

ASSESSMENT OF DRY ACID DEPOSITION IN CALIFORNIA

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Walter John, Stephen M. Wall and Jerome J. Wesolowski  
Air and Industrial Hygiene Laboratory  
California Department of Health Services  
2151 Berkeley Way  
Berkeley, California 94704

Submitted to: John Holmes, Ph.D., Chief  
Research Division  
California Air Resources Board  
P.O. Box 2815  
Sacramento, California 95812



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## ABSTRACT

The ambient concentration - deposition velocity method was selected for the development of monitoring techniques for dry acid deposition. Filter sampling trains containing cyclones, gaseous denuders and multiple filters, some chemically impregnated, were used to sample particulate strong acid, sulfate, ammonium, nitrate, nitric acid and ammonia. Hydrogen peroxide bubblers sampled sulfur dioxide. Oxides of nitrogen and meteorological variables were monitored in a mobile laboratory. Chemical analyses included acid titration, ion chromatography and ion-selective electrode.

Sampling was conducted in Martinez (high ammonia), San Jose (high oxides of nitrogen) and the Kern River canyon (high sulfur dioxide). At all three sites, concentrations of acidic species decreased in the order, oxides of nitrogen, sulfur dioxide, nitric acid and particulate strong acid. Especially in Kern Canyon, near-zero nighttime levels of nitric acid and sulfur dioxide indicate more efficient deposition mechanisms than for fine particles. Ion balances were obtained, showing that all major acidic and basic particulate species were sampled and that the samplers performed quantitatively. Some of the present techniques could be applied to monitoring but the full array is impractical. Calculation of reliable deposition fluxes from the ambient concentrations will require improvement in the knowledge of deposition velocities.



## INTRODUCTION

Acid precipitation has caused serious ecological damage in the Northeastern United States and in Scandinavia (1). Recent studies have shown that significant acid precipitation also occurs in California (2,3). In the South Coast Air Basin, measured acidities are typically 10 to 100 times greater than for unpolluted rain (2). While most studies have concerned wet deposition, dry deposition--that occurring in the absence of rain or snow--is also important (4-11). In the Northeastern United States, it is estimated that the wet/dry deposition ratio is about one in the summer and about two in the winter (12). However, Liljestrand has estimated that dry deposition in the South Coast Air Basin is more than 10 times that of wet deposition (6). Moreover, dry deposition of acidic particles is expected to impart a strong, localized dose of acid to a surface (5), consequently enhancing the potential for damage. Dry deposition occurs continually in the absence of rain which, in semi-arid California, is most of the year.

Prevailing westerly winds from the Pacific mean that in California, in contrast to most other areas, acid precipitation originates from sources within its own borders. These sources, principally combustion of fossil fuel by stationary and mobile sources, are located mainly in the coastal regions. In the urban, coastal areas, there is cause for concern for a possible hazard to health posed by acid aerosols. One study indicates that sulfuric acid aerosol causes significant alterations in mucociliary clearance rates in healthy nonsmokers (25). Acid aerosols also cause corrosion of metals and damage to masonry (26). Potential target areas in interior California, agricultural land, forests, and mountains are downwind of the coastal acid sources. The Sierras are especially vulnerable because their granitic rock does not neutralize the acid (1).

Because of the documented damage caused by acid deposition elsewhere, it is imperative to take steps to prevent such damage in California. This requires assessment of the magnitude of current acid deposition in California and the development of techniques for monitoring future acid deposition in order to guide control strategies.

## DRY DEPOSITION

There is a paucity of information on dry deposition due to technical difficulties with the required measurements; there is no accepted monitoring technique (13). Evaluation

of dry deposition is hampered by a lack of understanding of the detailed deposition mechanisms (13). Dry deposition includes the deposition of gaseous  $\text{SO}_2$  and  $\text{HNO}_3$  as well as acid particles. The latter may consist of droplets of sulfuric acid, acid adsorbed on particles and acid salts. The acidic particles are known to be predominately in the fine fraction, i.e., to have diameters less than  $2.5 \mu\text{m}$ . The settling velocities of these particles are too small to account for the observed deposition. Both the fine particles and  $\text{SO}_2$  must first be brought to the vicinity of the surface by atmospheric turbulence before deposition can take place (14-17). The actual deposition then depends on the nature of the surface and ground cover. Thus transport within a canopy and deposition on a specific surface are governed by meteorological variables and the geometry of the surface (18-22). The deposition of  $\text{SO}_2$  on plants depends on the stomatal (pore) resistance (23) to the entry of the gas. Particle deposition involves inertial impaction, interception and diffusion, (24) depending on the particle size.

The measurement techniques for dry deposition which are currently being studied by various investigators can be grouped into three general categories:

- (1) Ambient concentration measurements coupled with estimated deposition velocities
- (2) Micrometeorological techniques
- (3) Collection on surfaces

These three approaches will be discussed briefly here.

- (1) Ambient concentration - deposition velocity

The rate of dry deposition of gases or particles can be characterized by a parameter called the deposition velocity which, when multiplied by the ambient concentration (above the canopy) yields the deposition flux (27,28). For coarse particles ( $>2.5 \mu\text{m}$  diameter) the deposition velocity is the same as the settling velocity. However, most acidic particles are too small to have an appreciable settling velocity. Dry deposition has been modeled as a diffusion process such as that obtaining for heat transfer, with the diffusion coefficient replaced by an eddy diffusion coefficient. (24)

Essentially, the concentration method consists of measuring the ambient concentration of the species of interest and multiplying by a deposition velocity taken from the literature as appropriate to the topography, ground cover and meteorology of the site. The associated uncertainty could be as large as an order of magnitude, given the current lack of knowledge of deposition processes. Nonetheless, at present the concentration method may offer the most practical approach for monitoring. This was the conclusion of a recent workshop of workers in the field (13) (with a minority opinion supporting surface collectors) and is also the approach being taken by a current U.S.E.P.A. program. (29)

(2) Micrometeorological techniques

If the dry deposition is modeled as a heat or momentum transfer, then the deposition can be determined from micrometeorological variables. One method consists of combining certain meteorological parameters with measurements of the gradient of the pollutant concentration (8). Unfortunately this requires measuring the concentration at several heights to an accuracy of 1%. Another technique, called eddy correlation, involves separately sampling when the transport is downward towards the surface and when it is upwards to obtain the net transport (13). This technique requires pollutant sensors with a time response of a second or less.

Some limited success has been achieved with the micrometeorological techniques as a result of intensive efforts. However, this approach appears to be far away from any practical application. It has also been pointed out that the method only applies to sites which satisfy stringent criteria (30). The micrometeorological method is, however, an important research tool for the determination of deposition velocities and identification of the controlling parameters.

(3) Collection on surfaces

Studies have been made of direct particle deposition onto surrogate surfaces such as Teflon plates, filters or cups. The results have been widely criticized as being difficult to interpret in terms of real surfaces

(13). Also, the acid may be neutralized by ambient ammonia during the long exposure (typically several weeks) or by the alkalinity of coarse soil particles. Some work has also been done by washing deposits from real leaves with fairly consistent results.(31,32)

Collection on surfaces has the advantage of practicality and proponents believe the method to have promise (13). It would appear that the surface technique could be a useful adjunct to other measurements, if the method can be validated.

### OBJECTIVE AND APPROACH

The overall objective of the present project is a general assessment of the magnitude of dry acid deposition in California at the present time and the development of methods for monitoring the deposition in the future. Specific components of the objectives are:

1. To make baseline measurements of dry acid deposition at representative sites in California.
2. To develop measurement techniques suitable for long term monitoring of dry acid deposition.
3. To study the mechanisms of dry deposition in order to provide a better basis for monitoring methods.

After consideration of the current status of the field as described above, we have decided that, for a first approach, the concentration method is the most feasible. The measurements are to include all the major acidic gas and particle species and as many auxiliary pollutant and meteorological parameters as practicable. A large set of variables will then be available to facilitate the interpretation of the data.

The sites chosen for measurements include Martinez (San Francisco Bay Area), San Jose, an area known to have high nitric oxide emissions and Democrat Springs, in the Kern River canyon east of the strong sulfur dioxide sources near Bakersfield.

This report covers the findings of the concentration measurements at the three above sites. In continuing work under another ARB project, we have recently extended the measurements to sites in the Los Angeles area and begun to experiment with surface collectors. The work reported here constitutes Phase I of the program. Phases II and III are outlined briefly below:

### Phase II

**Objectives:** To extend the baseline measurements to the important Los Angeles basin. To explore several new techniques for sampling dry acid.

**Technical Plan:** Dry acid species will be sampled in western Los Angeles and in the eastern Los Angeles basin at Tanbark Flats. The particle size distributions will be measured with a new low pressure impactor including microtitration for acid and analysis for the associated species  $\text{NH}_4^+$ ,  $\text{SO}_4^-$  and  $\text{NO}_3^-$ . A thin metal film detector will collect acid particles and the acid-etched holes analyzed with an automated SEM. A new passive sampler (Nuclepore surrogate leaf) for  $\text{SO}_2$  and sulfate and nitrate particles will be tried. Potted Ligustrum plants will be exposed and the leaves washed for sulfate and nitrate deposits.

### Phase III

**Objectives:** To further develop the promising new techniques explored during Phase II and to address sampling problems revealed during Phases I and II.

**Technical Plan:**

1. Measurement of the size distributions of acidic particles in the ambient air of California in order to determine the appropriate deposition velocities.
2. Development of a spot test for ambient acidic particles which will detect the deposition of individual acidic particles and provide a measure of corrosivity for materials damage assessment.
3. Direct measurements of acidic particle deposition on leaves of Ligustrum, broad leaf trees and pine needles.

4. Further testing of a surrogate leaf based on a Nuclepore filter as a passive monitor for sulfur dioxide and as a means for determining the deposition of sulfur dioxide in a plant canopy.
5. Feasibility testing of a new design for an ammonia denuder which can tolerate ambient moisture.

## EXPERIMENTAL METHODS

### Experimental Arrangement

A 30-foot Gerstenslager van was acquired and extensively modified to support field work. The experimental arrangement is shown schematically in Figure 1. The van provides an air-conditioned environment for the continuous monitors and computer data system, laboratory bench space for sample preparation, filter changing, etc. and refrigerated/dry ice storage for samples. For all of the present work electrical power was obtained by cable from a 220V AC outlet at the sampling site.

A mast for meteorological instruments was mounted on the roof of the van, providing an 8 m elevation for the wind sensors. A 5cm-I.D. pyrex pipe conducted ambient air from an inlet above the van to a manifold inside which supplied the continuous monitors. A hi-vol blower provided flow in excess of that required for the monitors. Filter sampling trains were supported by a metal frame erected approximately 9 m from the van.

### Sampling Trains

The sampling trains are shown schematically in Figure 2. Inlets and connecting pipes were 5 cm I.D. pyrex. The cyclones are those developed at AIHL (36) with the addition of a Teflon coating (similar to no-stick cooking vessel coatings) on internal surfaces to minimize adsorption of gaseous nitric acid. Operated at 22 L/min, the cyclone provided a 50% cutpoint of 2.5  $\mu\text{m}$  to exclude coarse alkaline soil particles; 47 mm filters were held in polycarbonate Nuclepore filter holders. The carbon vane pumps were equipped with electronic or mechanical flow controllers and electronic flow sensors for computer-monitoring of flow rates. Flows were manually audited before and after

sampling with a rotameter attached to the inlets. This attention reduced the error in sampler flow rates to less than 3%. Individual sampling trains and methods of analysis are discussed below.

#### Acidic Particles, Ammonium and Sulfate

Following the cyclone, the sampling train (No. 1 in Fig. 2) for the total acidity of aerosol, ammonium and sulfate employed an ammonia denuder of the type developed by Stevens, et al. (33) The multiple glass tubes in parallel were coated inside with phosphorus acid. The efficiency for the removal of ammonia was measured with a permeation tube supplying ammonia at a concentration of 16 ppb. Samples taken before and after the denuder showed the efficiency to be 96%. This is less than the 99.9% predicted by the Gormley-Kennedy diffusion equation, but more than adequate for field sampling.

The aerosol was sampled onto 2  $\mu\text{m}$  pore size, 47mm Ghia Teflon membrane filters. After sampling, the filters were placed in air-tight plastic Petrie dishes, bagged in plastic and stored on dry ice. Blanks were carried through the entire procedure including loading into the sampler.

#### Gaseous Nitric Acid and Nitrate Particles

Gaseous nitric acid and nitrate particles were determined by the denuder difference method (37). Two identical sampling trains were operated side-by-side, one having a nitric acid denuder as shown in Figure 2 (Trains No. 2 and 3). The denuder was similar to the ammonia denuder described above, except that the glass tubes were coated internally with MgO and the tube lengths were increased to account for the smaller diffusion coefficient of nitric acid. The denuder collection efficiency was calculated to be >99.9%. In order to reduce nitrate particle loss by sedimentation and to prevent MgO contamination of the sample, the denuder was mounted vertically with the filter at the top. To set the air flows in the two sampling trains as closely as possible to the same value, a differential flow meter was constructed. Flow constrictors placed in the two inlets produced small pressure drops which were connected to a differential pressure gage. This enabled the flows to be set within 1% of each other.

The method used here for nitric acid sampling is based on work in this laboratory by Appel, et al. (37-39) A 2  $\mu\text{m}$  pore-size Teflon membrane filter (Ghia Corp., Zefluor) is used to collect particles, followed by a NaCl-impregnated Whatman 41 cellulose filter to collect gaseous nitric acid. Appel, et al. (37) determined the efficiency of the Whatman 41-NaCl filter for gaseous nitric acid collection to be 98%. They also found the Teflon prefilter not to retain nitric acid; however, atmospheric particulate matter retained some nitric acid, amounting to about 20% for a particle loading of one mg. on a 47 mm dia. filter. For determination of nitrate particles, the Teflon filters minimize the positive artifact, i.e., conversion of gaseous nitrogen compounds to nitrate. However, they are subject to negative artifact, i.e., loss of nitrate by volatilization. The nitrate lost in the form of  $\text{HNO}_3$  is recovered on the Whatman 41-NaCl backing filter and added in to obtain the total nitrate.

The sampling scheme for the inorganic nitrogen compounds can be summarized:

- (1) Particulate nitrate is obtained from the sum of the nitrate on the two filters of sampling train No. 2 (Fig. 2).
- (2) Gaseous nitric acid is obtained from the difference between the nitrate on both filters of sampling train No. 3 and that from both filters of sampling train No. 2.
- (3) Ammonium is obtained from the filter of sampling train No. 1 plus a correction for loss by volatilization of ammonium nitrate. This correction is obtained from sampling train No. 2 where the volatilized nitrate is recovered on the backing filter. The correction is made for the set of filters from each run.

#### $\text{SO}_2$ Bubbler Sampler

Ambient concentrations of  $\text{SO}_2$  below 1 ppb are significant for dry deposition. Since this is below the detection limit of continuous monitors, a bubbler was used to collect  $\text{SO}_2$  by oxidation to sulfate in  $\text{H}_2\text{O}_2$  solution. This method has been used extensively and is relatively simple. (14) The bubbler samples were analyzed for sulfate by ion chromatography. This  $\text{SO}_2$  method, collection in  $\text{H}_2\text{O}_2$  solution and analysis by ion chromatography, is highly sensitive, quantitative, stable and has no known interferences, as shown by the work of Mulik, et al. (40). The latter consider this method to be a

candidate as a replacement for the Federal Reference Method (FRM). The FRM, a modified West-Gaeke method, suffers from temperature-dependent losses.

Shown in Figure 3, the all glass bubblers used a coarse glass frit to produce good gas-liquid contact. Two bubblers were cascaded as a precaution, although almost all of the sulfate was recovered from the first bubbler. The second bubbler would be needed in hot, dry sites where the evaporation loss would be high. The 1%  $H_2O_2$  in water solution was refrigerated until use. Each bubbler was filled with 40 ml of the solution. After sampling, the solution and a small addition from rinsing of the bubbler was stored in a capped polyethylene tube in a refrigerator.

#### Gaseous Ammonia

A quartz fiber prefilter was used to filter particulate matter, which contains ammonium salts, from the air stream. Quartz was chosen to minimize volatilization of ammonium, although it is not definitely known to be better than Teflon in this regard. The quartz filter was followed by two acid-washed glass fiber filters impregnated with oxalic acid to collect gaseous ammonia. Two filters were necessary to ensure complete collection. Filters were prepared and kept under an argon atmosphere before use, to prevent exposure to ambient ammonia. After sampling, the filters were demounted in a glove box filled with Argon and then stored on dry ice.

#### Fine and Coarse Particle Fractions

Sierra 244 Dichotomous samplers equipped with the nominal 15  $\mu m$  cutpoint inlet were used to sample the fine and coarse aerosol (cutpoint 2.5  $\mu m$ ). The 2  $\mu m$  pore-size Ghia Teflon membrane filters were equilibrated overnight in an environmental chamber controlled at 50% R.H. and 20°C and weighed on a Cahn 25 microbalance. Some of the samples were further analyzed to provide additional data on chemical species.

#### Continuous Monitors for Nitrogen Oxides and Sulfur Dioxide

A TECO 14T chemiluminescent monitor was used to measure concentrations of  $NO$ ,  $NO_2$  and  $NO_x$ . These were recorded by the data logger described below.

Sulfur dioxide concentrations were monitored with a Monitor Lab 8450 chemiluminescent monitor. Most of the time the sulfur dioxide concentrations were too low (less than

5ppb) for reliable measurements with this monitor, but the monitor was run in case high concentrations should occur.

The monitors were calibrated against standard gases by the AIHL group which regularly calibrates the ARB monitoring instruments. Routine field checks were performed with span and zero gases at each site.

### Meteorological Sensors

Wind speed and wind direction were measured with a Met One 010 assembly. A platinum RTD sensor for temperature and a LiCl-RTD sensor for dew point were mounted in a General Eastern aspirated radiation shield.

### Data Acquisition and Analysis

Data from sensors was logged by a Fluidyne 750 programmable data recorder. Variables included the time, nitrogen oxides, sulfur dioxide, temperature, dew point, wind direction, wind speed and air flow rates in filter sampling trains. Analog voltages from the sensors were digitized and punched on paper tape once per minute and printed once every five minutes. Chart recorders were used to display several variables.

The punched tapes were analyzed at the University of California, Berkeley computer center. Time series were plotted and tables of average value, maximum, minimum and standard deviation for each variable and each run. Run averages were combined with chemical analysis data and time series plots made on the AIHL HP-85 computer.

### Analytical Procedures

Filter samples were removed from dry ice storage just prior to extraction in 15 ml polystyrene centrifuge tubes. Teflon filters were extracted in 5 ml of double glass-distilled water by agitation for 10 minutes in an ultrasonic bath followed by one hour on a rotating mixer. Glass fiber, quartz and cellulose filters were extracted in 5 to 8 ml of double glass-distilled water by vigorous shaking for one hour to break up the fiber matrix. All sample preparation was performed under an inert argon atmosphere to inhibit ammonia contamination. Extraction studies indicated recoveries of all major cations and anions to be greater than 96% by the above procedures.

Water extracts of the filter samples were analyzed for strong acid and ammonium ion immediately after extraction. The stability of nitrate and sulfate allowed analysis for these ions to be performed the following day. The same extracts were used for all the analyses in order to minimize extraction volume and maximize sensitivity. Microtitration for strong acid was performed under Argon using an Autoburette AB12 manufactured by Radiometer of Denmark. Strong acids ( $pK_a < 4$ ) were distinguished from weaker organic acids by use of Gran's plots, which display a linear relationship between hydrogen ion concentration and the volume of titrant (NaOH) added. The Gran's plots were generated on a chart recorder directly from the titration electrode potential with a high precision antilog signal processor of AIHL design. The titration endpoint was determined by extrapolation of the linear portion of the curve to the base line. Weaker acids produce a curved tail on the plot which can be used to estimate the amount of weak acid. Most of the samples showed less than 10% of weak acid; an occasional sample had as much as 30%. The acid determination limit (as  $H_2SO_4$ ) was 0.2  $\mu g/ml$  with a reproducibility of 10%.

Ammonium ion was analyzed by specific ion electrode under Argon. The electrode was calibrated with standards in the same concentration range as the samples. The determination limit was 0.2  $\mu g/ml$  and the reproducibility 20%. Sulfate and nitrate were analyzed by ion chromatography (Dionex). The determination limits for sulfate and nitrate were 0.5  $\mu g/ml$  and the reproducibility 10%. Based on six hours of sampling at 22 L/min, the determination limits in  $nequiv/m^3$  were: strong acid, 2; ammonium, 12; sulfate, 3; and nitrate, 5.

## SAMPLING LOCATIONS AND CONDITIONS

### Martinez

Sampling was conducted from July 20 to July 23, 1982 at the Mountain View Sanitary District, Martinez, CA. The van and samplers were located on a paved area near the northern edge of the sanitary district. The prevailing wind came from NW, the direction of the Carquinez Strait, the immediate approach being over an open, marshy area. At night the winds sometimes came from the west over the nearby petrochemical refinery. The 680 freeway just to the NE of the site was a source of automotive emissions.

The aerating tanks of the sanitary district were a possible source of ammonia. During the sampling period the days were warm and clear. Night periods were cool, calm and foggy.

Sampling periods of approximately six hours were used to separate day and night regimes which have different pollutant chemistry and deposition rates.

