ACQUISITION OF ACID VAPOR AND AEROSOL CONCENTRATION DATA FOR USE IN DRY DEPOSITION STUDIES IN THE SOUTH COAST AIR BASIN

Volume I

by

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ABSTRACT

An atmospheric monitoring network was operated throughout the South Coast Air Basin in the greater Los Angeles area during the year 1986. The primary objective of this study was to measure the spatial and temporal concentration distributions of atmospheric gas phase and particulate phase acids and bases in support of the California Air Resources Board's dry deposition research program. Gaseous pollutants measured include HNO_3, HCl, HF, HBr, formic acid, acetic acid and ammonia. The chemical composition of the airborne particulate matter complex was examined in three size ranges: fine particles (less than 2.2μm aerodynamic diameter, AD), PM_{10} (less than 10μm AD) and total particles (no size discrimination).

Upwind of the air basin at San Nicolas Island, gas phase acids concentrations are very low: averaging 0.3μg m^{-3} (0.1 ppb) for HNO_3, 0.8μg m^{-3} for HCl, 0.13μg m^{-3} for HF, and 2.6μg m^{-3} for formic acid. Annual average HNO_3 concentrations ranged from 3.1μg m^{-3} (1.2 ppb) near the Southern California coast to 6.9μg m^{-3} (2.7 ppb) at an inland site in the San Gabriel Moountains. HCl concentrations within the South Coast Air Basin averaged from 0.8μg m^{-3} to 1.8μg m^{-3} during the year 1986. Long-term average HF concentrations within the air basin are very low, in the range from 0.14 to 0.22μg m^{-3} between monitoring sites. Long-term average formic acid concentrations are lowest near the coastline (5.0μg m^{-3} at Hawthorne), with the highest average concentrations (10.7μg m^{-3}) observed inland at Upland.

Ammonia concentrations at low elevation within the South Coast Air Basin average from 2.1μg m^{-3} to 4.4μg m^{-3} at all sites except Rubidoux. Rubidoux is located directly downwind of a large ammonia source created by dairy farming and other agricultural activities in the Chino area. Ammonia concentrations at Rubidoux average 30μg m^{-3} during 1986, a factor of approximately 10 higher than elsewhere in the air basin.

Annual average PM_{10} mass concentrations within the South Coast Air Basin ranged from 47.0μg m^{-3} along the coast to 87.4μg m^{-3} at Rubidoux, the farthest inland monitoring site. Five major aerosol components (carbonaceous material, NO_3^-, $SO_4^=$, NH_4^+ and soil-related material) accounted for greater than 80% of the annual average PM_{10} mass concentration at all on-land monitoring stations. A peak 24-h average PM_{10} mass concentration of 299μg m^{-3} was observed at Rubidoux during 1986. That value is a factor of 2 higher than the federal 24-h average PM_{10} concentration standard, and a factor of 6 higher than the State of California PM_{10} standard. More than 40% of the PM_{10} aerosol mass measured at Rubidoux during that peak day event consisted of aerosol nitrates plus ammonium ion. Reaction of gaseous nitric acid to form aerosol nitrates was a major contributor to the high PM_{10} concentrations observed in the Rubidoux area near Riverside, California.

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CHAPTER 1. INTRODUCTION

Given the infrequent occurrence of rainfall in Southern California, deposition of acidic air pollutants at the earth's surface in the Los Angeles area is thought to be dominated by dry deposition processes. Liljestrand (1) and McRae and Russell (2) have estimated that the total dry flux of the major acidic species in the Los Angeles area is about an order of magnitude greater than the wet flux of these species to the earth's surface. Liljestrand (1) estimated the average annual dry acid flux of SO_2, NO_2, NO, NH_3, aerosol NO_3^- and SO_4^{-2} in downtown Los Angeles to be 3840, 5630, 1370, -1060, 8.8 (NO_3^-+SO_4^{-2}) equivalents/ha-yr, respectively.

The dry flux of acid gases and aerosols to the earth's surface can be estimated if the atmospheric concentration of the pollutants of interest is known in conjunction with meteorological conditions and ground surface characteristics. Unfortunately, many key atmospheric acid gases (e.g., HNO_3, HCl) have not been measured by routine air monitoring networks in the past. As a result, the long-term pattern of atmospheric concentration data required for even rough estimates of long-term average acid flux to the earth's surface is unavailable.

Short-term special studies in the Los Angeles basin have measured HNO_3 levels during a few days in past summer months (3-9). In the most recent short-term study HNO_3, NH_3 and aerosol nitrate concentrations were measured during two weeks in September, 1985 (8, and Appendix C, Volume I of this report). Nitric acid levels (24-h averages) within the South Coast Air Basin (SOCAB) during that study ranged from less than 1μg m^{-3} (0.4 ppb HNO_3) to about 27μg m^{-3} (10.5 ppb), while total particulate nitrate concentrations ranged from about 2.6 to 33.1μg m^{-3}. On the most polluted day, 14 September, 1985, HNO_3 levels (24-hr average) varied from 11.1μg m^{-3} (4.3 ppb) near the coast at Lennox to 26.7μg m^{-3} (10.4 ppb) at Claremont to 6.4μg m^{-3} (2.5 ppb) at Rubidoux, near Riverside. Rubidoux is an inland site where high concentrations of HNO_3 would normally be expected. However, this area

experiences extremely high NH_3 concentrations and as a result, NH_4NO_3 aerosol is formed and HNO_3 is removed from the gas phase. The maximum 24-hr average NH_3 concentration observed at Rubidoux during the September, 1985 study was 38.3μg m^{-3} (55.1 ppb). Maximum mid-afternoon HNO_3 levels (4-hr average) observed at Claremont during September, 1985 were approximately 41-50μg m^{-3} (15.9-19.5 ppb) depending on the sampling technique employed (8). Aerosol nitrate concentrations (24-hr average) on 14 September, 1985, ranged from 7.0μg m^{-3} at Lennox to 12.3μg m^{-3} at Claremont to 33.1μg m^{-3} at Rubidoux. Therefore, as can be seen, the distribution of inorganic nitrate between the gas and particle phases can vary considerably throughout the SOCAB.

From the above results, it is clear that HNO_3, NH_3 and particulate NO_3^- are present at concentrations high enough to affect the net dry flux of acids and bases to the suface of the South Coast Air Basin. The actual dry flux of these materials will depend critically on the distribution of inorganic nitrate between the gas and aerosol phases (i.e., HNO_3 and particulate nitrate, respectively) and on the details of the aerosol size distribution. The deposition velocities for gases and particles generally differ considerably. For example, deposition velocities reported by Pierson et al. (9) at Claremont, California were ~1.3cm sec^{-1} for gas phase HNO_3 and ~0.2cm sec^{-1} for total aerosol nitrate. The reaction of HNO_3 with alkaline species in the atmosphere can result in a complex size distribution for the aerosol nitrates that consists of both fine particle and coarse particle nitrates. This in turn affects deposition rates because coarse particles (d_p > 2.0μm aerodynamic diameter) are generally removed from the atmosphere at a more rapid rate than fine particles in the size range between 0.1-2.0μm diameter. Nitric acid reacts with NH_3 to form NH_4NO_3, which is primarily a fine particle species (10-14). The equilibrium relationship between HNO_3, NH_3 and NH_4NO_3 is complex and dependent on at least temperature, relative humidity, and other species present (7,15-17). Ammonia is the only major

alkaline pollutant present in the gas phase, and it can play a decisive role in the neutralization of acidic species in the atmosphere. Coarse particle nitrates are formed when HNO_3 reacts with coarse particle sea salt and soil dust aerosols (10-13,18,19). The reaction of HNO_3 with NaCl and other similar species (e.g., PbBrCl salts emitted from automobiles which use leaded fuel) might result in the release of HCl, HBr, and HF to the atmosphere. Even less is known about atmospheric levels of HCl, HF and HBr.

In addition to the inorganic acids just discussed, there is evidence that organic acids may be present in the atmosphere in quantities sufficient to affect the acidity of dew (9). Again, very little information is available at present on the relative abundance, spatial distribution, and seasonal concentration patterns for organic acids in the Los Angeles atmosphere.

Finally, the particle formation potential of acid gases like HNO_3 is important for reasons in addition to effects on acid deposition phenomena. Aerosol nitrates are a major contributor to Los Angeles area airborne particle concentrations and may contribute to visibility reduction. Information on aerosol nitrate concentrations in particle sizes less than 10μm aerodynamic diameter is needed to assist the development of cost-effective control strategies for compliance with newly adopted PM_{10} regulatory standards (20,21).

The primary objective of this study was to measure the spatial and temporal concentration distributions of the major gas and particulate phase acids and bases in the South Coast Air Basin in support of the California Air Resources Board's (ARB) dry deposition research program. Gas phase species were collected by the denuder difference method and by the tandem filter method using treated or reactive backup filters (3,5,6,8,22-26). Particulate matter was collected on appropriate filter media in three size ranges: fine particles (less than 2.2μm AD), PM_{10} (less than 10μm AD) and total particles (no size discrimination).

Samples were collected over a one-year period at nine locations (eight in the South Coast Air Basin and one at an offshore background location on San Nicolas Island). These samples were analyzed to determine the atmospheric concentrations of fine particle and PM_{10} mass and the concentrations of the major gaseous and particulate acidic and basic species (i.e., gaseous: HNO_3, HCl, HBr, HF, HCOOH, CH_3COOH and NH_3; particulate: NO_3^-, SO_4^{-2}, Br^-, Cl^-, F^-, $HCOO^-$, CH_3COO^-, and NH_4^+). Sodium ion and Mg^{2+} concentrations were measured to obtain a nearly complete ion balance on the water soluble portion of the aerosol. Analysis of 34 major and trace elements (by x-ray fluorescence (XRF)) plus organic and elemental carbon was obtained to achieve a nearly complete material balance on the chemical composition of the collected fine and PM_{10} aerosols. Determination of the ionic species concentrations in the total airborne particulate complex also was pursued.

The sole supported objective of this project was to acquire acid vapor and aerosol concentration data in time and space for subsequent use in dry deposition studies in the South Coast Air Basin. Statistical analysis, data interpretation, and modeling of acid dry deposition fluxes to the surface of the air basin is reserved for future research efforts. The intended scope of this research project was exceeded in order to furnish a preliminary analysis of a small portion of the data in two important cases: the HNO_3/aerosol nitrate system (see Appendix A, Volume I), and PM_{10} aerosols (see Appendix B, Volume I). The concentration patterns of HNO_3, HCl, HF, formic acid, acetic acid and NH_3 are summarized in pictorial and tabular form but without a formal discussion in Chapter 3 of this report.

Further analysis of the pollutant concentration data collected here should allow the assessment of the partition of acidic and basic species between the aerosol and gas phases, and the estimation of pollutant dry fluxes to soils, vegetation and materials present in Southern California. The PM_{10} data collected here presently are being employed by the South Coast Air Quality Management District

to design the official PM_{10} control program for the greater Los Angeles area. The fine particle data reported in Volume II of this work will permit similar control strategy planning efforts to proceed rapidly if proposed air quality standards for fine particles (i.e., PM_2) are adopted in future years (see reference 20, 40 CFR Part 50).

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CHAPTER 2: EXPERIMENTAL PROCEDURES

Air Monitoring Network

During the calendar year 1986, a monitoring network designed to measure the concentration of gas phase acids, ammonia and atmospheric particulate matter was operated at nine sampling sites located throughout the Los Angeles area. The station locations are illustrated in Figure 2.1. All sites except Tanbark Flats and San Nicolas Island were co-located with present South Coast Air Quality Management District (SCAQMD) continuous air monitoring stations. A description of the SCAQMD sites is given by the U.S. Environmental Protection Agency (1,2).

The Tanbark Flats site was located in the mountains north of San Dimas, in the Angeles National Forest at an elevation of approximately 870m. This site was chosen to determine the concentration of acidic pollutants present in the national forests which surround Los Angeles, and because air quality modeling calculations suggest that substantial amounts of nitric acid can be produced at higher elevations (3,4). The ninth site was located at the meteorological station on San Nicolas Island (SNI) and was approximately 140km southwest of the Los Angeles coastline. This remote, off-shore location was chosen to determine background pollutant levels entering Los Angeles from the upwind marine environment. At four of the sites (Burbank, Downtown Los Angeles, Long Beach and Upland) the sampling systems were placed on the roofs of one or two story buildings. At the other monitoring stations, the systems were placed with inlets located 2-3m above ground level. All sites except Tanbark Flats were below an elevation of 390m above sea level.

Sampler Design and Sampling Protocol

Gas phase acids and bases and atmospheric particulate matter samples in three size ranges (i.e., fine, PM_{10}, and total particles) were obtained using the sampling system that is illustrated schematically in Figure 2.2. Included in this figure are the

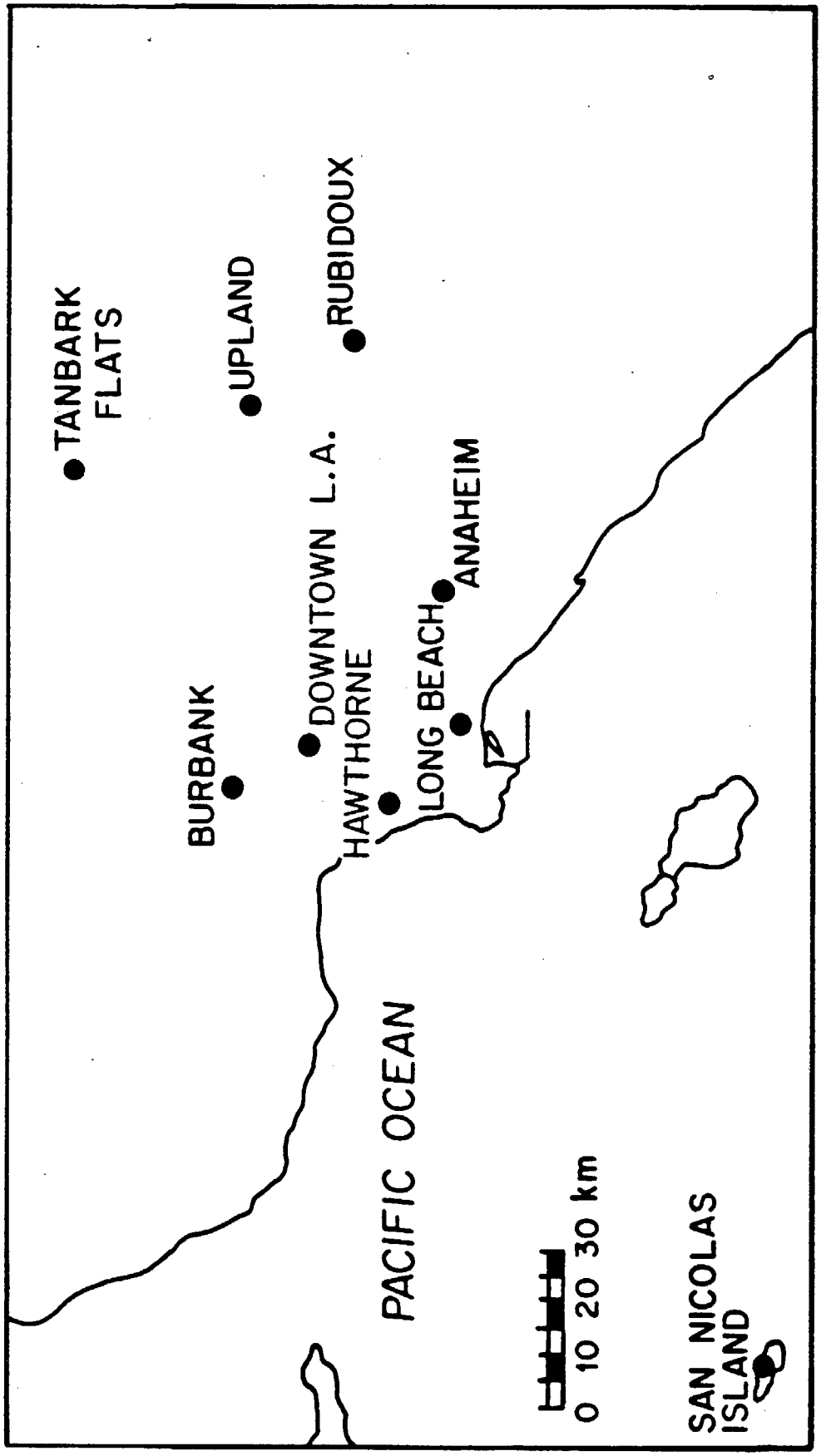
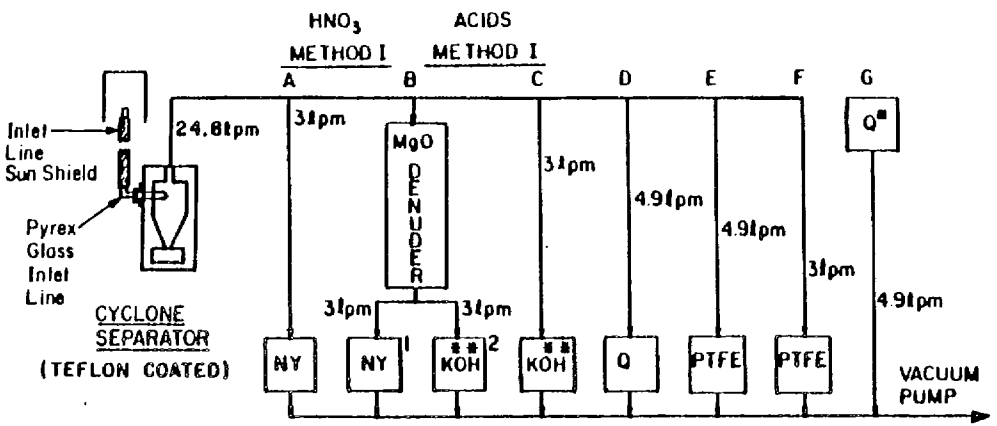
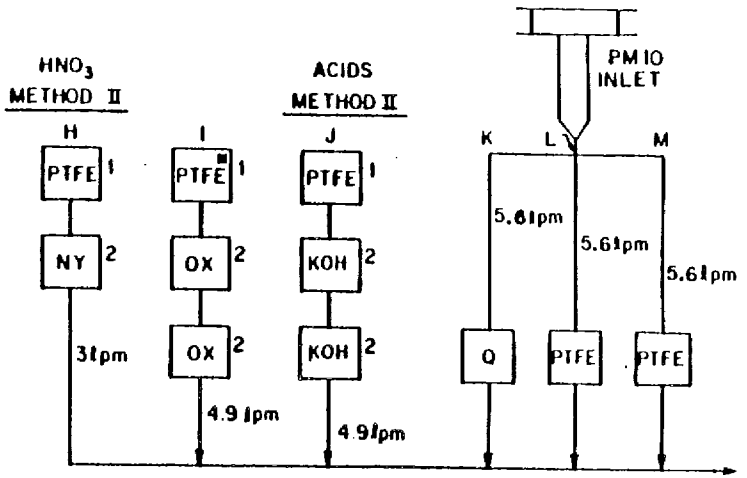


Figure 2.1. Los Angeles area monitoring network. All sites are at an elevation within 400m of sea level except Tanbark Flats which is at an elevation of 870m in the San Gabriel Mountains.

EXPERIMENTAL DESIGN





A
- HNO_3
- AEROSOL NO_3^-
- HCl
- AEROSOL Cl^-

B
1
- AEROSOL NO_3^-
- AEROSOL Cl^-

2**
- NO_3^-
- Cl^-
- Br^-
- F^-
- $HCOO^-$
- CH_3COO^-

C**
- NO_3^-
- Cl^-
- Br^-
- F^-
- $HCOO^-$
- CH_3COO^-
- NITROGEN OXIDES
- HCl
- HBr
- HF
- HCOOH
- CH_3COOH

D
- ELEMENTAL CARBON
- ORGANIC CARBON

E
- MASS
- TRACE ELEMENTS BY XRF

F
- $SO_4^=$
- NO_3^-
- Br^-
- Cl^-
- F^-
- NH_4^+
- Na^+
- Mg^{++}

G
- ELEMENTAL CARBON
- ORGANIC CARBON

H
1
- STORAGE

2
- HNO_3

I
1
- MASS
- TRACE ELEMENTS BY XRF

2
- NH_3

J
1
- $SO_4^=$
- NO_3^-
- Cl^-
- Br^-
- F^-
- NH_4^+
- Na^+
- Mg^{++}

2
- NITROGEN OXIDES
- HCl
- HBr
- HF
- HCOOH
- CH_3COOH

K
- ELEMENTAL CARBON
- ORGANIC CARBON

L
- MASS
- TRACE ELEMENTS BY XRF

M
- $SO_4^=$
- NO_3^-
- Cl^-
- Br^-
- F^-
- NH_4^+
- Na^+
- Mg^{++}

NY Nylon Filter

Q Quartz Fiber Filter (Preboked)

PTFE Polytetrafluoroethylene Filter

OX Oxalic Acid Impregnated Glass Fiber Filter

KOH Potassium Hydroxide Impregnated Quartz Fiber Filter (Preboked)

■ Funding was not supplied for chemical analysis of these filters.

** Reserved for alternative acids measurements if necessary.

Figure 2.2

nominal flow rates and a listing of the species analyzed on each filter. Gas phase species were collected by two methods: 1) the denuder difference method (DD) (5-11) and 2) the tandem filter method (TF) (6-8,10-13). The sampling protocol was designed to permit duplicate measurements, by different methods, of several of the gas phase pollutants of interest and to obtain a nearly complete material balance on the chemical composition of fine (d_p<2.2μm AD), PM_{10} (d_p<10μm AD), and total (no size discrimination) aerosols.

In the sampling system located on the left side of Figure 2.2, ambient air passed under a polypropylene rain cap and was pulled at a nominal flow rate of 24.8 lpm through an acid (HCl) washed, Pyrex glass inlet line (1/2" ID x 40" long) that was protected from the sun. The air then passed through a Teflon coated AIHL-design cyclone separator which, when operated at a flow rate of 24.8 lpm, removes coarse particles with diameters larger than 2.2μm AD (14). The airstream containing only fine particles and gases then entered a Teflon-coated sampling manifold where it was split into six portions and ducted (via the shortest possible Teflon tubing) to seven separate low-volume filter holder assemblies. Four of these filter assemblies were associated with the denuder difference method for acid gas measurement (sampling lines, A, B1, B2, and C; Figure 2.2), while the other three sampling lines (D, E and F; Figure 2.2) collected fine particles for subsequent chemical analysis. The flow rates through each filter were controlled by a critical orifice. The Teflon coating on the inside of the cyclone and manifold was used to prevent the loss of HNO_3 and other acidic gases to the aluminum surfaces of the sampling system.

The denuder difference method employing nylon filters was used to measure atmospheric HNO_3 concentrations. One nylon filter (sampling line A; Figure 2.2) collected fine particle nitrate plus HNO_3, while the other nylon filter, located behind a MgO-coated diffusion denuder (designed to quantitatively remove HNO_3) collected

only fine particle nitrate (sampling line B1; Figure 2.2). Nitric acid concentration data were obtained from the difference between nitrate ion measured on these two nylon filters. As a consequence of this method, fine particle nitrate concentration measurements also were obtained from nylon filter B1 which did not suffer from major positive or negative nitrate artifact problems (12).

In the tandem filter method, gas phase acids and bases were collected on reactive or treated backup filters after particles were removed by the use of open face, inert polytetrafluoroethylene (PTFE) prefilters (H1, I1 and J1; Figure 2.2). Nitric acid and HCl were collected on a nylon backup filter (H2; Figure 2.2). HCl, HF, HBr, CH_3COOH and HCOOH were collected on two KOH impregnated filters in series (14-17) (J2; Figure 2.2), and NH_3 was collected on two oxalic acid impregnated filters in series (11-13,18-20) (I2; Figure 2.2). For the collection of nitric acid, the tandem filter method has been shown to suffer from a positive artifact due to the loss of NO_3^-, as HNO_3, from the PTFE prefilter, with the subsequent collection of that HNO_3 on the nylon backup filter (9-12,21). A similar bias may exist for the collection of NH_3 by the tandem filter method since volatilization of NH_4NO_3 from the PTFE prefilter is likely to be the major source of the artifact HNO_3 (9-12,21,22). In the absence of a large data base on organic acids concentrations in the Los Angeles atmosphere, the quantity of KOH used to prepare the alkaline impregnated filters had to be estimated initially. Analysis of the earliest samples taken showed excessive breakthrough of organic acids from filter J2 (top) to filter J2 (bottom) in Figure 2.2. The quantity of KOH spiked onto each filter was increased to 1 ml of 0.1M KOH in distilled, deionized water, and for the final 8 months of 1986, the collection of organic acids data proceeded without incident.

The denuder difference method, employing potassium hydroxide impregnated filters (14-17) also was built into the sampling system (sampling lines B2 and C). This second set of filters provided insurance against a major loss of HNO_3 data, and

possibly could be used to obtain a second set of data on the atmospheric concentrations of the other major gas phase acids, specifically HCl, HBr, HF, CH_3COH, and HCOOH. One KOH impregnated filter collected both gas and aerosol phase acids (sampling line C; Figure 2.2), while the other, located behind the MgO-coated diffusion denuder (sampling line B2; Figure 2.2) collected only aerosol acids. The characteristics of MgO-coated diffusion denuders have not been evaluated for the removal of acid gases other than HNO_3. The objective of the present study is to use existing methods for acid gas determination, and therefore only the HNO_3 data obtained by the denuder difference method are used here.

The accuracy and precision of the denuder difference and tandem filter methods for HNO_3 and aerosol nitrate determination recently were evaluated during the Nitrogen Species Comparison Study held in Claremont, California, 1985 (10,11). The sampling systems employed during the 1986 field experiment detailed in the present report were tested as part of the Claremont study, and the results of that evaluation are discussed in detail in Appendix C to this report and in reference (10).

Airborne particulate matter samples were collected in three different size ranges: fine (d_p<2.2μm AD), PM_{10} (d_p<10μm), and total particulate matter (no size discrimination). The fine particle samples were obtained from filter holders D, E and F in Figure 2.2 that were located downstream of a cyclone separator that removed the coarse particles with nominal aerodynamic diameters greater than 2.2μm. PM_{10} aerosol samples were collected downstream of a size-selective inlet (10μm inlet TM, Model SA-246b, Sierra-Andersen) which, when operated at a flow rate of $1 m^3 h^{-1}$, had a nominal cutpoint of 10μm AD (23). The PM_{10} inlet was followed by a 3-way flow-splitter that ducted equal air volumes to three separate low-volume filter holder assemblies (sampling lines K, L, and M; Figure 2.2). Total particle concentrations were obtained from the open face prefilters of the tandem filter units used for collecting gas phase species (sampling lines G, H, I and J; Figure 2.2).

The open face filters were protected by a Teflon coated dry fallout and sun shield.

Several different filter substrates were used to collect particulate matter in each of the three size ranges. Pretreated quartz fiber filters (i.e., baked at 750°C for at least 3 hours) were used for determining atmospheric carbonaceous aerosol concentrations. Polytetrafluoroethylene (PTFE) filters were employed to obtain atmospheric particulate matter samples for mass concentration determination and for subsequent measurement of a wide variety of major and trace elements (in the fine and PM_{10} aerosols), and water soluble anions and cations (in all 3 particle size ranges). This was done to obtain a nearly complete material balance on the chemical composition of the fine and PM_{10} size fractions, and to permit construction of an ion balance on the composition of the aerosol in all three particle size ranges. Measurement of particle mass concentration, trace elements and carbonaceous aerosols in the total particle size fraction was not funded as part of this project.

It is important to note that the use of PTFE filters for the collection of particulate matter will result in a lower limit determination of atmospheric aerosol nitrate concentrations. This negative artifact for aerosol nitrate has been well documented and is most likely due to the vaporization of fine particle NH_4NO_3 from the inert PTFE filter substrate (9,11,12,21,22). Therefore, fine particle nitrate measured on the PTFE filter F in Figure 2.2 was used only to estimate the long-term average magnitude of this negative artifact by comparison to the fine particle nitrate measured by an artifact-free method on the nylon filter behind the diffusion denuder (filter B1; Figure 2.2). The results of this comparison are discussed in detail in Appendix A of this report. In addition, total particulate nitrate concentrations were corrected for nitrate loss from the PTFE filter by subtracting fine particle nitrate concentrations determined from PTFE filter F and adding fine particle nitrate concentrations obtained from nylon filter B1 (i.e., total particulate nitrate equals NO_3^- concentrations measured by J1-F+B1). Coarse particle nitrate concentrations are obtained by

difference between total and fine particle nitrate concentrations (corrected total particulate nitrate less fine particle nitrate collected on nylon filter B1).

Samples were collected every six days for 24-h sampling periods during the calendar year 1986. The first sample was collected on 2 January to coodinate this acid, dry deposition network with the National Air Surveillance Network high-volume sampling schedule. Filters were installed the day prior to, and removed the day after, sample collection. Flow rates were monitored before and after sampling with a rotameter which had been factory calibrated with an accuracy of 1 percent full scale. Rotameter calibration remained unchanged during the study. The flow rate checks were done to ensure that filter holders were not leaking and to determine that filter clogging had not occurred. Filter clogging did not occur even on the days with the highest particulate matter loadings. As an additional precaution to help ensure the integrity of the samples after collection, the filters were stored in self-sealing, plastic petri dishes, sealed with Teflon tape, and refrigerated until sample analysis.

Sample Analysis

Particle mass. Atmospheric fine and PM_{10} mass concentrations were measured gravimetrically by weighing the specified PTFE filter (sampling lines E and L; Figure 2.2) before and after sample collection. A mechanical microgram balance with a 1μg sensitivity (Model M-5S-A, Mettler Instruments) was employed for this purpose. Unexposed and collected PTFE filters were equilibrated at 22±3°C and 50±3 percent relative humidity for at least 24 h prior to weighing the filter. To track the calibration of the balance between initial and final weighings, a series of metal calibration weights and control filters (three unexposed and three loaded with atmospheric particles) were weighed at the beginning and end of each daily weighing period.

Filter extraction. Nylon filters were leached by lightly shaking each of them in 20ml of a $CO_3^{=}/HCO_3^{-}$ buffer (eluent for the ion chromatograph) for 3 hours or more

at 10°C. Reduced temperatures were used for the extraction to avoid loss of volatile species (i.e., NO_3^-, NH_4^+) during the sample preparation process. Polytetrafluoroethylene filters first were wetted with 0.2-0.25ml of ETOH (100 percent) to reduce the hydrophobic nature of this material (24). A Teflon rod was placed on top of each filter to keep them submerged, and then the PTFE filters were leached with distilled, deionized water in the same manner as the nylon filters. Oxalic acid and KOH impregnated filters also were leached with distilled, deionized water in the same manner as the nylon filters.

Gas phase acids and ionic aerosol species. After extraction, the concentrations of HNO_3 and HCl measured as NO_3^- and Cl^- on nylon filters (A, B1, H2; Figure 2.2) and the concentrations of HCl, HBr, HF, HCOOH, and CH_3COOH measured as Cl^-, Br^-, F^-, $HCOO^-$, and CH_3COO^- on KOH impregnated quartz filters (J2; Figure 2.2) were determined using ion chromatography (Models 2020i and 10, Dionex Corp.) (25,26). The concentration of NH_3 measured as NH_4^+ on oxalic acid filters (I2; Figure 2.2) was determined by an indophenol colorimetric procedure employing a rapid flow analyzer (RFA-300 TM, Alpkem Corp.) (27,28). The concentrations of the major water soluble particulate species (SO_4^{-2}, NO_3^-, Cl^-, Br^-, F^-) were determined from the extracts of one of the PTFE filters in each particle size range (Filters E and L; Figure 2.2) using ion chromatography (25,26). The same PTFE filter extracts also were analyzed for particulate ammonium ion (NH_4^+) by an indophenol colorimetric procedure (27,28) and for water soluble Na^+ and Mg^{++} by flame atomic absorption (Model AA-6, Varian Techtron).

Organic and elemental carbon. Organic carbon (OC) and elemental carbon (EC) concentrations in fine and PM_{10} aerosols were determined from the specified quartz fiber filters (D and K; Figure 2.2) by the thermal/optical method of Johnson et al. (29) as further developed by Cary (30). Prior to sample collection these filters were heat treated at 750°C in air for at least 3 h to lower their carbon blank levels. Com-

pensation for the pyrolytic conversion of organic carbon to elemental carbon during the thermal analysis is achieved by continuously monitoring the optical reflectance of the sample during analysis as described in references (29,30). The analysis of organic and elemental carbon is important because of the effect that elemental carbon can have on visibility through the atmosphere.

Trace elements. The bulk concentrations of 34 major and minor trace elements were determined by x-ray fluorescence (31,32). The species determined were Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Ga, As, Se, Br, Rb, Sr, Y, Zr, Mo, Pd, Ag, Cd, In, Sn, Sb, Ba, La, Hg, and Pb. The same PTFE filter employed for mass determination was used for this analysis. It has been established that certain elements and species can be used as tracers for emissions from individual source types (e.g., lead in particulate matter acts as a tracer for particles emitted from automobiles burning leaded gasoline; Si and Al act as tracers for soil dust, Ni acts as a tracer for fuel oil fly ash; Na is a tracer for sea salt; As is a tracer for copper smelters, etc.) (33-36). Therefore, considerable insight into source-receptor relationships can be gained if a nearly complete chemical characterization of the aerosol is obtained.

Quality Assurance/Quality Control

Quality assurance/quality control (QA/QC) measures were implemented to ensure high quality data. Preliminary QA/QC involved participation in the Claremont Nitrogen Species Comparison Study (10,11). Results from the Claremont study, which employed the same equipment used in the 1986 year-long acid gas measurement program are detailed in Appendix C of this report and in reference (10).

Field sampling. Samples remained in the field for as short a time period as possible (i.e., they were installed the day before and removed the day after sample collection). All filters were stored in pre-labeled, self-sealing petri dishes prior to sample collection. In addition, reactive and treated filters were stored at reduced

temperatures (-4°C). After sample collection, all filters were placed back into their original pre-labeled petri dish, sealed with Teflon tape and stored at reduced temperatures (-30°C for KOH filters and 4-10°C for other filters). Samples remained at reduced temperatures until they were analyzed for the species of interest.

Air flow rates through all filter trains were measured before and after sample collection to ensure that the filter holders were not leaking and that the filters did not become overloaded with particles. Each system had a 24-hour, seven-day timer along with a separate elapsed timer. A vacuum gauge was used in-line between the sample line manifold and the pump to ensure that the pump was functioning properly. All field data were immediately entered into a field log book (one log book for each site) at the site when the measurement was obtained. The glass inlet line and open face filter holders were protected from the sun and from wet or dry fallout.

Field blanks equal in number to 10% of the actual ambient samples were taken at periodic intervals throughout the sampling program. Two types of field blanks were obtained during the year. In the first type, filters were loaded, the sampler turned on for 10 seconds, the filters removed, and then stored by the same procedures as just described for the ambient samples. Four sets of these filters were obtained throughout the year at each site. Field blanks of the second type were left on the idle sampler for 48 hours. In the latter case, this process included filter placement and removal, flow rate checks, and sample storage. Two sets of field blanks of this type were obtained at each monitoring site immediately following completion of the sampling program. All filter blank values were averaged.

Chemical analysis. The concentrations of all chemical species were determined relative to primary or secondary laboratory standards of known concentration. Aqueous standards were diluted daily from more concentrated solutions prepared monthly from ACS grade analytical reagents. Whenever possible, the matrix of the daily standards matched that of the leaching solution. Standard log

sheets were filled out each time standards or reagents were prepared. For strong acids analysis, an independent QC standard was obtained from Dionex and routinely analyzed during the last half of the year. Accuracy, relative to this standard was typically better than 5 percent.

A summary of the filter blank values, the precision of the analytical measurements, and the instrument detection limits (IDL) for the major gas and aerosol phase species is presented in Table 2.1(A-D). For all water soluble species, the analytical precision was defined as the average coefficient of variation obtained from many pairs (typically n>50) of duplicate (split filters analyzed separately) or replicate (repeat analysis of a filter extract) measurements. The precision values for the x-ray fluorescence and organic and elemental carbon data were supplied by the analytical laboratories performing those analyses (NEA Inc. for x-ray fluorescence; Sunset Laboratories for EC and OC). For gravimetric mass determination, the reproducibility of the initial and final weighing was determined by reweighing a large number (n>200) of the filters prior to and after sample collection. The precision for either weighing was found to be approximately 5μg per filter. These weighing errors first were propagated with the inherent precision of the balance (specifications set by the manufacturer; 1σ = 15μg), and then the initial and final weighing errors were combined to obtain the precision for sample mass determination. Final error bound estimates were obtained by the statistical propagation of the sample, filter blank, and sampling volume precisions.

All PTFE and nylon filters were obtained from two sources; Membrana Corporation, no longer in business, and Gelman Sciences, Inc. Several lots of each filter type were employed throughout the year. Differences in filter blank values between lots are noted in Table 2.1(A-D). For example, no difference between lots was observed for NO_3^- measured on PTFE filter blanks, however, a considerable difference was observed between lots for NO_3^- measured on nylon filters. During

Table 2.1A. Summary of analytical measurements for chemical composition determination of gas phase species.

Species Determined	Species Analyzed	Instrument Detection Limit (IDL)	Filter Type	Lot Number	Filter Blank ($\bar{x}\pm\sigma_b$ in μg/filter)[a]	Analytical Precision[b]
HNO_3	NO_3^-	0.6μg/filter	nylon	4222	0.6±0.3	4.2%
				K07025E	0.6±0.2	
				84800	2.4±0.6	
HCl	Cl^-	0.1	KOH[c]		0.6±0.8	4.5
			nylon	4222	4.8±1.6	4.5
HF	F^-	0.3	KOH[c]		0.3±0.2	23.6
HCOOH	$HCOO^-$	0.9	KOH[c]		3.6±1.5	2.8
CH_3COOH	CH_3COO^-	2.3	KOH[c]		23±17	4.6
NH_3	NH_4^+	0.3	OX[d]		0.4±0.3	8.0

a. For species which were detectable in the filter blanks, the sample detection limit is equal to 2 times the standard deviation (σ_b) of the reported filter blank value.

b. Based on duplicate or replicate analysis of a large number of filters (typically n>50).

c. KOH impregnated prebaked quartz fiber filters.

d. Oxalic acid impregnated glass fiber filters.

Table 2.1B. Summary of analytical measurements for chemical composition determination of fine particle species (d_p<2.2μm AD).

Species Determined[a]	Instrument Detection Limit (IDL)	Filter Type	Lot Number	Filter Blank ($\bar{x}\pm\sigma_b$ in μg/filter)[b]	Analytical Precision[c]
mass	10μg/filter	PTFE		<IDL	5.4μg m^{-3}
organic carbon (OC)	2.5	prebaked quartz		0.4±0.2	3.5%
elemental carbon (EC)	2.5	prebaked quartz		<IDL	6.5
$SO_4^{=}$[d]	0.6μg/filter	PTFE		<IDL	5.6
NO_3^-[d]	0.6			<IDL	5.7
NO_3^-(CD)[d,e]	0.6	nylon	4222	0.6±0.3	4.2
			K07025E	0.6±0.2	
			84800	2.4±0.6	
Cl^-[d]	0.1	PTFE		0.35±0.19	18.2
NH_4^+[d]	0.8			<IDL	3.9
Na^+[d]	0.2			0.43±0.24	17.6
Mg^{++}[d]	0.2			<IDL	33.6
Al	110ng/filter			<IDL	<1
Si	70			<IDL	<1
Fe	23			0.069±0.040	<1
Ca	40			<IDL	<1

a. Other trace species determined by XRF: P, S, Cl, K, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Ga, As, Se, Br, Rb, Sr, Y, Zr, Pd, Ag, Cd, In, Sn, Sb, Ba, La, Hg, and Pb.

b. For species which were detectable in the filter blanks, the sample detection limit is equal to 2 times the standard deviation (σ_b) of the reported filter blank value.

c. Based on duplicate or replicate analysis of a large number of filters (typically n>50) except for Al, Si, Fe, and Ca which were obtained from the commercial laboratory (NEA Labs, Beaverton, OR, Dr. J. Cooper, President, personal communication).

d. Water soluble fraction only.

e. Nitrate concentrations were measured on a nylon filter located behind a Teflon-coated cyclone and a MgO diffusion denuder.

Table 2.1C. Summary of analytical measurements for chemical composition determination of PM_{10} species

Species Determined[a]	Instrument Detection Limit (IDL)	Filter Type	Filter Blank ($\bar{x}\pm\sigma_b$ in μg/filter)[b]	Analytical Precision[c]
mass	10μg/filter	PTFE	<IDL	2.78μg m^{-3}
organic carbon (OC)	2.5	prebaked quartz	4.0±1.8	3.5%
elemental carbon (EC)	2.5	prebaked quartz	<IDL	6.5
$SO_4^{=}$[d]	0.6	PTFE	<IDL	4.8
NO_3^{-}[d]	0.6		<IDL	4.1
Cl^{-}[d]	0.1		0.31±0.22	11.9
NH_4^{+}[d]	0.8		<IDL	3.9
Na^{+}[d]	0.2		0.41±0.19	4.8
Mg^{++}[d]	0.2		<IDL	8.4
Al	110ng/filter		<IDL	<1
Si	70		<IDL	<1
Fe	23		0.069±0.040	<1
Ca	40		<IDL	<1

a. Other trace species determined by XRF: P, S, Cl, K, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Ga, As, Se, Br, Rb, Sr, Y, Zr, Pd, Ag, Cd, In, Sn, Sb, Ba, La, Hg, and Pb.

b. For species which were detectable in the filter blanks, the sample detection limit is equal to 2 times the standard deviation (σ_b) of the reported filter blank value.

c. Based on duplicate or replicate analysis of a large number of filters (typically n>50) except for Al, Si, Fe, and Ca which were obtained from the commercial laboratory (NEA Labs, Beaverton, OR, Dr. J. Cooper, President, personel communication).

d. Water soluble fraction only.

Table 2.1D. Summary of analytical measurements for chemical composition determination of total particle species (no particle size fractionation).

Species Determined	Instrument Detection Limit (IDL)	Filter Type	Filter Blank ($\bar{x}\pm\sigma_b$ in μg/filter)[a]	Analytical Precision[b]
$SO_4^{=}$[c]	0.6μg/filter	PTFE	1.3±0.4	6.1%
NO_3^{-}[c]	0.6		2.5±0.8	5.0
Cl^{-}[c]	0.1		1.0±0.5	9.0
NH_4^{+}[c]	0.8		0.5±0.2	4.6
Na^{+}[c]	0.2		1.0±0.6	13.9
Mg^{++}[c]	0.2		0.28±0.15	28.5

a. For species which were detectable in the filter blanks, the sample detection limit is equal to 2 times the standard deviation (σ_b) of the reported filter blank value.

b. Based on duplicate or replicate analysis of a large number of filters (typically n>50).

c. Water soluble fraction only.

1986, nylon filter supplies were disturbed by the discontinuation of production at Membrana Corporation, and by very tight supply conditions due to a nationwide surge in nitric acid measurements induced by increased acid deposition research. Several batches of nylon filters obtained from Gelman Sciences, Inc. during 1986 had extremely high and non-reproducible Cl^- blanks (much greater than 200μg per filter) which made these filters useless for the determination of HCl as Cl^-. Fortunately, HCl measurements were successfully obtained by our second tandem filter method employing KOH impregnated filters.

As can be seen in Table 2.1(A-D), filters which were better protected from the atmosphere (i.e., located deep within the fine particle sampling system) had the lowest field blank values. The PTFE open face prefilter of the tandem filter units typically had higher dynamic filter blank values, thus confirming the need for our practice of installing and removing those filters as close to the sampling time as possible.

The present research represents a crash program to obtain a long term record of acid gas concentration data before the expiration of the legislative authority granted under the Kapiloff Acid Deposition Act. Formal analysis of these measurements is expected to occur as part of a subsequent data analysis effort. Chapter 3 of this report presents the gas phase acids and ammonia data in graphical and tabular form. A narrative description and preliminary analysis of the HNO_3, aerosol nitrate and PM_{10} data base is found in Appendices A and B of Volume I of this report.

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CHAPTER 3: SUMMARY OF GAS PHASE POLLUTANT CONCENTRATIONS

Gas phase pollutant concentrations are reported in this chapter in both tabular and graphical form. Annual or 8-month average (May-December) and maximum 24-h average concentrations are summarized in Tables 3.1-3.4, along with the number of sampling events used to calculate the long term average. Following each table, the spatial distributions of the long term average and 24-h average pollutant concentrations given in that table are illustrated on maps of the Los Angeles area. Then the time series graphs of the individual 24-h average concentrations of the gas phase acidic or basic species presented in the covering table are given at all nine sampling sites. The maps and time series plots are organized by pollutant species as follows:

HNO_3 (by DD)	Figures 3.1 through 3.11.
HNO_3 (by TF)	Figures 3.12 through 3.22.
HCl	Figures 3.23 through 3.33.
HF	Figures 3.34 through 3.44.
Acetate (see note below)	Figures 3.45 through 3.55.
Formic Acid	Figures 3.56 through 3.66.
NH_3	Figures 3.67 through 3.77.

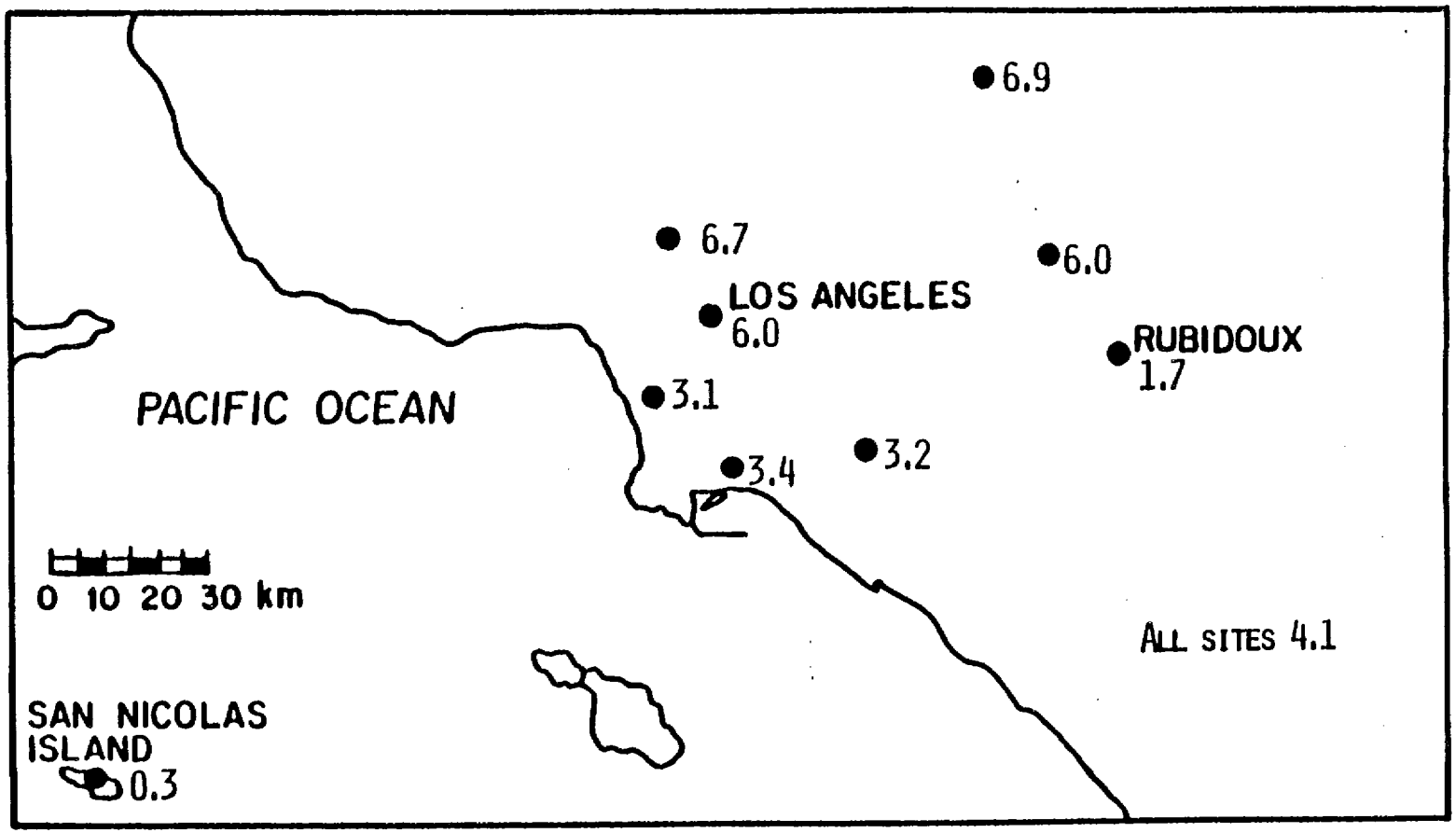
Nitric acid was measured by both the denuder difference method (DD) and by the tandem filter method (TF), and both data sets are illustrated in the tables and graphs that follow. Gas phase HCl, HF, HCOOH, CH_3COOH, and NH_3 data shown were obtained by the tandem filter method. Acetic acid measurements may be subject to a positive artifact induced by conversion of peroxyacetyl nitrate (PAN) to acetate on alkaline substrates. The actual extent of this potential artifact is unknown at present. Therefore, these data on CH_3COOH concentrations are stated as "acetate" values (the actual species measured on the filter), and should be treated as an upper limit on actual CH_3COOH concentrations in the atmosphere. Articles that describe the HNO_3 data and their significance are reproduced as Appendices A and C to this report, and the PM_{10} concentrations and composition measurements likewise are described in Appendix B.

Table 3.1. Gas phase nitric acid concentrations observed in the Los Angeles area, 1986 (concentrations in $\mu g\ m^{-3}$)

Site	HNO_3(DD)[a] Annual Average	HNO_3(DD)[a] Max 24-h Average	HNO_3(DD)[a] n[c]	HNO_3(TF)[b] Annual Average	HNO_3(TF)[b] Max. 24-h Average	HNO_3(TF)[b] n[c]
Burbank	6.7	17.4	61	10.4	23.3	61
Downtown LA	6.0	16.6	57	9.7	27.2	58
Hawthorne	3.1	13.0	60	5.8	28.4	59
Long Beach	3.4	15.7	58	6.5	31.7	58
Anaheim	3.2	13.5	59	7.1	28.6	60
Rubidoux	1.7	6.7	59	3.6	12.5	61
Upland	6.0	18.8	61	10.8	37.2	61
Tanbark Flats	6.9	21.0	55	10.0	34.3	57
San Nicolas Island	0.3	4.7	59	1.1	11.2	59

a. By denuder difference method employing nylon filters.
b. By tandem filter method employing a nylon backup filter.
c. Maximum number of sampling events is 61.

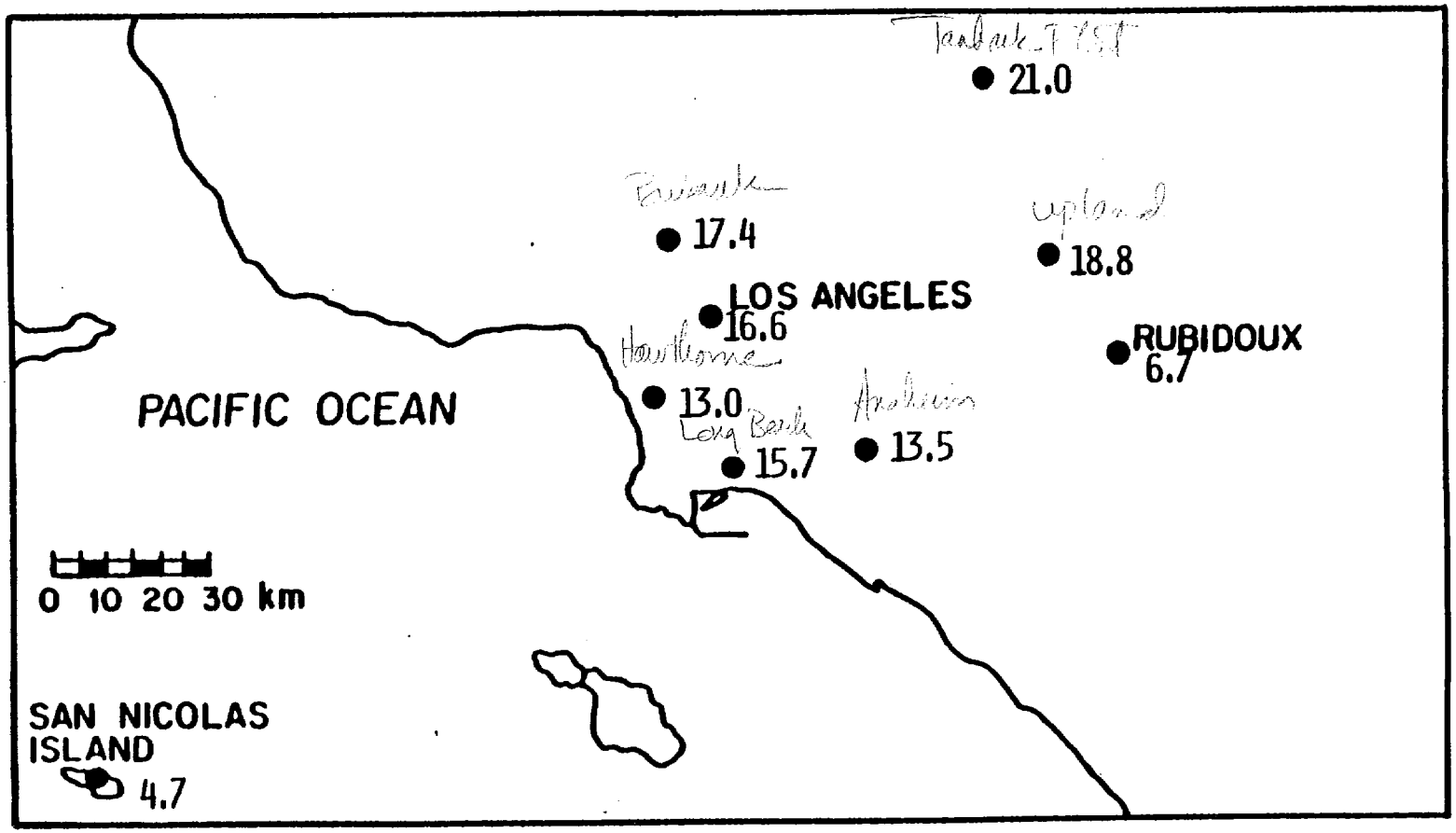
ANNUAL AVERAGE HNO_3 CONCENTRATIONS ($\mu g\ m^{-3}$) OBSERVED IN THE LOS ANGELES AREA, 1986. (HNO_3 BY DENUDER DIFFERENCE METHOD.)[A]



[A]EMPLOYING A NYLON BACKUP FILTER.

FIGURE 3.1

MAXIMUM 24-HOUR AVERAGE HNO_3 CONCENTRATIONS ($\mu g\ m^{-3}$) OBSERVED IN THE LOS ANGELES AREA, 1986. (HNO_3 BY DENUDER DIFFERENCE METHOD.)[A]



[A]EMPLOYING A NYLON BACKUP FILTER.

