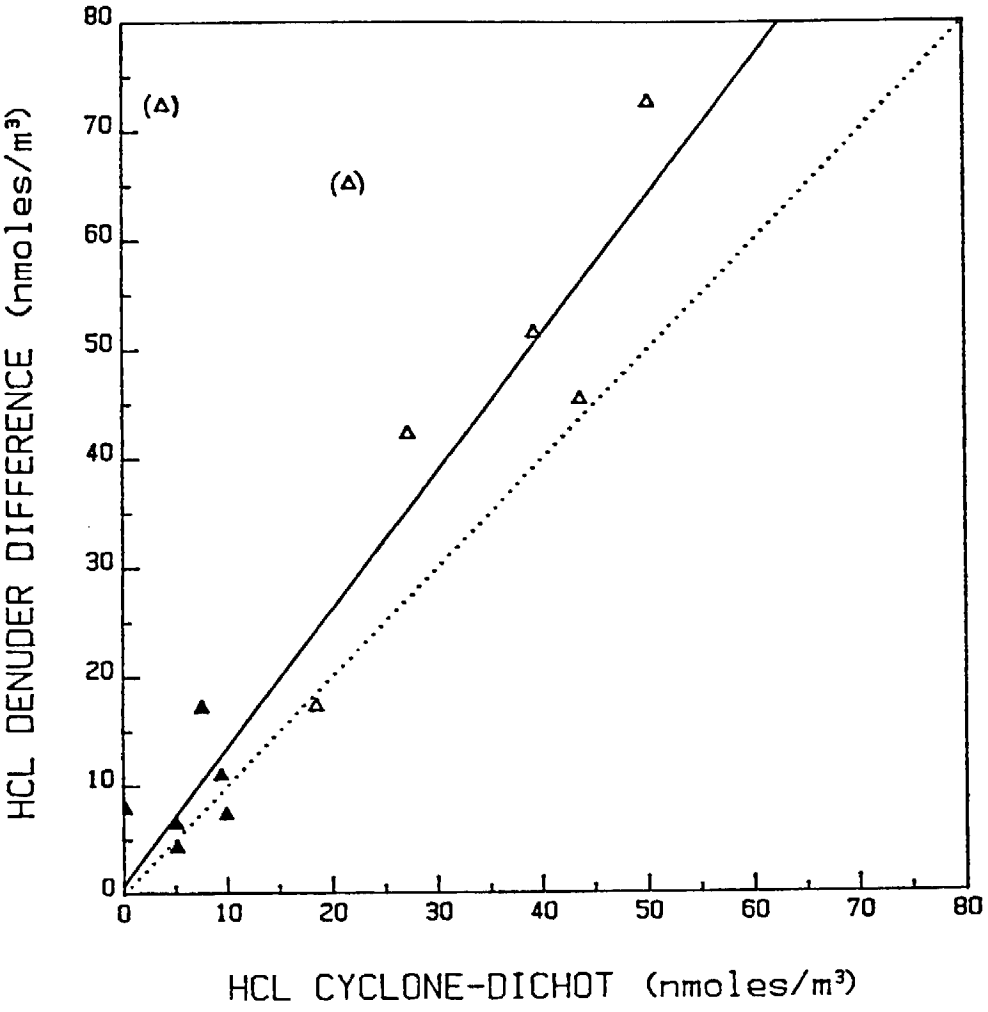

Figure 17.

Hydrochloric acid concentrations obtained from the MgO denuder difference method (B. Appel) vs. that from the cyclone-Dichotomous sampler difference method. The two outliers were omitted from the regression analysis.

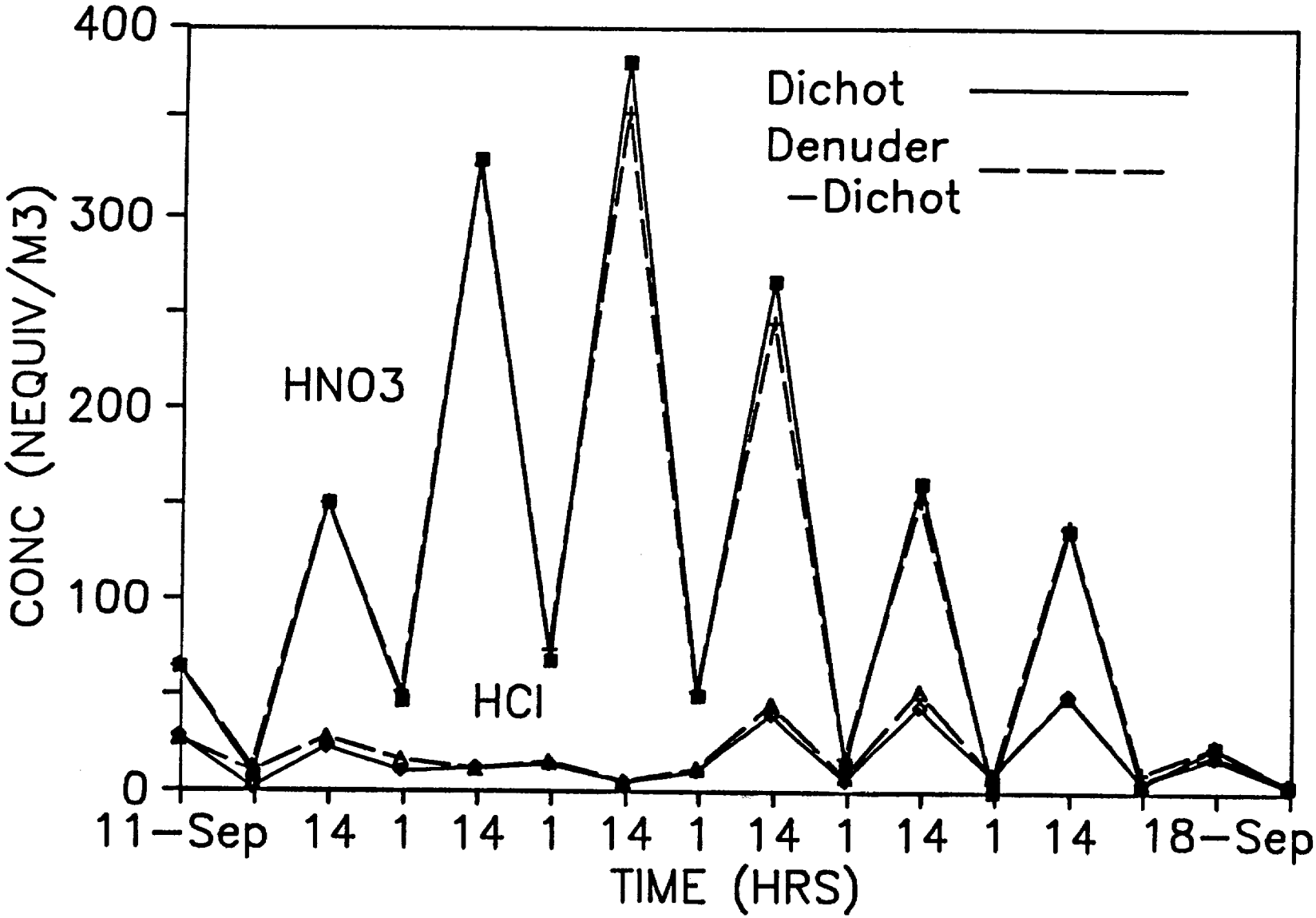

Figure 18. Comparison of hydrochloric acid to nitric acid concentrations.

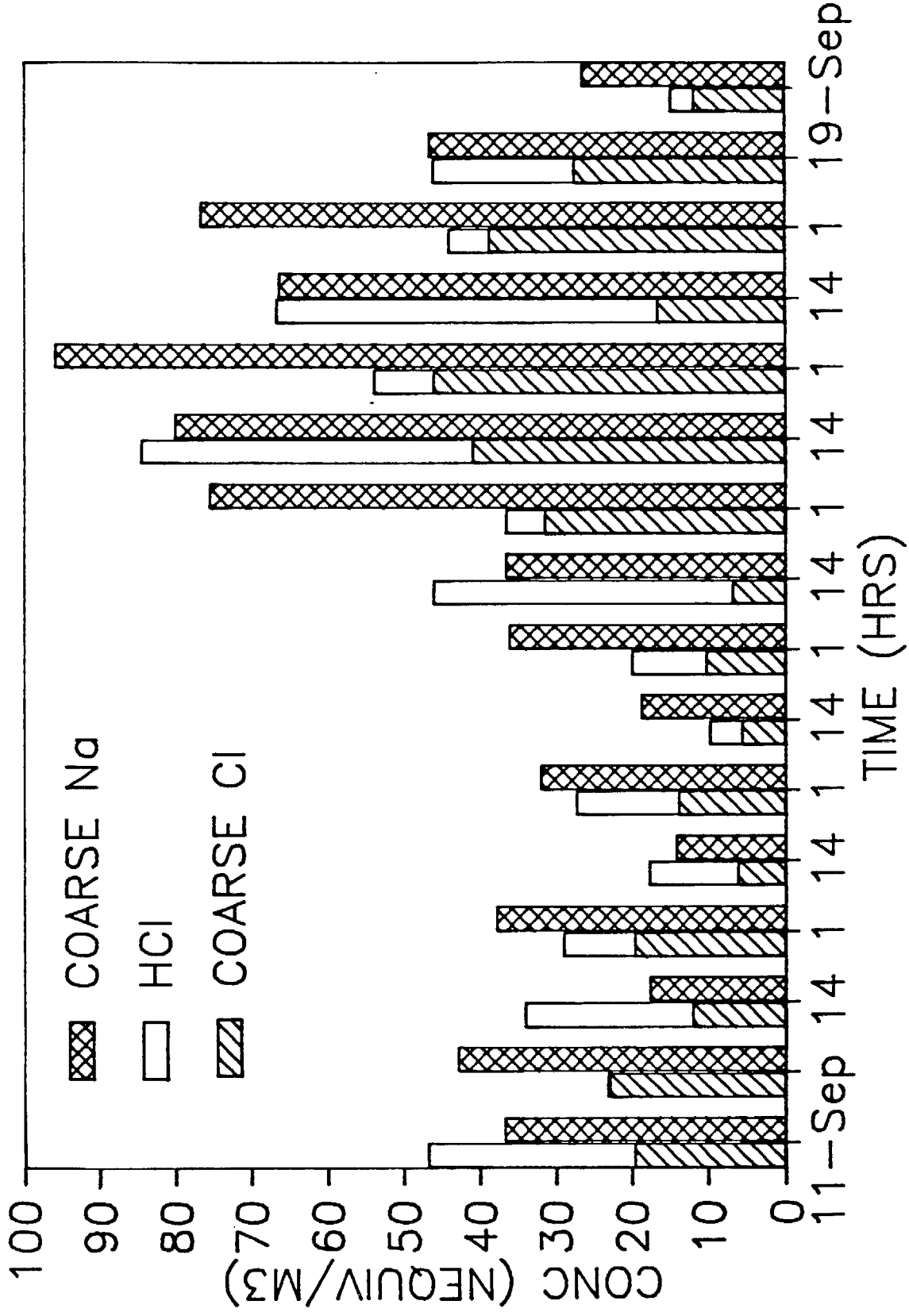

Figure 19. Histogram of coarse chloride, hydrochloric acid and coarse sodium concentrations.

III. MEASUREMENT OF AEROSOL SIZE DISTRIBUTIONS FOR NITRATE AND MAJOR IONIC SPECIES

Nitrate particles represent an important removal pathway for nitrogen oxide reaction products. Nitrate is found in both coarse and fine particles but as different chemical compounds indicating different formation pathways. Thermal evolution nitrate analysis performed by Yoshizumi (1985) on impactor samplers identified a volatile fine particle mode as ammonium nitrate and a non-volatile coarse mode nitrate associated with sodium. Unlike ammonium nitrate which can undergo dissociation under atmospheric conditions to produce nitric acid, non-volatile sodium nitrate serves as a permanent removal mechanism for nitric acid.

As early as 1956 Junge reported large particle nitrate to be formed when marine aerosol mixed with continental air in coastal areas. More recently, size selective sampling in coastal areas by Savoie and Prospero (1982), using a Hi-vol cascade impactor, and Harrison and Pio (1983), using a Hi-vol impactor/diffusion battery combination, determined the large nitrate particle mass distribution to be associated with the surface area distribution of sea salt aerosol, which could be explained by a direct surface reaction with HNO_3. Supporting evidence was provided by Bruynseels and Van Grieken (1985); using laser microprobe mass analysis, they found $NaNO_3$ only in the surface layers of 1-4 μm coastal aerosol.

In the present work, particle size distributions for nitrate and the other major ions were obtained with the Berner cascade impactor during the Nitrogen Species Methods Comparison Study, September 11-19, 1985. We have made similar measurements previously at other California locations (Wall, et al., 1984; John, et al., 1986). The purpose of the Claremont measurements was two-fold: to test improvements to the sampling technique, including the use of a nitric acid denuder and greased substrates, and to obtain detailed size distributions of the inorganic ions to permit interpretation of the relevant atmospheric chemistry.

Experimental

Nitrate particle size distributions were determined with the Berner impactor developed at the University of Vienna (Berner et al., 1979). The instrument has 9 multi-jet stages and operates at 30 L/min with nominal size cuts of 0.06, 0.125, 0.25, 0.50, 1.0, 2.0, 4.0, 8.0 and 16.0 μm aerodynamic diameter. The impactor was calibrated in the laboratory with monodisperse aerosol and the stage efficiencies reported elsewhere (Wang and John, 1986; John, Wall, Ondo and Wang, 1986). Wall losses were found to be less than 1% per stage and thin chemically inert coating (Halocarbon grease #25-5S), applied to the Tedlar impaction foils by solvent evaporation, was effective in reducing particle bounce. To eliminate interference from nitric acid in the field, an annular denuder of anodized aluminum, with a theoretical efficiency greater than 89%, preceded the impactor. The denuder was mounted vertically with a cylindrical wind screen surrounding the inlet to reduce wind effects on large particles. The impactor and denuder inlet are shown in Figure 1. Sampling was made with and without the denuder and with and without grease in order to examine effects on observed size distributions.