### San Jose

From August 9 to August 13, 1982 sampling was conducted in San Jose. The site was on the edge of Spartan Field, San Jose State University, at 10th and Humboldt Street. The samples were in a yard adjacent to a small laboratory building. Winds approached either over the grassy football field or the surrounding residential area. The weather was warm and visibility good. Oxidants were gradually building up during the sampling period but overall the air was relatively clean.

### Democrat Springs

Because of the oil fields in Oildale, the Bakersfield area has some of the highest sulfur dioxide concentrations in California. The Kern river canyon traverses the Sierra Nevada mountains from Bakersfield in the Central Valley to Lake Isabella near the summit to the east. The prevailing westerly winds during the daytime are expected to transport the sulfur dioxide up the Kern river canyon, a forested area in granitic rock, and hence susceptible to acid damage.

The primary sampling site was at Democrat Springs, a U.S. Forest Service fire station approximately half way up the Kern river canyon. The samplers were near the edge of a ridge. A dichotomous sampler was also operated at Shirley Meadows near the summit.

The sampling period, September 13 to September 16, 1982, was timed to overlap with a multi-group study of air quality, air chemistry and pollutant transport in the southern San Joaquin Valley and the Sierra Nevada slopes organized by C.D. Unger, ARB. F. Shair, California Institute of Technology, released SF<sub>6</sub> tracer gas from Oildale and took samples in a wide area around Bakersfield. M. Fosberg, U.S. Forest Service,

released tetroons (constant density balloons) which were tracked by radar. R. Flocchini, University of California, Davis made aerosol and meteorological measurements in Tehachapi Pass. P. Miller, U.S. Forest Service, operated wind gages at six sites in the Kern river canyon, monitored ozone and sulfur dioxide at Democrat Springs and placed Huey sulfation plates in forested areas. He also took soil and tree samples for analysis of sulfur isotope ratios.

The meteorological studies showed that, during the sampling period, the afternoon winds at Bakersfield were from the north rather than the west and that deep mixing occurred. Winds were light at the mouth of the Kern River Canyon. In the upper part of the canyon, surface winds showed well developed mountain and valley circulation, while the wind at Shirley Meadows was indicative of regional flow. These data suggested that the Oildale plume was vertically well mixed in the valley and then transported into the Sierra Nevada as an elevated plume. Our surface wind measurements at the Democrat Springs sampling site showed the expected westerly winds during the day and drainage flows at night. However, some vertical mixing probably occurred.

## RESULTS

### Concentrations, Time Dependences and Site Differences

All concentrations have been expressed in terms of equivalents to facilitate direct comparisons. (Equivalent weight = molecular weight/valence) Time series for the measured variables are shown in Figures 4 to 50, grouped by sampling site. Because of the large volume of data, a concise summary of concentration ranges and time dependences is given in Table 2.

Of all the chemical species, oxides of nitrogen were observed to have the highest concentrations at all three sites, with Kern showing considerably less than the other sites. Relatively high concentrations were also seen for sulfur dioxide, which can produce strong acidity when adsorbed on a neutral, hygroscopic surface. Although the Kern plot showed one high SO<sub>2</sub> peak, the overall levels were similar in magnitude at all three sites. The diurnal patterns having daytime peaks were similar at all locations but the most regular pattern appeared at Kern due to the tidal air flow in the canyon.

The nighttime minima were deepest at Kern. Since these minima were weak or absent for the particulate species,  $\text{SO}_2$  deposition was evidently more efficient than that of fine particles, consistent with published deposition velocities. A time correlation was not observed between sulfur dioxide and sulfate at any location. Particulate strong acid was also uncorrelated with  $\text{SO}_2$ , but at Martinez, high peaks occurred at the same time. Apparently sulfur dioxide concentration was not a limiting factor in the production of oxidized sulfur species.

Particulate strong acid reached similar maximum levels at all three sites, but were only 10 to 20% of the  $\text{SO}_2$  concentrations. Evidence of diurnal patterns was weak even at Kern, despite the tidal air flow there. This is consistent with low deposition velocities for particulate strong acid.

Fine particulate sulfate and ammonium were highly correlated at Martinez, San Jose and Kern. This would follow from the presence of ammonium sulfate and ammonium acid sulfate; however, these salts were not determined directly. Maximum sulfate concentrations were typically three to four times the particulate strong acid concentration and less than half the sulfur dioxide peak concentrations. At Kern, sulfate and ammonium levels slowly increased over the three sampling days whereas the sulfur dioxide concentration did not, instead showing a strong diurnal pattern consistent with the higher deposition velocity of sulfur dioxide. Rain in the Bakersfield area just prior to the sampling period had cleared the air of pollutants which subsequently built up again. This was reflected in the gradual buildup of fine particle species transported up the Kern river canyon from the Bakersfield area.

Fine particulate ammonium was not correlated with gaseous ammonia at Martinez or San Jose. A weak correlation was seen at Kern. Ammonia levels were extremely high at Martinez; even at San Jose and Kern they were 10 times higher than particulate strong acid. The high levels at Martinez may have been due to the nearby sewage treatment plant.

After sulfur dioxide, the largest contribution to atmospheric acid levels was made by nitric acid. Nitric acid peaked in midday to early afternoon and dropped to near zero at night. In Martinez, peak concentrations in nitric acid and nitrate did not correlate, but  $\text{NO}_x$  peaked whenever nitric acid or nitrate peaked. At San Jose the peaks in

$\text{HNO}_3$  lagged peaks in  $\text{NO}_x$  by about six hours. This time dependence is expected from the photochemical mechanism for nitric acid formation. The strongest diurnal pattern was observed in the Kern canyon. The reactive gases  $\text{SO}_2$  and  $\text{HNO}_3$  showed similar evidence of nighttime deposition. Although  $\text{NO}_x$  varied greatly from site to site, the  $\text{HNO}_3$  levels were comparable, suggesting that  $\text{HNO}_3$  production was not limited by  $\text{NO}_x$ .

At San Jose, particulate strong acid increased over the three day period as did most of the pollutants following several days of unusually high visibility. Several species including particulate strong acid and nitric acid peaked on the last day (8/12).

At Kern, the dichotomous samplers provided additional data on the fine and coarse particle fractions of several species. These show the  $\text{NH}_4$ ,  $\text{SO}_4$  and  $\text{NO}_3$  to be predominately in the fine fraction, the sole exception being  $\text{NO}_3$  at Democrat Springs. Possibly the soil of the Fire Station grounds contained nitrate fertilizer. The Democrat Springs data and the Shirley Meadows data have different trends as expected. Shirley Meadows, near the summit, received circulation more typical of the region including down-mixing, than did Democrat Springs in the valley.

### Ion Balance

In Figs. 51 to 54, the sum of the anions  $\text{SO}_4^-$  and  $\text{NO}_3^-$  is plotted vs. the sum of the cations, strong particulate acid and  $\text{NH}_4^+$ . If these ions were balanced, the points would lie along a  $45^\circ$  line through the origin. This type of plot affords a test of whether the major acidic and basic particulate species have been sampled and whether the samplers collect these species quantitatively. Figs. 51, 52 and 54 show that an ion balance was indeed achieved at Martinez, San Jose and Kern. For all three plots, the intercept of the regression line is not significantly different from zero at the 95% confidence limit and the slope is not significantly different from one.

Fig. 53 is a replot of the San Jose data without applying the correction to  $\text{NH}_4$  for volatilization loss of ammonium nitrate as explained above in the discussion of the sampling trains. Comparing Figs. 52 and 53, it is seen that without the correction the intercept is larger and the slope smaller. Furthermore, the correlation coefficient decreased from 0.95 to 0.81. This results from variation of the volatilization loss

from run to run, depending on conditions. The correction is made from the measured loss of nitrate in sampling train No. 2 for each run. In the past, some experimenters have sampled with Teflon filters without backup filters, obtaining good ion balances. This is misleading because the volatilization of ammonium nitrate will lead to equal losses of ammonium and nitrate. Indeed, trial plots using our data for Teflon filters only, lead to fairly good ion balances.

In the plot for Martinez there are four outliers for which we have no definite explanation. It is possible that another cation was present from a reaction with sea salt. Martinez represents an extreme case of a multiplicity of strong, nearby sources.

### Estimates of Dry Acid Deposition

The measured ambient concentrations can be used to estimate the deposition flux by multiplying by the appropriate deposition velocities. This will be done here as an illustrative exercise, with no expectation that the results will be better than order-of-magnitude estimates. The concentration data acquired during the present project represent a brief one-time sampling at each site. At all three sites the general air pollution levels ranged from clean to moderately clean. Therefore, the observed concentrations cannot be said to be representative of yearly averages or of episodic highs. Another source of major uncertainty is in the selection of deposition velocities because of the lack of definitive experimental data and theoretical understanding upon which to base the choice. Nevertheless, the exercise is instructive in forcing an examination of the factors involved in the evaluation of deposition velocities. The results are listed in Table 3.

To put the results for dry acid flux into perspective, a comparison with wet flux is illuminating. Liljestrang and Morgan (2) measured the strong acidity of rainwater in the Los Angeles basin for the 1978 - 79 season, obtaining approximately  $30 \mu\text{N} = 30 \text{ nequiv/cm}^3$ . They list the precipitation as  $20 \text{ in/yr} = 50 \text{ cm/yr}$ . To estimate the yearly average wet acid flux, we multiply the two factors:

$$30 \text{ nequiv/cm}^3 \times 50 \text{ cm/yr} = 1500 \text{ nequiv/cm}^2\text{yr}$$

For dry deposition of sulfur dioxide or nitric acid, we obtained (Table 3) about 1

$\text{nequiv/m}^2\text{s} = 3000 \text{ nequiv/cm}^2\text{yr}$ . This is twice the above estimated wet flux. Although the result is reasonable, we must emphasize again that we are making only crude estimates.

Obtaining more meaningful dry acid deposition fluxes will require several improved inputs. The major need is for data on deposition velocities for the various acidic species onto various surfaces. Since the deposition velocities depend on meteorological conditions, this dependency must be taken into account. Present data on deposition velocities is very sparse and even that is of questionable accuracy. The techniques for the measurement are still under development. The other input, ambient concentrations, will require sampling periodically through the year at various locations. The sampling must be coupled with meteorological measurements. A first approach might be to separate day and night sampling since both concentrations and deposition velocities are normally quite different. An estimate of the atmospheric stability category would be made for selection of the appropriate deposition velocity.

#### Critique of Sampling Techniques and Performance of Samplers

In this section, the sampling techniques and the performance of the samplers for the various chemical species will be critiqued, following the order of items in Table 1.

##### (1) Particulate strong acid

The  $\text{NH}_3$  denuder presented a serious operational problem due to the hygroscopicity of phosphorus acid. At times of high humidity the water accumulation is sufficient to block some of the tubes, necessitating remedial action. An improved  $\text{NH}_3$  denuder is definitely needed. Otherwise, no difficulties were encountered, although it should be mentioned that the microtitration is an exacting operation.

That a denuder is needed is confirmed by the high  $\text{NH}_3$  levels at all three sites. Moreover, the denuder-protected filter gave acid values typically about 20% higher than the unprotected filters of the nitrate sampling trains; occasionally values were twice as great.

(2)  $\text{SO}_4$

$\text{SO}_4$  was determined by analyzing the filters from the particulate sampling train and the prefilters of the nitrate sampling trains for comparison. At Martinez, the coefficient of variation averaged 7%. At Kern, the fine fraction from the dichotomous sampler gave sulfate values about 20% higher than the other samplers.

(3)  $\text{NH}_4$

As previously discussed, it was necessary to correct  $\text{NH}_4$  for volatilization loss. The addition of an oxalic acid impregnated after filter would allow recovery of the ammonia from the volatilized ammonium. This improvement is indicated for future work. This would be combined with an improved train for  $\text{NH}_3$ , as explained under (7), below. Based on previous work (37,38), Teflon is the preferred filter medium for the sampling of nitrogen compounds.  $\text{NH}_4$  determined from the quartz prefilter of the  $\text{NH}_3$  sampler roughly agreed with the other samplers at Kern, agreed poorly at San Jose and disagreed at Martinez.

(4)  $\text{NO}_3$

The nitrate sampling train is believed to be free of sampling artifacts. The MgO acid denuder for removal of  $\text{HNO}_3$  was relatively free of operational problems.

(5)  $\text{HNO}_3$

The denuder difference method employed here, although cumbersome to field and requiring the analysis of four filters for each  $\text{HNO}_3$  determination, produces unambiguous results. It is necessary to maintain the flow rates in the two sampling trains within 1% of each other, which can be accomplished by manual adjustments every few hours.

(6)  $\text{SO}_2$

The  $\text{H}_2\text{O}_2$  bubblers were essentially trouble-free. The only operational com-

plication is the requirement that the solutions be kept under refrigeration before and after sampling. The possible sampling time is limited to a day or so by evaporation loss. Judging from the data for the three sites, a sensitivity of about 10 nequiv/m<sup>3</sup> is needed and is achieved by the bubblers. This is equivalent to 0.25 ppb. By comparison, monitoring instruments have a sensitivity of about 1 ppb but are only reliable at 5 - 10 ppb. It should be noted that at the ppb level the acid deposition from SO<sub>2</sub> is comparable to that of wet deposition, in California.

(7) NH<sub>3</sub>

The NH<sub>3</sub> sampling train presented no operational problems. The filter handling, which must be done in an ammonia-free atmosphere, is tedious and time-consuming. NH<sub>3</sub> sampling is important however, the levels at all three stations being high compared to other chemical species.

Some volatilization loss of ammonium nitrate could have taken place from the quartz filter. The resulting error in the ammonia value would have been small because the NH<sub>4</sub> levels were very much smaller than those of NH<sub>3</sub>. The loss could be taken into account by a denuder difference sampling scheme analogous to that for nitric acid and nitrate. One sampling train would be the present No. 1 with an added backup filter. The two trains would be:

- (a) cyclone - ammonia denuder - Teflon filter - oxalic acid/glass fiber filter
- (b) cyclone - Teflon filter - oxalic acid/glass fiber filter

The ammonium from both filters of each train is summed. Ammonium is obtained from train (a). Ammonia is obtained from (b) minus (a). This arrangement would represent a definite improvement over our present arrangement, particularly if sampling were conducted where ammonia and ammonium had comparable levels.

## SUMMARY AND CONCLUSIONS

Dry acid deposition measurement methods were reviewed and the ambient concentration - deposition velocity method selected as the most feasible for application to monitoring. Advantages of this approach vs. other possible methods are:

- (1) It is possible to measure the ambient concentrations of all acidic chemical species of interest, using available techniques as a starting point. This cannot be said for the micrometeorological methods or surface collection methods.
- (2) The lack of data and theoretical understanding of deposition velocities is a drawback to the method. Meanwhile, ambient concentration data alone can be used for trend analysis and can be related to source controls.
- (3) The ambient concentration - deposition velocity method is probably the most useful for the assessment of dry acid impact on wide areas of the state. Micrometeorological methods apply only to a uniform site of a given type. Surface methods address only a specific target.

Of course, data from all approaches are valuable in the attack on this very difficult problem. The present work illustrates the need for supporting data from the other techniques.

An extensive dry acid sampling array, in fact, one of the most complete ever operated, has been assembled. Variables sampled included particulate strong acid,  $\text{SO}_4$ ,  $\text{NH}_4$ ,  $\text{NO}_3$ ,  $\text{HNO}_3$ ,  $\text{SO}_2$ ,  $\text{NH}_3$ ,  $\text{NO}_x$ , temperature, dew point, wind direction, wind speed and fine and coarse particulate mass. Sampling trains included cyclones to exclude coarse alkaline particles,  $\text{NH}_3$  and acid denuders as appropriate and double filters to eliminate sampling artifacts. Chemical species were analyzed by microtitration for acid, ion chromatography and ion-selective electrode. Continuous monitors, meteorological instruments and a computer data acquisition system were housed in a mobile laboratory.

Sampling was carried out in three locations, Martinez, San Jose and the Kern River valley. Martinez had multiple sources including strong ammonia, San Jose had the highest nitric acid and nitric oxide levels while the Kern site was distinguished by high

SO<sub>2</sub> from the Bakersfield-Oildale area. The three sites were also different in being progressively removed from maritime influence and in having different wind regimes.

Sampling was carried out for several days at each site with sufficient time resolution to detect diurnal variations. For important chemical species, redundant analyses were made on samples from several different sampling trains to evaluate the performance of denuders, etc. Time series were plotted for each of the variables.

Of all the chemical species, oxides of nitrogen had the highest concentrations at all three sites. Sulfur dioxide was also relatively high. In the tidal air flow of the Kern River canyon, sulfur dioxide showed a strong diurnal pattern with deeper minima than did fine particulate sulfate and ammonium. Whereas the fine particulate species showed an increase over three days, the sulfur dioxide did not. This is consistent with a higher deposition velocity for sulfur dioxide than fine particles, as expected. Sulfate was uncorrelated to sulfur dioxide but strongly correlated to ammonium, consistent with the presence of ammonium sulfate and ammonium acid sulfate.

After sulfur dioxide, nitric acid was the major acidic species at all sites. Nitric acid showed a strong diurnal pattern, the time lag relative to NO<sub>x</sub> being characteristic of photochemical production. Peak NO<sub>x</sub> levels varied greatly from site to site but HNO<sub>3</sub> levels did not, suggesting that nitric acid formation was not NO<sub>x</sub> limited. Nighttime levels of nitric acid were near zero, suggesting a relatively large deposition velocity. In Kern canyon the diurnal pattern was similar to that of sulfur dioxide.

Particulate strong acid was 10 to 20% of sulfur dioxide levels. Weak acids were less than 10% of the strong acid. The weak diurnal pattern of the particulate strong acid is consistent with a low deposition velocity. The dichotomous sampler data at Kern indicated that NH<sub>4</sub>, SO<sub>4</sub> and NO<sub>3</sub> were predominately in the fine particulate fraction.

At all three sites a balance was obtained between the sum of the anions SO<sub>4</sub> and NO<sub>3</sub> and the cations particulate strong acid and NH<sub>4</sub>, verifying that all major ions were sampled and that the sampling was quantitative. The ion balance was also used to show that volatilization of ammonium nitrate is significant, and that the precautions incorporated into the present sampling scheme are necessary.

Although the present sampling techniques proved satisfactory, some improvements are suggested. A non-hygroscopic ammonia denuder is needed. The sampling of ammonium would be improved by addition of an oxalic acid-glass fiber backup filter to that sampler. Use of the denuder difference technique for ammonia would eliminate particulate ammonium artifact in ammonia sampling. The sampling array was labor-intensive to operate. In about nine days of sampling, some 400 samples were collected requiring over 800 chemical determinations. While over-determinations were necessary for research purposes, clearly it would not be practical to field such a sampling array routinely.

The derivation of quantitative dry acid deposition fluxes from measured ambient concentrations of acidic species will require much more reliable and extensive data on deposition velocities than is currently available.

### RECOMMENDATIONS

It is evident that much work remains to be done in devising monitoring methods for dry acid deposition because of the large number of chemical species which must be measured, the technical difficulties attending the measurements and the embryonic state of research in this field. The research reported here covers the first year of a multiyear program. Some progress has been made and on the basis of the experience thus far, it is possible to make some specific recommendations for research especially needed as well as interim measures to begin the monitoring of dry acid.

- (1) Improved monitoring of  $\text{SO}_2$  should be instituted, because the continuous monitors currently in use have inadequate sensitivity. The  $\text{H}_2\text{O}_2$  bubbler technique, which was highly satisfactory in the present work, is recommended.
- (2) Nitric acid has significant levels in California. Consideration should be given to making periodic measurements, perhaps quarterly, on ambient  $\text{HNO}_3$  at important sites such as San Jose and Los Angeles. The denuder difference method is recommended.

- (3) Sulfate particles should be sampled on Teflon filters, using dichotomous samplers or cyclones.
- (4) Research is needed on the following topics:
  - (a) Deposition velocities of acidic gases and particles.
  - (b) Size distributions of acidic particles since deposition velocities are strongly size-dependent.
  - (c) Development of a non-hygroscopic ammonia denuder.
  - (d) Development of high sensitivity, real-time monitors for  $\text{SO}_2$ ,  $\text{HNO}_3$  and  $\text{NH}_3$ .
  - (e) Identification of the important receptors of dry acid in California to guide monitoring strategies.
  - (f) Basic mechanisms of dry acid deposition to provide a basis for the development of monitoring techniques.