FIGURE 3.2

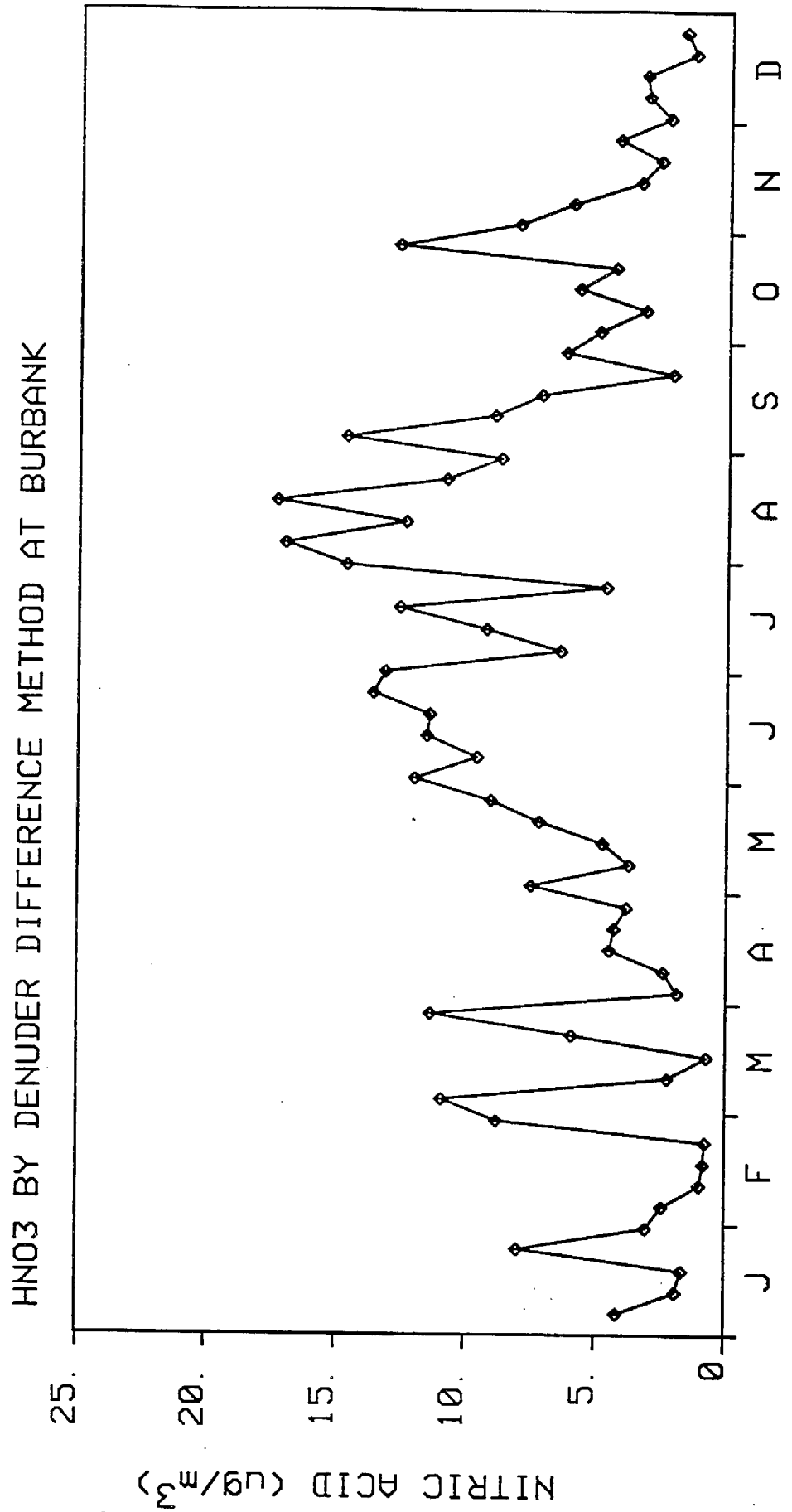

HNO3 BY DENUDER DIFFERENCE METHOD AT BURBANK
NITRIC ACID (ug/m3)
25.
20.
15.
10.
5.
0
J F M A M J J A S O N D
--1986--

FIGURE 3.3

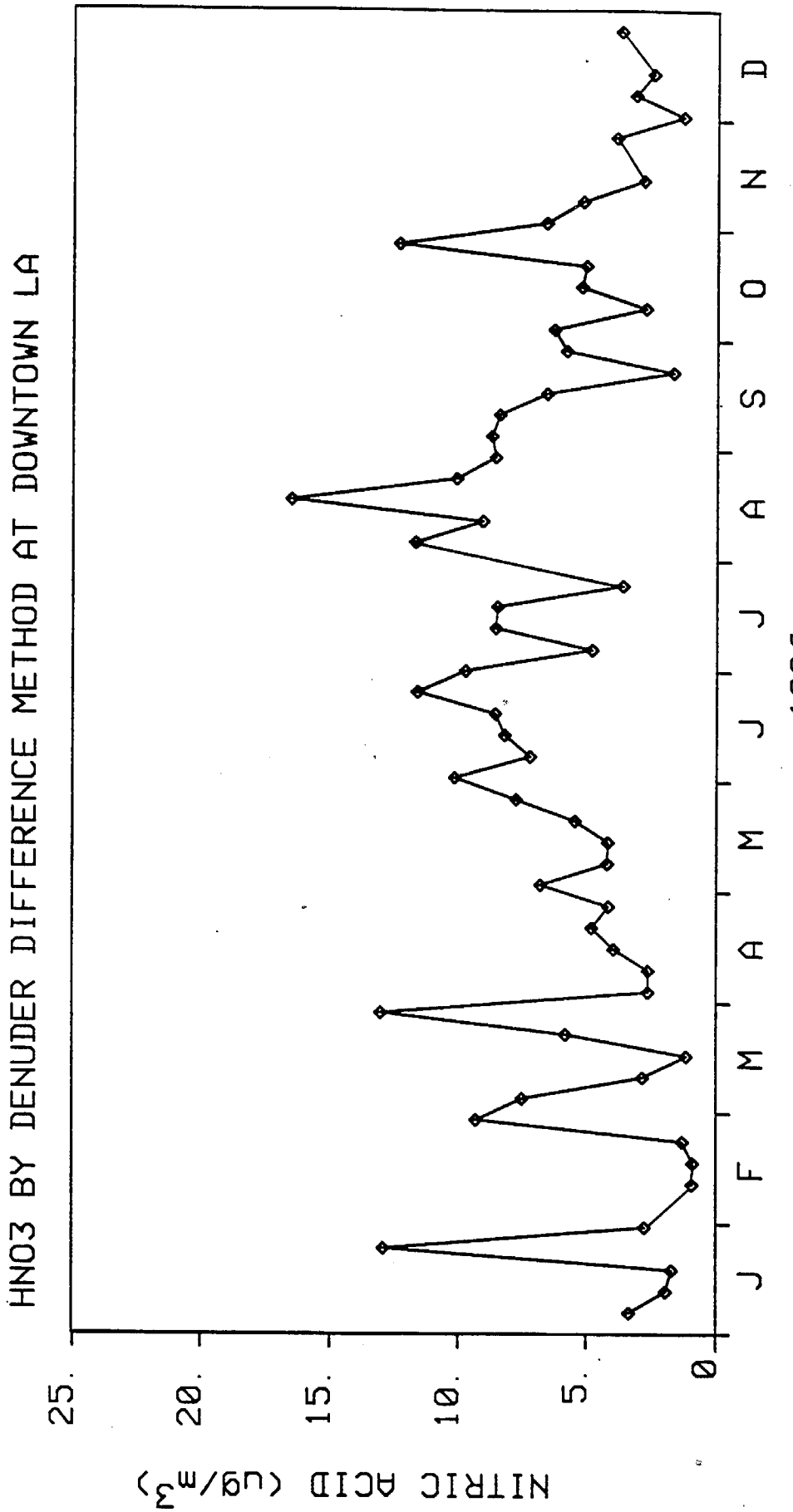

HNO3 BY DENUDER DIFFERENCE METHOD AT DOWNTOWN LA
NITRIC ACID (ug/m3)
25.
20.
15.
10.
5.
0
J F M A M J J A S O N D
--1986--

FIGURE 3.4

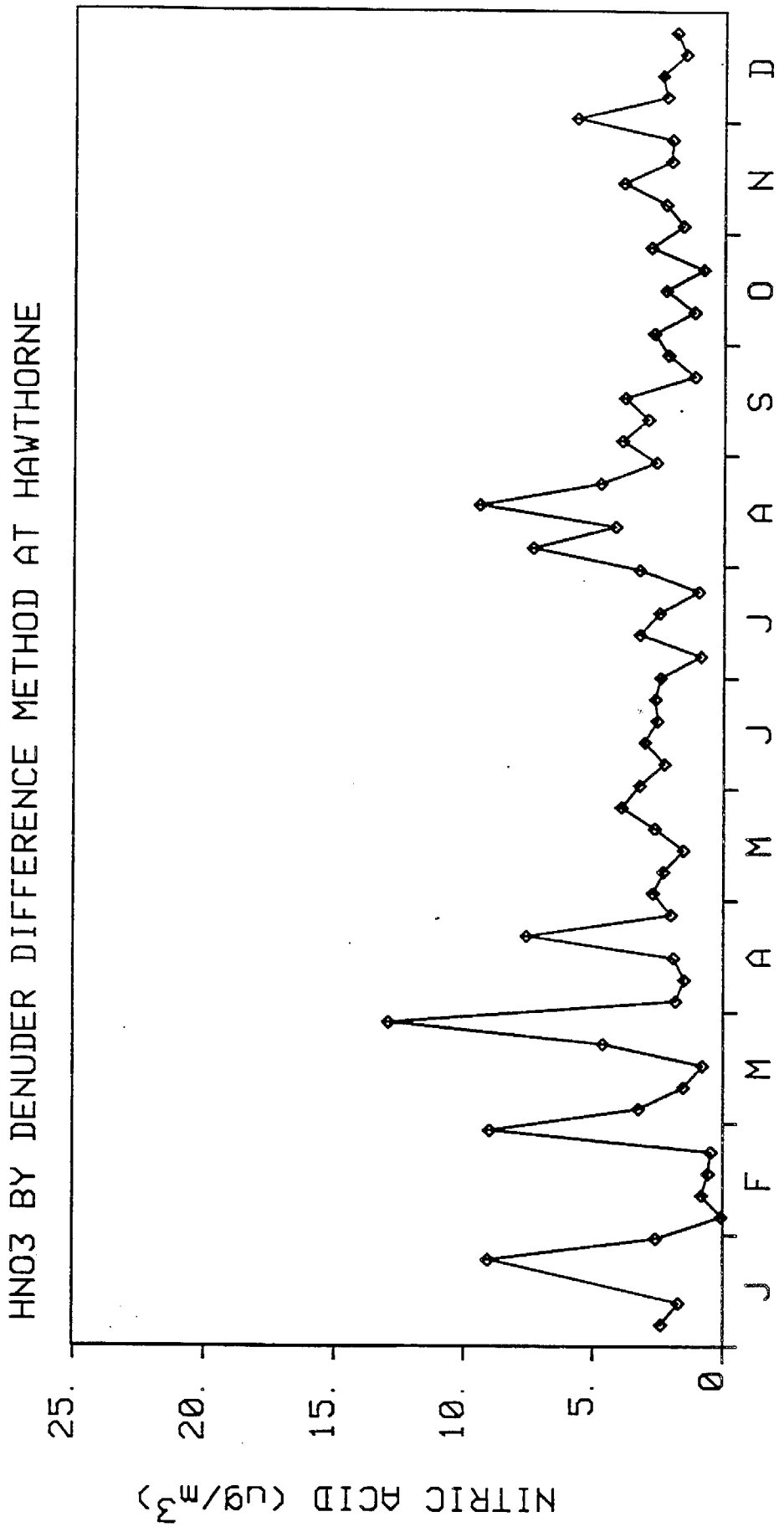

HNO3 BY DENUDER DIFFERENCE METHOD AT HAWTHORNE
NITRIC ACID (ug/m3)
25.
20.
15.
10.
5.
0
J F M A M J J A S O N D
--1986--

FIGURE 3.5

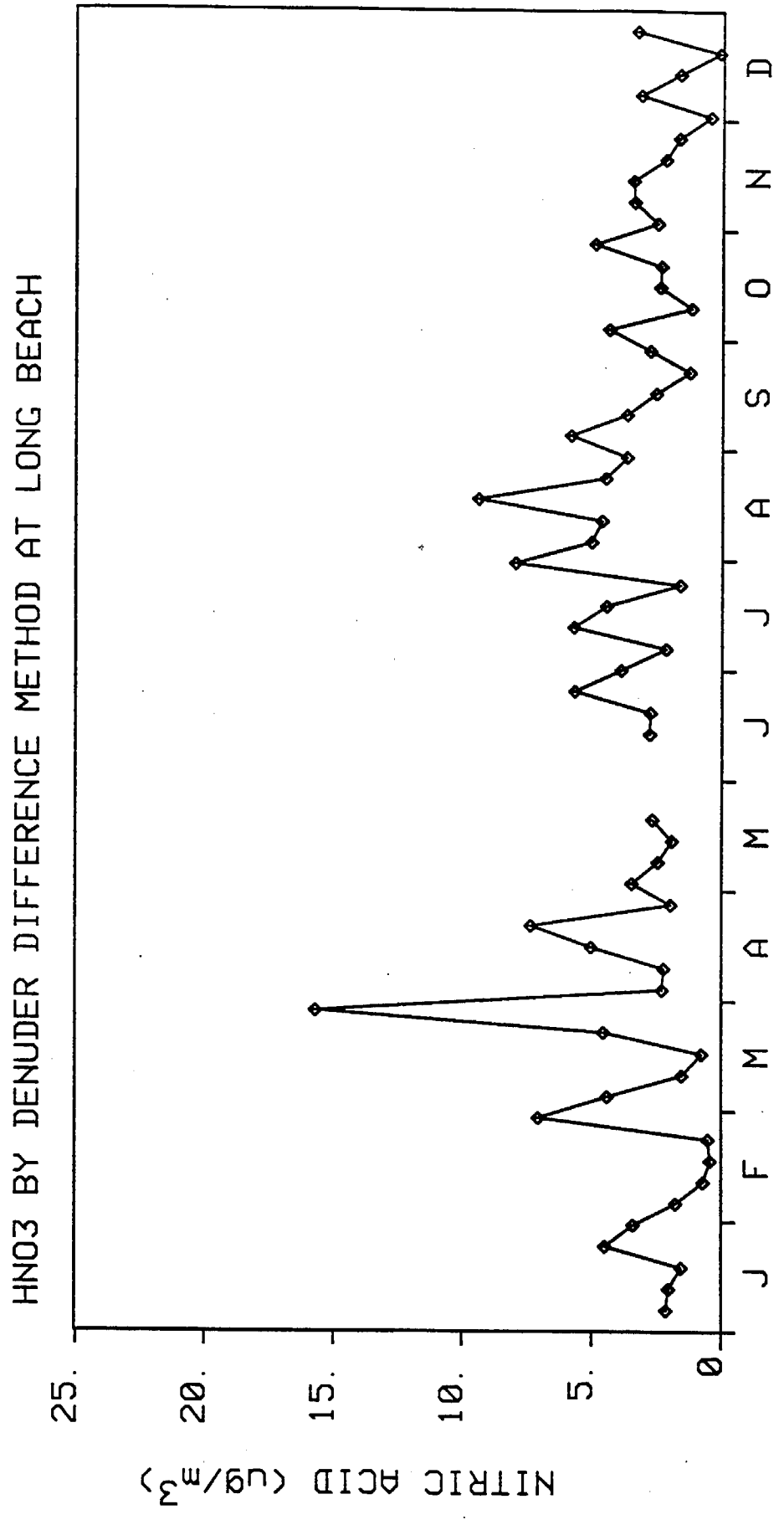

HNO3 BY DENUDER DIFFERENCE METHOD AT LONG BEACH
NITRIC ACID (ug/m3)
25.
20.
15.
10.
5.
0
J F M A M J J A S O N D
--1986--

FIGURE 3.6

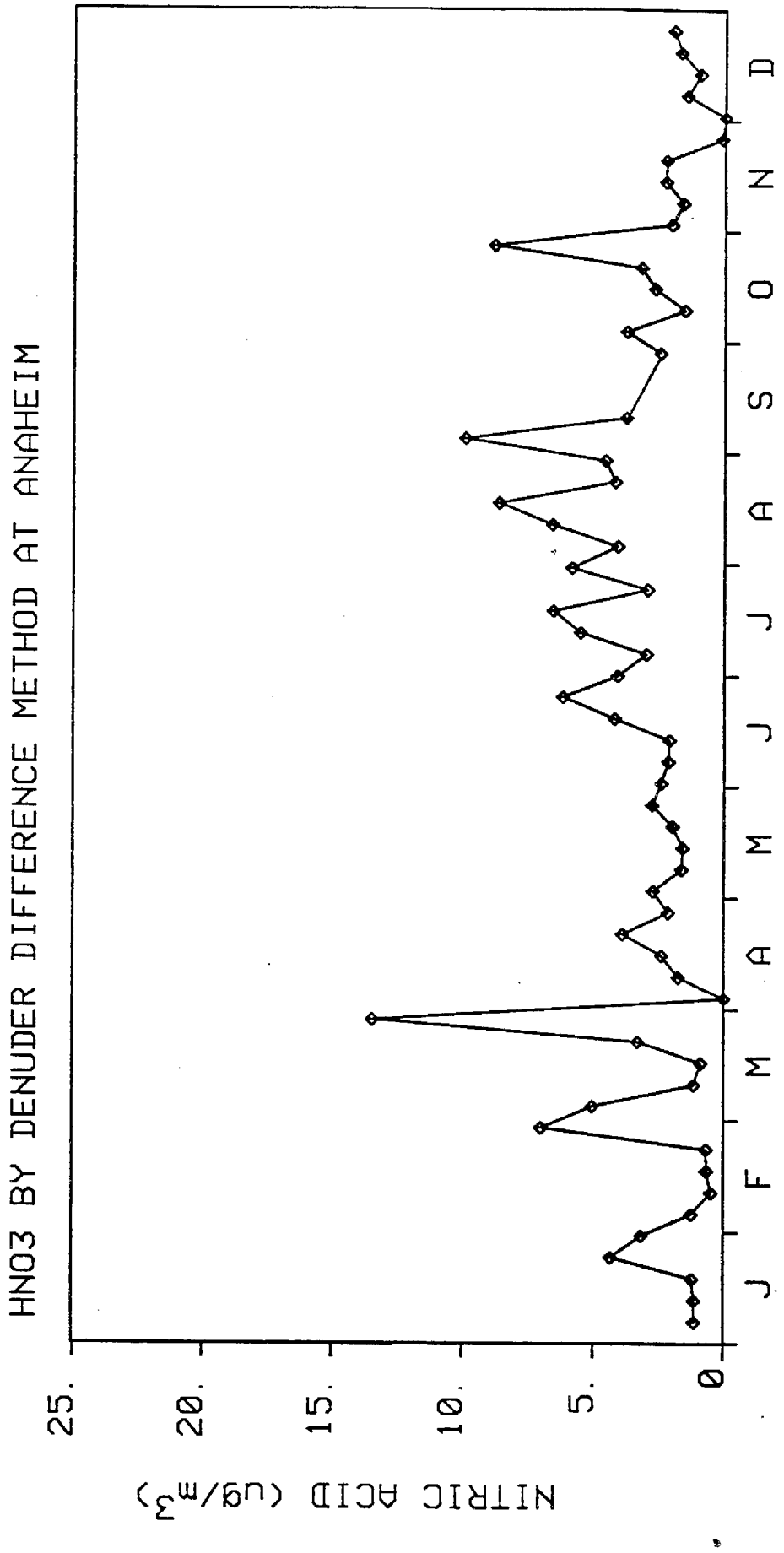

HNO3 BY DENUDER DIFFERENCE METHOD AT ANAHEIM
NITRIC ACID (ug/m3)
25.
20.
15.
10.
5.
0
J F M A M J J A S O N D
--1986--

FIGURE 3.7

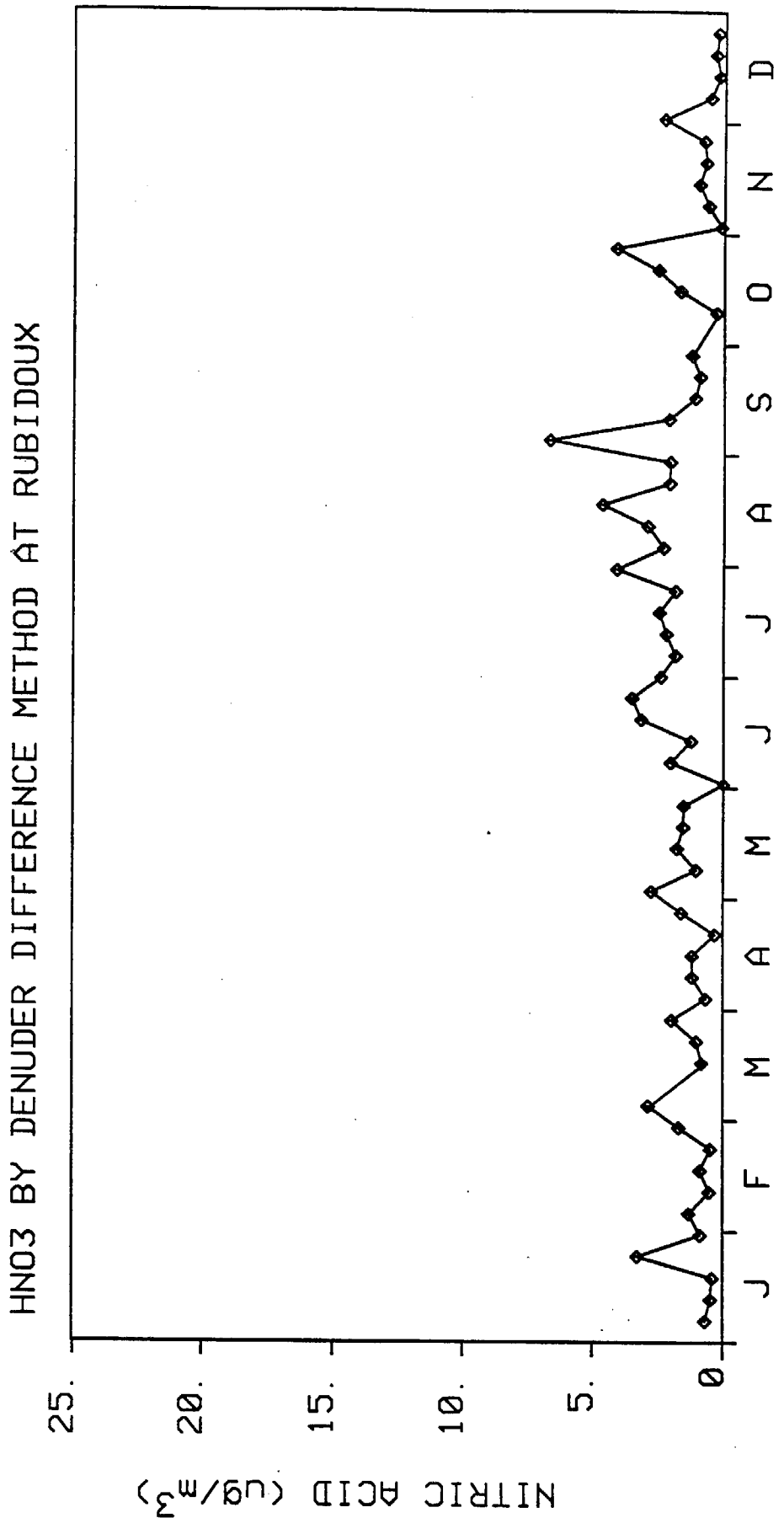

HNO3 BY DENUDER DIFFERENCE METHOD AT RUBIDOUX
NITRIC ACID (ug/m3)
25.
20.
15.
10.
5.
0
J F M A M J J A S O N D
--1986--

FIGURE 3.8

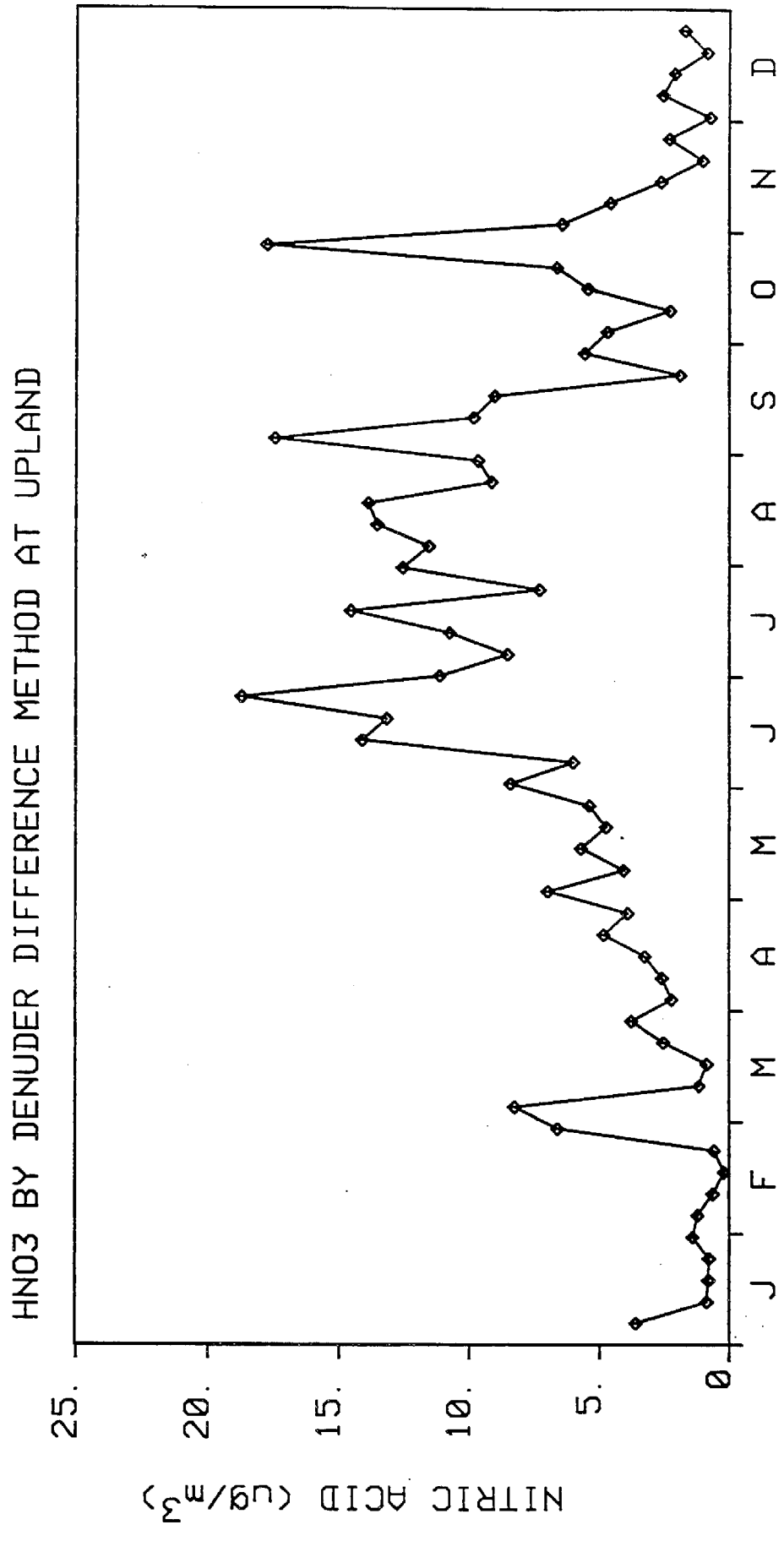

HNO3 BY DENUDER DIFFERENCE METHOD AT UPLAND
NITRIC ACID (ug/m3)
25.
20.
15.
10.
5.
0
J F M A M J J A S O N D
--1986--

FIGURE 3.9

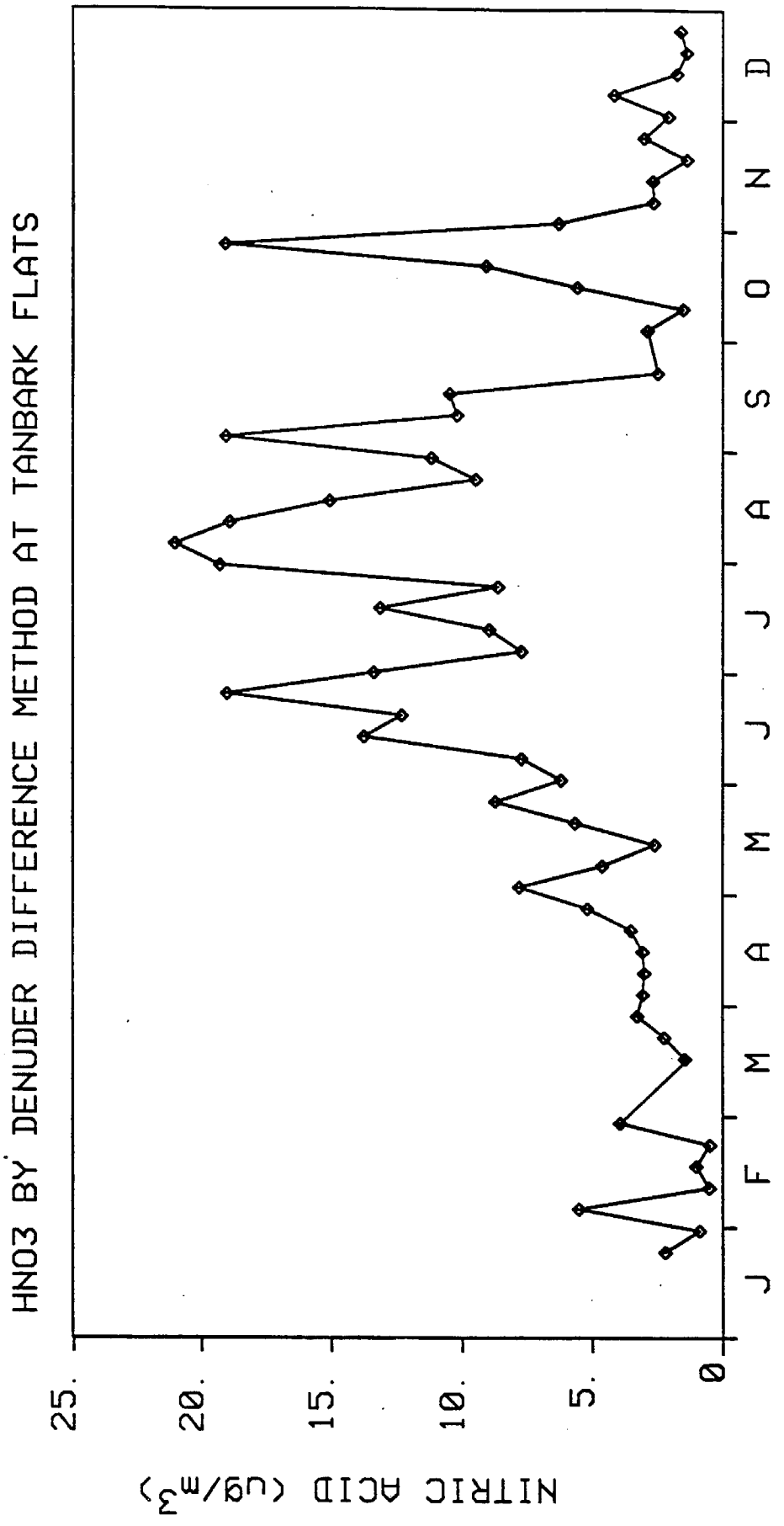

HNO3 BY DENUDER DIFFERENCE METHOD AT TANBARK FLATS
NITRIC ACID (ug/m3)
25.
20.
15.
10.
5.
0
J F M A M J J A S O N D
--1986--

FIGURE 3.10

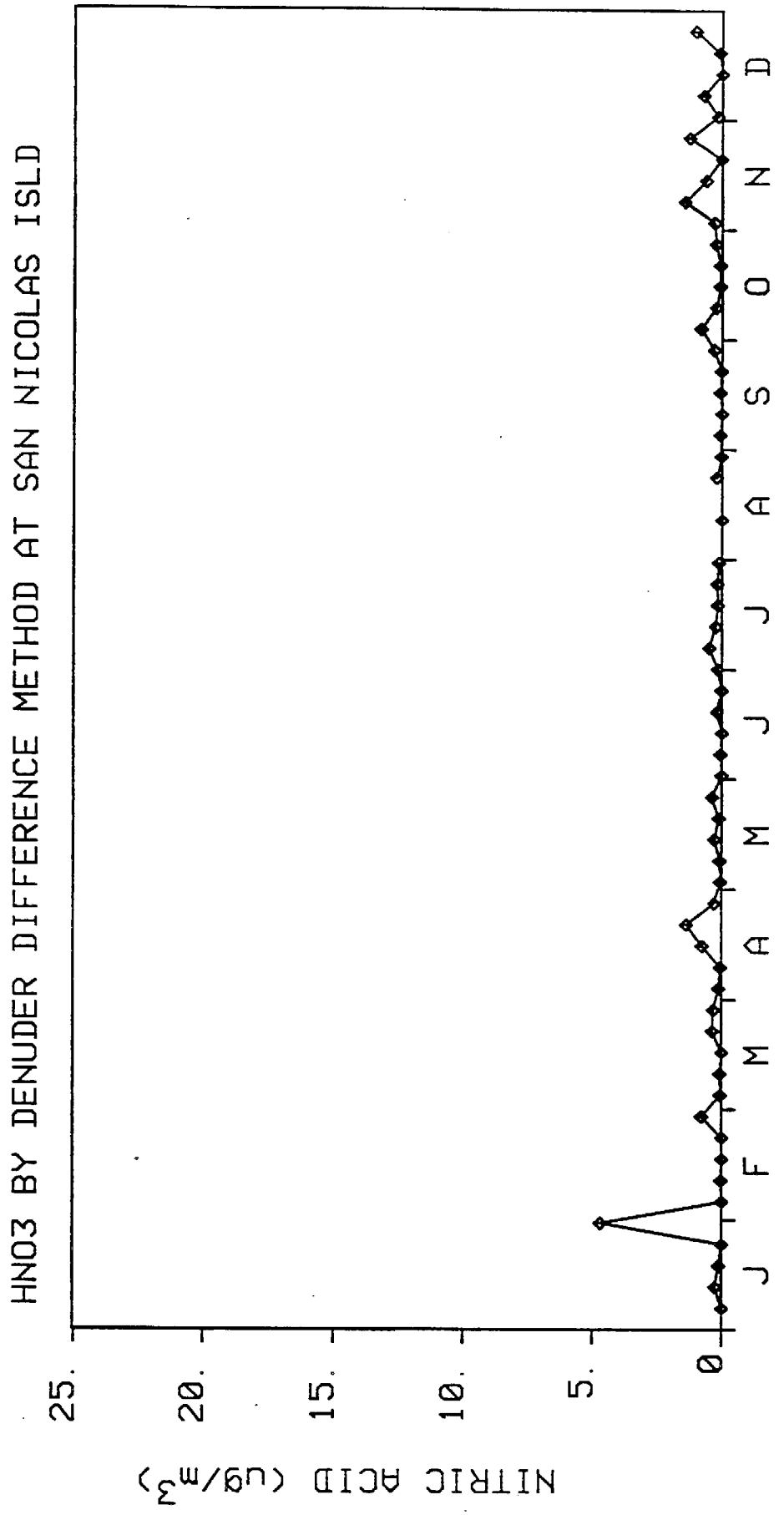
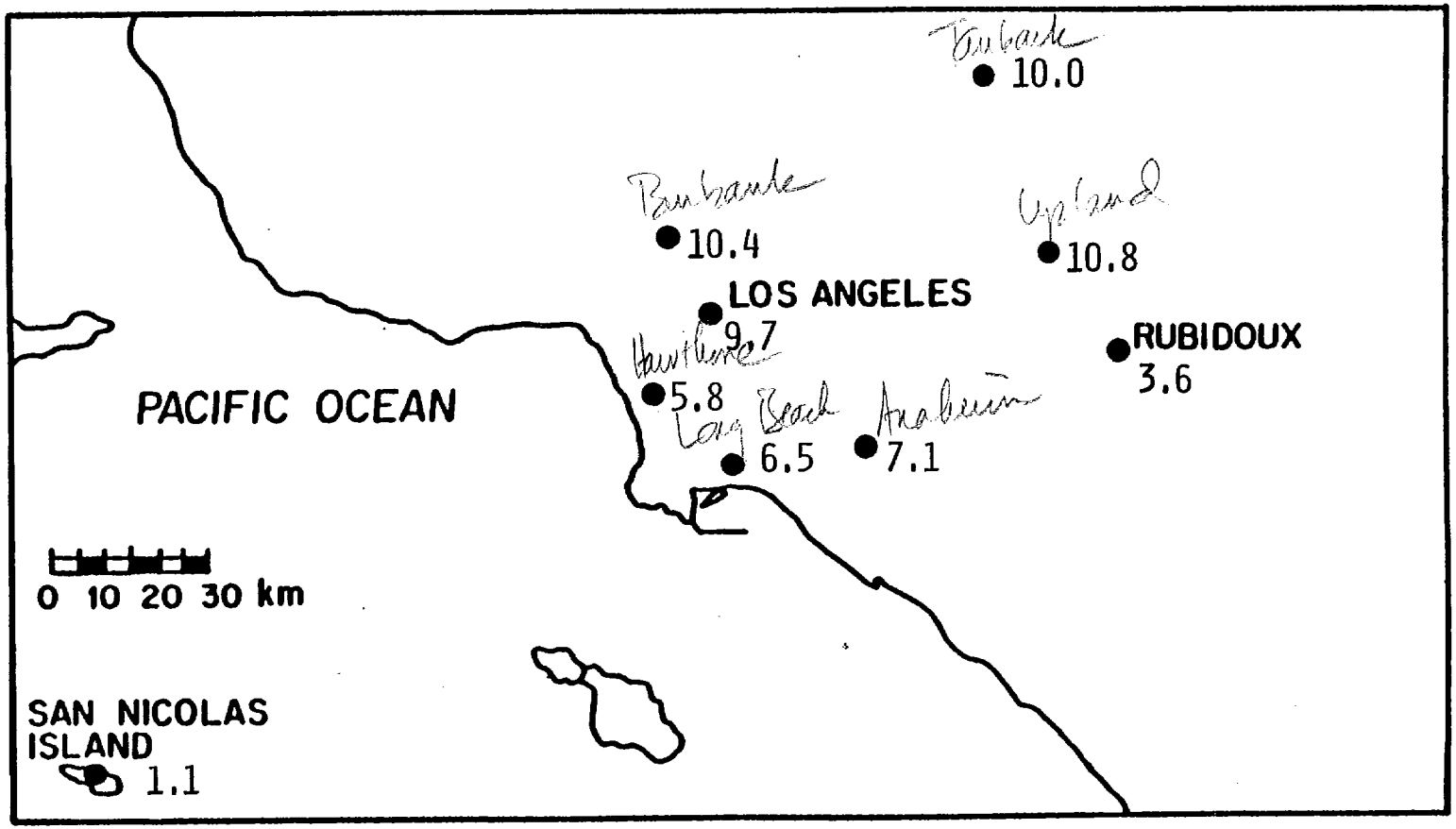

HNO3 BY DENUDER DIFFERENCE METHOD AT SAN NICOLAS ISLD
NITRIC ACID (ug/m3)
25.
20.
15.
10.
5.
0
J F M A M J J A S O N D
--1986--

FIGURE 3.11

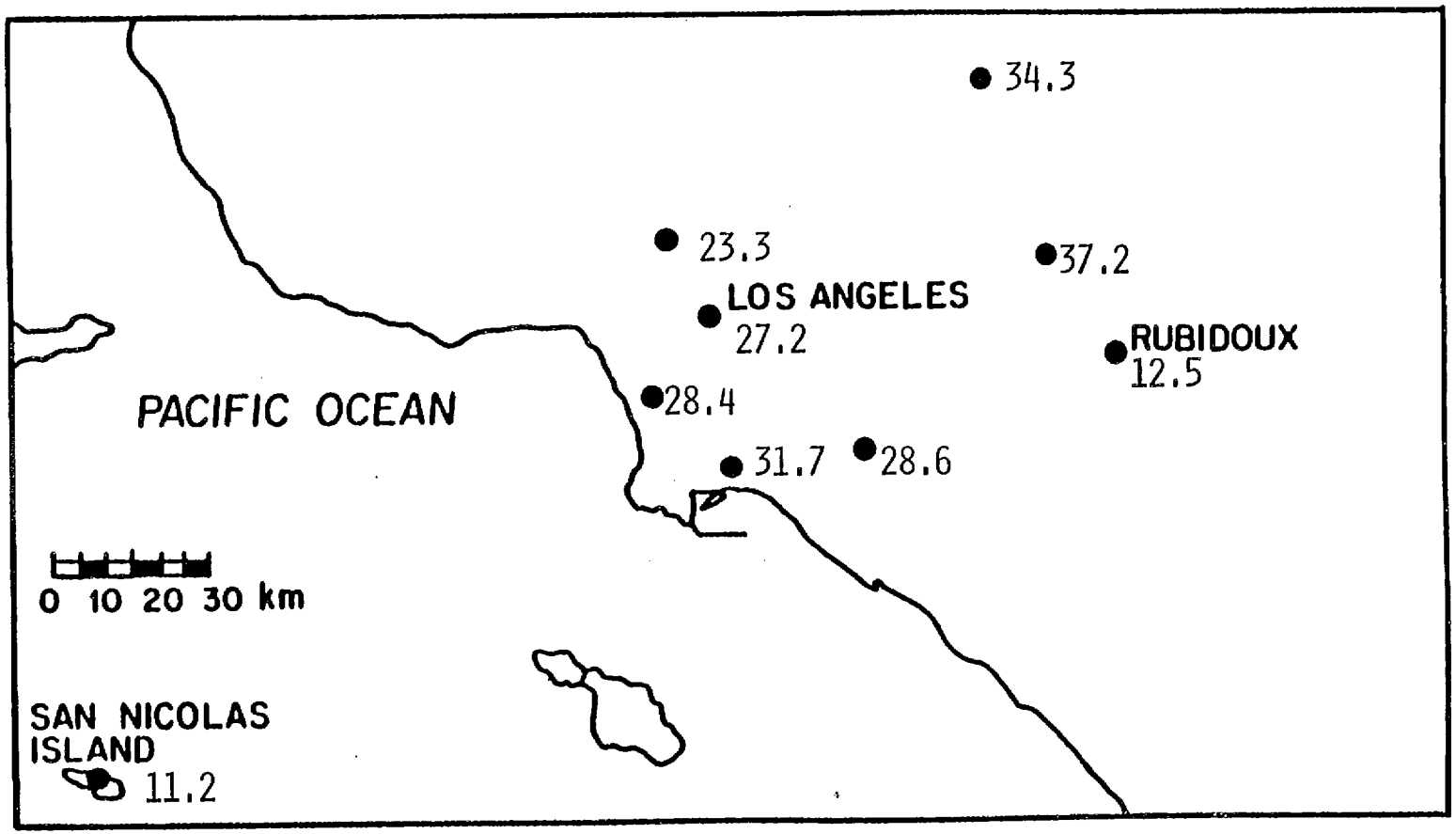
ANNUAL AVERAGE HNO_3 CONCENTRATIONS (UG M^{-3}) OBSERVED IN THE LOS ANGELES AREA, 1986. (HNO_3 BY TANDEM FILTER METHOD.)[A]



[A]EMPLOYING A NYLON BACKUP FILTER.

FIGURE 3.12

MAXIMUM 24-HOUR AVERAGE HNO_3 CONCENTRATIONS ($\mu G\ M^{-3}$) OBSERVED IN THE LOS ANGELES AREA, 1986. (HNO_3 BY TANDEM FILTER METHOD.)[A]



[A]EMPLOYING A NYLON BACKUP FILTER.

