

THE CHEMISTRY, DISPERSION AND TRANSPORT OF
AIR POLLUTANTS EMITTED FROM
FOSSIL FUEL POWER PLANTS IN CALIFORNIA
CHEMICAL ANALYSIS OF PARTICULATE SAMPLES FOR
SULFATE, NITRATE AND TRACE ELEMENT COMPOSITION
FINAL REPORT

By

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Abstract

This study is intended to assess the formation of sulfate and nitrate in SF₆-labelled power plant plumes emitted to otherwise clean and relatively polluted atmospheres. Results from field monitoring conducted in the vicinity of the Moss Landing power plant (near Monterey), on days when the power plant burned either natural gas or fuel oil were compared to those from sampling the plumes from the Haynes and Edison power plants at Alamitos Bay (near Long Beach). Ground level sampling employed an array of automated sequential particulate samplers, SO₂ and SF₆ monitors. Aerial particulate collection within and adjacent to the plume was also employed.

Particulate nitrate levels in ground level samples at both sites appeared to be independent of the plumes under study. Sulfate concentrations, however, did reveal contributions from the plumes except when sulfate levels were high (e.g. > 30 µg/m³). The sulfate contribution from the Southern California plumes were calculated to be 3-5 µg/m³ at ground level compared to 1.6-2.3 µg/m³ from the Moss Landing plant.

In Southern California, a correlation was found between mid-morning sulfate concentrations and early morning relative humidities. The mathematical equation relating the two follows that predicted for metal ion and ammonia catalyzed oxidation of SO₂ to sulfate in water droplets.

Based on aerial sampling, concentrations of sulfate at varying distances downwind of the stack ranged from 0.9 to 14.9 µg/m³. However the sampling protocol did not permit calculation of plume sulfate levels and, therefore, SO₂ conversion. A procedure is described for calculating SO₂ conversion in the plume which may be of use in future programs.

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I. Introduction

Stationary sources (power plants, refineries and chemical plants) are the principal origins of the sulfate precursor, SO_2 , in urban atmospheres. Results from the ARB-sponsored Aerosol Characterization Study suggest that > 30% of the SO_2 from all sources can be converted to particulate matter before leaving the South Coast Basin. The percentage conversion is substantially lower in areas such as St. Louis where photochemical smog is of lesser importance. Thus, the conversion efficiency of SO_2 may be markedly dependent on the presence of other pollutants as well as atmospheric conditions. Furthermore, the present fuel shortage will necessitate, in some cases, the use of fuels richer in sulfur for power generation. This may lead to hazardous concentrations of particulate sulfate in populated areas.

Accordingly a study was performed to determine the efficiency of formation of particulate sulfate from important stationary combustion sources of SO_2 as related to the nature of the fuel and the concentration of other pollutants. The program was conducted jointly by Rockwell International Science Center (RI), the Air and Industrial Hygiene Laboratory (AIHL), Meteorology Research Inc. (MRI), and the California Institute of Technology (CIT).

Previous monitoring of plumes from stationary combustion sources suggested that ground level monitoring alone was not as effective as a combination of ground and aerial monitoring; a plume was typically observed to remain aloft for a number of miles before reaching ground level. Therefore, a coordinated study combining meteorological data collection and forecasting, and a deliberately added plume tracer (SF_6) together with aerial monitoring and a network of ground level sampling stations was employed. Particulate matter sample collection was done primarily at the ground level sites but a limited number of samples were collected from the elevated plumes by the MRI aircraft.

This study was intended to include two important source types: one in which the effluent was mixed with ambient pollutants already present in relatively high concentration and one in which the source effluent remains relatively free of other pollutants. The first type, located at Alamitos Bay on the Pacific coast south of Long Beach, was represented by the Southern California Edison and Haynes power plants as the principal SO_2 sources. On the sampling days chosen, however, smog levels remained light along the trajectory of the Haynes - Edison power plant plume. Thus greatly enhanced oxidation of nitrogen and sulfur oxides due to photochemical oxidant could not be expected. Pollutant monitoring data from local APCD stations during the present study are included in this report.

The Edison and Haynes plants are sufficiently close together to cause relatively rapid merging of their plumes. Thus, while SF_6 labelling was done on one plant or the other for a given sampling day, the plume related materials (e.g., SO_2 , sulfate, vanadium) reflect both plants' contributions of primary pollutants.