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Table 1. Summary of Environmental Variables, Samplers and Methods of Analysis

Variable	Sampler or Sensor	Analysis
Particulate strong acid	Cyclone NH <sub>3</sub> Denuder, Teflon filter	Acid titration
SO <sub>4</sub>	"	Ion chromatography
NH <sub>4</sub>	"	Ion selective electrode
NO <sub>3</sub>	Cyclone, acid denuder, Teflon and Whatman 41- NaCl filters	Ion chromatography
HNO <sub>3</sub>	Denuder difference method	Ion chromatography
SO <sub>2</sub>	H <sub>2</sub> O <sub>2</sub> bubbler	Ion chromatography
NH <sub>3</sub>	Quartz filter, acid-washed glass fiber filters w/oxalic acid	Ion selective electrode
Nitric oxides	TECO 14 T monitor	--
Temperature	Platinum RTD in aspirated radiation shield	--
Dew point (for relative humidity)	LiCl-RTD in aspirated radiation shield	--
Wind direction, wind speed	Met One 010 assembly	--
Fine particulate mass	Cyclone, NH <sub>3</sub> denuder Teflon filter	Microbalance
Fine and coarse particulate mass	Sierra 244 Dichotomous Sampler, Teflon filters	Microbalance

Table 2. Summary of Concentration Ranges (nequiv/m<sup>3</sup>) and Time Dependences of Variables

Species	Martinez	San Jose	Kern
SO <sub>2</sub>	30-110 weak diurnal pattern high daytime	15-160 diurnal, high daytime	0-225 very strong diurnal, high daytime
Particulate Strong acid	0-25 weak diurnal, high daytime, no long term buildup	0-25 no diurnal, large evening peak last day	5-20 no diurnal, small long term increase
SO <sub>4</sub>	10-70 strong diurnal, morning peaks of constant magnitude	0-60 variable	10-80 weak diurnal, peak midday, long term increase
NH <sub>4</sub>	10-80 strong diurnal, morning peaks of constant magnitude correlated with SO <sub>4</sub>	0-70 variable, correlated with SO <sub>4</sub>	15-100 weak diurnal, peak midday, long term increase, correlated with SO <sub>4</sub>
NH <sub>3</sub>	140-900 strong diurnal, daytime peak of variable magnitude	20-250 sharp daytime, one nighttime peak of constant magnitude	70-150 daytime peak of variable magnitude
HNO <sub>3</sub>	0-70 variable, one peak midday	0-100 strong diurnal, afternoon peak of variable magnitude	0-50 very strong diurnal, afternoon peak
NO <sub>x</sub>	600-2200 irregular, daytime peaks	700-3800 irregular, morning peaks	100-500 no diurnal, multiday peak
NO <sub>3</sub>	20-90 daytime peaks of variable conc., largest peak morning	10-60 irregular morning peaks, correlated with NO <sub>x</sub>	10-20 no diurnal, multiday peak, correlated with NO <sub>x</sub>
Fine particulate mass	(not measured)	10-28 daytime peak, one exception	8-28 variable

Table 2. Summary of Concentration Ranges (nequiv/m<sup>3</sup>) and Time Dependences of Variables (continued)

Species	Martinez	San Jose	Kern
Wind direction	NNW constant	northerly, westerly at times	NE daytime (up valley), SW night (down valley)
Wind speed	4-13 mph diurnal, high daytime	0-9 mph diurnal, high daytime	2-5 mph diurnal, high daytime
Average Temperature	12-30°C diurnal, high daytime	13-29°C diurnal, high daytime	12-25°C diurnal, high daytime
Average Relative Humidity	26-82% diurnal, high nighttime	32-85% diurnal, high nighttime	30-70% diurnal, high nighttime

Table 3. Illustrative Calculation of Deposition Fluxes.  
Not to be Considered Quantitative

Species	Assumed deposition velocity		Midrange of measured concentration			Calculated Deposition Flux		
	cm/s		nequiv/m <sup>3</sup>	nequiv/m <sup>3</sup>	nequiv/m <sup>3</sup>	nequiv/m <sup>2</sup> s	nequiv/m <sup>2</sup> s	nequiv/m <sup>2</sup> s
			Martinez	San Jose	Kern	Martinez	San Jose	Kern
SO <sub>2</sub>	1.0	(1)	70	88	113	0.7	0.9	1.0
Particulate strong acid	0.05	(2)	23	23	13	0.01	0.01	0.007
SO <sub>4</sub>	0.05	(2)	45	30	45	0.02	0.02	0.02
HNO <sub>3</sub>	2.5	(3)	35	50	25	0.9	1.0	0.6
NO <sub>3</sub>	0.05	(2)	45	35	15	0.02	0.02	0.008
NO <sub>x</sub>	1.0	(4)	1400	2250	300	10	20	3.0

- (1) Estimated midrange of data in Ref. 28.
- (2) Estimated from data on deposition of particles to grass, assuming particle dia. approx. 0.3 μm, Refs. 27 and 28.
- (3) Measured daytime deposition velocity on pasture, Refs. 34 and 34.
- (4) Arbitrary guess. Published data range from minus to 0.5, one measurement on NO<sub>2</sub> gave 1.9 cm/s. Refs. 27 and 28.



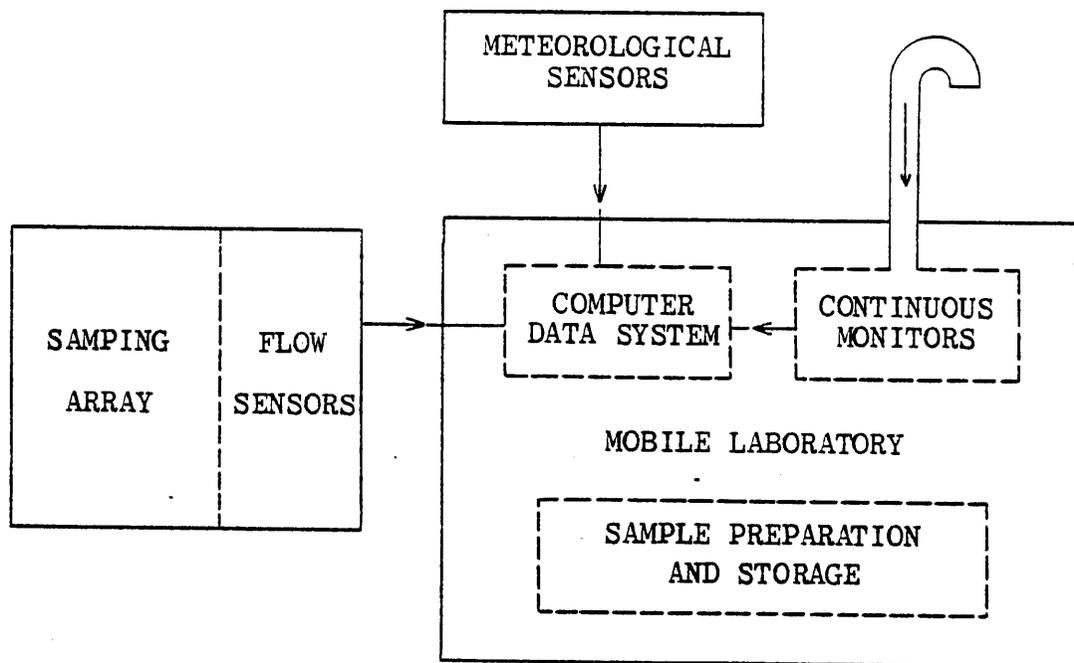


Figure 1. Diagram of sampling arrangement.

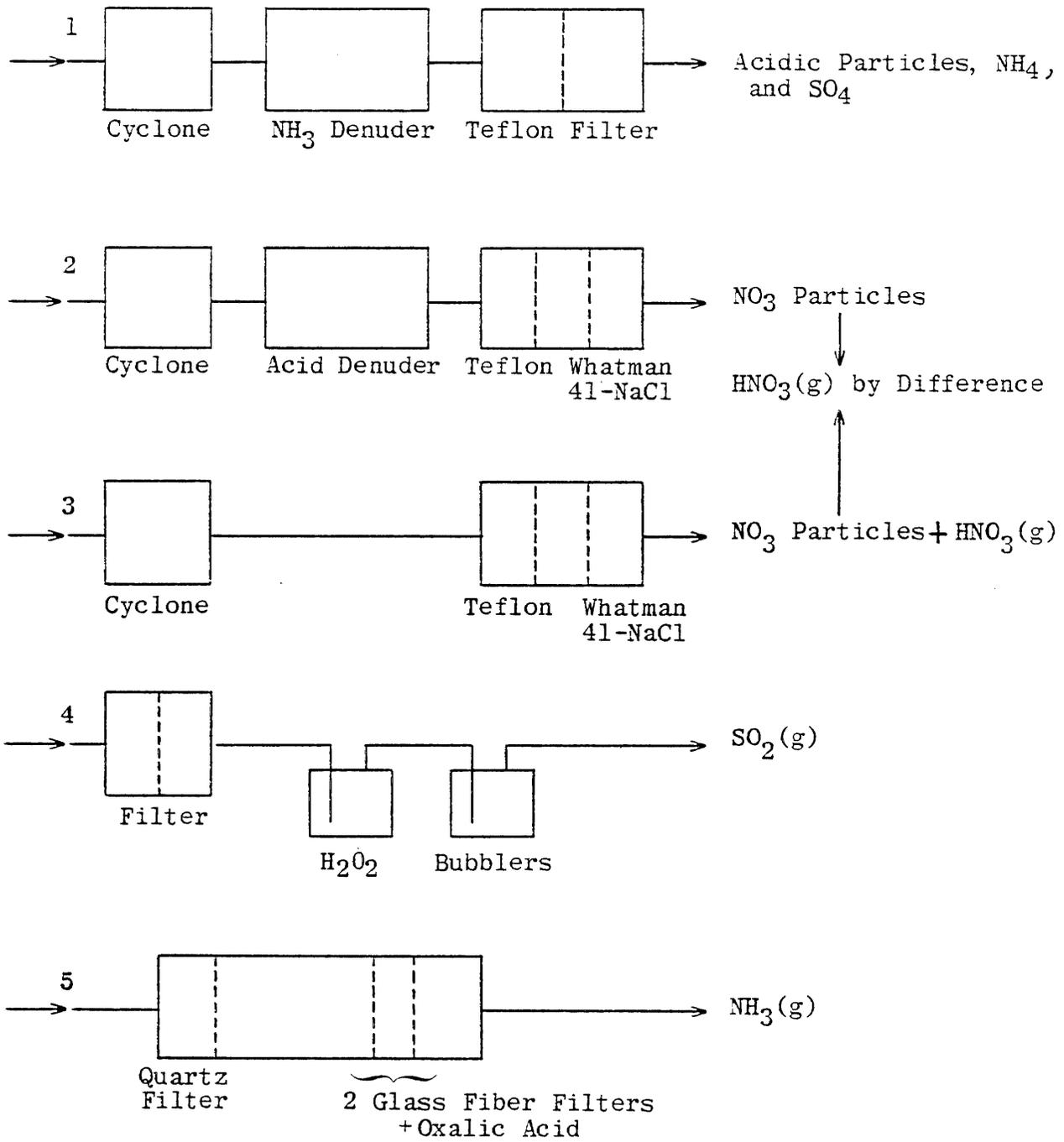


Figure 2. Schematic drawing of filter sampling trains.

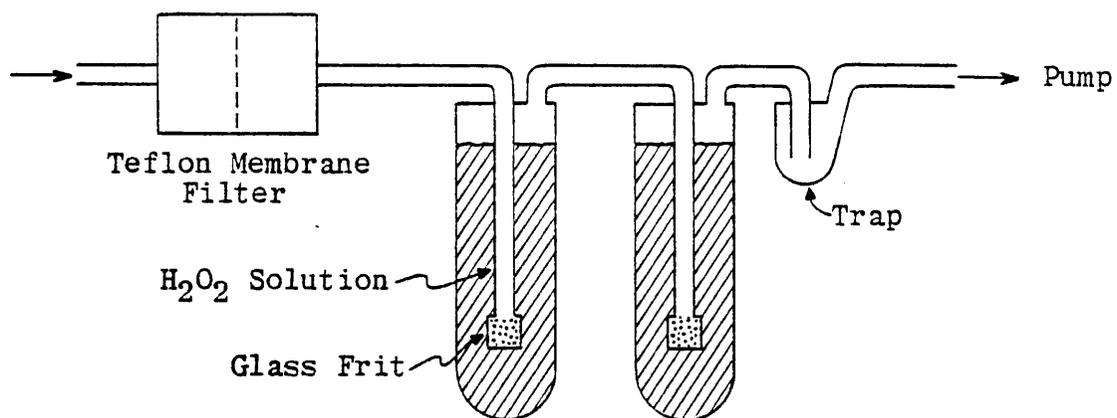


Figure 3. Bubblers for sulfur dioxide sampling.

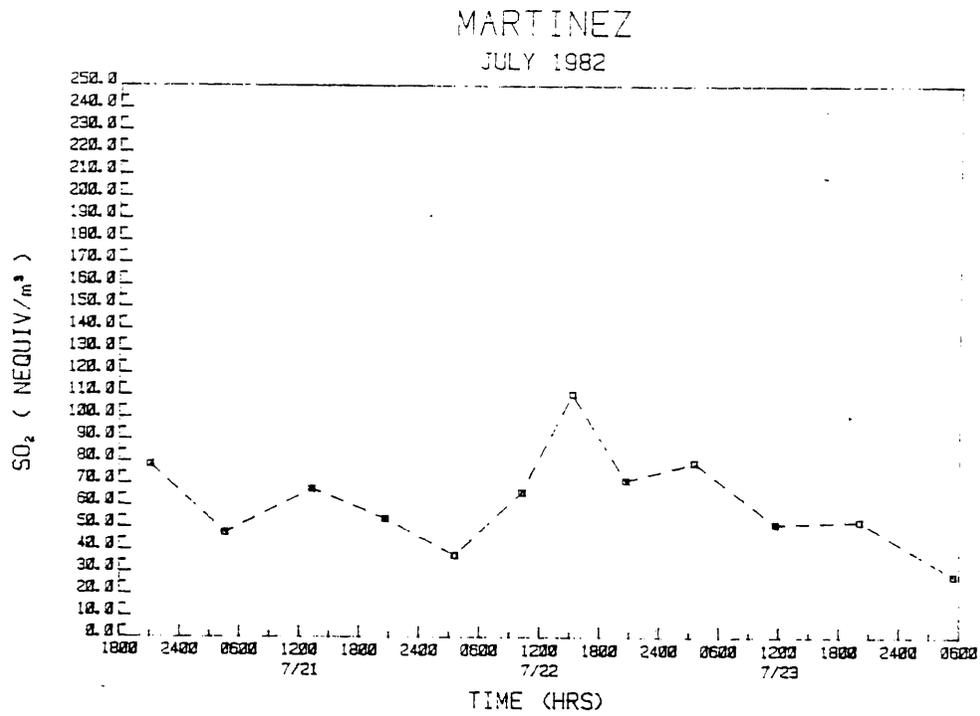


Figure 4. Sulfur dioxide concentration vs. time at Martinez.

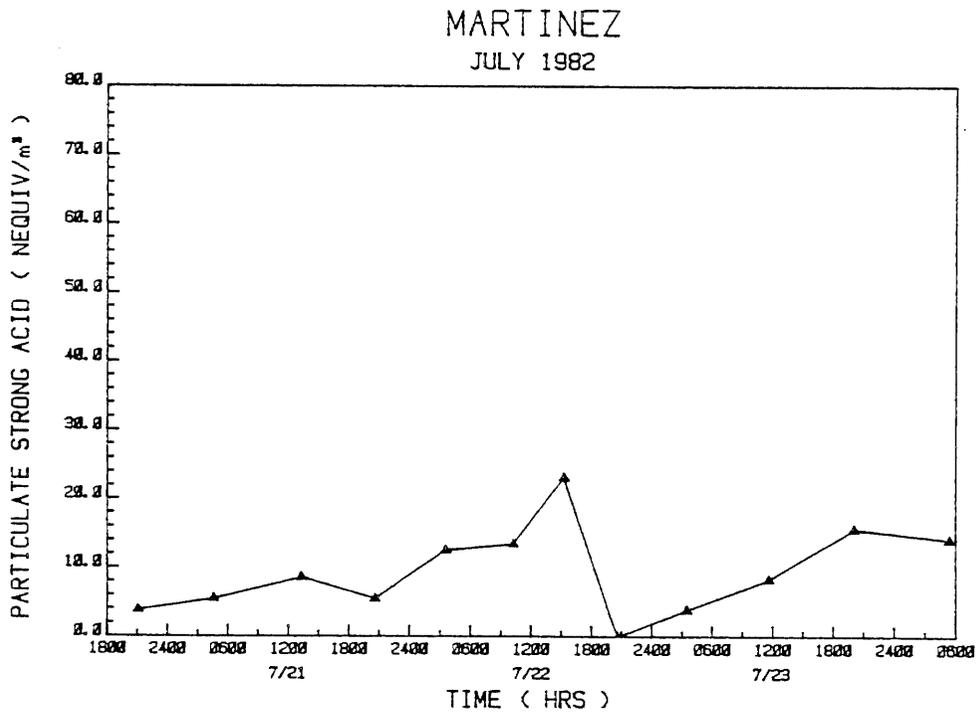


Figure 5. Strong acid concentrations from titration of the extract from the particle filter in sampling train No. 1.

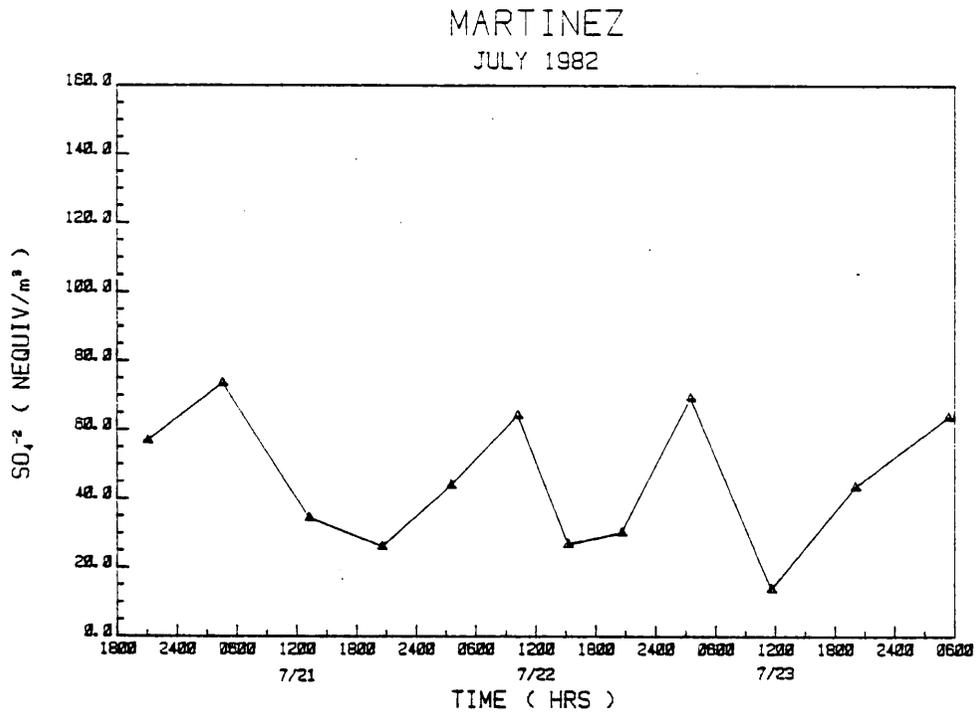


Figure 6. Fine particulate sulfate concentration vs. time at Martinez.

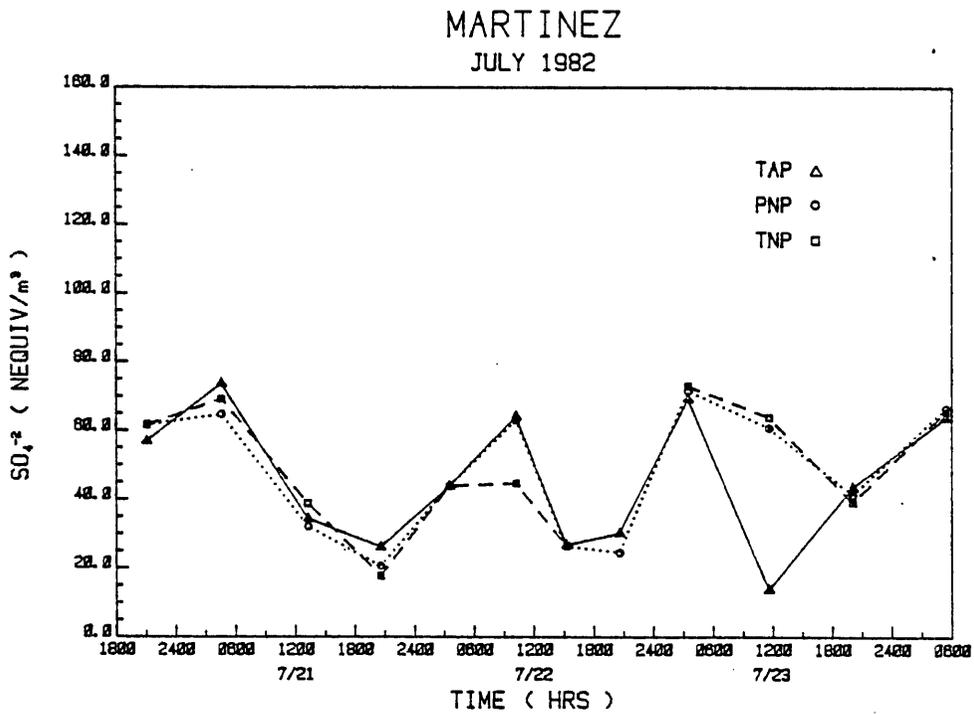


Figure 7. Comparison of sulfate concentrations from the Teflon filters in sampling train No. 1 in Fig. 2 (TAP), sampling train 2 (PNP) and sampling train 3 (TNP).