FIGURE 3.13

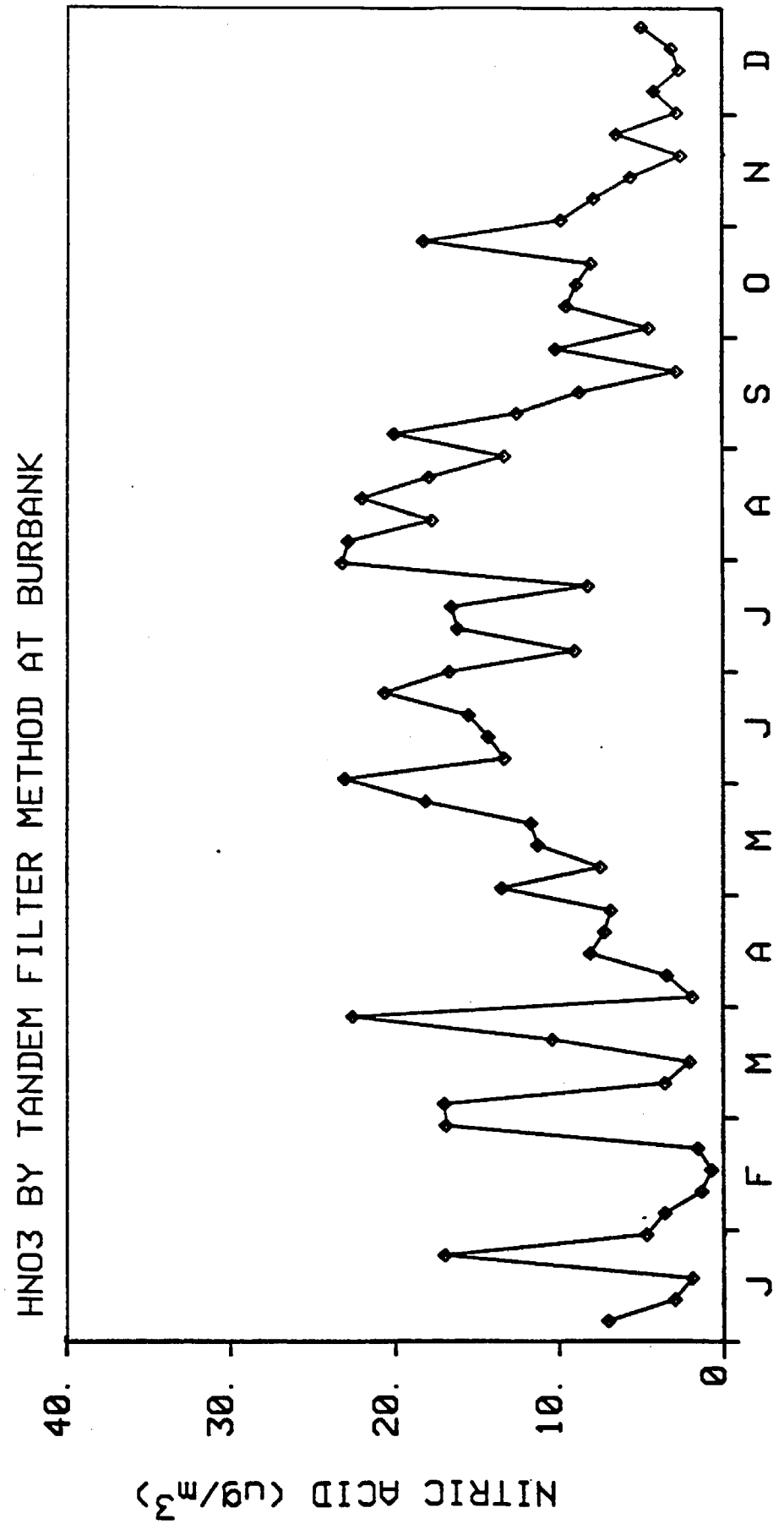

HNO3 BY TANDEM FILTER METHOD AT BURBANK
NITRIC ACID (ug/m3)
40.
30.
20.
10.
0
J F M A M J J A S O N D
--1986--

FIGURE 3.14

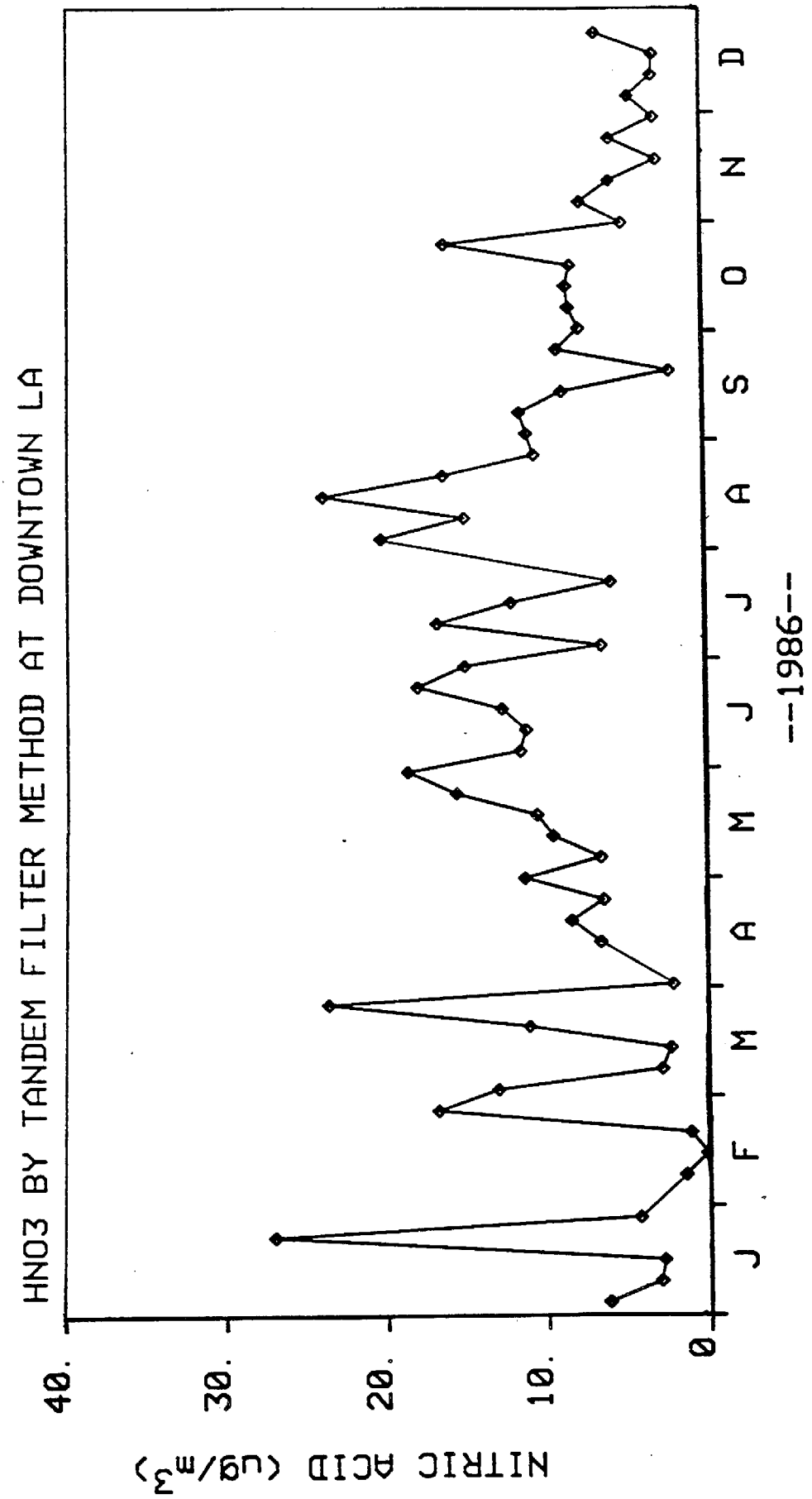

HNO3 BY TANDEM FILTER METHOD AT DOWNTOWN LA
NITRIC ACID (ug/m3)
40.
30.
20.
10.
0
J F M A M J J A S O N D
--1986--

FIGURE 3.15

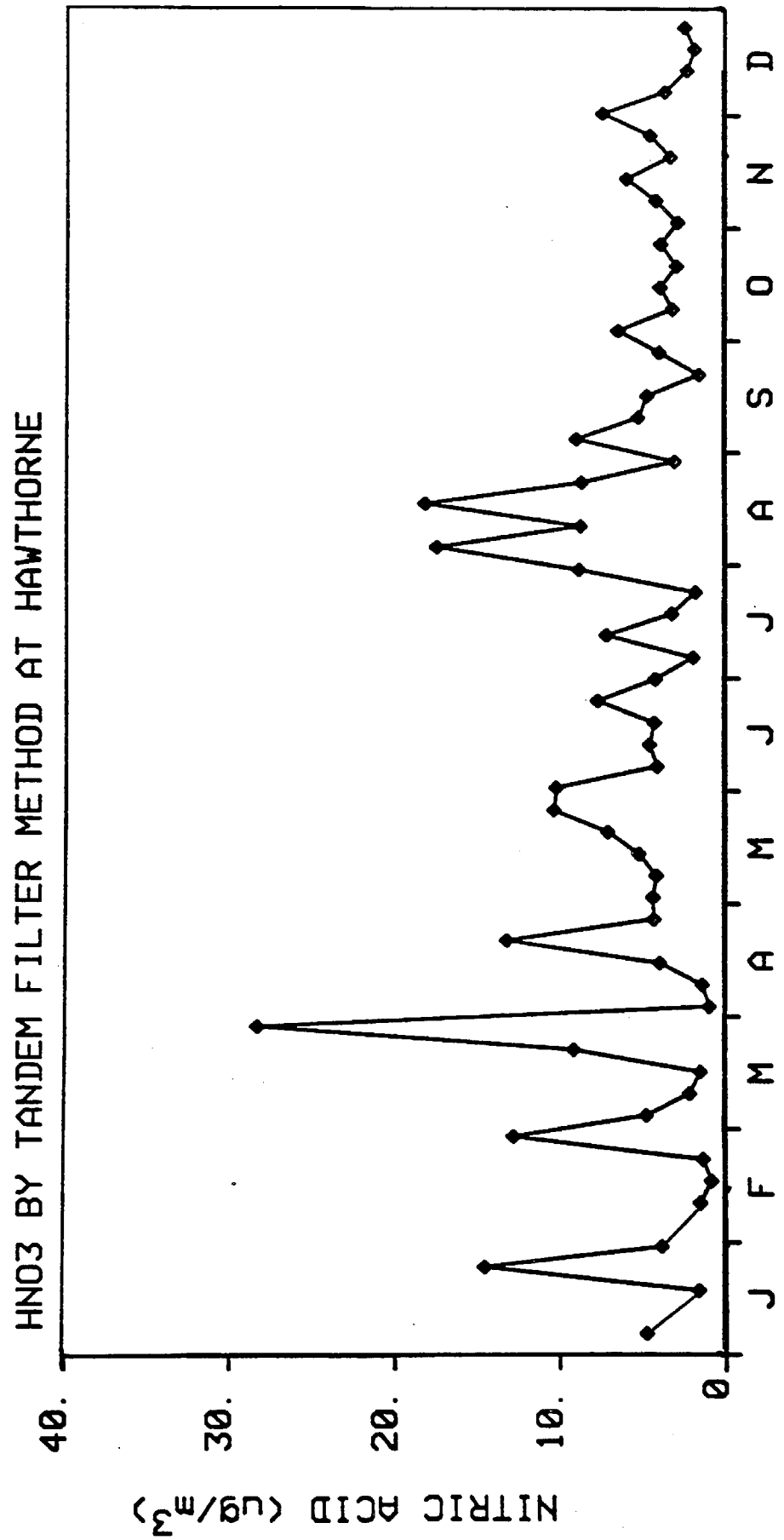

HNO3 BY TANDEM FILTER METHOD AT HAWTHORNE
NITRIC ACID (ug/m3)
40.
30.
20.
10.
0
J F M A M J J A S O N D
--1986--

FIGURE 3.16

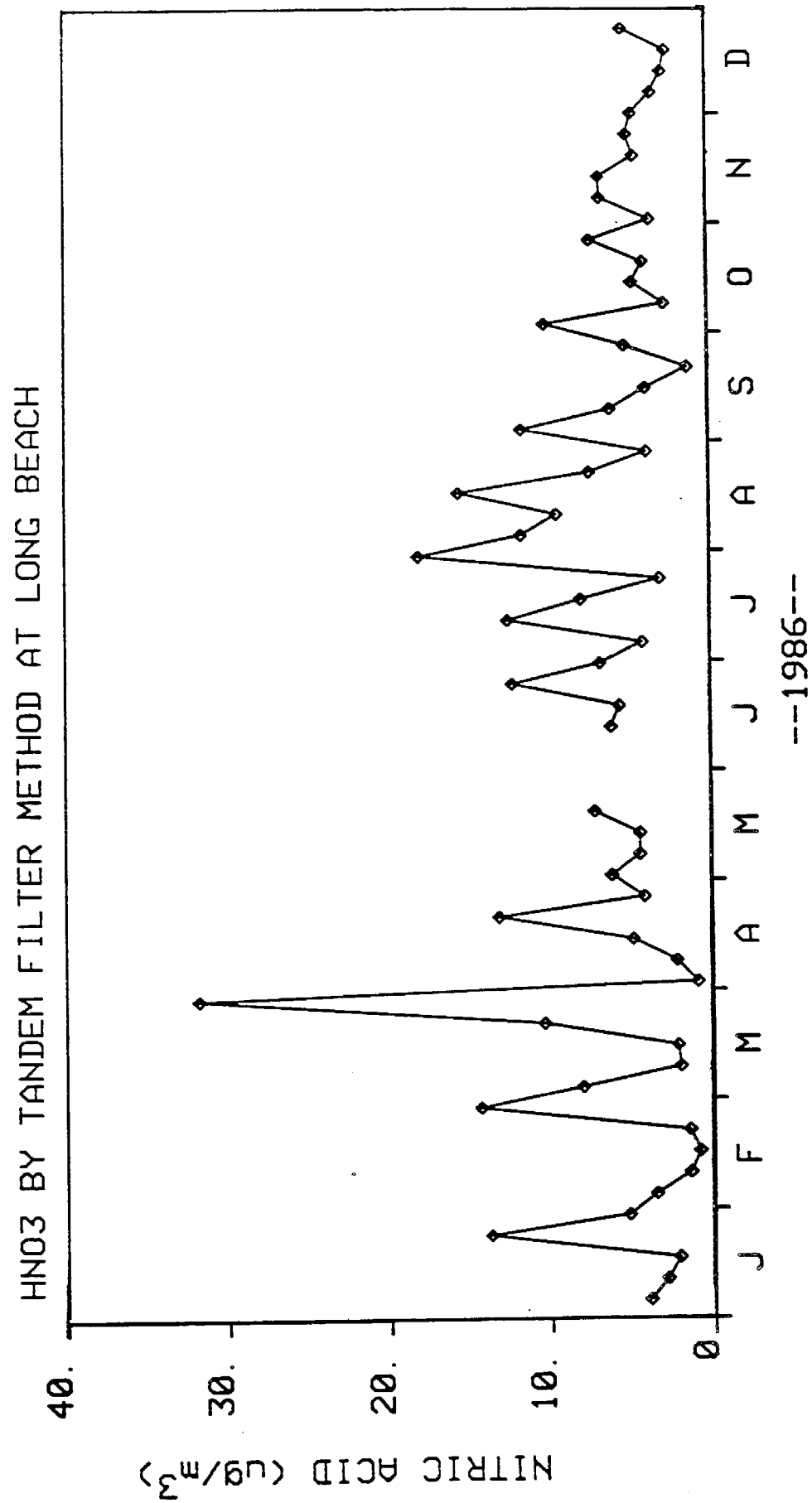

HNO3 BY TANDEM FILTER METHOD AT LONG BEACH
NITRIC ACID (ug/m3)
40.
30.
20.
10.
0
J F M A M J J A S O N D
--1986--

FIGURE 3.17

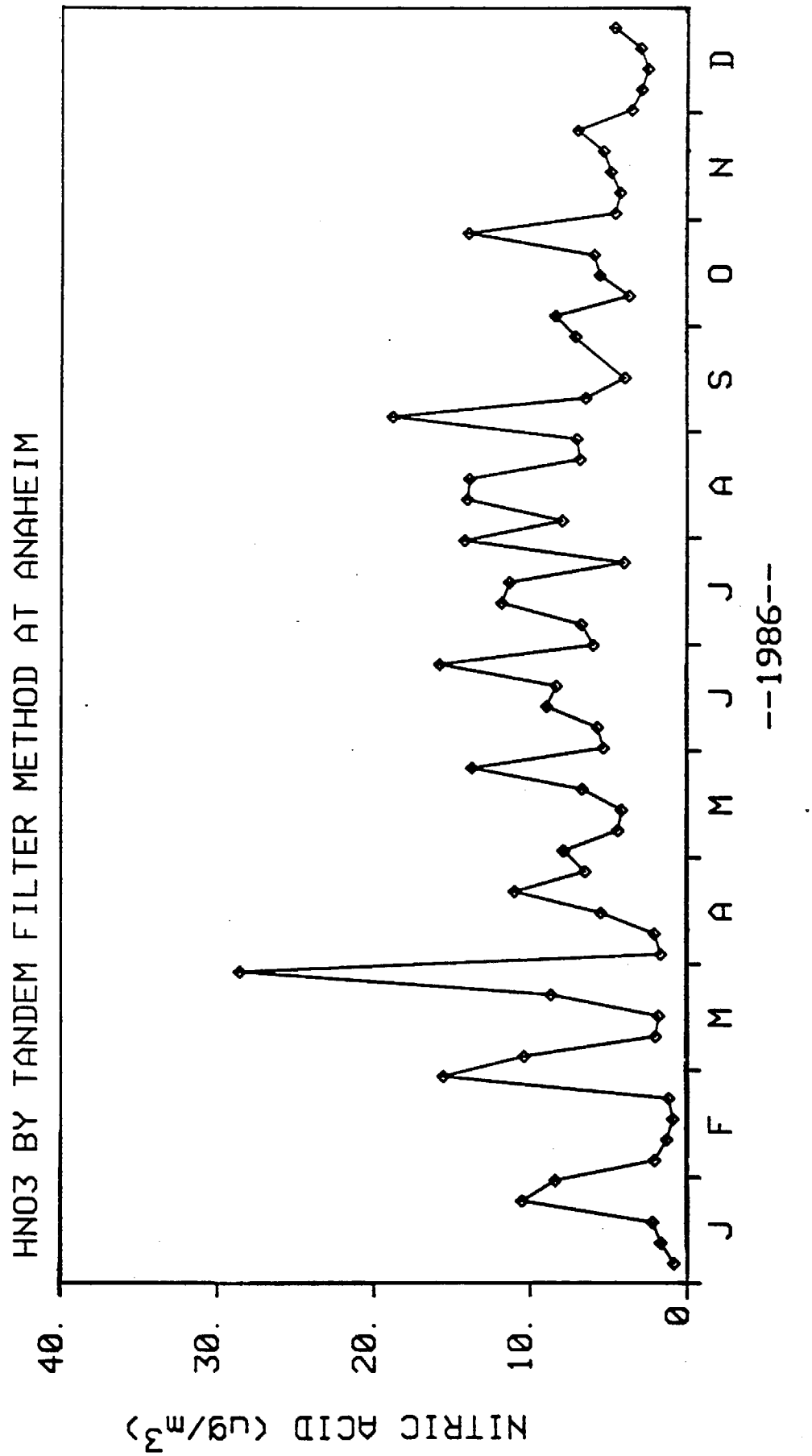

HNO3 BY TANDEM FILTER METHOD AT ANAHEIM
NITRIC ACID (ug/m3)
40.
30.
20.
10.
0
J F M A M J J A S O N D
--1986--

FIGURE 3.18

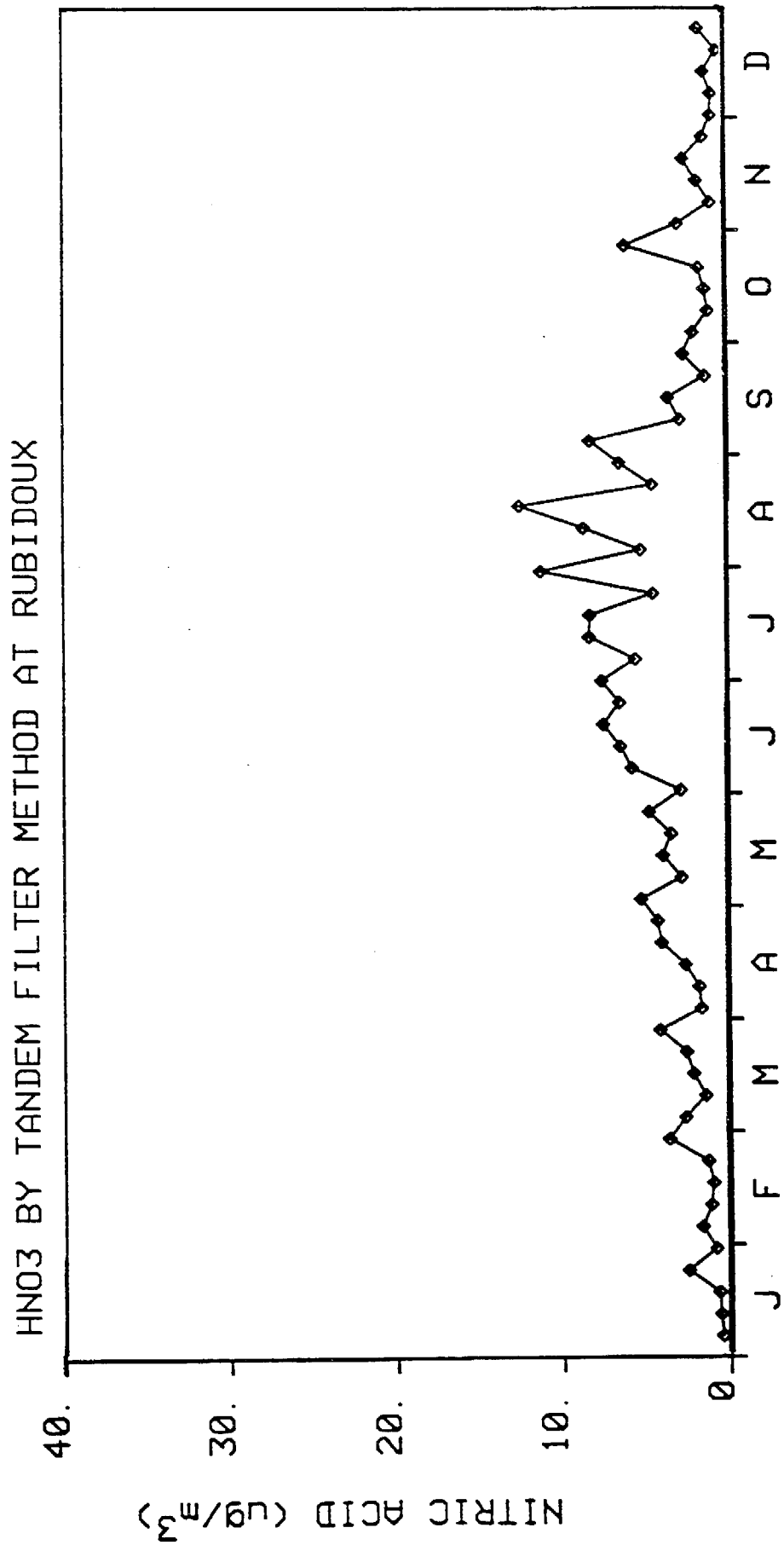

HNO3 BY TANDEM FILTER METHOD AT RUBIDOUX
NITRIC ACID (ug/m3)
40.
30.
20.
10.
0
J F M A M J J A S O N D
--1986--

FIGURE 3.19

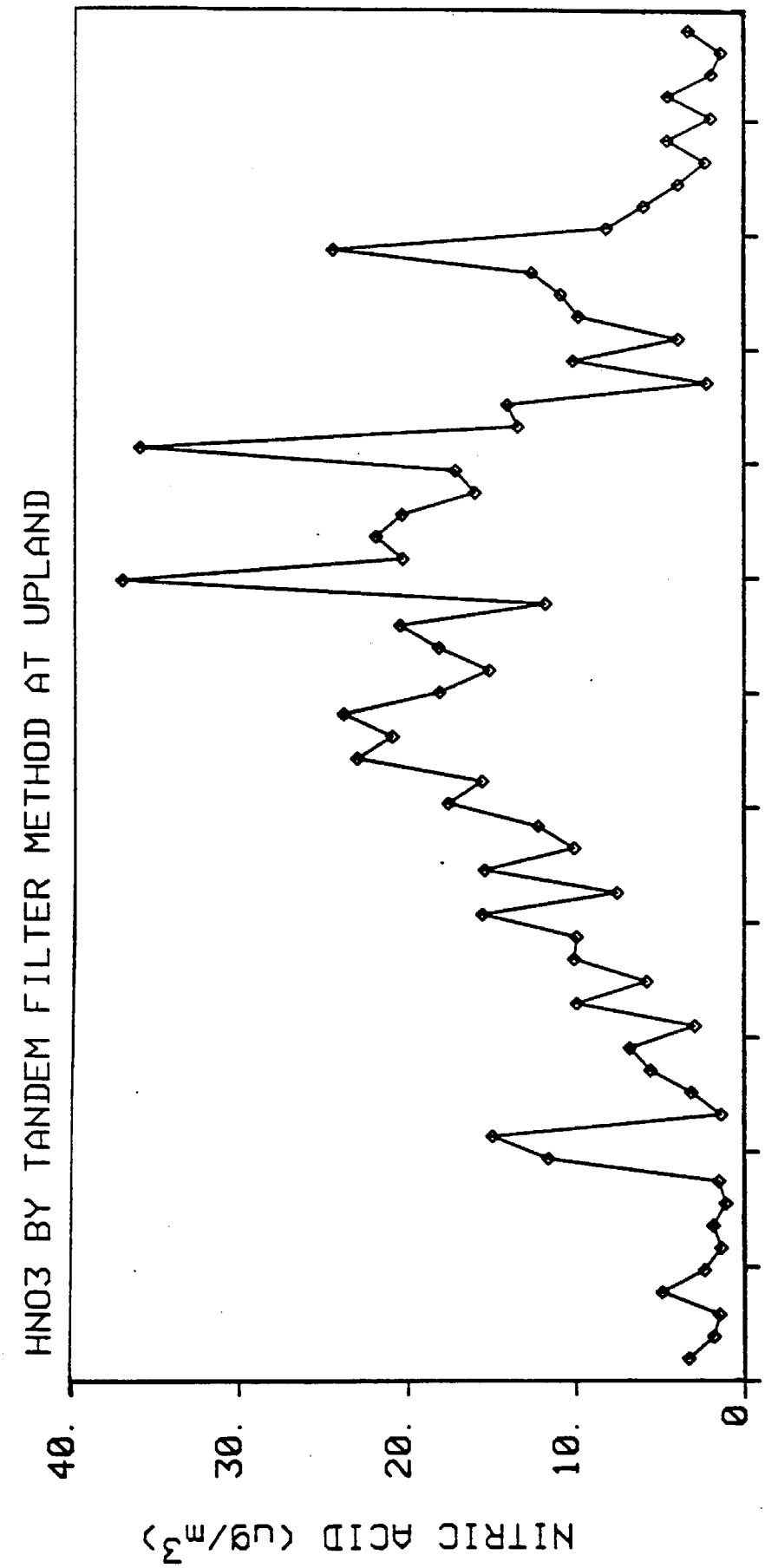

HNO3 BY TANDEM FILTER METHOD AT UPLAND
NITRIC ACID (ug/m3)
40.
30.
20.
10.
0
J F M A M J J A S O N D
--1986--

FIGURE 3.20

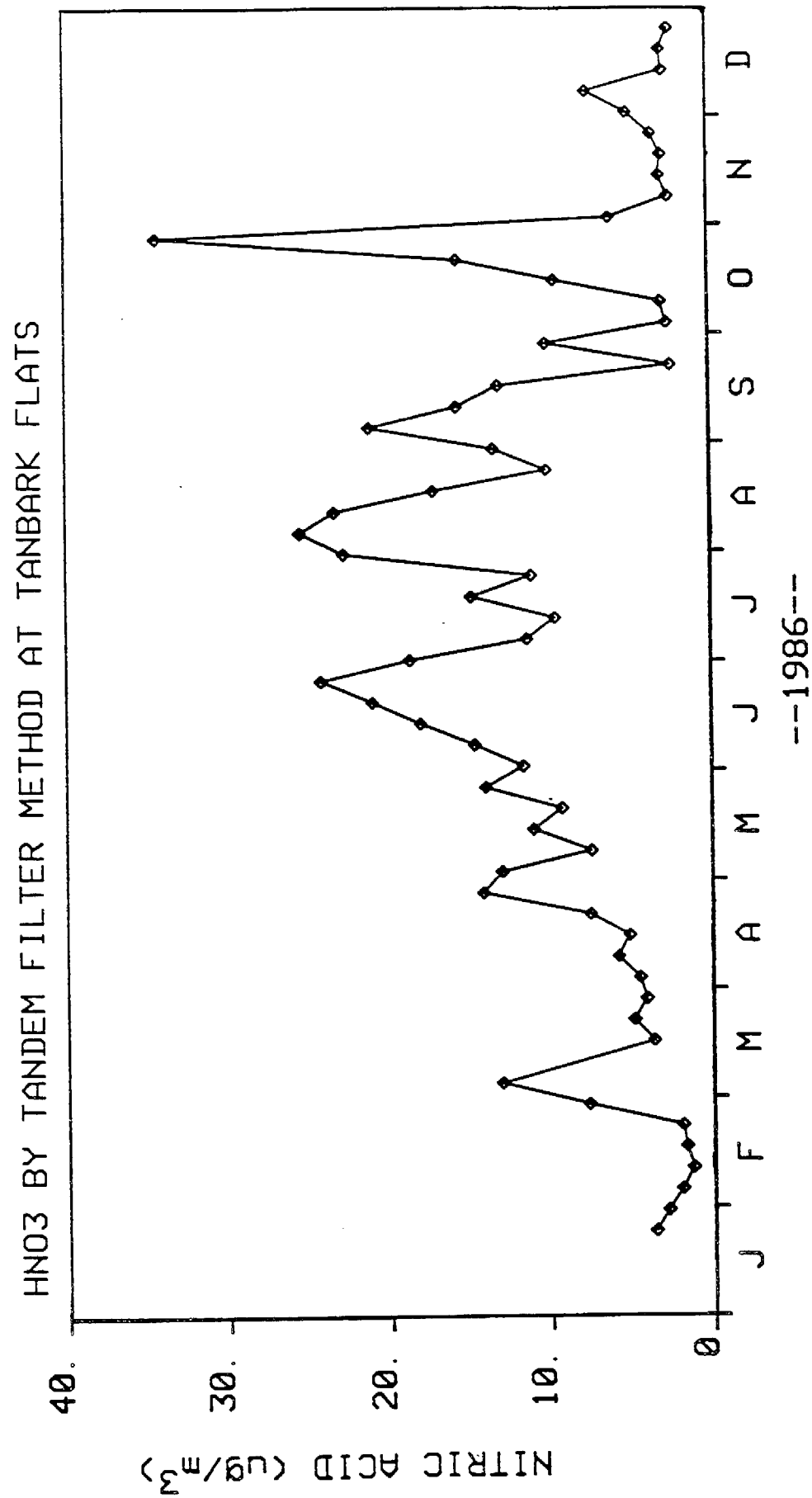

HNO3 BY TANDEM FILTER METHOD AT TANBARK FLATS
NITRIC ACID (ug/m3)
40.
30.
20.
10.
0
J F M A M J J A S O N D
--1986--

FIGURE 3.21

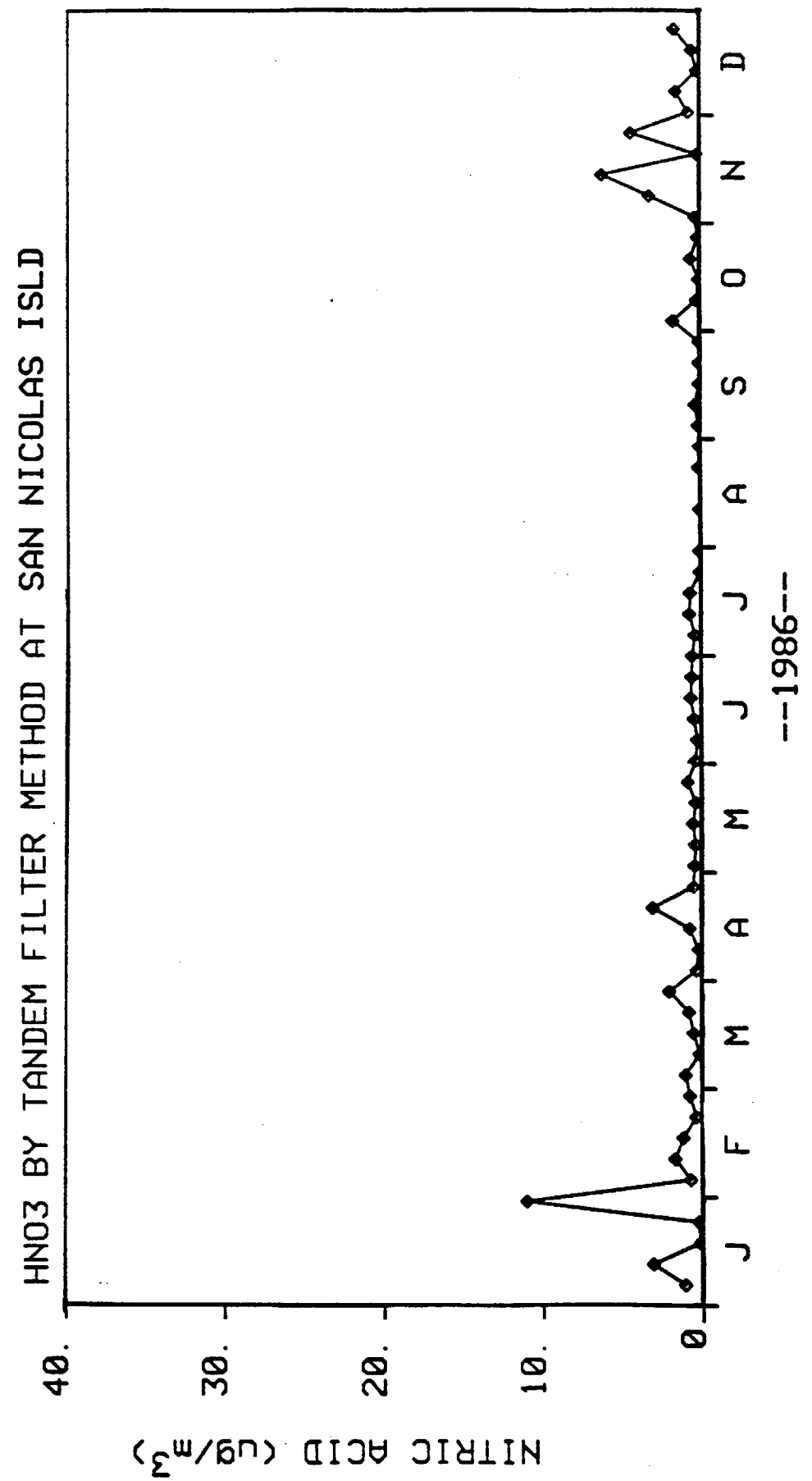

HNO3 BY TANDEM FILTER METHOD AT SAN NICOLAS ISLD
NITRIC ACID (ug/m3)
40.
30.
20.
10.
0
J F M A M J J A S O N D
--1986--

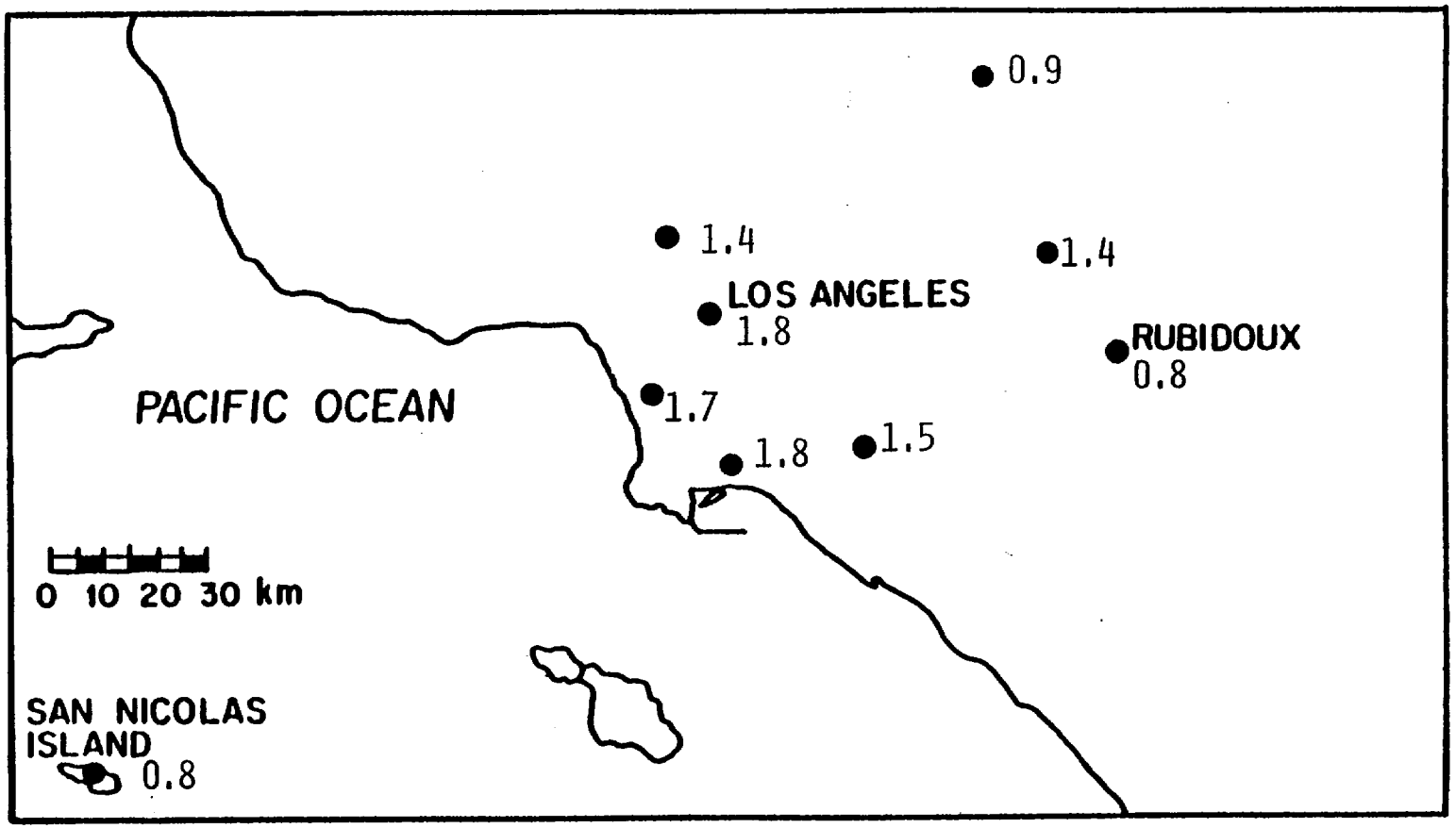
FIGURE 3.22

Table 3.2. Gas phase HCl and HF concentrations observed in the Los Angeles area, 1986 (concentrations in $\mu g\ m^{-3}$)

	HCl[a]			HF[b]		
Site	Annual Average	Max. 24-h Average	n[c]	8-Month Average[d]	Max. 24-h Average	n[e]
Burbank	1.4	4.2	61	0.16	0.51	38
Downtown LA	1.8	5.2	57	0.14	0.37	38
Hawthorne	1.7	5.5	59	0.16	1.33	38
Long Beach	1.8	6.3	58	0.16	0.50	37
Anaheim	1.5	5.3	58	0.16	0.58	38
Rubidoux	0.8	4.6	59	0.22	1.91	38
Upland	1.4	4.3	59	0.18	0.36	36
Tanbark Flats	0.9	3.3	57	0.18	0.34	38
San Nicolas Island	0.8	2.4	57	0.13	0.62	36

a. By tandem filter method employing nylon or KOH impregnated backup filters.
b. By tandem filter method employing KOH impregnated backup filters.
c. Maximum number of sampling events is 61.
d. May-December, 1986.
e. Maximum number of sampling events is 40.

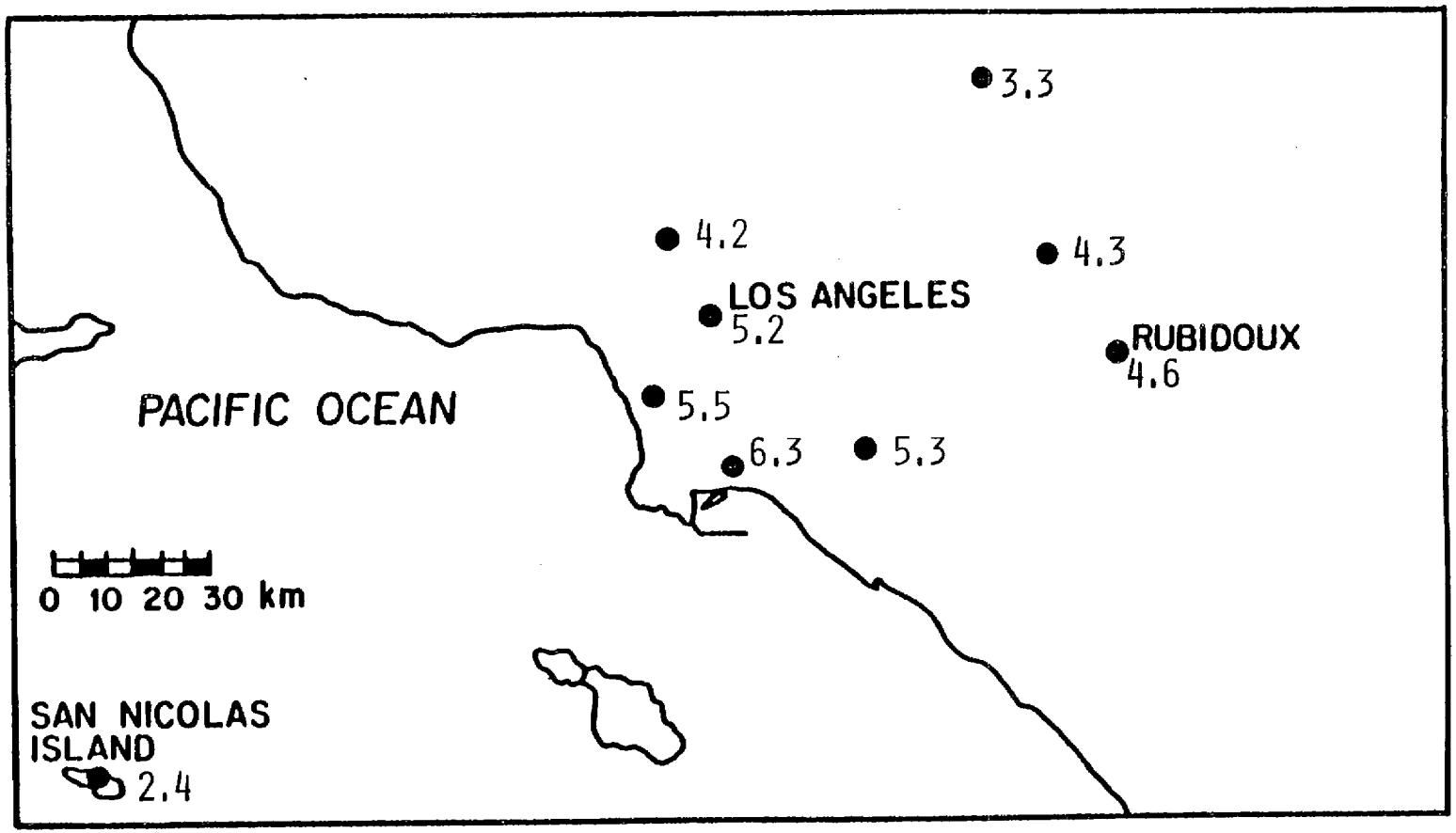
ANNUAL AVERAGE HCL CONCENTRATIONS ($\mu g\ m^{-3}$) OBSERVED IN THE LOS ANGELES AREA, 1986.[A]



[A]HCL BY TANDEM FILTER METHOD EMPLOYING NYLON OR KOH IMPREGNATED BACKUP FILTERS.

FIGURE 3.23

MAXIMUM 24-HOUR HCL CONCENTRATIONS ($\mu g\ m^{-3}$) OBSERVED IN THE LOS ANGELES AREA, 1986.[A]



[A]HCL BY TANDEM FILTER METHOD EMPLOYING NYLON OR KOH IMPREGNATED BACKUP FILTERS.

FIGURE 3.24

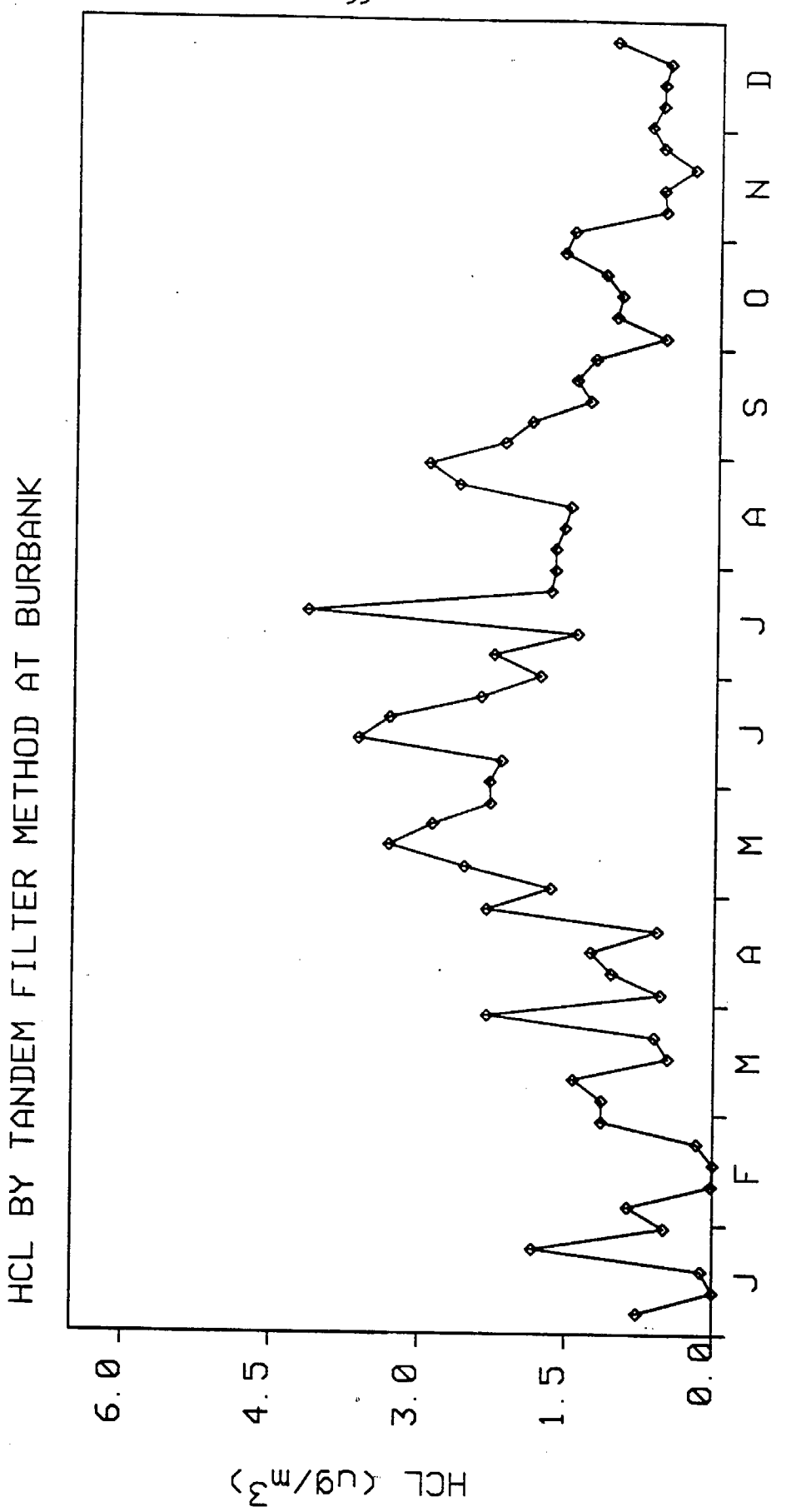

HCL BY TANDEM FILTER METHOD AT BURBANK
HCL (ug/m3)
6.0
4.5
3.0
1.5
0.0
J F M A M J J A S O N D
--1986--

FIGURE 3.25

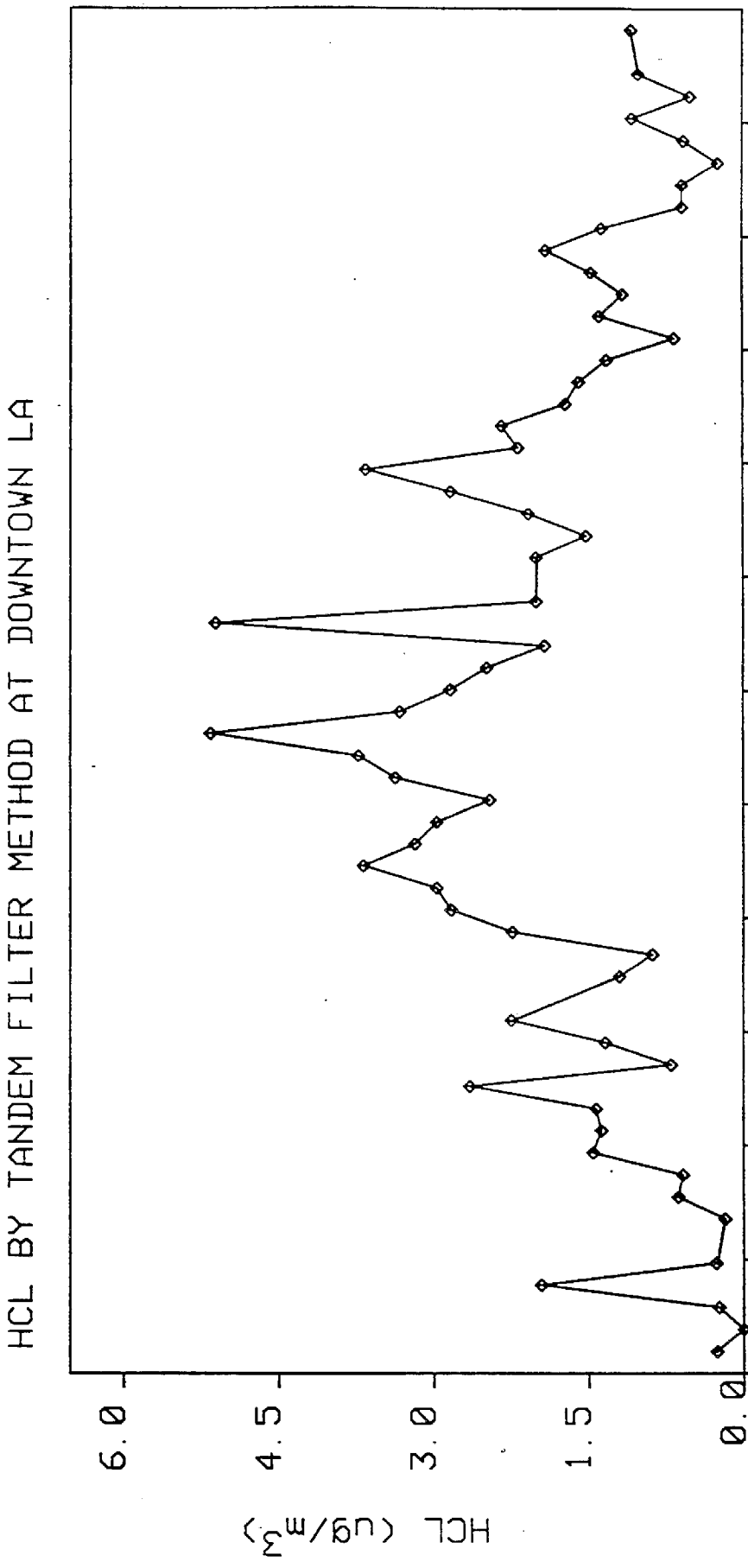

HCL BY TANDEM FILTER METHOD AT DOWNTOWN LA
HCL (ug/m3)
6.0
4.5
3.0
1.5
0.0
J F M A M J J A S O N D
--1986--

FIGURE 3.26

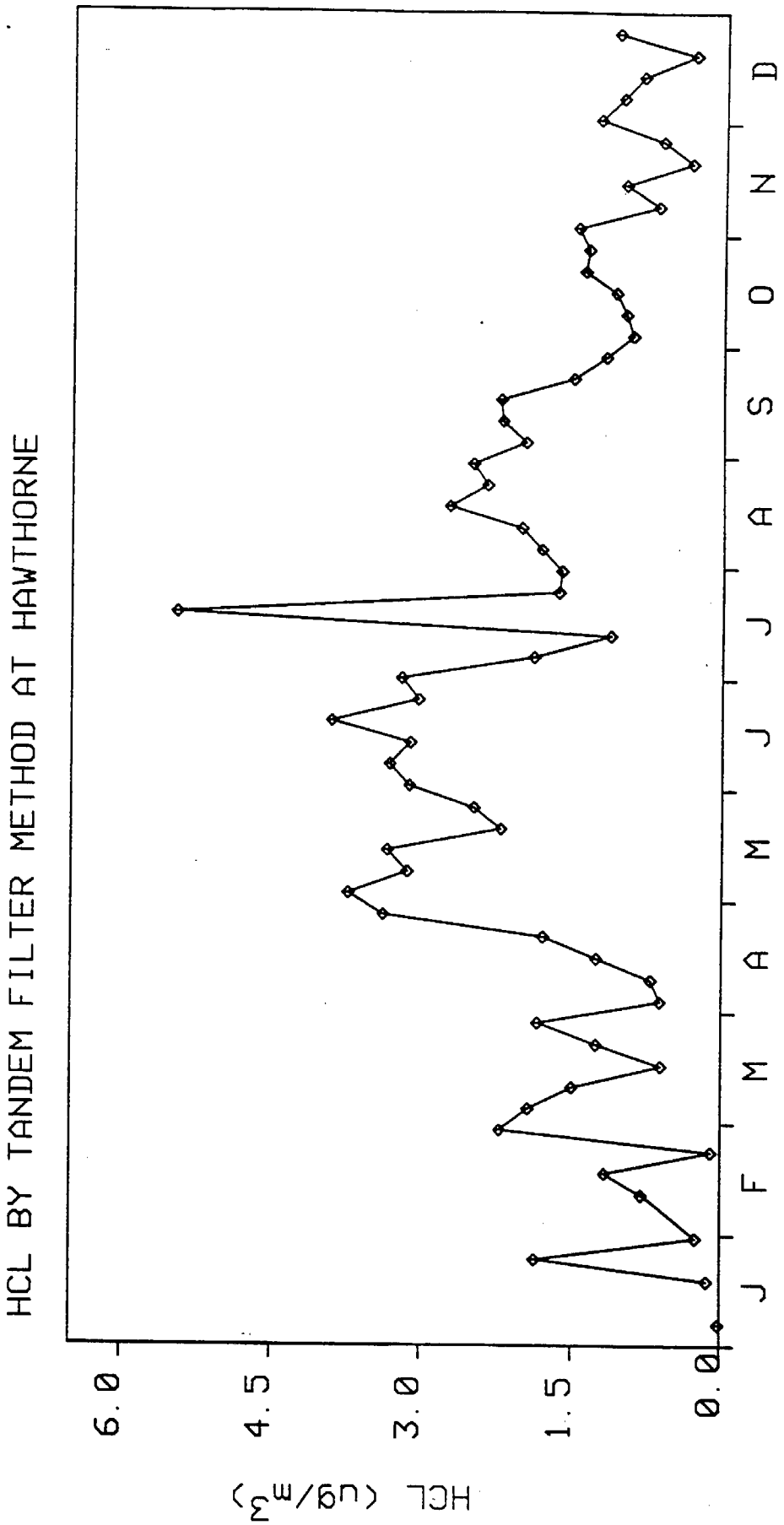

HCL BY TANDEM FILTER METHOD AT HAWTHORNE
HCL (ug/m3)
6.0
4.5
3.0
1.5
0.0
J F M A M J J A S O N D
--1986--

FIGURE 3.27

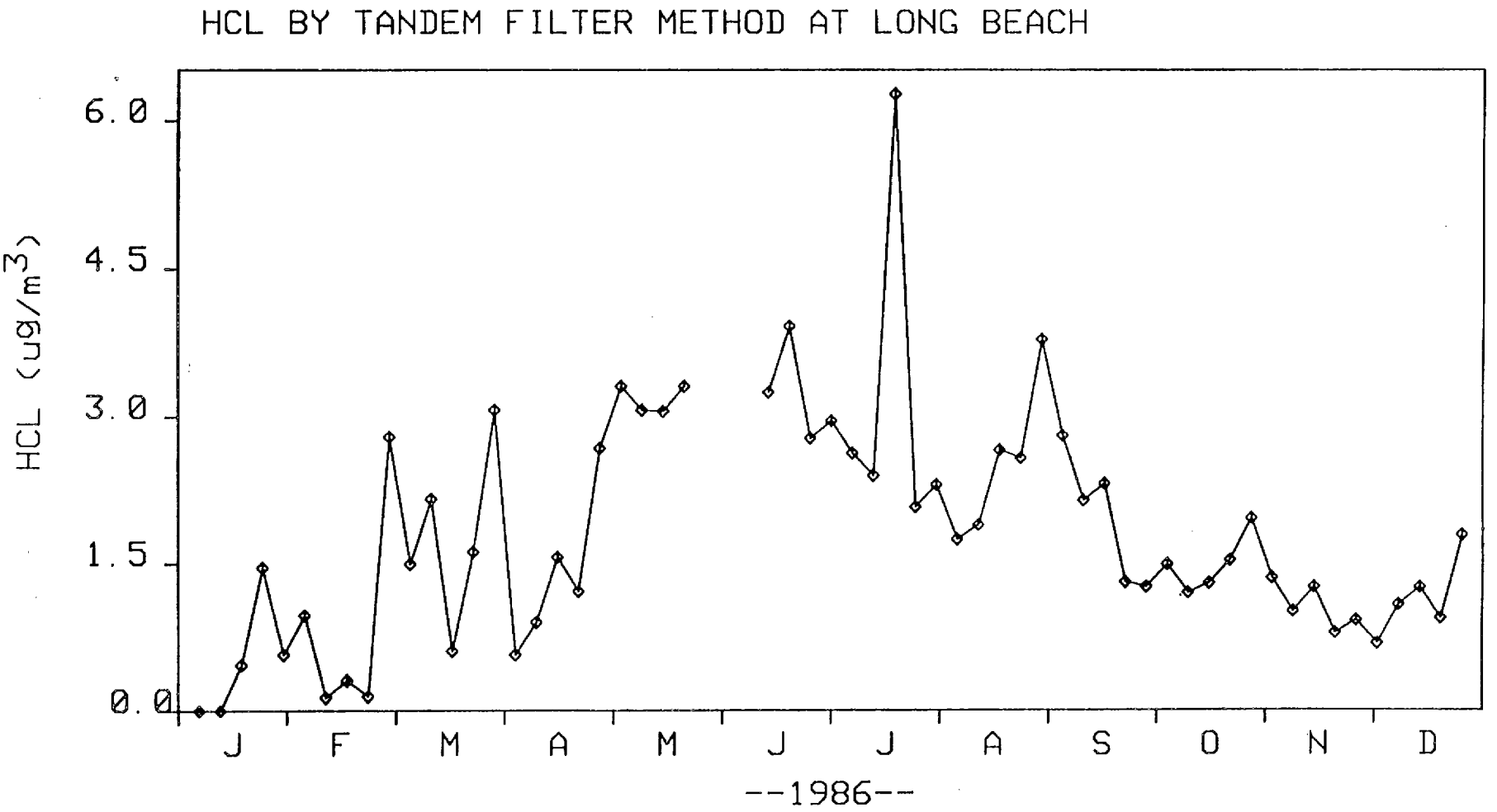

HCL BY TANDEM FILTER METHOD AT LONG BEACH
HCL (ug/m3)
6.0
4.5
3.0
1.5
0.0
J
F
M
A
M
J
J
A
S
O
N
D
--1986--

FIGURE 3.28

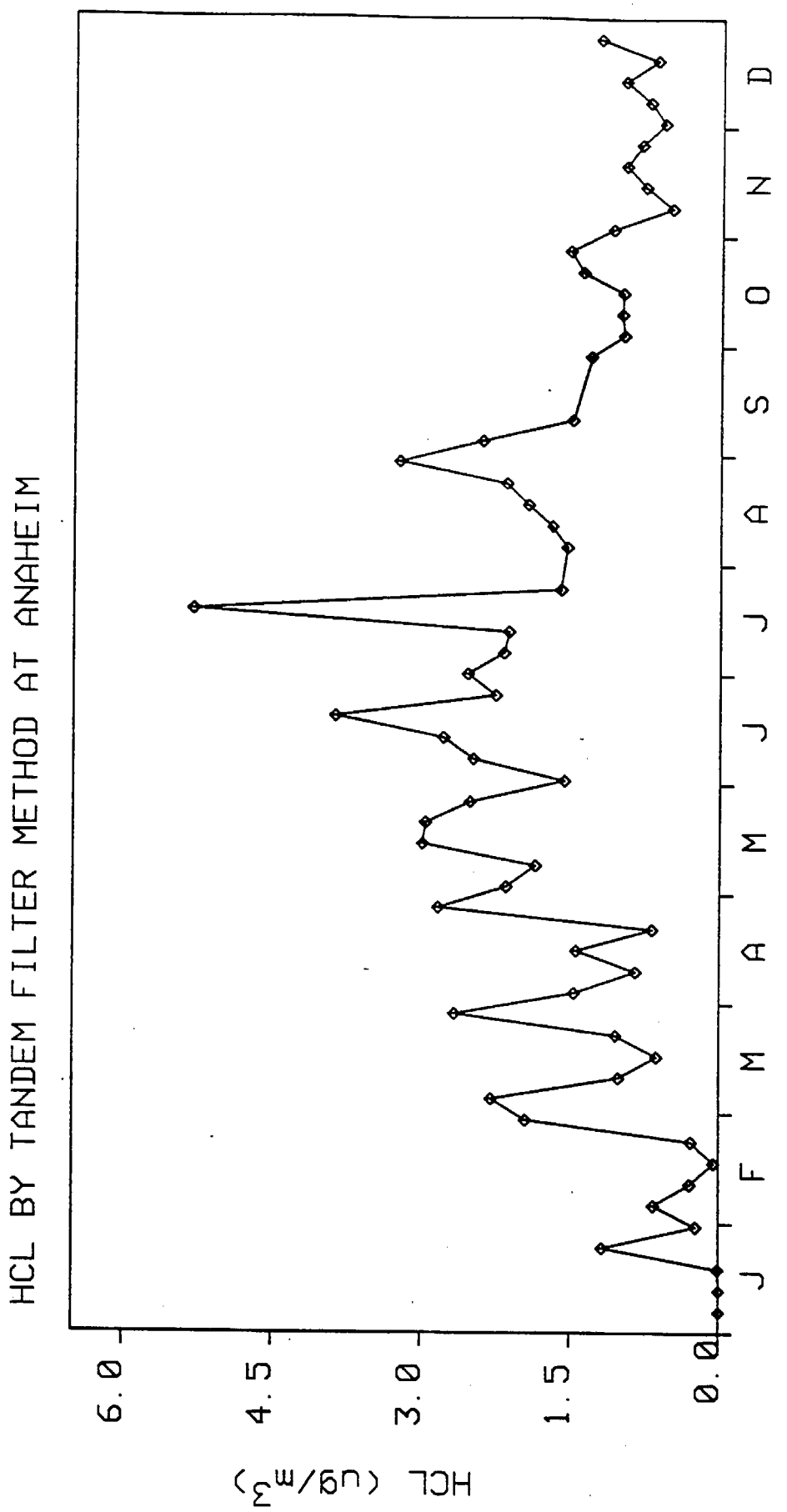

HCL BY TANDEM FILTER METHOD AT ANAHEIM
HCL (ug/m3)
6.0
4.5
3.0
1.5
0.0
J F M A M J J A S O N D
--1986--

FIGURE 3.29

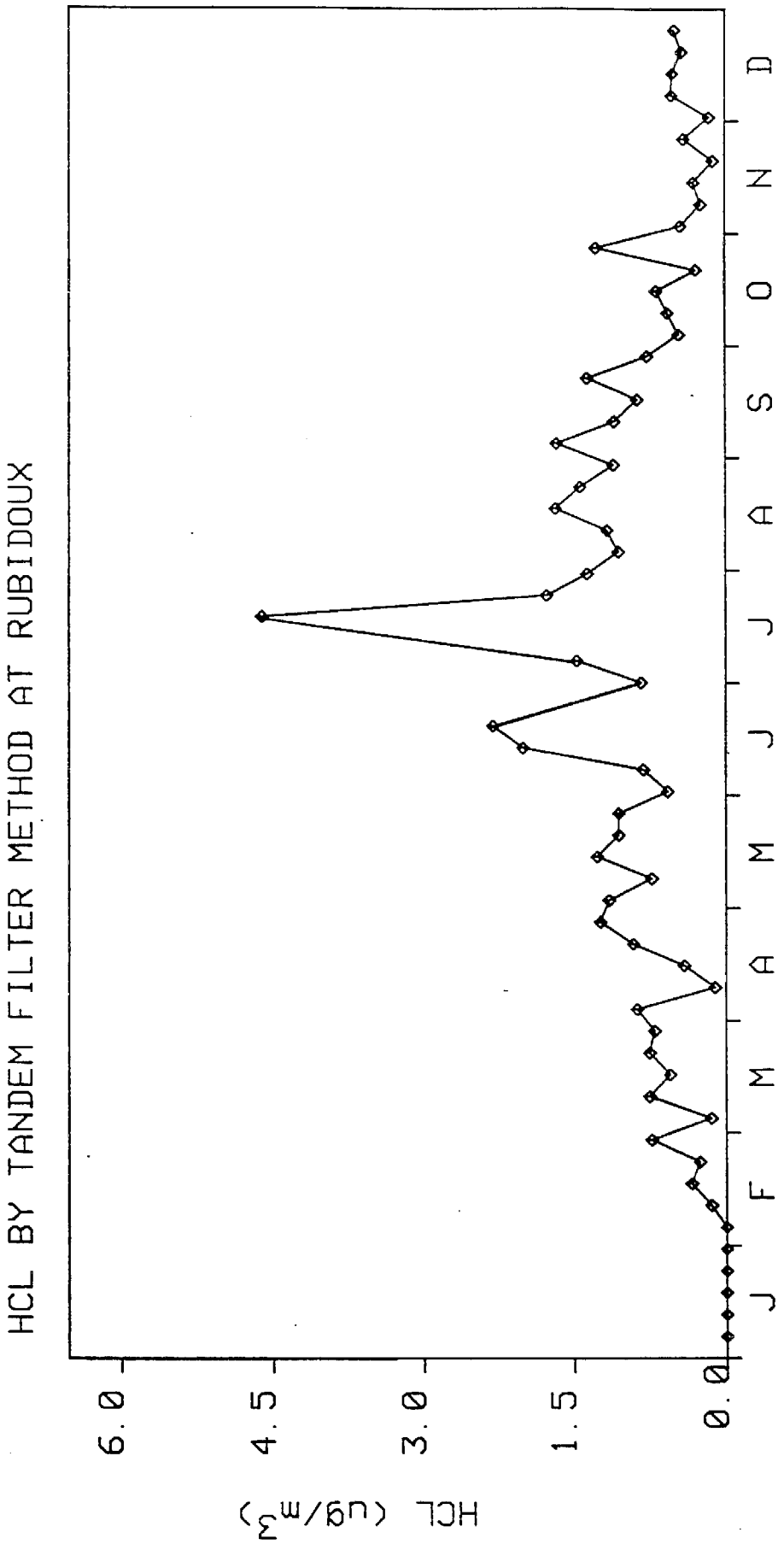

HCL BY TANDEM FILTER METHOD AT RUBIDOUX
HCL (ug/m3)
6.0
4.5
3.0
1.5
0.0
J F M A M J J A S O N D
--1986--

FIGURE 3.30

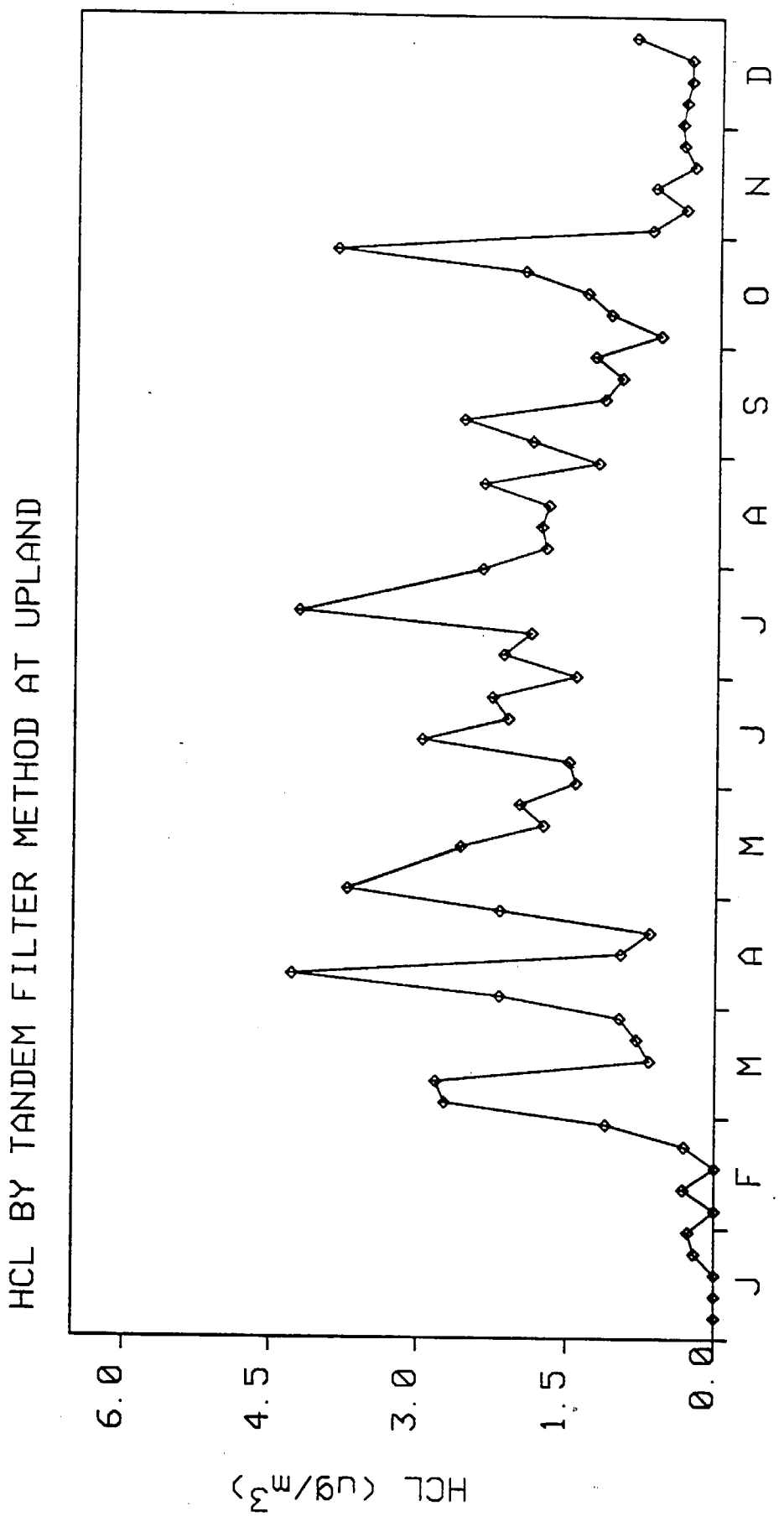

HCL BY TANDEM FILTER METHOD AT UPLAND
HCL (ug/m3)
6.0
4.5
3.0
1.5
0.0
J F M A M J J A S O N D
--1986--

FIGURE 3.31

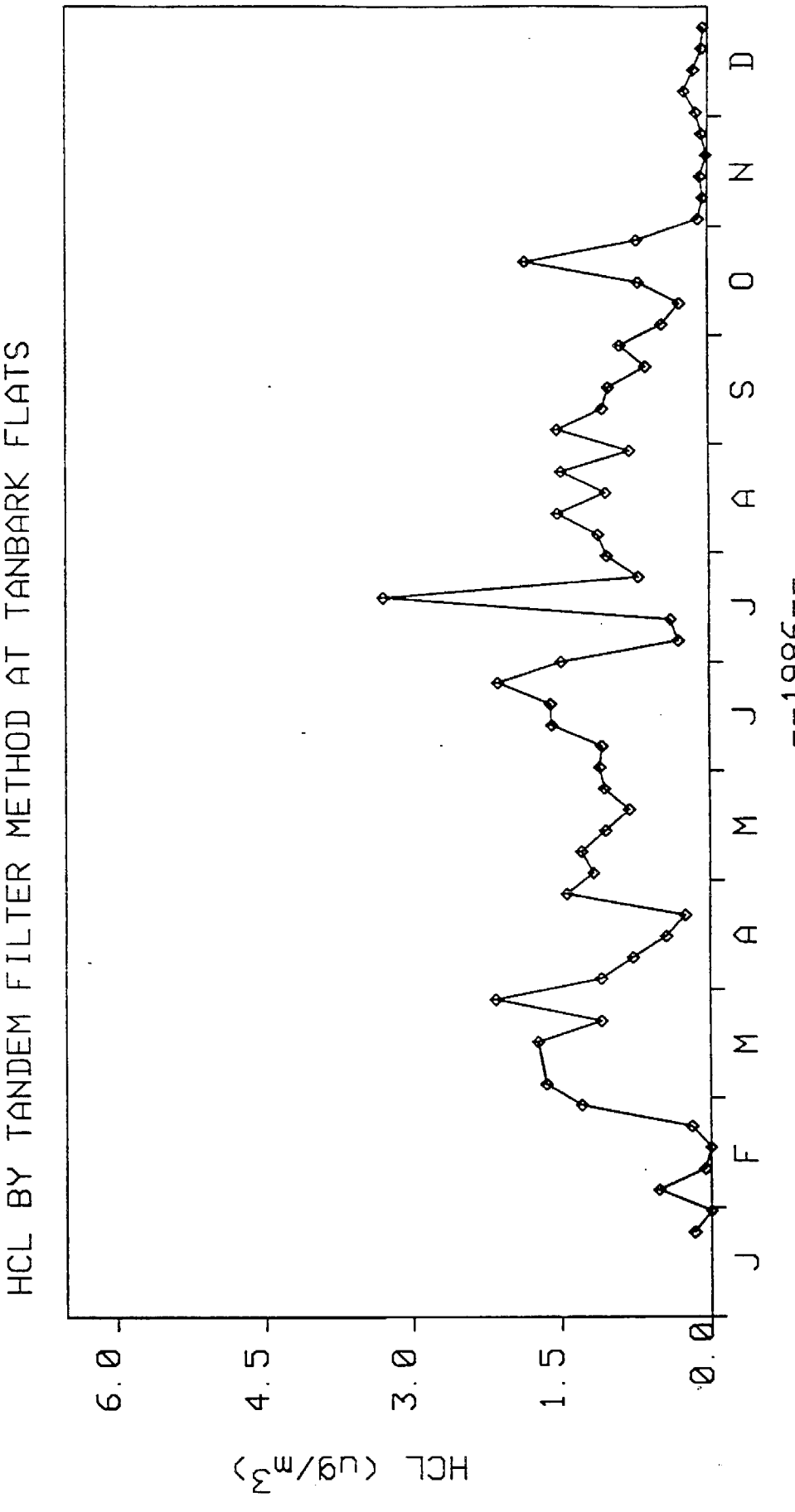

HCL BY TANDEM FILTER METHOD AT TANBARK FLATS
HCL (ug/m3)
6.0
4.5
3.0
1.5
0.0
J F M A M J J A S O N D
--1986--

FIGURE 3.32

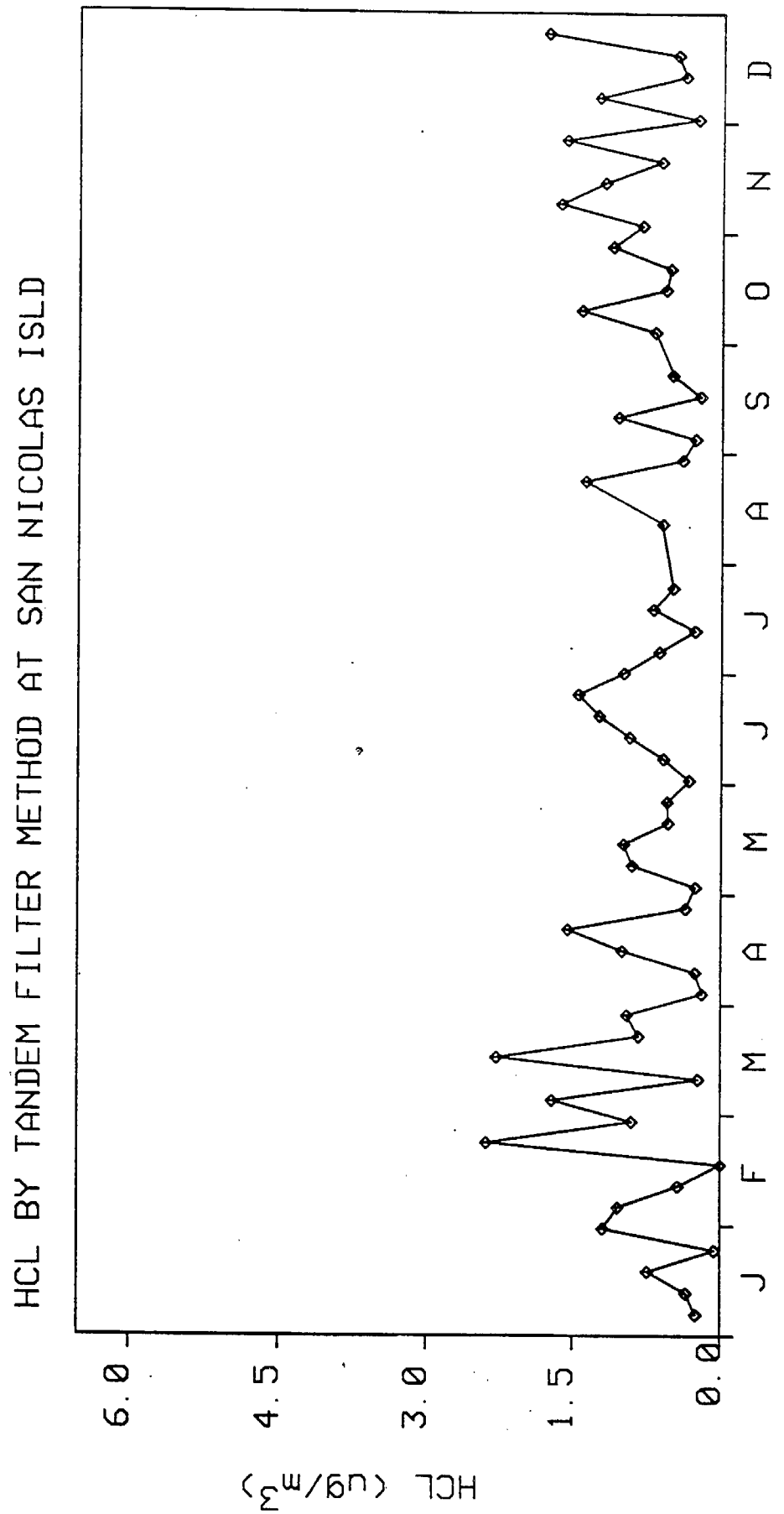
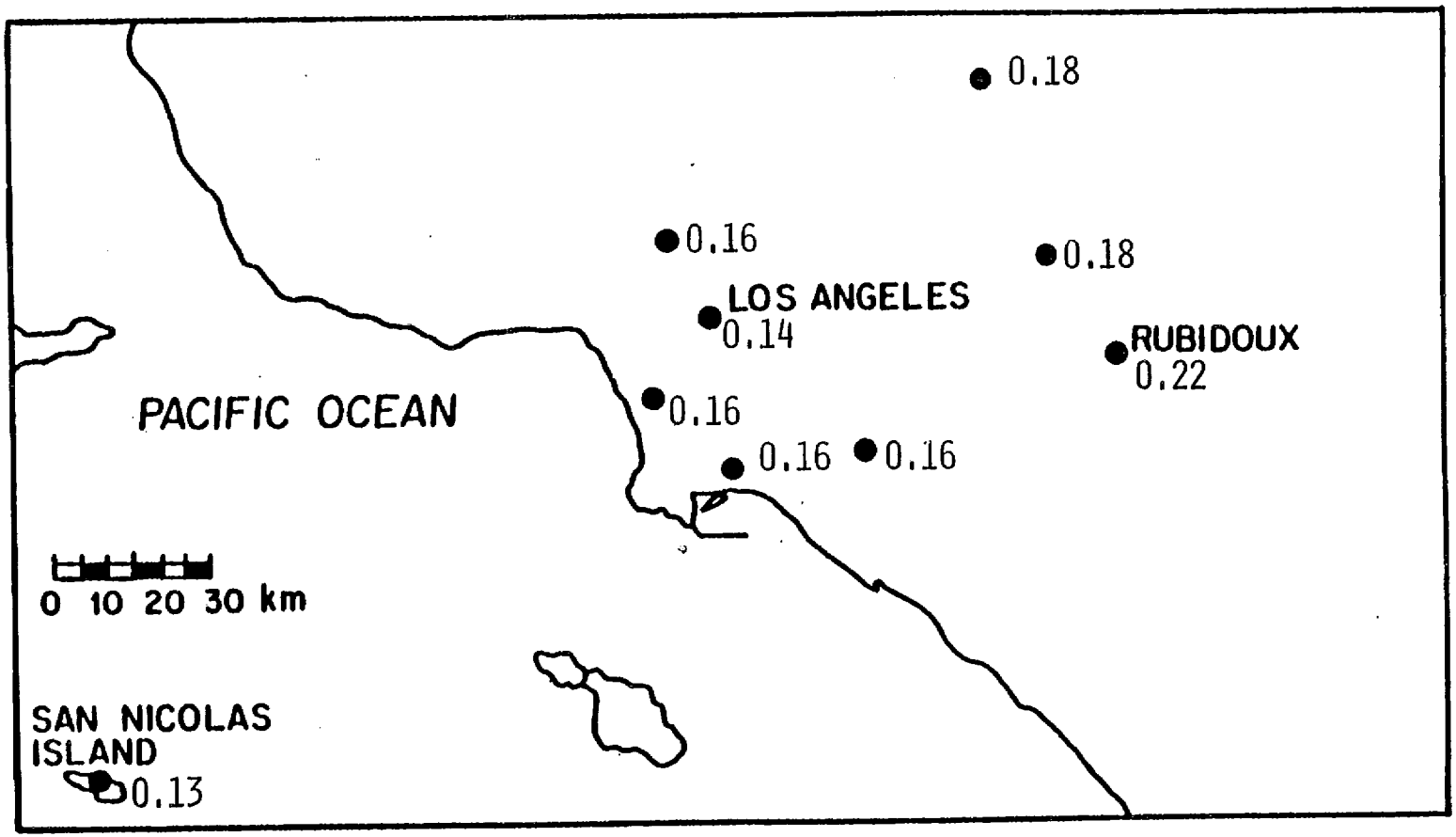

HCL BY TANDEM FILTER METHOD AT SAN NICOLAS ISLD
HCL (ug/m3)
6.0
4.5
3.0
1.5
0.0
J F M A M J J A S O N D
--1986--

FIGURE 3.33

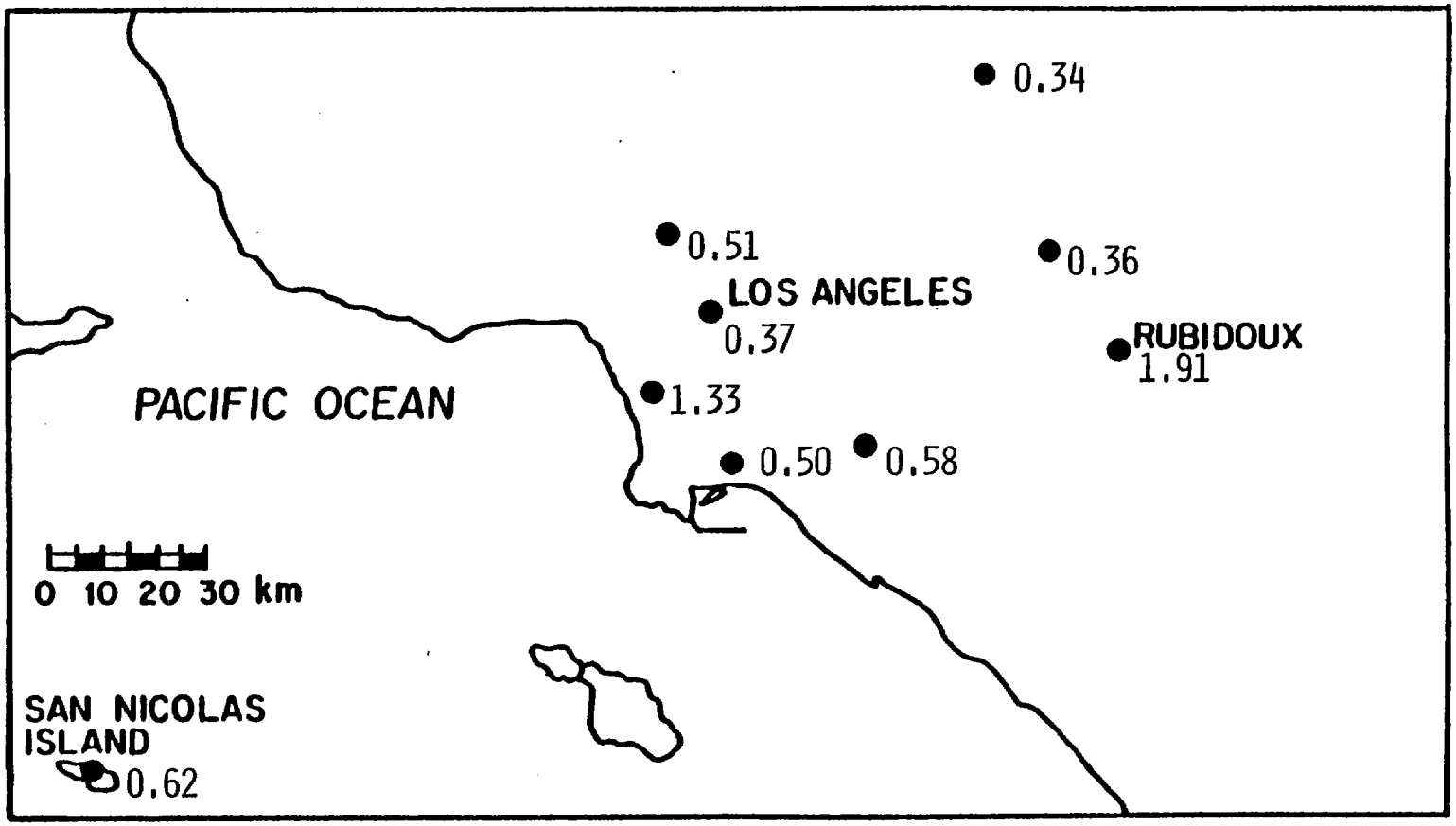
ANNUAL AVERAGE HF CONCENTRATIONS ($\mu g\ m^{-3}$) OBSERVED IN THE LOS ANGELES AREA, 1986.[A]



[A]HF BY TANDEM FILTER METHOD EMPLOYING KOH IMPREGNATED FILTERS.

FIGURE 3.34

MAXIMUM 24-HOUR AVERAGE HF CONCENTRATIONS ($\mu g\ m^{-3}$) OBSERVED IN THE LOS ANGELES AREA, 1986.[A]



[A]HF BY TANDEM FILTER METHOD EMPLOYING KOH IMPREGNATED FILTERS.