The second source type is represented by the Moss Landing Pacific Gas and Electric power plant near Monterey. The effluent from Moss Landing during the summer months is typically transported inland during daylight hours, especially southeast to Salinas and Gonzales. Transport eastward toward Hollister is also possible. In either case, photochemical smog concentrations were light. Again, monitoring data from local APCD stations will be cited.

AIHL was funded to assist in the sampling by providing sampling media, log books etc., and to perform chemical analyses for samples at both Moss Landing and the Los Angeles Basin sources. Operation of samplers was the responsibility of RI, CIT and MRI.

The ground level sampling units consisted of an array of 10 sampling stations operating in conjunction with MRI's monitoring aircraft. The 10 ground level sampling sites were selected by RI. The objective in situating these sampling stations was to obtain two linear arrays of 5 each. Ideally, each array would be located at different distances downwind of the stack such that the plume contents aged 1-2 hours between sampling sets.

Each ground level station used sequential filter samplers, detailed in RI's Final Report,¹ to collect particulate matter. Filter changes were made automatically every two hours during daylight hours to obtain diurnal patterns in total particulate mass and chemical composition. Simultaneously, a Meloy sulfur analyzer obtained continuous data on total gas phase sulfur and samples were collected on an hourly basis for SF₆ analysis. Details of the SF₆ technique and tabulated data are given in CIT's Final Report.² The MRI airplane-mounted filters and pollutant gas analyzers sampled the plume close to the source and at two or more distances further downwind.

A portion of each ground level filter sample was analyzed at AIHL for water soluble sulfate and nitrate by colorimetric methods. Another section from each filter was analyzed by alpha particle induced x-ray fluorescence (AIXE) by the Crocker Nuclear Laboratory, University of California (Davis) for about 15 elements. In addition to sulfur, vanadium and nickel were of the greatest interest since they can serve as a natural tracer for fuel oil combustion. The aerial filter samples were analyzed at AIHL for water soluble sulfur using a flash vaporization-flame photometric detector technique.

At Moss Landing a total of 3 days of sampling was done including 2 days in which the plant burned fuel oil and, for comparison, one day with natural gas. The latter fuel contains negligible quantities of sulfur and ash. In the South Coast Basin fuel oil or a combination of fuel oil and natural gas was used for each of seven days of sampling. The sulfur ash and vanadium contents of the fuel oils used for each sampling day are given in Table 1.

Based in part on the CIT SF₆ results, two Moss Landing and two Southern California episodes were selected for detailed evaluation. These include

Table 1 AIHL Analyses of Sulfur, Vanadium and Fly Ash Contents of
Fuel Oils Burned During Study

<u>Date</u>	<u>Power Plant</u>	<u>% S (w/w)</u>	<u>% Ash (w/w)</u>	<u>V, ppm (w)</u>	<u>V as % of Ash</u>
9-10-74 ^a	Moss Landing	0.35 ± .03	0.027 ± .002	13.6 ± 3.4	5.0
9-11-74 ^a	Moss Landing	0.40 ± .006	0.016 ± .001	13.4 ± 1.3	8.4
9-12-74	Moss Landing	Burned natural gas			
10-1-74 ^b	Haynes	0.45 ± .01	0.0075 ± .0007	9.1 ± .5	12
10-4-74	Haynes	0.45	0.008	11.3	15
10-11-74 ^b	Haynes	0.46 ± .01	0.0075 ± .0007	10.7	14
10-17-74 ^b	Haynes	0.455 ± .005	0.0075 ± .002	10.6 ± 1.1	14
10-25-74	Edison	0.44	0.007	14.5	21
10-30-74	Edison	0.45	0.006	13.4	22
11-7-74	Edison	0.45	0.012	20.5	17

a. Analyses shown for this date are means for 6 samples

b. Separate samples taken for each of two boiler units operating on sampling day. Values shown are means for the two units.

September 11 and 12, 1974 (Moss Landing) and October 1 and November 7, 1974 (Haynes-Edison). The Moss Landing episodes include one with natural gas and one with oil as the power plant fuel. The September 10th Moss Landing episode was notable for the low level of plume pollutants reaching ground level (97% of all SF₆ samples < 10 ppt). Accordingly it was rejected from further scrutiny. The Southern California episodes generally revealed plume impact zones to the north or northeast of the stacks and away from a majority of the particulate samplers. In only one case (November 7, 1974) was evidence found for plume touch-down in the Santa Ana Canyon (where many of the particulate samplers were located).²⁾* Accordingly November 7th was considered an important episode for evaluation. In addition the October 1st episode was selected because of the high sulfate levels found on this day and because it appeared typical of most of the Southern California episodes in regards to the locations for plume touch-down.