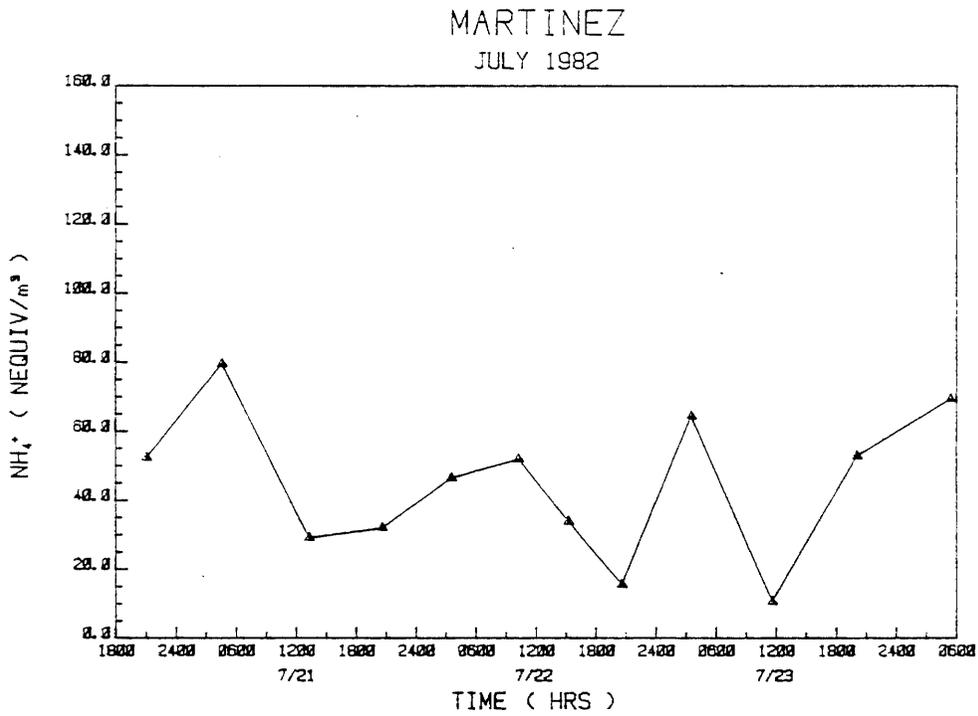


Figure 8. Fine particulate ammonium concentration vs. time in Martinez.

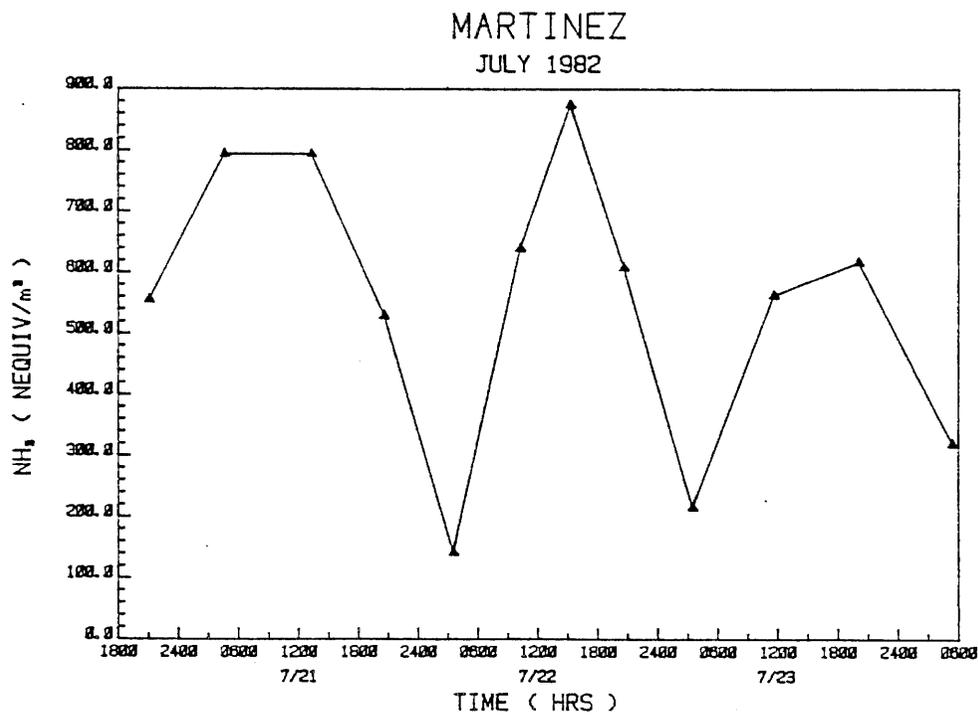


Figure 9. Ammonia concentration vs. time at Martinez.

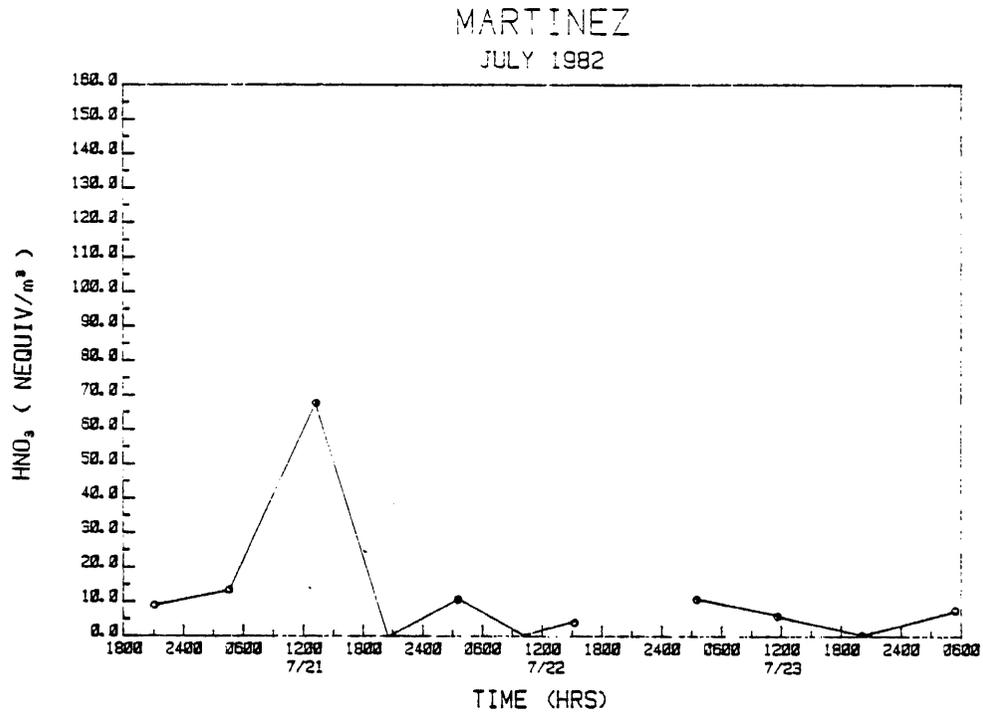


Figure 10. Nitric acid concentration vs. time at Martinez.

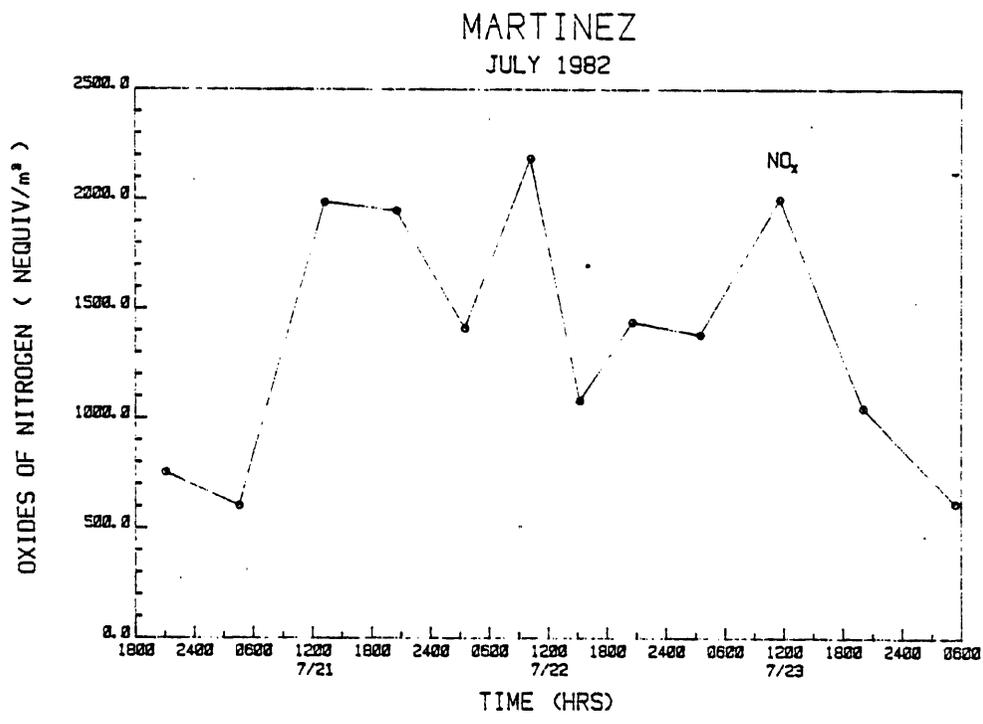


Figure 11. Concentration of oxides of nitrogen vs. time at Martinez.

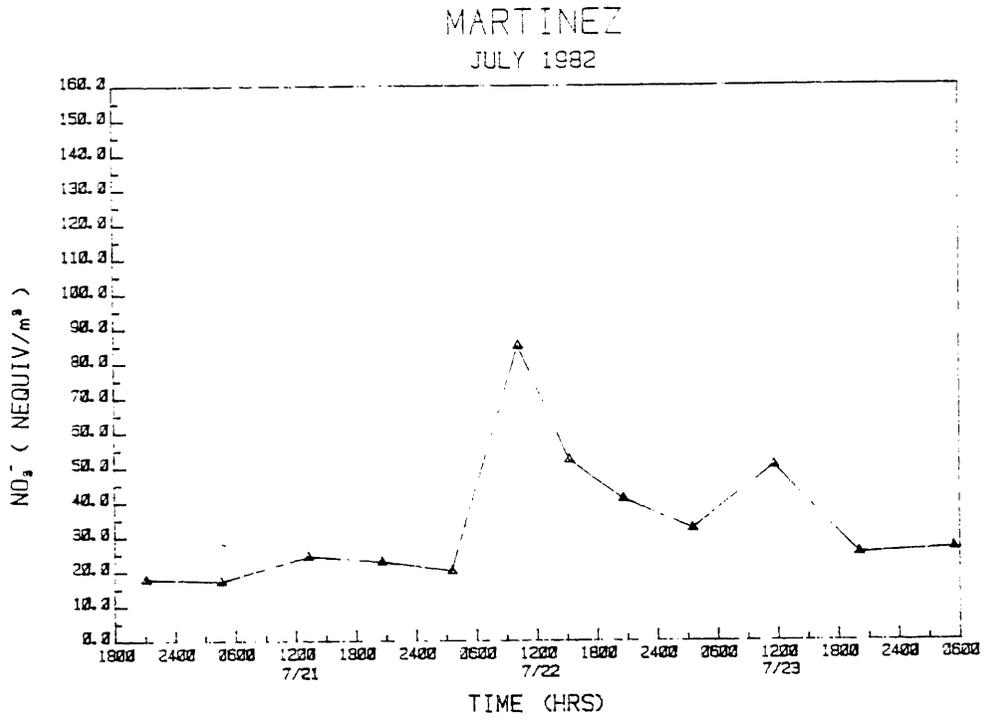


Figure 12. Fine particulate nitrate concentration vs. time at Martinez.

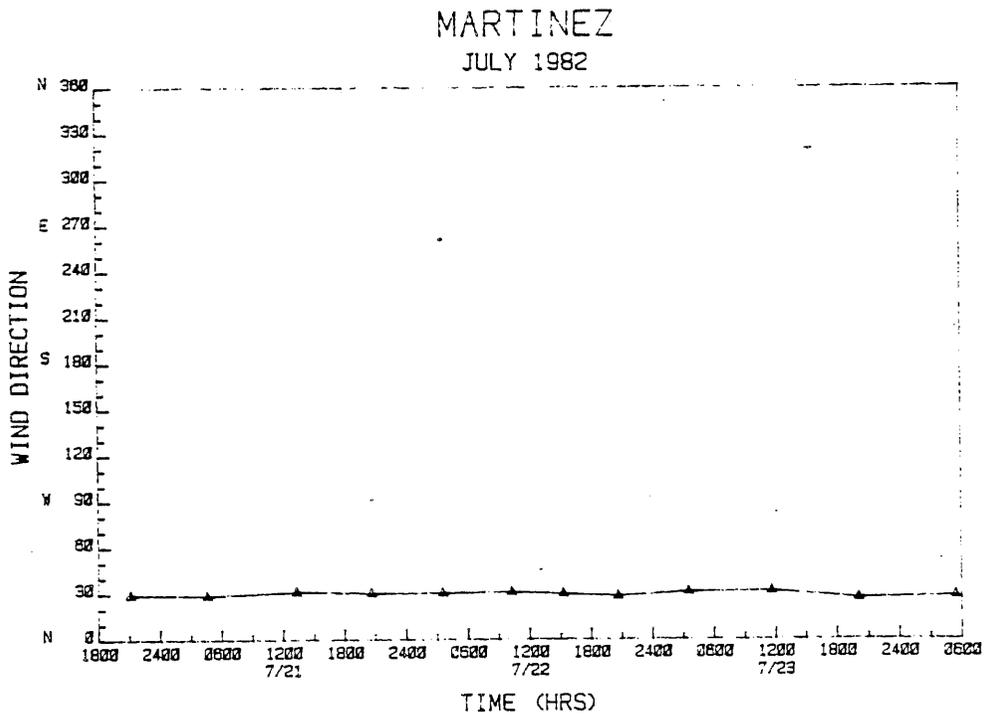


Figure 13. Wind direction vs. time at Martinez.

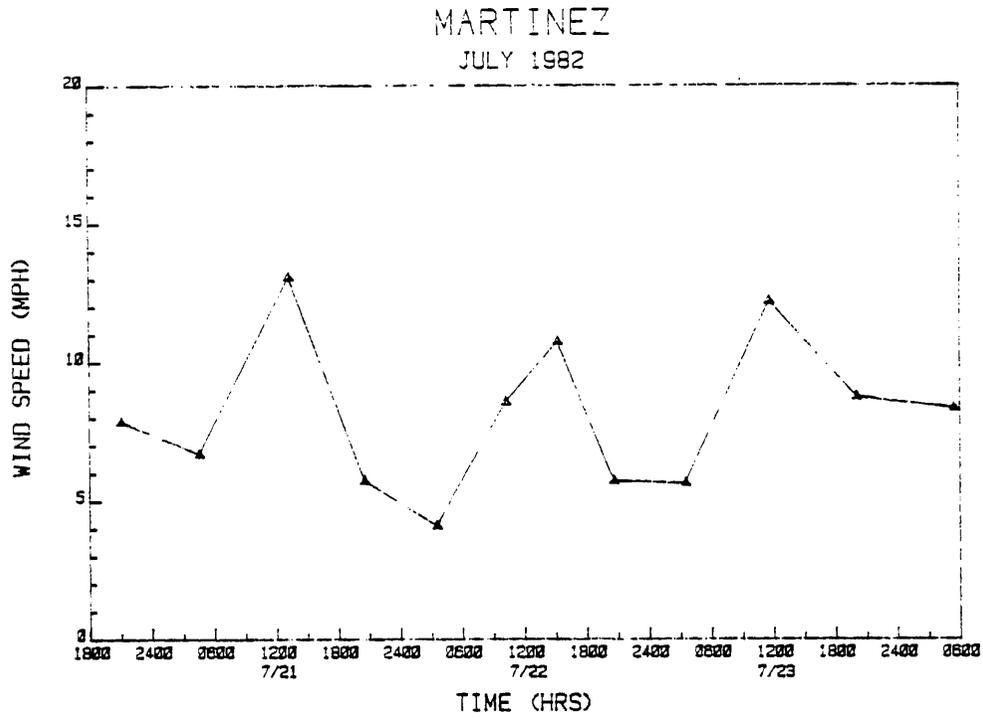


Figure 14. Wind speed vs. time at Martinez.

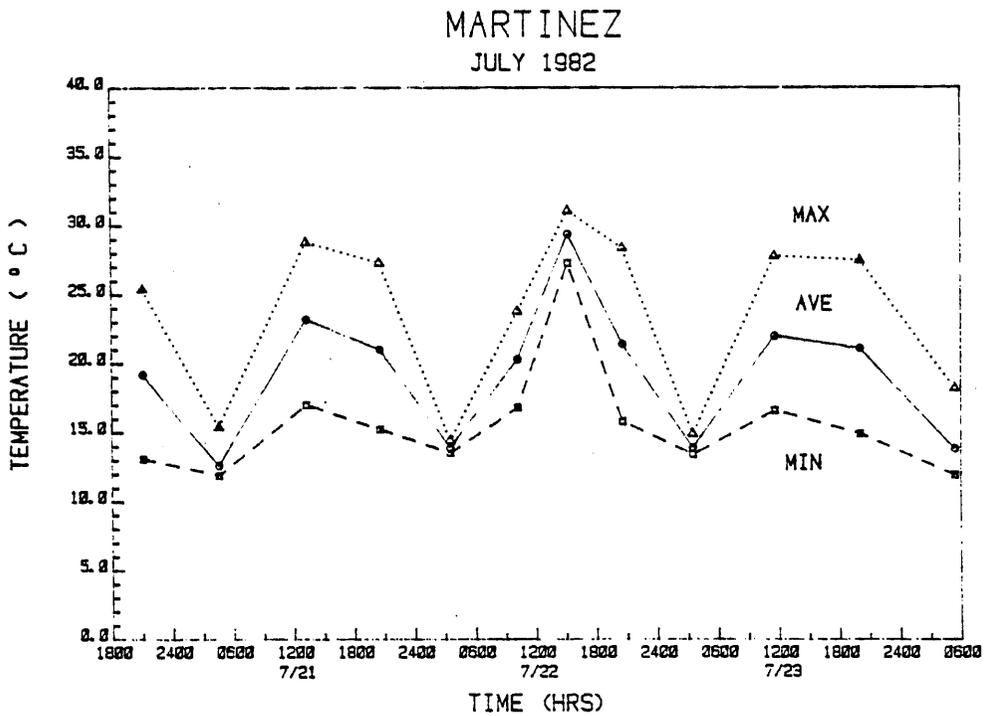


Figure 15. Temperature vs. time at Martinez.

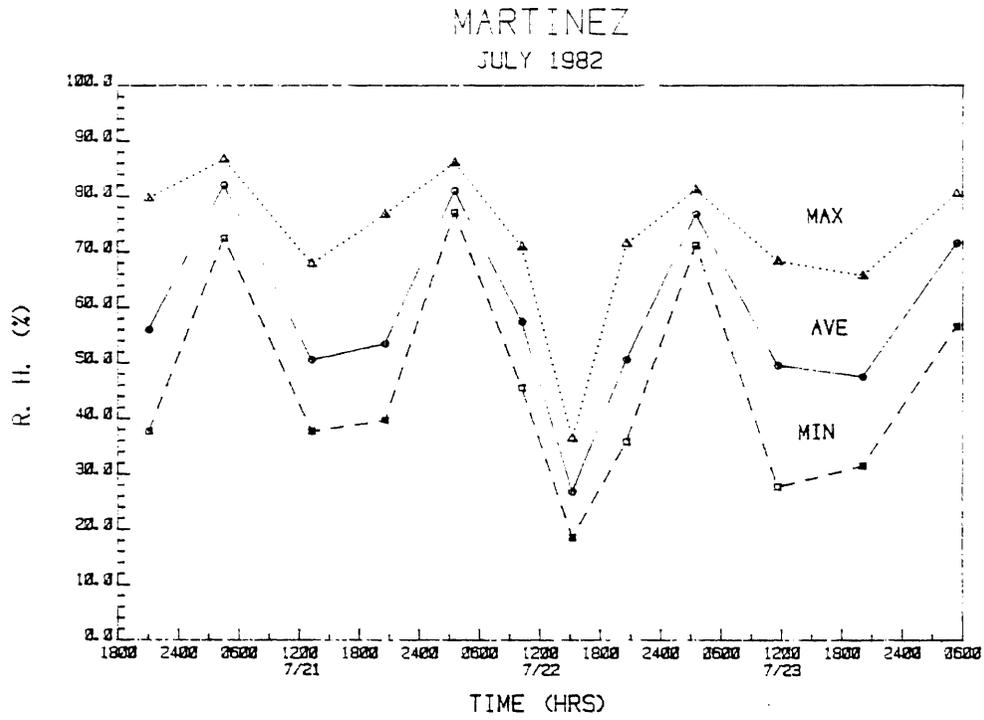


Figure 16. Relative humidity vs. time at Martinez.