At Claremont the impactor was operated during daytime (0800-2000 hrs) and nighttime (2000-0600 hrs) as well as combined periods. Impactor samples were stored in polypropylene extraction tubes under dry ice until extracted with water for analysis in the laboratory. Ion chromatography was used to determine the major anion and cation species including: Cl^-, $SO_4^=$, NO_3^-, NO_4^+, K^+, Na^+, Ca^{++} and Mg^{++} as well as a semi-quantitative measure of formate which may include some contribution from acetate. Field blank levels were below the determination limit of 1 μg/sample for all species except nitrate. A consistent nitrate blank of only 3 μg/sample was traced to a specific batch of ex-traction tubes but no blank correction was applied due to the analytical uncertainty at this low level and since no effect on the reported nitrate distributions would result. Hydrogen ion concentrations were determined by pH electrode which was found to provide a better measure of strong acid than Gran's titration. Gran's titration yielded up to a four-fold higher strong acid level than the total acidity measured by pH electrode on the sample extract, clearly in error. Overestimation of strong acidity by Gran's titration was greatest at the higher pH levels found

on the larger particle stages of the impactor. These shortcomings of Gran's titration are in accord with the findings of Keene and Galloway (1985). Laboratory experiments were conducted to verify that impactor field deposits could be quantitatively extracted from the halocarbon grease substrates. Continuous size distributions were derived from the data using an inversion technique (Markowski, 1986) with curve fitting constraints set by the uncertainty in the chemical analysis. The inversion procedure makes no assumptions as to the functional form of the distribution.

Results

Artifacts and Sampler Comparisons

Size selective nitrate sampling is subject to volatility losses and nitric acid gas absorption which can alter the particle size distribution. From the size distributions taken with and without the nitric acid denuder, no qualitative nitric acid adsorption effects were apparent. Since ambient conditions vary between runs, this comparison is not quantitative. A more rigorous comparison was afforded by a Dichotomous sampler with Nylon filters run in parallel, which has been shown to sample particulate nitrate quantitatively (John, Wall and Ondo, 1987). When the impactor size distributions were integrated above and below the Dichotomous sampler cutpoint, good agreement was obtained for both coarse ($> 2.5\ \mu m$) and fine ($\leq 2.5\ \mu m$) nitrate fractions as shown in Figures 2a and 2b. This comparison covered a range of 5 to 200 nequil/m^3 nitric acid with temperatures from 14 to 30°C, and relative humidi-ties of 30 to 100%. The fine nitrate loss was only 8%, consistent with laboratory tests which showed that the Berner impactor lost 7% of precollected submicron ammonium nitrate particles under hot (35°C) and dry (18% RH) conditions producing 87% loss from a Teflon filter (John, Wall, Ondo and Wang, 1986). Regression coefficients for similar comparisons of the other ions are included at Table 1, with slopes greater that 1 indicating undersampling by the impactor. In general, the agreement is quite good. The slight oversampling of chloride by the impactor may be due to the incomplete sampling of volatile chloride by the Nylon filters of the dichotomous sampler (Appel, 1987).

The presence of grease on the substrates might influence the results by suppressing particle bounce or by affecting the extraction of the deposit for analysis. However, comparisons of the size distributions with and without grease, and the comparison to the Dichotomous sampler show no apparent effect.

Ion Balance

In Figure 3 the sum of the anions - chloride, sulfate, nitrate and formate - are plotted vs. the cations - sodium, ammonium, hydrogen ion, calcium and magnesium. (In the Berner impactor, smaller stage numbers collect smaller size fractions.) Formate is included since the hydrogen ion concentration includes a contribution from organic acids, primarily formic. Hydrogen ion was obtained by pH measurement since Gran's titration was found to be subject to larger errors due to interferences from weak organic acids as reported by Keene and Galloway (1985). The comparison of ion sums provides an indication of whether the major ionic species were determined quantitatively. Ion balance was achieved within 12%, with a small deficit of anions. The anion carbonate, which was not determined, has been reported in soil samples (Kelley, Dore and Page, 1941). The major cations were determined, including potassium, which if present never exceeded the detection limit of 1 μg/sample.

Atmospheric Regimes

Sampling occurred under distinctly different atmospheric regimes which included mixtures of marine and continental influence as evidenced by the wind direction and concentrations of the coarse mode ionic species shown in Figures 4a and 4b. Coarse mode aerosols (here to be differentiated from coarse particle fraction as measured by the Dichotomous sampler) were obtained by integrating the size distribution down to the intermodal minimum (approx. 1.5 μm). Twenty-four hour averages are shown to reveal overall trends. All mineral species (for this comparison) were corrected for marine contribution based on the seawater composition, assuming all of the sodium to be of marine origin. Carbonate was estimated as the large particle anion deficit. The initially strong influence of dry continental air is associated with

non-marine calcium and magnesium. Maritime influence becomes increasingly important during the second half of the study as indicated by sodium. Mineral levels were lower during this period. The last study day was relatively clean after a light rain storm scavenged photochemical pollutants. Examples of different characteristic particle size distributions observed for these separate regimes are shown in Figures 5,6, and 7.

Fine Ammonium Nitrate

Fine nitrate and fine ammonium, which were correlated, were major features of the size distributions. Ammonium nitrate predominated the aerosol during the initial days when the coarse mode was small. The main fine nitrate peak ranged from 0.52 to 0.67 μm, with a smaller peak present during the last half of the study period in the range 0.1 to 0.3 μm. The main ammonium peak was as small as 0.33 μm, but was usually near 0.6 μm. A smaller ammonium peak occurred frequently in the 0.17 to 0.29 μm range. The relatively small amount of nitrate below 0.3 μm has been explained on the basis of the Kelvin effect (Bassett and Seinfeld, 1983). Below 0.3 μm the particle curvature becomes sufficient to increase the vapor pressure over smaller particles. The effect would not alter the ammonium nitrate dissociation constant, but would shift the fine mode nitrate distribution toward larger diameters as observed. The bimodal distribution of fine nitrate indicates different formation processes such as gas phase reaction of nitric acid with ammonia to form the 0.1 - 0.3 μm mode and reaction of nitric acid with pre-existing fine particles to form the 0.5 - 0.7 μm mode.

Surface Reactions of Nitric Acid

Coarse mode nitrate, although present to some degree in all of the samples, is primarily associated with the high sodium levels of maritime air prevalent during the last half of the study. The coarse nitrate peaks consistently at 3 μm, smaller than the sodium mode as evident in Figures 6 and 7. Figure 7 is a good example from the relatively clean period of maritime air. The coarse nitrate peak does not extend to as large a particle size as sodium and chloride, and chloride is depleted relative to sodium, especially near the nitrate peak. Coarse ammonium

is totally absent from the data shown in Figure 7. These features of the coarse mode indicate the reaction of nitric acid with the surfaces of sea salt particles:

$$HNO_3 + NaCl \rightarrow NaNO_3 + HCl \qquad (1)$$

From the large equilibrium constant, the reaction is expected to go to completion with sufficient surface area.

If the reaction went to completion, all of the NaCl would be converted to $NaNO_3$, and the coarse NO_3^- size distribution would follow the sodium mass dis-tribution, neglecting the mass difference between Cl^- and NO_3^-. If the reaction is only partial the small NaCl particles would be converted to $NaNO_3$ but the larger particles, having a smaller surface-to-volume ratio, would be only partially converted. We find, in fact, that the coarse nitrate consistently peaks where the product of the sodium mass and surface distributions peaks. An example is shown in Figure 8. (It can be shown that the product peaks at the crossover point of the mass and surface distributions, if the distributions are lognormal). This suggests that the reaction rate is dependent on the NaCl surface area presented to the nitric acid and also on the mass of sodium chloride available to react.

Additional evidence for the reaction in Equation (1) can be obtained by accounting for the loss of chloride from the sea salt. John, et al. (1986) measured the airborne HCl at Claremont by the denuder difference method. In Figure 9, chloride lost from the coarse mode is plotted vs. HCl (gas) and fine mode particle chloride. A good correlation is obtained by not including the data points (shown in parentheses) for purely nighttime sampling when deposition of HCl to the ground is expected. Airborne HCl could react with ammonia to form fine ammonium chloride aerosol or it could react with the surfaces of accumulation mode particles. The fine chloride peaked near 0.09 μm in eight cases, in three of which ammonium was absent. During the last two days, the fine chloride peak was somewhat larger.

Unlike nitrate, submicron chloride is not always associated with ammonium ion due to a significantly higher ammonium chloride dissociation

constant, which is 73 ppb^2 compared to 27 ppb^2 for ammonium nitrate at 25°C and humidities less than 60%, as calculated using the approach of Stelson and Seinfeld (1982). For example, in Figure 7, the fine chloride peak is at 0.17 μm and clearly not correlated with ammonium. Since the surface distribution of the accumulation mode of urban aerosol peaks at 0.19 μm (Whitby, 1978), this case is consistent with the surface reaction of HCl with pre-existing aerosol. Even in the other cases where ammonium is present, it is not clear whether it is associated with chloride.

Ammonium appears in the coarse mode in more than half of the distributions, peaking at the same particle size as the nitrate. If coarse ammonium nitrate were wind-generated, it seems unlikely that the particle size would coincide with that from the reaction in Equation (1). Also we do not believe coarse ammonium nitrate is due to agglomeration of submicron particles with coarse mode aerosol, since submicron ammonium occurs without coarse ammonium as shown in Figure 7. Instead, we suggest that ammonia reacts with nitric acid on the surface of marine aerosol, probably in the presence of moisture. This mechanism is important since substantial amounts of nitrate can be added to marine particles, in excess of the chloride available for displacement by reaction with nitric acid.

Coarse nitrate can also be produced by the reaction of nitric acid with the surfaces of soil particles (Wolff, 1984). During the initial days of the study, coarse nitrate exceeded sodium, and ammonium was low or absent (see Figure 5). Ca and Mg contributed significantly to the cations associated with coarse nitrate on some days, as shown in Figure 13. Soil particles may be less efficient than sea salt in removing nitric acid since Ca peaked at larger particle sizes than Na.

Sulfate

Sulfate particles occurred primarily in two submicron modes with modal diameters 0.17 to 0.25 μm and 0.60 to 0.65 μm. (One case at 0.31 μm). In two cases, both submicron modes were present simultaneously (Figure 6a). The smaller mode has been ascribed to homogeneous gas phase reac-

tions and the larger mode to the reaction of sulfur dioxide with pre-existing accumulation mode particles (Hering, 1982). Strong acid, which was always fairly low in concentration, tended to be associated with the smaller sulfate mode. According to Hering (1982), the larger mode is produced by the oxidation of sulfur dioxide in liquid droplets. The mode grows to larger particle size than the original accumulation mode from the addition of a significant mass of sulfate. In the case of chloride discussed above, the mass added is insufficient to shift the mode appreciably. Evidence of liquid water was found only in the impactor deposits of stages 3 and 4, which correspond to the larger submicron sulfate mode attributed to droplet phase reaction of sulfur dioxide.

Coarse sulfate, which consistently occurred in excess of that expected from sea salt, was generally distributed in a broad peak extending up to the large particle sizes with sodium and calcium. Colloidal calcium sulfate is reported in the alkali soils which lie to the northeast of the sampling site. Both are sufficiently water soluble to have been completely dissociated in the aqueous extract. In about half of the distributions, coarse sulfate, although broad, peaked at 3 μm with the coarse nitrate. This is consistent with some formation of sulfate by the reaction of SO_2 with sea salt droplets. Significant coarse mode sulfate derived from submicron sulfuric acid is unlikely due to the small amount of the strong acid available and since accumulation mode aerosol is known not to react appreciably with coarse mode aerosol (Willeke and Whitby, 1975).

Coarse Mode Species and Mass Balances

The above evidence of the reaction of nitric acid with sea salt was based on the particle size distributions. Additional strong evidence is provided by accounting for all the major species in the reaction including nitric acid and hydrochloric acid, which were sampled and reported in a companion paper (John, Wall and Ondo, 1987). Coarse and fine species <u>modal</u> concentrations were determined by integrating the species distributions above or below the intermodal minimum, which was consistently near 1.5 μm. Such a clean separation of coarse and fine aerosol <u>modes</u> is not possible with the Dichotomous sampler which cuts at 2.5 μm,

thus including a substantial portion of the coarse mode with the fine fraction.

Since different sampling periods were used for the impactor and filter samplers, twenty-four hour average values were used for the analysis. From Figure 10, during the initial dry period nitric acid concentrations are high but coarse mode nitrate is low, as is sodium. The later infusion of maritime air brings increased sodium levels which correlate closely with increases in both coarse mode nitrate and hydrochloric acid. In order to quantitatively account for chloride attributable to the reaction, the total chloride, aerosol and HCl, was calculated for each individual sampling period and compared to the coarse sodium in Figure 11. The unit slope of the regression line verifies that essentially all the chloride present in the gas and particle phase can be considered to be derived from sodium chloride. Only a few nighttime periods (identified by brackets) were excluded as outliers. The diurnal variation of hydrochloric acid (John, et al., 1987) indicates probable deposition to the ground, similar to nitric acid. This deposition loss cannot be included here.

Interferences from deposition losses can be avoided by accounting for the non-volatile large particle nitrate created when chloride is lost from marine particles. Coarse mode nitrate can be from several different sources including sodium nitrate from the reaction of nitric acid with sea salt, ammonium nitrate from the reaction of ammonia and nitric acid on the surface provided by sea salt particles, and calcium and magnesium nitrates from the reaction of nitric acid with soil derived particles. The amount of sodium nitrate present was calculated from the total coarse nitrate by subtracting contributions from calcium and magnesium nitrate as well as ammonium nitrate. Calcium and magnesium nitrate was estimated as the total calcium and magnesium present after subtraction of soil related sulfate and carbonate. Ammonium nitrate was estimated as the coarse ammonium present. In Figure 12, the portion of nitrate attributable to the reaction of nitric acid and marine sodium chloride is plotted against the chloride lost. Excellent agreement is obtained for <u>all</u> sampling periods as well as, a wide range of sodium levels. Points nearer the origin correspond to low sodium days.

The cations associated with coarse mode nitrate are shown in Figure 13 for individual sampling periods. Both volatile and non-volatile species are present. Non-volatile nitrates function as a permanent removal mechanism for nitric acid. The major non-volatile constituent is sodium from the reaction of nitric acid with sea salt, but soil derived calcium and magnesium are substantial when sodium is low. Ammonium represents the volatile nitrate fraction. However, because of the relatively small surface area and high deposition velocity, coarse ammonium nitrate is expected to deposit to the ground more efficiently than fine ammonium nitrate.

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TABLE 1. Correlation of Integrated Impactor Samples with Dichotomous Sampler Fractions*

	Species	Slope	Intercept	R	Approx. Max Conc. (nequiv/m^3)
Fine < 2.5 μm	$SO_4^=$	1.06	-2.33	0.97	120.00
	NO_3^-	1.08	3.23	0.99	240.00
	Cl^-	0.86	0.03	0.95	50.00
Coarse > 2.5 μm	$SO_4^=$	1.09	0.02	0.97	40.00
	NO_3^-	1.06	3.20	0.99	240.00
	Cl^-	0.88	3.35	0.98	50.00
	Na^+	1.02	4.50	0.97	110.00

* Slopes greater than one indicate undersampling by the impactor.