Although only selected data are discussed in this report, all of the analytical results are included in an accompanying data tape and listing.

*A recent re-analysis of these data¹⁾ suggests that even in this case plume touchdown in the Santa Ana Canyon is insignificant.

II. Ground Level Studies

Approximately 607 filter samples were collected including 70 filters from the 10-4-74 run when there was no labelled plume and 112 filters initially lacking flow data. The latter problem was corrected by joint Rockwell-AIHL efforts. Rockwell provided estimates of the flow data based upon the grand mean flow rates. For all filters a grand mean of 3.4 ± 0.25 cfm (C.V. = 7.2%) was calculated.

Sampling stations were coded for use in a filter coding system detailed in Appendix A. A separate station coding system was used by Prof. F. Shair and co-workers in connection with SF₆ sampling. Table 2 lists the equivalent station codes in the two systems. Only the AIHL-RI filter coding system will be used in this report.

Figures 1 and 2 include maps of the two sampling areas indicating placement of the filter sampling sites.

A. Data Analysis - Moss Landing Sites

Selected gaseous pollutant levels at local Air Pollution Control District stations are shown in Table 3 for Salinas, Gonzales and Hollister. The maximum hourly average oxidant level reported was 0.08 ppm at Hollister. Along the dominant plume trajectory through Salinas and Gonzales, oxidant 1 hour maxima ranged from 0.04-.06 ppm. Thus we infer that photochemical smog levels were indeed low in this area.

Figures 3-5 include comparisons of sulfate distributions with SF₆ values for two Moss Landing episodes. Wet chemical sulfate values are shown with three-hour average isopleths for SF₆ as calculated by Dr. Shair and co-workers.* The latter are expressed as a fraction of the SF₆ concentration in the stack. Since SF₆ is unreactive this technique provides a means of locating the plume and measuring concentration decreases due only to dilution. For comparison with CIT's three hour average SF₆ isopleths three hour average values were approximated** from two 2-hour sulfate values. The plume was considered to lie within the 10⁻⁶ SF₆ isopleth.

*As stated in Reference 2, "Solid lines indicate contours well supported by the data sampling network. The dashed lines indicate approximate contours either outside the sampling network or at some distance from any sampling point."

**
$$\frac{(SO_4^{=})_A + \frac{1}{2}(SO_4^{=})_B}{1.5} = 3 \text{ hour average including two hours from period A and one hour from period B. Where A and B are two hour sampling periods.}$$

Table 2 EQUIVALENT DESIGNATIONS FOR SAMPLING SITES USED BY ROCKWELL-AIHL FOR PARTICLE SAMPLING AND BY CIT FOR SF₆ SAMPLING

<u>Site</u>	<u>RI-AIHL Number</u>	<u>CIT Number</u>
	0	3
	1	5
	2	4
	3	2
	4	6
Moss Landing	5	17
	6	16
	7	15
	8	14
	9	18
So. California	0	4
	1	2
	2	3
	3	8
	4	7
	N4 ^a	5
	5	9
	N5 ^a	17
	6	14
	7	19
N7 ^a	16	
8	20	
9	21	

a. For Episodes on October 25, 30 and November 7, AIHL stations 4, 5, and 7 were moved to different CIT sites as indicated.

TABLE 3

Maximum Hourly Average Concentration of Pollutants at
 Selected ARB Stations During Sampling Periods at
 Moss Landing (September 1974), ppm

Place and Contaminant	Day of Month		
	10	11	12
Salinas-Alisal			
oxidant	.04	.05	.05
oxides of nitrogen	.06	.07	.04
Gonzales-High School			
oxidant	.06	.05	.06
Hollister			
oxidant	.05	.08	.05
oxides of nitrogen	.06	.04	.01

*Abstracted from "California Air Quality Data, California Air Resources Board", Vol. VI, without any corrections to ozone (or oxidant) values.