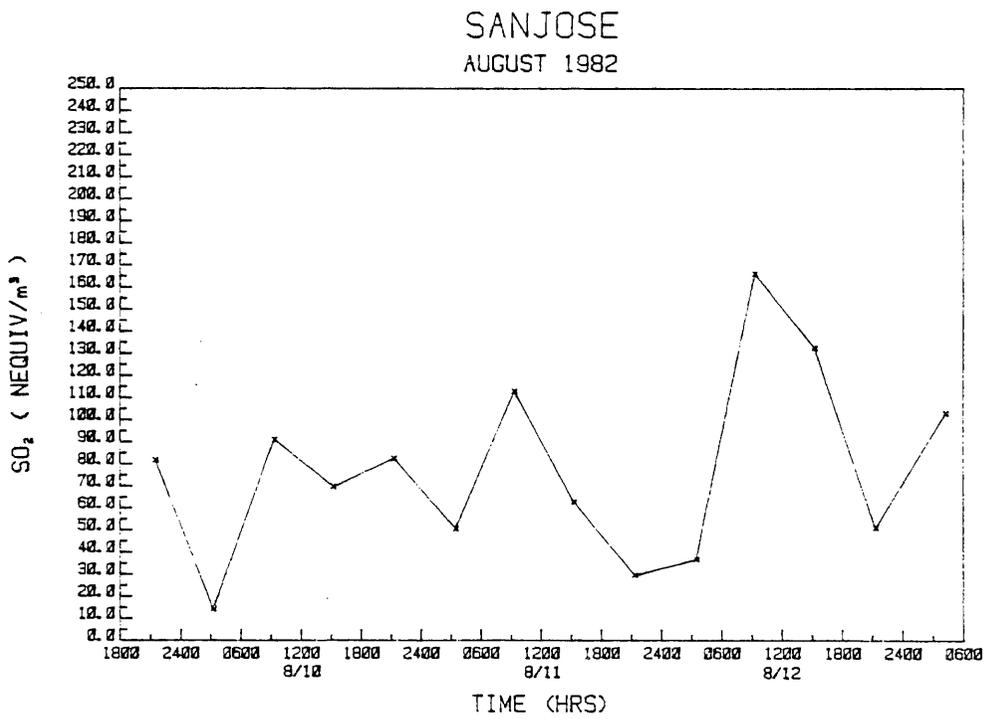


Figure 17. Sulfur dioxide concentration vs. time at San Jose.

SAN JOSE  
AUGUST 1982

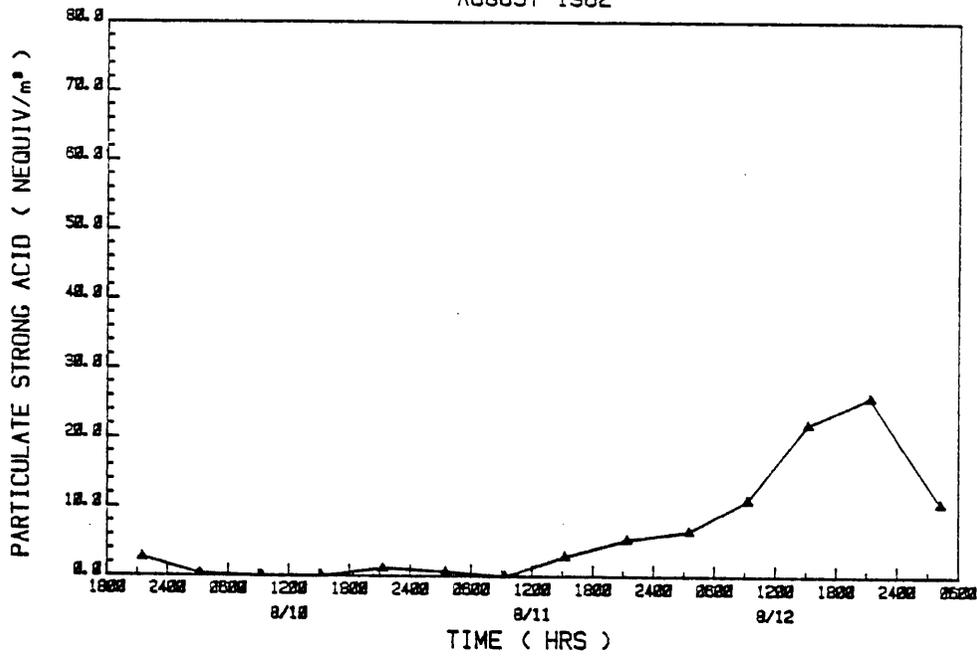


Figure 18. Fine particulate strong acid vs. time at San Jose.

SAN JOSE  
AUGUST 1982

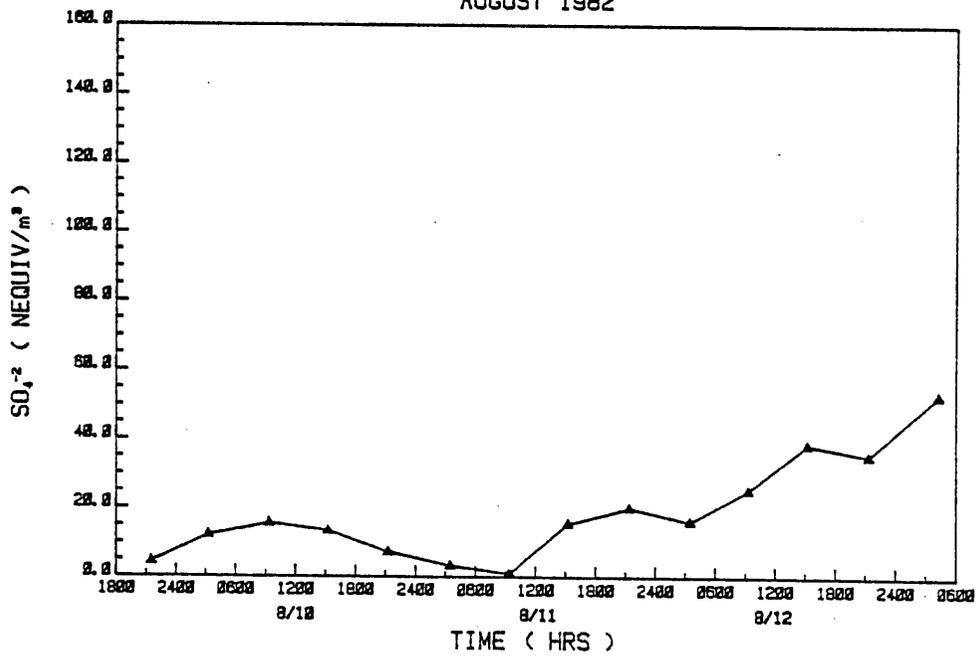


Figure 19. Fine particulate sulfate concentration vs. time at San Jose.

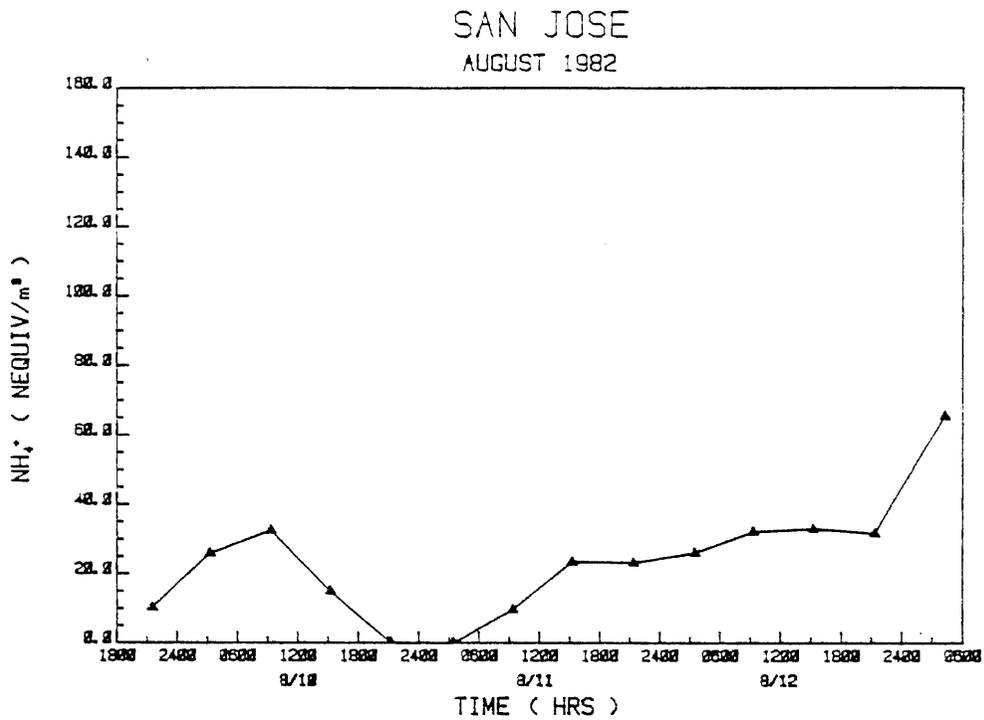


Figure 20. Fine particulate ammonium concentration vs. time at San Jose.

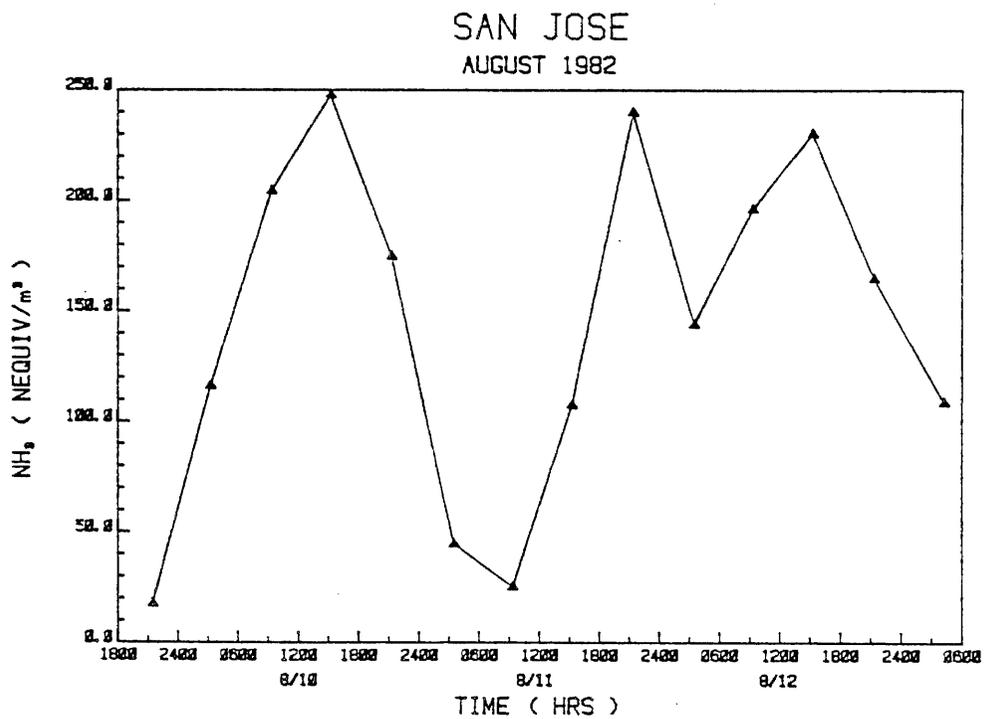


Figure 21. Ammonia concentration vs. time at San Jose.

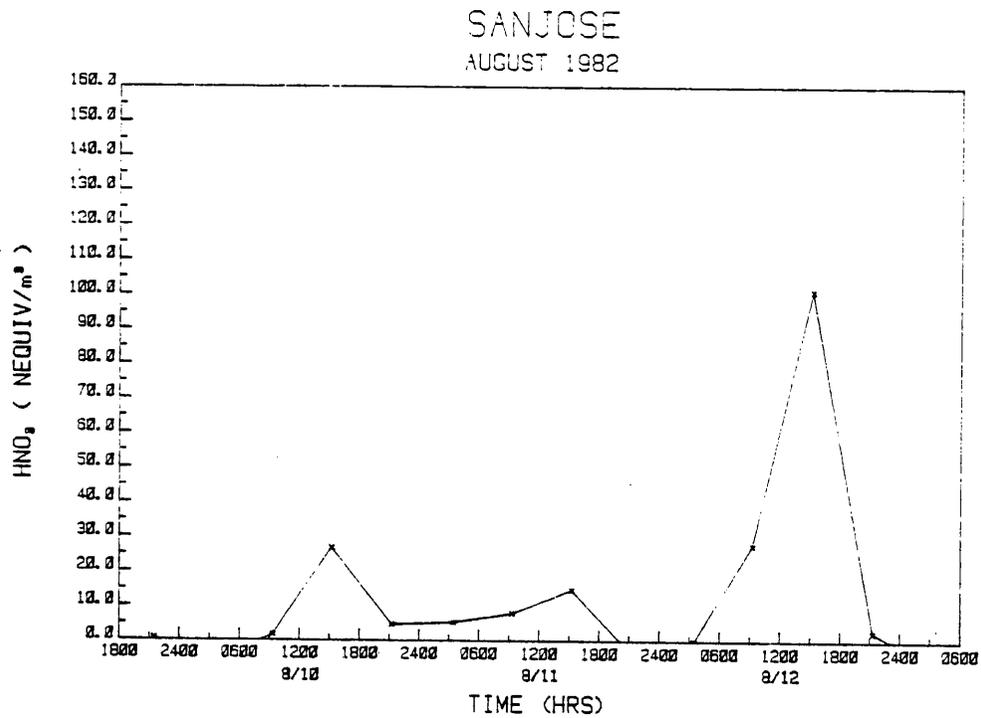


Figure 22. Nitric acid concentration vs. time at San Jose.

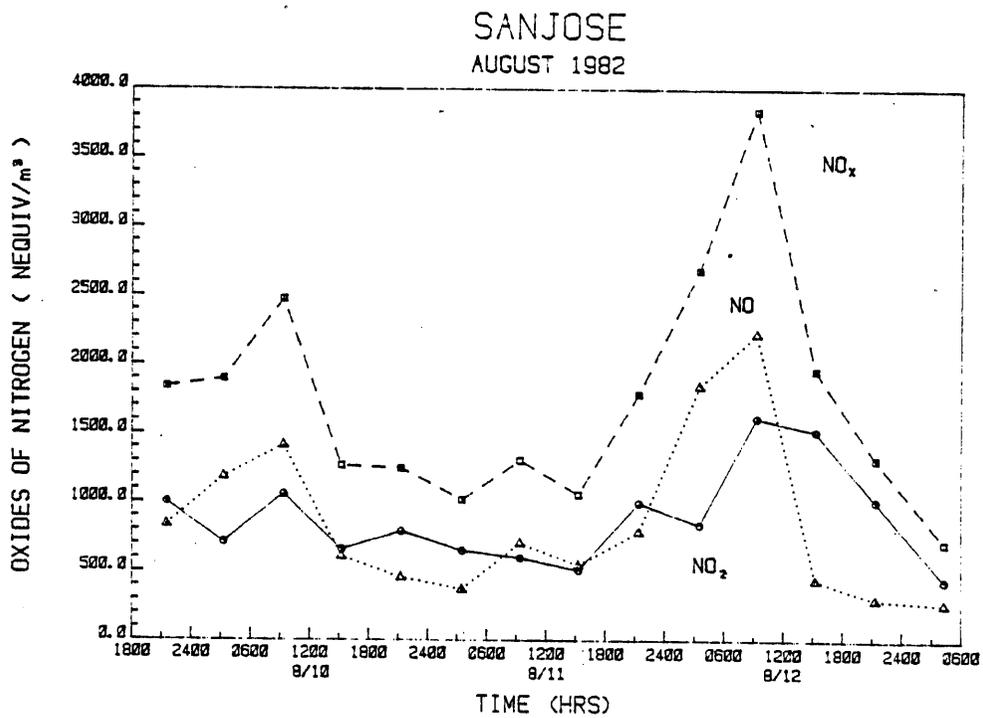


Figure 23. Concentrations of NO<sub>x</sub>, NO, and NO<sub>2</sub> at San Jose.

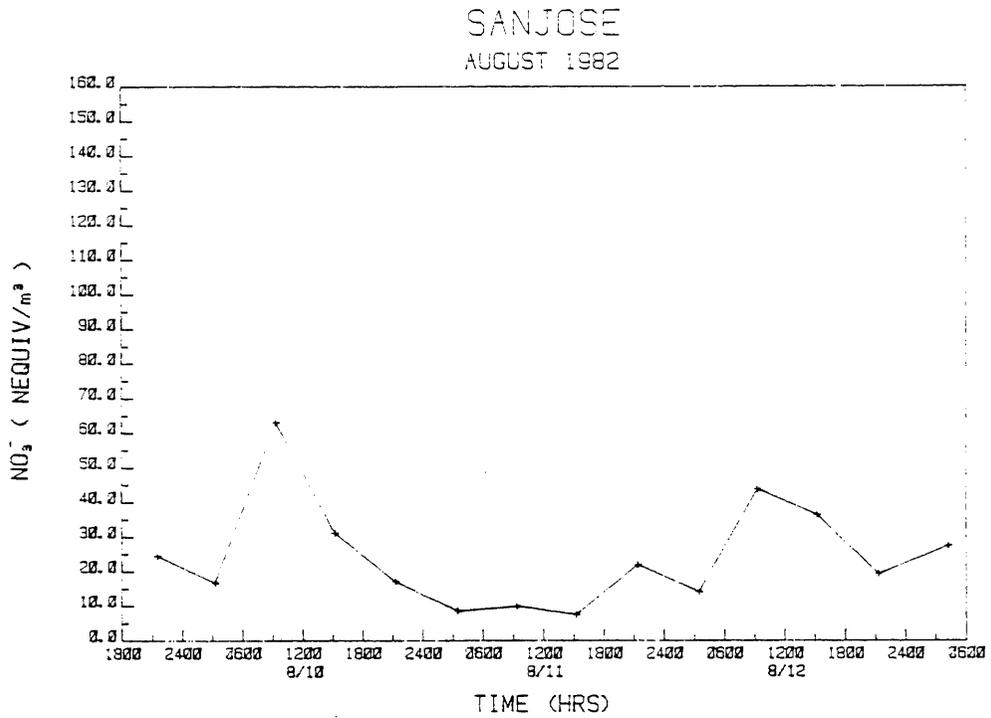


Figure 24. Fine particulate nitrate concentration vs. time at San Jose.

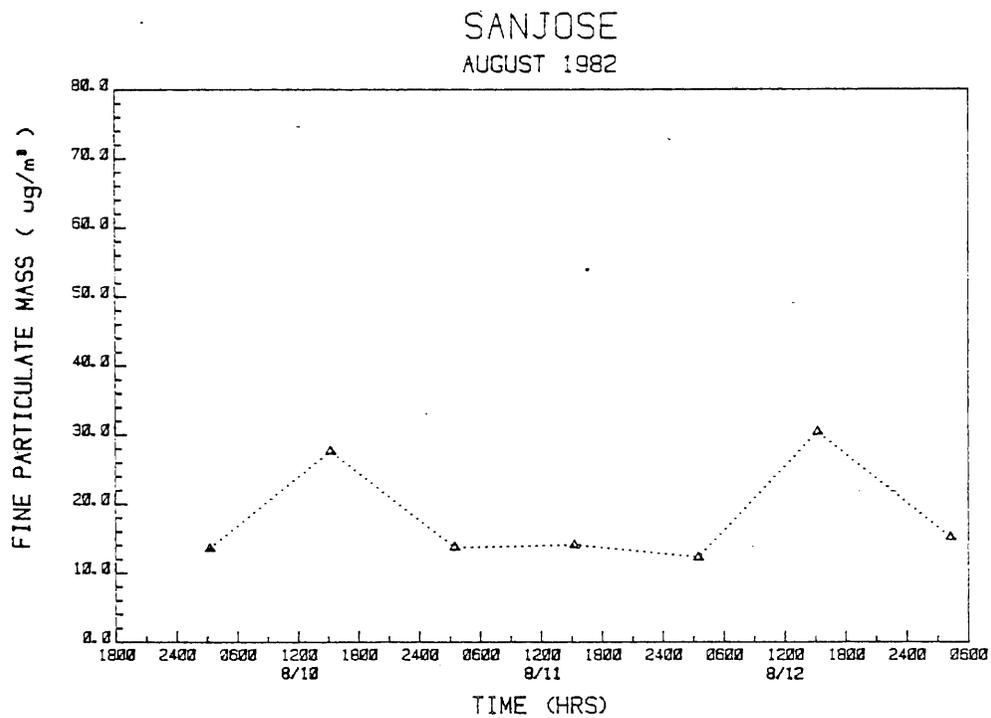


Figure 25. Mass of particles with aerodynamic diameters less than  $2.5 \mu\text{m}$ , from sampling train No. 1.