FIGURE 3.35

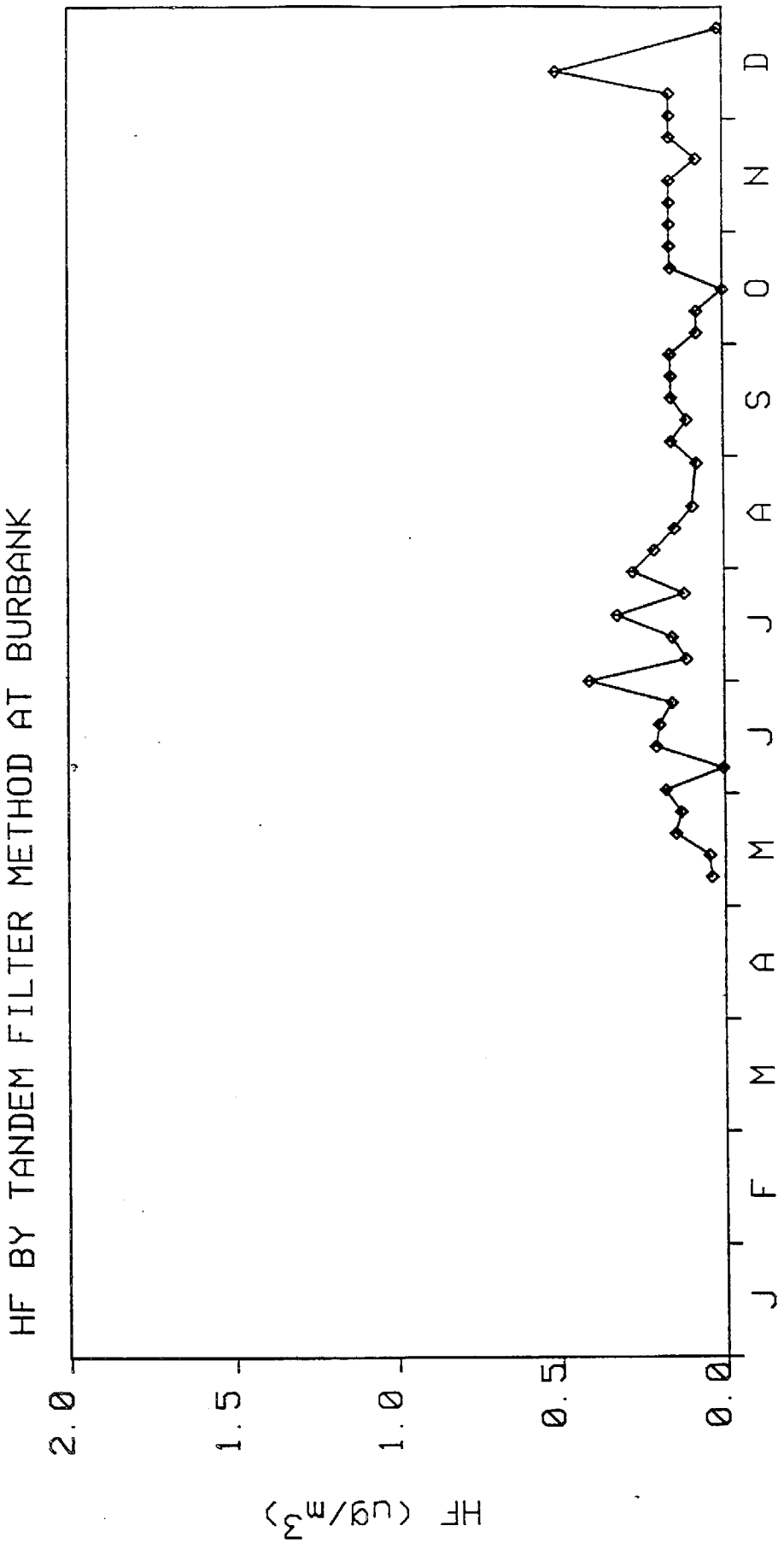

HF BY TANDEM FILTER METHOD AT BURBANK
HF (ug/m3)
2.0
1.5
1.0
0.5
0.0
J F M A M J J A S O N D
--1986--

FIGURE 3.36

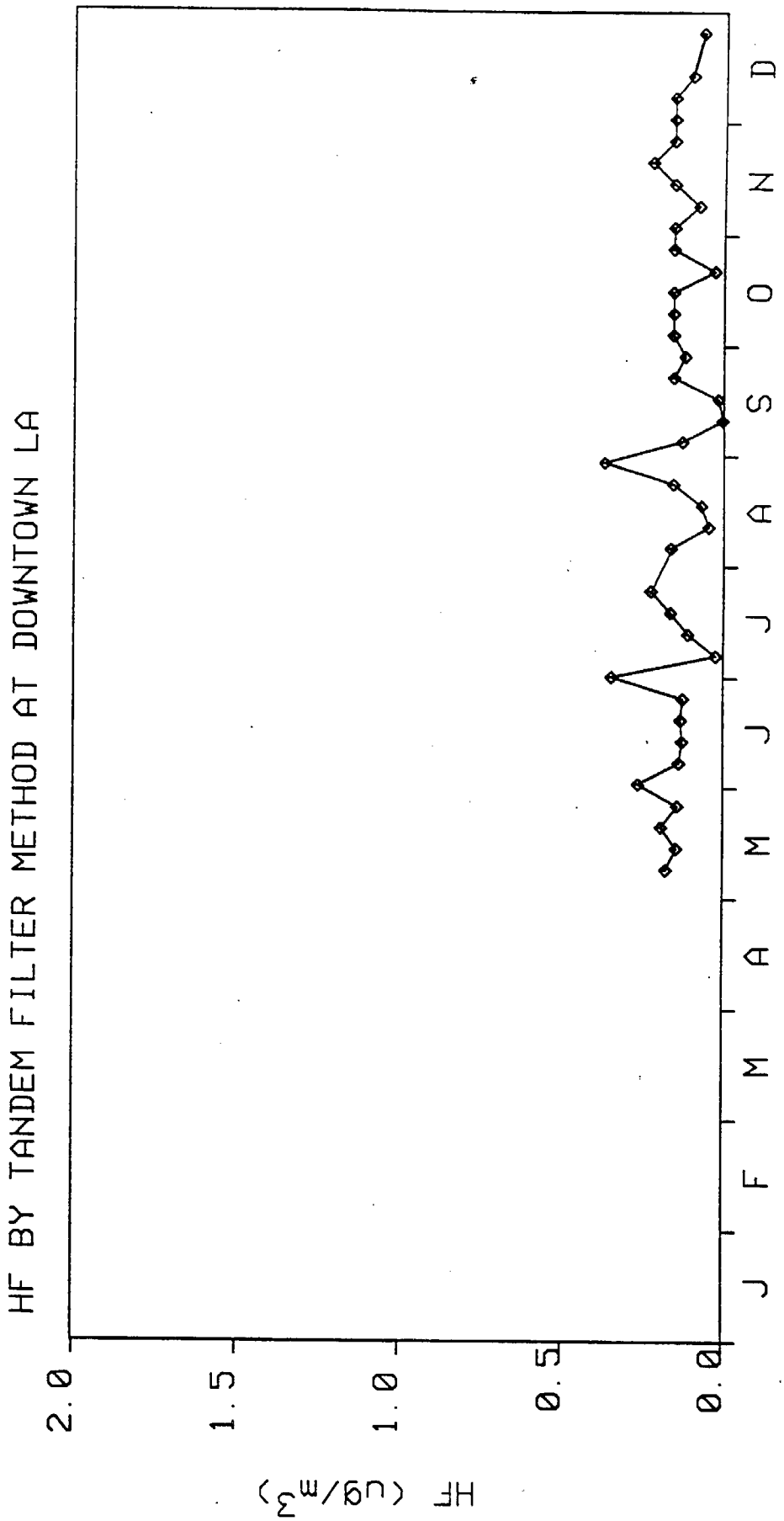

HF BY TANDEM FILTER METHOD AT DOWNTOWN LA
HF (ug/m3)
2.0
1.5
1.0
0.5
0.0
J F M A M J J A S O N D
--1986--

FIGURE 3.37

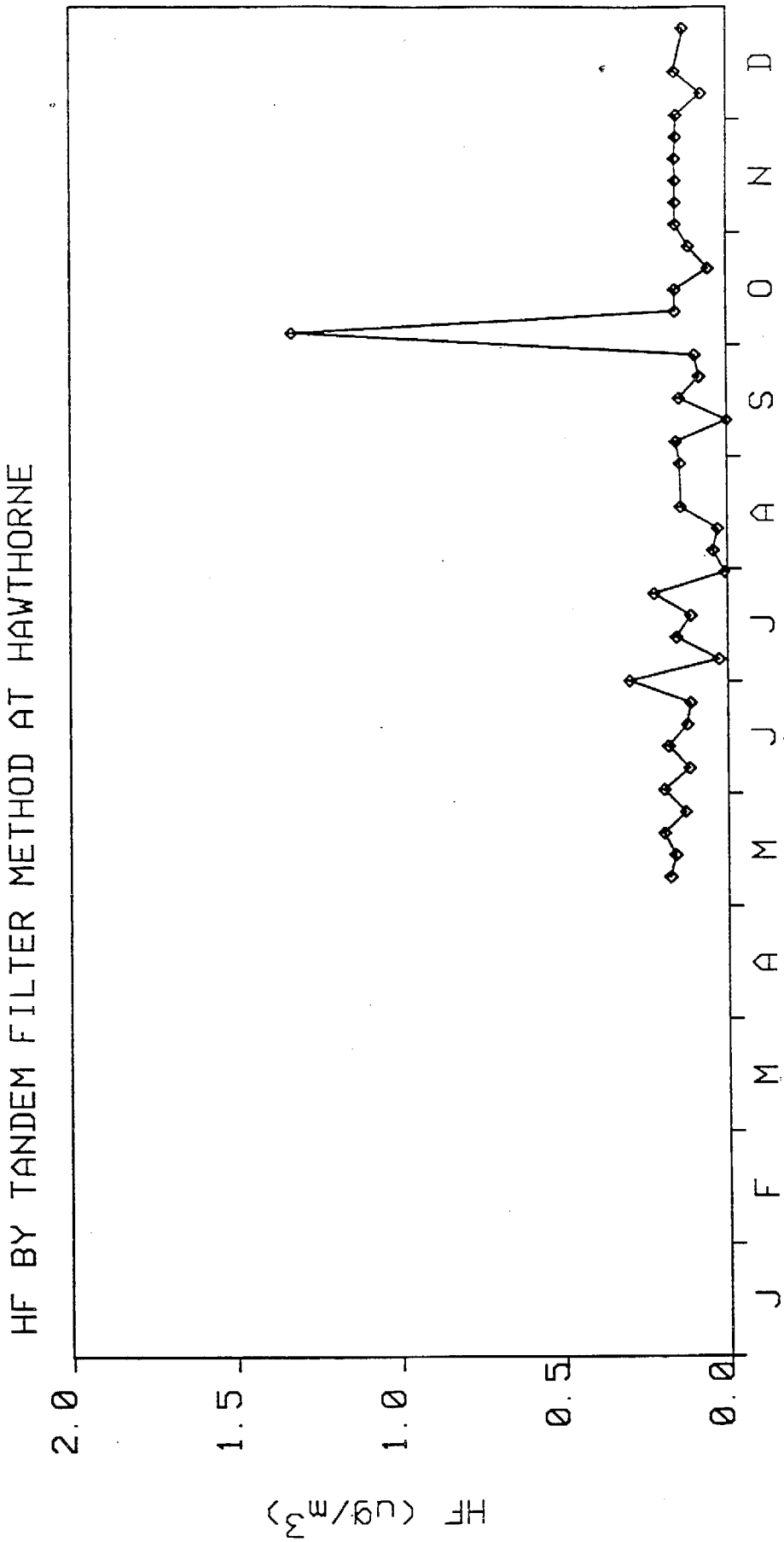

HF BY TANDEM FILTER METHOD AT HAWTHORNE
HF (ug/m3)
2.0
1.5
1.0
0.5
0.0
J F M A M J J A S O N D
--1986--

FIGURE 3.38

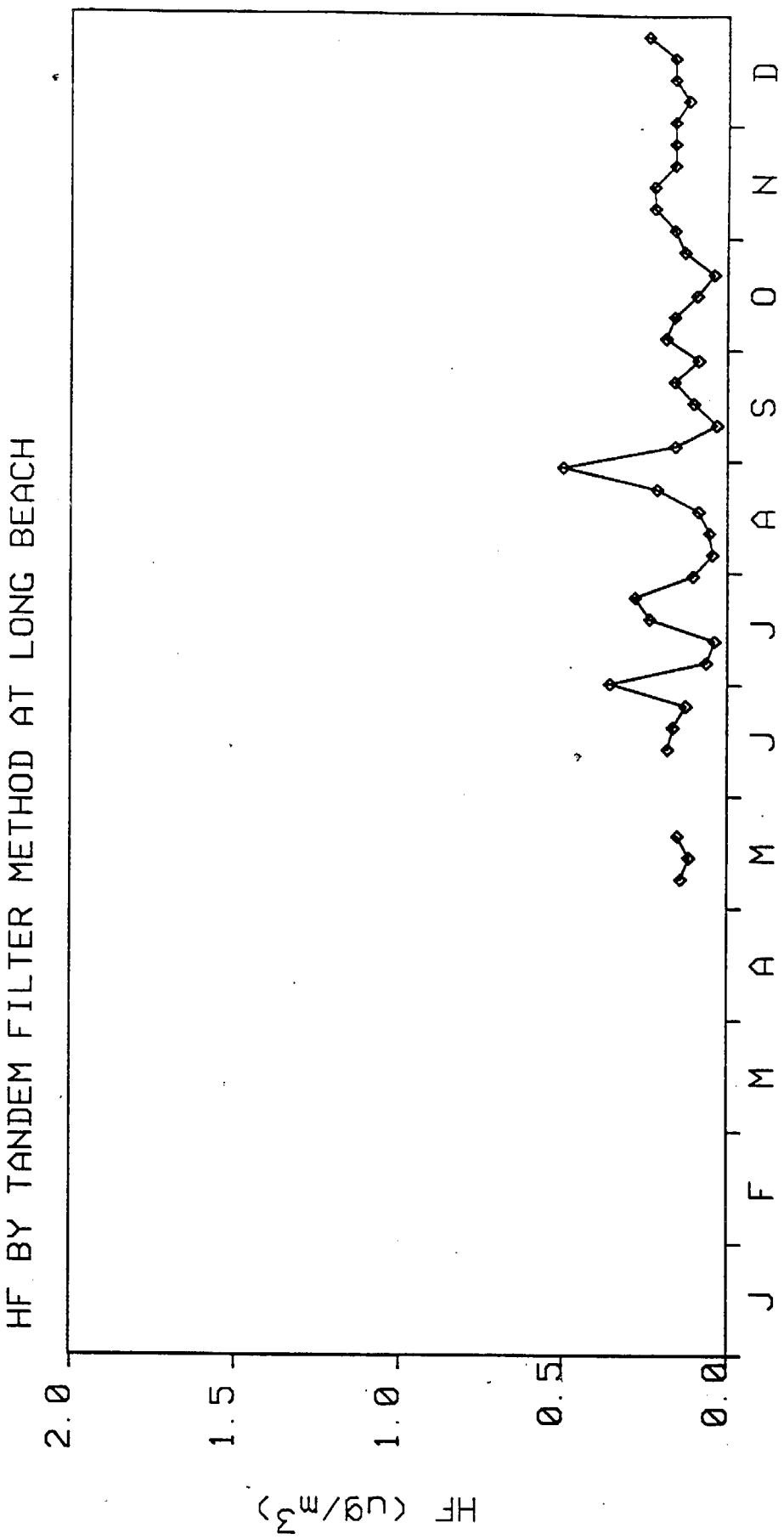

HF BY TANDEM FILTER METHOD AT LONG BEACH
HF (ug/m3)
2.0
1.5
1.0
0.5
0.0
J F M A M J J A S O N D
--1986--

FIGURE 3.39

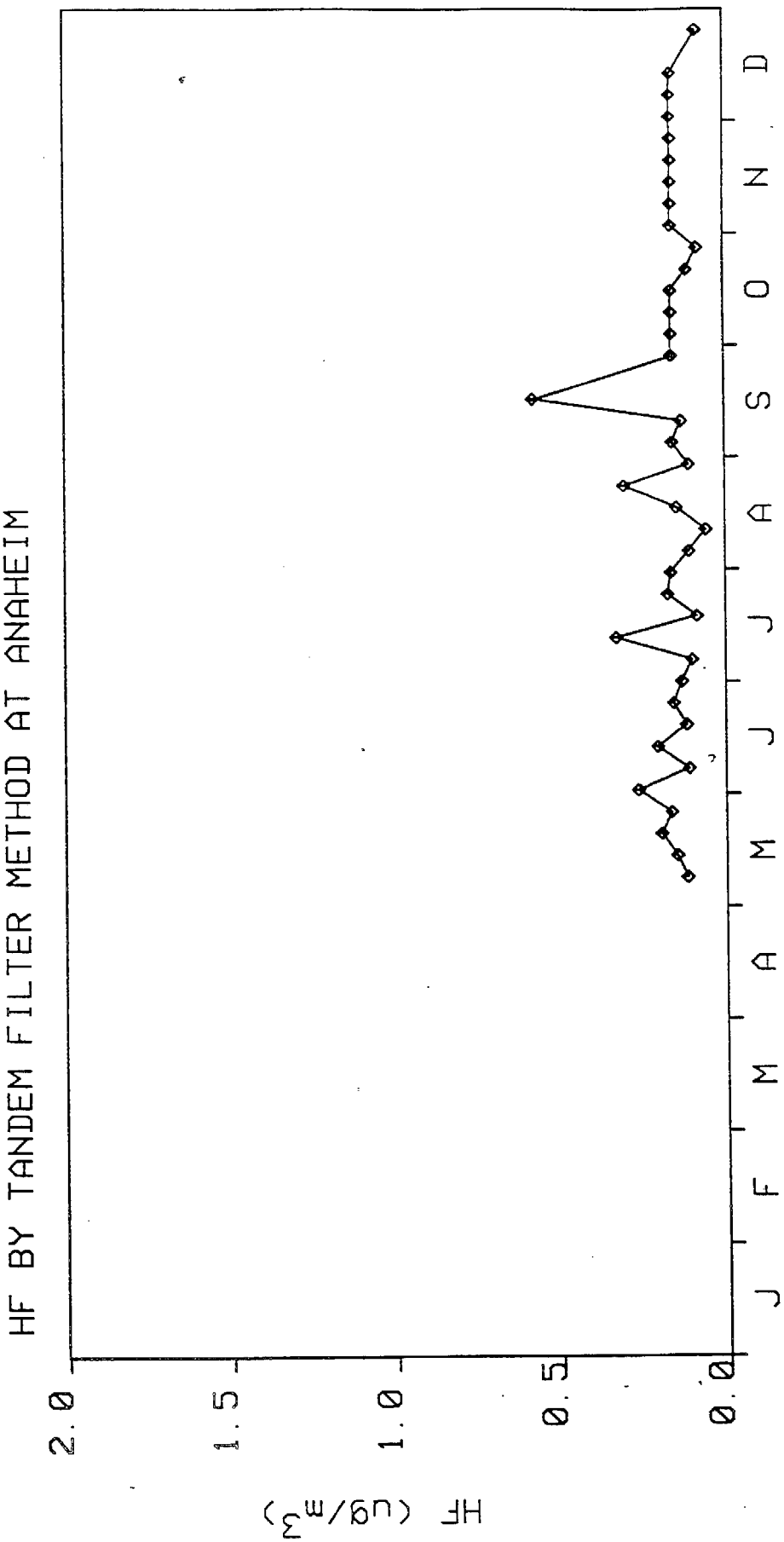

HF BY TANDEM FILTER METHOD AT ANAHEIM
HF (ug/m3)
2.0
1.5
1.0
0.5
0.0
J F M A M J J A S O N D
--1986--

FIGURE 3.40

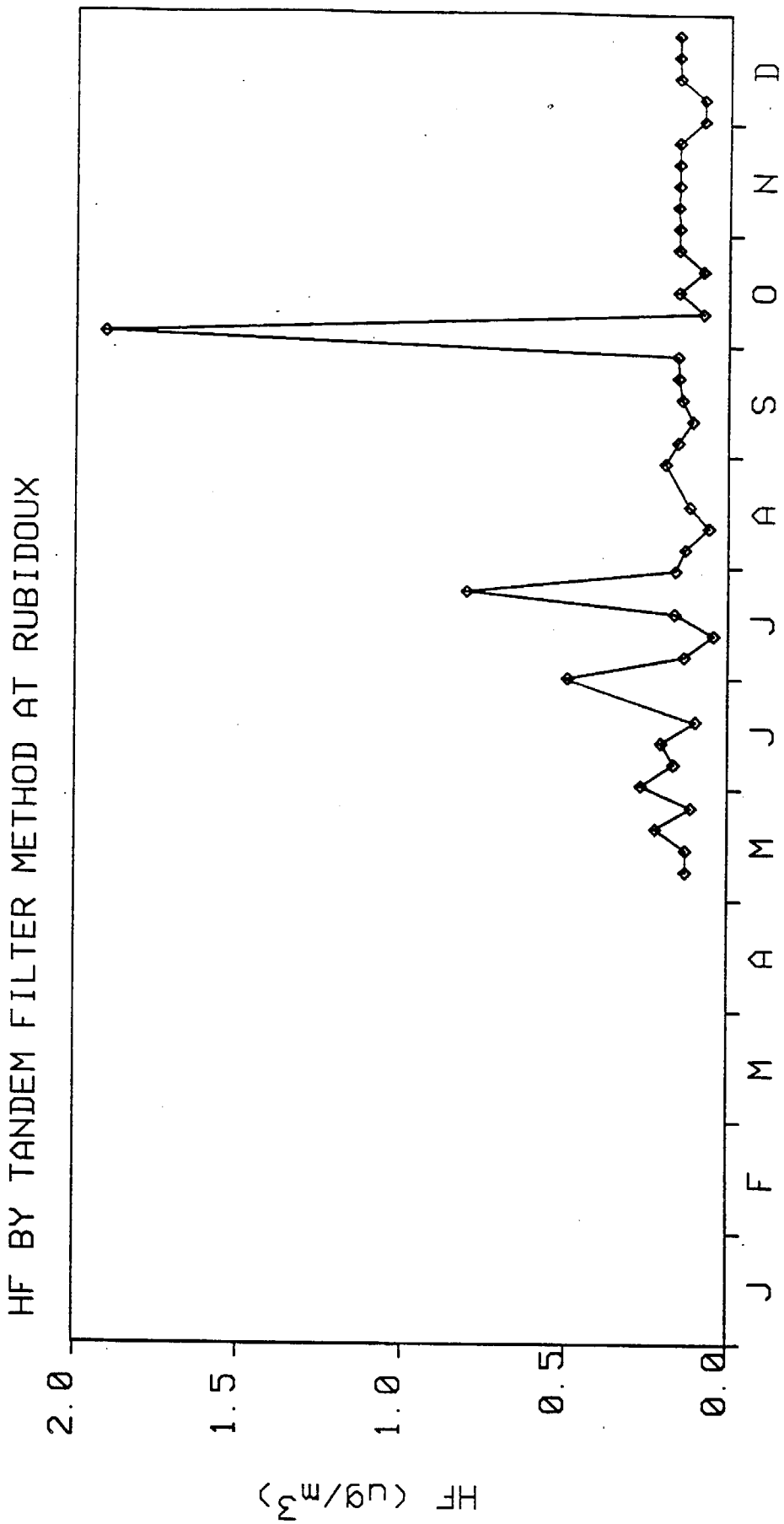

HF BY TANDEM FILTER METHOD AT RUBIDOUX
HF (ug/m3)
2.0
1.5
1.0
0.5
0.0
J F M A M J J A S O N D
--1986--

FIGURE 3.41

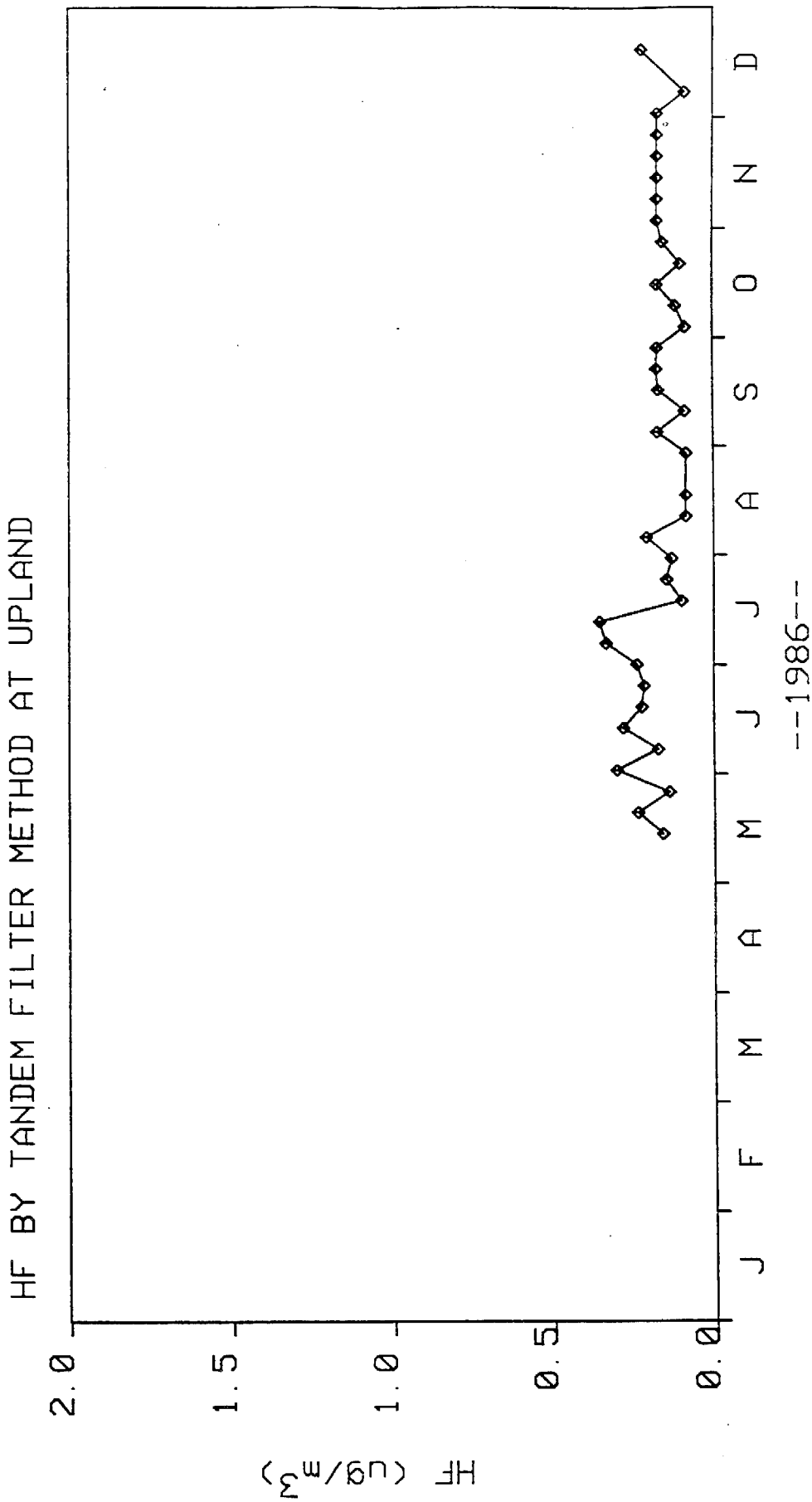

HF BY TANDEM FILTER METHOD AT UPLAND
HF (ug/m3)
2.0
1.5
1.0
0.5
0.0
J F M A M J J A S O N D
--1986--

FIGURE 3.42

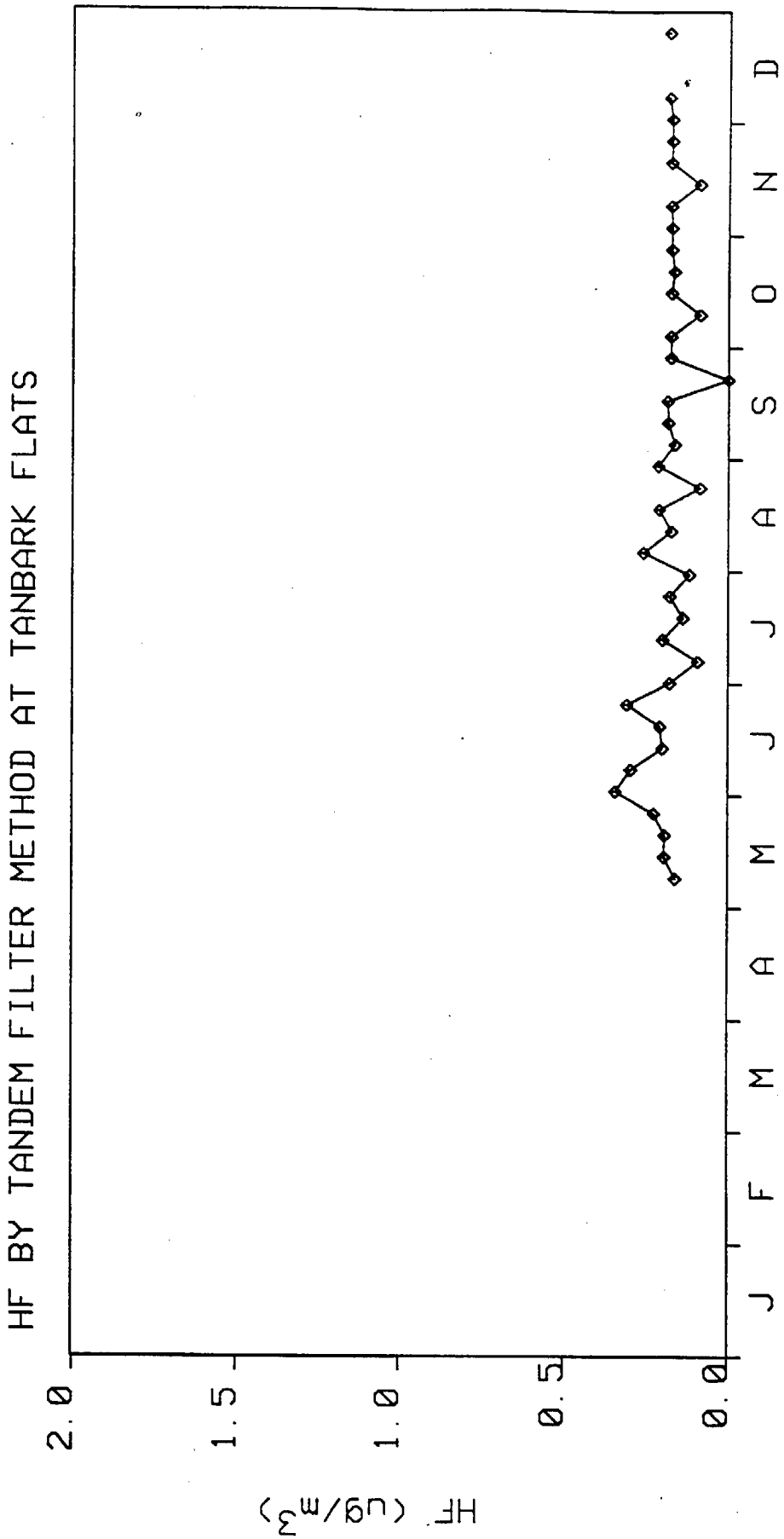

HF BY TANDEM FILTER METHOD AT TANBARK FLATS
HF (ug/m3)
2.0
1.5
1.0
0.5
0.0
J F M A M J J A S O N D
--1986--

FIGURE 3.43

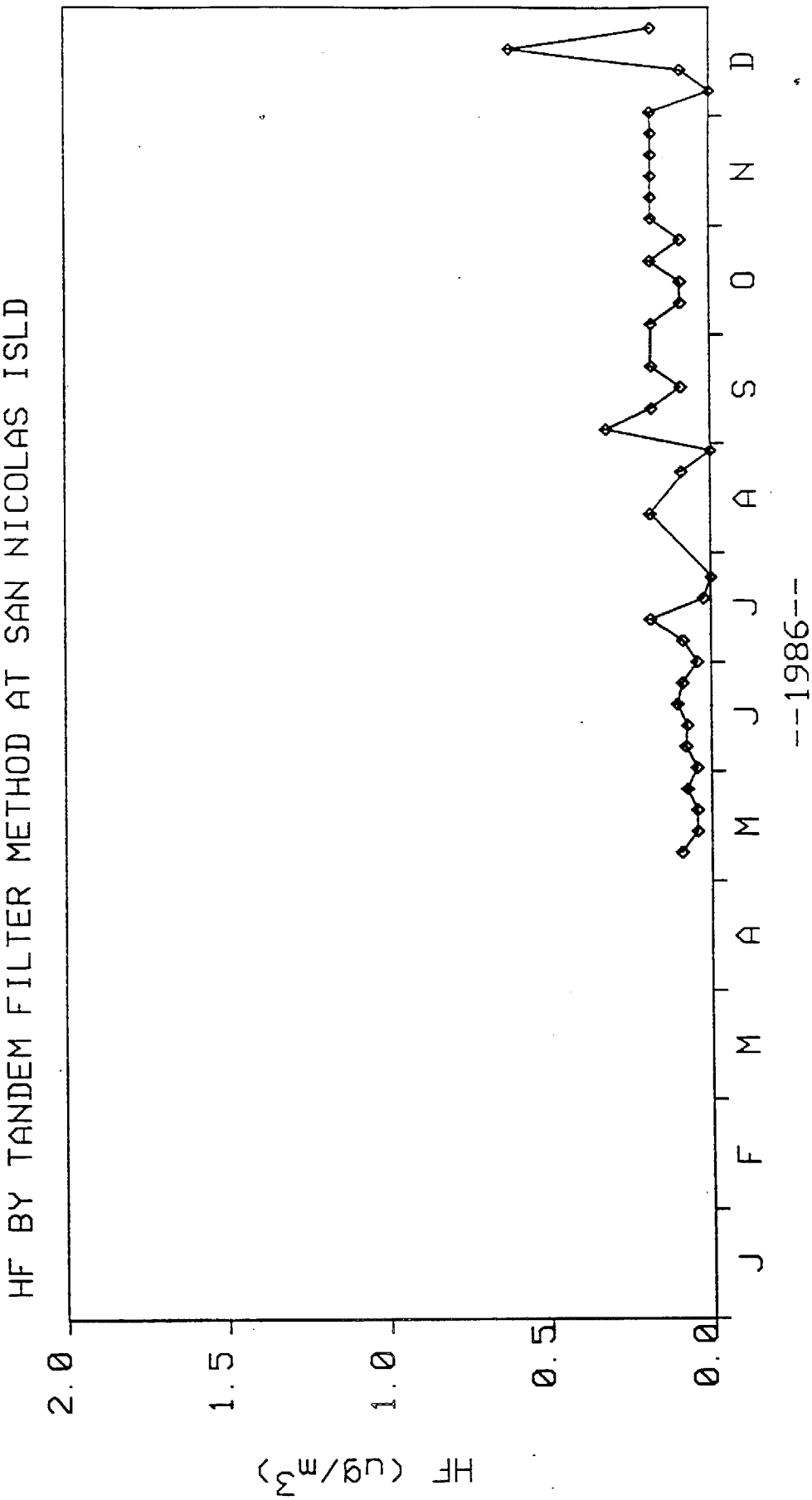

HF BY TANDEM FILTER METHOD AT SAN NICOLAS ISLD
HF (ug/m3)
2.0
1.5
1.0
0.5
0.0
J F M A M J J A S O N D
--1986--

FIGURE 3.44

Table 3.3. Gas phase organic acids concentrations observed in the Los Angeles area, 1986 (concentrations in $\mu g\ m^{-3}$)

Site	CH_3COOH[a,d]			HCOOH[a]		
	8-Month Average[b]	Max. 24-h Average	n[c]	8-Month Average[b]	Max. 24-h Average	n[c]
Burbank	19.0	39.8	38	10.0	17.4	39
Downtown LA	17.4	31.4	37	9.2	16.0	37
Hawthorne	13.4	30.3	39	5.0	9.5	40
Long Beach	15.4	31.5	36	6.1	10.4	37
Anaheim	15.6	30.3	39	7.0	11.3	39
Rubidoux	14.8	36.8	37	6.8	17.4	39
Upland	19.5	42.1	38	10.7	25.1	39
Tanbark Flats	18.5	50.7	37	9.8	23.4	40
San Nicolas Island	2.9	14.9	35	2.6	7.4	36

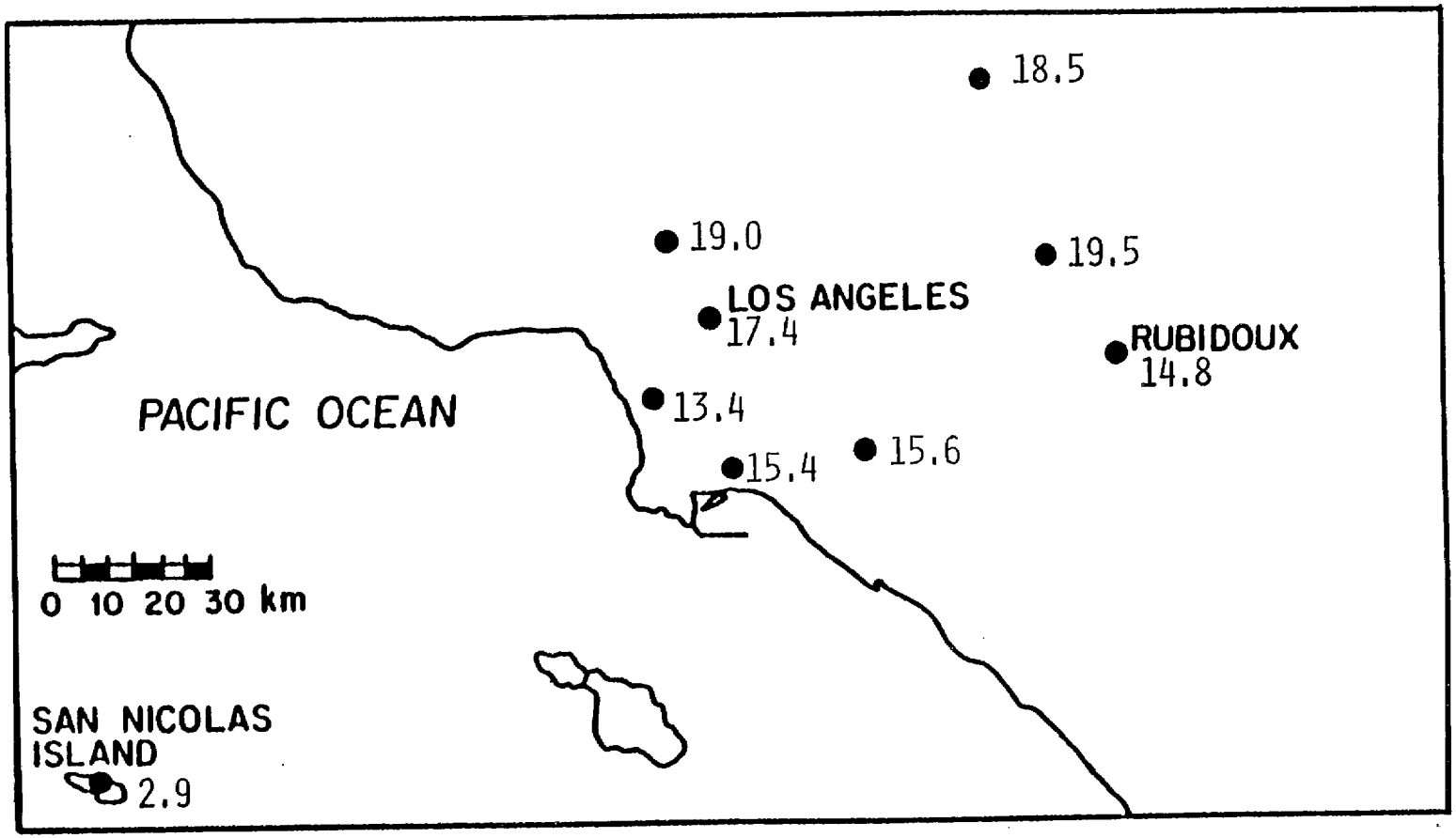
a. By tandem filter method employing KOH impregnated backup filters.

b. May-December, 1986.

c. Maximum number of sampling events is 40.

d. CH_3COOH measurements may be subject to a positive artifact induced by conversion of peroxyacetyl nitrate (PAN) to acetate on alkaline substrates. The actual extent of this potential artifact is unknown at present. These data on CH_3COOH concentrations should be treated as an upper limit on actual CH_3COOH concentrations in the atmosphere.

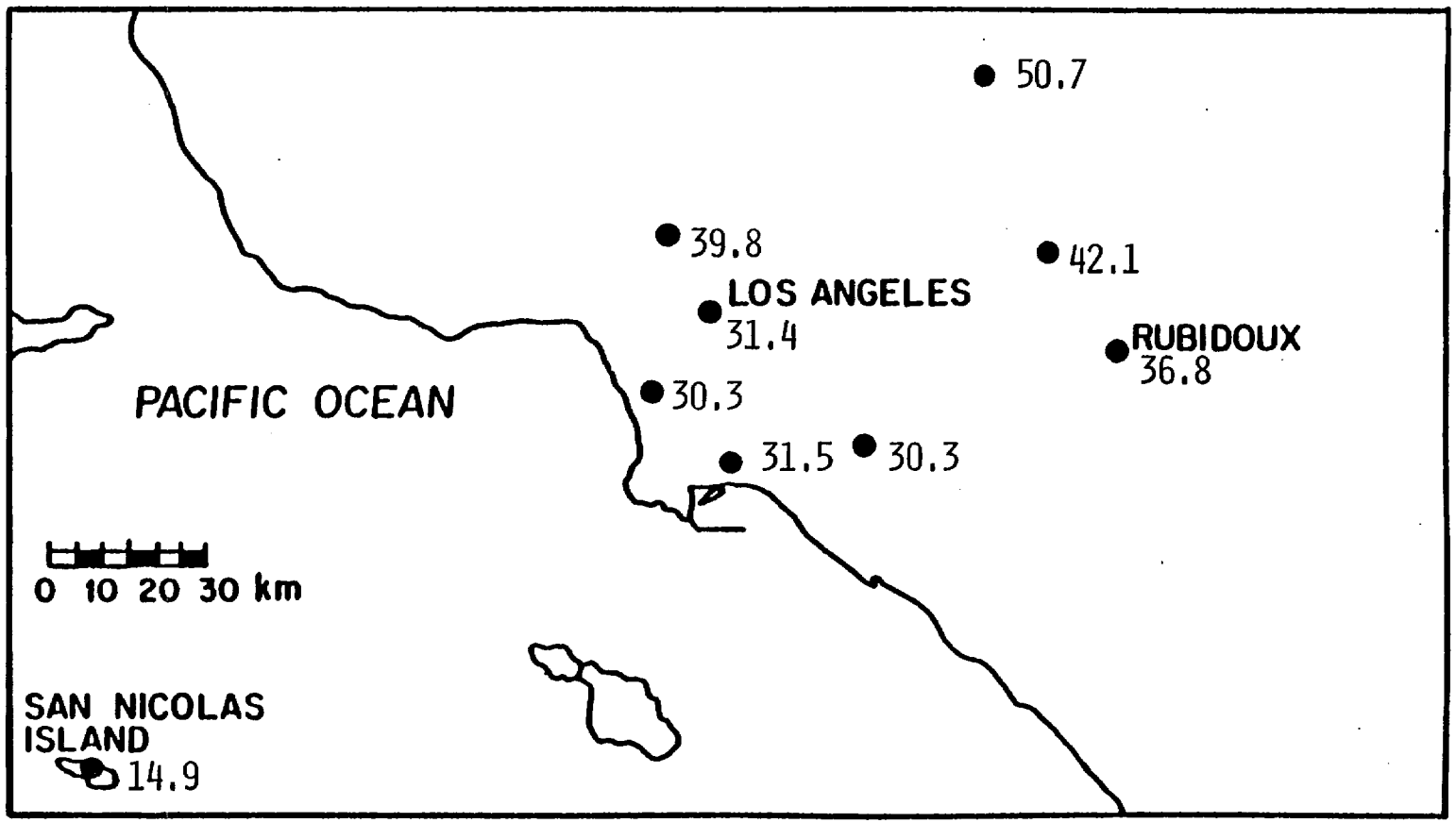
ANNUAL AVERAGE GASEOUS ACETATE CONCENTRATIONS ($\mu g\ m^{-3}$, AS ACETIC ACID) OBSERVED IN THE LOS ANGELES AREA, 1986.[A]



[A]GASEOUS ACETATE BY TANDEM FILTER METHOD EMPLOYING KOH IMPREGNATED BACKUP FILTERS.

FIGURE 3.45

MAXIMUM 24-HOUR AVERAGE GASEOUS ACETATE CONCENTRATIONS ($\mu g\ m^{-3}$, AS ACETIC ACID) OBSERVED IN THE LOS ANGELES AREA, 1986.[A]



[A]GASEOUS ACETATE BY TANDEM FILTER METHOD EMPLOYING KOH IMPREGNATED BACKUP FILTERS.