Figure 1. LOCATION OF SEQUENTIAL FILTER SAMPLERS, BY NUMBER, IN THE MOSS LANDING-SALINAS AREA.

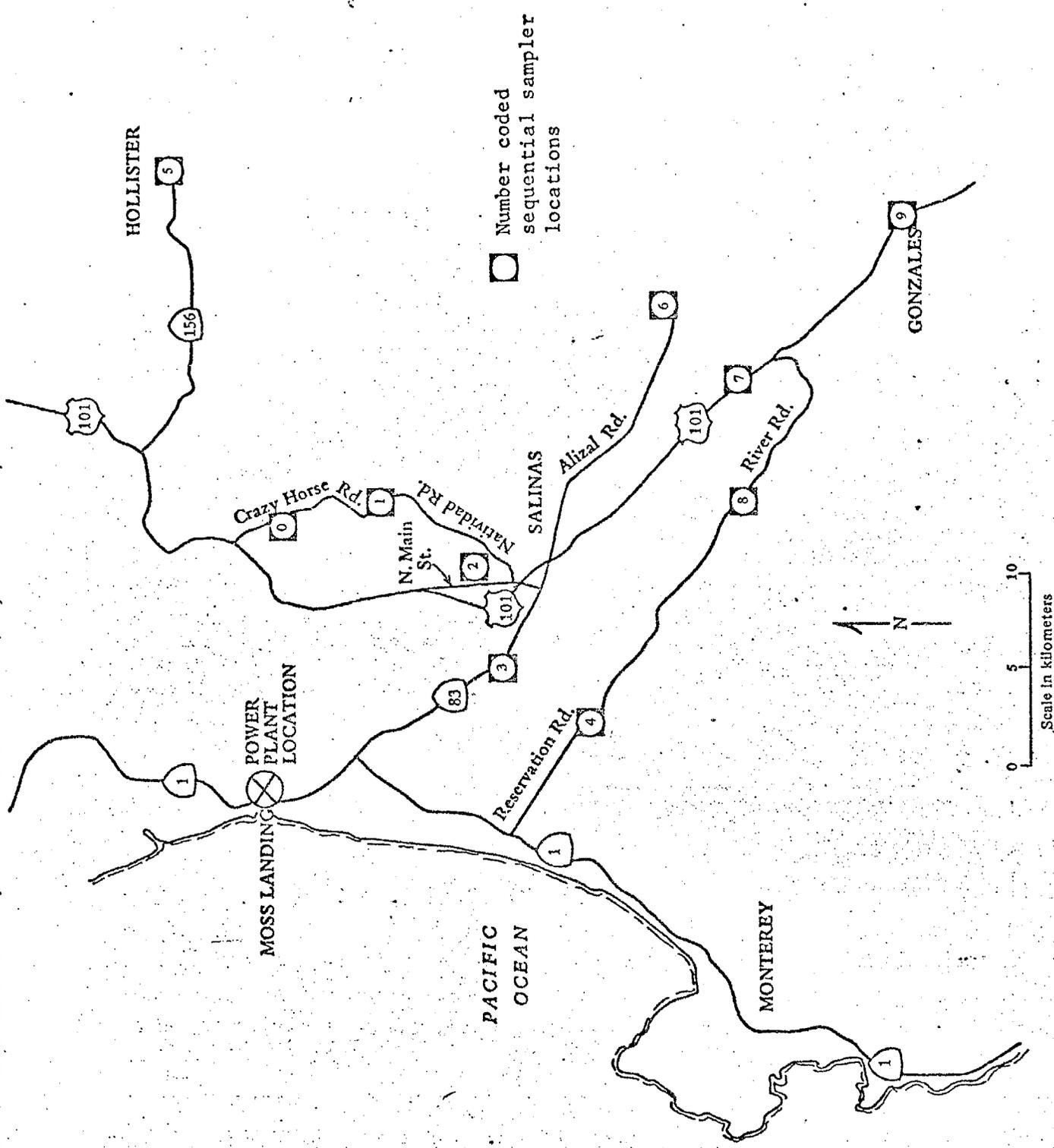


Figure 2. LOCATION OF SEQUENTIAL FILTER SAMPLERS, BY NUMBER, IN THE LOS ANGELES SOUTH COAST BASIN.