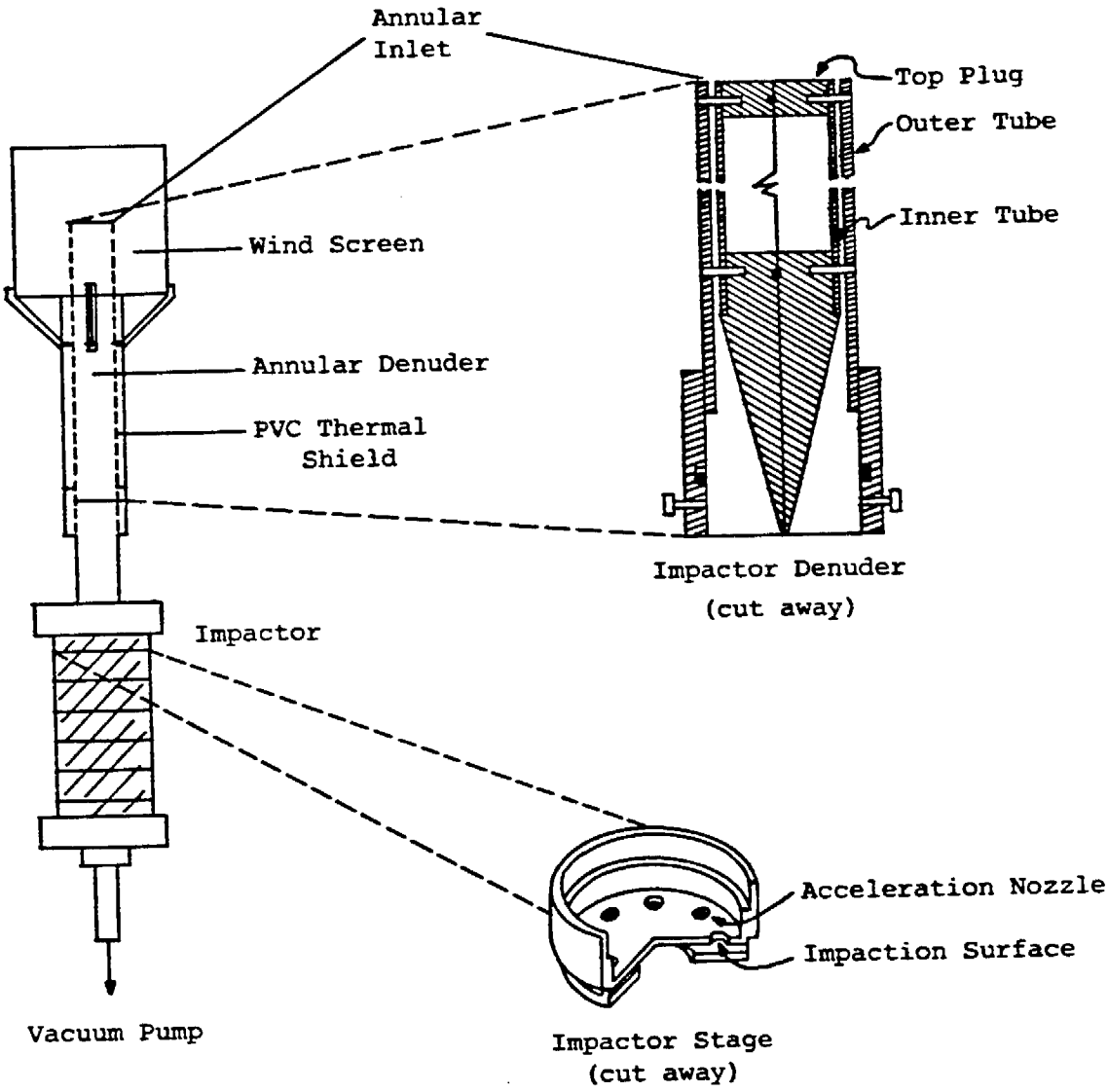

Figure 1.

Berner impactor showing inlet wind screen and annular denuder of anodized aluminum.

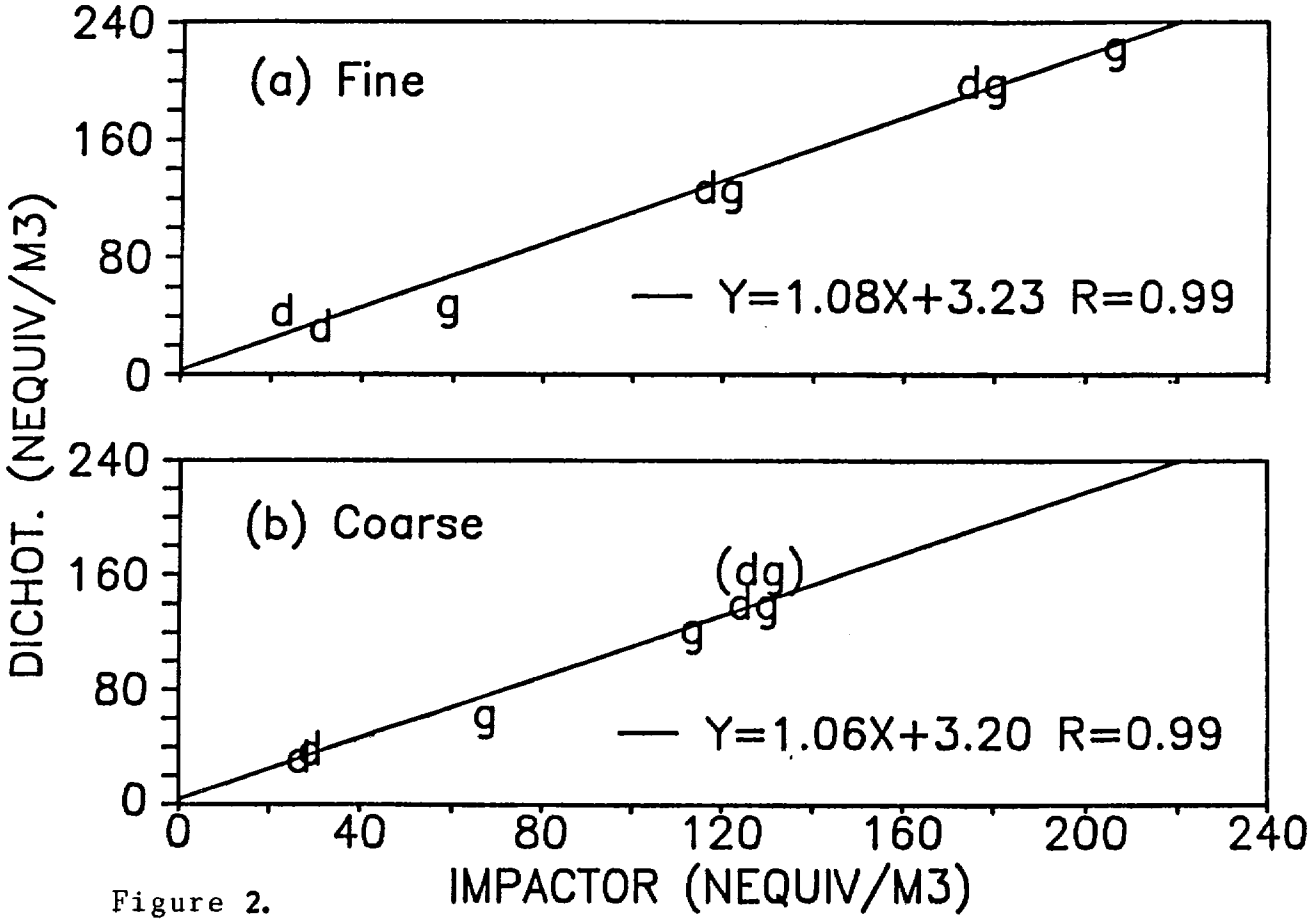

Figure 2.

Comparison of integrated Berner impactor samples with size fractions from a Dichotomous sampler using Nylon filters for (a) fine fraction nitrate and (b) coarse fraction nitrate. Denuder (d), greased stage (g), and both denuder and grease (dg) usage is indicated.

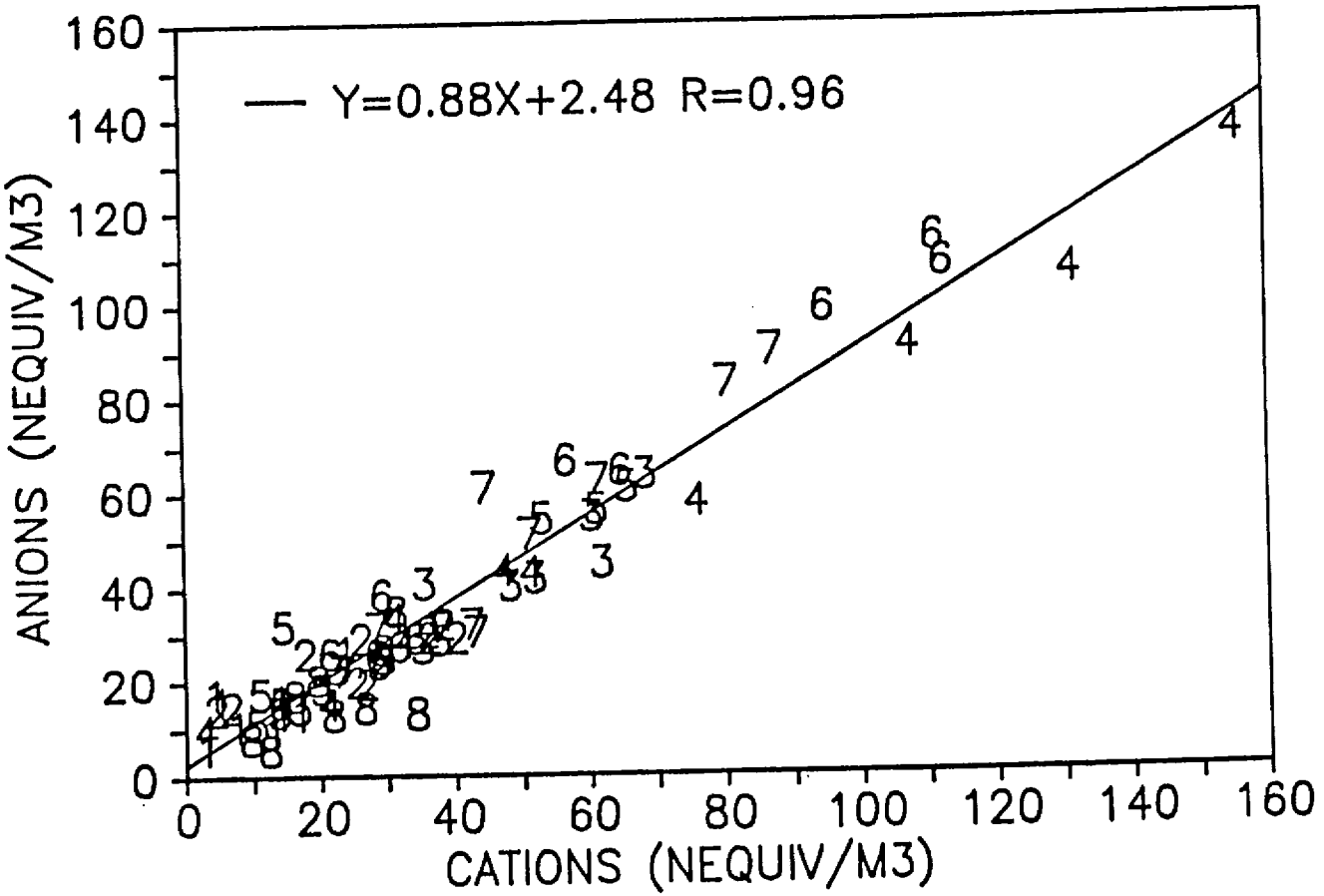

Figure 3. Ion balance for individual impactor stages with smaller stage numbers representing smaller size fractions.

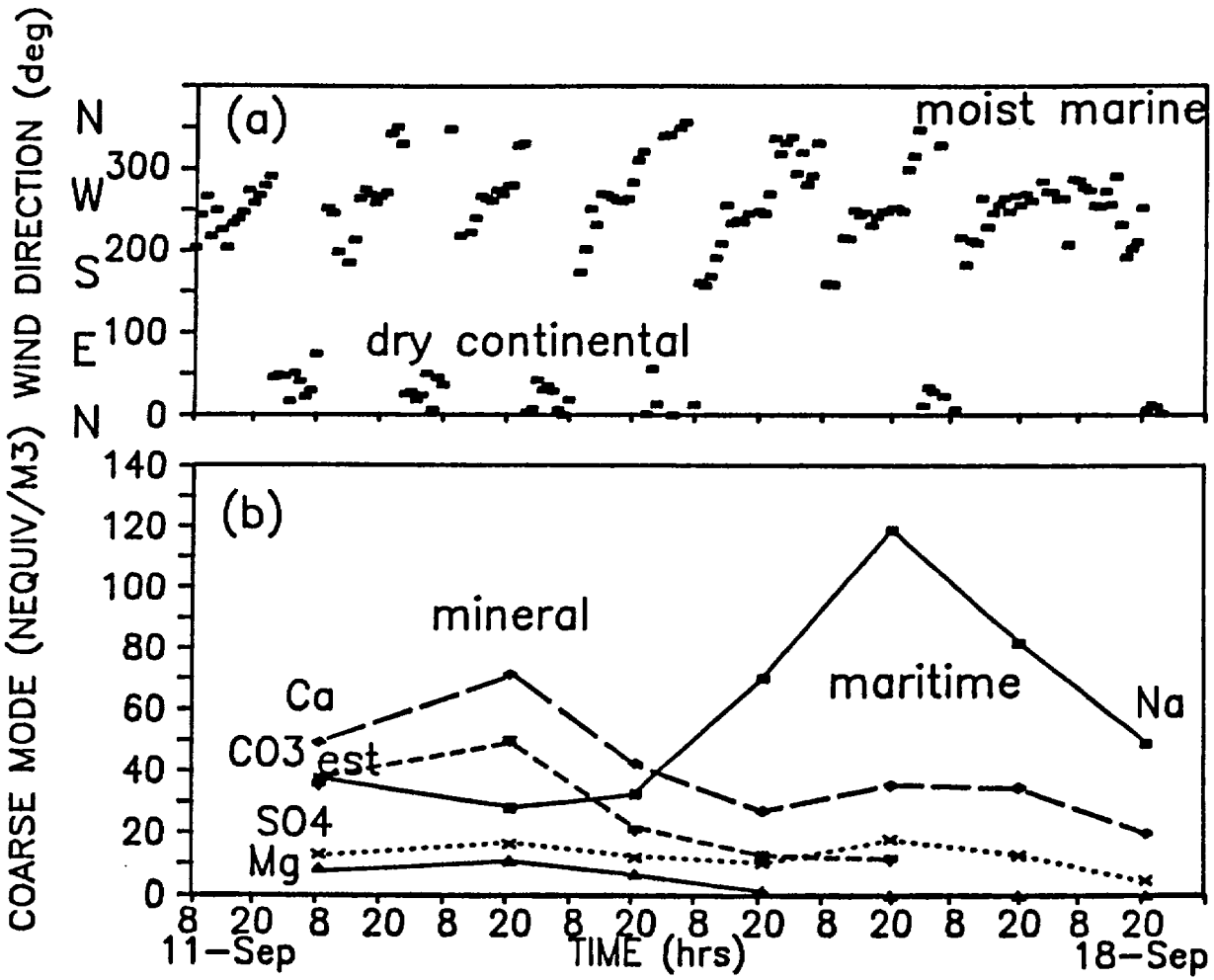

Figure 4. (a) Wind direction (C. Ellis, private comm.), and (b) coarse mode species indicating the occurence of minerals with dry inland continental air and sodium with moist marine air.