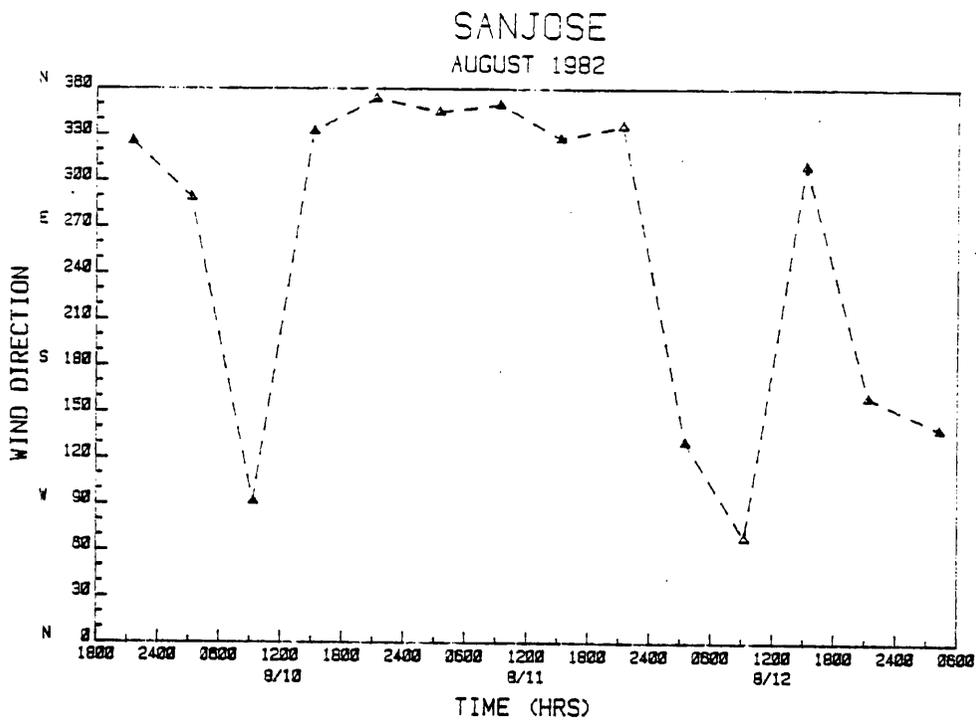


Figure 26. Wind direction vs. time at San Jose.

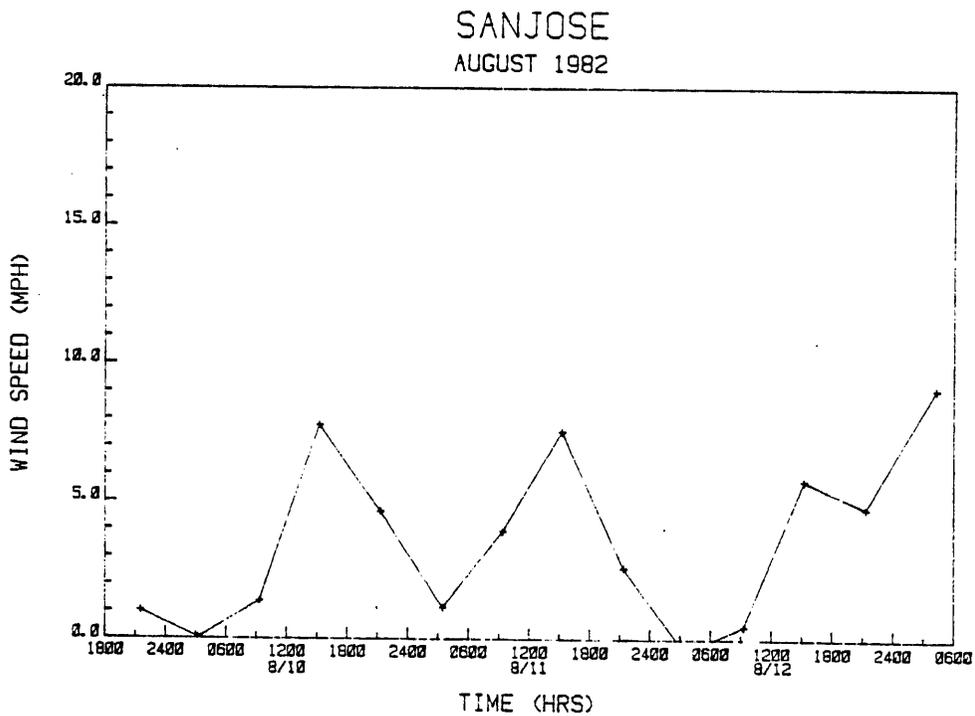


Figure 27. Wind speed vs. time at San Jose.

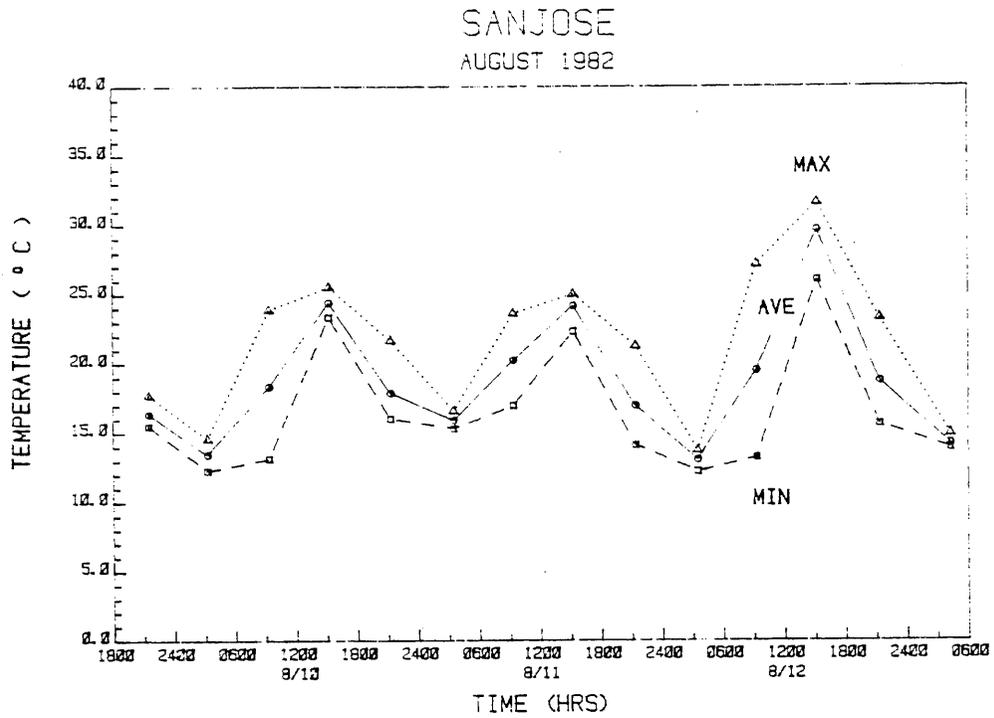


Figure 28. Temperature vs. time at San Jose.

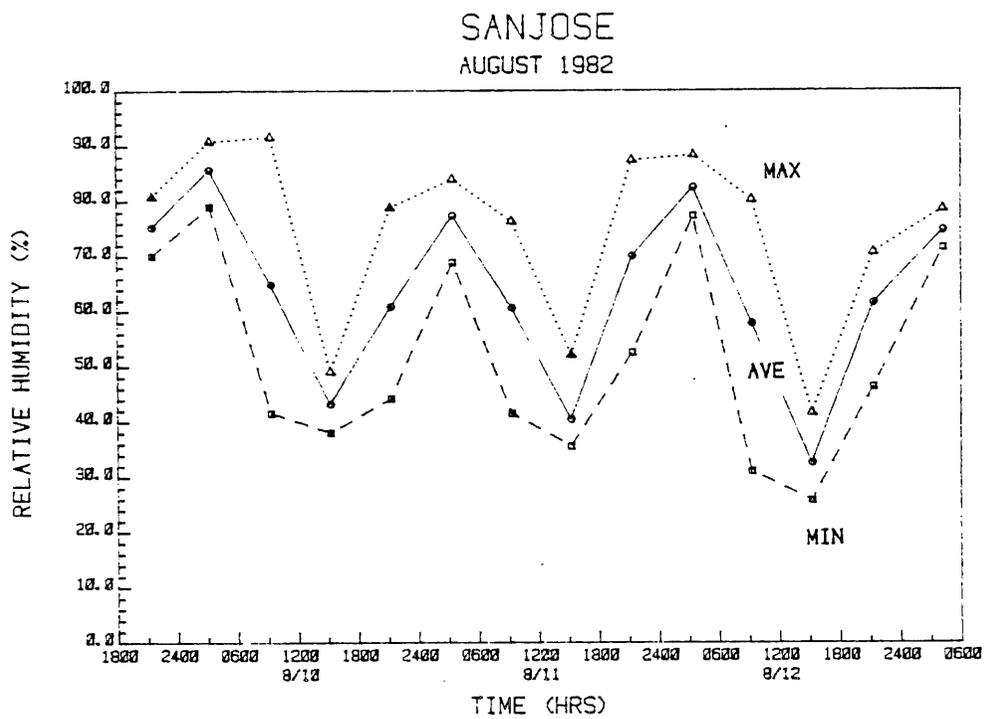


Figure 29. Relative humidity vs. time at San Jose.

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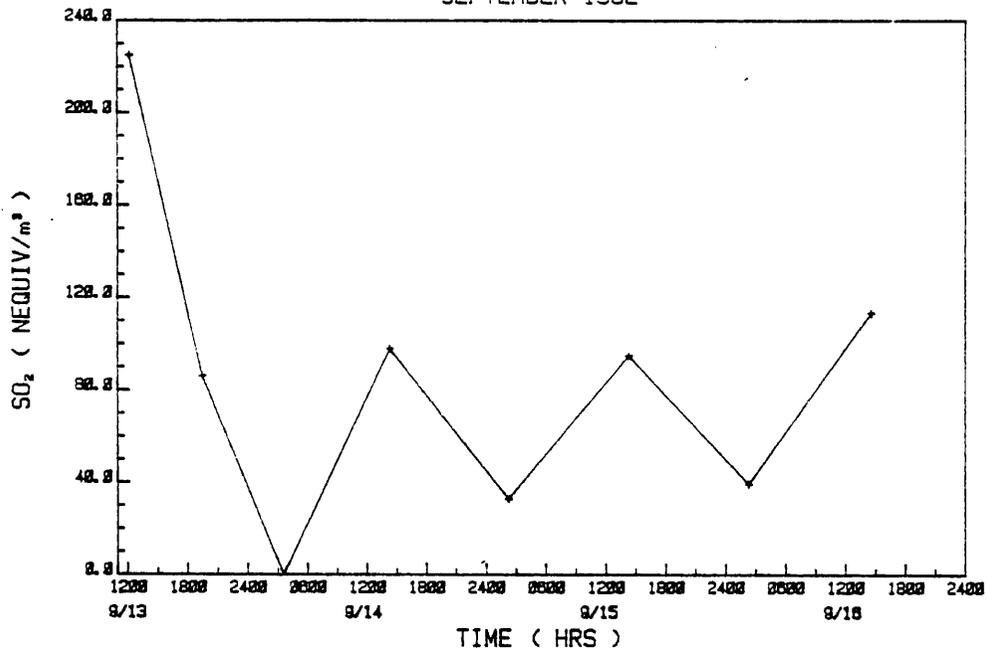


Figure 30. Sulfur dioxide concentration vs. time at Democrat Springs.

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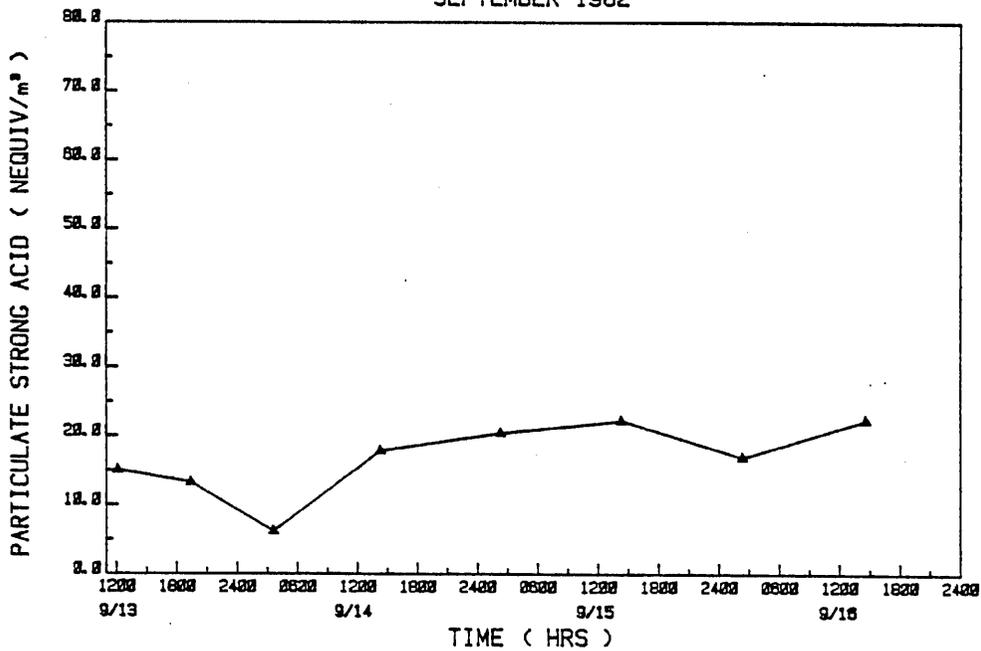


Figure 31. Fine particulate strong acid concentration vs. time at Democrat Springs.

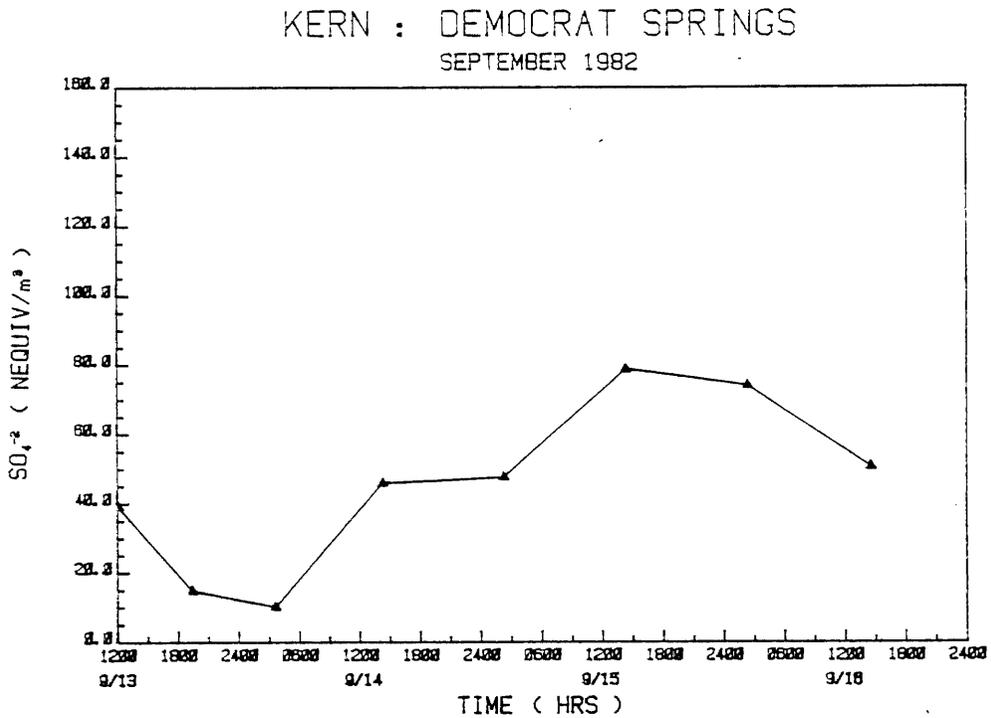


Figure 32. Fine particulate sulfate concentrations vs. time at Democrat Springs.

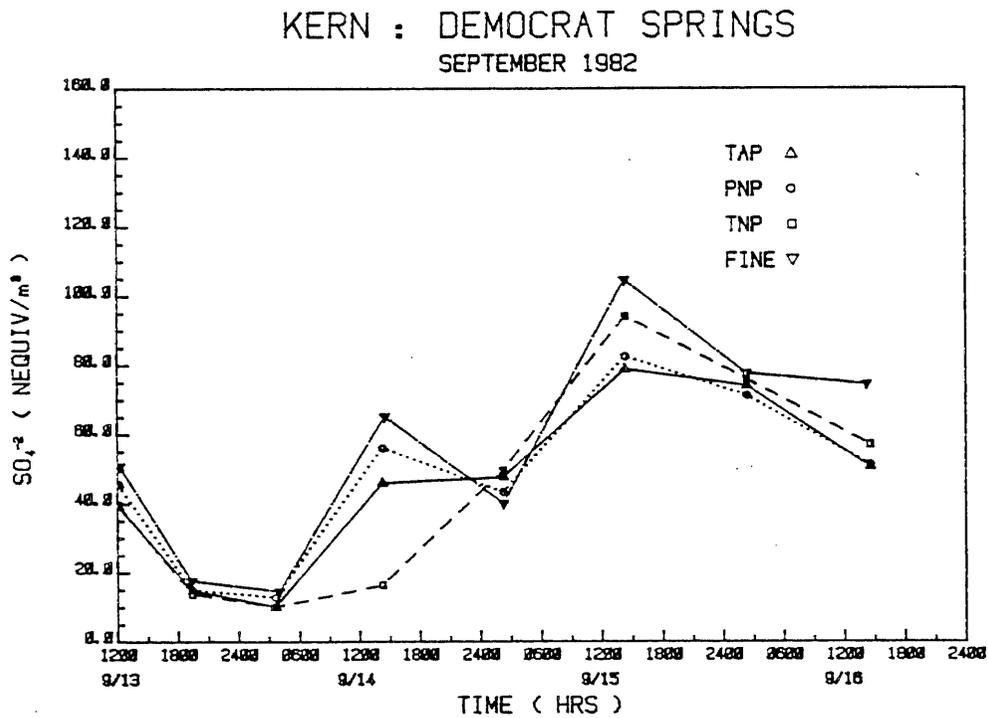


Figure 33. Comparison of sulfate concentrations from the Teflon filters of sampling trains No. 1 (TAP), No. 2 (PNP), No. 3 (TNP) and the fine fraction of a dichotomous sampler (FINE).

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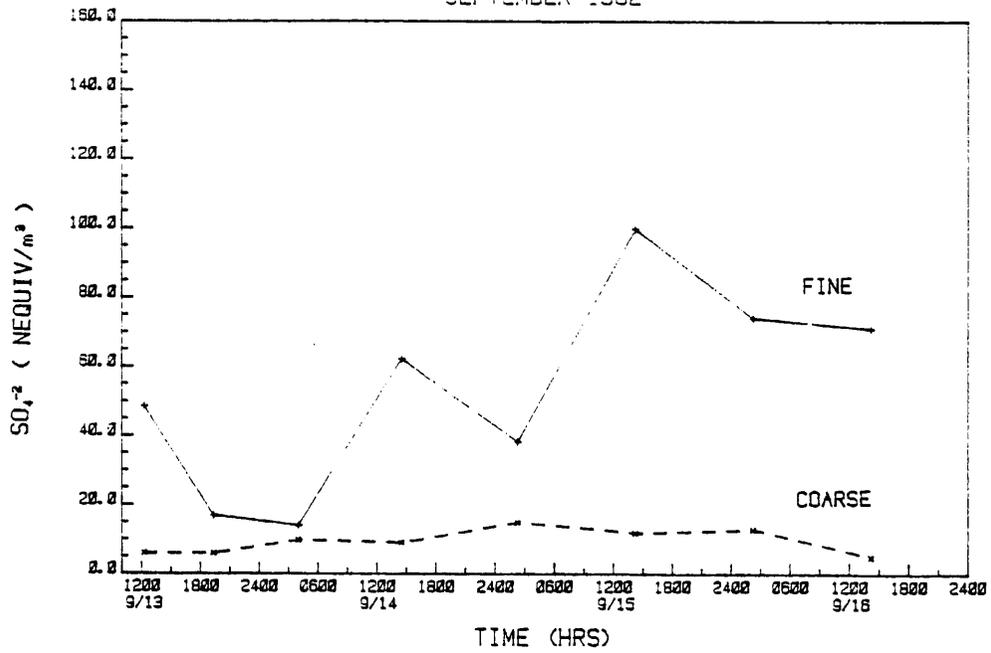


Figure 34. Fine and coarse sulfate concentrations from a dichotomous sampler.

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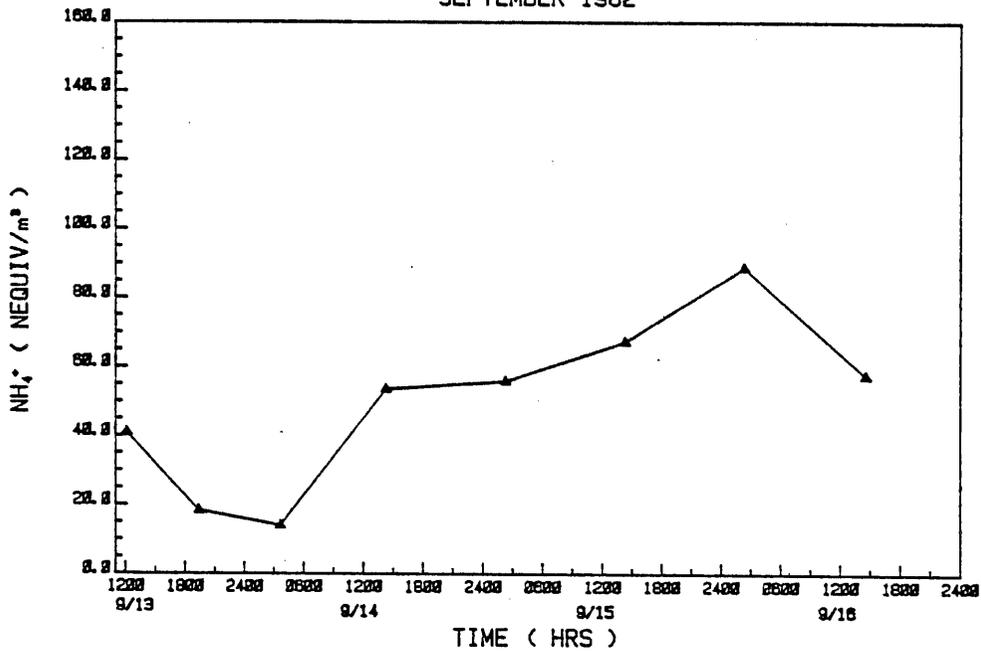


Figure 35. Fine particulate ammonium concentration vs. time at Democrat Springs.