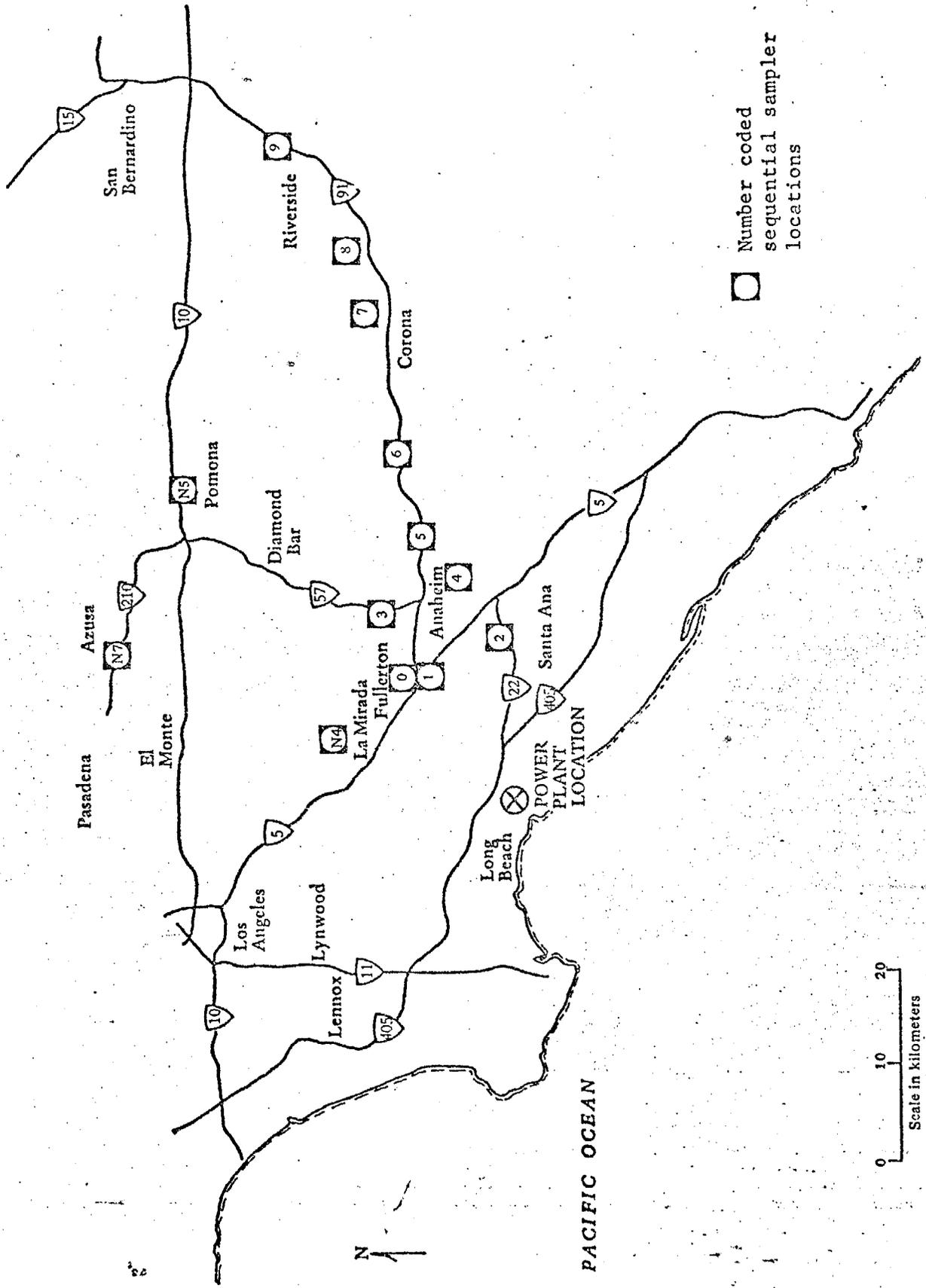