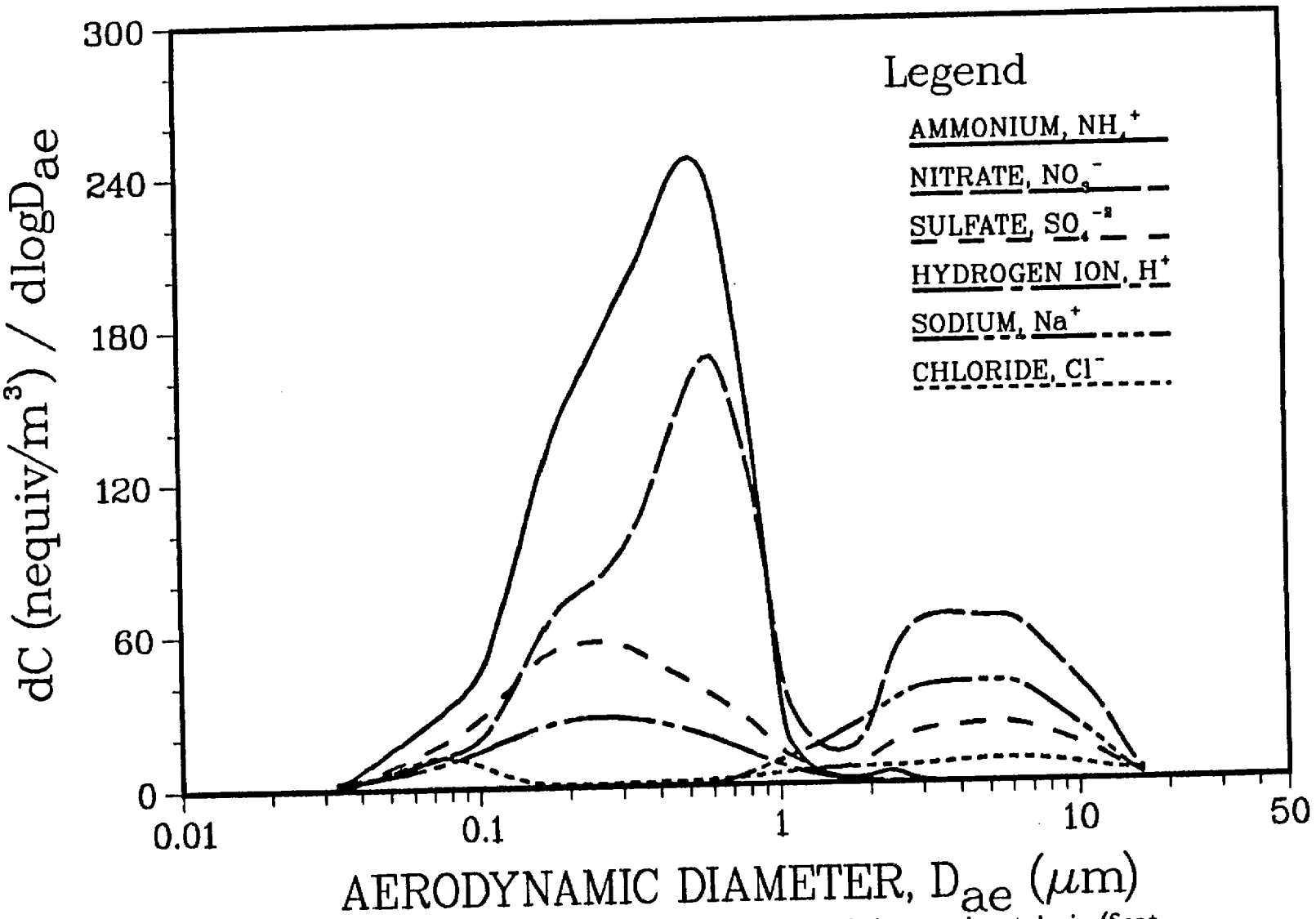

Figure 5. Major ion size distributions during the initial period of dry continental air (Sept. 13), sampling with both denuder and greased stages.

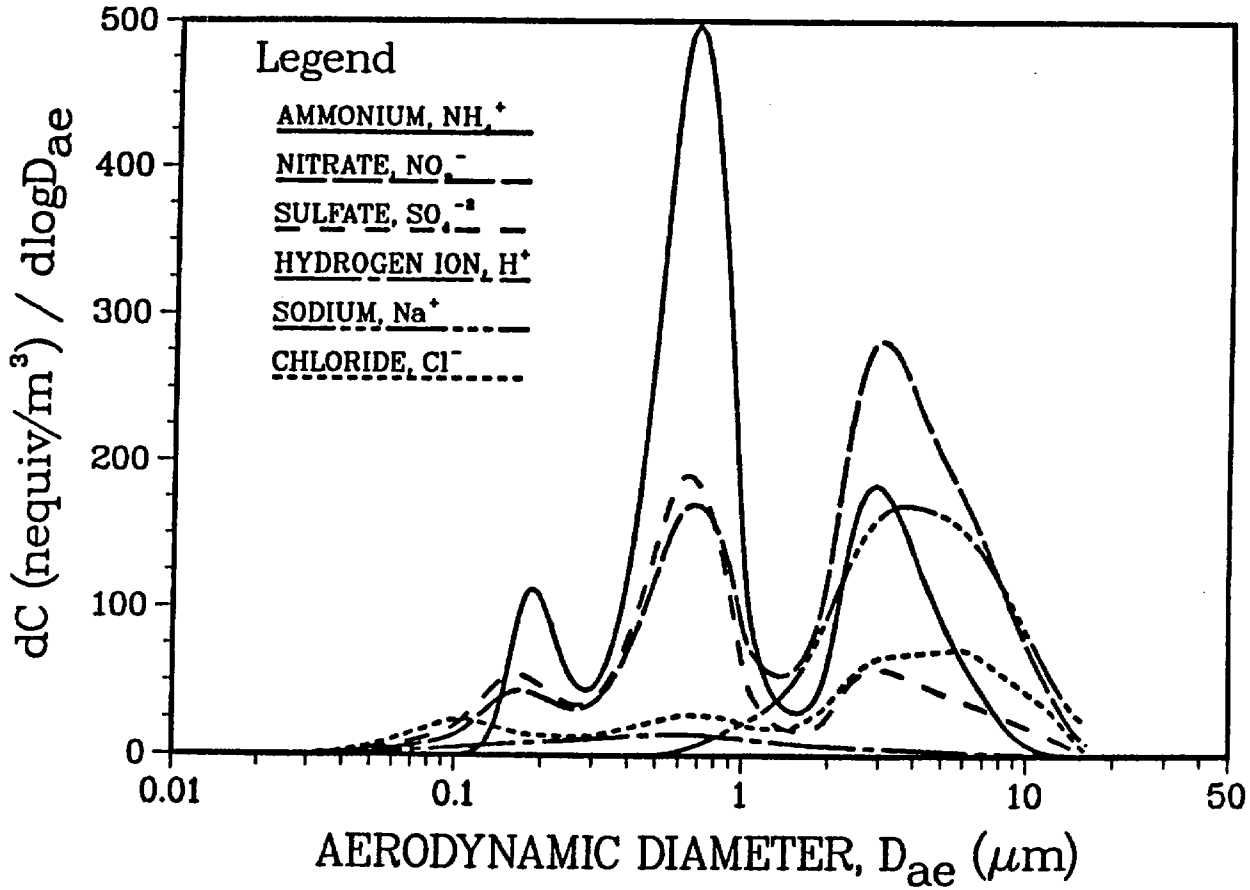

Figure 6 a. Representative size distributions for the period of strong marine sodium influence with both denuder and grease (nighttime, Sept. 16).

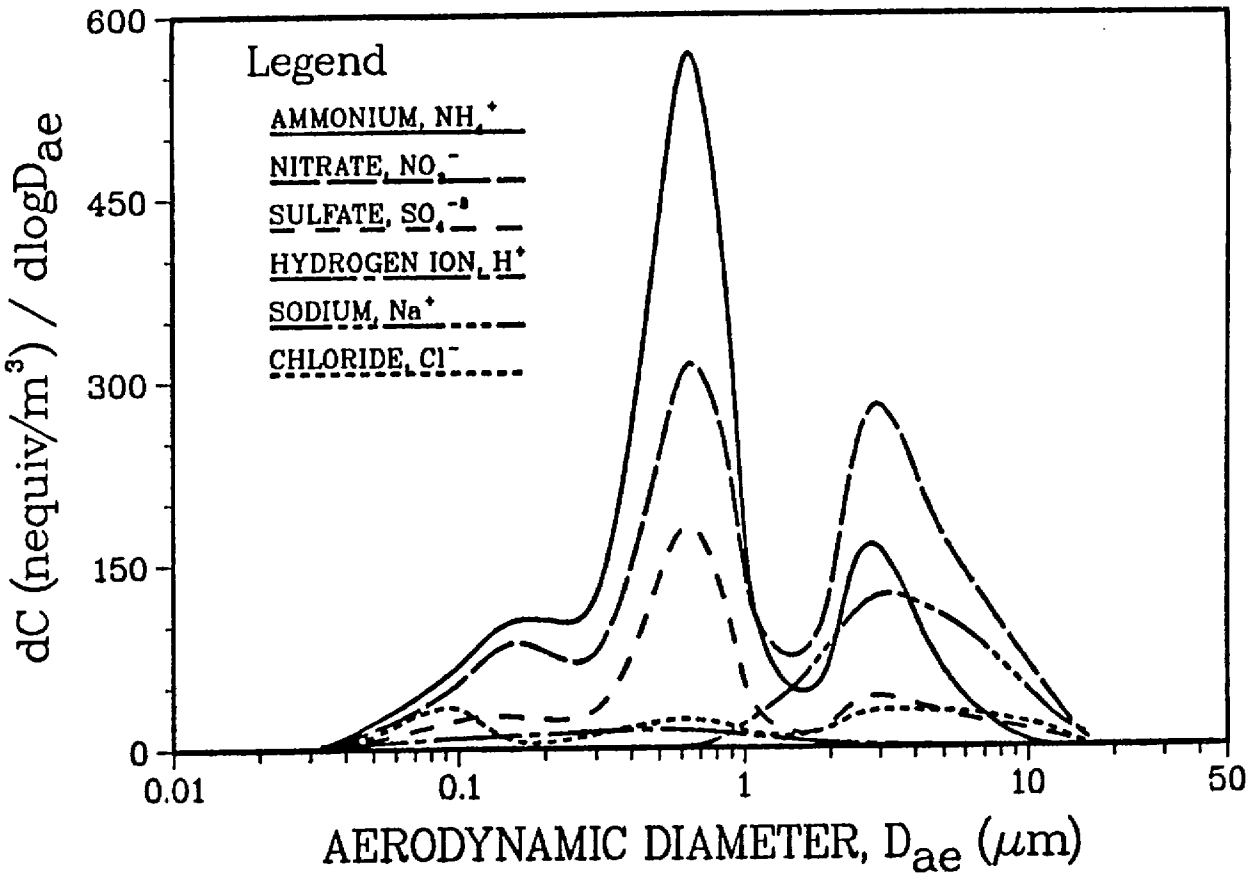

Figure 6 b. Similar to Fig. 6a, but with grease and no denuder, daytime, September 17.

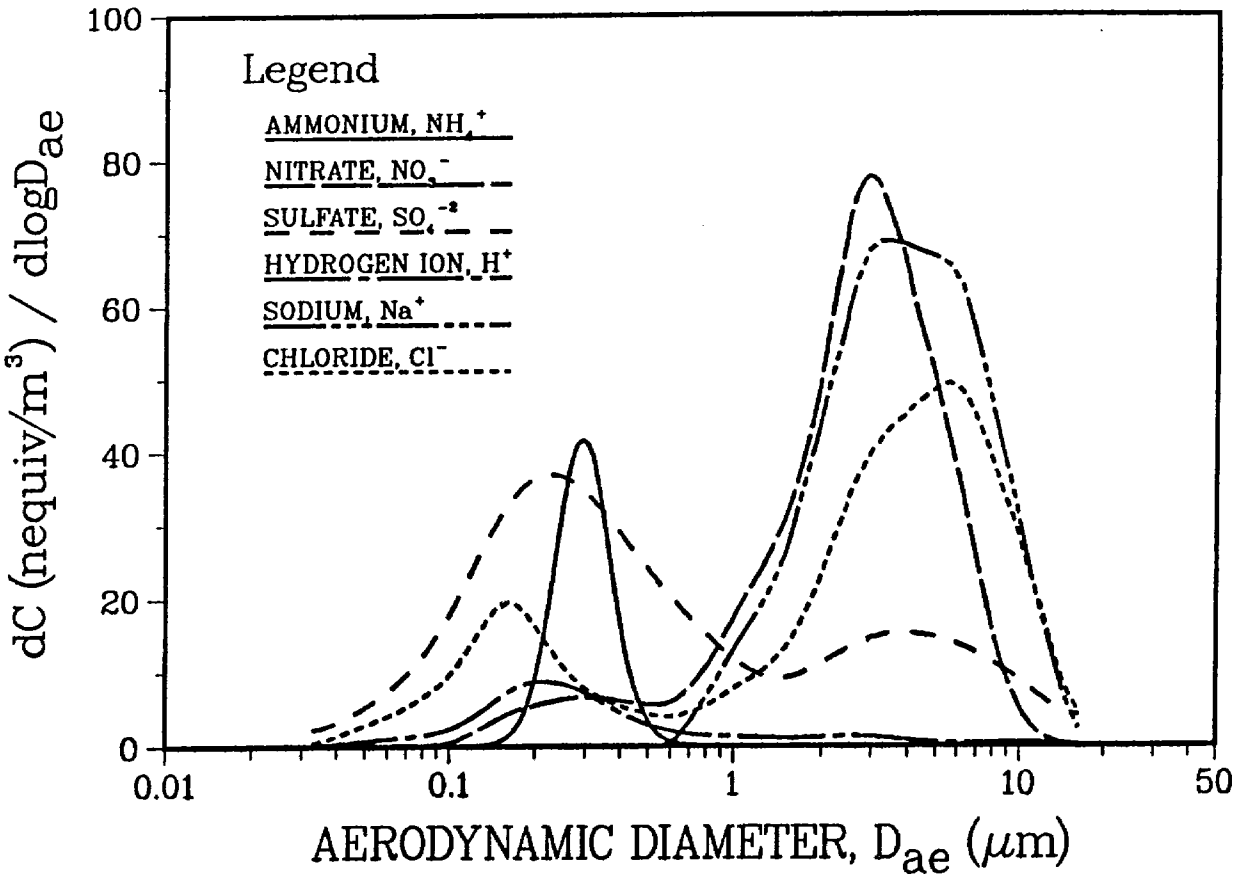

Figure 7. Size distribution for last study day of less polluted maritime air with denuder and no grease. (daytime, Sept. 18).