FIGURE 3.46

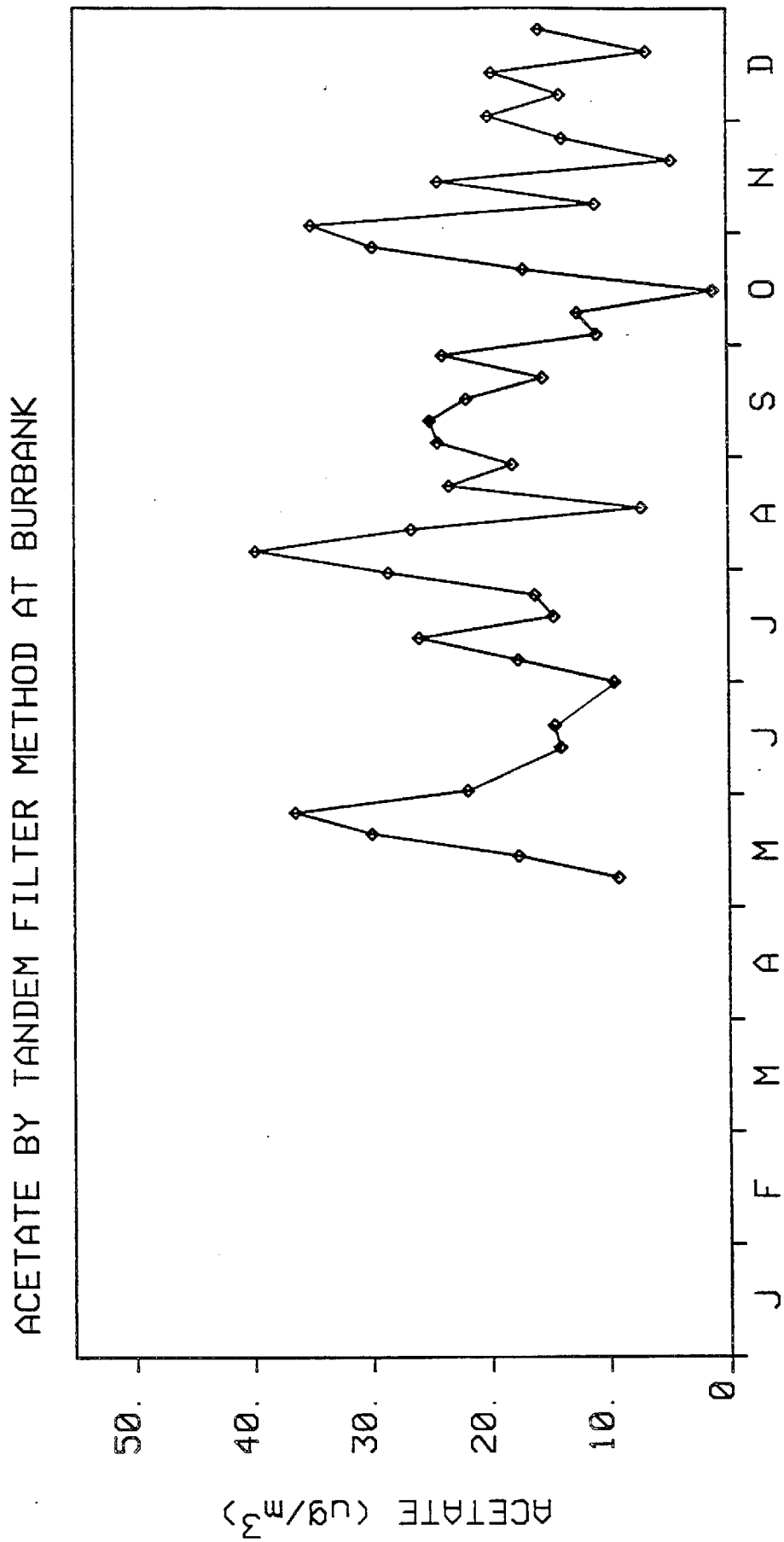

ACETATE BY TANDEM FILTER METHOD AT BURBANK
ACETATE (ug/m3)
50.
40.
30.
20.
10.
0
J F M A M J J A S O N D
--1986--

FIGURE 3.47

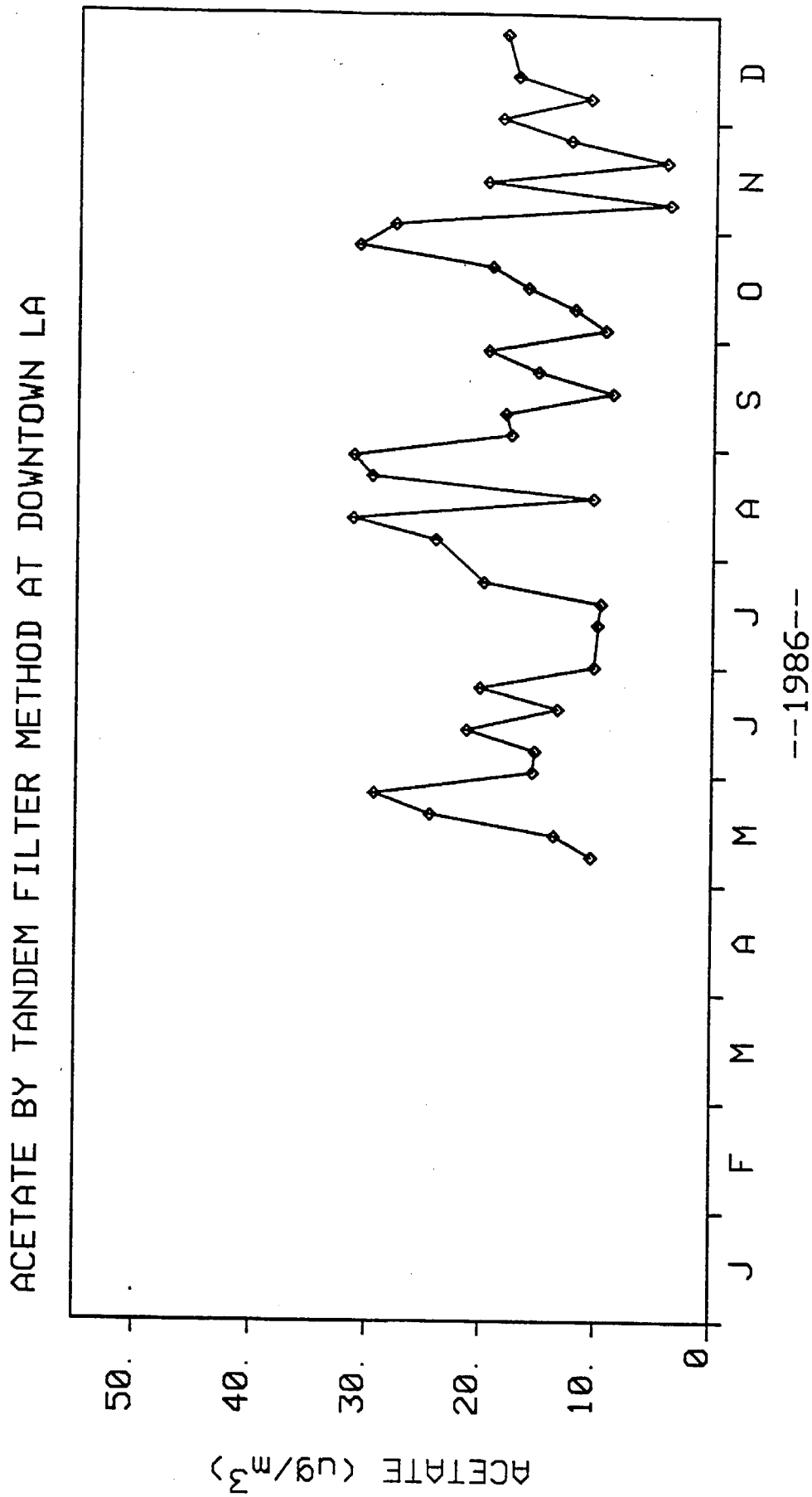

ACETATE BY TANDEM FILTER METHOD AT DOWNTOWN LA
ACETATE (ug/m3)
50.
40.
30.
20.
10.
0
J F M A M J J A S O N D
--1986--

FIGURE 3.48

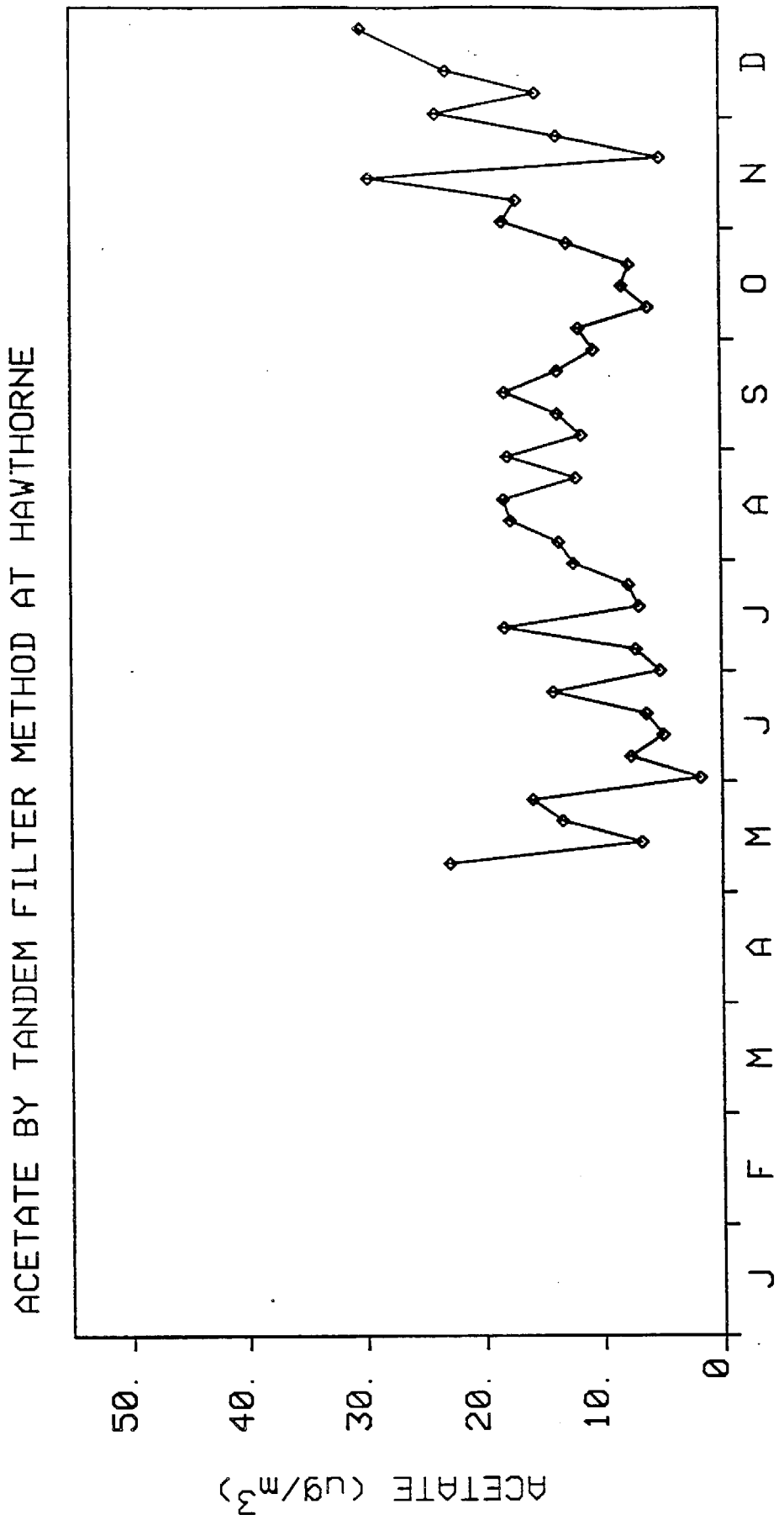

ACETATE BY TANDEM FILTER METHOD AT HAWTHORNE
ACETATE (ug/m3)
50.
40.
30.
20.
10.
0
J F M A M J J A S O N D
--1986--

FIGURE 3.49

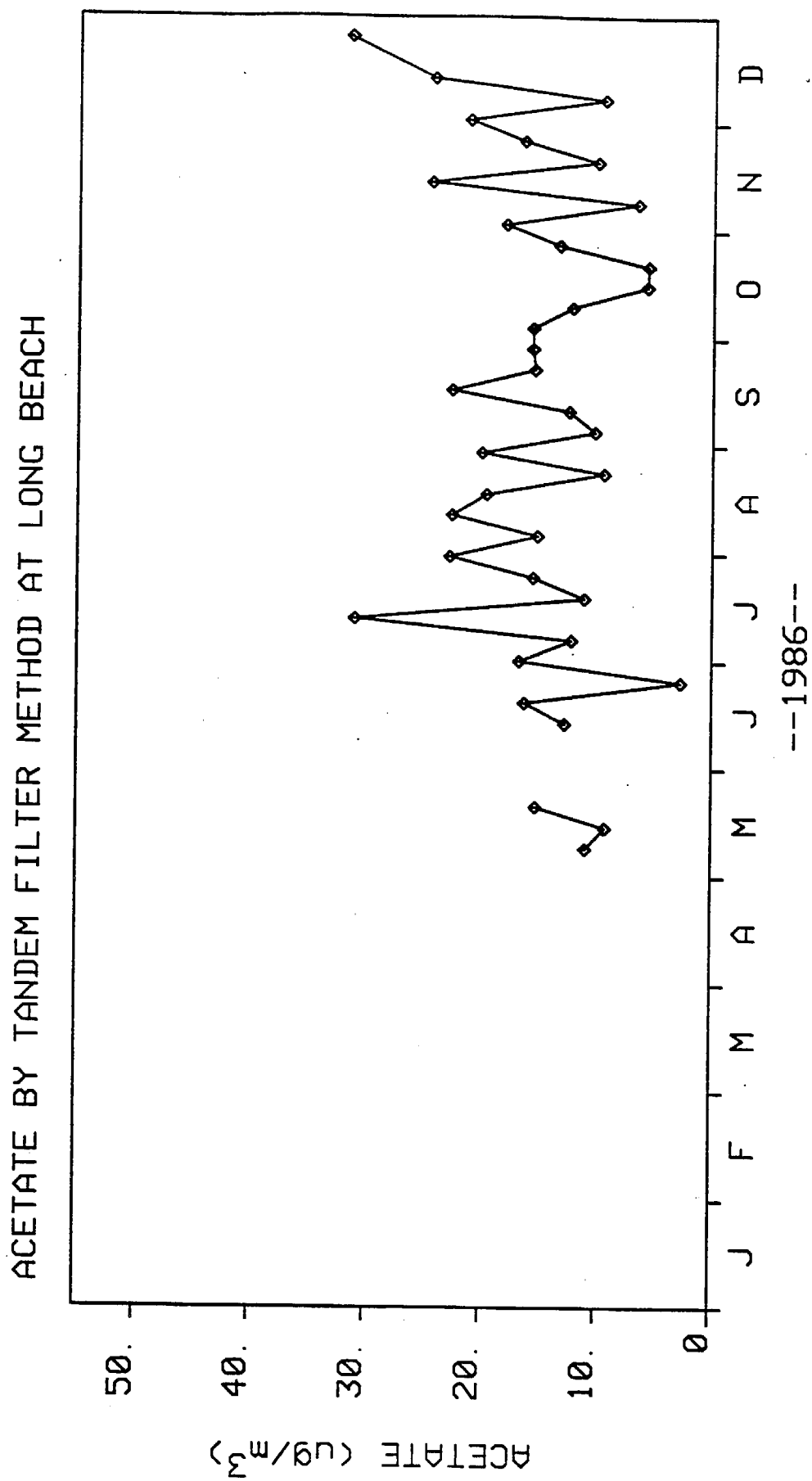

ACETATE BY TANDEM FILTER METHOD AT LONG BEACH
ACETATE (ug/m3)
50.
40.
30.
20.
10.
0
J F M A M J J A S O N D
--1986--

FIGURE 3.50

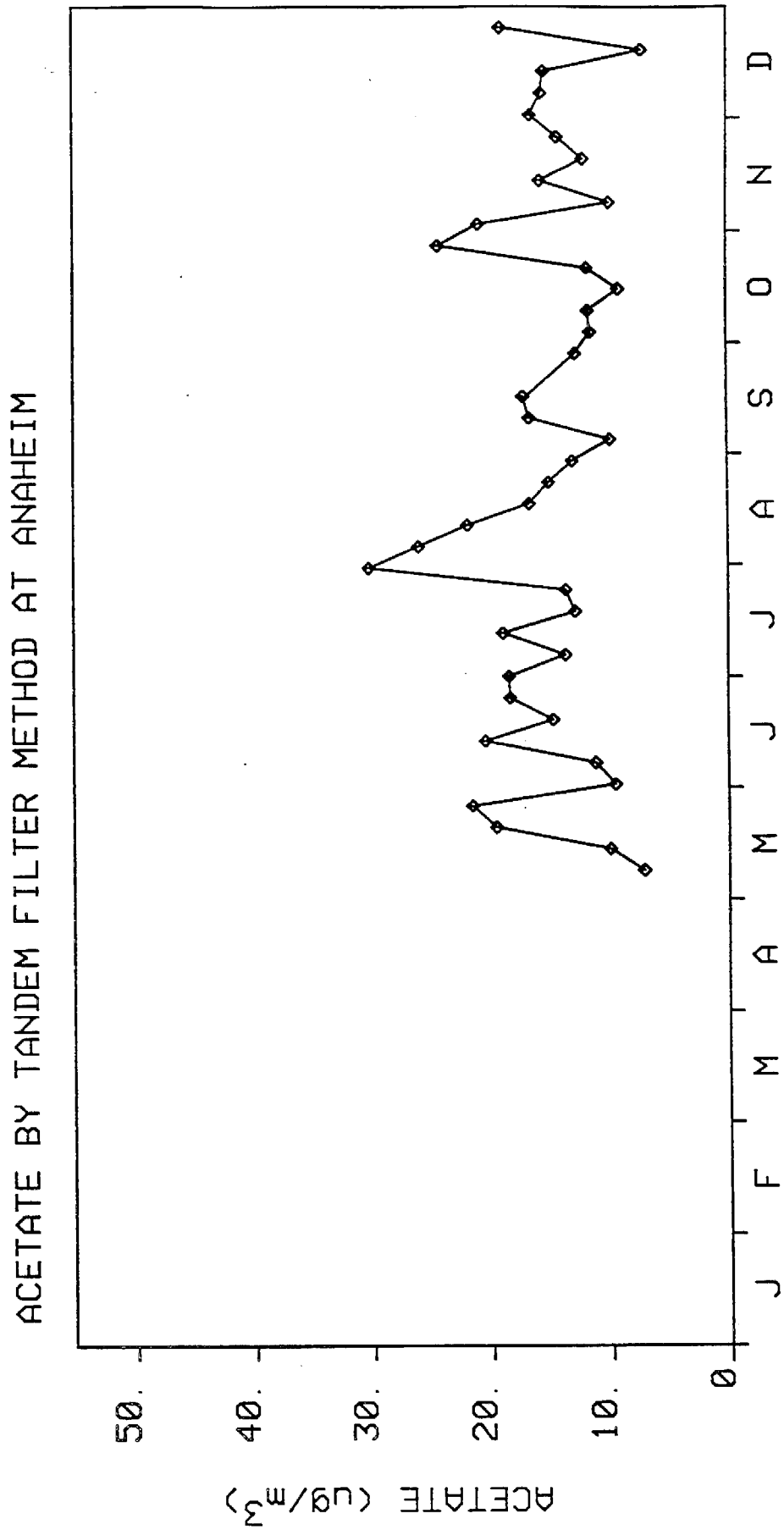

ACETATE BY TANDEM FILTER METHOD AT ANAHEIM
ACETATE (ug/m3)
50.
40.
30.
20.
10.
0
J F M A M J J A S O N D
--1986--

FIGURE 3.51

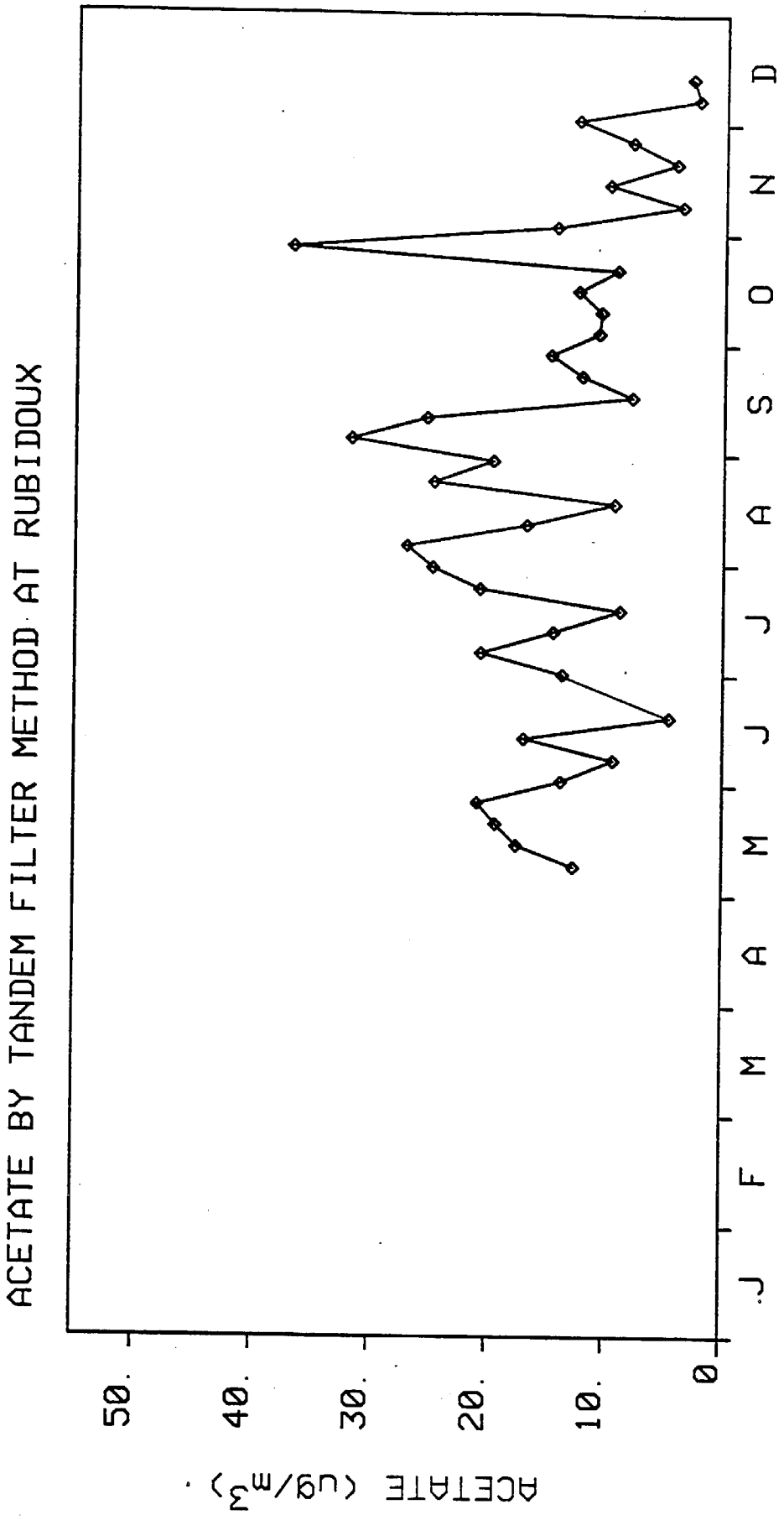

ACETATE BY TANDEM FILTER METHOD AT RUBIDOUX
ACETATE (ug/m3)
50.
40.
30.
20.
10.
0
J F M A M J J A S O N D
--1986--

FIGURE 3.52

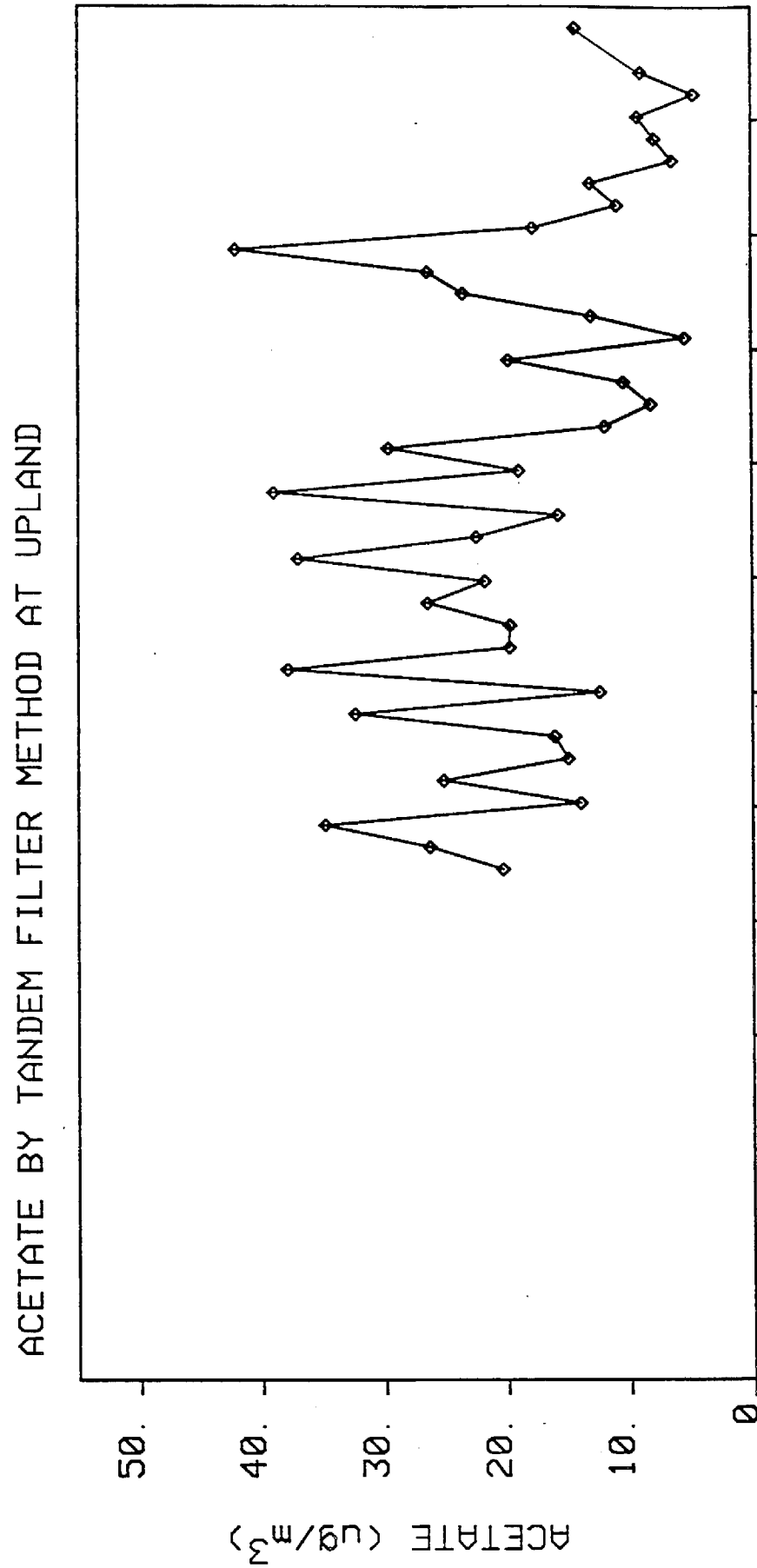

ACETATE BY TANDEM FILTER METHOD AT UPLAND
ACETATE (ug/m3)
50.
40.
30.
20.
10.
0
J F M A M J J A S O N D
--1986--

FIGURE 3.53

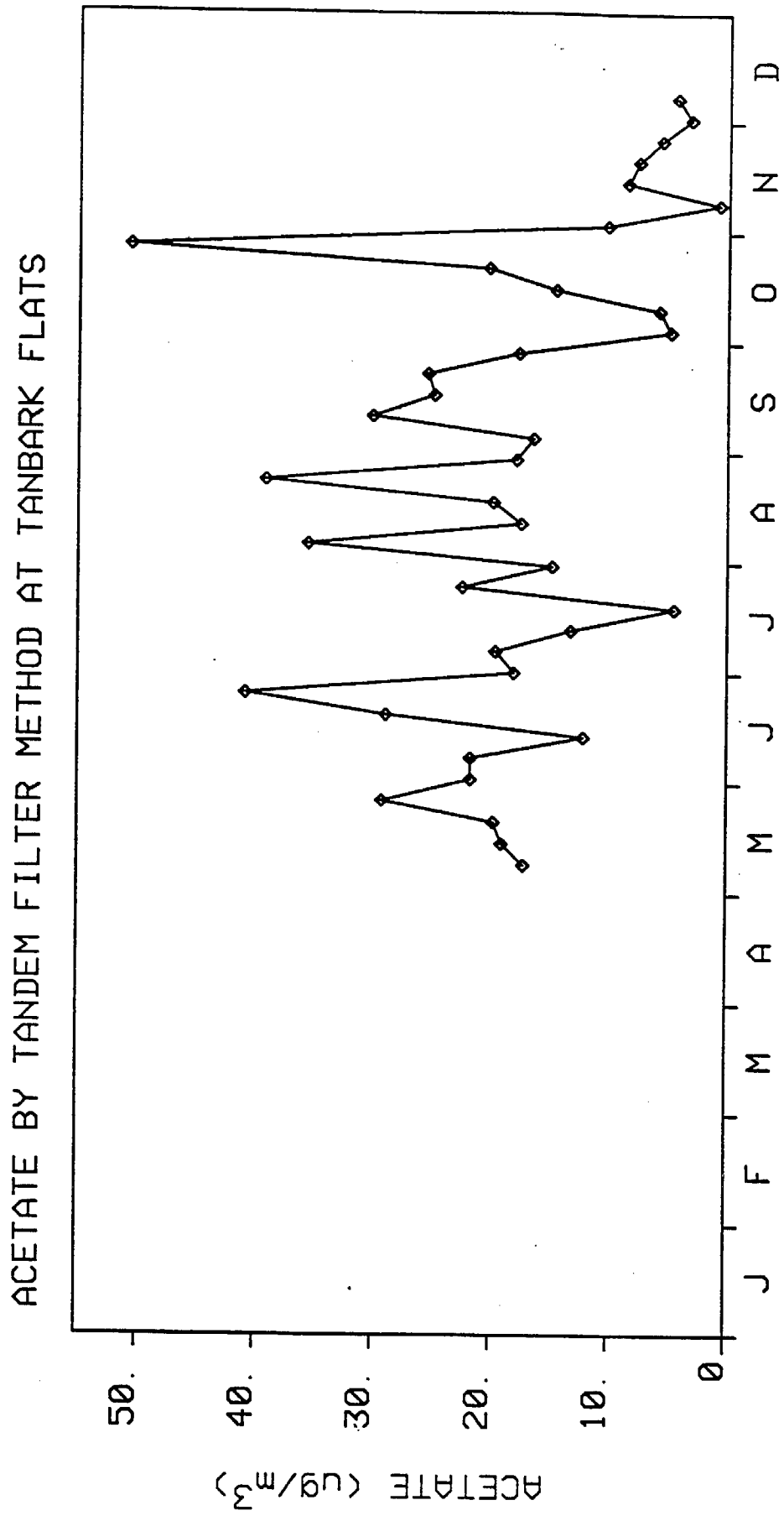

ACETATE BY TANDEM FILTER METHOD AT TANBARK FLATS
ACETATE (ug/m3)
50.
40.
30.
20.
10.
0
J F M A M J J A S O N D
--1986--

FIGURE 3.54

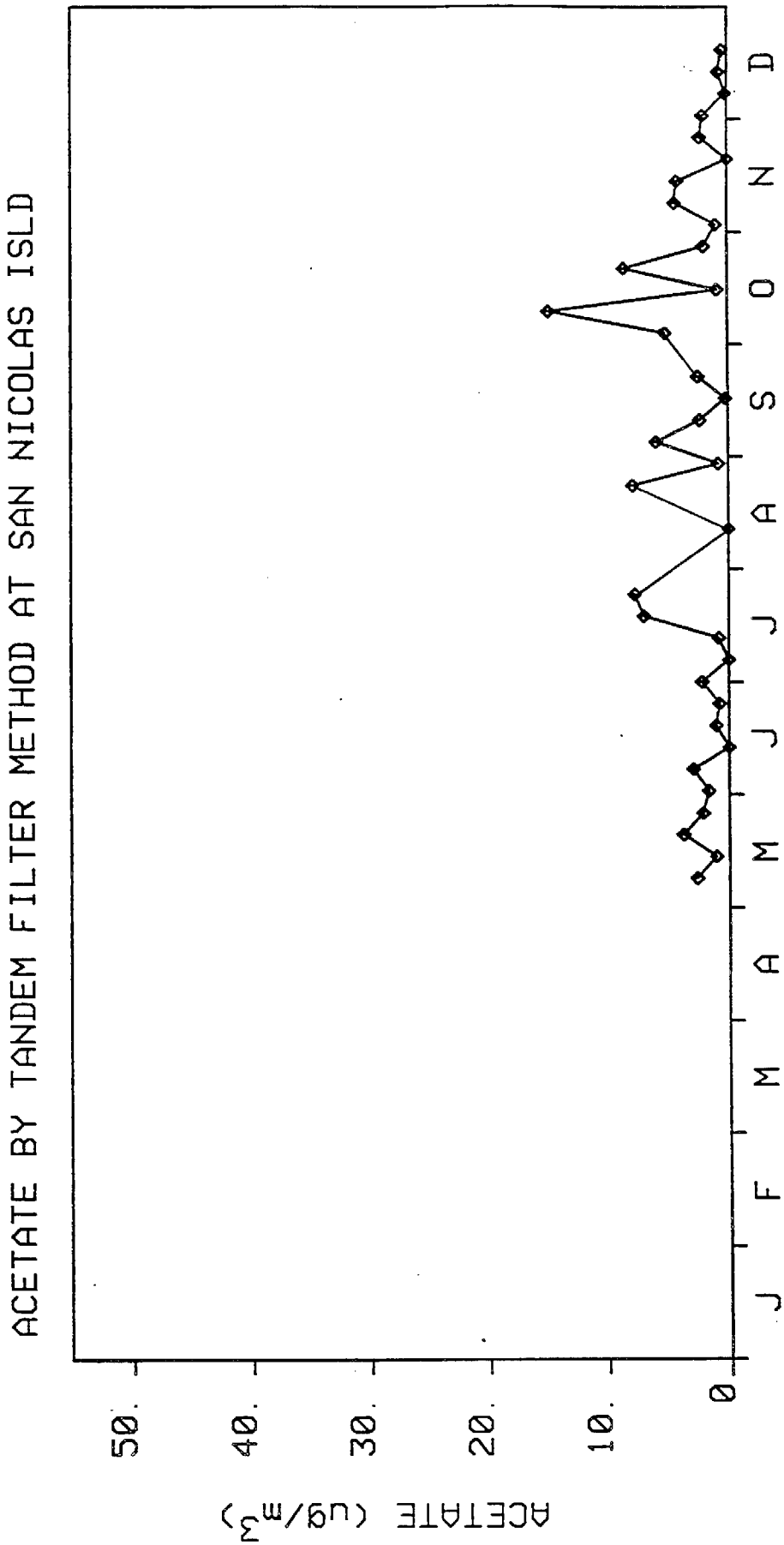
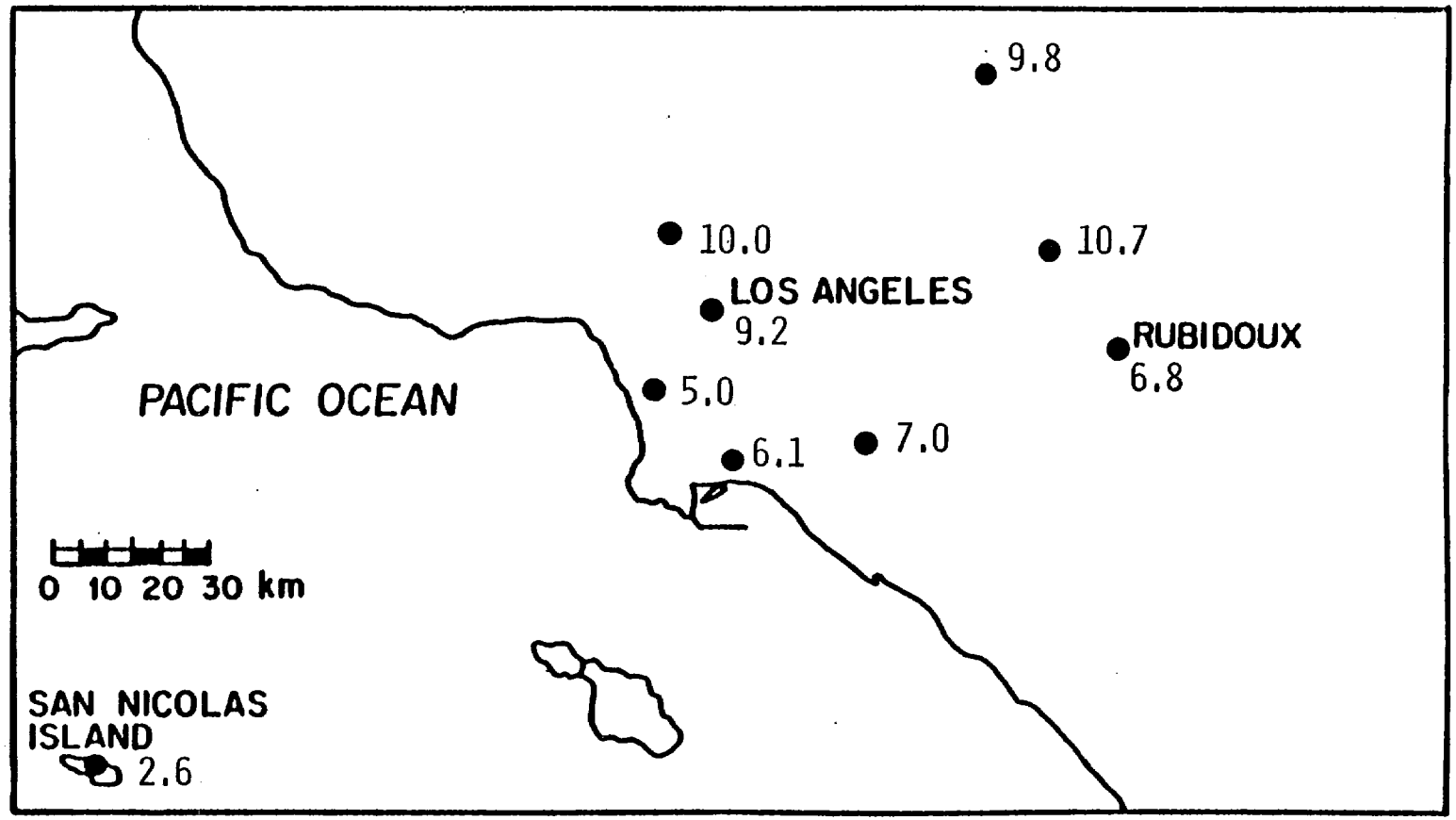

ACETATE BY TANDEM FILTER METHOD AT SAN NICOLAS ISLD
ACETATE (ug/m3)
50.
40.
30.
20.
10.
0
J F M A M J J A S O N D
--1986--

FIGURE 3.55

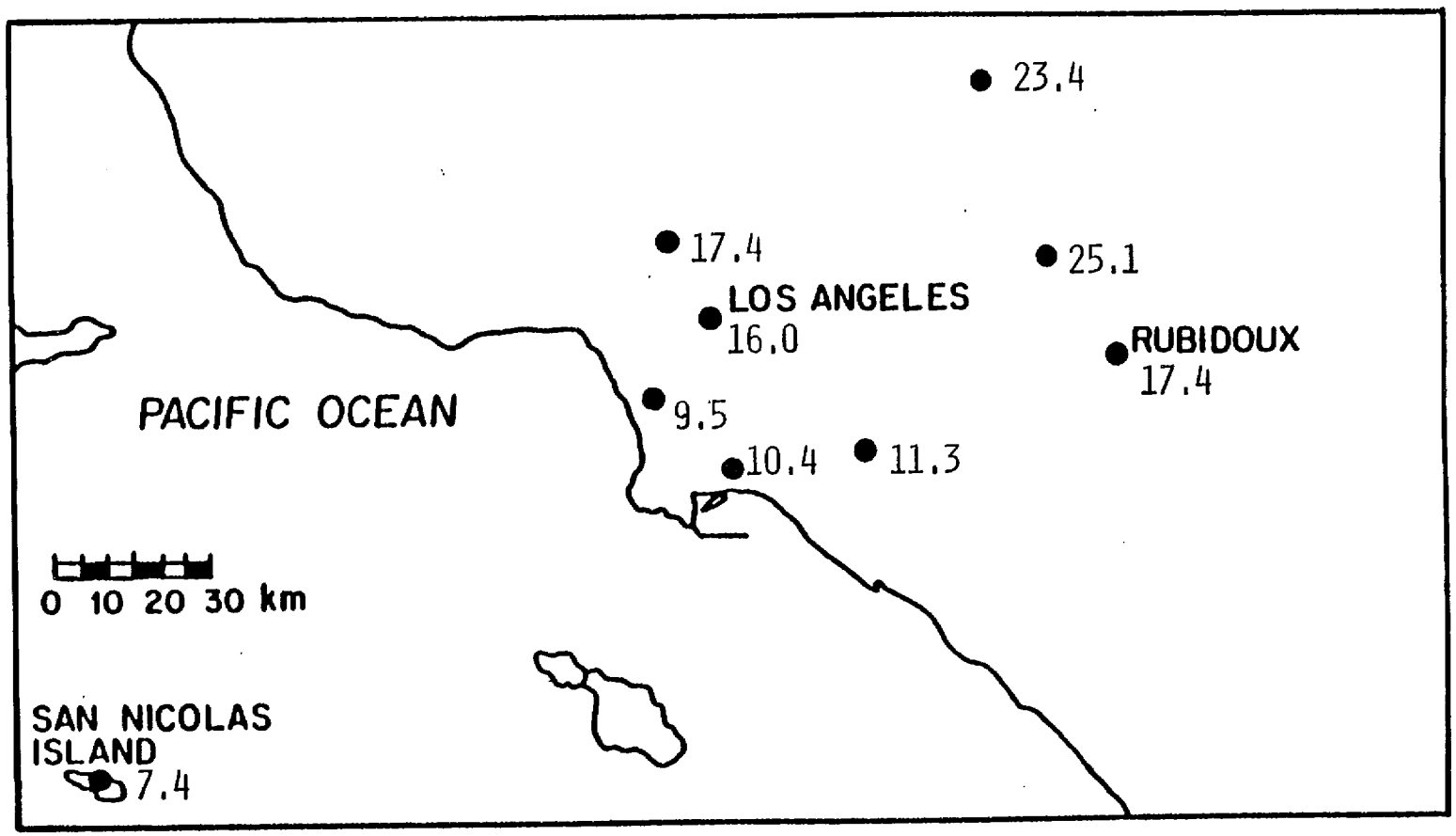
ANNUAL AVERAGE FORMIC ACID CONCENTRATIONS ($\mu g\ m^{-3}$) OBSERVED IN THE LOS ANGELES AREA, 1986.[A]



[A]FORMIC ACID BY TANDEM FILTER METHOD EMPLOYING KOH IMPREGNATED BACKUP FILTERS.

FIGURE 3.56

MAXIMUM 24-HOUR AVERAGE FORMIC ACID CONCENTRATIONS ($\mu g\ m^{-3}$) OBSERVED IN THE LOS ANGELES AREA, 1986.[A]



[A]FORMIC ACID BY TANDEM FILTER METHOD EMPLOYING KOH IMPREGNATED BACKUP FILTERS.

FIGURE 3.57

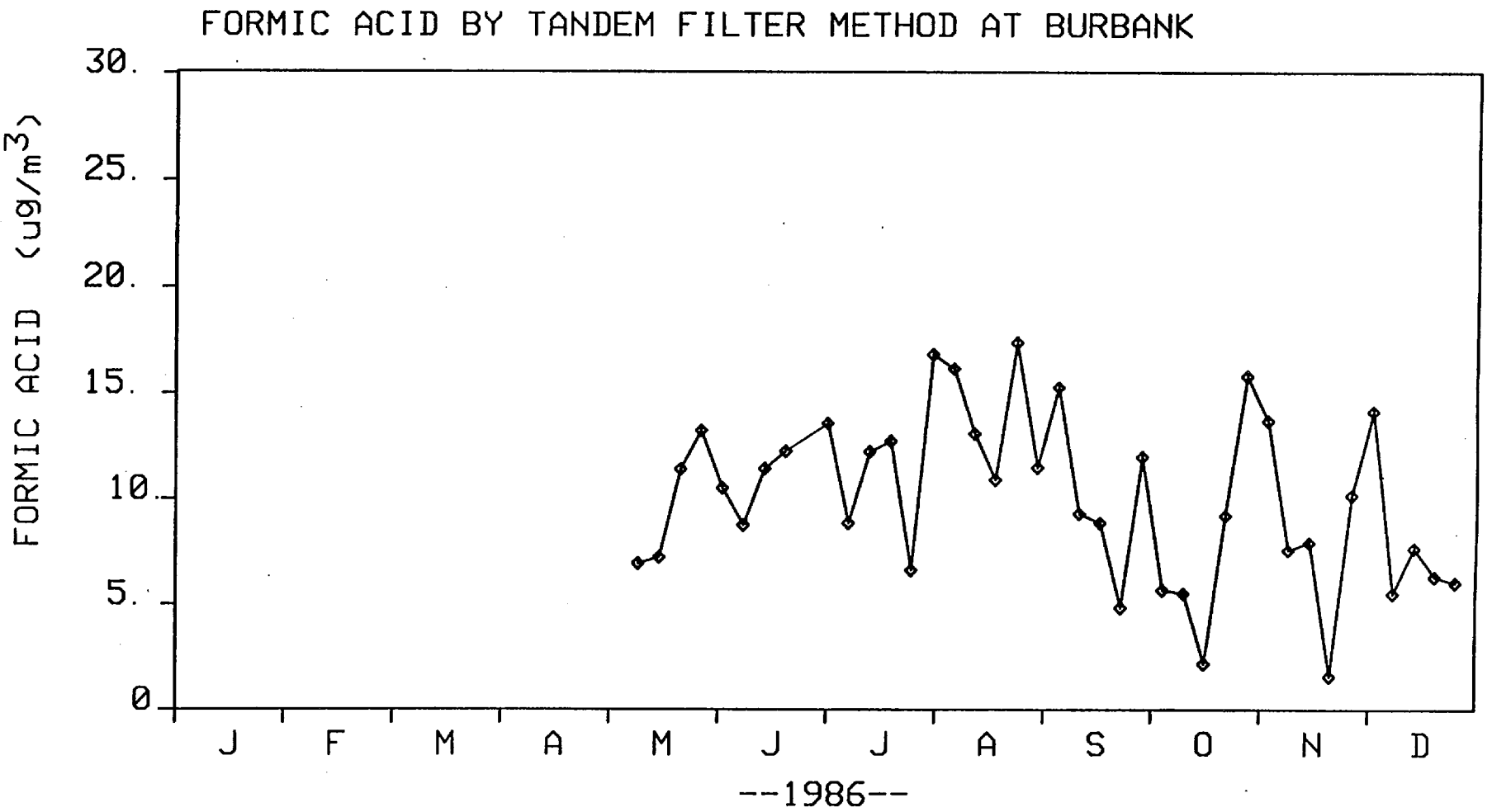

FORMIC ACID BY TANDEM FILTER METHOD AT BURBANK
FORMIC ACID (ug/m3)
30.
25.
20.
15.
10.
5.
0
J
F
M
A
M
J
J
A
S
O
N
D
--1986--

FIGURE 3.58

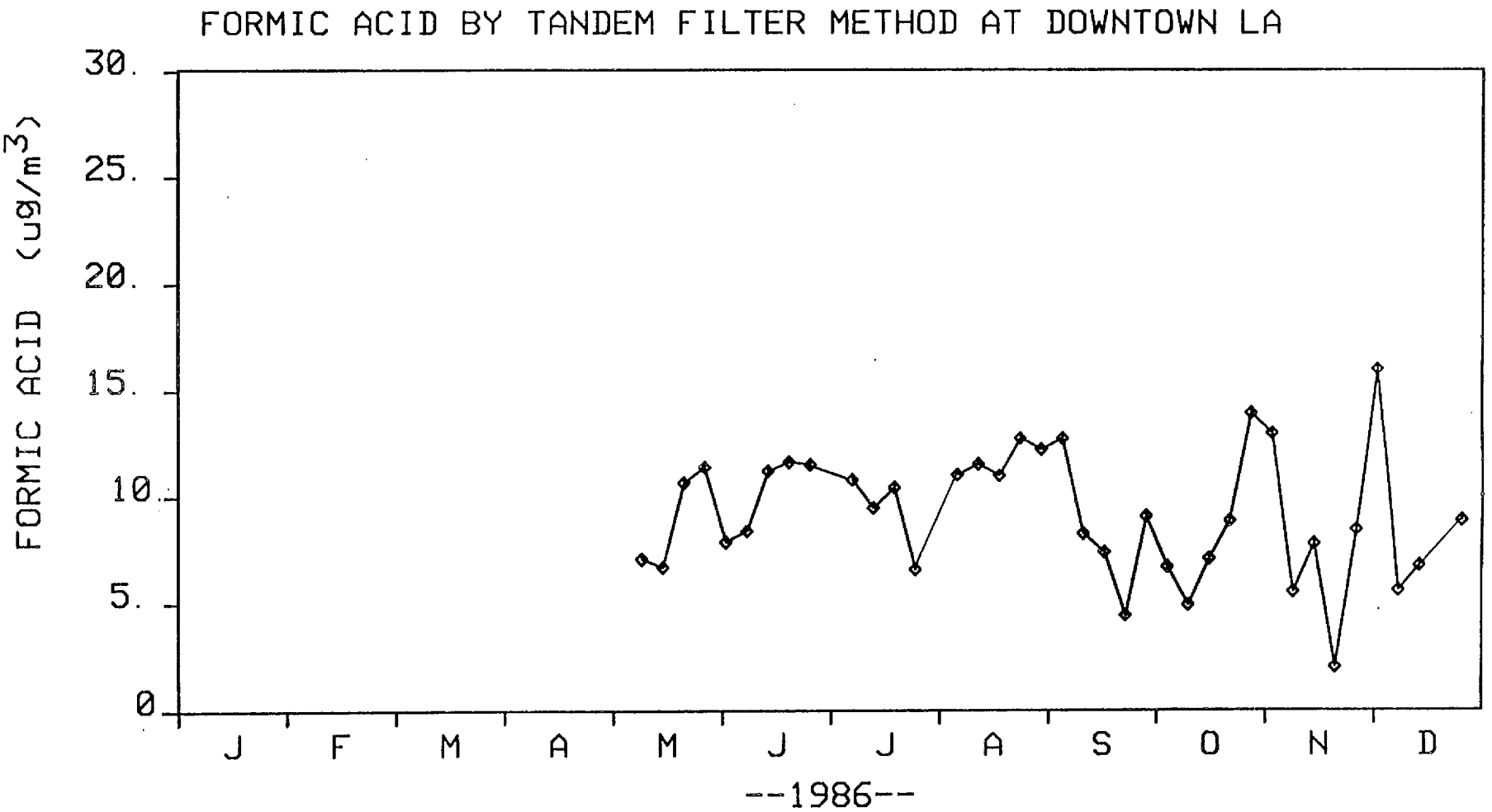

FORMIC ACID BY TANDEM FILTER METHOD AT DOWNTOWN LA
FORMIC ACID (ug/m3)
30.
25.
20.
15.
10.
5.
0
J
F
M
A
M
J
J
A
S
O
N
D
--1986--

FIGURE 3.59

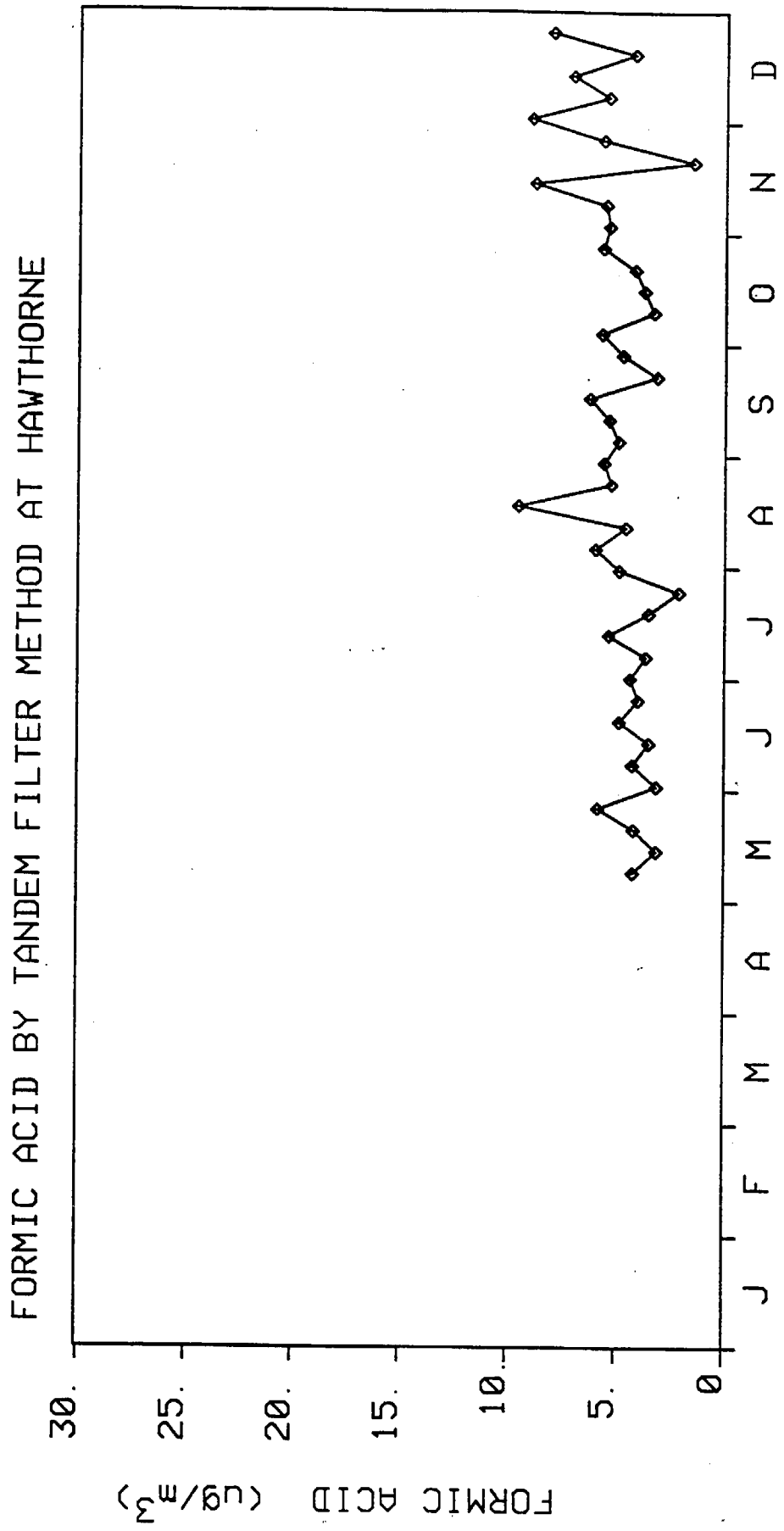

FORMIC ACID BY TANDEM FILTER METHOD AT HAWTHORNE
FORMIC ACID (ug/m3)
30.
25.
20.
15.
10.
5.
0
J F M A M J J A S O N D
--1986--

FIGURE 3.60

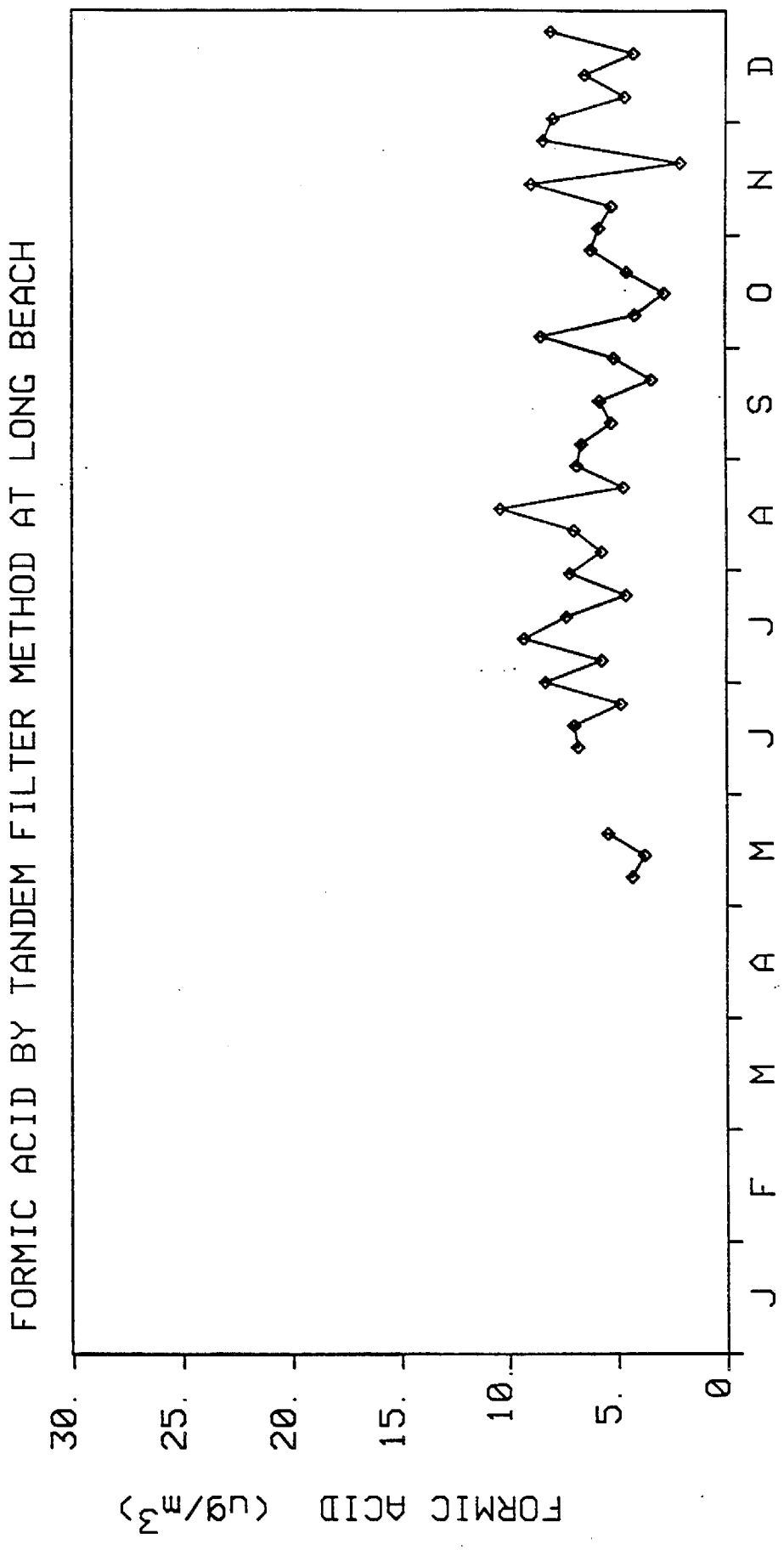

FORMIC ACID BY TANDEM FILTER METHOD AT LONG BEACH
FORMIC ACID (ug/m3)
30.
25.
20.
15.
10.
5.
0
J F M A M J J A S O N D
--1986--

FIGURE 3.61

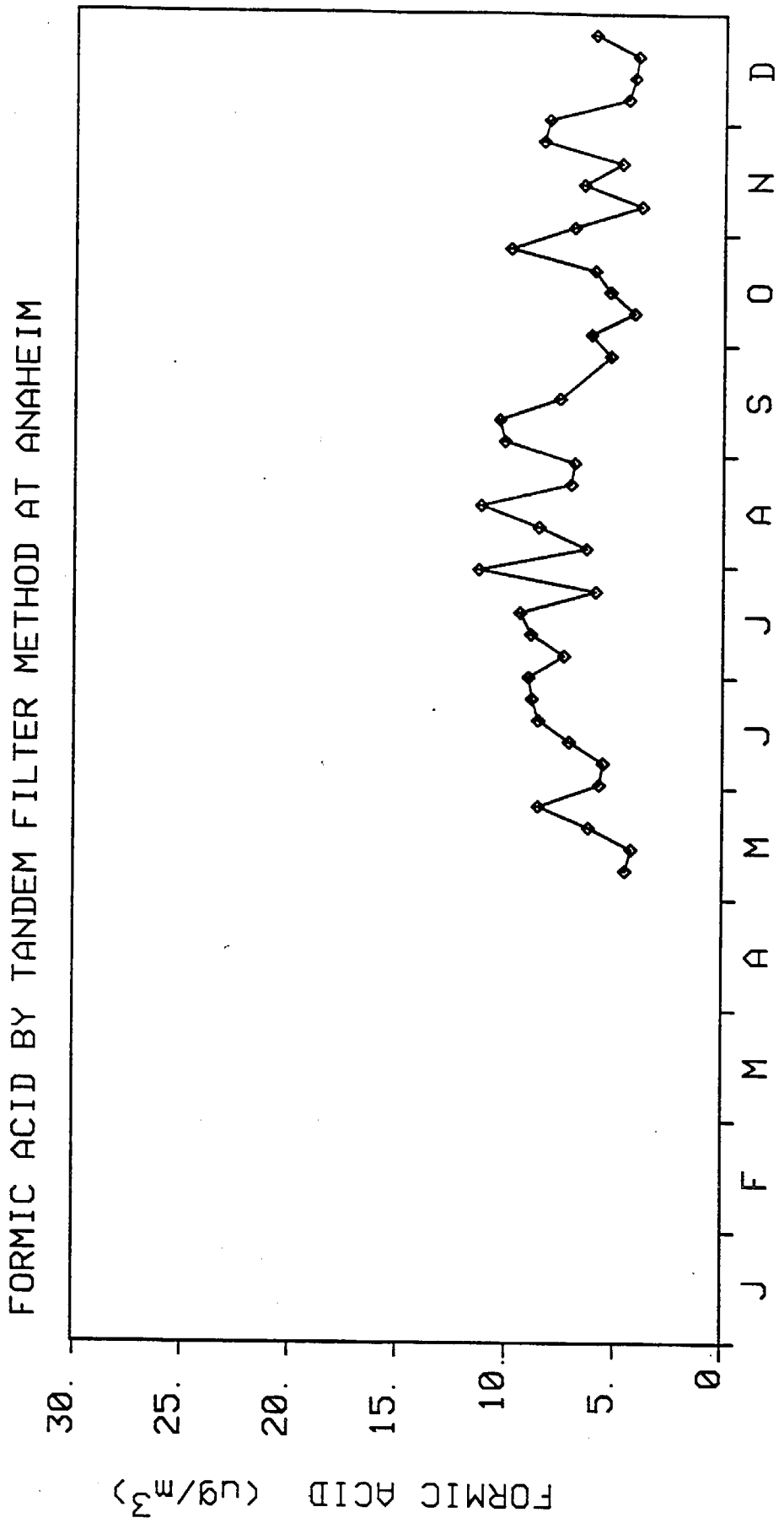

FORMIC ACID BY TANDEM FILTER METHOD AT ANAHEIM
FORMIC ACID (ug/m3)
30.
25.
20.
15.
10.
5.
0
J F M A M J J A S O N D
--1986--

FIGURE 3.62

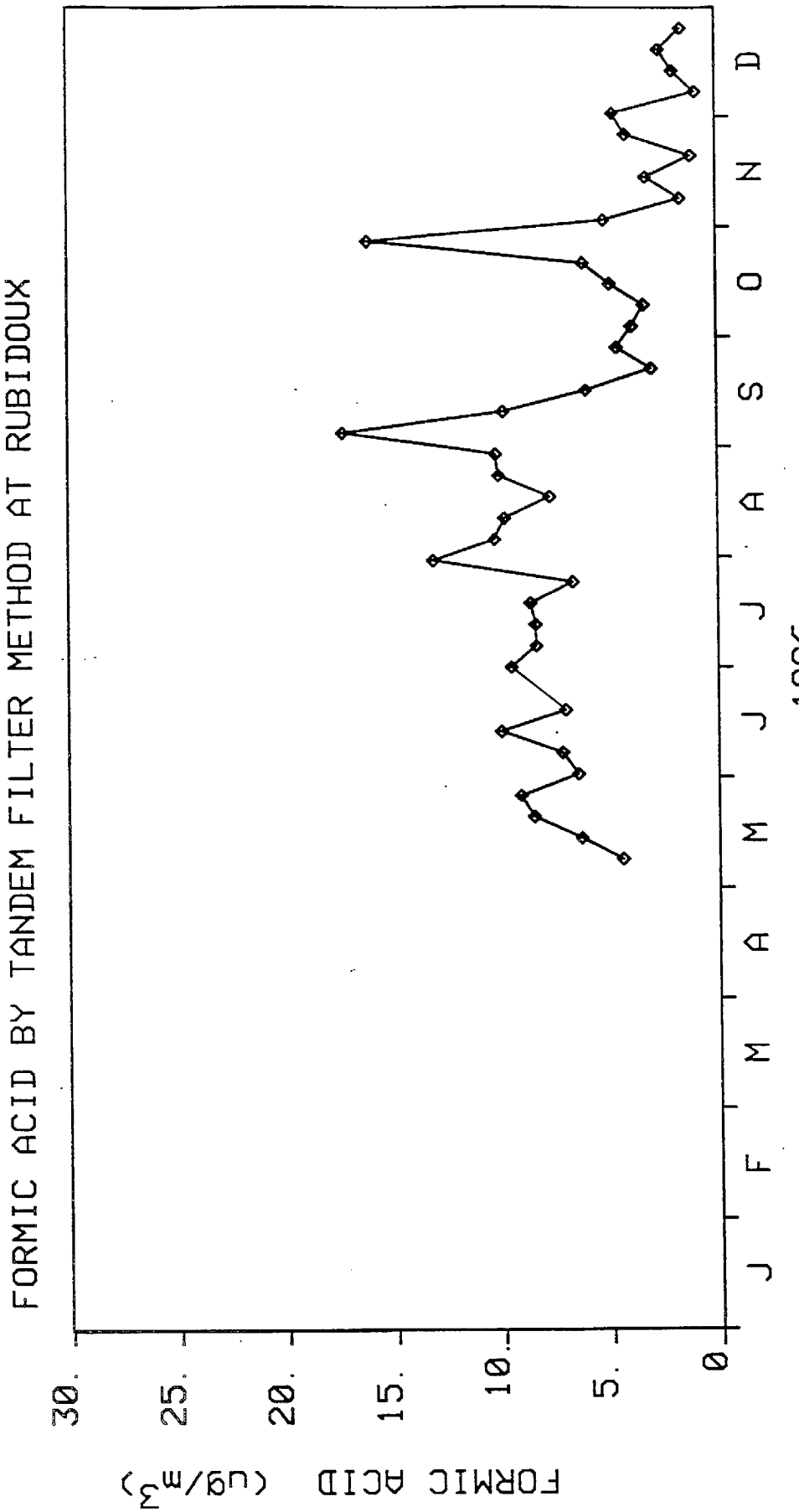

FORMIC ACID BY TANDEM FILTER METHOD AT RUBIDOUX
FORMIC ACID (ug/m3)
30.
25.
20.
15.
10.
5.
0
J F M A M J J A S O N D
--1986--

FIGURE 3.63

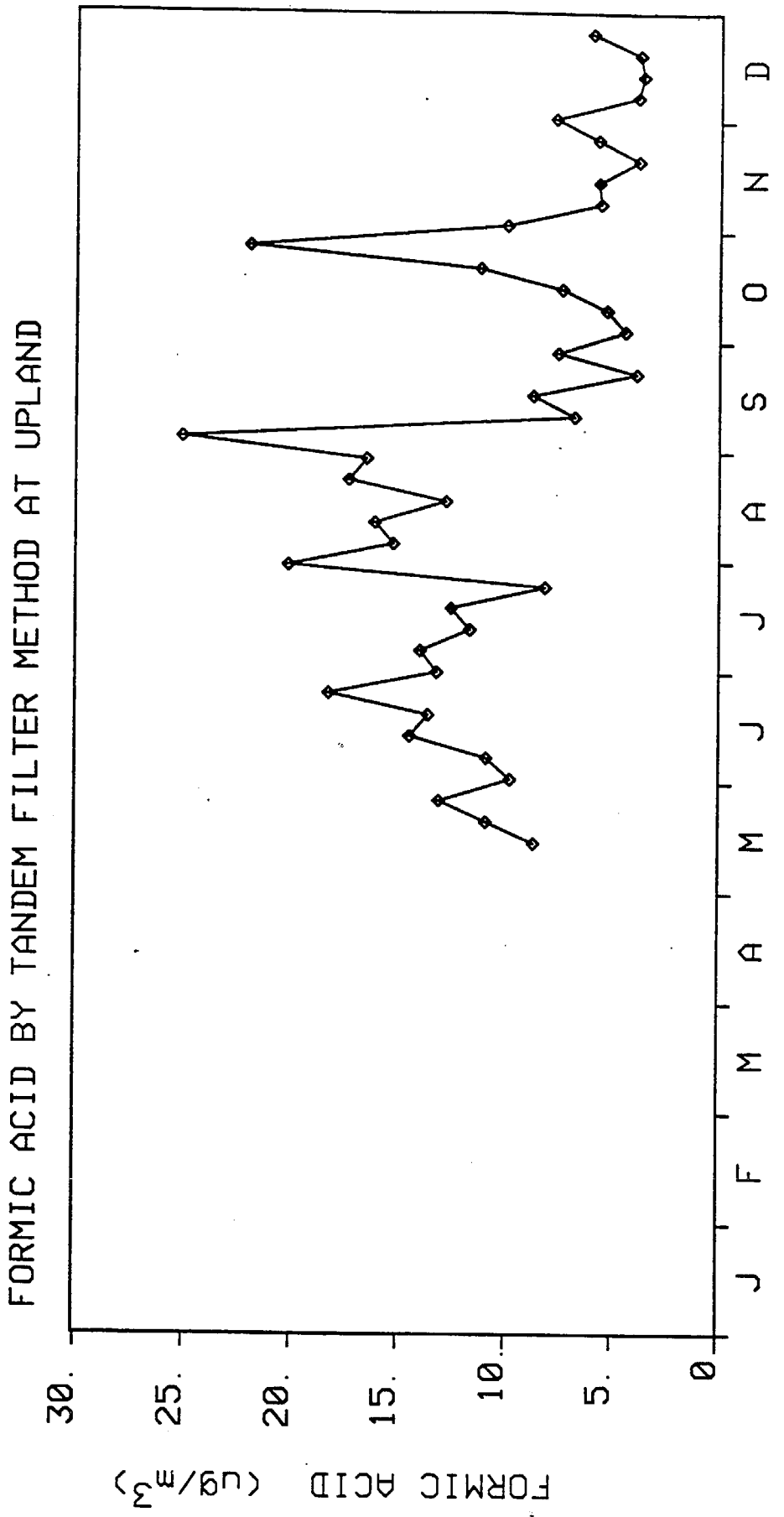

FORMIC ACID BY TANDEM FILTER METHOD AT UPLAND
FORMIC ACID (ug/m3)
30.
25.
20.
15.
10.
5.
0
J F M A M J J A S O N D
--1986--

FIGURE 3.64

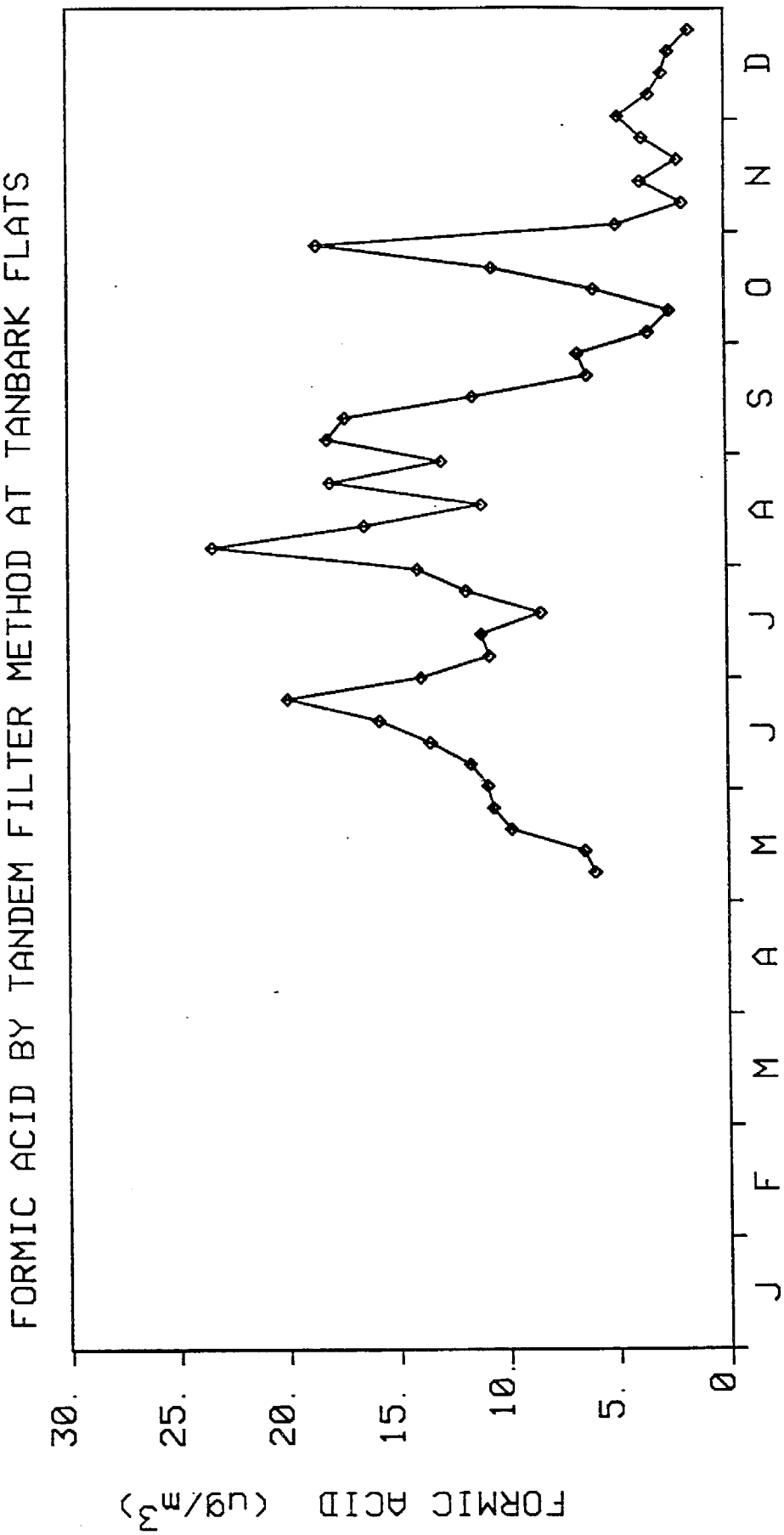

FORMIC ACID BY TANDEM FILTER METHOD AT TANBARK FLATS
FORMIC ACID (ug/m3)
30.
25.
20.
15.
10.
5.
0
J F M A M J J A S O N D
--1986--

FIGURE 3.65

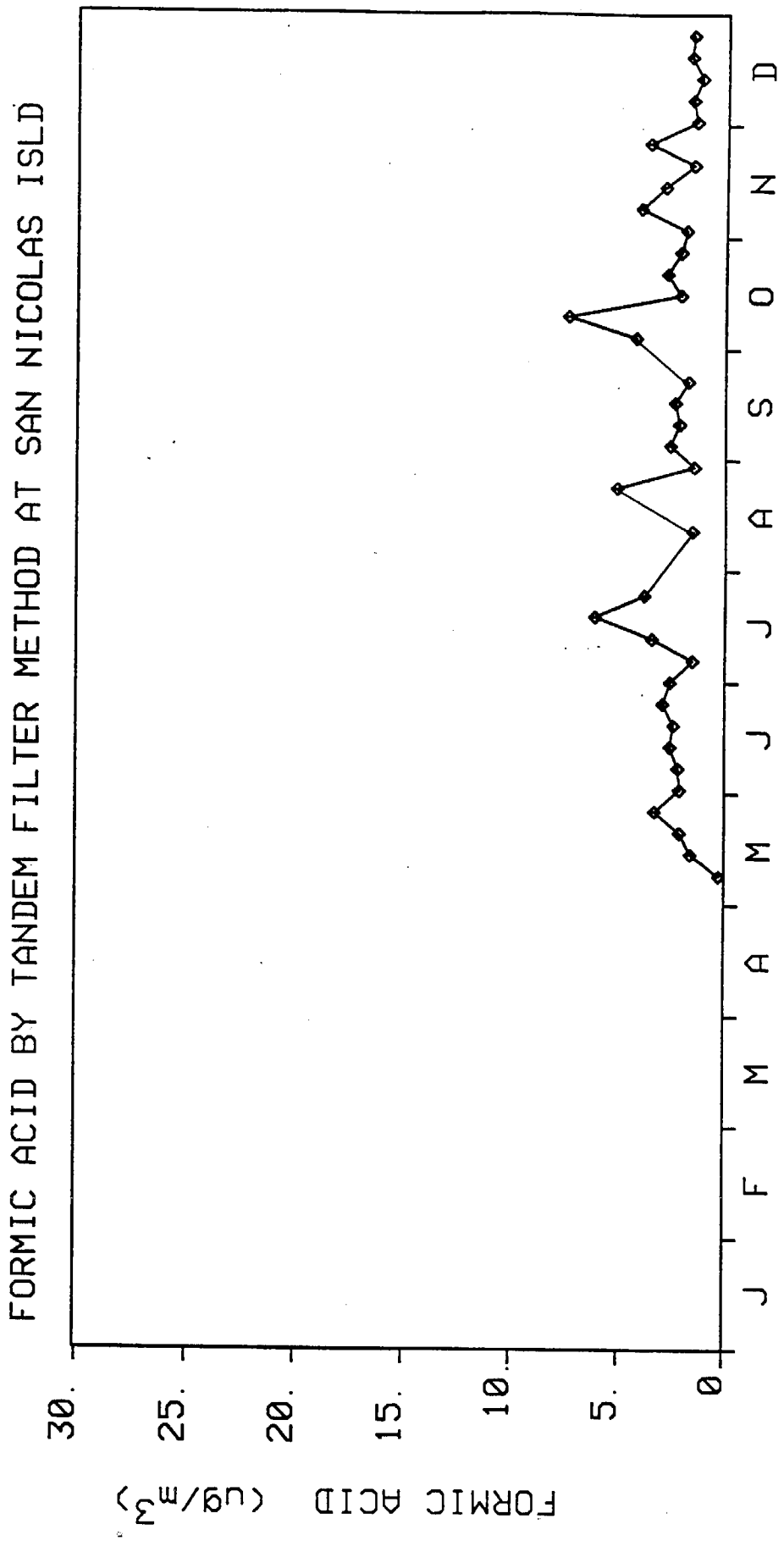

FORMIC ACID BY TANDEM FILTER METHOD AT SAN NICOLAS ISLD
FORMIC ACID (ug/m3)
30.
25.
20.
15.
10.
5.
0
J F M A M J J A S O N D
--1986--

FIGURE 3.66

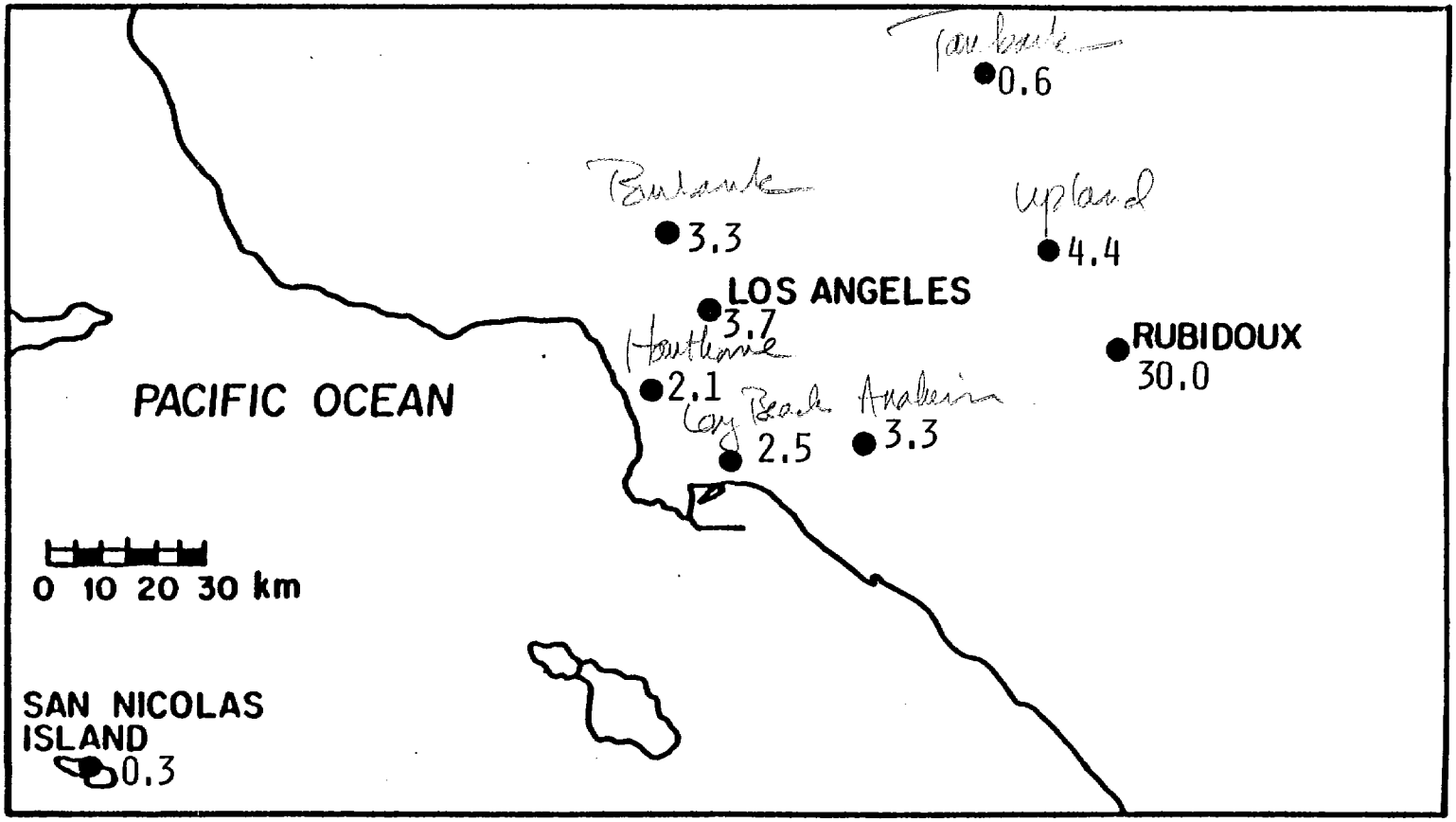
Table 3.4. Gas phase ammonia concentrations observed in the Los Angeles area, 1986 (concentrations in $\mu g\ m^{-3}$)

Site	NH_3 [a] Annual Average	NH_3 [a] Max. 24-h Average	n[b]
Burbank	3.3	6.4	60
Downtown LA	3.7	6.6	57
Hawthorne	2.1	12.7	61
Long Beach	2.5	10.2	58
Anaheim	3.3	9.3	60
Rubidoux	30.0	77.9	60
Upland	4.4	23.1	61
Tanbark Flats	0.6	1.8	55
San Nicolas Island	0.3	1.7	60

a. By tandem filter method employing oxalic acid impregnated backup filters.

b. Maximum number of sampling events is 61.