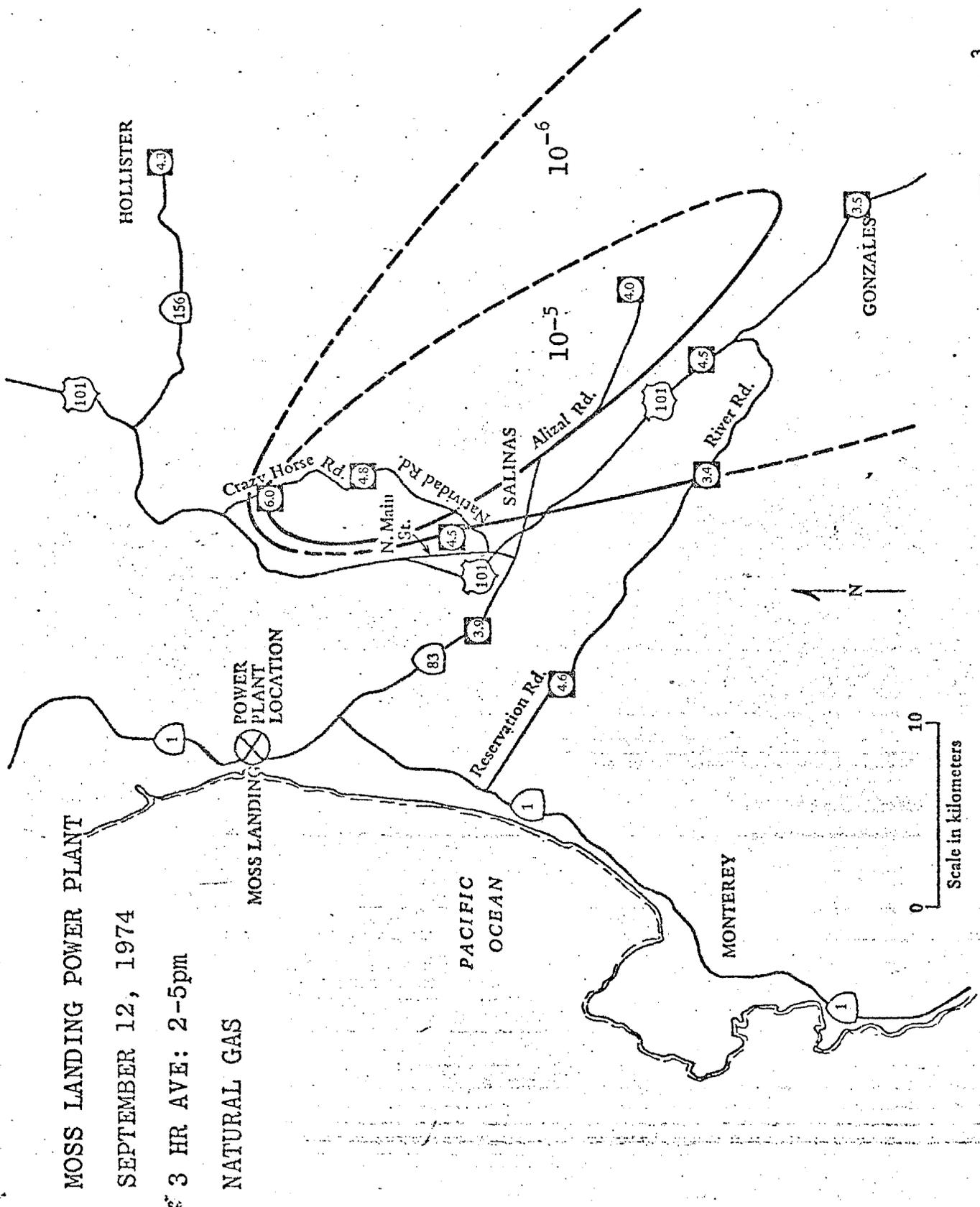