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SEPTEMBER 1982

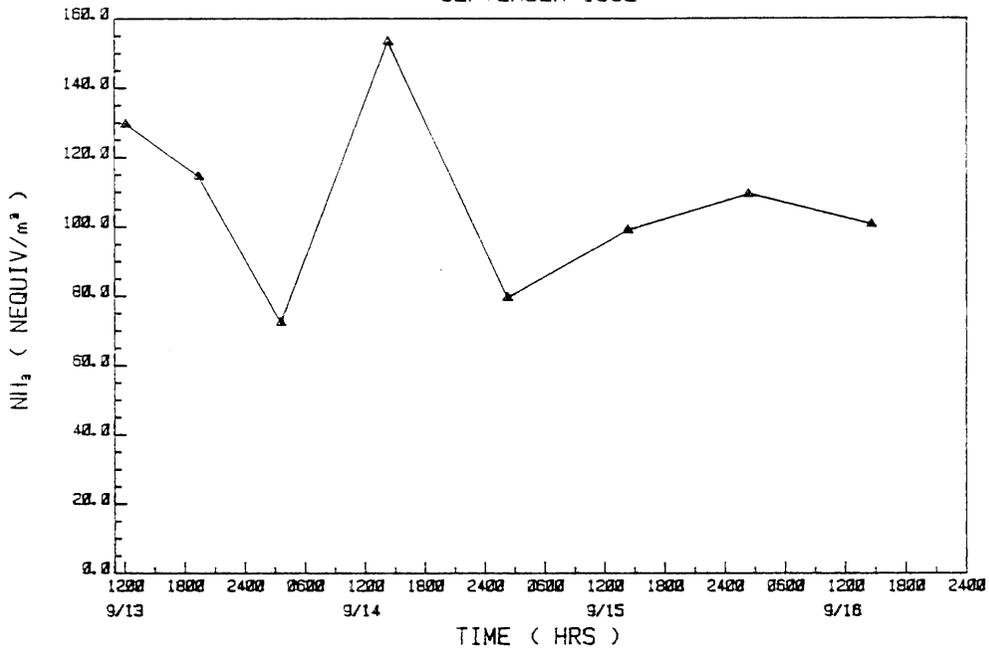


Figure 36. Ammonia concentration vs. time at Democrat Springs.

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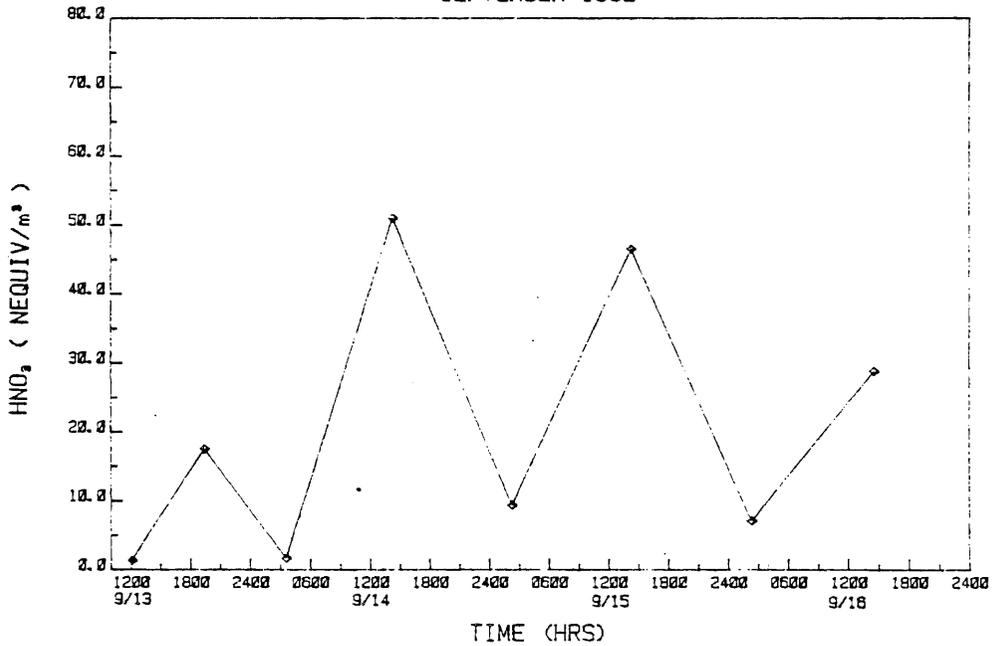


Figure 37. Nitric acid concentration vs. time at Democrat Springs.

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 SEPTEMBER 1982

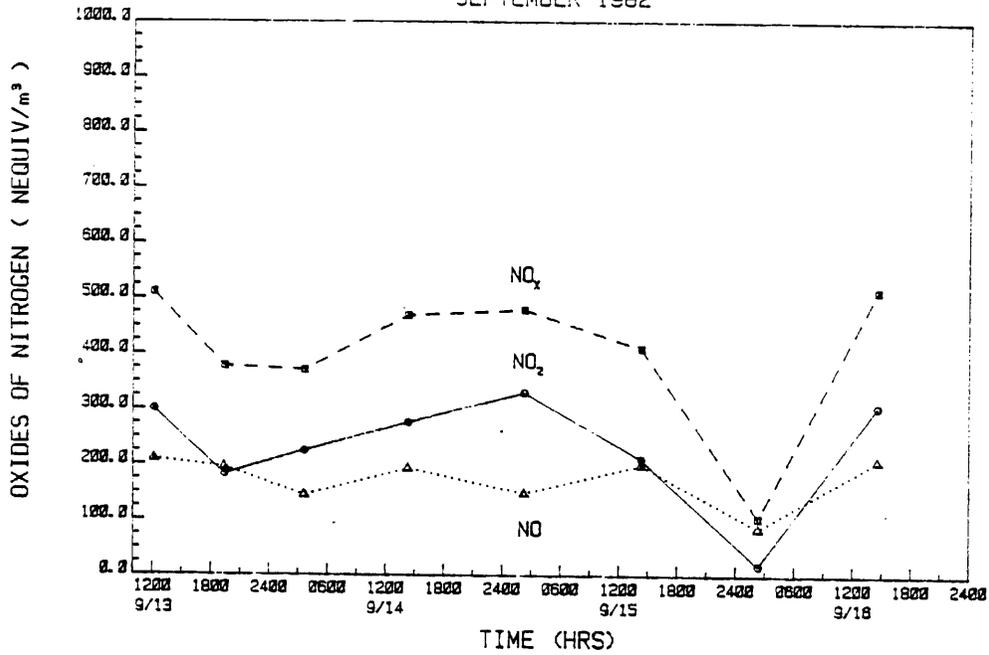


Figure 38. Concentrations of NO<sub>x</sub>, NO<sub>2</sub>, and NO vs. time at Democrat Springs.

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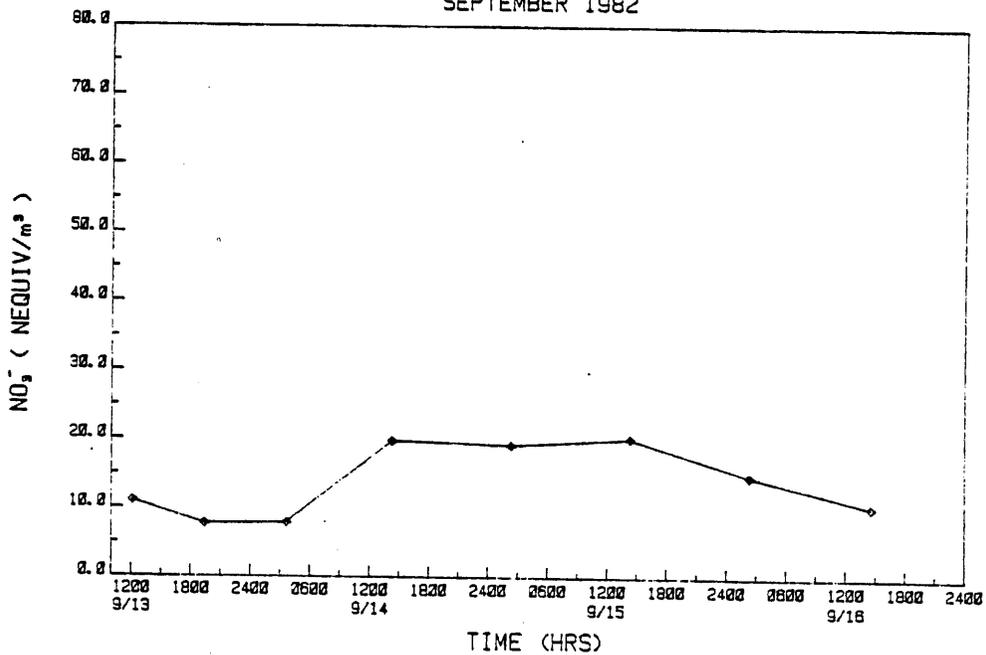


Figure 39. Fine particulate nitrate concentration vs. time at Democrat Springs.

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 SEPTEMBER 1982

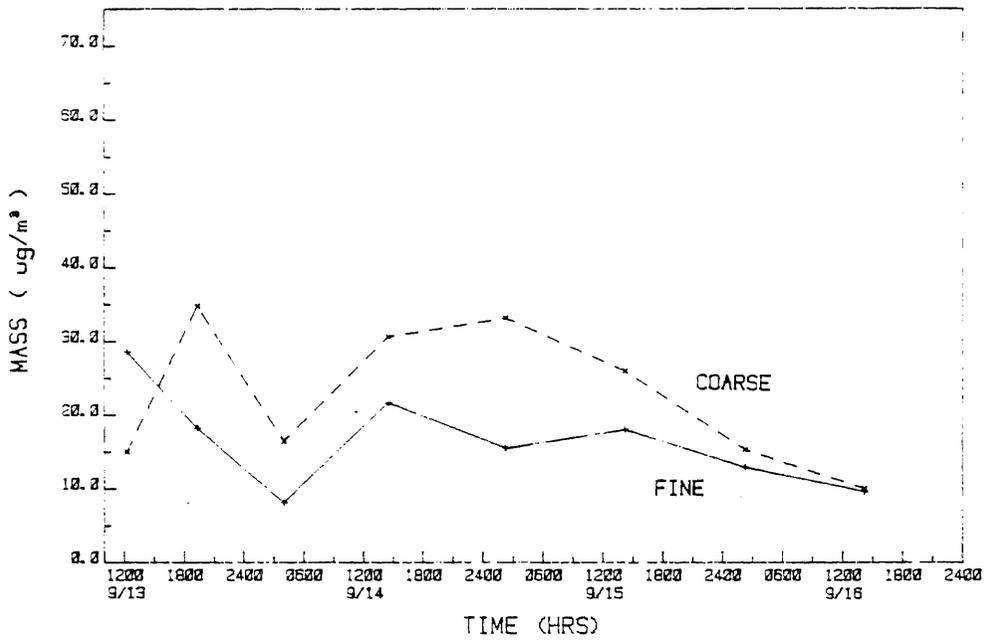


Figure 40. Fine and coarse particulate mass from a dichotomous sampler at Democrat Springs.

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 SEPTEMBER 1982

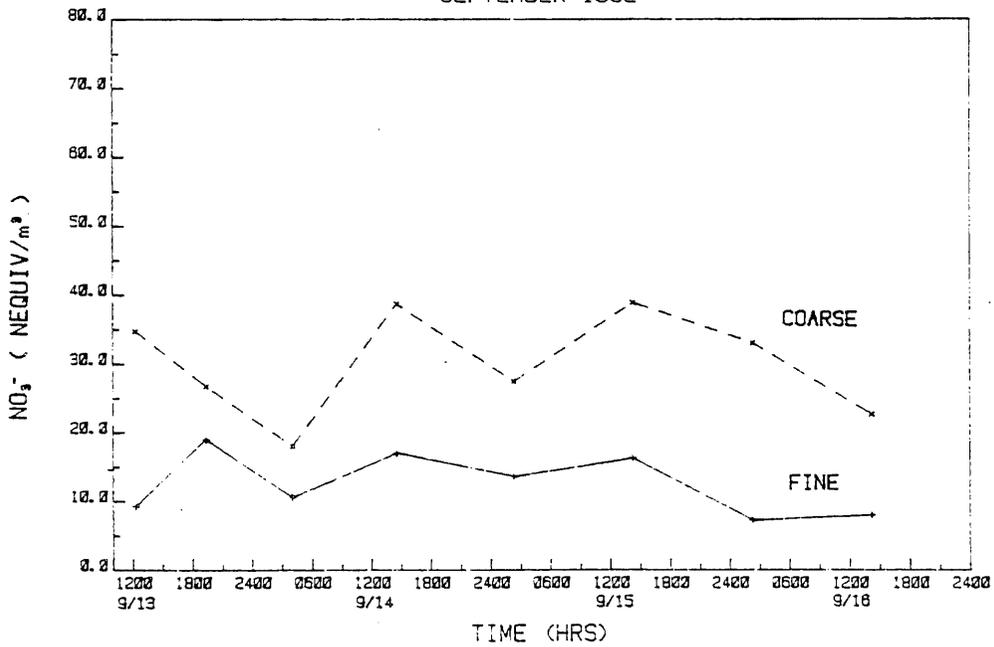


Figure 41. Fine and coarse nitrate from a dichotomous sampler at Democrat Springs.

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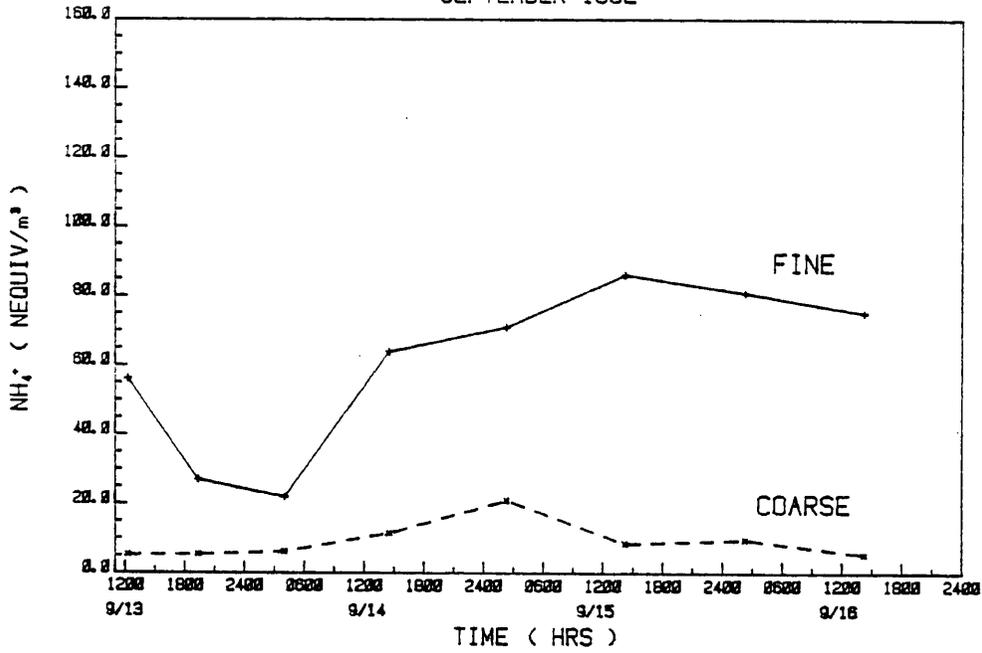


Figure 42. Fine and coarse ammonium from a dichotomous sampler at Democrat Springs.

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 SEPTEMBER 1982

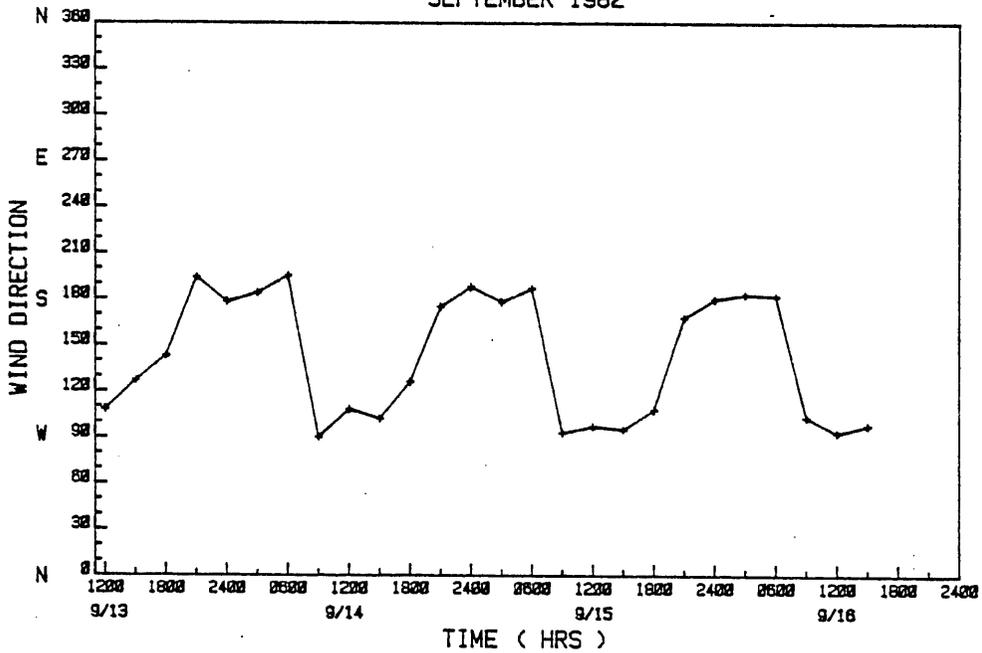


Figure 43. Wind direction vs. time at Democrat Springs.

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SEPTEMBER 1982

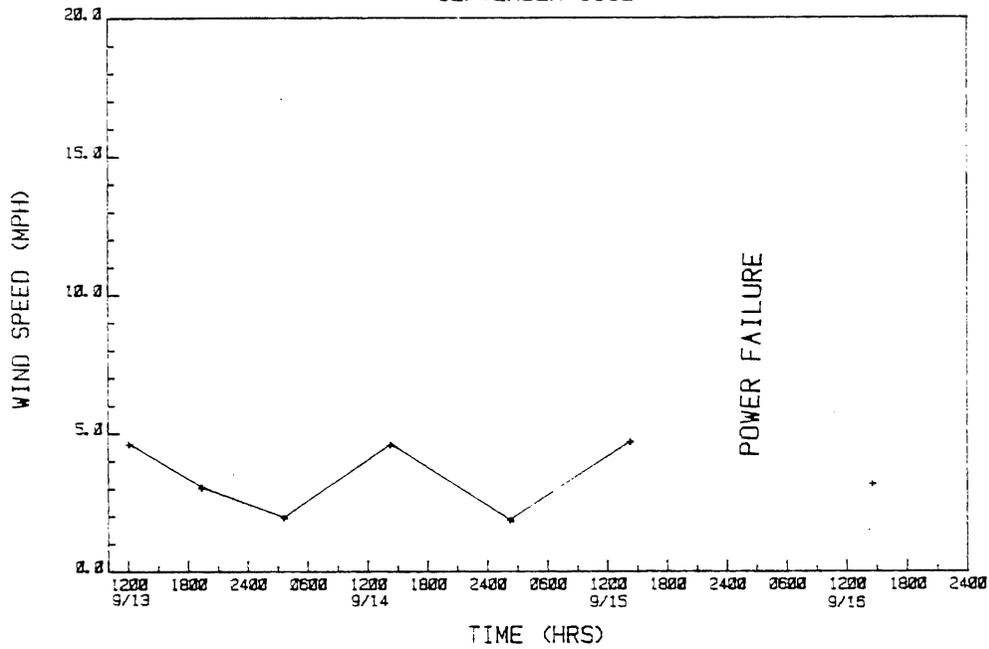


Figure 44. Wind speed vs. time at Democrat Springs.

KERN : DEMOCRAT SPRINGS  
SEPTEMBER 1982

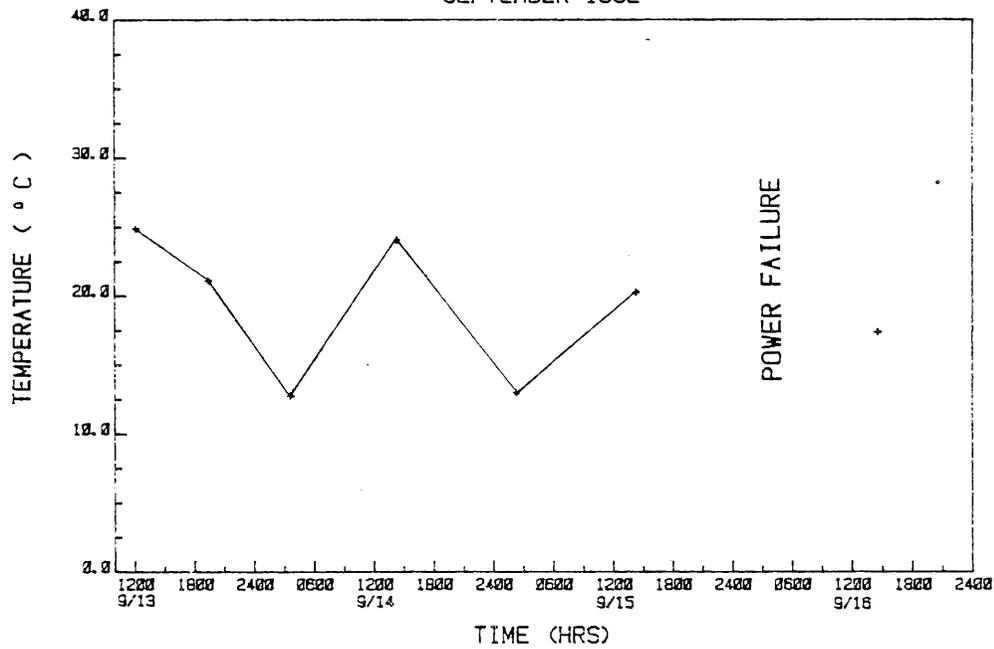


Figure 45. Temperature vs. time at Democrat Springs.