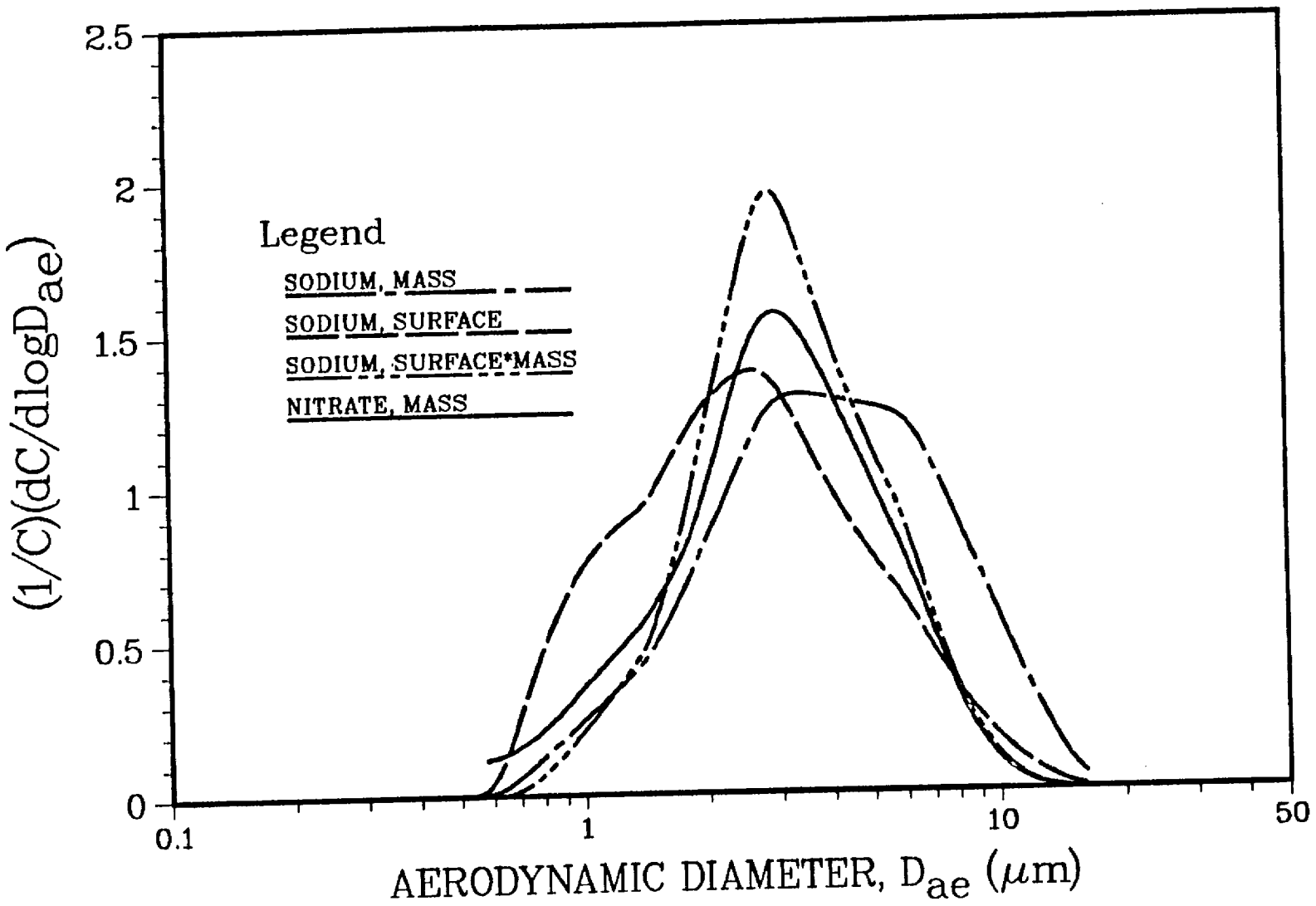

Figure 8. Normalized surface and mass distributions for sodium and their product, which peaks with nitrate. From Sept. 18 (Figure 7).

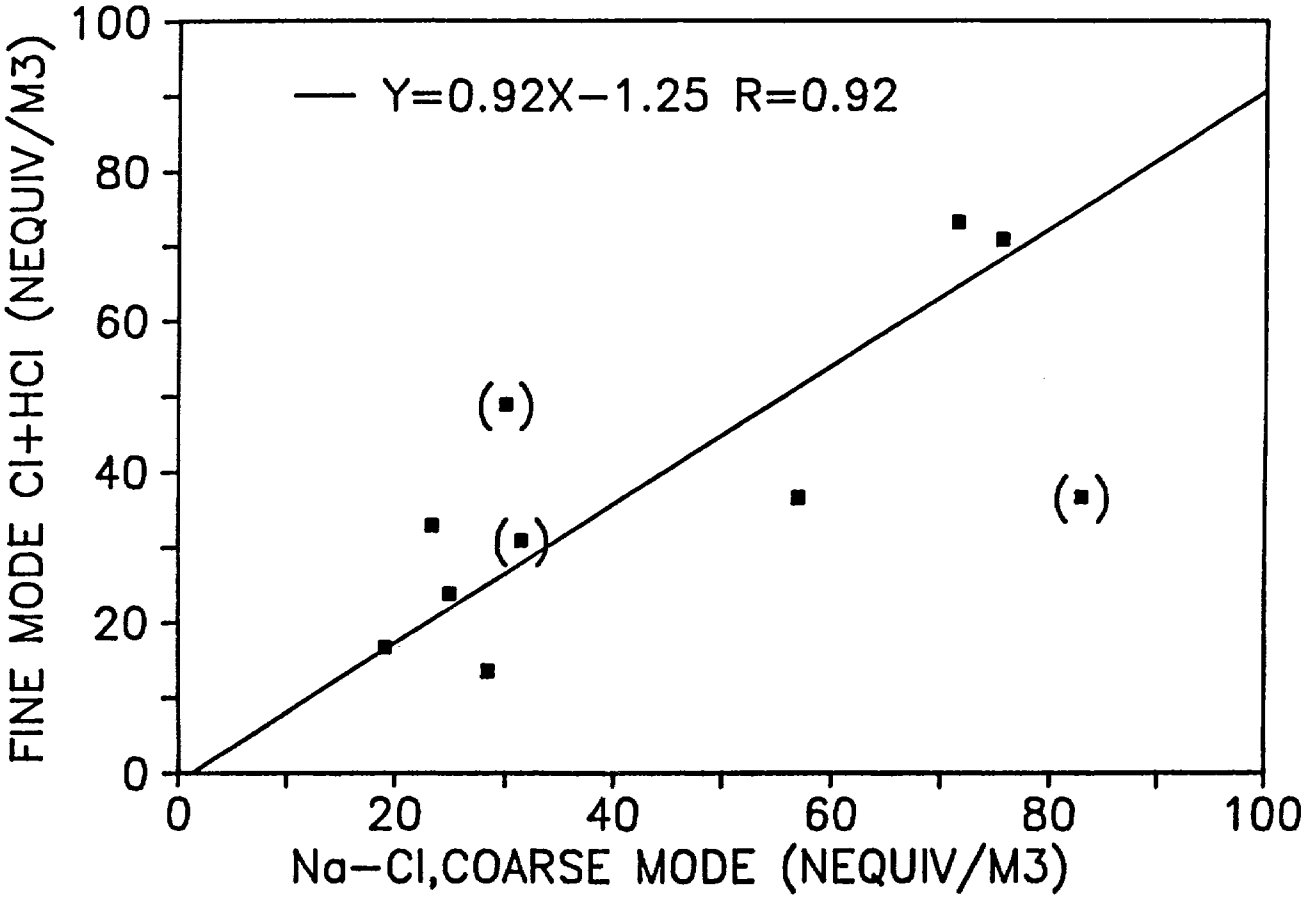

Figure 9. Coarse mode chloride lost from sea salt vs. HCl (gas) and fine mode particle chloride. Nighttime-only sampling periods are excluded from the regression analysis.

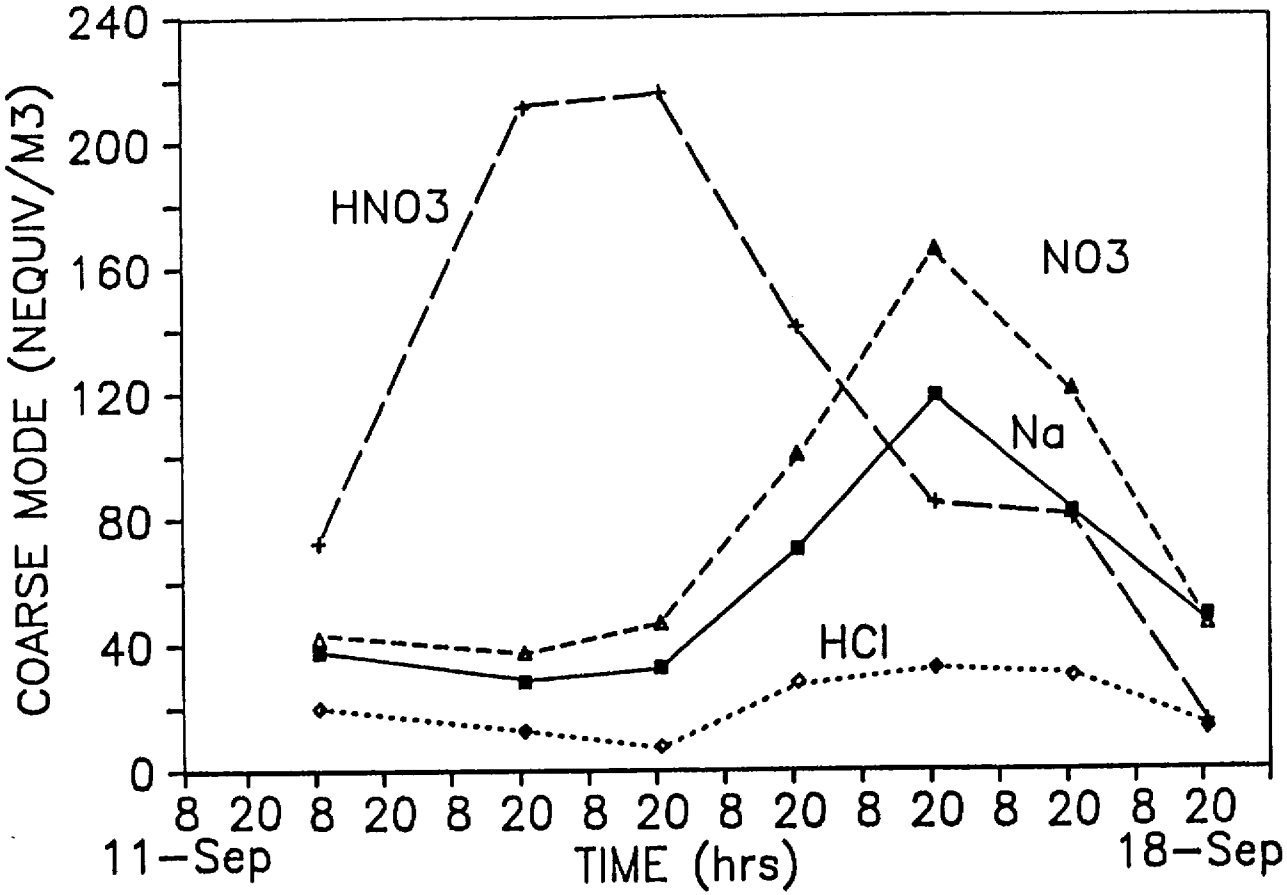

Figure 10. Twenty-four hour average values for the major ions in the reaction of nitric acid with sea salt particles, obtained by integrating above the intermodal minimum.