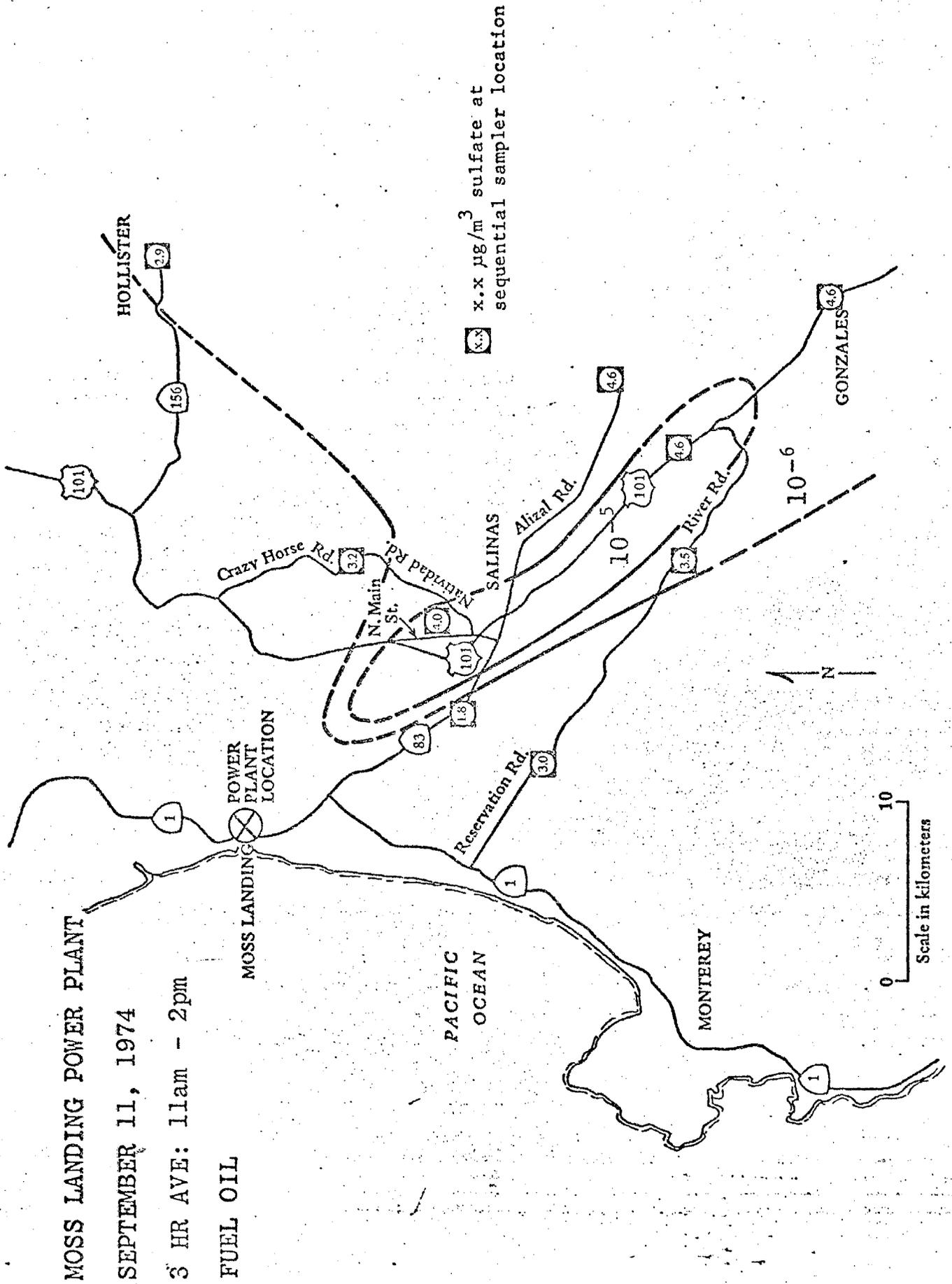
Figure 3. GROUND LEVEL DISTRIBUTION OF SF₆* AND CORRESPONDING SULFATE LEVELS.