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 SEPTEMBER 1982

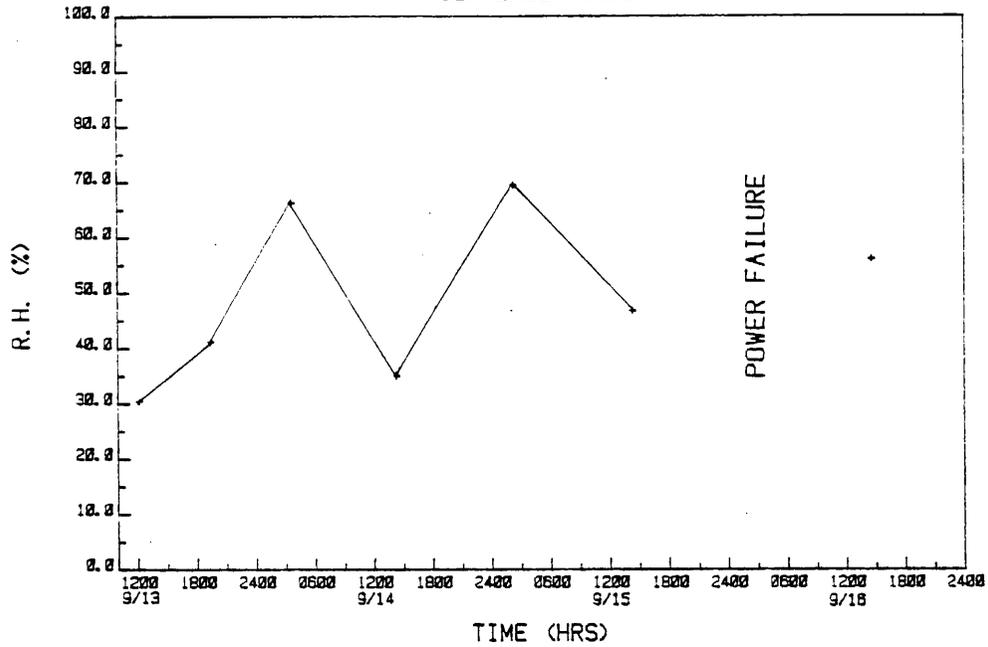


Figure 46. Relative humidity vs. time at Democrat Springs.

KERN - SHIRLEY MEADOW  
 SEPTEMBER 1982

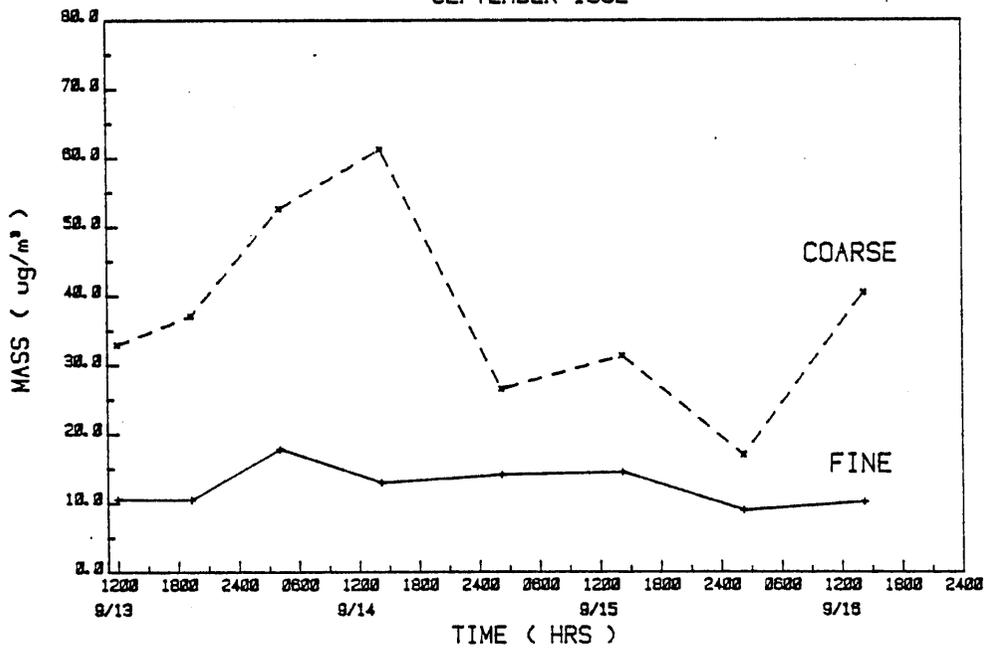


Figure 47. Fine and coarse particulate mass from a dichotomous sampler at Shirley Meadow.

KERN - SHIRLEY MEADOW  
 SEPTEMBER 1982

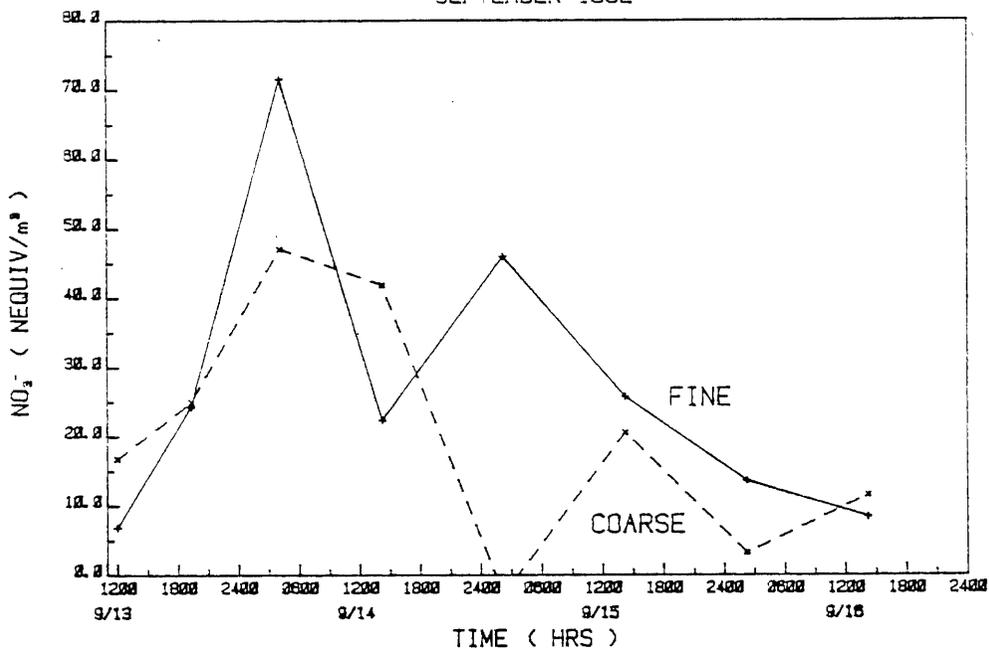


Figure 48. Fine and coarse nitrate at Shirley Meadow.

KERN - SHIRLEY MEADOW  
 SEPTEMBER 1982

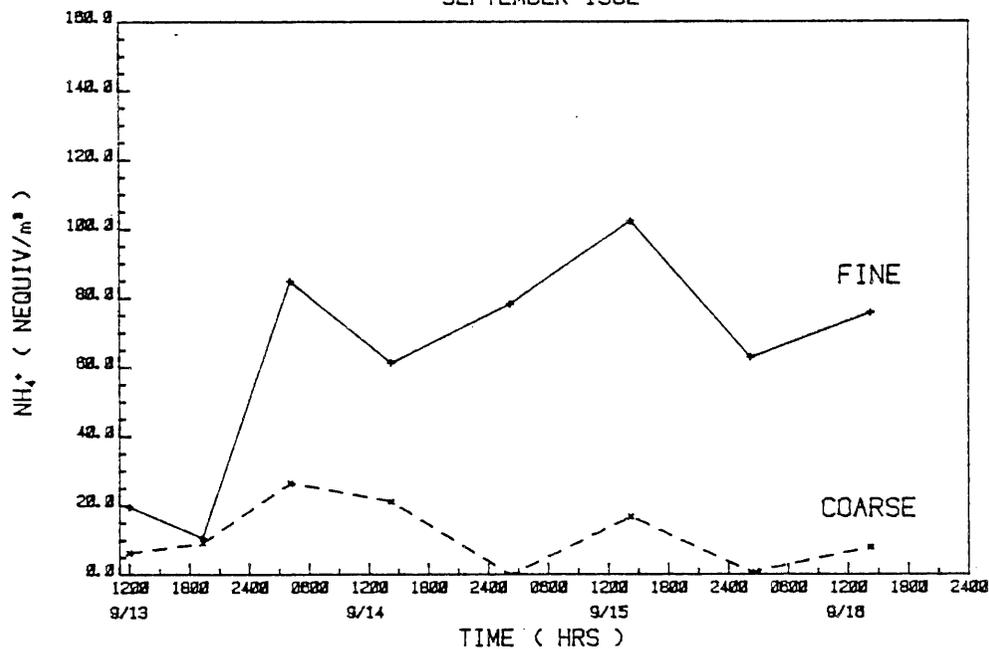


Figure 49. Fine and coarse ammonium at Shirley Meadow.

KERN - SHIRLEY MEADOW  
SEPTEMBER 1982

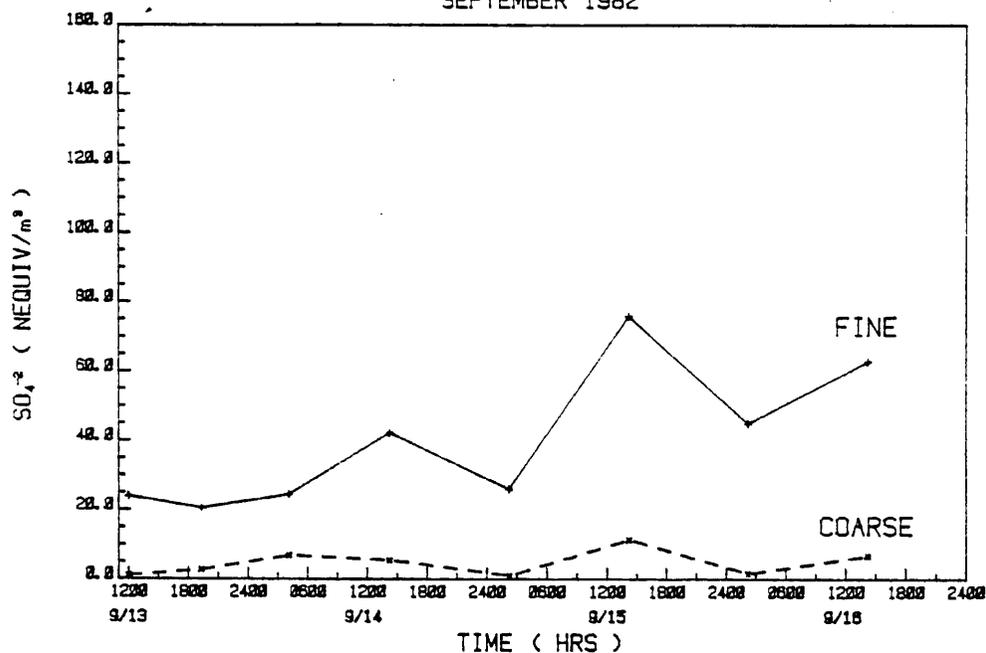


Figure 50. Fine and coarse sulfate at Shirley Meadow.

CORRELATION PLOT  
MARTINEZ - JULY 1982

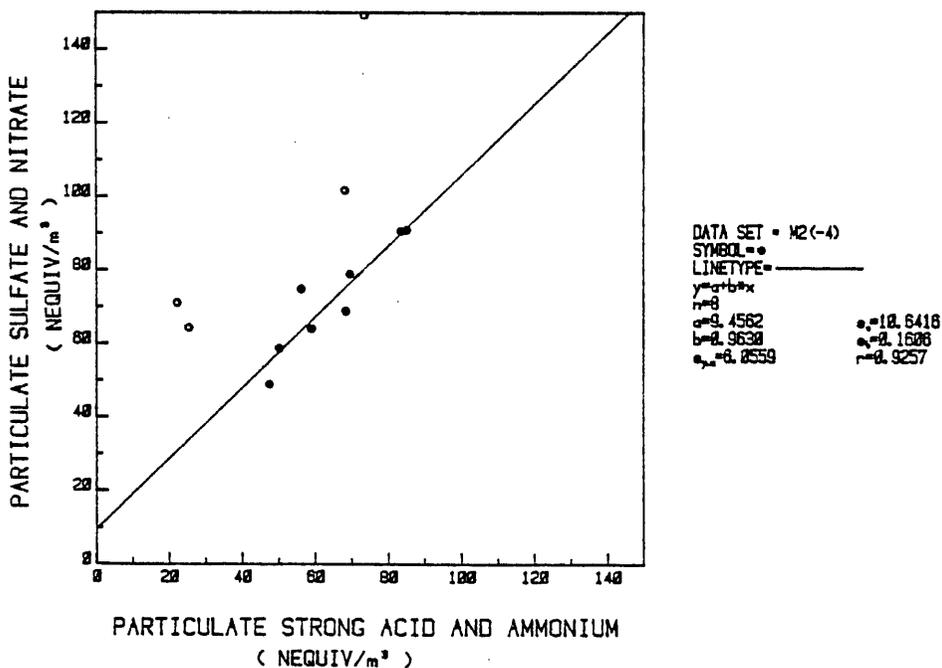


Figure 51. Anion vs. cation concentrations at Martinez. The regression line was fitted to the closed circles, omitting the outliers (open circles).

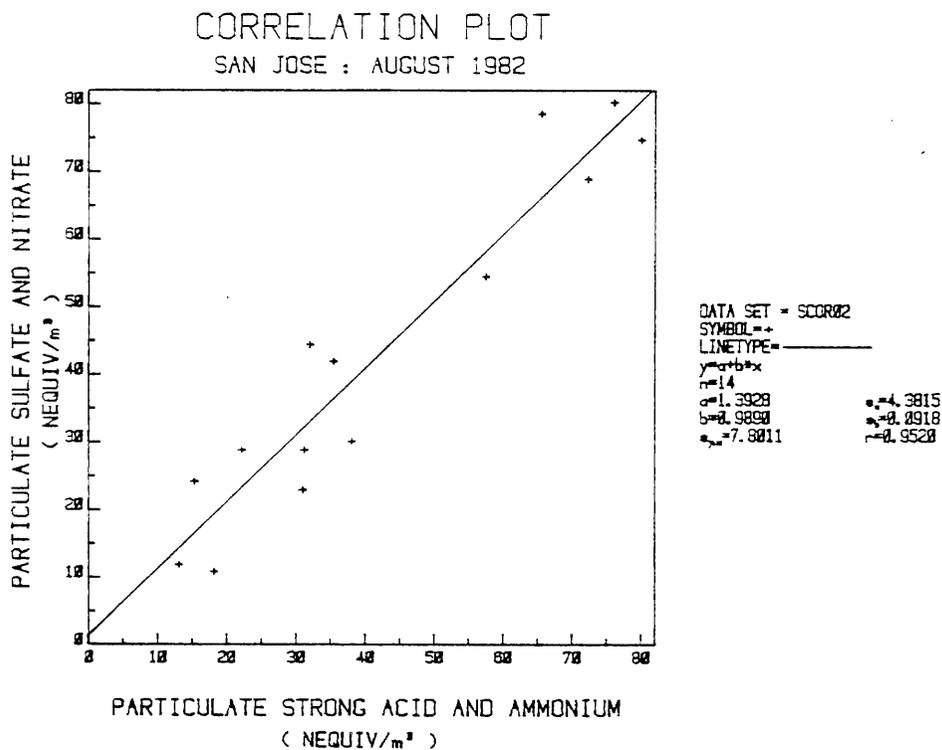


Figure 52. Anion vs. cation concentrations at San Jose.

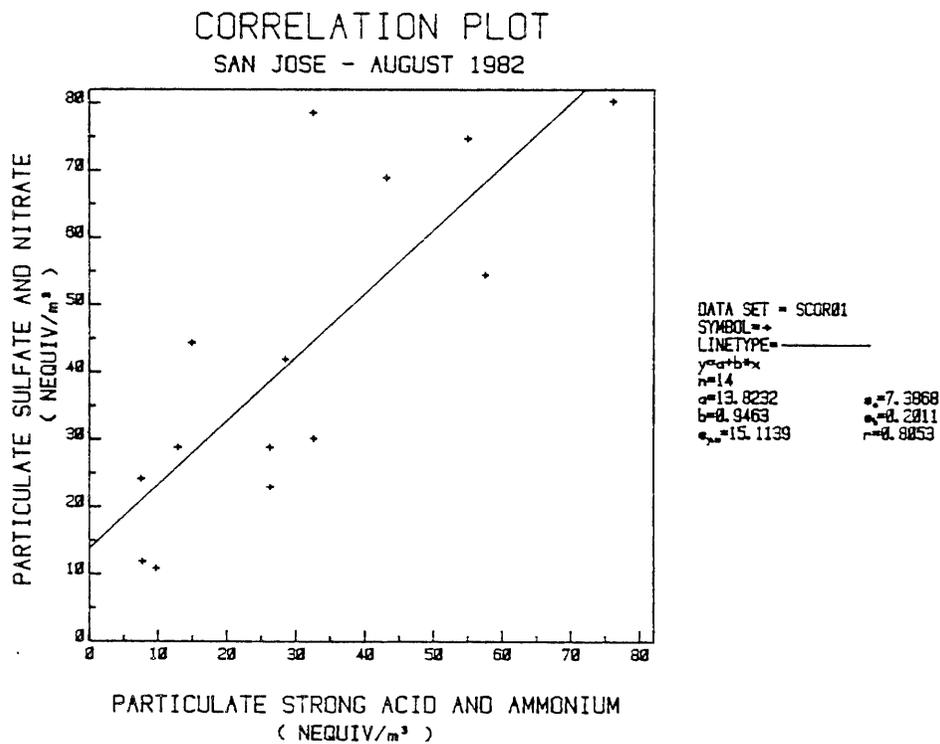


Figure 53. Anion vs. cation concentrations at San Jose without correction for volatilization of ammonium (compare to Fig. 52).

# CORRELATION PLOT

KERN - SEPTEMBER 1982

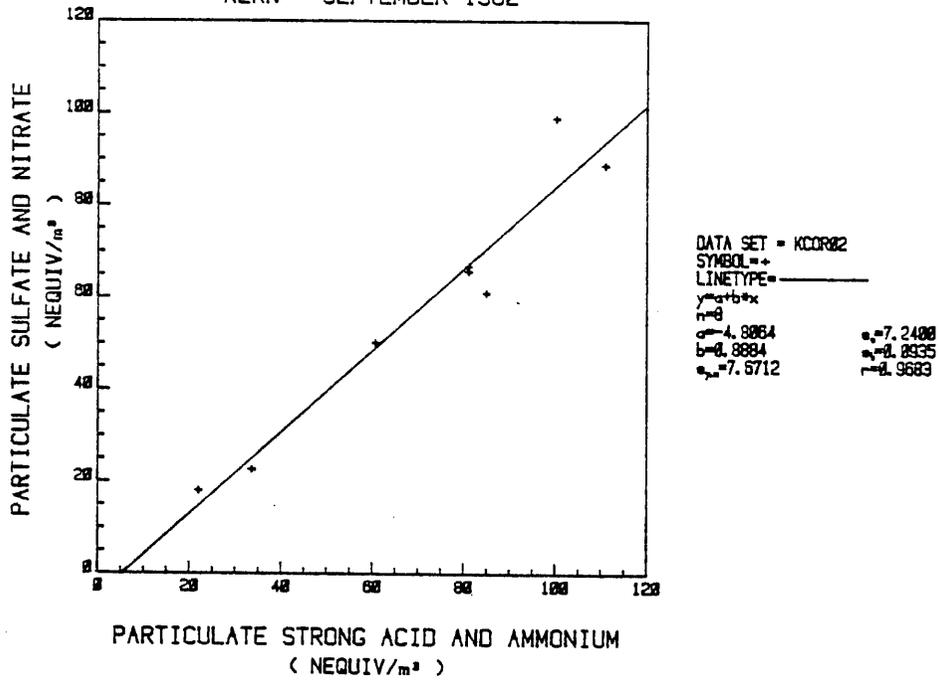


Figure 54. Anion vs. cation concentrations at Kern.