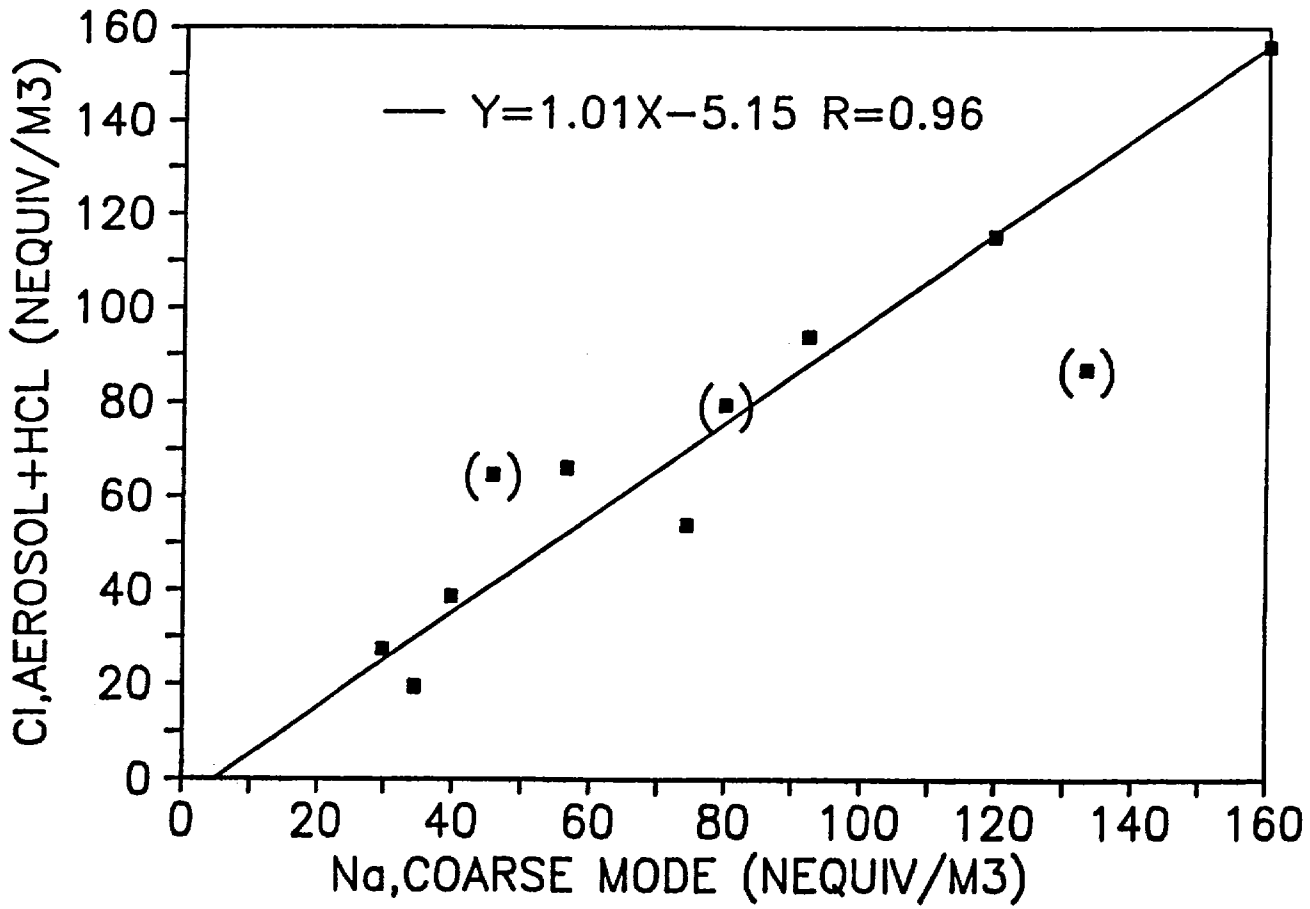

Figure 11. Coarse mode Na vs. HCl (gas) and particle phase chloride showing most of chloride to be of marine origin. Nighttime-only sampling periods are excluded from the regression analysis.

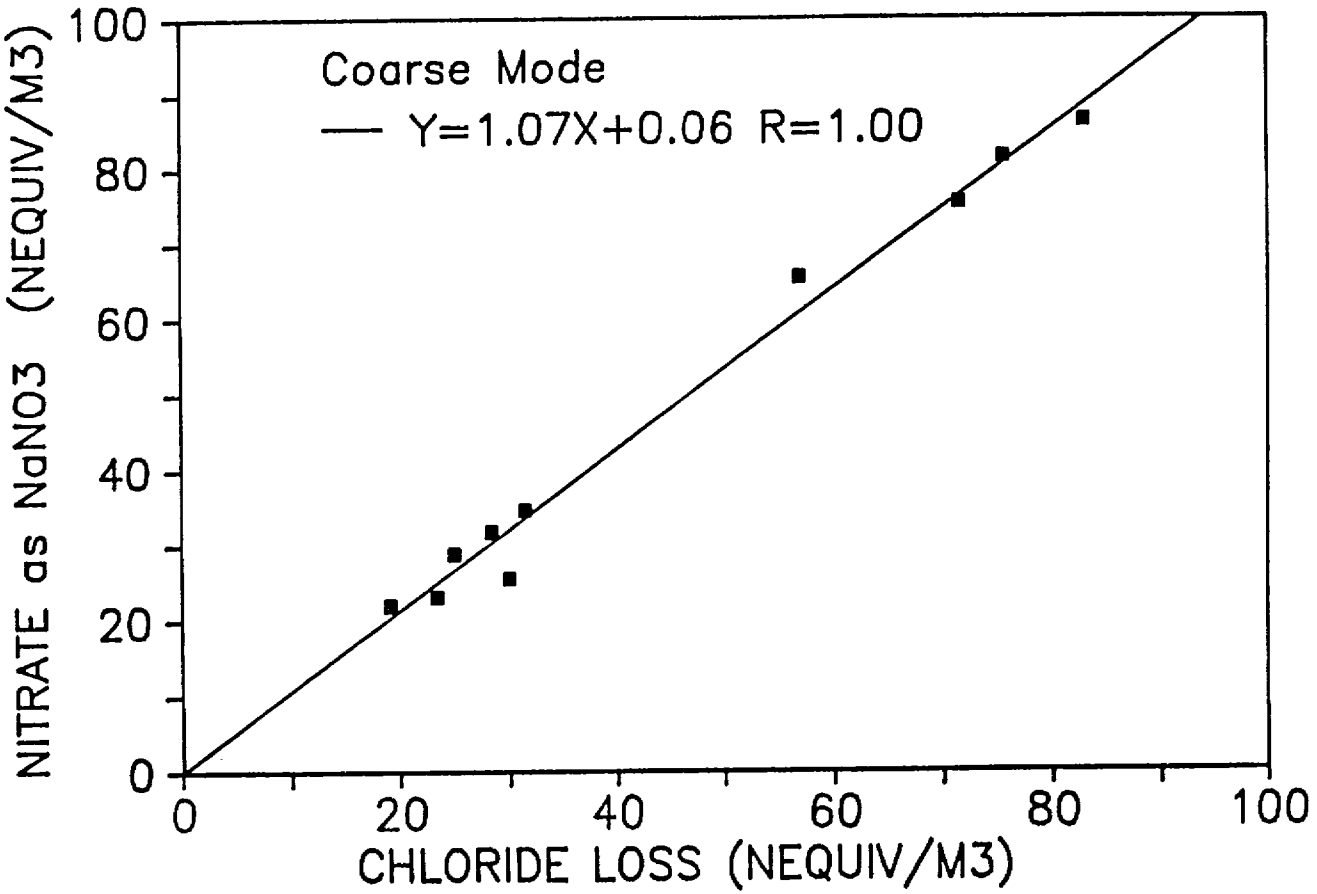

Figure 12. Loss of coarse mode chloride vs. coarse mode nitrate produced by nitric acid reaction with sea salt.

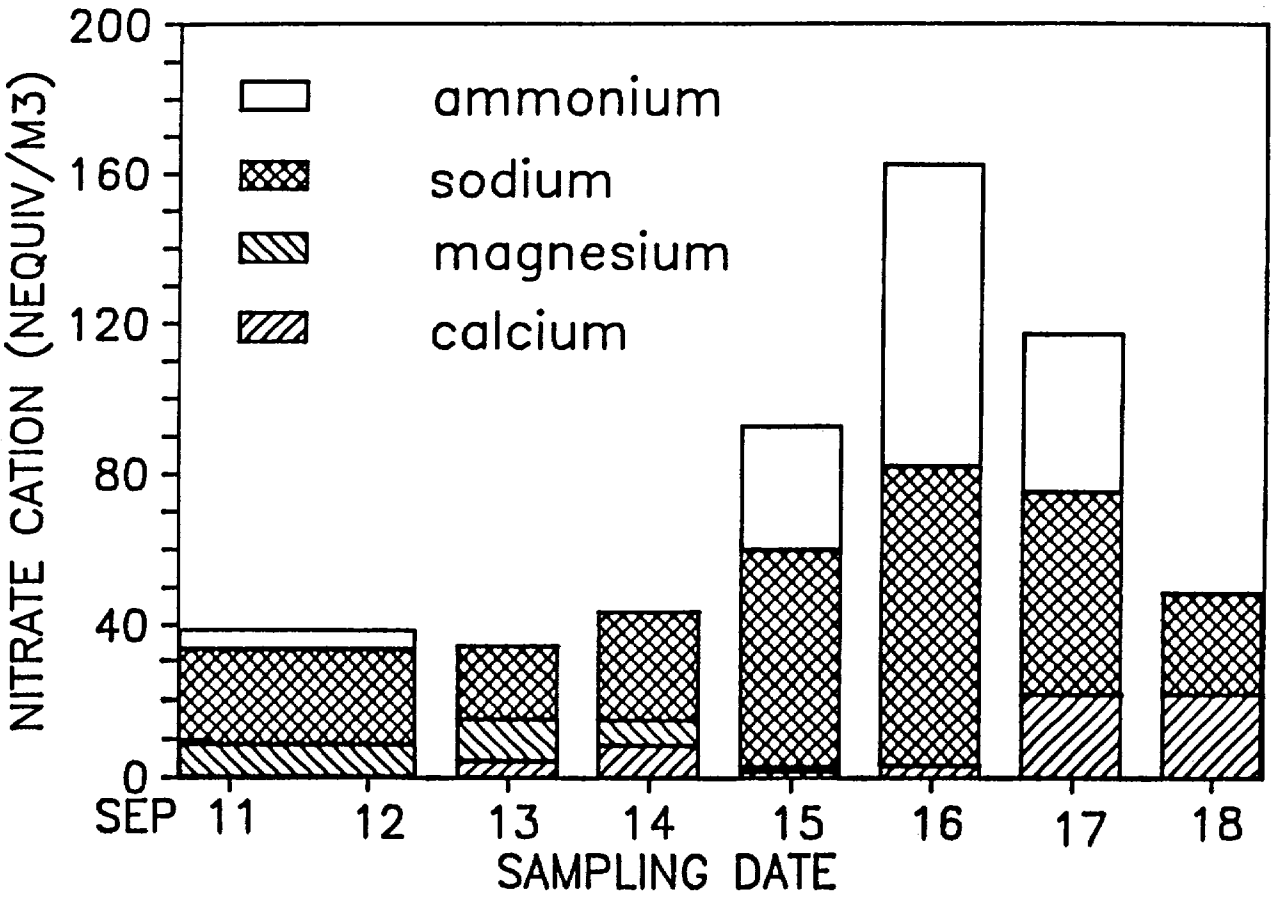

Figure 13. Histogram showing cations associated with coarse mode nitrate during each sampling period.

IV. DRY DEPOSITION OF PARTICLES ONTO SURFACES AT CLAREMONT

A direct measurement of dry deposition of acidic particles on leaves can be made by washing off the deposit and analyzing the extract. If the ambient particle concentration is measured during the exposure, deposition velocities can be derived. In previous work (1,2) we have demonstrated the feasibility of this technique, using potted plants of Ligustrum and Pinus. The potted plants can be transported to different sites for comparison of deposition under different conditions.

Details of the extraction and analysis procedures have been given previously (1). Experiments were performed to verify that material was extracted from the exterior leaf surface without significant leaching from the interior (1). However, it is not know whether any appreciable exudates are present and extracted. At Oildale in 1984, exposures for periods up to 62 days under unchanging atmospheric conditions yielded deposition velocities independent of exposure time, except that periods less than 7 days sometimes gave higher deposition velocities for unknown reasons (3).

We have also exposed plastic surrogate surfaces for comparison to the plants. We use foils of Tedlar, a fluorocarbon material with low affinity for gases. The top and bottom surfaces can be analyzed separately, providing useful information on the deposition process.

The Nitrogen Species Methods Comparison Study at Claremont was a good opportunity to measure particle deposition during a period with well-documented ambient particulate concentrations. Pierson, et al. (4), also exposed surrogate surfaces to study the deposition of particulate nitrate and nitric acid, the latter with Nylon membrane surfaces.

Experimental

The surface collectors were placed on the roof of the astronomical observatory of Pomona College, located approximately 150 m northeast of the air sampling site of the methods comparison study (see Figure 1). The surrogate surface collectors consisted of Tedlar foil in plastic

35 mm film slide holders. Potted plants included Pinus coulteri, Ligustrum japonicum and Ligustrum ovalifolium.

Two Tedlar foils were exposed for four days, another pair for the three following days and a third pair for the entire 7 days. Plant leaves were exposed for the first four days and another set for the entire seven day period. The exposures were ended on the morning of the last day when a misting rain began. Moisture could be seen on some of the surfaces but no dripping occurred.

At the beginning of an exposure period, the leaves or needles were washed with water and rinsed with distilled water. Blanks were taken to check the washing. After an exposure, the sample harvest consisted of five leaves, eight leaves and ten needles from each of three plants of L. japonicum, L. ovalifolium and P. coulteri, respectively. The leaves were extracted in 50 ml of distilled water and analyzed by ion chromatography. For Tedlar foils, the top and bottom surfaces were extracted separately in 10 ml of distilled water. The leaves were placed on graph paper and photocopied for determination of the surface area. The area used for the surface deposition included both sides of the leaf. Needle surface areas were determined from the diameter and length, using a formula developed by P. Coyne (5). For the calculation of deposition velocities, the surface deposition was divided by the ambient concentration of the appropriate species, averaged over the exposure period. The ambient concentrations were taken from the Dichotomous sampler data (Chapter II), i.e., PM-10 measurements.

Results

The observed deposition velocities for nitrate and sulfate are summarized in Table 1. For the leaves and needles, Cl, Na, NH_4 and K were less than the blank levels. For the Tedlar surfaces, Cl, PO_4, NH_4 and K were less than the blank (there was a trace of 7d K). Three and four day Na were less than the blank on Tedlar; however, 7d Na was 2.6 times the blank, giving a deposition velocity of 0.16 ± 0.06 cm/s for Na on Tedlar.

The four day P. coulteri exposure appeared to give a higher deposition velocity than the seven day exposure, although the errors are large. The results for Ligustrum were inconsistent or below detection limit. The exposures were generally insufficient to obtain meaningful results on Ligustrum. As we have observed in previous experiments, deposits on the bottom surfaces of the Tedlar foils were insignificant (Table 1). On the top surfaces, the sum of the four day and three day deposits were equal, within error, to the seven day deposits (Table 2). This confirms that no wash off by the rain occurred.

In Table 3, the nitrate deposition velocities obtained for the surrogate surfaces are compared to those from Pierson, et al. The data from the latter work were obtained by averaging the 12 hour data in their Table III; some of the nights were missing. Overall, the deposition velocities from Pierson, et al. are somewhat higher than ours, although the differences are not statistically significant. The ratio between the two sets of data should be further increased by approximately 23% because Pierson, et al. used ambient concentrations based on open face filter sampling while ours is based on PM-10. Thus their concentration data included essentially all particle sizes while ours excluded particles larger than 10 μm, aerodynamic diameter. One reason for the higher deposition velocities of Pierson, et al. might be the location of their collectors near the edge of the roof (Figure 1) where turbulence could have enhanced deposition. Another reason is our much longer exposure times which could have resulted in losses of ammonium nitrate by volatilization. The previously mentioned consistency of our three, four and seven day exposure data indicates that the volatility loss, if any occurs over a period of less than three days.