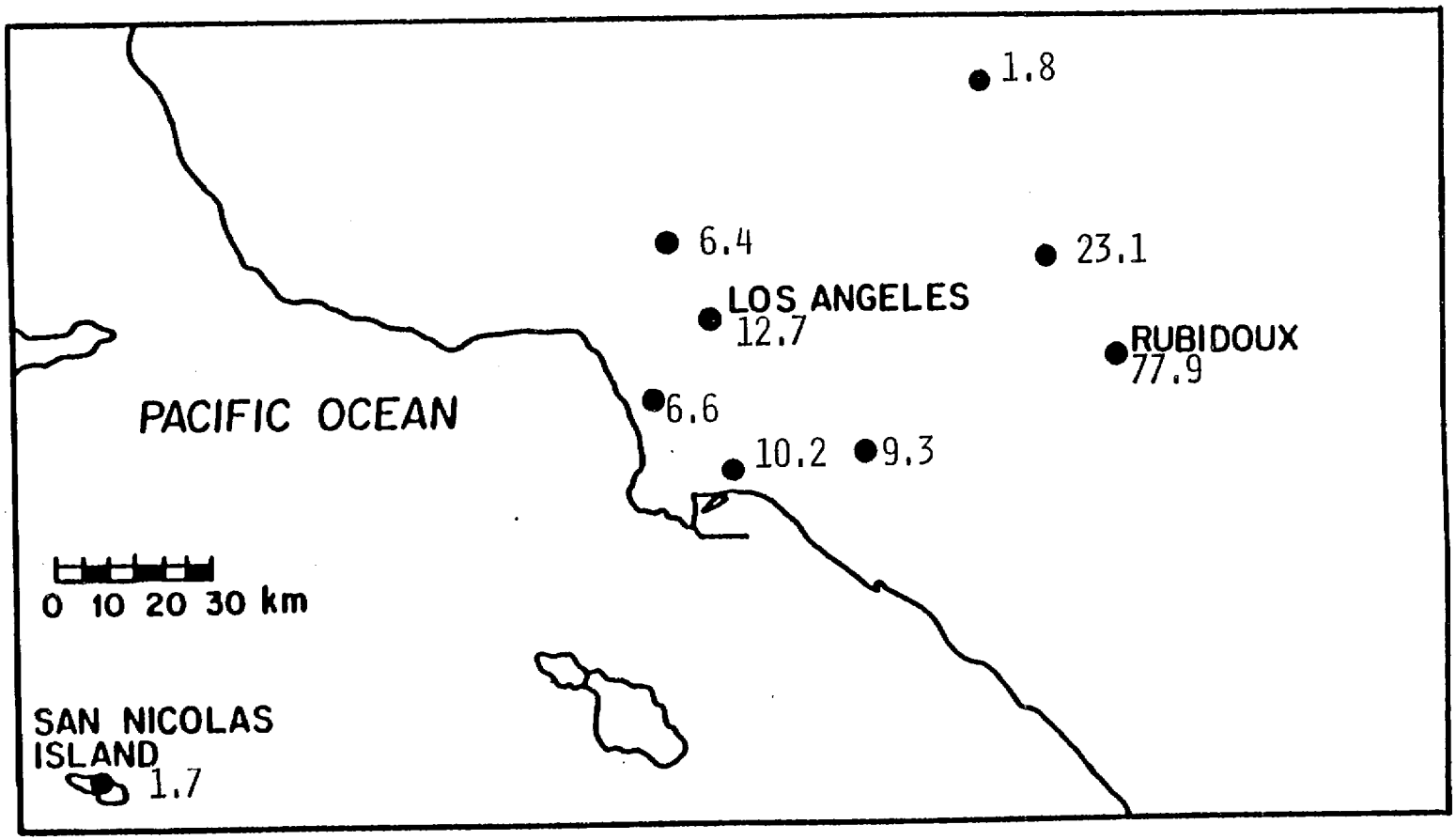
ANNUAL AVERAGE NH_3 CONCENTRATIONS ($\mu g\ m^{-3}$) OBSERVED IN THE LOS ANGELES AREA, 1986.[A]



[A]NH_3 BY TANDEM FILTER METHOD EMPLOYING OXALIC ACID IMPREGNATED BACKUP FILTERS.

FIGURE 3.67

MAXIMUM 24-HOUR AVERAGE NH_3 CONCENTRATIONS ($\mu G\ M^{-3}$) OBSERVED IN THE LOS ANGELES AREA, 1986.[A]



[A] NH_3 BY TANDEM FILTER METHOD EMPLOYING OXALIC ACID IMPREGNATED BACKUP FILTERS.

FIGURE 3.68

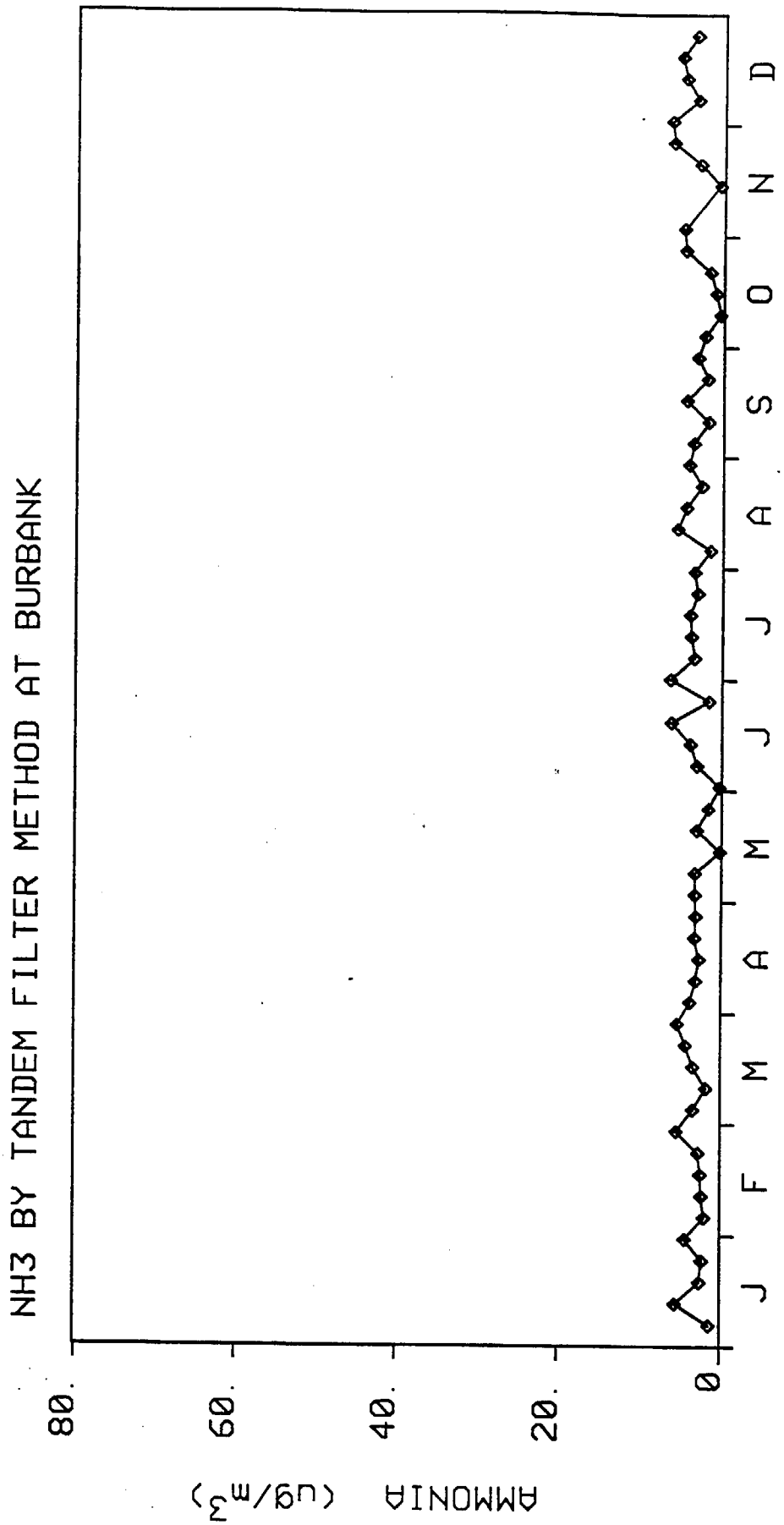

NH3 BY TANDEM FILTER METHOD AT BURBANK
AMMONIA (ug/m3)
80.
60.
40.
20.
0
J F M A M J J A S O N D
--1986--

FIGURE 3.69

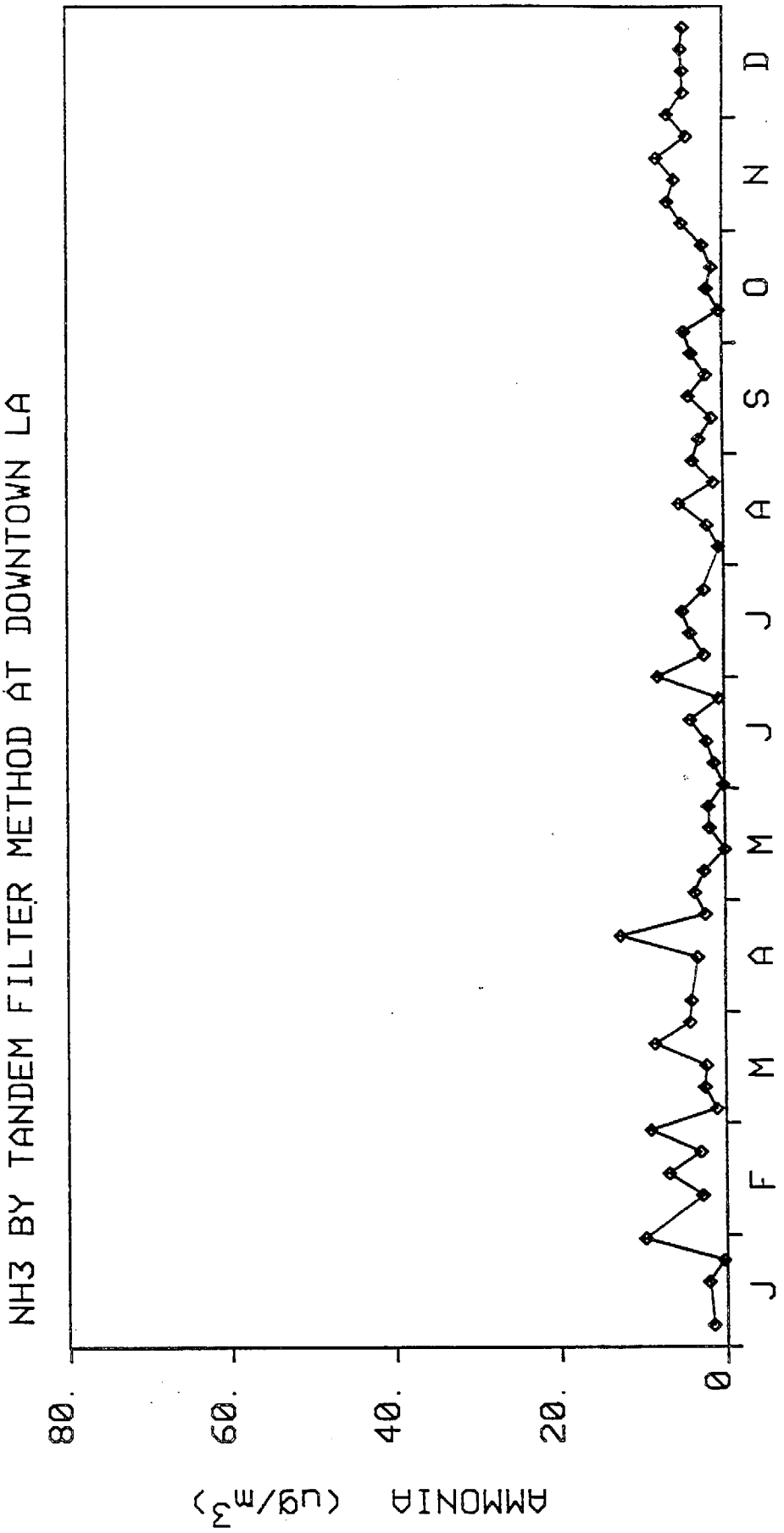

NH3 BY TANDEM FILTER METHOD AT DOWNTOWN LA
AMMONIA (ug/m3)
80.
60.
40.
20.
0
J F M A M J J A S O N D
--1986--

FIGURE 3.70

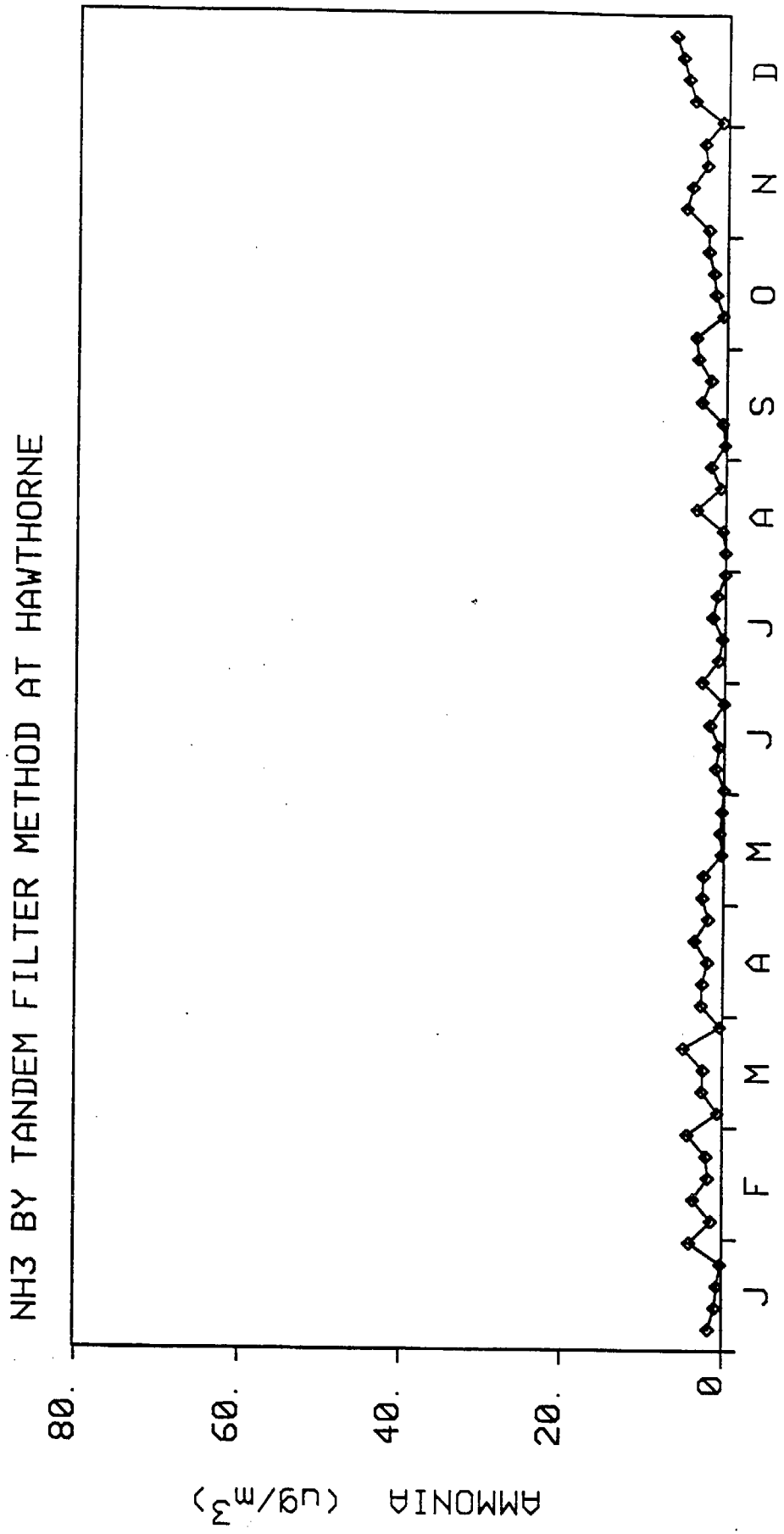

NH3 BY TANDEM FILTER METHOD AT HAWTHORNE
AMMONIA (ug/m3)
80.
60.
40.
20.
0
J F M A M J J A S O N D
--1986--

FIGURE 3.71

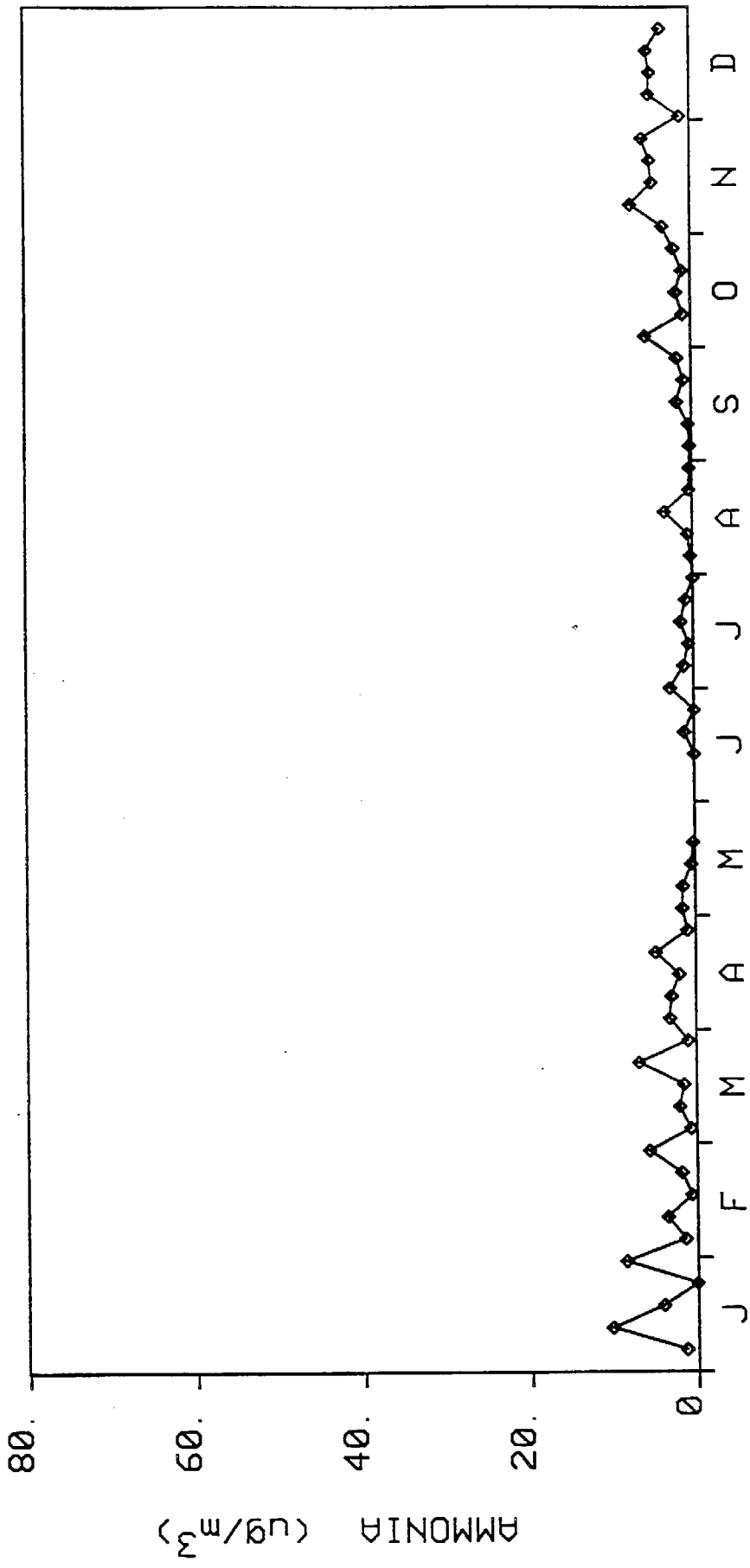

NH3 BY TANDEM FILTER METHOD AT LONG BEACH
AMMONIA (ug/m3)
80.
60.
40.
20.
0
J F M A M J J A S O N D
--1986--

FIGURE 3.72

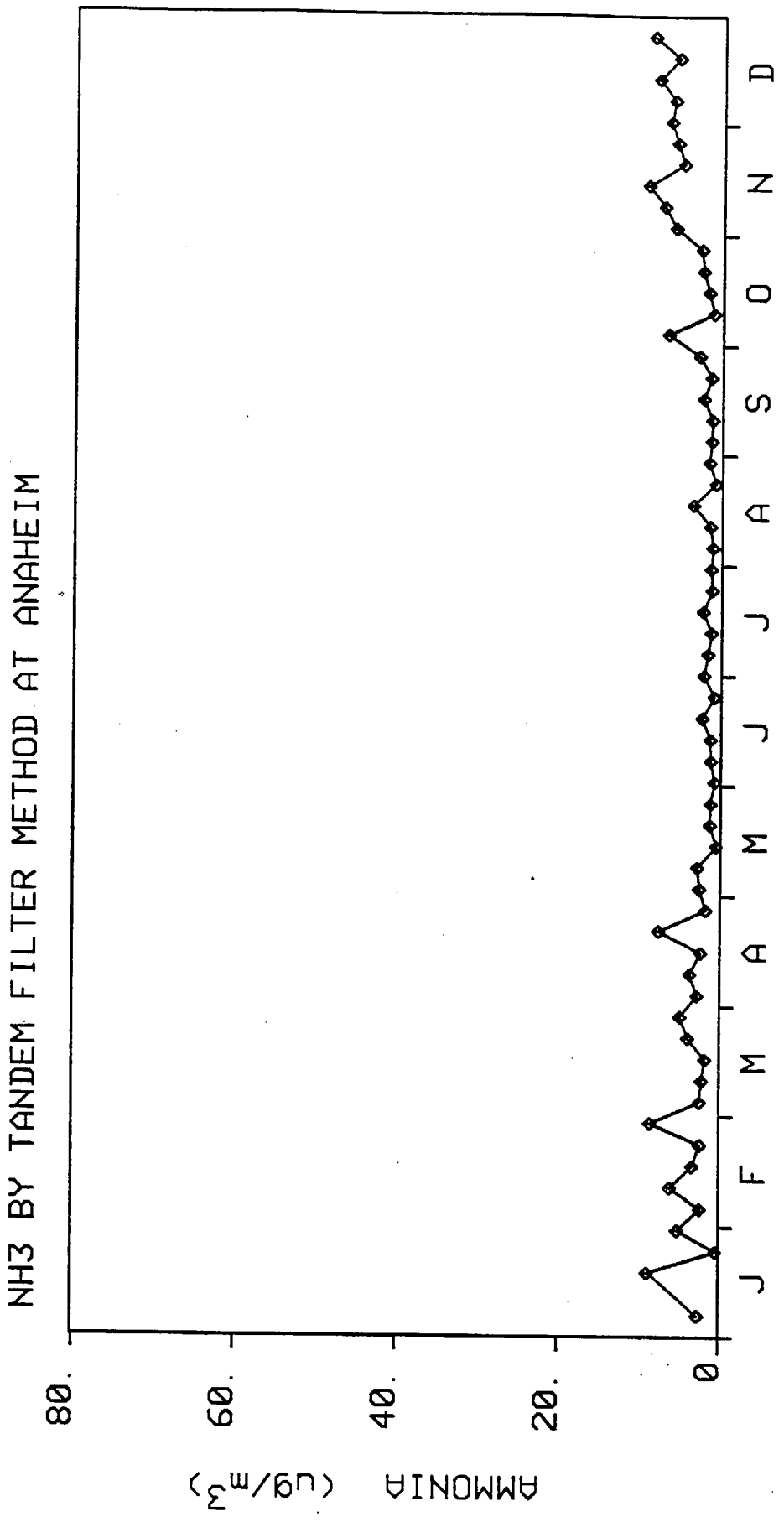

NH3 BY TANDEM FILTER METHOD AT ANAHEIM
AMMONIA (ug/m3)
80.
60.
40.
20.
0
J F M A M J J A S O N D
--1986--

FIGURE 3.73

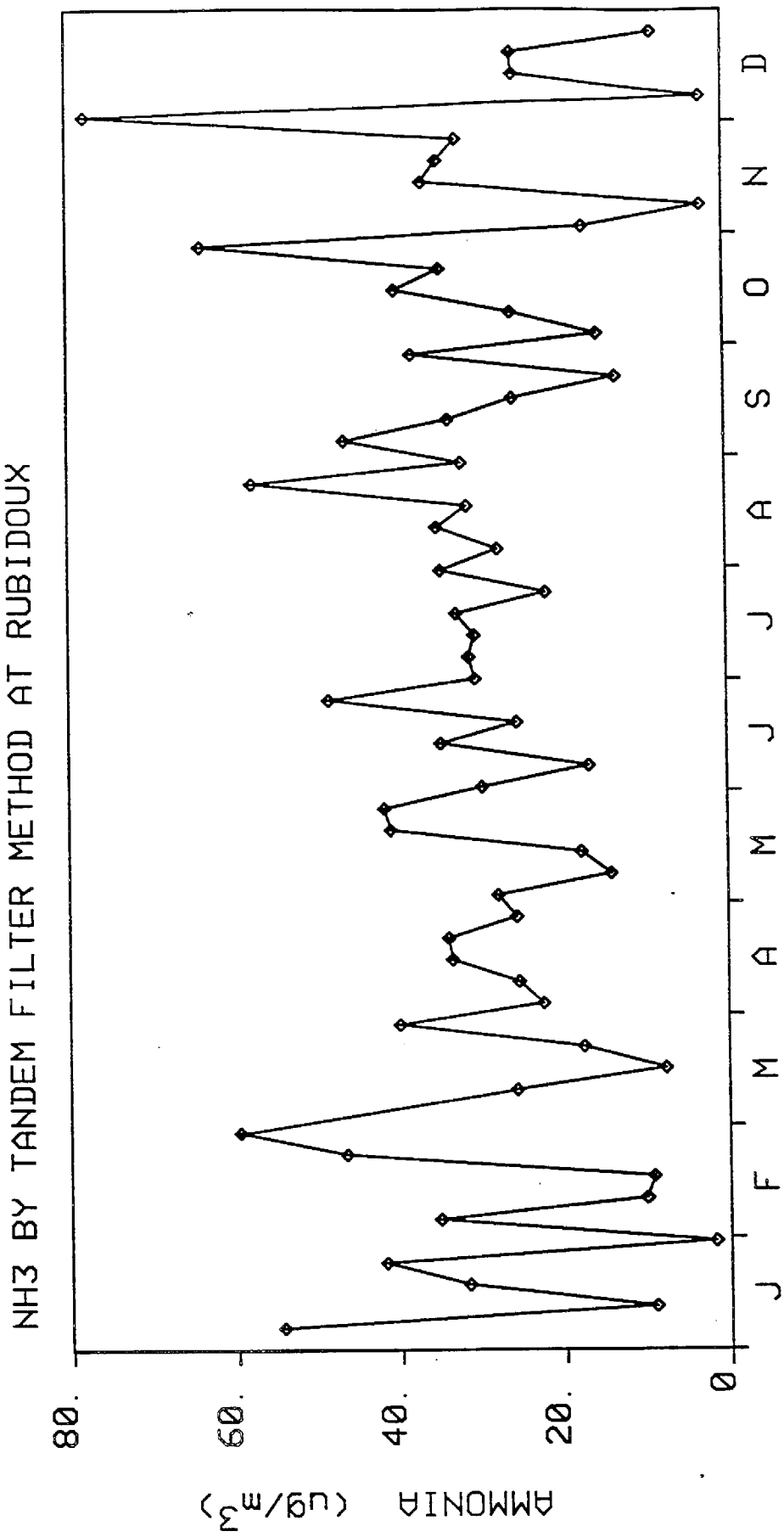

NH3 BY TANDEM FILTER METHOD AT RUBIDOUX
AMMONIA (ug/m3)
80.
60.
40.
20.
0
J F M A M J J A S O N D
--1986--

FIGURE 3.74

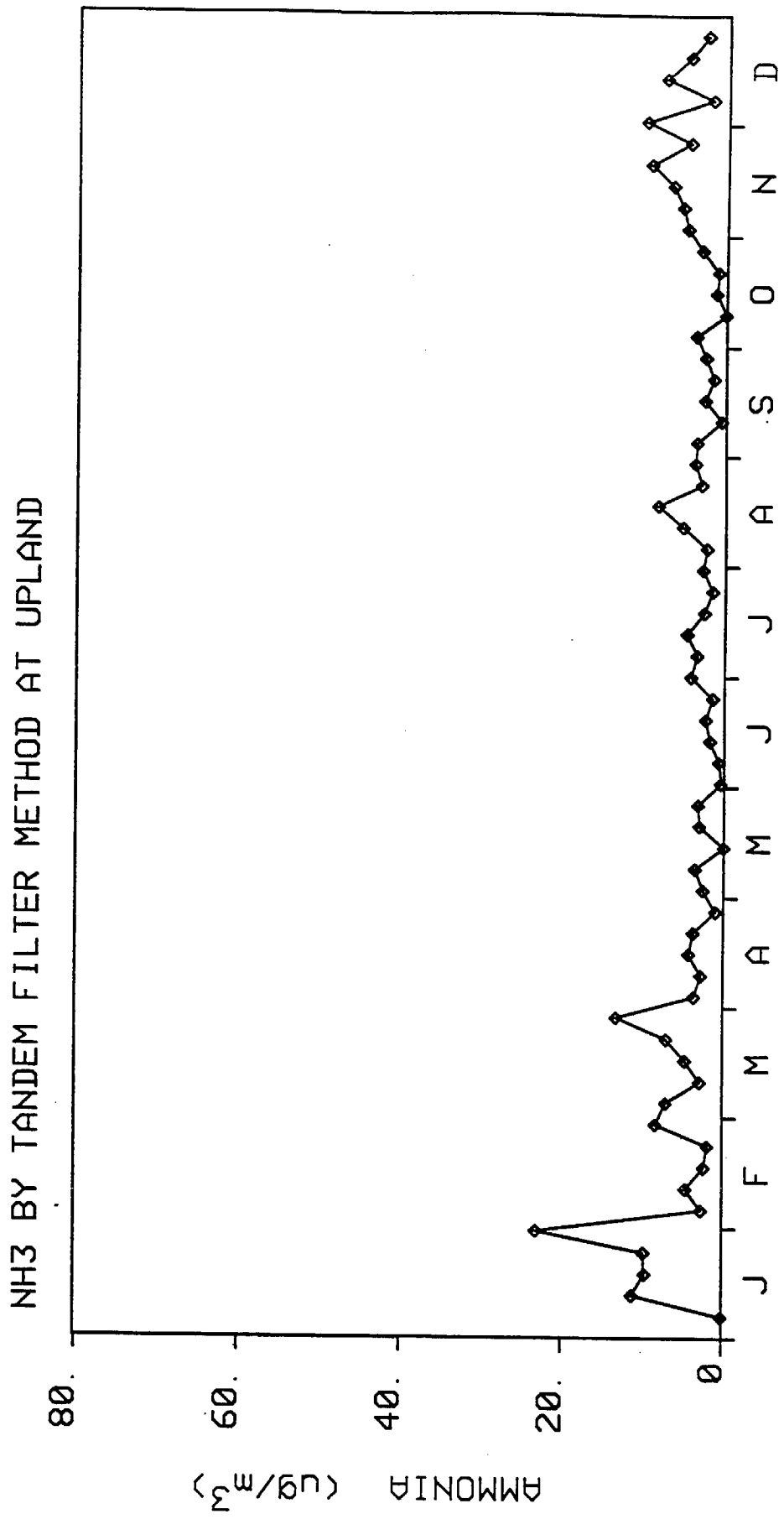

NH3 BY TANDEM FILTER METHOD AT UPLAND
AMMONIA (ug/m3)
80.
60.
40.
20.
0
J F M A M J J A S O N D
--1986--

FIGURE 3.75

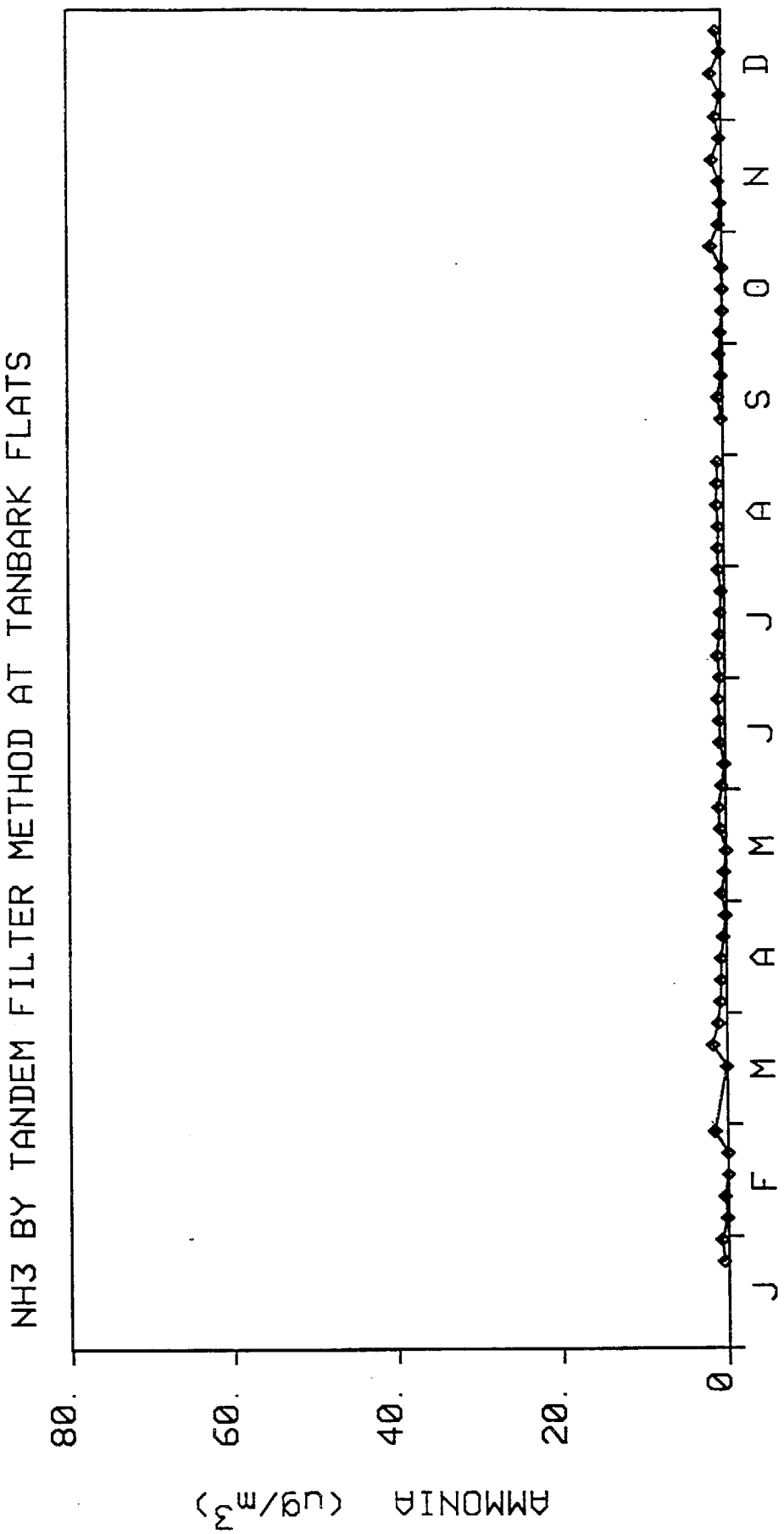

NH3 BY TANDEM FILTER METHOD AT TANBARK FLATS
AMMONIA (ug/m3)
80.
60.
40.
20.
0
J F M A M J J A S O N D
--1986--

FIGURE 3.76

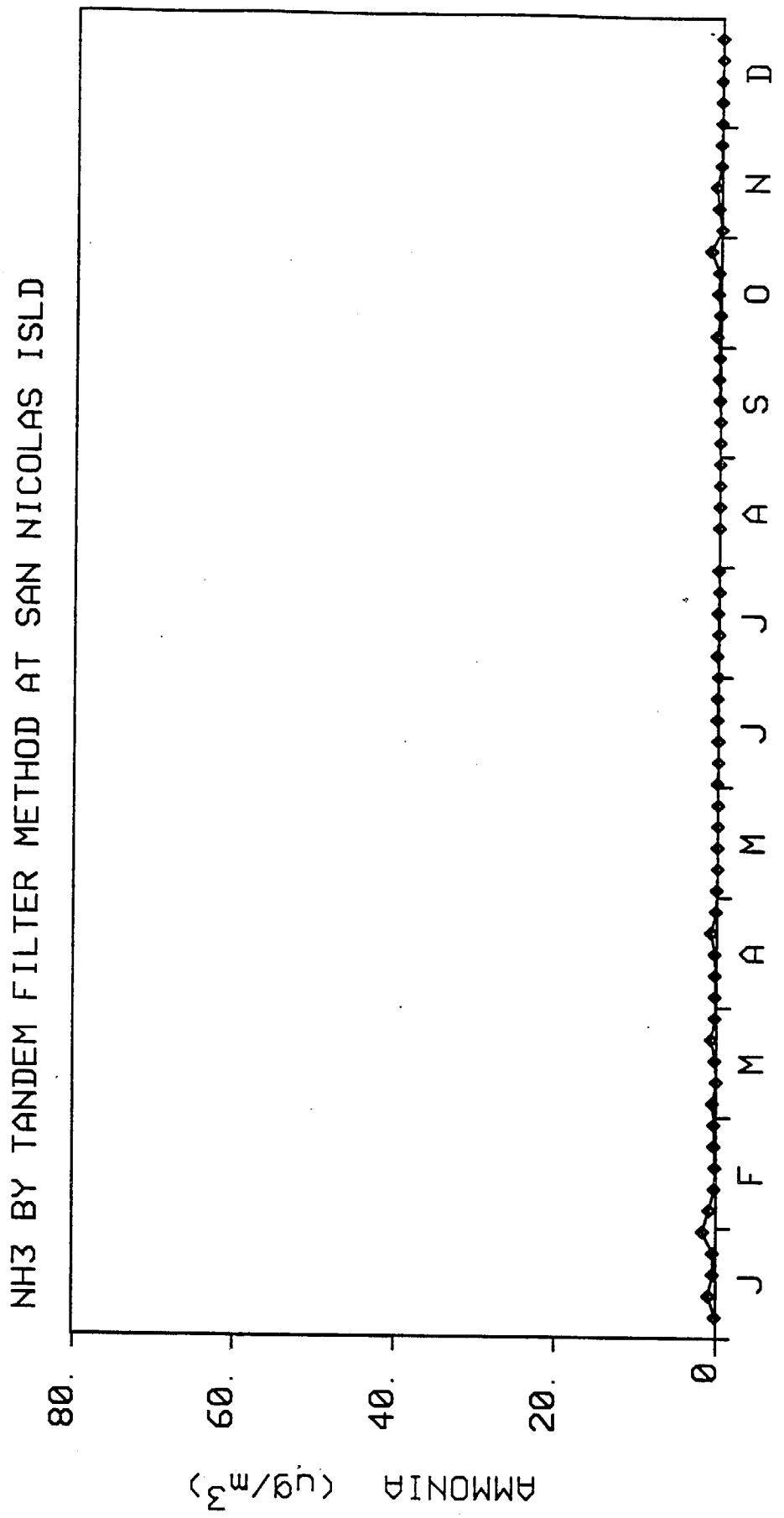

NH3 BY TANDEM FILTER METHOD AT SAN NICOLAS ISLD
AMMONIA (ug/m3)
80.
60.
40.
20.
0
J F M A M J J A S O N D
--1986--

FIGURE 3.77

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

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Environmental Quality Laboratory
California Institute of Technology
Pasadena, CA 91125

ABSTRACT

A one year atmospheric measurement program was conducted throughout the South Coast Air Basin in the greater Los Angeles area during 1986, to determine the long-term average concentration patterns of gaseous HNO_3 and aerosol nitrates. Upwind of the air basin at San Nicolas Island, HNO_3 levels are very low, averaging 0.3μg m^{-3} (0.1 ppb) over the year 1986. Annual average HNO_3 concentrations ranged from 3.1μg m^{-3} (1.2 ppb) near the Southern California coast to 6.9μg m^{-3} (2.7 ppb) at an inland site in the San Gabriel Mountains. At most monitoring stations, a majority of the inorganic nitrate (HNO_3 plus its reaction product: aerosol nitrates) was in the aerosol phase. Conversion of HNO_3 to aerosol nitrates was most pronounced at Rubidoux, near Riverside, CA, where on average 94% of the inorganic nitrate was found in the aerosol phase, and where fine particle nitrate concentrations exceeded 109μg m^{-3} during the peak 24-h period examined.

[a]Present address: Atmospheric Science Group, Pacific Gas and Electric, San Ramone, CA

INTRODUCTION

The atmospheric oxides of nitrogen, including nitric acid vapor, are major contributors to the dry deposition flux of strong acids to the earth's surface in Southern California (1,2). Nitric acid vapor also may react with ammonia to produce visibility-reducing fine aerosol nitrates and with sea salt or soil dust particles to produce coarse particle nitrates (3-11). While a number of short-term studies have been conducted in the Los Angeles area to measure ambient HNO_3 levels (6,12-17), data reported to date are for the summer season. No long-term record exists from which to examine seasonal trends and annual average values.

The present paper describes the results of a one-year field experiment in which HNO_3 plus fine particle and coarse particle nitrate were measured throughout the Los Angeles area. Measurements made in the urban area will be compared to observations at a remote background site on an offshore island and to data taken at a high elevation receptor site in the mountains downwind of the metropolitan area. Spatial and temporal trends in pollutant concentrations will be discussed in light of the transport patterns and atmospheric processes that govern the HNO_3/aerosol nitrate system.

EXPERIMENTAL

Sampling Sites

During calendar year 1986, a monitoring network designed to measure gas phase HNO_3 and atmospheric particulate matter was operated at nine sampling sites located throughout the South Coast Air Basin (SOCAB) which surrounds the Los Angeles area as shown in Figure 1. All sites except Tanbark Flats and San Nicolas Island were colocated with present South Coast Air Quality Management District (SCAQMD) continuous air monitoring stations. A description of the SCAQMD sites is given by the U.S. Environmental Protection Agency (18,19).

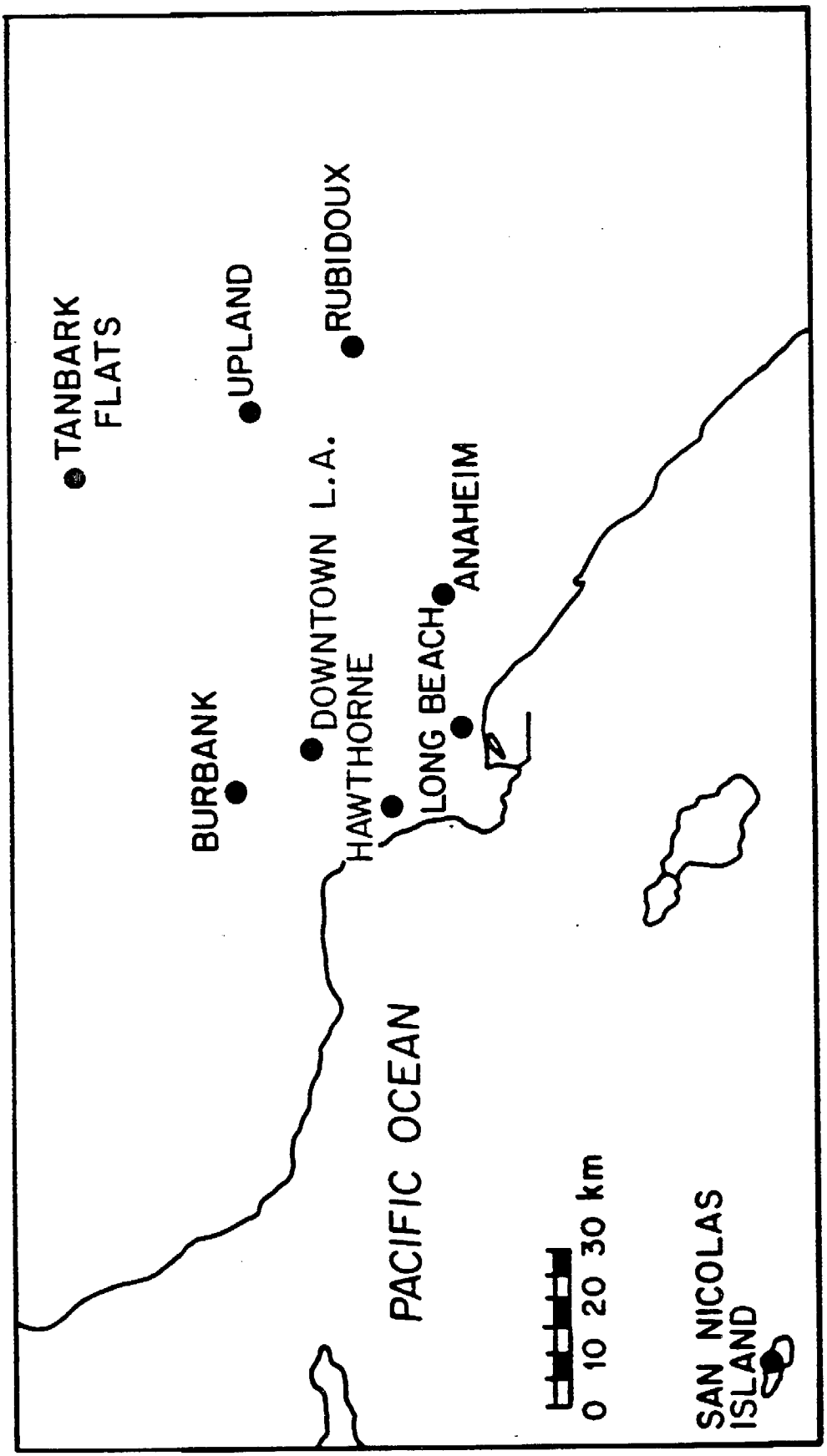


Figure 1. Los Angeles area monitoring network. All sites are at an elevation within 400m of sea level except Tanbark Flats which is at an elevation of 870m in the San Gabriel Mountains.

The Tanbark Flats site was located in the mountains north of San Dimas, in the Angeles National Forest, at an elevation of approximately 870m. This site was chosen to determine the concentration of acidic pollutants present in the national forests to the north of Los Angeles, and because air quality modeling calculations suggest that nitric acid concentrations may be different at higher elevations than is observed near the ground within the urban area (20). The ninth site was located at the meteorological station on San Nicolas Island (SNI), approximately 140km southwest of the Los Angeles coastline. This remote, off-shore location was chosen to determine background pollutant levels present in the marine environment upwind of Los Angeles. At four of the sites (Burbank, Downtown Los Angeles, Long Beach, and Upland) the sampling systems were placed on the roofs of one or two story buildings. At the other sites the systems were placed with inlets 2-3m above ground level. All sites except Tanbark Flats were below an elevation of 390m above sea level.

Sampler Design and Sample Collection

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

The denuder difference apparatus deployed during this study is illustrated at the left side of Figure 2, and its design has been described in detail elsewhere (16). In this series of experiments, ambient air was drawn at a rate of 24.8 lpm through a Teflon-coated AIHL-design cyclone separator (26) and a 1 l Teflon-coated manifold. Coarse particles with aerodynamic diameter greater than 2.2μm were removed by the cyclone. The airflow then was divided between several parallel filter holders. One filter holder (sampling line A, Figure 2) held a nylon filter (1.0μm pore size, 47mm diameter; Membrana Corp. and Gelman Sciences) that acted as a perfect sink

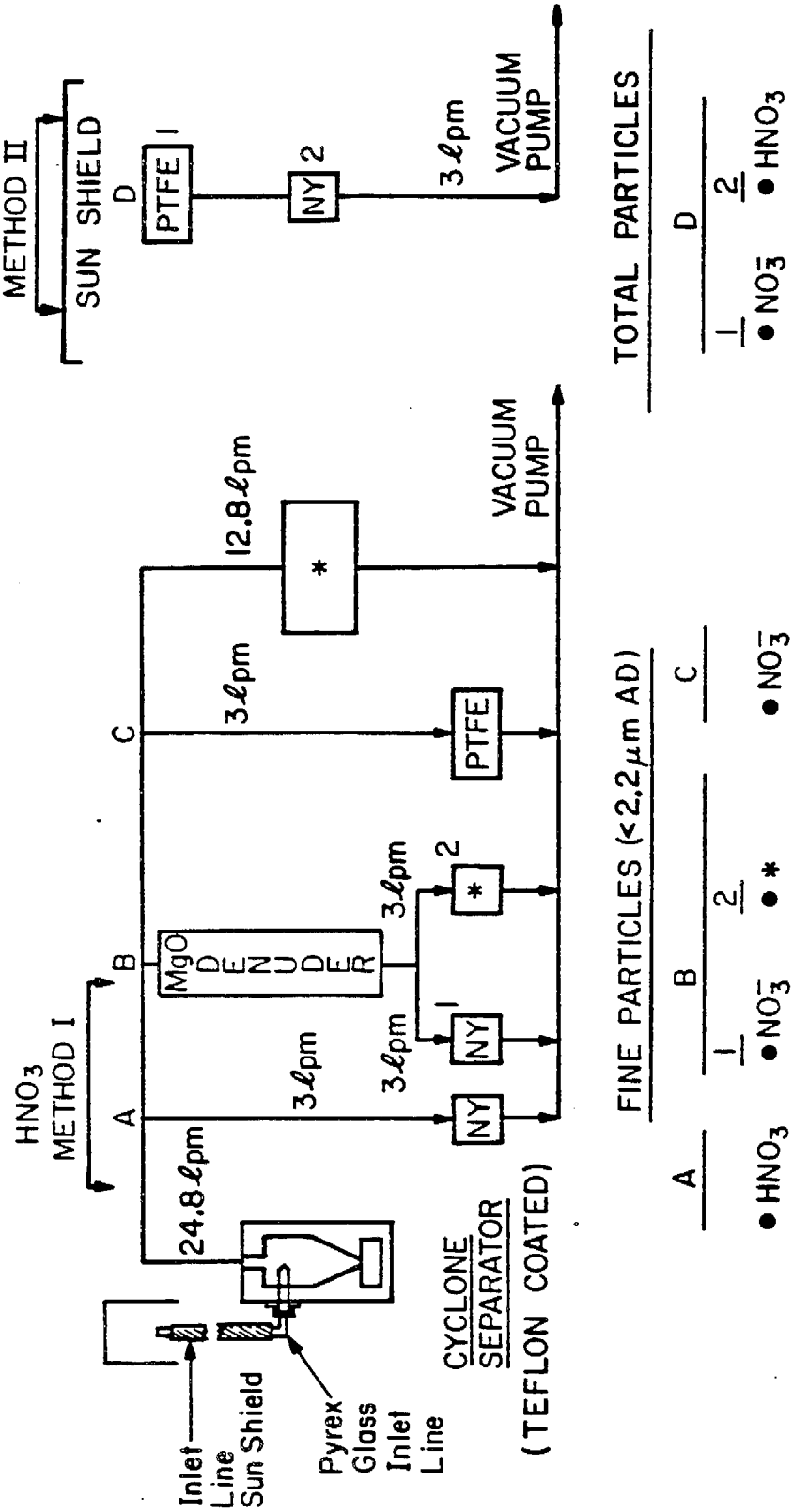


Figure 2. Sampler and sampling protocol.

for both fine particle nitrate and nitric acid vapor. A second nylon filter (sampling line B1) was used as a backup filter beneath a MgO-coated diffusion denuder that was designed to remove gas phase HNO_3. Thus nylon filter B1 collected only fine particle nitrate. Nitric acid was determined by the difference between the nitrate ion concentration measured on these two nylon filters (A-B1).

In the tandem filter method (sampling line D, Figure 2), nitric acid was collected on a nylon backup filter (D2) after particles (including aerosol nitrate) were removed by the use of an open face, inert polytetrafluoroethylene (PTFE) prefilter (D1) (2.0μm pore size, 47mm diameter, Membrana Corp.). This method has been shown to produce HNO_3 measurements that are artificially high due to the decomposition of NH_4NO_3 collected on the PTFE prefilter, releasing additional HNO_3 which is collected on the nylon backup filter (12,15,16,25,27,28).

Aerosol nitrate concentrations were measured in several size ranges using the system just described. Fine particle nitrate collected on nylon filter B1 (Figure 2), located below the diffusion denuder, provided a measure of fine particle nitrate concentrations that did not suffer from major positive or negative artifact problems (25,27,28). To gauge the magnitude of the aerosol nitrate loss from Teflon filters, fine particle nitrate concentrations also were measured from samples collected on a PTFE filter (sampling line C, Figure 2) located downstream of the cyclone separator. Total particulate nitrate concentrations (fine particle nitrate plus coarse particle nitrate) were measured from the nitrate ion collected on the open faced Teflon filter that preceeded the nylon filter in the tandem filter sampler (filter D1, Figure 2). Total particulate nitrate concentrations reported here were corrected, to the extent possible, for the previously mentioned loss of aerosol nitrate from filter D1. It was assumed that nitrate losses from the PTFE filter were due mainly to decomposition or volatilization of NH_4NO_3 which is found mostly in the fine particles (25,27,28). An estimate of fine aerosol nitrate volatilization from PTFE filters was obtained dur-

ing each sampling event based on the difference between fine particle nitrate concentrations measured on filters B1 and C on that day at that site. The estimate of volatilized aerosol nitrate was then added to the total particle nitrate value measured on PTFE filter D1 on that day at that site to arrive at a corrected total particulate nitrate concentration. Coarse particle nitrate concentrations were obtained by difference between corrected total particulate nitrate concentrations and the fine particle nitrate concentrations measured on the nylon filter located below the diffusion denuder in Figure 2.

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

The average blank values and analytical precisions for the measurement of nitrate ion on the nylon and PTFE filters employed in this study are listed in Table I. Both filter types were obtained from two sources: Membrana Corporation, no longer in business, and Gelman Sciences, Inc. Three lots of each filter type also were employed throughout the year. No difference between lots was observed for NO_3^- measured on PTFE filter blanks, however a considerable difference (almost 2μg/filter) was observed between lots for NO_3^- measured on nylon filter blanks.

Table I. Summary of filter blanks and relative analytical precision for NO_3^-.

Filter Location	Filter Type.	Analytical Precision[c]	Filter Blank[d] (μg/filter) (lot #, source)
cyclone-denuder system[a]	nylon	4.2%	0.53±0.17 (K07025E, Gelman Sciences)
			1.57±0.54 (84800, Gelman Sciences)
	PTFE(0.5μm)	5.7%	<0.6 (4215 & 2326, Membrana Corp.)
tandem filter unit[b]	nylon	4.2%	0.63±0.33 (4222, Membrana Corp.)
			2.38±0.55 (84800, Gelman Sciences)
	PTFE(2.0μm)	5.0%	2.5±0.8 (092, Membrana Corp.)

a. Filters located following a 1m acid-washed glass inlet line, a Teflon coated cyclone separator and manifold, and/or a MgO diffusion denuder.

b. Open face PTFE prefilter with the nylon filter located about 1" further downstream.

c. Based on duplicate analysis of many split filters (n typically >50).

d. The detection limit was defined as two times the standard deviation of the filter blank when the filter blank was greater than the instrument detection limit for NO_3^- of 0.6μg/filter.

Dynamic field blanks were obtained during the year in an amount equal to one-tenth of the actual number of ambient samples taken.

As can be seen in Table I, filters which were better protected from the atmosphere (i.e., buried within the cyclone-denuder system, left side of Figure 2) had the lowest filter blank. In contrast, the PTFE open face prefilter had a much higher dynamic blank value. This may be due to wind blown dust particles which settle on the filter during times when the filters were loaded onto the sampler but the sampler was not running, and in spite of the fact that a particle fallout and sun shield was positioned to protect the open faced filter holders. This observation reinforces our decision to install and remove the filters as close to the sampling event as possible.

Sample Analysis

Nylon filters were leached by lightly shaking each of them in 20ml of a $CO_3^=/HCO_3^-$ buffer (eluent for the ion chromatograph) for 3 hours or more at 10°C. Polytetrafluoroethylene filters first were wetted with 0.2-0.25ml of ETOH (100 percent), to reduce the hydrophobic nature of this material (29) and then leached in the same manner as the nylon filters. The leachate was analyzed by ion chromatography for nitrate ion. Concentrations were determined relative to standards of known concentrations prepared daily from more concentrated standards. The high concentration standards were prepared new at least every 30 days from ACS analytical reagent grade $NaNO_3$.

Approximately 10 percent of the filters were cut in half and each half was analyzed separately (i.e., a duplicate measurement). The coefficient of variation obtained for all nylon filters analyzed in this manner was about 4.2 percent, and for PTFE fine and total particle filters was 5.0 and 5.7%, respectively. The accuracy of our NO_3^- measurements from nylon PTFE filters was determined during a previous

study (15,16). In that study, the California Air Resources Board supplied nylon and PTFE filters containing quantities of nitrate ion known only to the filter supplier. Results from that quality assurance study indicated an accuracy of better than ±10 percent for NO_3^- determination over the concentration range tested. The detection limit for NO_3^- measured on the nylon filters employed in this study ranged from 0.3 to 1.1μg/filter. This detection limit was based on 2 times the standard deviation of the average filter blanks and depended on the filter lot employed. PTFE filter blanks were lower than the instrument detection limit for NO_3^-, which was 0.6μg/filter.

RESULTS

Comparison of Nitric Acid and Aerosol Nitrate Measurement Methods

Nitric acid was measured by the denuder-difference method (DD; HNO_3 method I, Figure 2) and by the tandem filter method (TF; HNO_3 method II, Figure 2), both of which are described in the experimental section of this manuscript. Linear regression analysis was employed to compare these two techniques for the measurement of ambient HNO_3 concentrations. The resulting regression equation, based on nearly all sampling periods, at all sites was: TF = 1.48 (DD) + 1.09μg m^{-3}; r = 0.932; n = 514. This result indicated that, on the average, the tandem filter method yielded HNO_3 concentrations that were greater than those obtained by the denuder-difference method. Although there appeared to be a systematic error, the two methods were highly correlated, with a correlation coefficient (r) of 0.932. These results are consistent with those obtained during the 1985 Claremont Nitrogen Species Comparison Study (15,16). In that field experiment, both of the methods employed here were compared to measurements of ambient HNO_3 concentrations made by Fourier transform infrared spectroscopy (FTIR). The conclusion from the 1985 Claremont study was that the denuder difference method yielded reasonably unbiased estimates of atmospheric HNO_3, while the tandem filter

method overestimated atmospheric HNO_3 concentrations. This postive HNO_3 artifact, observed when using the tandem filter method, has been studied previously (25,27,28,30). This artifact is believed to be due to release of HNO_3 from the decomposition of NH_4NO_3 aerosol previously collected on the PTFE prefilter with the subsequent collection of that HNO_3 on the nylon backup filter.

Fine particle nitrate was measured in two ways: 1) by collection on a nylon filter located downstream of a cyclone separator that was followed by a diffusion denuder (the cyclone-denuder method, CD; see sampling line B1, Figure 2) and 2) by collection on a PTFE filter located downstream of a cyclone separator (the cyclone only method, CY; see sampling line C, Figure 2). Linear regression analysis also was used to compare these two methods for measuring ambient fine particle nitrate concentrations (method CD versus CY). The resulting regression equation, based on nearly all sampling periods, at all sites was: CY = 0.82 (CD) - 1.98μg m^{-3}; r = 0.920; n = 526. This result indicated that, on the average, the use of PTFE filters as a collection substrate leads to an underestimation of atmospheric fine particle nitrate concentrations, again most probably due to vaporization of NH_4NO_3 collected on the PTFE filter. Although there is a systematic difference, the results obtained by these two methods are highly correlated.

On an absolute basis, when comparing the denuder difference and the tandem filter methods for HNO_3 measurement, the amount of nitrate observed as an increase in HNO_3 due to aerosol nitrate loss from the PTFE prefilter D1 in Figure 2 was 3.1μg m^{-3}, averaged over all samples taken. The loss of fine particle NO_3^- from the PTFE fine particle filter (sampling line C, Figure 2) relative to fine particle NO_3^- measured by the cyclone-denuder method (sampling line B1, Figure 2) was 3.5μg m^{-3}, averaged over all samples taken. The smaller loss of particulate nitrate from the open face PTFE filter (an average loss of 3.1μg m^{-3}) relative to the PTFE filter behind the cyclone (an average loss of 3.5μg m^{-3}) might have been due to the reac-

tion of HNO_3 with coarse particle sea salt or soil-related particles which were collected on the open face filter but which were largely removed by the cyclone separator and thus were present to a much lesser degree on the fine particle PTFE filter.

The above observations suggest that the denuder difference method for HNO_3 and the cyclone-denuder method for fine particle nitrate determination are superior to the tandem filter method. That finding was consistent with the results of previous studies (15,16,25,27,28). Therefore, the analysis of Los Angeles air quality that follows was based on the denuder difference method results for HNO_3 and the cyclone-denuder method results for fine particle nitrate. Total particulate nitrate concentrations collected on PTFE filters were corrected for nitrate aerosol volatilization to the extent possible by the method outlined earlier in this paper.

Nitric Acid Concentrations

Daily average nitric acid concentrations observed during 1986 are shown in time series in Figure 3. At San Nicolas Island, located in the prevailing upwind direction, HNO_3 levels are very low, with an average HNO_3 value of approximately 0.3μg m^{-3} (0.1 ppb). Peak single day events at San Nicolas Island are observed on rare occasions with HNO_3 concentrations approaching 5μg m^{-3} (2 ppb).

Near the coastline at Hawthorne and at Long Beach, nitric acid levels are typically less than 5μg m^{-3} (2 ppb) during most days of the year. 24-h periods with HNO_3 concentrations approaching 10μg m^{-3} (4 ppb) occur on isolated days during the winter, spring and summer, but there is no pronounced summer seasonal peak in HNO_3 concentrations near the coast.

Moving inland to Burbank, Downtown Los Angeles, Upland, and Tanbark Flats, a summer seasonal peak in HNO_3 levels is observed. 24-h average HNO_3 concentrations in the range 15-20μg m^{-3} (6-8 ppb) are seen on numerous occasions during the

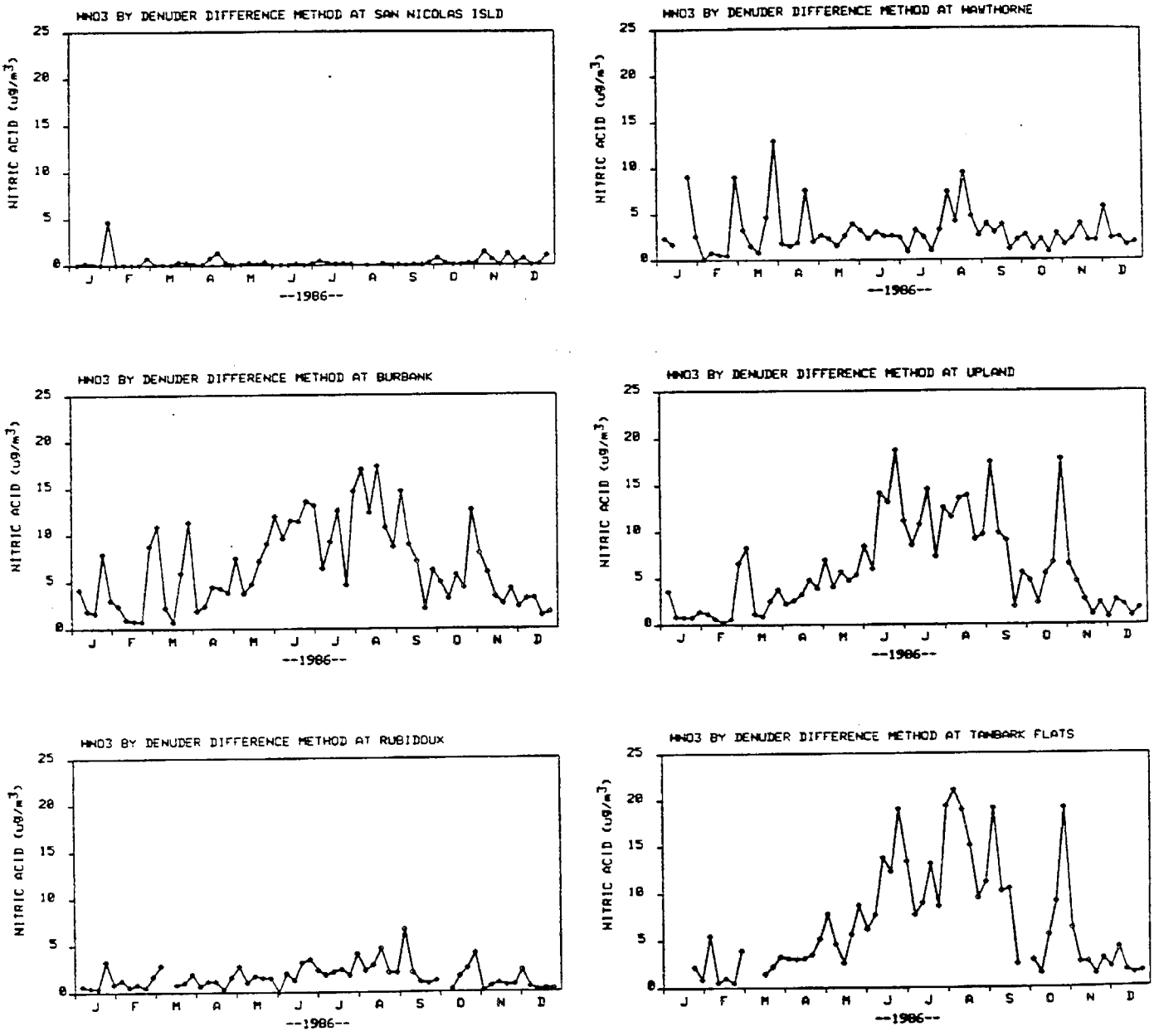


Figure 3. Daily HNO_3 concentrations at selected sites in the Los Angeles area. HNO_3 was measured by the denuder difference method.

period June-September 1986. Although lower values prevail on average during the spring, fall and winter season, Figure 3 shows that 24-h average HNO_3 concentrations in the range 10-15μg m^{-3} (4-6 ppb) can be observed at these inland sites on isolated days during most seasons of the year.

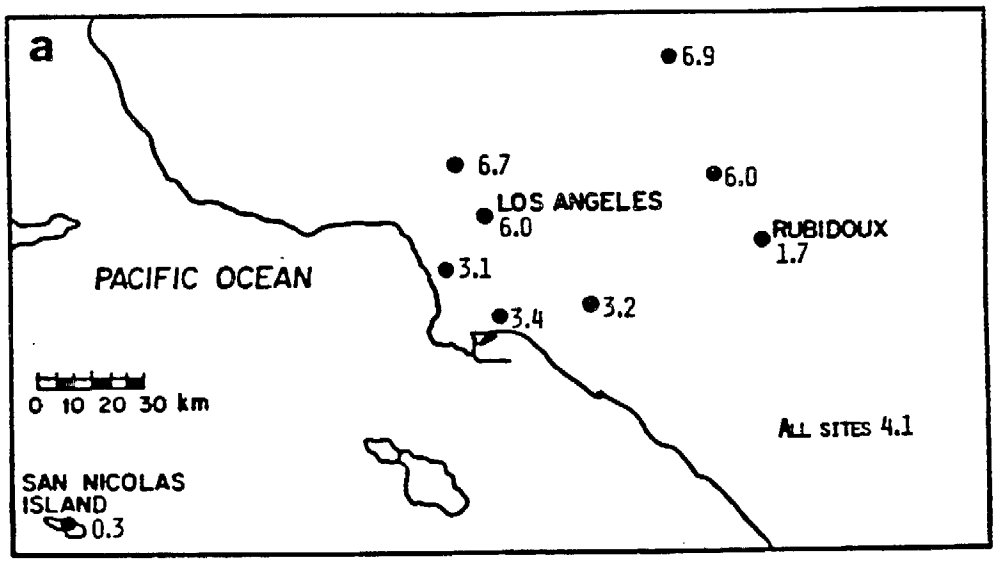
Nitric acid concentrations measured at Rubidoux stand in direct contrast to the pattern of increasing nitric acid concentrations with increasing distance in the prevailing downwind direction (inland) over the urban area. Unlike the other sites in the eastern portion of the air basin, HNO_3 levels at Rubidoux are very low during all seasons of the year, typically less than 2μg m^{-3} (<1 ppb).

Annual average and maximum 24-h average HNO_3 concentrations are displayed in Figure 4. Annual average HNO_3 levels at near-coastal sites are in the range 3-4μg m^{-3} (1.2-1.6 ppb) rising to 6-7μg m^{-3} (2.3-2.7 ppb) at inland locations like Downtown Los Angeles, Burbank, Upland and Tanbark Flats. Once again, Rubidoux shows the lowest annual average and 24-h average HNO_3 concentrations of any on-land monitoring site.

Total Inorganic Nitrate Concentrations

Annual average and maximum 24-h average total inorganic nitrate concentrations (HNO_3 plus its further reaction product, aerosol nitrates) are shown in Figure 5. Annual average values range from a low of 3μg m^{-3} at San Nicolas Island to 16-18μg m^{-3} at near coastal sites, to 24μg m^{-3} at Los Angeles and Burbank, rising to 27-29μg m^{-3} at the farthest inland urban sites, Upland and Rubidoux. Peak 24-h average inorganic nitrate concentrations follow a similar pattern, with the highest 24-h average value of 139.5μg m^{-3} measured at Rubidoux.

Subtraction of HNO_3 concentrations (Figure 4) from total inorganic nitrate concentrations (Figure 5) shows that the majority of the inorganic nitrate is found in the aerosol phase at all sites except the high elevation mountainous site at Tanbark



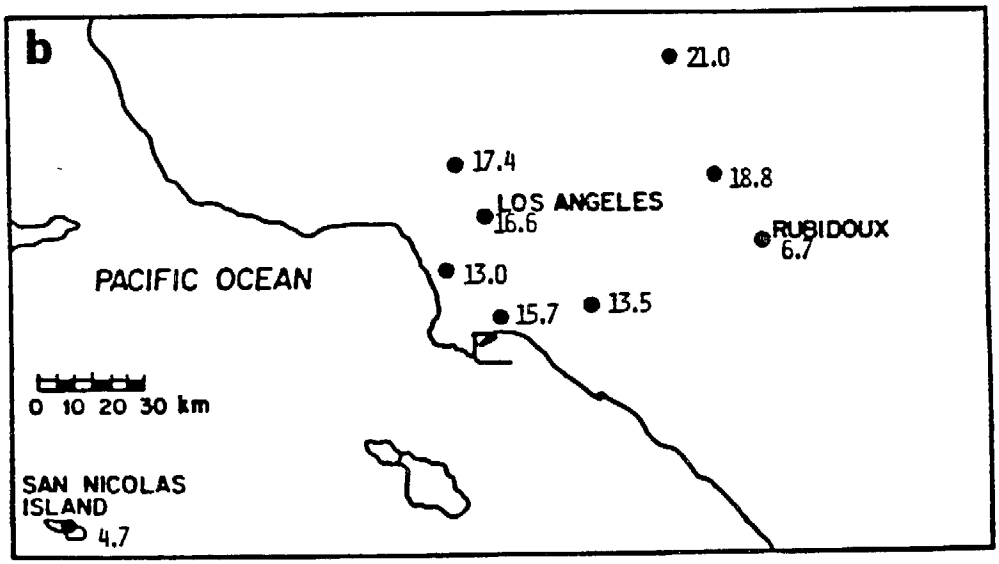


Figure 4. HNO_3 concentrations ($\mu g\ m^{-3}$) observed in the Los Angeles area, 1986. HNO_3 was measured by the denuder difference method. (a) Annual averages. (b) Maximum 24-h average.

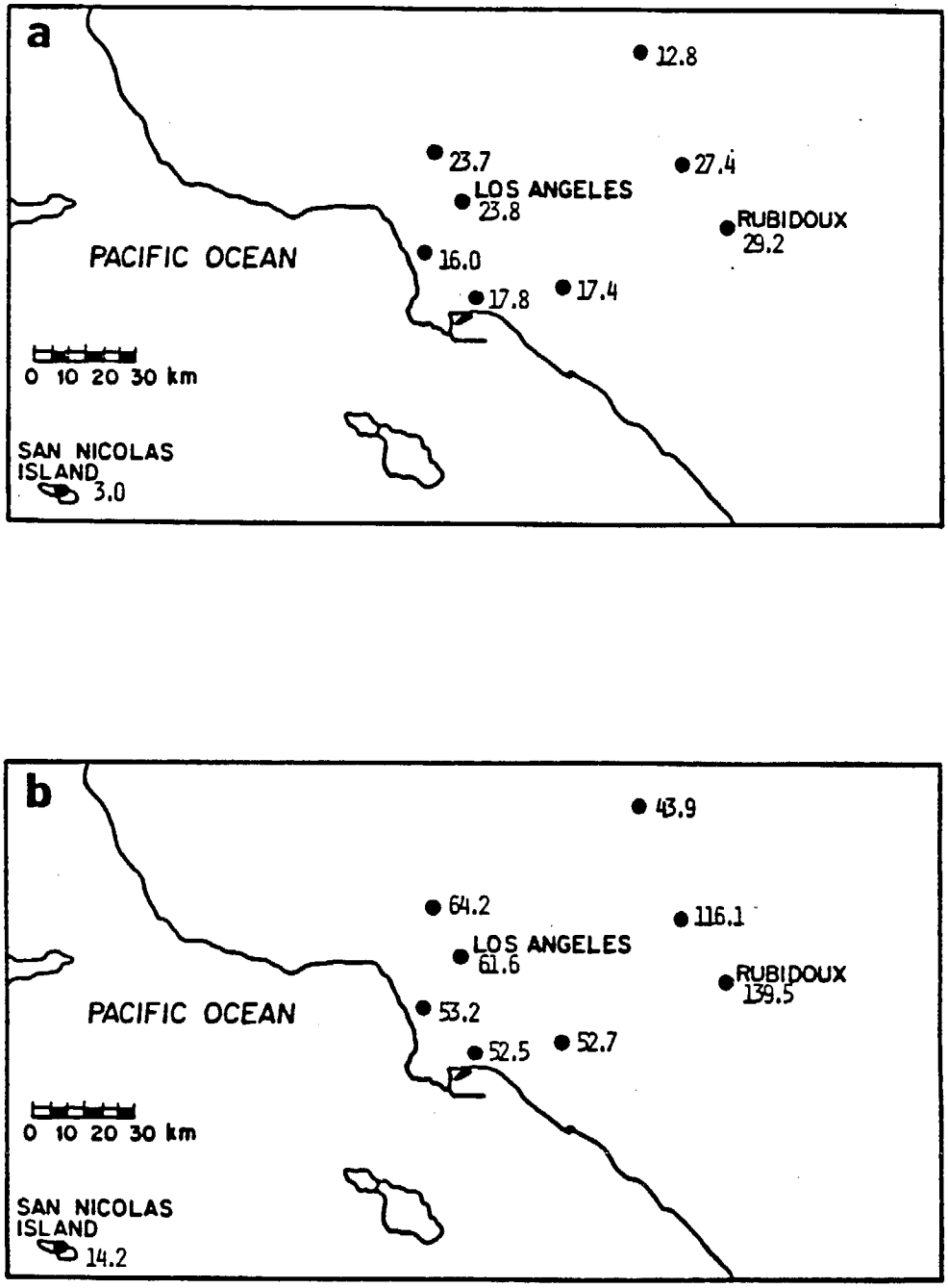


Figure 5. Total inorganic nitrate (i.e., sum of gas phase HNO_3 plus aerosol nitrate) observed in the Los Angeles area, 1986. (a) Annual averages. (b) Maximum 24-h average.

Flats. The spatial distribution of total particulate nitrate (fine plus coarse particle fractions) is shown in Figure 6. At Rubidoux, 94 percent of the annual average inorganic nitrate concentration is found in the aerosol phase. At the other urban sites, aerosol nitrates contribute from 72% (Burbank) to 82% (near the coast) of the total inorganic nitrate concentrations observed. At Tanbark Flats, 46% of the inorganic nitrate is in the aerosol phase. Clearly aerosol nitrate formation is a major sink for atmospheric HNO_3.

Fine and Coarse Particle Nitrate Concentrations

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

The importance of the contribution of fine particle nitrate during peak pollution periods is clearly seen in Table II. The highest 24-h average fine particle nitrate concentration observed in the SOCAB was 109.0μg m^{-3} at Rubidoux. Other peak day fine particle nitrate values, within the Los Angeles metropolitan area, ranged from 37.7 to 78.0μg m^{-3}. Maximum 24-h coarse particle nitrate values exhibed a much smaller range from 14.4 to 38.2μg m^{-3} within the metropolitan area, including Rubidoux. These high aerosol nitrate concentrations are of particular importance for the Los Angeles area because they affect compliance with the new 24-h average federal (150μg m^{-3}, ref. 31) and existing State of California (50μg m^{-3}, ref. 32) PM_{10} standards. The highest fine particle NO_3^- concentration observed during this study represents 73 percent of the allowable 24-h average federal PM_{10} standard and more than two times the State of California 24-h average PM_{10} standard.

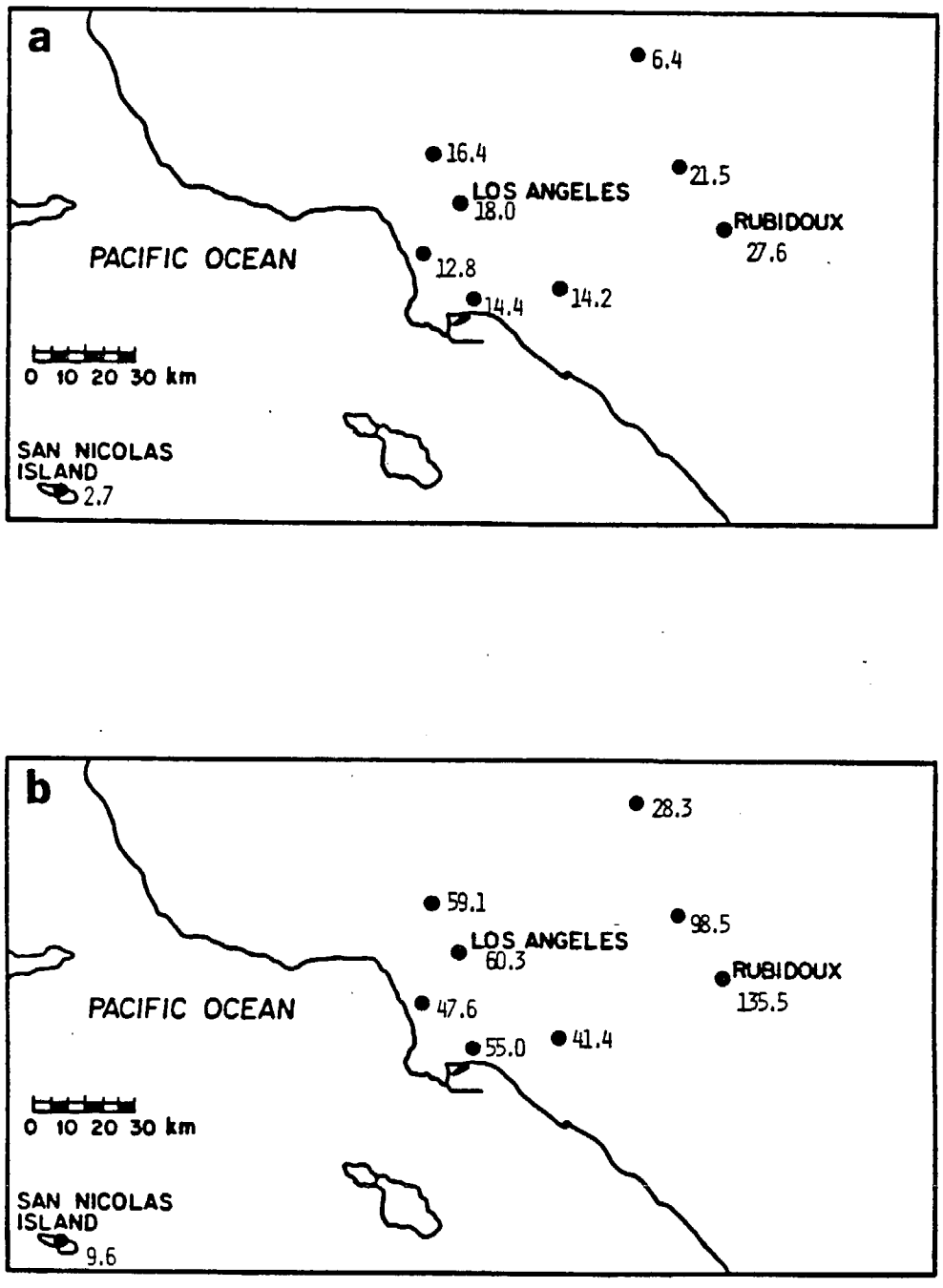


Figure 6. Total particulate nitrate (fine particle plus coarse particle nitrate) observed in the Los Angeles area, 1986. (a) Annual average. (b) Maximum 24-h average.

Table II. Annual and peak 24-hour average fine[a] and coarse[b] particle nitrate concentrations ($\mu g\ m^{-3}$) observed at each site.

Site	Annual Average		Maximum 24-h Average	
	Fine Particle NO_3^-	Coarse Particle NO_3^-	Fine Particle NO_3^-	Coarse Particle NO_3^-
		metropolitan area		
Burbank	9.5	7.4	50.8	17.1
Downtown LA	9.7	8.0	56.3	18.6
Hawthorne	6.2	6.3	39.4	18.3
Long Beach	7.6	7.0	42.7	15.5
Anaheim	8.6	5.9	37.7	14.4
Rubidoux	18.2	9.0	109.0	38.2
Upland	13.3	8.1	78.0	29.1
		inland, high elevation		
Tanbark Flats	4.0	2.1	25.2	7.8
		background		
San Nicolas Island	1.1	1.7	6.7	5.4

a. Fine particles are particles in sizes less than 2.2μm aerodynamic diameter.

b. Coarse particles are particles in sizes greater than 2.2μm aerodynamic diameter.

DISCUSSION

Nitric acid and aerosol nitrate concentration patterns in the Los Angeles area have been examined previously by means of short-term photochemical air quality models that are capable of explaining the observed concentration patterns on a cause and effect basis (20,33-35). The findings of the present long-term monitoring study are consistent with these prior air quality model predictions. Referring to Figure 3 of reference (35), the highest NO_2 concentrations accumulate near the coast in the western portion of the air basin overnight and during the early morning hours. As the day proceeds, NO and NO_2 typically are advected eastward across the air basin; NO_2 is oxidized to form nitric acid, and high nitric acid concentrations are predicted to occur in the middle portion of the air basin (e.g., at Burbank and Upland in the present study). As the nitric acid-laden air mass passes over the Chino dairy area (just to the west of Rubidoux), large amounts of ammonia are injected into the atmosphere from livestock waste decomposition and from other agricultural activities. Ammonia measurements made at the same time as the present study show a 1986 annual average NH_3 concentration of 30μg m^{-3} downwind of Chino at Rubidoux. This is approximately ten times higher than the NH_3 concentrations measured at upwind sites in the western portion of the air basin during 1986 (36). The available nitric acid reacts to form large amounts of ammonium nitrate aerosol, resulting in the extremely high aerosol nitrate concentrations and the low HNO_3 levels measured farther downwind at Rubidoux. The modeling study of Russell et al. (35) predicts that Rubidoux should have the highest aerosol nitrate concentrations and the lowest HNO_3 concentrations of any routine monitoring site in the air basin during 1982 summertime conditions. The present monitoring study shows that this is a year-round condition at Rubidoux during the year 1986.

Monthly average time series graphs of HNO_3, fine and coarse particle nitrate,

and total inorganic nitrate at Hawthorne, Downtown Los Angeles and Upland are illustrated in Figure 7. As seen in Figure 7, inorganic nitrate production almost always is in great excess of the amount of HNO_3 in the atmosphere, with average fine particle nitrate concentrations in winter typically higher than in the summer. Since all aerosol nitrate was once HNO_3, these results suggest that the pronounced summertime peak in HNO_3 observed at inland sites is apparently due to factors governing the partition of inorganic nitrate between the gas and aerosol phases, rather than strictly due to an increased production of inorganic nitrate during the summer as compared to the winter. Based on thermodynamic considerations, it is predicted that atmospheric HNO_3 and NH_3 often are in equilibrium with NH_4NO_3 aerosol and that the equilibrium dissociation constant for NH_4NO_3 often governs the concentration product of HNO_3 times NH_3 in the atmosphere and the partition of inorganic nitrate between the gas and aerosol phases (3-5,33). The NH_3-HNO_3-NH_4NO_3 equilibrium condition is very sennsitive to temperature, with greatly increased ambient HNO_3 concentrations predicted to be in the gas phase at higher ambient temperatures (3-5,33). Aerosol NH_4NO_3 formation also is sensitive to the absolute magnitude of the concurrently observed NH_3 concentrations, and measured NH_3 concentrations at most of the monitoring sites studied here are lowest during the summer months (36). Therefore, it is likely that the broad summer seasonal HNO_3 peak observed at inland low elevation monitoring sites (e.g., Burbank; Upland) results from the higher summer temperatures and lower summer NH_3 concentrations that shift the NH_4NO_3-HNO_3-NH_3 equilibrium toward higher concentrations of HNO_3. Conversely, the increased fine particle nitrate levels observed at most sites during the winter, most likely result from the lower winter temperatures and higher winter NH_3 levels shifting the NH_4NO_3-HNO_3-NH_3 equilibrium toward the aerosol phase. Nearest to the coast, seasonal temperature extremes are moderated by the presence of the ocean, and there is little seasonal pattern in the HNO_3 con-

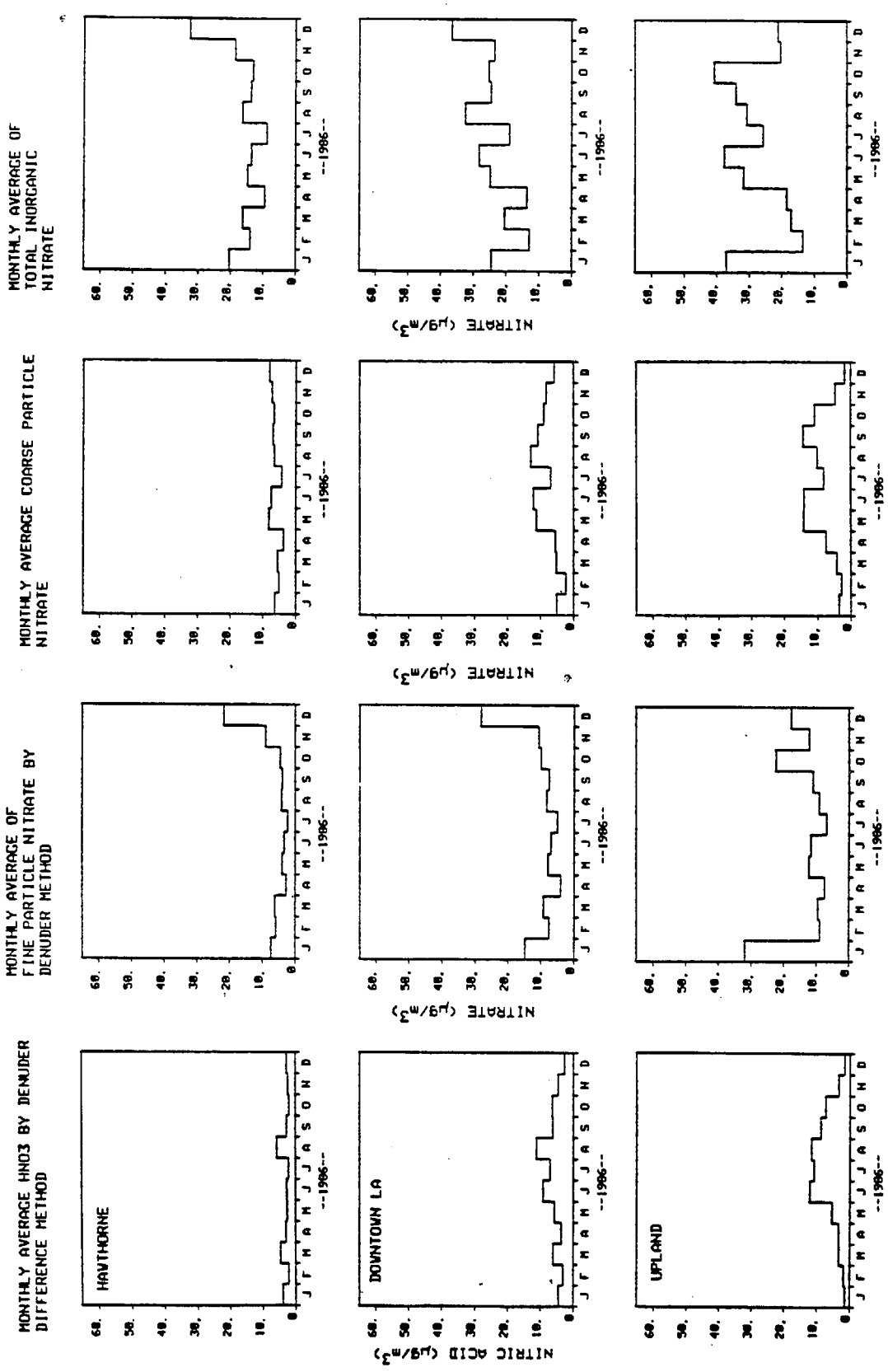


Figure 7. Monthly average HNO_3, fine particle nitrate, coarse particle nitrate, and total inorganic nitrate at Hawthorne, Downtown Los Angeles, and Upland.

centrations.

Coarse particle nitrate concentrations during 1986 were found to be comparable in many cases to the fine particle nitrate concentrations observed (see Table II and Figure 7). Chemical analyses of samples collected in the Los Angeles area and elsewhere have shown (7,8,11,37) that the coarse particle nitrates are largely composed of the reaction products of HNO_3 with sea salt or soil dust, while the fine particle nitrates are largely composed of NH_4NO_3. Coarse particle nitrate formation has been examined via photochemical modeling calculations (34) in which nitric acid transport to the surface of the sea salt or soil dust particle is the governing factor limiting coarse particle nitrate formation. As seen in Figure 7, coarse particle nitrate concentrations display approximately the same seasonal variation as HNO_3 concentrations, with a flat seasonal distribution near the coast and a summer seasonal peak at inland sites such as Burbank and Upland. This is consistent with the pattern expected if coarse particle nitrate formation is limited by HNO_3 diffusion to an existing coarse particle surface which acts as an irreversible sink for HNO_3; coarse particle nitrate formation is driven by the availability of HNO_3 in the gas phase.

The highest HNO_3 levels observed in this air basin in 1986 occurred at the high elevation monitoring site at Tanbark Flats, while total inorganic nitrate concentrations at that site are much lower than at the nearest monitoring stations on the floor of the populated valleys below. The most likely explanation for this increased HNO_3 concentration at high elevation in the presence of lower total inorganic nitrate concentrations is that aerosol nitrate formation has been suppressed. Previous modeling studies have shown that ammonia concentrations should be much higher at low elevations at night and in the early morning hours than at higher elevations (33). This is because NH_3 is released principally from ground level sources located on the floor of the air basin. Nitrogen oxides emissions may be

produced by both ground level sources and elevated sources. Hence there is a mechanism by which the ratio of NO_x to NH_3 may vary with elevation in the atmosphere. Ambient NH_3 measurements made concurrently with the present study show that annual average NH_3 concentrations at Tanbark Flats are very low (only 0.6μg m^{-3}), compared to 2.1-4.4μg m^{-3} at most other urban sites and 30μg m^{-3} at Rubidoux. The high HNO_3 concentrations observed at Tanbark Flats when compared to the other sites are consistent with suppression of NH_4NO_3 formation due to the near absence of available ammonia in the gas phase.

ACKNOWLEDGEMENTS

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APPENDIX B
Chemical Characteristics of PM_{10} Aerosols Collected in the Los Angeles Area

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ABSTRACT

A PM_{10} monitoring network was established throughout the South Coast Air Basin (SOCAB) in the greater Los Angeles region during the calendar year 1986. Annual average PM_{10} mass concentrations within the Los Angeles metropolitan area ranged from 47.0μg m^{-3} along the coast to 87.4μg m^{-3} at Rubidoux, the furthest inland monitoring station. Measurements made at San Nicolas Island suggest that regional background aerosol contributes between 28 to 44 percent of the PM_{10} aerosol at monitoring sites in the SOCAB over the long term average. Five major aerosol components (carbonaceous material, NO_3^-, $SO_4^=$, NH_4^+, and soil-related material) account for greater than 80% of the annual average PM_{10} mass at all on-land monitoring stations. Peak 24-h average mass concentrations of nearly 300μg m^{-3} were observed at inland locations, with lower peak values (~130-150μg m^{-3}) measured along the coast. Peak-day aerosol composition was characterized by increased NO_3^- ion and associated ammonium ion levels, as compared to the annual average. There appears to be only a weak dependence of PM_{10} mass concentration on season of the year. This

lack of a pronounced seasonal dependence results from the complex and contradictory seasonal variations in the major chemical components (carbonaceous material, nitrate, sulfate, ammonium ion and crustal material). At most sites within the Los Angeles metropolitan area, PM_{10} mass concentrations exceeded both the annual and 24-h average federal and State of California PM_{10} regulatory standards.

INTRODUCTION

On July 31, 1987 the U.S. Environmental Protection Agency (EPA) promulgated new primary and secondary national ambient air quality standards (NAAQS) for suspended particulate matter (1). Previous ambient air quality standards, defined in terms of Total Suspended Particulate Matter (TSP) (2), were replaced by a new indicator defined in terms of particulate matter in sizes smaller than or equal to 10μm aerodynamic diameter, referred to as PM_{10} (1). Earlier, a separate PM_{10} standard had been adopted by the State of California (3). The motivation for developing the recently approved standards is to protect against the risks of potential adverse health effects from particles small enough to penetrate the thoracic region (both the tracheobronchial and the sensitive alveolar regions) of the human respiratory tract (4,5) (primary NAAQS) and to protect the public welfare (e.g., climate, visibility, etc.; secondary NAAQS).

As PM_{10} concentrations have not been measured widely in the past, the adoption of these new air quality standards raises a series of questions. Most obviously, which areas of the United States are out of compliance with the PM_{10} concentration objectives, and what is the extent of excursions above the standards? Since the Los Angeles area is recognized as having one of the most serious air pollution problems in the nation, it is likely that PM_{10} concentrations measured downwind of Los Angeles may establish a yardstick against which other difficult PM_{10} control problems should be compared. Secondly, to meet these PM_{10} concentration objectives in areas that exceed the standards, emissions from mobile, stationary, and fugitive sources may need to be controlled. In order to develop cost-effective emission control strategies, the fraction of the problem that is due to each major source type, including background material, must be determined. Atmospheric measurement procedures are needed that help to identify the source origin of the PM_{10} aerosol, and that result in a data base that is specifically designed for use with receptor-

oriented and source-oriented mathematical models. These models then can be employed to estimate the source contributions at each monitoring site (6-9).

This paper describes the spatial and temporal distribution of PM_{10} concentrations in the South Coast Air Basin (SOCAB) in the greater Los Angeles region during the year 1986. The air sampling protocol employed was structured to obtain a nearly complete material balance on the chemical composition of the collected PM_{10} mass. Chemical analysis procedures were selected that determine key tracer species needed for source contribution identification. Annual and seasonal trends in PM_{10} mass concentration and composition will be discussed in detail, along with individual 24-h periods with unique pollution characteristics. A background air monitoring site was established on an island off the coast of Southern California, and an inland, high elevation mountainous monitoring site was selected in order to provide PM_{10} data that can be contrasted with results obtained within the Los Angeles urban area.

EXPERIMENTAL

Sampling Sites

During the calendar year 1986, a monitoring network designed to measure the spatial and temporal distribution of PM_{10} aerosols was operated in the Los Angeles area. There were nine sampling sites and their locations are illustrated in Figure 1. All sites except Tanbark Flats and San Nicolas Island were colocated with present South Coast Air Quality Management District (SCAQMD) continuous air monitoring stations. A description of the seven SCAQMD stations is given by the U.S. Environmental Protection Agency (10,11). The Tanbark Flats site was located in the mountains, north of San Dimas, in the Angeles National Forest at an elevation of approximately 870 m. This site was chosen to determine the concentration of pollutants present in the national forests to the north of Los Angeles. The ninth site was

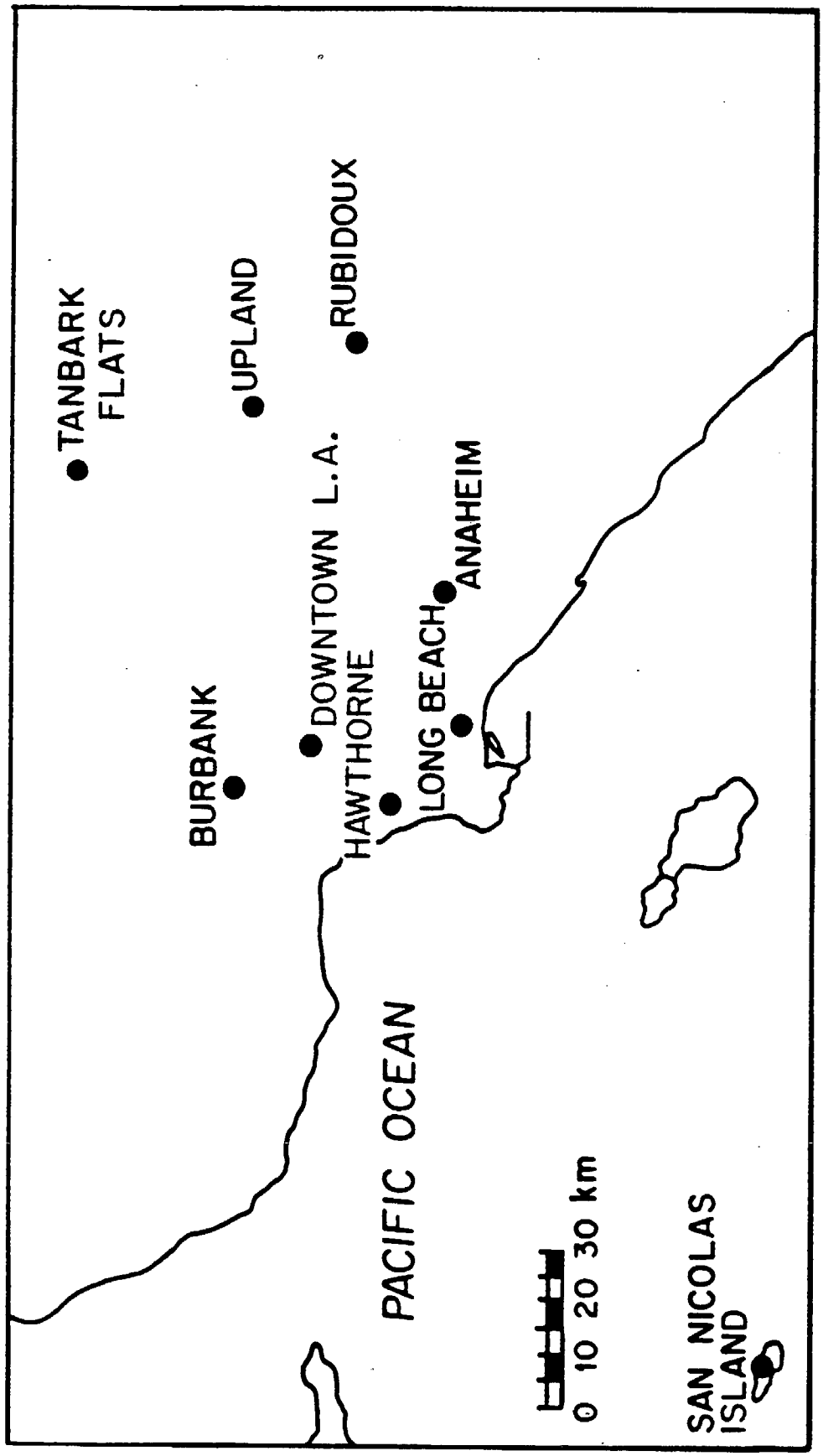

Figure 1. PM_{10} aerosol monitoring network. All sites are at an elevation within 400m of sea level except Tanbark Flats which is at an elevation of 870m in the San Gabriel Mountains.

located at the meteorological station on San Nicolas Island (SNI) and is approximately 140 km southwest of the Los Angeles coastline. This remote, off-shore location was chosen to estimate background pollutant levels entering the Los Angeles area from the upwind marine environment. A previous study by Gray et al. (12) found that as much as 25 percent of the fine particle mass present in the Los Angeles atmosphere may already be present in near-coastal marine air before it enters the SOCAB.

The sampling systems were placed on the roofs of one or two story buildings at Burbank, Downtown Los Angeles, Long Beach and Upland. At the other 5 sites the sampler inlets were located about 2 to 3m above ground level. All sites except Tanbark Flats were located at an elevation of 390m or less above sea level.

Sampler Design and Sampling Schedule

The PM_{10} aerosol sampling unit employed in this study is illustrated in Figure 2. The PM_{10} inlet (10μm inlet TM, Model SA-246b, Sierra-Andersen) has a nominal 10μm cutpoint (i.e., 50 percent collection efficiency for particles with an aerodynamic diameter of 10μm) when operated at a flow rate of 1 $m^3\ h^{-1}$ (16.7 l min^{-1}) (13). The air passing through the inlet was divided evenly between 3 parallel filter holder assemblies. A specially designed flow splitter was used that consisted of a converging nozzle with a triangularly symmetric transition to the three filter holder inlet lines. An equal allocation of the air flow rates between the 3 filters was found to be necessary in order to obtain an equal distribution of the larger particles (d_p~2.5-10μm) between the three filter holders. The nominal flow rate through each filter was 0.34 $m^3\ h^{-1}$ (5.6 l min^{-1}). One filter holder contained a single 47mm diameter quartz fiber filter (2500 QAO, Pallflex Corp.), while the other two filter holders each contained a single polytetrafluoroethylene filter (PTFE; 2.0μm pore size, ringed, 47mm diameter, Gelman Sciences). The use of the 3 filters (one quartz and two PTFE) was chosen for compatibility with particular physical and chemical analysis

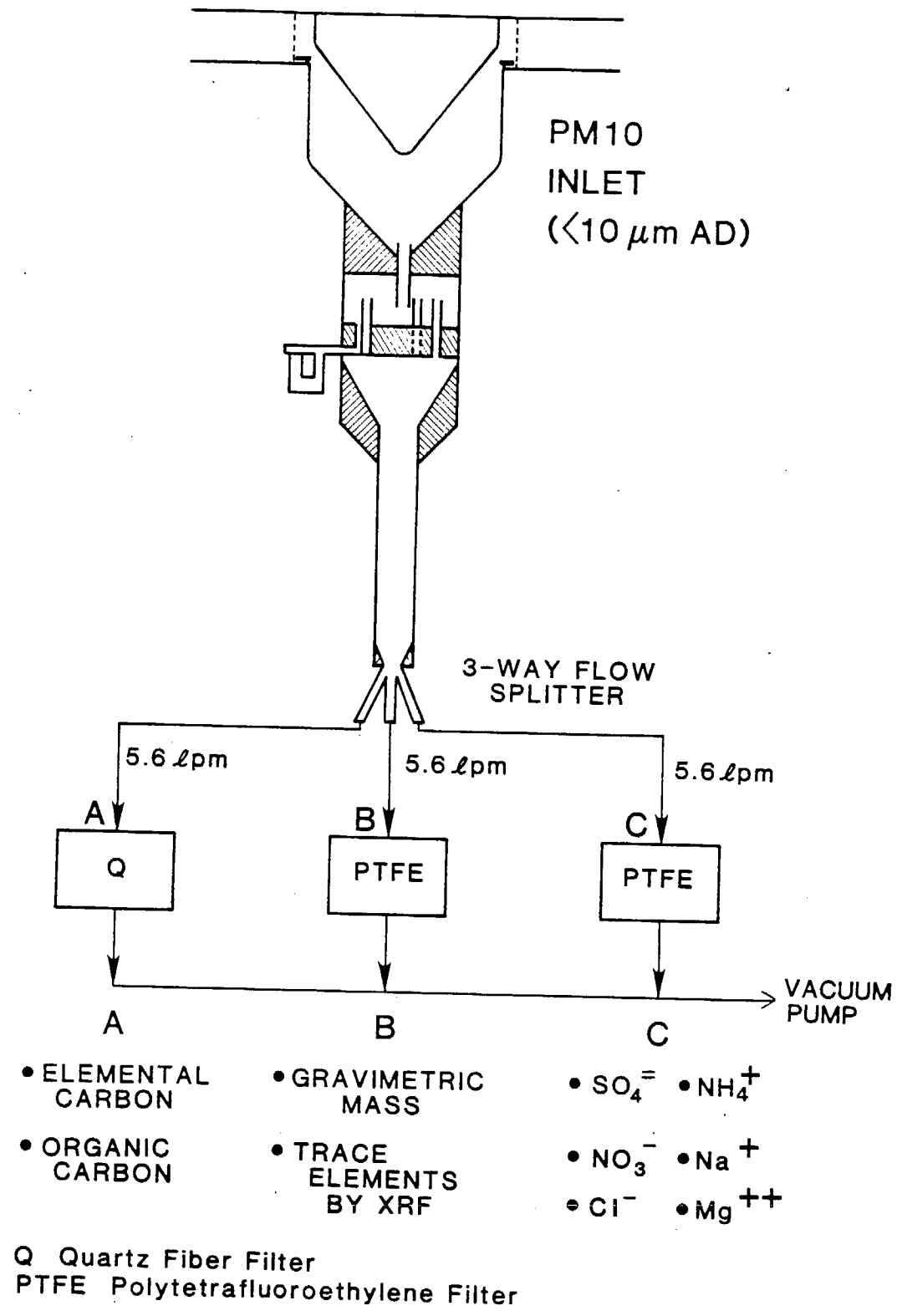

Figure 2. Ambient PM_{10} sampler and sampling protocol.

procedures that lead to a nearly complete material balance on the chemical composition of the collected PM_{10} aerosol.

Samples were collected every sixth day for 24-h sampling periods during the calendar year 1986. The first sample was collected on 2 January to coordinate this PM_{10} network with the National Air Surveillance Network (NASN) high-volume sampling schedule. Filters were installed the day prior to, and removed the day after, sample collection. Flow rates were monitored before and after every sampling period with a rotameter which was factory calibrated with an accuracy of 1 percent full scale. The flow rate checks were made before and after each sampling event to ensure that filter holders were not leaking and to determine that filter clogging had not occurred. All filters were stored in self-sealing plastic petri dishes, sealed with Teflon tape, and refrigerated until sample analysis. Dynamic field blanks equal to 10% of the atmospheric samples taken were obtained during the year.

Sample Analysis

The ambient concentrations of PM_{10} mass, organic and elemental carbon, six water soluble anions and cations, and 34 bulk composition trace elements were determined from the filter samples as shown in Figure 2. A summary of the species determined and the analytical techniques employed is given in Table 1.

Atmospheric PM_{10} mass concentrations were obtained gravimetrically by weighing the PTFE filters (sampling line B, Figure 2) before and after sample collection. A mechanical microgram balance with a 1μg sensitivity (Model M-5S-A, Mettler Instruments) was employed for this purpose. Unexposed and collected PTFE filters were equilibrated at 22±3°C and 50±3 percent relative humidity for at least 24 h prior to weighing the filter. To track the calibration of the balance between initial and final weighings, a series of metal calibration weights and control filters (three unexposed and three loaded with atmospheric particles) were weighed at the beginning and end of each daily weighing period.

Table 1. Summary of analytical measurements for chemical composition determination of PM_{10} aerosols.

Species Determined[a]	Analytical Technique	(Reference)	Instrument Detection Limit (IDL)	Filter Blank ($\bar{x}\pm\sigma_b$ in μg/filter)[b]	Analytical Precision[c]
mass	gravimetric	(—)	10μg/filter	<IDL	2.78μg m^{-3}
organic carbon	thermal/ optical	(14)	2.5	0.40±0.18	3.5 %
elemental carbon	thermal/ optical	(14)	2.5	<IDL	6.5
SO_4^{-2}[d]	ion chromatography	(16)	0.6	<IDL	4.8
NO_3^-[d]	ion chromatography	(16)	0.6	<IDL	4.1
Cl^-[d]	ion chromatography	(16)	0.1	0.31±0.22	11.9
NH_4^+[d]	colorimetric	(17)	0.8	<IDL	3.9
Na^+[d]	flame AAS	(—)	0.2	0.41±0.19	4.8
Mg^{+2}[d]	flame AAS	(—)	0.2	<IDL	8.4
Al	XRF	(18)	110 ng/filter	<IDL	<1
Si	XRF	(18)	70	<IDL	<1
Fe	XRF	(18)	23	0.069±0.040	<1
Ca	XRF	(18)	40	<ID	<1

(a) Other trace species determined by XRF: P, S, Cl, K, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Ga, As, Se, Br, Rb, Sr, Y, Zr, Pd, Ag, Cd, In, Sn, Sb, Ba, La, Hg, Pb.

(b) For species which were detectable in the filter blanks, the sample detection limit was defined as equal to 2 times the standard deviation of the reported filter blank value (σ_b).

(c) Based on duplicate or replicate analysis of a large number of filters (typically n>50). The precision of sample air volume determination is about 1 percent.

(d) Water soluble fraction only.

Organic carbon (OC) and elemental carbon (EC) concentrations were determined on the quartz fiber filters (sampling line A, Figure 2) by a thermal/optical method (14). Prior to sample collection these filters were heat treated at 750°C in air for at least 3 h to lower their carbon blank levels. Compensation for the pyrolytic conversion of organic carbon to elemental carbon during the thermal analysis is achieved by continuously monitoring the optical reflectance of the sample during analysis as described in reference (14).

Water soluble anions and cations were determined from the analysis of the PTFE filters (sampling line C, Figure 2). Prior to the addition of the leaching solution, the PTFE filters were wetted with 0.2 ml of ethanol (ETOH, 100 percent) to reduce the hydrophobic nature of this material (15). A Teflon rod was then placed on top of each filter to keep it submerged in the leaching solution. The PTFE filters were leached by lightly shaking each of them in 20 ml of distilled, deionized water for at least 3 h. This was done at reduced temperatures (10°C) to avoid loss of volatile species (i.e., NO_3^-, NH_4^+) during the aration process. One to five ml of the leachate w ons by ion chromatography (16) (Model 20 by a modified indophenol colorimetric me (Model RFA-300, Alpkem Corp.), and Na^+ a flame atomic absorption spectroscopy (Mo

The bulk con elements were determined by x-ray fluo ting). The PTFE filter, first employed for m analysis. The choice of this technique allo ...ation of specific tracer elements (e.g., Pb for automobiles, Si and Al for soil, etc.) required for source-receptor modeling analysis (6-9).

The concentration of all chemical species was determined relative to primary

or secondary laboratory standards of known concentration. For water soluble species, aqueous standards were diluted daily from more concentrated solutions prepared monthly from ACS grade analytical reagents. Whenever possible, the matrix of the daily standards matched that of the leaching solution.

A summary of the instrument detection limits (IDL), filter blank values, and the precision of the analytical measurements is also presented in Table I. Duplicate or replicate analysis of approximately 10% of the filters for each species was performed to determine the analytical precision. For gravimetric mass determination, the reproducibility of the initial and final weighing was determined by reweighing a large number (n>200) of the filters both prior to and after sample collection. The precision for either weighing was found to be approximately 5μg per filter. These weighing errors first were propagated statistically with the inherent precision of the balance (specifications set by the manufacturer; 1σ = 15μg), and then the initial weighing and final weighing errors were combined to obtain the precision for sample mass determination. For other species, the analytical precision was defined as the average coefficient of variation obtained from many pairs (typically n>50) of duplicate or replicate measurements. Filter blank values, for each species, are the average of all dynamic field blanks obtained during the study, including 10-sec and 2-day field blanks. There was no discernable difference between the short- and long-term dynamic field blanks.

RESULTS AND DISCUSSION

Annual Average Mass Concentration and Composition

Average PM_{10} mass concentrations observed throughout the monitoring network ranged from 21 to 87μg m^{-3}, annual arithmetic mean (AAM), and from 17 to 76μg m^{-3}, annual geometric mean, for the year 1986 (see Figure 3 and Table II). The lowest annual average of 20.8μg m^{-3} AAM was observed upwind of the air basin at

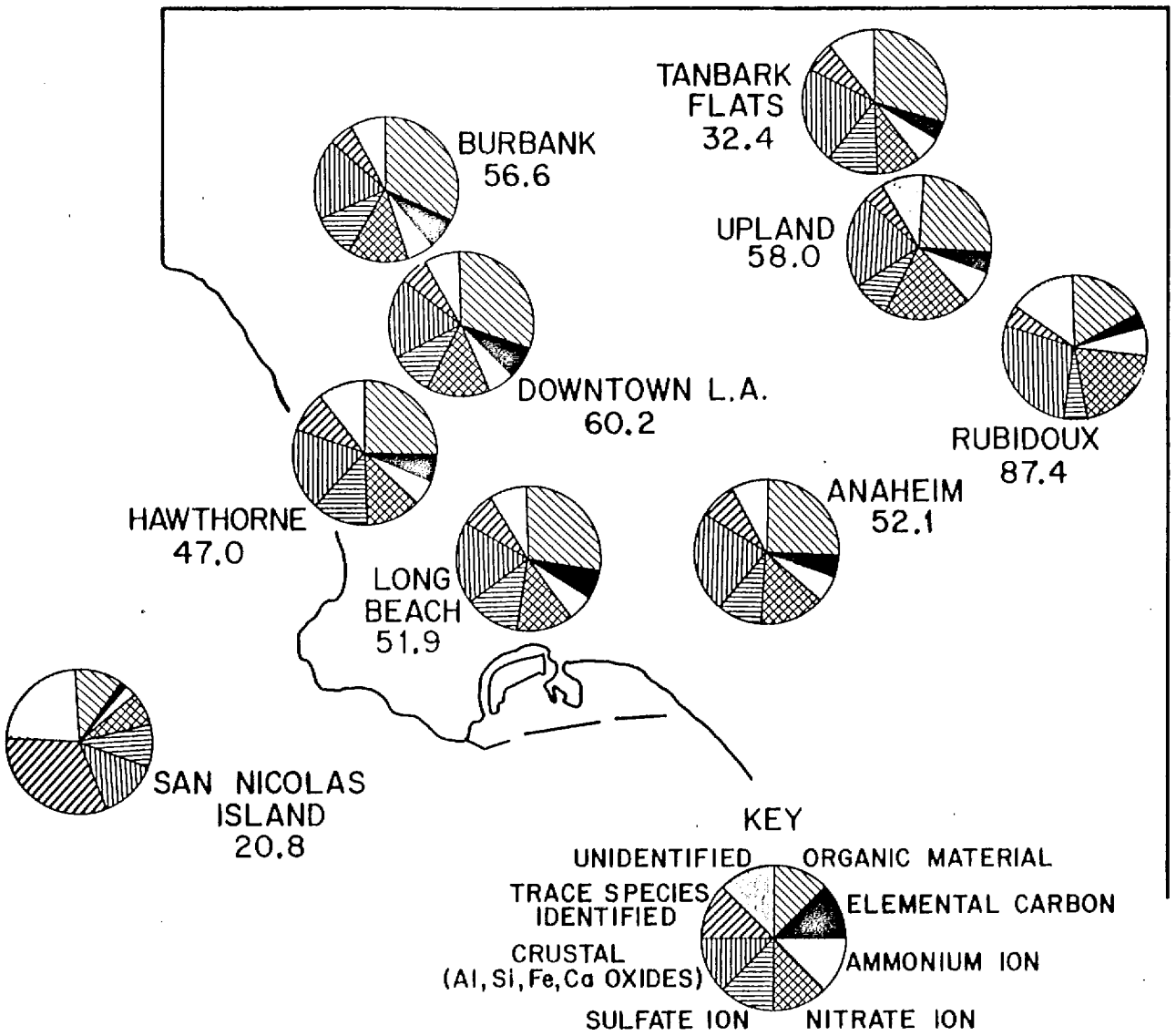

Figure 3. Material balance on the chemical composition of annual average PM_{10} aerosols collected in the South Coast Air Basin during 1986. Values indicate annual arithmetic mean PM_{10} mass concentrations in $\mu g\ m^{-3}$.

Table II. Annual average and 24-hour maximum PM_{10} mass concentrations throughout the South Coast Air Basin in the greater Los Angeles region, 1986.

Site	Annual Average PM_{10} Mass ($\mu g\ m^{-3}$)		Highest 24-h PM_{10} Mass		2nd Highest 24-h PM_{10} Mass		Percent of Days Greater than the 24-h Standard		Number of Sampling Events in Average[e]
	Arithmetic Mean[a]	Geometric Mean[b]	($\mu g\ m^{-3}$)	Date	($\mu g\ m^{-3}$)	Date	Federal[c] ($150\mu g\ m^{-3}$)	State of California[d] ($50\mu g\ m^{-3}$)	
Burbank	56.6	51.2	187	Dec 4	138	Jan 2	1.6	54.1	61
Downtown LA	60.2	55.5	187	Dec 4	122	Jan 2	1.7	66.1	59
Hawthorne	47.0	42.9	146	Dec 4	106	Dec 28	0	26.7	60
Long Beach	51.9	48.0	131	Mar 27	130	Dec 4	0	39.3	56
Anaheim	52.1	47.5	130	Dec 4	121	Mar 27	0	34.4	61
Rubidoux	87.4	75.5	299	Oct 29	225[h]	Nov 16	9.8	80.3	61
Upland	58.0	50.7	209	Oct 29	188	Jan 2	5.0	56.7	60
Tanbark Flats[f]	32.4	26.9	75.1	Oct 29	66.4	Jan 20	0	20.8	53
San Nicolas Island[g]	20.8	17.4	84.8	Jan 26	61.0	Feb 25	0	5.2	58

a. The federal annual primary and secondary PM_{10} standards are both $50\mu g\ m^{-3}$ arithmetic mean (1).

b. The State of California's annual primary PM_{10} standard is $30\mu g\ m^{-3}$ geometric mean (3).

c. The federal 24-h primary and secondary PM_{10} standards are both $150\mu g\ m^{-3}$ with no more than one expected excursion above that value per year (1).

d. The State of California's 24-h primary PM_{10} standard is $50\mu g\ m^{-3}$ with no measured values allowed above that level (3).

e. The maximum number of sampling events in 1986 was 61.

f. Located in the San Gabriel Mountains, north of San Dimas, at an elevation of 870m.

g. A background site, located approximately 140km SW of the Los Angeles coastline.

h. The chemical material balance on this day does not come close to explaining the gravimetrically determined mass concentration, and therefore this data point may be incorrect. The next lowest day at Rubidoux was $170\mu g\ m^{-3}$ on January 2, 1986.

San Nicolas Island, while the highest value of 87.4μg m^{-3} AAM was observed inland at Rubidoux. Of the on-land monitoring stations, the lowest annual arithmetic average PM_{10} mass concentration of 32.4μg m^{-3} was observed at Tanbark Flats, a site located in the mountains at an elevation about 500-850m above that of the other monitoring stations. At the remaining six sites within the Los Angeles metropolitan area, annual arithmetic average PM_{10} mass concentrations were in the range 47.0 to 60.2μg m^{-3}, varying by only 13.2μg m^{-3} between monitoring stations. Of those six sites, the three most affected by the marine environment (Hawthorne, Long Beach and Anaheim) were at the lower end of the stated range, whereas the inland locations (i.e., Burbank, Downtown Los Angeles and Upland) were at the upper end.

For each location, a material balance on the chemical composition of the PM_{10} aerosol was constructed by summing the annual average concentrations of the individual chemical species measured. Prior to the summation, major trace elements (e.g., Al, Si, Fe, Ca, K, Cr, and Pb) were converted to their oxides, and organic carbon concentrations were converted to an estimate of the mass of organic material present (i.e., organic carbon concentrations were multiplied by 1.4 to account for the O and H associated with organic matter) (12). Sulfur was assumed to be in the form of water soluble sulfate, and therefore the sulfate values determined by ion chromatography were employed. Data on the concentrations of elemental carbon, nitrate, sulfate and ammonium ion, and minor trace elements, were added directly to the material balance. Only samples for which all scheduled chemical analyses were available were included in the material balance calculation. At all on-land sites, except Rubidoux, between 91.0 and 93.7 percent of the gravimetrically measured mass was accounted for on an annual basis by the chemical analyses of the individual species. At Rubidoux and San Nicolas Island 85.7 and 78.0 percent, respectively, of the measured annual average mass concentration could be accounted for on the basis of the species measured. A portion of the unidentified

mass concentration is probably due to water present in the aerosol samples despite desiccation. Witz and co-workers (19) have determined the water content of PM_{10} aerosols collected at several locations in the Los Angeles basin during June and July, 1987. Their results indicate that from about 1 to 7% of the gravimetrically measured PM_{10} mass (equilibrated at 45% RH) may be due to water associated with the collected particles. On the average (n=10), they observed a water content of 4.7 and 2.1 percent of the PM_{10} mass at Long Beach and Riverside, respectively. Therefore, at most sites, when water is included it appears that greater than 95% of the collected PM_{10} mass has been identified, including major contributors and trace species important for source identification and for source-receptor modeling.

As can be seen in Figure 3 and Table III, at all sites except San Nicolas Island, carbonaceous aerosol (organic material plus elemental carbon) and crustal material (the sum of Al, Si, Ca, and Fe oxides) along with the major water-soluble ionic species (NH_4^+, NO_3^-, and $SO_4^=$) account for greater than 80 percent of the measured annual average PM_{10} mass. At most on-land sites, the relative chemical composition is similar to that seen at Downtown Los Angeles, where the aerosol consisted of 30.9% organics, 7.1% elemental carbon, 5.9%, 14.5% and 9.4% ammonium, nitrate and sulfate ions, respectively; 18.1% crustal, 7.7% other trace elemental species, and 6.3% unidentified material (a portion of which undoubtedly is water associated with hygroscopic species such as NH_4NO_3, $(NH_4)_2SO_4$, and NaCl). The major exception to this pattern was observed at Rubidoux. At Rubidoux the samples appear lower in relative carbon content only because the annual PM_{10} mass concentration there is higher. On an absolute concentration basis, Rubidoux actually has the 3rd highest annual average carbonaceous material concentration of the sites studied in the basin (see Table III). The PM_{10} mass concentration is higher at Rubidoux because of the larger (about a factor of 2) absolute amounts of aerosol nitrate and crustal species observed there as compared to the other monitoring sites (see Table III).

Table III. Comparison of the major components comprising the material balance on peak 24-h and annual average PM_{10} concentrations at each site (concentrations in $\mu g\ m^{-3}$).

Site	Organic Material[a]	Elemental Carbon	NH_4^+	NO_3^-	$SO_4^=$	Crustal[b]	Trace Species I.D.[c]	Fraction Chemically Identified (%)
Peak 24-h Average at Each Site								
Burbank	53.8	16.2	15.5	54.0	3.9	24.5	5.1	92.4
Long Beach[d]	29.8	4.7	13.3	15.0	21.7	13.4	3.0	77.0
Hawthorne	29.7	8.7	16.3	49.1	7.1	16.0	4.7	90.0
Downtown LA	47.8	13.6	16.4	52.8	4.9	30.1	6.6	92.1
Rubidoux	41.3	8.3	39.1	85.6	19.8	35.9	5.2	78.7
Upland	37.1	7.3	23.9	67.2	15.7	21.9	4.9	85.3
Anaheim	29.9	9.2	11.9	38.2	3.9	19.6	5.2	90.9
Tanbark Flats	24.9	3.8	5.7	10.8	7.5	8.8	2.6	85.3
Annual Average at Each Site								
Burbank	18.2	3.9	3.4	7.9	5.3	10.3	3.8	93.3
Long Beach	14.4	3.3	3.1	7.3	6.0	9.4	4.8	93.6
Hawthorne	12.0	2.8	2.9	6.2	6.0	8.6	4.9	91.5
Downtown LA	18.6	4.3	3.6	8.8	5.7	10.9	4.6	93.7
Rubidoux	15.5	2.8	5.6	17.5	5.1	24.1	4.4	85.7
Upland	14.5	2.6	4.3	11.3	4.8	11.9	3.3	91.8
Anaheim	13.3	2.6	3.1	7.8	5.3	11.9	4.6	93.4
Tanbark Flats	9.8	1.2	1.9	3.1	3.9	7.0	2.6	91.0

a. Organic carbon measured by the thermal/optical technique (14) multiplied by 1.4 to compensate for O and H associated with organic matter.

b. Crustal material is estimated as the sum of Al, Si, Ca, and Fe oxides.

c. Trace species identified is equal to the sum of all species analyzed by XRF (except for S, Al, Si, Ca, and Fe) plus Na^+ and Mg^{++} as determined by AAS.

d. Second highest 24-h average concentration at Long Beach (PM_{10} mass = 130$\mu g\ m^{-3}$) had the following composition: organic material, 27.8$\mu g\ m^{-3}$; elemental carbon, 8.3$\mu g\ m^{-3}$; NH_4^+, 14.2$\mu g\ m^{-3}$; NO_3^-, 46.6$\mu g\ m^{-3}$; $SO_4^=$, 5.2$\mu g\ m^{-3}$; crustal, 14.8$\mu g\ m^{-3}$; trace species I.D., 4.9$\mu g\ m^{-3}$; fraction chemically identified, 93.9%.

The unusually high aerosol nitrate levels observed at Rubidoux have been documented by other authors (12,20-22) who attribute the high nitrate levels to Rubidoux's location in the SOCAB. Rubidoux is far enough downwind of the major industrial and urban pollution sources to experience high total inorganic nitrate (HNO_3 + aerosol nitrate) levels and is also directly downwind of a large, sharply defined source of fresh NH_3 emissions from agricultural activities (12,20,21; also see the NH_3 emission pattern in Figure 6 of ref. 22). Nitric acid and ammonia react to form aerosol NH_4NO_3. The higher airborne crustal material concentrations at Rubidoux are most likely due to the local soil surface conditions (dry, vacant land with sparse vegetation) in the vicinity of that particular monitoring site.

The aerosol at San Nicolas Island is quite different from that found over the on-land portion of the air basin. The dominant contributor to the mass balance there is the identified trace species category, which includes NaCl from sea salt. Estimates based on the measured NaCl at San Nicolas Island indicate that nearly 85% of the trace species category or 28% of the PM_{10} mass is sea salt (i.e., NaCl). On an absolute basis, the concentrations of the other chemical species comprising the mass balance at San Nicolas Island are from 2.5 to 10 times lower than the values observed at the on-land air monitoring locations. This suggests that San Nicolas Island is a reasonable choice for a regional marine background site for use in air quality studies in the Los Angeles metropolitan area.

An ion balance on the water-soluble portion of the aerosol shows that between 70 and 85 percent of the NO_3^- and $SO_4^=$ is associated with NH_4^+ at all on-land locations and that about 50 percent of the NO_3^- plus $SO_4^=$ is associated with NH_4^+ at San Nicolas Island. Lower ratios of NH_4^+ to NO_3^- plus $SO_4^=$ equivalent concentrations (~70%) is observed near the coast, while higher ratios (80-85%) are observed inland. These results indicate that metal cations (probably Na^+) are probably more important to the aerosol formation process near the coast, while NH_4^+ is more important

at inland sites. On an ionic charge equivalent basis, $SO_4^{=}$ concentrations are greater than NO_3^- concentrations at locations nearest the coast (including San Nicolas Island), and also at Tanbark Flats. At Rubidoux and Upland, however, NO_3^- equivalent concentrations are much greater than $SO_4^{=}$. The reasons for the high nitrate values at the eastern, low elevation sites were explained earlier. While Tanbark Flats is also at the eastern end of the air basin, recent results indicate that a significant fraction of the inorganic nitrate at that site remains in the gas phase as HNO_3 (23,24). This is undoubtedly due to reduced amounts of NH_3 at the higher elevations (23).