Both sets of data show that the nitrate deposition velocity was higher by roughly a factor of two during the first four days of the study compared to the following three days (Table 3). As discussed in Sections II and III, the wind was from the east during the first period and the aerosol had continental characteristics. During the second period the wind was predominately from the west, accompanied by marine aerosol. These quite different atmospheric conditions resulted in different deposition velocities.

Table 4 summarizes the nitrate and sulfate deposition data we have obtained at four California locations. Although the standard deviations are large, the averages suggest that deposition velocities to L. japonicum are larger than to L. ovalifolium. The two have quite different leaf surfaces and structure. L. ovalifolium leaves have a lengthwise fold, the angle between the two halves varying with atmospheric conditions. When they are relatively closed, the projected area is smaller, which would reduce deposition. This is not taken into account by our measurement of the leaf area which is for open leaves. Under microscopic examination, the surfaces of japonicum leaves are seen to have short projections of waxy material which may increase the collection efficiency for particles. The needles of P. coulteri seem to have a higher deposition velocity that Ligustrum, although more data are needed for a definite conclusion. The average deposition velocity for nitrate is larger than that for sulfate to foliar or Tedlar surfaces. This is probably due to particle size, since nitrate has a major coarse mode (see Section III).

TABLE 1. Nitrate, Sulfate and Sodium Deposition Velocities

Surface	Exposure, Days*	Deposition Velocity**, cm/s Sodium	Nitrate	Sulfate
Tedlar, top	4	-	0.17 ± 0.01	0.12 ± 0
Tedlar, top	3	-	0.11 ± 0.03	0.24 ± 0.07
Tedlar, top	7	0.16 ± 0.06	0.13 ± 0.01	0.14 ± 0.01
Tedlar, bottom	4		0.03	<0.06
Tedlar, bottom	3		<0.01	0.03
Tedlar, bottom	7		<0.01	<0.03
P. coulteri	4		0.24	0.20
P. coulteri	7		0.13 ± 0.03	0.10 ± 0.03
L. japonicum	4		0.02	-
L. japonicum	7		<0.05	0.15
L. ovalifolium	4		0.20	-
L. ovalifolium	7		0.05 ± 0.01	<0.05

* 4 day exposure from 0820 Sept. 11 to 0855 Sept. 15, 1985.
3 day exposure from 0900 Sept. 15 to 0945 Sept. 18, 1985.
7 day exposure from 0820 Sept. 11 to 0945 Sept. 18, 1985.

** Errors quoted are standard deviations of repeated measurements, two for surrogate surfaces, three for plants.

TABLE 2. Comparison of the Sum of 4 Day* and 3 Day Deposits to 7 Day Deposits on Tedlar Surfaces**

Substance	Deposits, μg/cm2				$\frac{4+3}{7}$	Average Ratio
	4 day	3 day	4 + 3	7 day		
Nitrate	0.66	0.38	1.04	1.05	0.99	
	0.57	0.56	1.13	0.97	1.16	1.08 ± 0.12
Sulfate	0.13	0.17	0.30	0.41	0.73	
	0.14	0.27	0.41	0.35	1.17	0.95 ± 0.31

* See Table 1 footnote for dates and times.

** Deposit on top surface.

TABLE 3. Comparison of Nitrate Deposition Velocities onto Surrogate Surfaces, Present Measurements vs. Pierson, et al. (4)

Exposure Days	Nitrate Deposition Velocity, cm/s	
	Present	Pierson, et al.*
Sept. 11-14	0.17 ± 0.01	0.25 ± 0.09
Sept. 15-17	0.11 ± 0.03	0.11 ± 0.01
Sept. 11-17	0.13 ± 0.01	0.20 ± 0.12

* Average of available data, some nights missing.

TABLE 4. Comparison of Deposition Velocities (cm/s) Measured at Four Locations

Location	Exposure	Sulfate				Nitrate			
		L. japon.	L. oval.	P. coul.	Tedlar*	L. japon.	L. oval.	P. coul.	Tedlar
W. Los Angeles	4 days	0.69**	0.64**	-	0.14	0.24	0.15	-	0.24
Tanbark Flats	4 days	0.06	0.03	-	<0.06	0.10	0.06	-	0.16
Oildale	6-7 days	0.14	0.10	0.15	0.14	0.33	0.15	0.50	0.18
Claremont	7 days	<0.15	<0.05	0.10	0.14	<0.05	0.05	0.13	0.14
Average***		0.10 ±0.06	0.07 ±0.05	0.13 ±0.04	0.14 ±0	0.22 ±0.12	0.10 ±0.06	0.32 ±0.26	0.18 ±0.04
		Average 0.10 ± 0.03				Average 0.21 ± 0.11			

* Top surface of Tedlar only. Deposits on bottom surface negligible.

** High value attributed to SO_2 deposition.

*** Excluding the two sulfate outliers and lower limits.

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1. John, W., Wall, S.M. and Ondo, J.L. Dry acid deposition on materials and vegetation: Concentrations in ambient air. Final report, Interagency agreement (ARB No. A1-160-32), Air and Industrial Hygiene Laboratory Report CA/DOH/AIHL/SP-34), California Department of Health Services, May 1985. Available from NTIS, Report No. PB85-241206/WEP.

2. Ondo, J.L., John, W. and Wall, S.M. Dry acid deposition on leaves of ligustrum and a new surrogate leaf. 77th Annual Meeting of the Air Pollution Control Association, San Francisco, CA, June 24-29, 1984, Paper No. 84-108.3.

3. John, W., Wall, S.M., Ondo, J.L. and Wang, H.C. Dry deposition of acidic gases and particles. Final report, Interagency agreement (ARB No. A3-108-32), Air and Industrial Hygiene Laboratory Report CA/DOH/AIHL/SP-40), California Department of Health Services, February 1986.

4. Pierson, W.R., Brachaczek, W.W., Japar, S.M. and Cass, G.R. Dry deposition and dew chemistry in Claremont, California during the 1985 nitric acid intercomparison study. Atmos. Environ. (to be published).

5. Miller, P. Private communication.

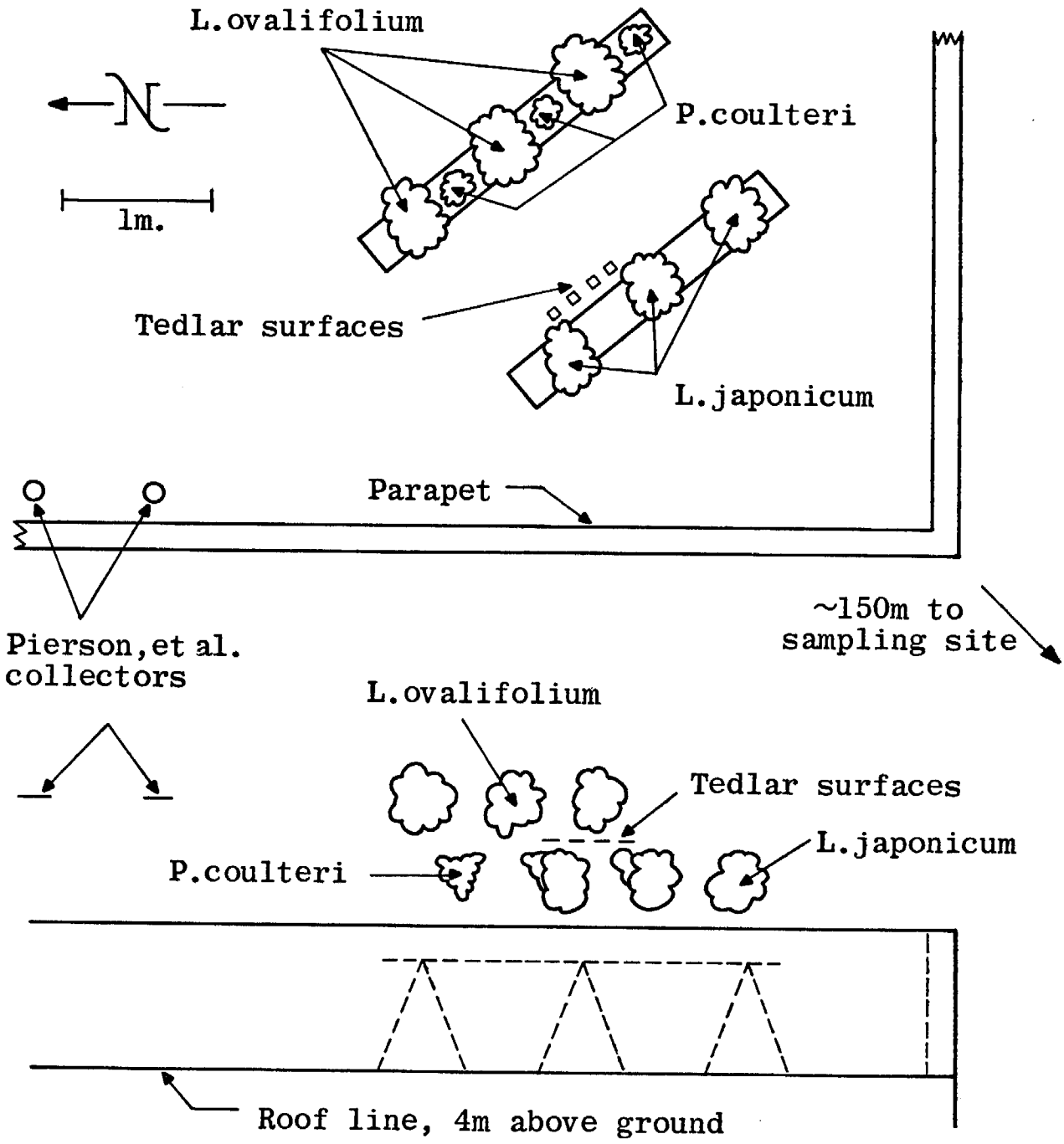

Figure 1. Arrangement of surface collectors at Claremont.

V. NITRIC ACID DENUDING EFFICIENCY OF THE DICHOTOMOUS SAMPLER: LABORATORY TESTS

The denuding efficiency of the Dichotomous sampler for nitric acid was measured in the laboratory under controlled conditions. The walk-in AIHL environmental chamber at Emeryville allowed the entire sampler to be equilibrated at a chosen temperature, a more realistic test than merely sampling conditioned air. However, the sampler did not sample chamber air, but was supplied via a manifold so that the relative humidity and nitric acid content could be controlled. The manifold was in temperature equilibrium with the chamber so that the sampling air was within about 1°C of the chamber air.

Nitric Acid Generator

A nitric acid generator was constructed, based on a design by Unisearch-Canada. A Teflon permeation tube (from Scintrex) passed over a 3:2 mixture of concentrated sulfuric:nitric acid inside a glass vessel. Nitric acid diffusing through the wall of the Teflon tube mixed with dry nitrogen flowing through the tube at 40 cm^3/min. The entire unit was housed in a temperature-controlled oven. The generator output was measured by bubbling the gas through a 0.01 N NaOH solution for 30 min. An aliquot of this solution was injected into an ion chromatograph for nitrate determination.

The output of the generator is a strong function of temperature, as shown in Figure 1. From the slope of the graph, the output increases about 5%/°C at 325°K (52°C). This high temperature sensitivity and lack of sufficient resolution on the temperature control made it difficult to set the temperature reproducibly. This is reflected in the spread of the data points in Figure 1. However, when the generator was operated at a fixed temperature, the output was relatively stable, constant within ± 3% at 35°C (7 runs) and ± 4% at 40°C (4 runs). In the chamber tests, the output of the generator was mixed with 90 L/min of clean sampling air. From audit filters (Nylon membranes), the variation in nitric acid concentration was 5 to 10%.

Chamber Tests

The sampling air was conducted in 3.8 cm dia. Pyrex tubing and branched to the Dichotomous sampler and an open faced audit filter assembly. The annular slit on the inlet of the Dichotomous sampler was fitted with a collar of PVC sealed to the sampler with O-rings. An opening on one side admitted the sampling air. The inner surface of the PVC collar was coated with fluorocarbon grease to prevent nitric acid absorption. The Dichotomous sampler and the audit filter each sampled at 16.7 L/min; the excess air was vented outside the chamber. Before starting, the glass tubing was washed with detergent and rinsed with distilled water and dried in a clean air stream. In the first few runs, only about 20% of the expected nitric acid reached the audit filter. This gradually increased to about 90% after three weeks. Evidently the glass walls absorbed nitric acid until they became equilibrated.

Initially, the Dichotomous sampler was replaced by another audit filter in order to compare the nitric acid concentrations at the two ports which did not have the same glass tubing geometry. The Dichotomous sampler port consistently yielded values 13% lower than the audit filter port; therefore, the data were corrected by this factor. Air containing nitric acid (approx. 20 $\mu g/m^3$) was supplied to the Dichotomous sampler for three days in order to equilibrate the sampler before any data was taken. The Dichotomous sampler was operated with the modified filter holders as described above in Section II. A 37 mm Teflon membrane filter was followed by a 37 mm Nylon membrane filter. A similar filter pack, with 47 mm filters, was used in the audit filter assembly. The Teflon and Nylon filters were extracted separately and analyzed for nitrate and ammonium ions by ion chromatography.

Each tests run was conducted for 23 hours with a nominal nitric acid concentration of 18 $\mu g/m^3$. This is moderately high but within the range observed in the ambient air of the Los Angeles air basin. For example, during the 1985 Claremont study (Section II), nitric acid ranged from 0 to 25 $\mu g/m^3$. Data were taken with a Dichotomous sampler which was still dirty from the Claremont study and with a second Dichotomous sampler which was cleaned beforehand. Temperatures were varied in the exposure chamber system from 13.5°C to 30°C and the relative humidity from 25% to

75%. One set of runs was made with the inlet (10 μm particle fractionation unit) removed from the Dichotomous sampler. Finally, runs were made with clean air to investigate to what extent previously deposited nitrate would be re-emitted from the sampler walls.

Results

On the Nylon audit filters, the ratio of ammonium to nitrate ion in equivalents averaged 0.44 ± 0.22. It is to necessary consider the significance of this relatively high occurrence of ammonium before the data on denuding efficiency can be interpreted. None of the Teflon filters on the Dichotomous sampler had any significant nitrate or ammonium ion. Therefore there were no ammonium nitrate particles < 10 μm, aerodynamic diameter, in the sampled air. The Teflon audit filter-catch averaged 2.6 ± 2.9% of the nitrate and 6.1 ± 5.7% of the ammonium (14 runs) on the audit Nylon filters. This suggests that some ammonium nitrate particles larger than 10 μm were possibly present; however, the ratio of ammonium to nitrate (in equivalents) on the audit Teflon filters ranged from 0 to 1.9, indicating that gaseous nitric acid and/or ammonia deposited on the Teflon filters. This is consistent with the much larger deposits of nitrate and ammonium on the Nylon audit filters downstream of the Teflon filters. The presence of the ammonium requires explanation. The efficiency of a clean Nylon membrane filter for gaseous ammonia is unknown; however, we believe it likely that the acidification of a Nylon filter by the absorption of nitric acid would sensitize it for a basic gas such as ammonia. This would also explain the absence of ammonium on the Nylon filters in the Dichotomous sampler since the nitric acid is denuded in the sampler. The remaining question concerns the origin of the gaseous ammonia. The most plausible source is from volatilization of ammonium nitrate previously deposited on the walls of the glass tubing in the chamber exposure system. In summary, it does not appear that the presence of substantial amounts of gaseous ammonia affected the measurements of nitric acid denuding efficiency.

The nitric acid concentrations measured by the Dichotomous sampler were calculated from the nitrate on the Nylon afterfilter and the flow rate. For the coarse fraction, the flow rate was taken to be 16.7 L/min and for the fine fraction, 15 L/min. This places the nitric acid artifact

on the same sampling basis as nitrate particles so that the penetration data can be interpreted directly in terms of ambient concentrations. The results are tabulated in Table 1, where the listed uncertainties are from duplicate runs at each condition.

These data, averaged over all the test conditions, show that nitric acid penetration of the Dichotomous sampler was 0.3% on the coarse fraction filter and 0.5% on the fine. These high denuding efficiencies confirm the field test results. There was no significant effect of temperature and relative humidity over the wide range tested. The data for the clean and dirty Dichotomous samplers were virtually identical. Without the inlet (10 μm Andersen SA-246B), the penetration to the fine filter was 7.4 ± 3.0%. Assuming the overall penetration to be the product of the penetration of the inlet and the penetration of the rest of the sampler, it can be calculated that the inlet alone allows a penetration of 8 ± 4%; i.e., the inlet and the rest of the sampler have about equal denuding efficiencies.

The results of the tests with clean air are listed in Table 2. The first two tests were conducted in the environmental chamber. The Nylon audit filter showed that a substantial background of nitric acid was emitted from the walls of the tubing upstream of the sampler. The remaining clean air tests were conducted in the aerosol laboratory with a clean system. The audit filter data show much lower background. For each run, the nitrate expected at the Dichotomous sampler filter is listed, based on the 0.5% penetration previously measured. The excess nitrate on the filters is presumed to have been emitted from the sampler walls. All of the tests showed substantially less than 1 neq/m^3 of nitrate on the Dichotomous sampler filters. For comparison, at Claremont fine nitrate ranged from 30 to 280 neq/m^3 and coarse nitrate ranged from 30 to 150 neq/m^3. Therefore, the observed re-emission is negligible. The results were similar for both the initially clean sampler and the sampler previously used in ambient air. The latter had 22 days in the ambient air and 8 days in the chamber, a total of 30 days operation. It is not known how much longer the sampler could be operated before the denuding efficiency would fall; however, we believe it might be substantially longer because the inlet alone denudes 92% of the nitric acid and the sampler has a large internal surface area.

TABLE 1. Measured Penetration of Nitric Acid Through a Dichotomous Sampler

Condition	Temperature	Relative Humidity	% Penetration Coarse	% Penetration Fine
Clean sampler	20°C	25%	0.2 ± 0.0	0.7 ± 0.1
Clean sampler	20°C	25%	0.2 ± 0.1	0.4 ± 0.1
Clean sampler	20°C	50%	0.3 ± 0.2*	0.5 ± 0.1*
Clean sampler	20°C	70%	0.5 ± 0.1	0.8 ± 0.1
Clean sampler	13.5°C	75%	0.3 ± 0.1	0.6 ± 0.1
		Average	0.3 ± 0.1	0.6 ± 0.2
Dirty sampler	30°C	25%	0.1 ± 0	0.5 ± 0.1
Dirty sampler	20°C	50%	0.14 ± 0.06*	0.4 ± 0.2*
Dirty sampler	13.5°C	70%	0.3 ± 0.1	0.5 ± 0.1
		Average	0.2 ± 0.1	0.5 ± 0.1
(Combined clean and dirty)		Average	0.3 ± 0.1	0.5 ± 0.1
Clean sampler, no inlet	20°C	50%	0.8 ± 0.3	7.4 ± 3.0

* 4 runs, all others 2 runs.

TABLE 2. Tests with Clean Air. Concentrations in nequiv/m³

Prior exposure of Dichotomous sampler	Test conditions	Nitric Acid conc. from audit filter	Nitrate expected at filter*	Nitrate Observed	
				Coarse Filter	Fine Filter
Initially clean,	20°C, 50% RH	58.8	0.3	0.38	0.70
10 days chamber acid	20°C, 50% RH	59.0	0.3	0.37	0.56
" plus 4 more days in chamber acid	20°C, 25% RH	8.8	0.04	0.07	0.10
	20°C, 25% RH	3.4	0.02	0.22	0.41
Dirty sampler,	20°C, 25% RH	3.4	0.02	0.15	0.42
14 days Berkeley ambient	20°C, 25% RH	1.7	0.01	0.17	0.75
8 days Claremont ambient					
8 days chamber acid					
			Average, dirty sampler	0.16 ±0.01	0.59 ±0.23

* Assuming 0.5% penetrates the sampler.

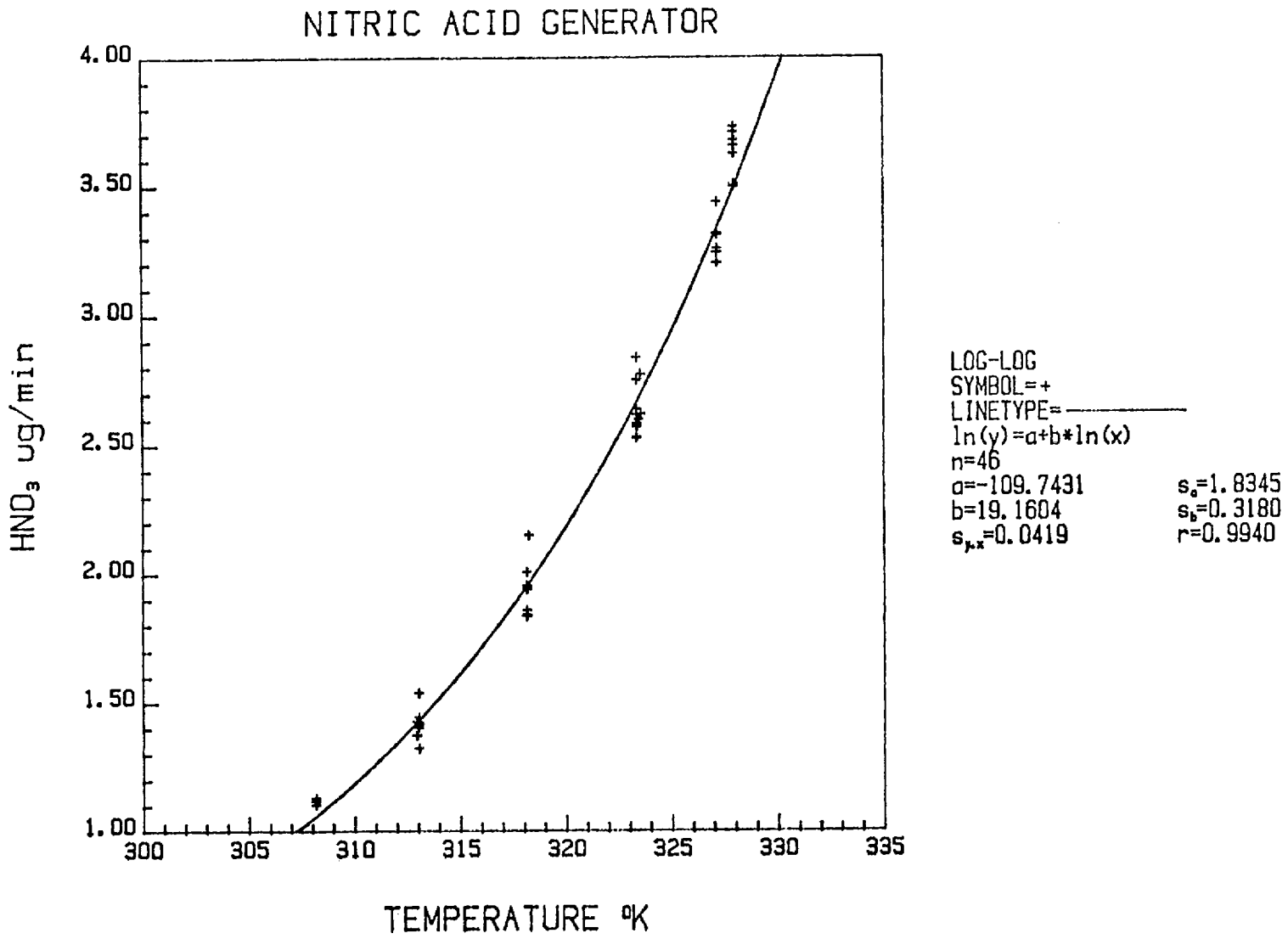

Figure 1. Output of the nitric acid generator vs. temperature.

VI. CONCLUSIONS

Parallel sampling during the Claremont Nitrogen Species Methods Comparison Study demonstrated that the Dichotomous sampler collects the same amount of fine particulate nitrate as a sampler with a conventional MgO denuder, i.e., the Dichotomous sampler efficiently denudes nitric acid. The addition of an aluminum denuder to the Dichotomous sampler did not increase the denuding action. Nitric acid was determined accurately by the difference method, using the Dichotomous sampler and an AIHL cyclone. The sampling covered a wide range of atmospheric conditions.

Tests with a nitric acid generator in an environmental chamber showed that the nitric acid penetration to the coarse fraction filter was 0.3% and 0.5% to the fine fraction filter. No significant effect was observed when the temperature and relative humidity were varied over the range 13.5°-30°C and 25-75% RH. An initially clean sampler and one used previously at Claremont showed nearly identical results. Without the inlet, the denuding efficiency was 93% and since the entire sampler had a denuding efficiency of 99.5%, the inlet alone has a calculated efficiency of 92%. Tests with clean air showed re-emission of nitrate from the walls of a dirty sampler to be less than 1 neq/m^3, which is negligible compared to ambient nitrate concentrations. The dirty sampler, which was still denuding nitric acid efficiently, had a total operating time of 22 days in ambient air and 8 days in the chamber.

The Dichotomous sampler used in this work was a standard commercial model with the filter holders modified to use a Teflon membrane followed by a Nylon membrane afterfilter. Besides eliminating the nitrate artifact, this arrangement permitted sampling for all the major ionic species. It was found that the coarse nitrate at Claremont was comparable in concentration to fine nitrate when the wind was from the ocean. Strong evidence was obtained for the reaction of nitric acid with sea salt producing coarse particulate nitrate and hydrochloric acid. Additional experimentation is needed to validate the method for hydrochloric acid. Thus, the Dichotomous sampler, coupled with the AIHL cyclone, affords a simple quantitative method for the sampling of nitric

acid and particulate ionic species, including both fine and coarse fractions.

Nitrate size distributions were also measured during the Claremont study. The Berner impactor was shown to lose less than 10% of the fine nitrate by comparison to a Dichotomous sampler. The comparison showed good agreement for all the major ions. No apparent effects of sampling with or without greased stages and with or without a nitric acid gas denuder were observed. Nevertheless, these precautions are recommended for general sampling since the field data comparison was only semi-quantitative.

Nitrate was bimodal during both day and nighttime periods. Fine mode nitrate was correlated with ammonium while coarse mode nitrate correlated with both ammonium and sodium. The coarse nitrate mode occurred consistently near 3 μm, smaller than the Na mode, and is interpreted as a product of the reaction of HNO_3 with marine aerosols. The fate of the chloride released from the NaCl particles is accounted for as gas phase HCl and fine mode particles. Unlike NO_3^-, fine Cl^- is not always associated with NH_4^+, consistent with a large dissociation constant for NH_4Cl. The fine chloride peak possibly results from the reaction of HCl with the surfaces of accumulation mode particles. The observed coarse ammonium suggests that additional coarse mode NO_3^- may be formed by reaction of NH_3 and HNO_3 on the surface of marine aerosol.

Sulfate particles were primarily in two submicron modes which were seen separately or together. The smaller sulfate mode has been ascribed to homogenous gas phase reactions and the larger submicron mode to the reaction of SO_2 with pre-existing accumulation mode particles. Strong acid, always low in concentration, tended to be associated with the smaller sulfate mode. Coarse sulfate was attributed to soil particles and, possibly, to the reaction of SO_2 with the surface of marine aerosol.

Analysis of nitrate deposition on the Tedlar surface collectors exposed at Claremont yielded a deposition velocity of 0.13 cm/s, averaged over seven days. Over the first four days, when easterly winds brought continental air to the site, the deposition velocity was about twice

that during the last three days, when marine air came from the west. Nitrate deposition was also measured by washing leaves and needles of potted plants, but sulfate deposits, which were measured on the Tedlar surfaces, were generally too small for analysis on the plant surfaces. The Claremont results, combined with our previous findings at other sites, further attest to the usefulness of surface collectors for direct measurements of particle deposition fluxes.

VII. RECOMMENDATIONS

The Air Resources Board should consider the deployment of a number of Dichotomous samplers in the routine monitoring network for the following reasons:

(1) The Dichotomous sampler has been shown to be capable of sampling particulate nitrate, an important pollutant, without positive artifact from nitric acid or negative artifact from volatilization of ammonium nitrate. These artifacts render the nitrate data currently being collected invalid.

(2) The Dichotomous sampler permits the sampling of both the fine and coarse nitrate. Coarse nitrate is important since it is produced by the reaction of nitric acid with sea salt and it has a high deposition velocity.

(3) The Dichotomous sampler can be used to sample all the major inorganic ions.

(4) The Dichotomous sampler has been validated as a PM-10 sampler by the U.S. Environmental Protection Agency.

(5) The ARB already has a large number of Dichotomous samplers on hand.

The leaf and needle washing technique, supplemented by artificial surface collectors, can be used for direct determination of particle deposition fluxes. This technique should be applied to exploratory studies of acidic particle deposition to California forests.

VIII. ACKNOWLEDGEMENTS

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