The total carbon to elemental carbon ratio (TC/EC) is a useful indicator for detecting the presence of any large enrichment in secondary organic aerosols that are formed in the atmosphere from condensation of the low vapor pressure products of atmospheric chemical reactions involving gas-phase hydrocarbons. The TC/EC ratio is useful because elemental carbon concentrations observed in the atmosphere are strictly due to direct (primary) emissions of particles from sources, while organic carbon levels may be due to either primary emissions or to secondary aerosol formation. Gray and co-workers (12) measured TC/EC ratios in fine particle sizes (< 2.1μm AD) during 1982 at many of the same sites used in this study. The fine particle TC/EC ratios during 1982 ranged from 2.43 at Lennox (near Hawthorne) to 2.97 at Azusa and 2.92 at Rubidoux. While these values are less than the TC/EC ratio of 3.2 estimated for basin-wide primary aerosol emissions in 1980 (25), Gray and co-workers still determined that at inland locations up to 22% of the total carbonaceous material may be due to the formation of secondary organics in the atmosphere. Annual average PM_{10} TC/EC ratios for the year 1986 ranged from 4.1 at Hawthorne, Long Beach and Downtown Los Angeles to 5.0 at Rubidoux and Upland, again showing an increasing trend with distance inland in the prevailing downwind direction of air transport. These values for the TC/EC ratio in PM_{10} aerosols are

higher than those observed in the fine particles during 1982. This is to be expected, in part, because EC is found almost solely in fine particles, while noticeable amounts of OC are found in the added coarse particle material (i.e., in the 2 to 10μm size range) due to the presence of plant fragments, humic material in soils, etc. However, fine particle measurements of the TC/EC ratio made at Downtown Los Angeles during 1986 (23) also are higher than in 1982; 3.83 in 1986 versus 2.59 in 1982, and the mass of total carbon in PM_{10} aerosols at Downtown Los Angeles is only 14 percent higher than that observed in the fine particles. These results indicate that most of the carbonaceous material is in particles with aerodynamic diameters of less than 2.5μm. The implication is that secondary organics concentrations in 1986 were higher than in 1982, indicating the potential for year to year variability.

Daily and Seasonal Characteristics

The time series of individual 24-h average PM_{10} mass concentrations at Hawthorne, Downtown Los Angeles, Rubidoux, and Tanbark Flats are shown in Figure 4. The largest day-to-day fluctuations, on an absolute basis, occurred during October and November at the low elevation, inland sites like Rubidoux where higher overall concentrations are observed. The lowest single day PM_{10} mass concentrations were observed at San Nicolas Island and at Tanbark Flats and are around 4-5μg m^{-3}. At the other sites, those located in the Los Angeles metropolitan area, the lowest single day concentration values were approximately 15-20μg m^{-3}. Maximum 24-h average PM_{10} mass concentrations of nearly 200μg m^{-3} were observed at coastal locations, whereas at the eastern end of the air basin (Rubidoux) this value rose to 299μg m^{-3}.

Seasonal variations can more easily be observed by computing monthly average values from the individual 24-h data. This was done for PM_{10} mass and for each of the chemically determined species. A material balance then was constructed

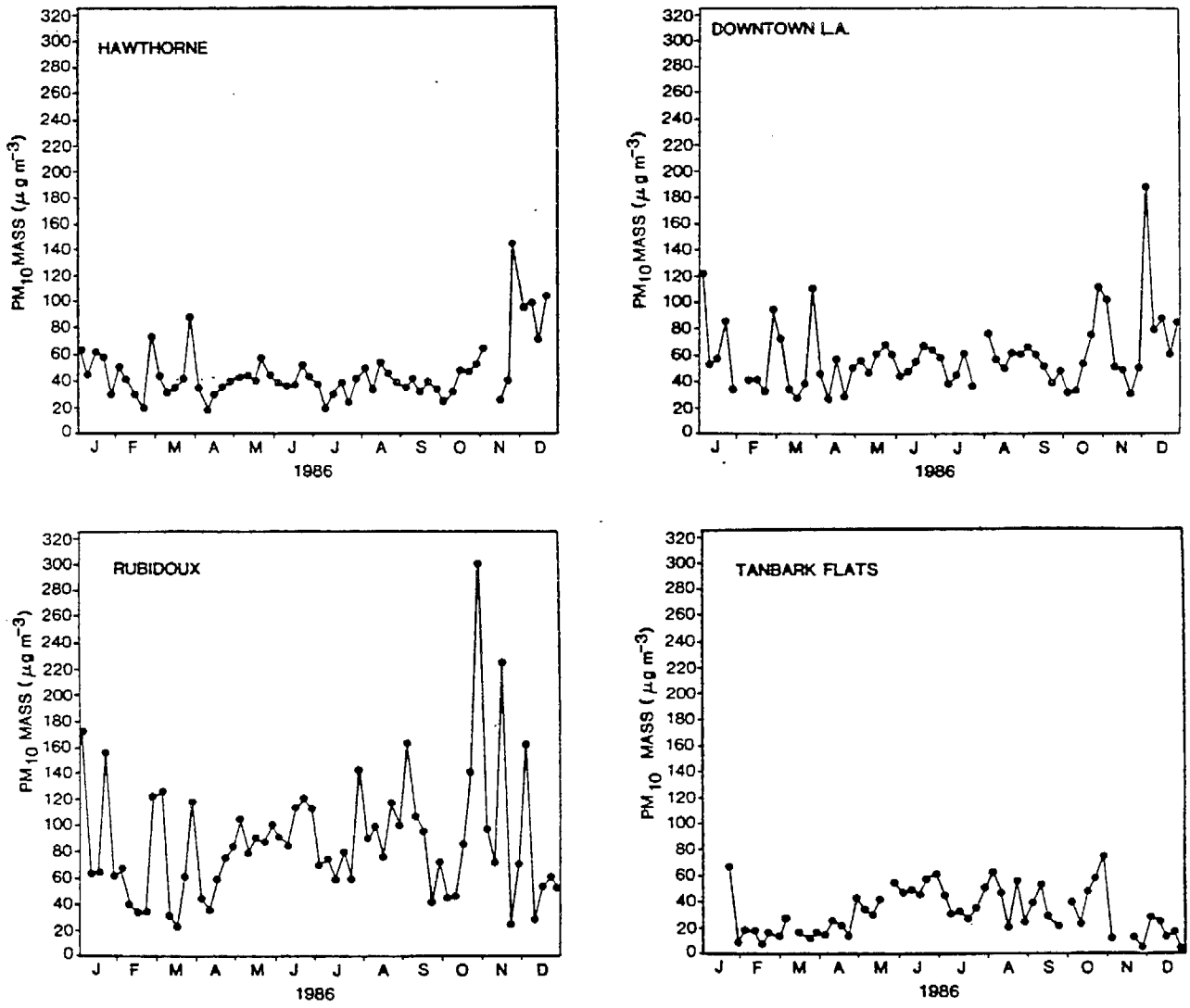

Figure 4. Daily PM_{10} mass concentrations at selected sites in the Los Angeles area.

from the monthly average values and the results are shown for all nine monitoring locations in Figure 5. The same calculations and assmptions were employed here as were used to obtain the annual average mass balance results. The top of each shaded column in Figure 5 represents the gravimetrically measured PM_{10} mass concentration for that month. The undetermined portion indicates the fraction of the gravimetric mass which was not accounted for by chemical analysis.

The monthly average results for San Nicolas Island, presented in Figure 5, show that the concentrations of all species are relatively low and, for 1986, there appears to be no systematic variation in PM_{10} mass or composition with season. At Hawthorne, the maximum mass concentrations occur in the winter (December and January), with December, 1986 being an exceptionally high month. Lower mass concentrations, which fluctuate only slightly from month-to-month are observed during the rest of the year. The weak dependence of PM_{10} mass on time of year at Hawthorne during the spring, summer and fall is due to strong and contradicting seasonal trends in the individual chemical components which make up the aerosol. Carbonaceous material and nitrate ion concentrations are highest during the winter months, falling to a minimum in the summer. These results are similar to fine particle ($<2.1\mu$m AD) carbon and nitrate data taken in the Los Angeles area by Gray et al. (12) in 1982 and by Solomon et al. (23) in 1986. This pattern of high winter and low summer aerosol carbon values is typical of primary vehicular pollutants like CO and lead measured at Lennox, a nearby monitoring site adjacent to a major freeway (26). High winter aerosol nitrate levels are favored by the higher total NO_x levels observed in the Los Angeles area in the winter (26) and by the fact that the partition of inorganic nitrate between HNO_3 and ammonium nitrate is driven toward aerosol nitrate at low ambient temperatures (22). On the other hand, maximum sulfate concentrations are observed in the summer, partially off-setting the lower carbon and nitrate levels. In the summer, sulfate concentrations at Hawthorne average 1.5-3

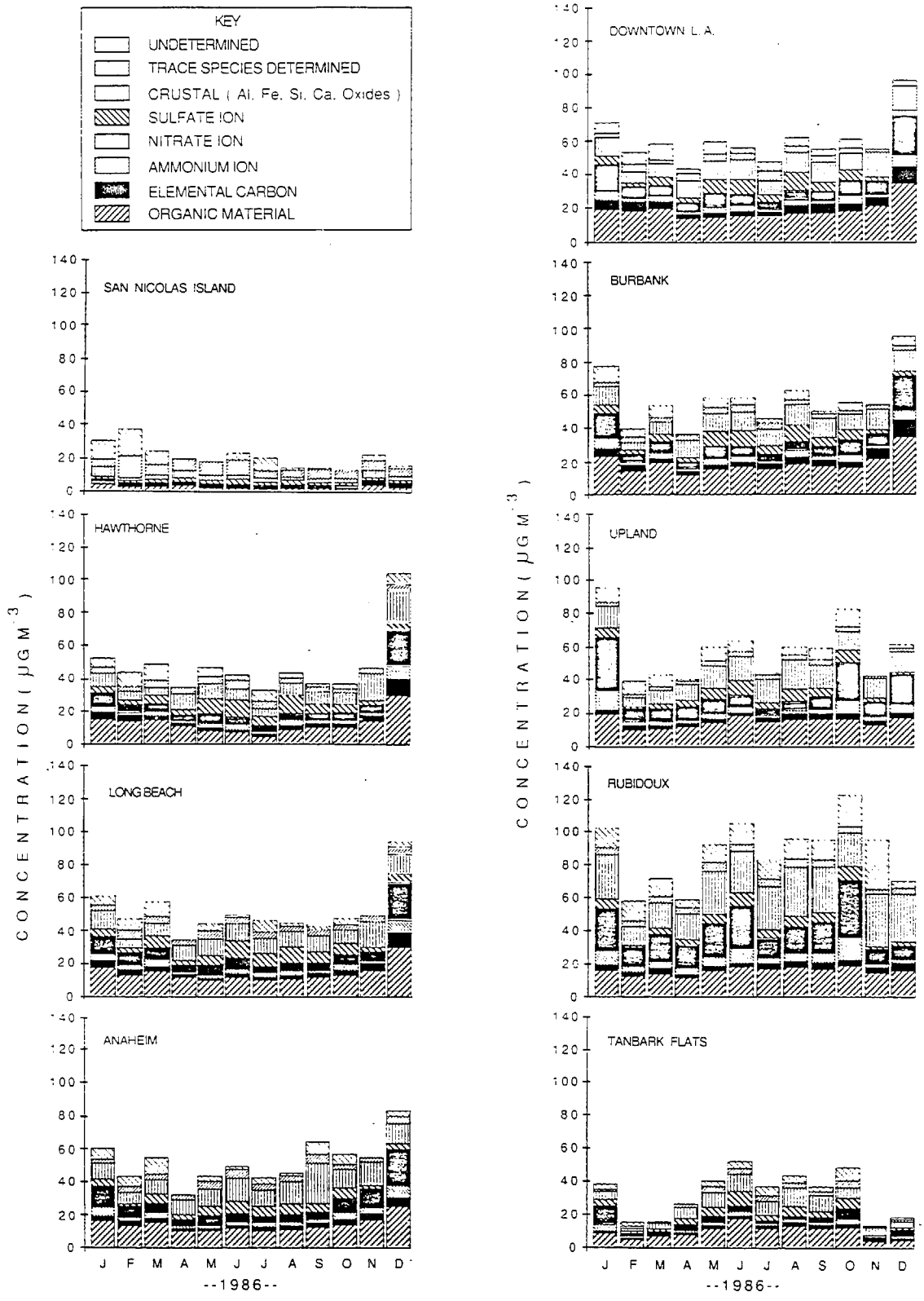

Figure 5. Material balance on the chemical composition of monthly average PM_{10} aerosols collected in the South Coast Air Basin during 1986.

times greater than the aerosol nitrates, while in the winter the reverse is true. Crustal material, which can account for over 20% of the observed PM_{10} mass at Hawthorne, is 2-3 times higher in November and December than during the rest of the year. There are at least two reasons for the wintertime maximum in crustal material observed at Hawthorne. First, during the winter air masses arriving at Hawthorne typically have had a longer residence time over land than is true during summer, when ocean breezes are stronger and of longer duration. Secondly, during the winter the average night through early morning mixing depth is lower than in the summer, thereby concentrating the primary crustal aerosol emissions (e.g., from road dust).

In terms of PM_{10} mass, the seasonal variations at Long Beach, Anaheim, Downtown Los Angeles and Burbank are similar to those observed at Hawthorne. That is, maximum PM_{10} mass concentrations are observed in the winter months of January and December with lower concentrations observed during the rest of the year (see Figures 4 and 5). The predominant difference between stations is found in seasonal trends in the individual chemical components. Moving inland toward Downtown Los Angeles and Burbank from Hawthorne, the strong seasonal dependence in carbonaceous material concentration weakens while that of the aerosol nitrates becomes stronger.

Proceeding further inland to Upland and Rubidoux, the seasonal variation in PM_{10} mass concentration begins to change with monthly average summer and fall values approaching and even exceeding winter ones (see Figure 5). The pronounced summer minimum in aerosol carbon concentrations observed at sites located further west is absent at these eastern monitoring stations. At Upland, the months that show a pronounced increase above the annual average (i.e., January and October) are distinguished by a major increase in aerosol nitrates during those months. At Rubidoux, on the average, the summer PM_{10} mass concentrations are

higher than the winter values. However, individual days during the late fall and winter months show much higher concentrations than any summertime values (see Figure 4). In fact, the highest 24-h average PM_{10} concentration observed throughout the SOCAB during 1986, was at Rubidoux on 29 October, and was equal to 299μg m^{-3}. This day will be discussed in more detail in the next section. On an absolute basis, there is much more aerosol nitrate and soil-related material in the air at Rubidoux than at the other monitoring locations; reasons for this were given earlier. Nitrate levels at Rubidoux follow a complex seasonal pattern. Unlike any of the other sites, there is a peak in the monthly average aerosol nitrate concentration during the summer at Rubidoux. The high monthly average aerosol nitrate concentrations in January and in October are due to one or two very high days (NO_3^- > 60μg m^{-3}), while during the summer NO_3^- concentrations are constantly found in the range of 20-30μg m^{-3} (e.g., in June the daily values were 27.9, 25.7, 24.4, 22.8 and 28.4μg m^{-3}).

Peak Day Composition

The highest and second highest 24-h average PM_{10} mass concentrations observed at each site are listed in Table II. As can be seen, the peak PM_{10} levels typically occurred in the late fall and early winter: late October through January. As with the annual averages, peak 24-h concentrations were higher at inland locations than along the coast, except at Tanbark Flats (the high elevation inland site). The maximum 24-h PM_{10} mass concentration observed in the SOCAB, during the study period was 299μg m^{-3} at Rubidoux.

For each site, a material balance was constructed from chemical composition data taken on the day of the maximum 24-h average PM_{10} concentration measurement. The same assumptions were used here as were employed in the mass balance calculations reported earlier. The peak day material balance results for all on-land monitoring locations are presented in Figure 6 and in Table III. In comparing the

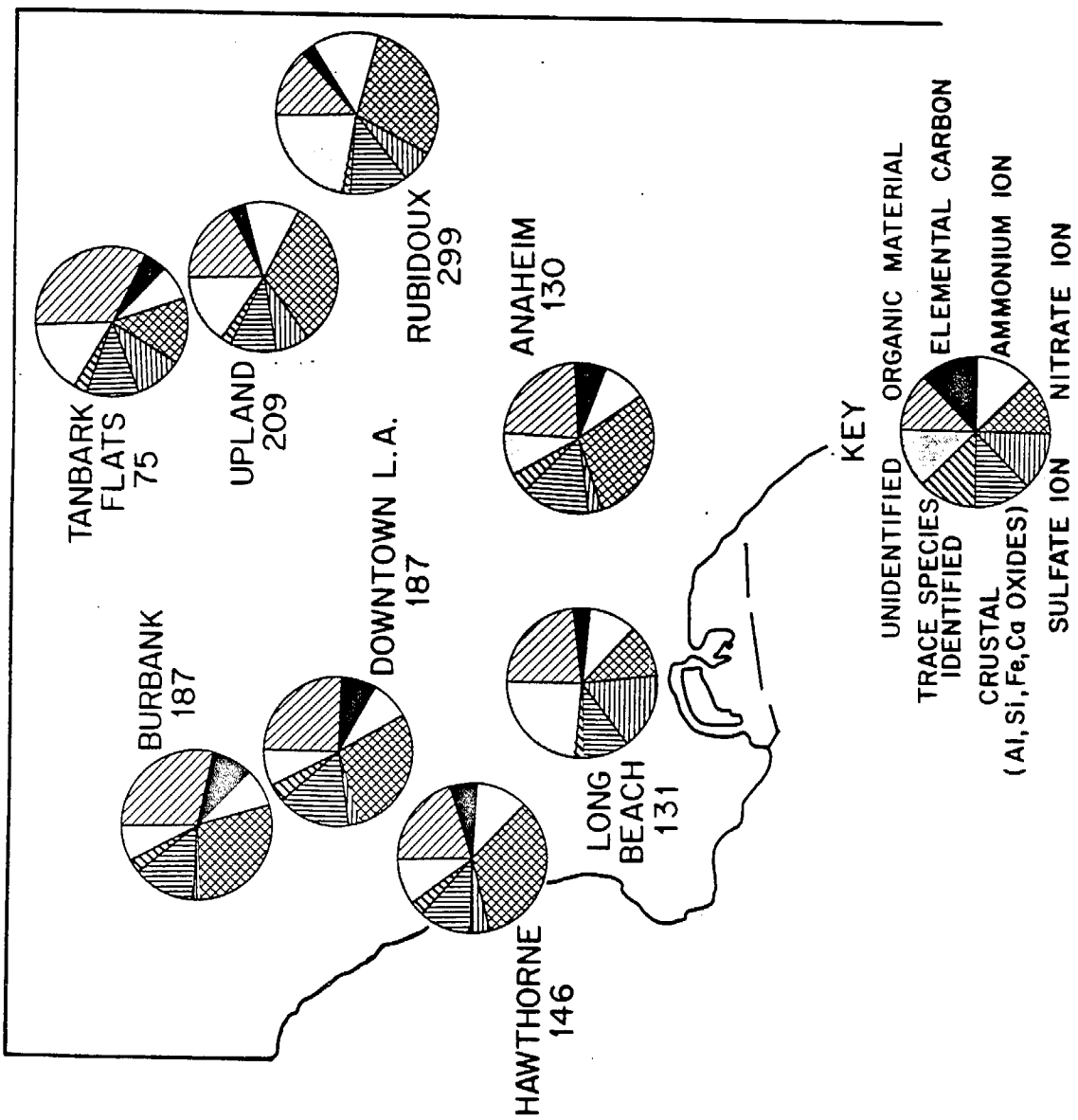

Figure 6. PM_{10} aerosol composition during the highest 24-h average concentration event at each monitoring station, 1986 (concentrations in $\mu g\ m^{-3}$).

peak day material balance results to those of the annual average (see Figure 3), it is seen that the relative chemical composition of the PM_{10} aerosol over these two averaging times is quite different. For example, NO_3^- and associated NH_4^+ play a much more important role during high single day pollution events, while $SO_4^=$, at least in the western portion of the air basin, plays a considerably less important role during peak single day high PM_{10} episodes. These findings indicate that to reduce the peak PM_{10} mass concentrations in the SOCAB, aerosol NO_3^- levels will probably have to be reduced. This is of special concern at inland locations, such as Rubidoux, where for example, the NO_3^- plus NH_4^+ ion concentrations are more than 100μg m^{-3} higher during the peak day than observed for the annual average.

PM_{10} Standards and Measured PM_{10} Mass Concentrations

The annual average PM_{10} standards set by the federal government (1) and the State of California (3) are 50μg m^{-3} arithmetic mean and 30μg m^{-3} geometric mean, respectively. As can be seen in Table II, the annual average PM_{10} mass concentrations (arithmetic and geometric means) measured at most sites are greater than both the federal and state particulate matter standards. At Tanbark Flats, the inland, high elevation site and San Nicolas Island, the background monitoring station, both the state and federal annual PM_{10} standards are met. The yearly average PM_{10} mass concentration measured at Hawthorne, the on-land site closest to the ocean, was slightly less than allowed by the federal standard, but considerably above the allowable level set by the State of California.

The federal and state governments also have set 24-h PM_{10} standards which are 150μg m^{-3} with no more than one expected excursion above that value per year and 50μg m^{-3} with no measurements above that value per year, respectively. Once again, Tanbark Flats, San Nicolas Island, and those stations closest to the coastline do not exceed the federal 24-h PM_{10} standard, while all areas, including San Nicolas Island, exceed the state 24-h average PM_{10} standard. The highest percentage of days

exceeding the state and federal 24-h standards occurred at Rubidoux, with over 80% of the days sampled exceeding the state PM_{10} standard of 50μg m^{-3}. In addition, the highest individual 24-h PM_{10} concentration during the entire study occurred at Rubidoux and exceeded the federal and state standards by roughly a factor of 2 and 6, respectively. As was mentioned earlier, these extreme particulate matter levels observed at Rubidoux are due to the addition of much more aerosol nitrate and soil related materials than is observed elsewhere in the SOCAB.

SUMMARY AND CONCLUSIONS

The promulgation of new air quality standards for particulate matter has prompted the immediate need for the measurement of the spatial distribution of PM_{10} aerosols on a daily and annual average basis in cities throughout the United States. Of particular importance is the determination of the chemical composition of these aerosols in a way that will assist both the assessment of the origin of this material and the development of cost-effective emission control strategies in areas where pollutant levels exceed the new standards. Data also are needed on regional background PM_{10} concentrations and composition in order to determine the fraction of the PM_{10} concentrations which would not be affected by local emission control measures.

In anticipation of this need, a PM_{10} aerosol monitoring network was established in the South Coast Air Basin in the greater Los Angeles region during the calendar year 1986. A remote background station at San Nicolas Island was included in this network. A sampling protocol was developed which allowed for the detailed chemical characterization of the collected samples so that a nearly complete material balance was obtained on the chemical composition of the samples taken at all on-land monitoring stations (i.e., 86-94 percent of the gravimetrically measured mass was chemically identified).

Virtually all portions of the Los Angeles urban area exceed both the federal and State of California ambient air quality standards for PM_{10} over an annual average, with annual concentrations at urban sites other than Rubidoux in the range 47-60$\mu g\ m^{-3}$. Rubidoux, located at the eastern end of the air basin, had the highest annual average PM_{10} mass concentration (87.4$\mu g\ m^{-3}$). This was due to larger amounts of NO_3^- and soil-related material in the aerosol at Rubidoux than elsewhere. Five major chemical components (carbonaceous material, nitrate, sulfate, and ammonium ion, and crustal material) accounted for greater than 80 percent of the gravimetrically measured mass at all on-land monitoring stations. Measurements made at San Nicolas Island suggest that 20.8$\mu g\ m^{-3}$ of the PM_{10} aerosol in the South Coast Air Basin, over the long term average, may be present in the absence of local urbanization (i.e., 28% to 44% of the annual average PM_{10} concentrations at the individual on-land monitoring sites). This contribution due to regional background is less than observed in the eastern United States, where 35 to 80 percent of the measured PM_{10} mass has been attributed to long distance transport of source contributions which cannot be controlled at a local level (27).

Peak 24-h average PM_{10} concentrations as high as 299$\mu g\ m^{-3}$ were measured at Rubidoux, CA during October, 1986. Increases in aerosol nitrate levels appear to be the most important factor that distinguishes the peak 24-h PM_{10} events from a typical day at nearly all sampling locations.

Since five major chemical components (carbonaceous material, nitrate, sulfate, ammonium ion, and crustal material) are needed to account for the bulk of the PM_{10} aerosol, emission control strategies directed at some combination of the sources of these particular substances will be needed if PM_{10} standards are to be met. Procedures for the engineering design of deliberate air pollution abatement programs for sulfates, nitrates and primary carbon particles have been demonstrated previously in the Los Angeles area (28-32). For these pollutants, ambient concentration

improvements of up to about 50% could be achieved in the Los Angeles area via identifiable emission controls, which is in the range of the improvement needed to meet the federal PM_{10} standards at Rubidoux.

ACKNOWLEDGEMENTS

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APPENDIX C

BASINWIDE NITRIC ACID AND RELATED SPECIES CONCENTRATIONS OBSERVED DURING THE CLAREMONT NITROGEN SPECIES COMPARISON STUDY

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ABSTRACT

In conjunction with the Claremont Nitrogen Species Comparison Study, tandem filter units designed to collect HNO_3/total aerosol (TA) NO_3^- and NH_3/TA NH_4^+ were operated at seven locations throughout the Los Angeles area, including Claremont. The sampling methods used were related to the comparison study via intensive short-term and long-term measurements made at Claremont by both the tandem filter method and the denuder difference method. Between methods, 4-h and 6-h duration HNO_3 samples taken by the tandem filter method were higher (~20%) than the HNO_3 results obtained by the denuder difference method. As sampling duration increased to 22 h, the tandem filter method HNO_3 and NH_3 concentration measurements increased, while the 22-h denuder difference method HNO_3 values remained indistinguishable from the average of simultaneous short-term 4- and 6-h average samples.

Analysis of the basinwide data showed that Claremont experienced the highest measured HNO_3 concentrations in the Los Angeles area during the period of the comparison study, confirming that Claremont was a wise choice for the main site of the study. In contrast, an alternative site near Riverside experienced the lowest HNO_3 levels in the air basin, accompanied by high aerosol nitrate and very high NH_3 concentrations.

Keywords: Nitric acid (HNO_3), ammonia (NH_3), tandem filter method, denuder difference method, Los Angeles.

Introduction

During the early planning stages of the 1985 Claremont Nitrogen Species Comparision Study (NSC) (Hering, 1986) the question was raised, "Where in the Los Angeles area should the experiment be conducted in order to maximize the chance of encountering the highest available atmospheric nitric acid levels?" At various times, monitoring sites at El Monte, Claremont, and Riverside, CA, were considered seriously. An unambiguous answer to that siting question could not be supplied in advance of the study because no large data base existed that describes HNO_3 concentration gradients based on measurements taken simultaneously at many sites throughout Southern California over a long period of time.

In order to assist the siting of future studies, and to determine in retrospect whether or not Claremont was a wise choice for the HNO_3 measurement methods comparison study, an air monitoring network was established at seven locations in Southern California, as shown in Figure 1. Tandem filter units (Spicer, 1979; Spicer et al., 1982; Appel et al., 1980; Grosjean, 1983; Russell and Cass, 1984) designed to collect HNO_3/total aerosol (TA) NO_3^- and NH_3/TA NH_4^+ were operated for 24-h sampling periods every second day at those sites from September 10-18 during the course of the NSC study at Claremont. The sampling methods used were related to the Claremont study via intensive short-term and long-term average measurements made at Claremont.

At Claremont, two methods for the collection of HNO_3 were employed: (1) the denuder-difference method and (2) the tandem filter method (Spicer, 1979; Spicer et al., 1982; Appel et al., 1980; Forrest et al., 1982; Shaw et al., 1982; Grosjean, 1983; Russell and Cass, 1984). The tandem filter method also was used for the collection of NH_3 (Richards and Johnson, 1979; Appel et al., 1980; Cadle et al., 1980; Russell and Cass, 1984). In addition, fine and TA nitrate and sulfate, and TA ammonium ion samples were collected. Fine and TA sulfate and TA ammonium ion concentration

LOS ANGELES AREA MONITORING NETWORK

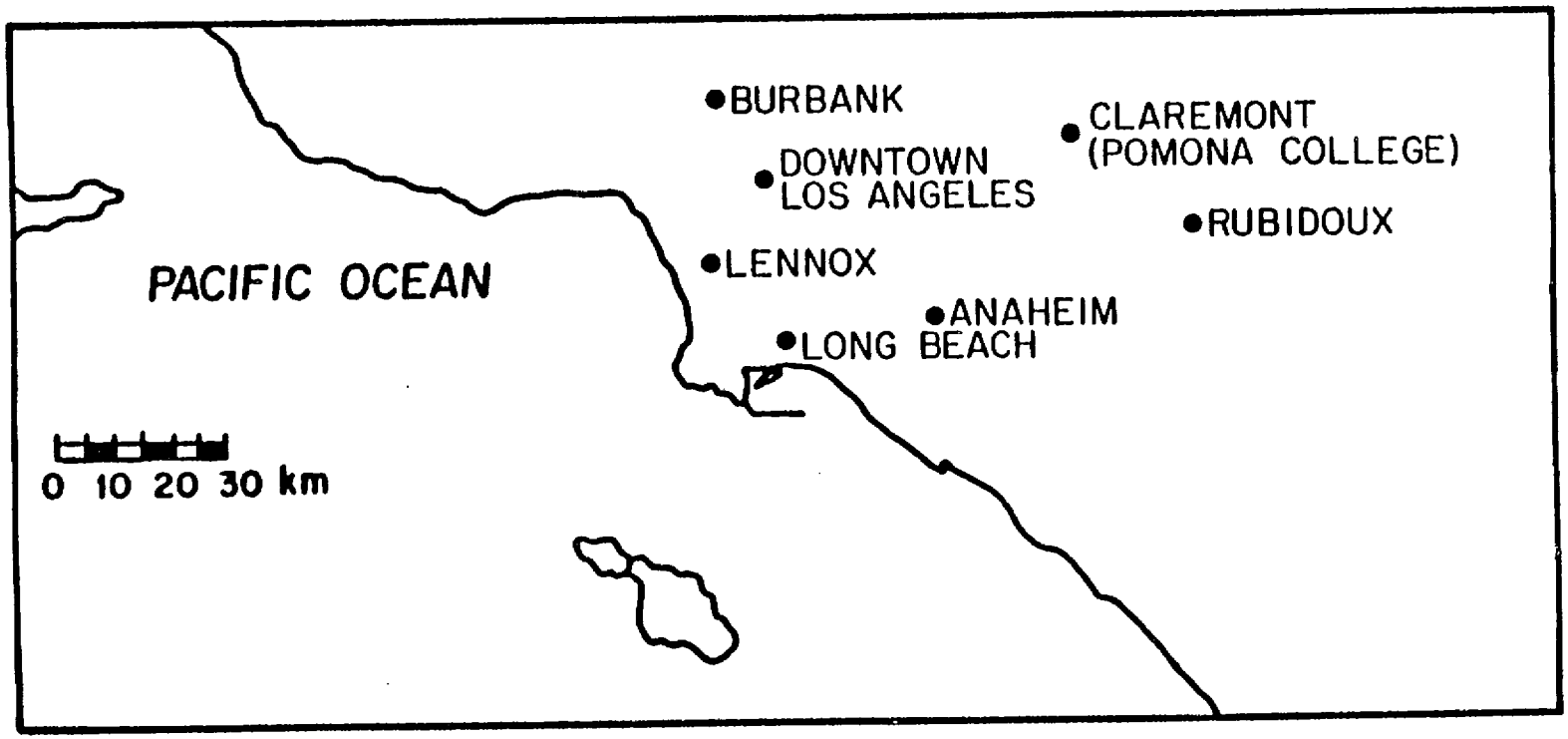


Figure 1. Air monitoring sites in the South Coast Air Basin that surrounds Los Angeles, CA and employed during the Nitrogen Species Comparison Study, September 1985. Sites other than Claremont were colocated with South Coast Air Quality Management District continuous monitoring stations (U.S. Environmental Protection Agency, 1973; 1978).

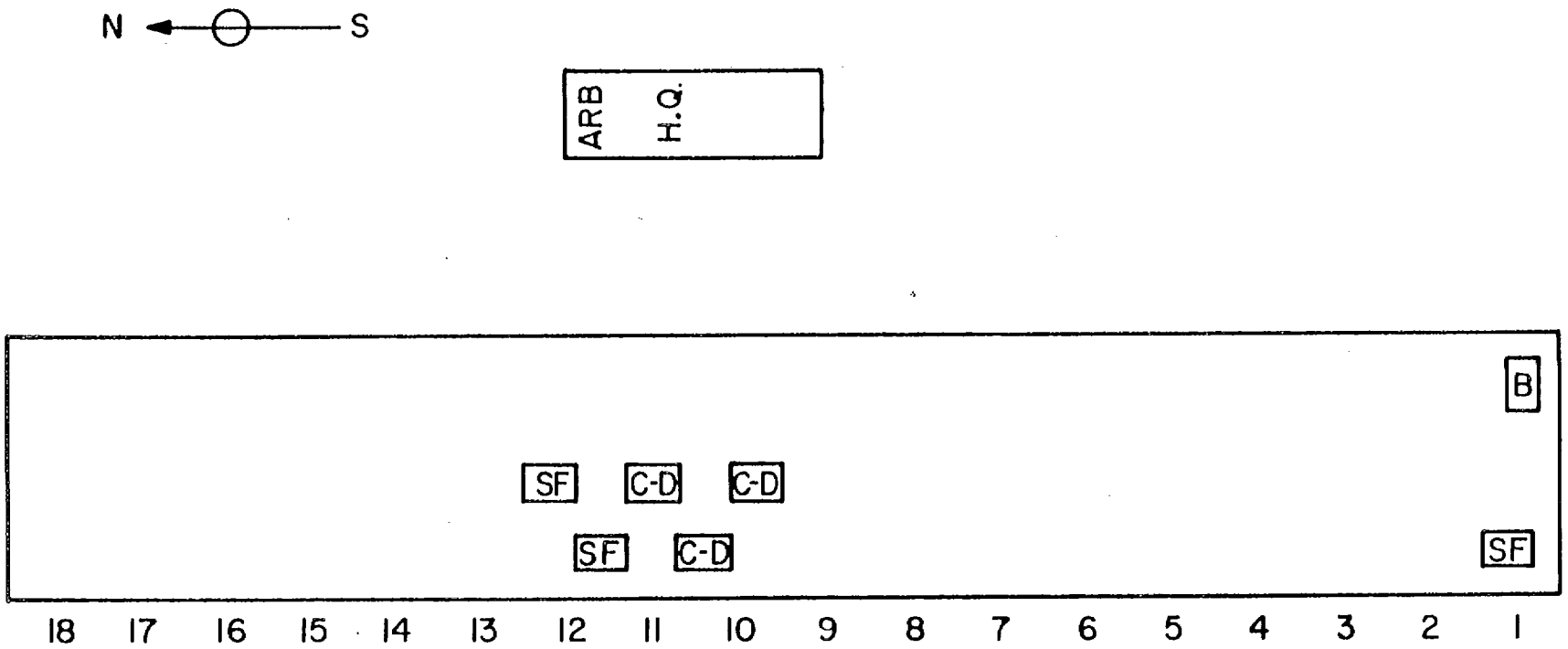
data will not be discussed here, but the measured values can be found in Hering (1987). Three sampling systems of each type were employed at Claremont (at locations shown in Figure 2) in order to assess the reproducibility of measurements within and between methods, and to determine the effect of sampling duration. Two sampling systems of each type ran according to the 4- and 6-h schedule established by the NSC study design. The third sampler of each type collected 22-h continuous samples that can be compared to the weighted average of the short-term 4- and 6-h samples collected during the same day. By siting replicate samplers at two widely separated points along the NSC sampling platform, it was also possible to assess whether or not HNO_3 and NH_3 concentration gradients existed horizontally along the sampling platform.

Sampler Design

A schematic diagram of the samplers used in this study is given in Figure 3. These sampling systems are relatively inexpensive, field-ready devices, designed for semi-automated 24-h integrated sampling (i.e., the flow rates were optimized according to the amount of material estimated to be collected in 24 hours and to the capabilities of the analytical procedures used for sample analysis). During the comparison study, when called upon to collect 4- and 6-h samples those short duration samples were taken by the unmodified samplers at the flow rates shown in Figure 3. The samplers were operated with an inlet line configuration suited to all-weather use in the field.

The tandem filter units deployed at Claremont and throughout the 7-station network are illustrated on the right side of Figure 3 (sampling lines D and E). In the tandem filter method, a standard polycarbonate, multiple filter holder (47 mm, Nuclepore Corp.) was used to hold several filters in series. Nitric acid was collected on a nylon (1.0 μm pore size, 47mm diameter, Nylasorb, Membrana Corp., Lot #4221)

SAMPLER LOCATION ON PLATFORM AT CLAREMONT HNO_3 STUDY (9/85)

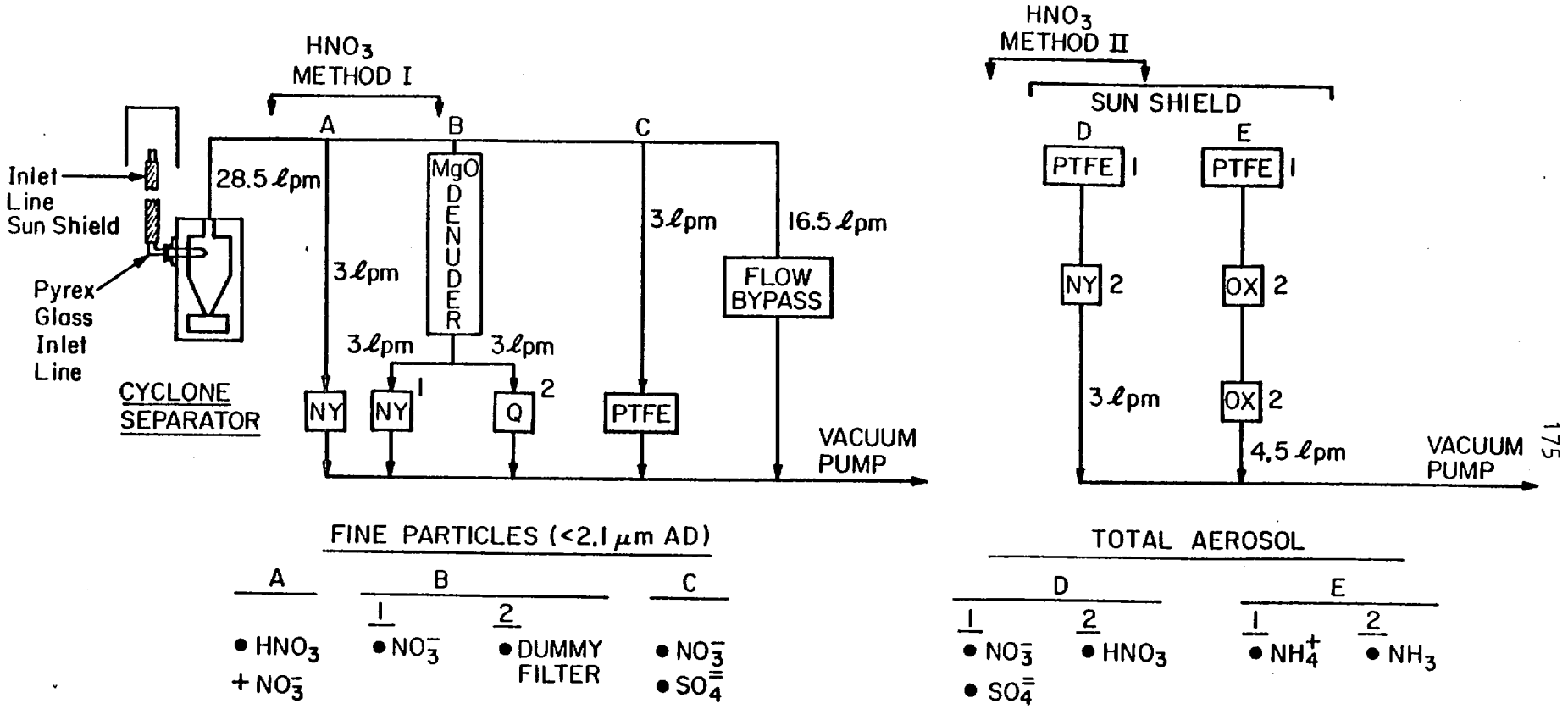


SF: STACKED FILTER UNITS

C-D: CYCLONE-DENUDER SYSTEM

B: STACKED FILTER UNITS, BASINWIDE NETWORK

Figure 2. Location of the Caltech sampling systems on the Nitrogen Species Comparison Study sampling platform at Claremont. The platform was 125 feet in length and there was 80 feet between position 1 and 12, the locations of the two spatially separated sampling systems.



NY Nylon Filter

PTFE Polytetrafluoroethylene Filter

OX Oxalic Acid Impregnated Glass Fiber Filter

Q Quartz Fiber Filter (not analyzed)

Figure 3. Schematic of sampling apparatus employed at the Nitrogen Species Comparison Study, September 1985. The two filter trains labeled D and E were employed at the seven basinwide sampling locations.

backup filter after particles (including total aerosol nitrate) were removed by the use of an open-face inert polytetrafluoroethylene (PTFE) prefilter (2.0 μm pore size, 47mm diameter, Membrana Corp.) (sampling line D, Fig. 3). Ammonia and total aerosol ammonium ion samples also were collected by an analogous method. In this case, ammonia was collected on two glass fiber filters (Type A/E, 47mm diameter, Gelman Sciences, Inc.), each impregnated with oxalic acid (1.0 ml of 5 percent oxalic acid) after particles were removed by a PTFE prefilter (sample line E, Fig. 3). The filter units used for HNO_3/TA NO_3^- and NH_3/TA NH_4^+ collection operated at nominal flow rates of 3.0 and 4.5 l/min, respectively, and both were protected from the sun by a large Teflon®-coated sunshield.

The HNO_3 diffusion denuder systems placed at Claremont are shown on the left side of Figure 3. One nylon filter (B1) was used as a backup filter beneath a MgO-coated diffusion denuder designed to remove HNO_3. This nylon filter collected only fine particle nitrate. The other nylon filter (A) collected total inorganic nitrate (HNO_3 plus fine particle nitrate). The difference between the NO_3^- ion concentrations measured on the two nylon filters (A – B1) yields a measure of gas phase nitric acid. In order for the denuder difference method to work, two requirements must be met: (1) the nitrate aerosol concentration reaching nylon filters A and B1 in Figure 3 must be the same, and (2) HNO_3 must be removed completely by the denuder but must not be collected unintentionally on other surfaces inside the sample. In order to meet these requirements, attention must be paid to materials of construction, flow rates, and aerosol loss mechanisms. In the system shown in Figure 3, ambient air passed under a polypropylene rain cap and was pulled at a flow rate of 28.5 lpm through an acid (HCl) washed Pyrex glass inlet line that was protected from the sun (1/2" ID, 40" long). The air stream then passed through a Teflon®-coated AIHL cyclone with a 2.1μm aerodynamic diameter cutpoint (50 percent collection efficiency) (John and Reischl, 1980). The cyclone was used to remove

large nitrate-containing particles (>2.1 μm AD) which, if not removed at this point, would be preferentially collected by inertial deposition within the diffusion denuder assembly that is directly upstream of filter B1, thereby violating design requirement (1) above. The acid washed inlet line and Teflon®-coated cyclone were used to suppress HNO_3 deposition on those parts of the sampler other than the MgO-coated denuder assembly. From the cyclone, the air flow and fine particles (<2.1 μm AD) entered a one liter Teflon®-coated sampling manifold where the flow and particles were split between several parallel filter holder assemblies and a flow bypass needed to obtain the desired total flow of 28.5 lpm. Two of these filter holders contained nylon filters (1.0 μm pore size, 47 mm diameter, Nylasorb, Membrana Corp., lot #4221) with a nominal flow rate through each filter of 3 l/min (sample lines A and B1, Fig. 3). In addition to the two nylon filters, a PTFE filter (0.5 μm pore size, 47 mm diameter, Membrana Corp.), operating at a nominal flow rate of 3 l/min, was placed in parallel with the total nitrate filter behind the cyclone (sample line C, Fig. 3). This filter was analyzed for fine particle nitrate and sulfate, and was intended to allow for the comparison of fine particle nitrate collected on a Teflon® filter to that collected on a nylon filter located behind the diffusion denuder. The purpose of this comparison was to obtain, under the conditions of this experiment, an estimate of the loss of particulate nitrate from Teflon® filters (Appel et al., 1980, 1981; Forrest et al., 1980). The dummy filter (sample line B2, Figure 3) occupied a filter holder that was already a part of the existing field-ready samplers used in this study but which was not needed by the present set of experiments.

Flow rates were measured on each of the tandem filter units at the beginning of every sampling period to ensure that the Nuclepore filter holders were not leaking. Flow rates on the denuder difference systems were monitored once each morning. Flow rate measurements were made using a rotameter that had been factory calibrated with an accuracy of 1 percent full scale. Periodically during sampling,

additional flow checks were made on both systems in order to determine if filters were clogging or if filter holders were leaking. These tests indicated that neither of these problems occurred.

Several precautions were taken to ensure the integrity of the samples both before and after sample collection. Reactive and treated filters were stored in self-sealing, plastic petri dishes, sealed with Teflon® tape, stored in Ziploc poly bags, and refrigerated at all times. PTFE filters also were stored in the same type of petri dishes and Ziploc bags, but sealed with Teflon® tape and refrigerated only after the samples were collected.

Dynamic field blanks were collected once each day on all samplers. The filters were loaded, the samplers turned on for 10 seconds, and the filters were removed. Storage and analysis of the field blanks was identical to that of the samples. The average blank (μg/filter) determined for each of the filter types and for each species are as follows: PTFE — NO_3^- (0.30), $SO_4^=$ (0.2) and NH_4^+ (<0.3); nylon — NO_3^- (0.26), and oxalic acid impregnated glass fiber filters — NH_4^+ (0.15).

Sample Analysis

Nylon filters were leached by lightly shaking each of them in 10 ml of a $CO_3^=$/ HCO_3^- buffer (eluent for the ion chromatograph) for about 15 hours. PTFE filters were first wet with 0.2 ml of EtOH (100 percent), in order to reduce the hydrophobic nature of this filter medium (Derrick and Moyers, 1981). They then were leached in the same manner as the nylon filters except for the use of a PTFE rod (47 mm x 10 mm) required to keep the filters submerged in the leaching solution. Glass fiber filters impregnated with oxalic acid were leached by lightly shaking each of them in 10 ml of water (distilled, deionized) for about 15 hours.

The leachate from the nylon filters A, B1 and D2 and the PTFE filters C and D1 (Figure 3) were analyzed by ion chromatography (Dionex Corp.) for nitrate and

sulfate (Mulik et al., 1976). The leachate from the PTFE and two oxalic acid backup filters (E, E1 and E2, Figure 3) were analyzed for NH_4^+ ion by a modified indophenol colorimetric procedure (Bolleter, 1961) employing an Alpkem rapid flow analyzer. The concentrations of NO_3^-, $SO_4^=$ and NH_4^+ ions were determined relative to standards of known concentration which were diluted daily from more concentrated solutions. These concentrated standards were prepared new from ACS grade analytical reagent K_2SO_4, $NaNO_3$ and NH_4NO_3. For all samples analyzed, the matrix of the daily standards matched the matrix of the combined leaching solution and filter impregnating agent (if any).

Approximately 10 percent of the filters were cut in half and run in duplicate. The coefficient of variation for all filters analyzed in this manner was 5 percent for NO_3^-, 4 percent for $SO_4^=$, and 5 percent for NH_4^+ ion. Reproducibility obtained from replicate analysis of standards and samples yielded a relative error of 2 percent for NO_3^-, 3 percent for $SO_4^=$, and 3 percent for NH_4^+ ion. The accuracy of the NO_3^- and $SO_4^=$ measurements from PTFE and nylon filters was obtained from analysis of blind spiked calibration filters supplied by the California Air Resources Board. These results indicated an accuracy of better than 10 percent for both NO_3^- and $SO_4^=$ over the concentration range tested. No spiked calibration filters were supplied for NH_4^+ ion analysis.

Results and Discussion

Short-term 4- and 6-h average HNO_3 and NH_3 concentrations measured at Claremont are shown in time series in Figure 4. As can be seen in this Figure, HNO_3 concentrations observed at Claremont ranged from less than 100 neq/m^3 at the beginning (September 11) and at the end (September 18) of the study to almost 800 neq/m^3 on September 14. Ammonia concentrations remained rather constant, generally ranging from 200-400 neq/m^3, except for 3 short episodes of very high con-

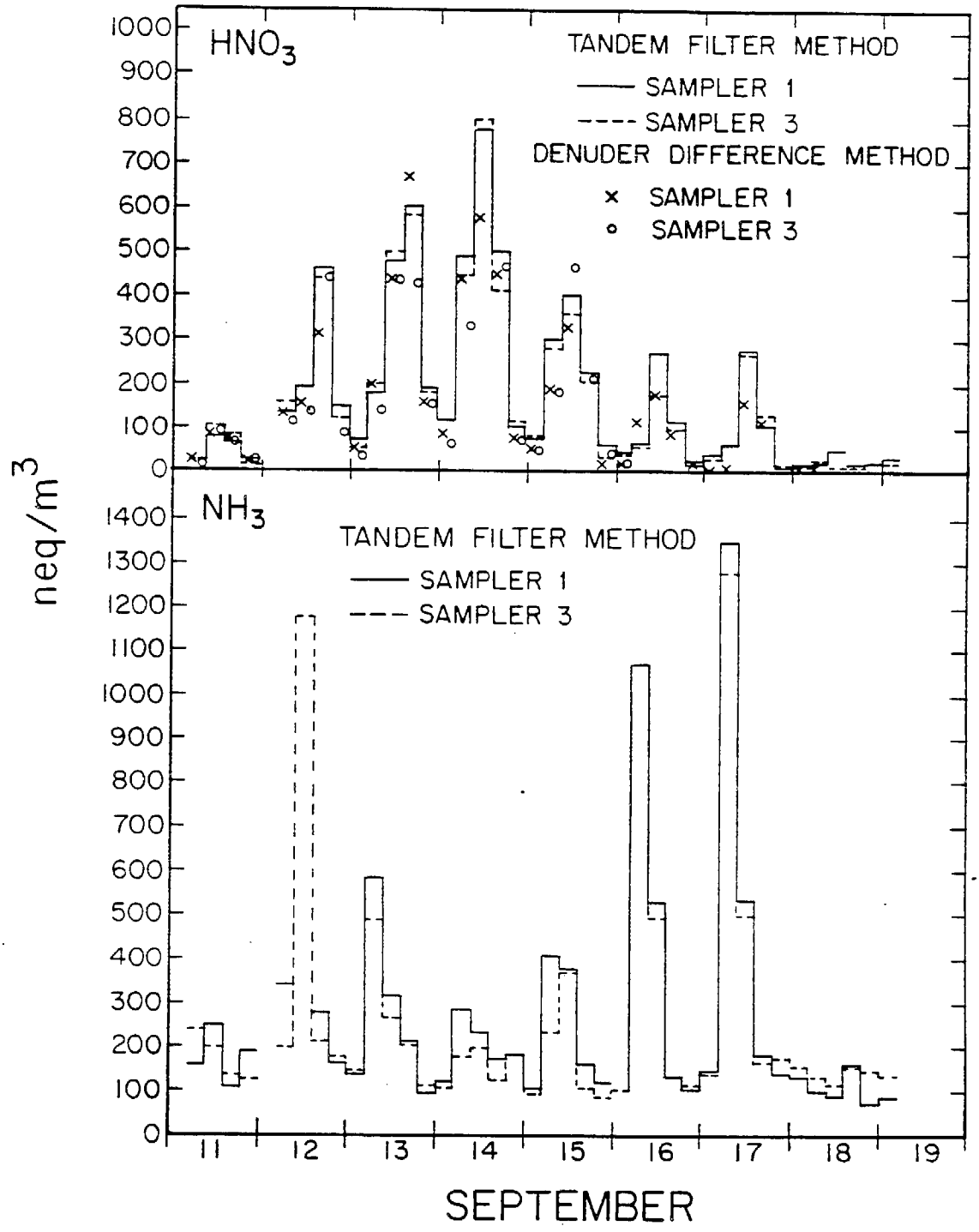


Figure 4. Time series of 4- and 6-h HNO_3 measurements by the diffusion denuder method and the tandem filter method (upper). Time series of the 4- and 6-h NH_3 measurements by the tandem filter method (lower).

centrations (>1000 neq/m^3), which could have been due to transport from nearby dairy farms. Statistical evaluation of data from the two co-located denuder difference samplers operating over 4- and 6-h averaging times shows that the two replicate data sets are related with a correlation coefficient of 0.91, and a paired t-test shows that the mean values of those data sets are not significantly different at the 95% confidence level. The two tandem filter units that were operated at widely separated points on the sampling platform (see Figure 2) correlate with each other exceptionally well (r = 0.99), and analyses of those data by Hering and Lawson et al. (1987) show that there were no appreciable differences between those data sets due to horizontal position along the sampling platform. An analysis of variance performed on the records of both denuder systems and both tandem filter systems showed, however, that the short-term HNO_3 concentrations measured by the tandem filter method are significantly different (in a statistical sense) from the HNO_3 values obtained by the denuder difference method. The tandem filter method values measured over 4- and 6-h periods average about 20 percent higher than the HNO_3 levels measured by the denuder difference method.

The effect of sampling duration on the collection of HNO_3 by the tandem filter and denuder difference methods and on the collection of NH_3 by the tandem filter method is shown in Figure 5 and in Table 1. Samples collected on the 22-h continuous schedule are plotted against the weighted average of the 4- and 6-h samples collected over the same 22-h sampling period. If two short-term samplers of the same type were in operation, their results were averaged to obtain the 22-h value used. As seen in Table 1, there was no statistically significant difference (paired t-test at 95% confidence level) between the mean of the daily average of 4- and 6-h HNO_3 samples versus the mean HNO_3 concentration measured by continuous 22-h sampling using the denuder difference method. Using the tandem filter method, the mean values of the 22-h continuous HNO_3 and NH_3 samples were both systemati-

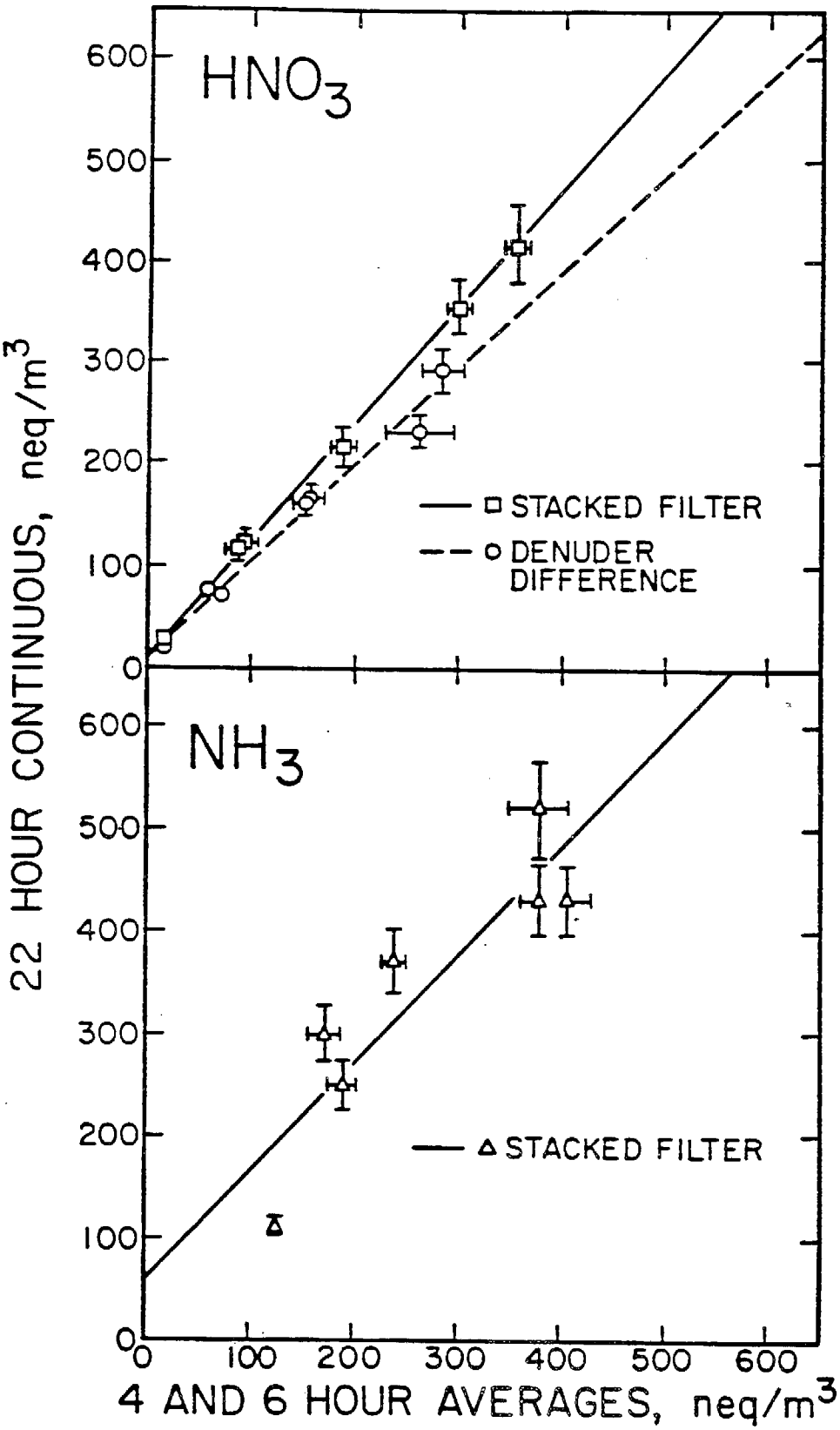


Figure 5. 22-h continuous versus 22-h average of daily 4- and 6-h HNO_3 and NH_3 samples collected at the Claremont Nitrogen Species Comparison Study, September 1985.

Table 1.
Analysis of the Effect of Sampling Duration
(Concentrations in neq/m^3)

Case	Number of Observations	Correlation Coefficient	22-h samples mean (standard error of mean)	4-, 6-h samples mean (standard error of mean)	Difference of means (standard error of difference)	Means differ with >95% probability[a]
1. Comparison of 22-h denuder difference (DD) HNO_3 samples to daily average of 4-, 6-h DD samples	7	0.99	145 (36)	140 (38)	5 (6)	No
2. Comparison of 22-h tandem filter (TF) HNO_3 samples to daily average of 4-, 6-h TF samples	6	0.99	207 (62)	170 (54)	37 (8)	Yes
3. Comparison of 22-h tandem filter (TF) NH_3 samples to daily average of 4-, 6-h TF samples	7	0.90	344 (52)	270 (45)	74 (23)	Yes

Note (a) by paired t-test

cally higher than the 22-h average of simultaneous 4- and 6-h HNO_3 and NH_3 values obtained by identical sampling systems (see Table 1). Over the seven day period for which this comparison was made, the mean HNO_3 concentration measured by continuous 22-h tandem filter sampling was 207 neq/m^3, while the average of the short-term 4- and 6-h sampling results was 170 neq/m^3, a difference relative to the average of the daily means of 20 percent. For NH_3, the 7-day average of continuous 22-h samples was 344 neq/m^3, versus 270 neq/m^3 for the mean of the daily short-term 4- and 6-h samples, a difference relative to the average of the daily means of 24 percent.

Appel et al. (1980, 1981) and Forrest et al. (1980) present data which suggest that these differences are, in part, due to the vaporization of NH_4NO_3 aerosol collected on the Teflon® prefilter used in the tandem filter system. Vaporization of NH_4NO_3 aerosol would result in a positive artifact for HNO_3 and NH_3 and a negative artifact for aerosol NO_3^- and NH_4^+. This loss of aerosol nitrate from Teflon filters was confirmed using other observations made during this study. Fine particle NO_3^- collected on nylon filters (sampler line B1, Figure 3) was compared to fine particle NO_3^- collected on a parallel Teflon® filter (sampler line C, Figure 3). On the average, for 4- and 6-h samples, the fine particle NO_3^- collected on the Teflon® filter was 57 percent of that collected on the nylon filter. For 22-h samples the same ratio was 41 percent.

Results from the basinwide monitoring network are shown in Tables 2-4. HNO_3 concentrations (Table 2) throughout the Los Angeles area began the time period of interest at low levels with an average concentration of 30.6 neq/m^3 or lower. Nitric acid values peaked at all sampling sites on September 14, followed by a decline over the next several days to very low HNO_3 concentrations. This pattern was similar to that experienced at Claremont. HNO_3 concentrations at Claremont were either the highest or second highest observed throughout the network on each day sam-

TABLE 2

HNO_3

BASINWIDE CONCENTRATIONS

(neq/m^3)

CITY	Sept 10	Sept 12	Sept 14	Sept 16	Sept 18
Burbank	30.6	179	326	132	45.2
Downtown LA	30.6	255	340	111	30.6
Lennox	–	111	176	45.2	24.2
Long Beach	9.7	–	234	41.9	17.7
Anaheim	24.2	158	252	66.1	17.7
Rubidoux	–	51.6	102	59.7	14.5
Claremont	–	202	424	111	30.7

pled, and the basinwide 24-h average peak HNO_3 value of 424 neq/m^3 was observed at Claremont on September 14. These results confirm that Claremont was a wise choice for the main site of the Nitrogen Species Comparison Study. In contrast, choice of the alternate site at Riverside, near Rubidoux, would have yielded the lowest HNO_3 concentrations observed basinwide. HNO_3 concentrations at Rubidoux reached only 102 neq/m^3 on September 14, which is below the detection limits of some of the methods being tested by investigators at the NSC. As can be seen in Table 3, total inorganic nitrate concentrations (HNO_3+TA NO_3^-) at Claremont and at Rubidoux were approximately equal. At Claremont, 68% of the total nitrate was present as HNO_3 while at Rubidoux only 16% of the total nitrate was present as HNO_3. As seen in Table 4, NH_3 concentrations observed at Rubidoux were nearly a factor of four to a factor of twenty times higher than NH_3 values observed at the other basinwide monitoring sites. This finding is consistent with the spatial distribution of ammonia emissions presented by Russell et al. (1983) which shows a large spike in the NH_3 emission inventory due to dairy farming operations located just to the west of Rubidoux. These observations (i.e., high NH_3, and a low ratio of HNO_3 to total inorganic nitrate) suggest that conversion of HNO_3 to aerosol nitrate was the probable cause of the low HNO_3 values characteristic of the Rubidoux (Riverside) area.

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TABLE 3
TOTAL INORGANIC NITRATE
(HNO_3 + AEROSOL NO_3^-)
BASINWIDE CONCENTRATIONS
(neq/m^3)

CITY	Sept 10	Sept 12	Sept 14	Sept 16	Sept 18
Burbank	105	329	476	519	147
Downtown LA	100	478	511	364	127
Lennox	–	313	289	260	102
Long Beach	51.6	–	440	121	75.8
Anaheim	74.2	292	392	282	79.0
Rubidoux	–	297	636	374	157
Claremont	–	402	622	476	129

TABLE 4

NH_3

BASINWIDE CONCENTRATIONS
(neq/m^3)

CITY	Sept 12	Sept 14	Sept 16	Sept 18
Burbank	250	430	170	160
Downtown LA	460	390	240	260
Lennox	330	230	140	100
Long Beach	–	250	100	160
Anaheim	350	300	110	110
Rubidoux	1880	2250	2000	1810
Claremont	500	290	400	110

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