□ x.x μg/m³ sulfate at sequential sampler location

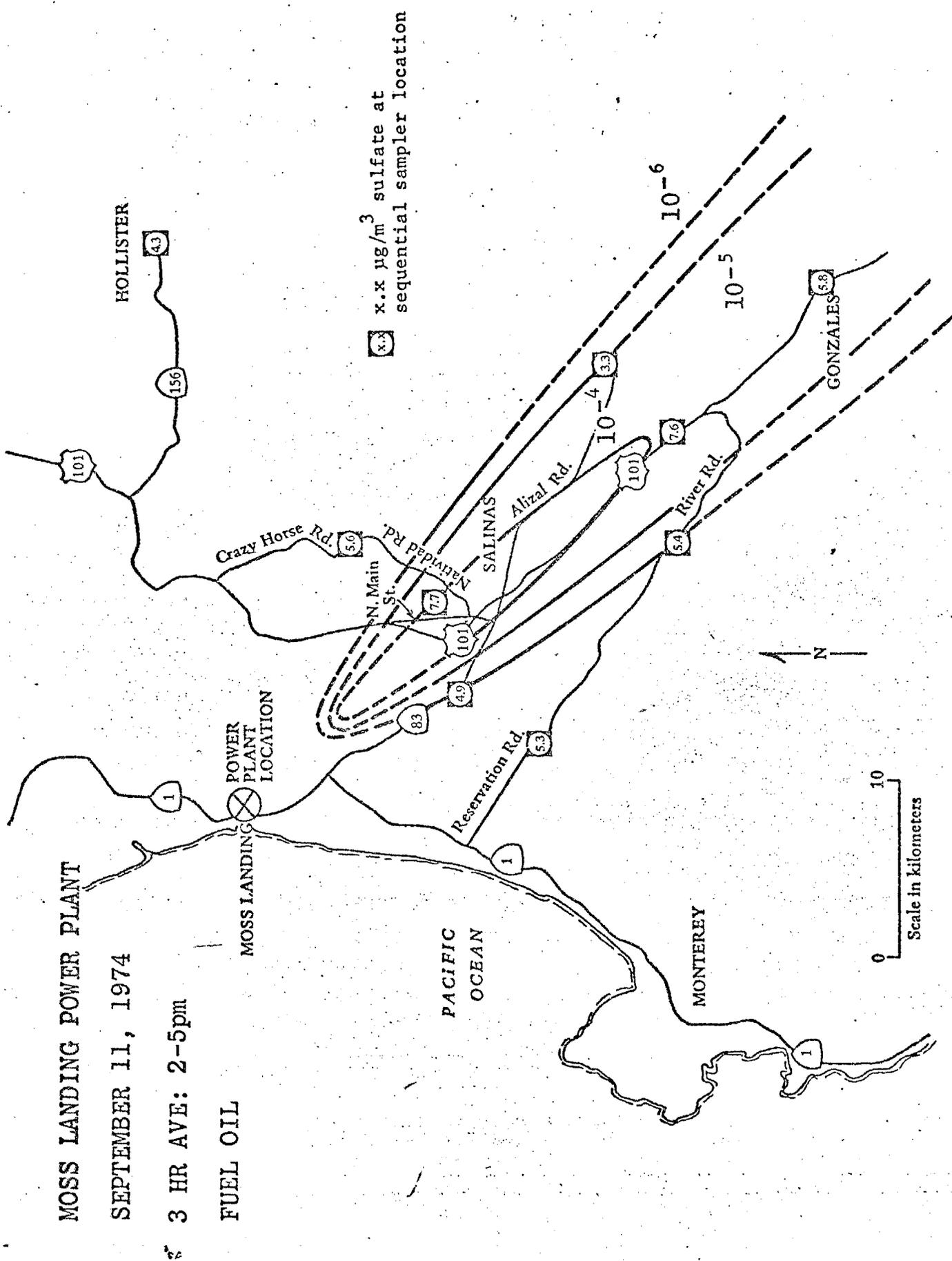
* SF₆ isopleth levels expressed as fraction of original stack concentration

Figure 4. GROUND LEVEL DISTRIBUTION OF SF₆* AND CORRESPONDING SULFATE LEVELS.



* SF₆ isopleth levels expressed as fraction of original stack concentration
 Dashed lines indicate approximate contours

Figure 5. GROUND LEVEL DISTRIBUTION OF SF₆* AND CORRESPONDING SULFATE LEVELS.



* SF₆ isopleth levels expressed as fraction of original stack concentration
 Dashed lines indicate approximate contours

Considering first Figure 3 for Moss Landing on a day when the power plant was burning natural gas, ground level sulfate values ranged from 3.4 to 6.0 $\mu\text{g}/\text{m}^3$. There was no significant difference* between sulfate concentrations within and outside the plume at ground levels, as expected from the absence of significant sulfur in the power plant fuel.

These values can be used to establish a baseline for comparison with days when fuel oil was burned and plume touchdown occurred. September 11 was such a day. Figures 4 and 5 illustrate the SF_6 - $\text{SO}_4^{=}$ correspondence for two time periods. In the midday period, with moderate SF_6 ground level concentrations, $\text{SO}_4^{=}$ values ranged from 2.9-4.6 $\mu\text{g}/\text{m}^3$. Comparing the mean $\text{SO}_4^{=}$ level for the area of plume touchdown defined by the 10^{-6} isopleth, $4.3 \pm .5 \mu\text{g}/\text{m}^3$, to that outside the plume, $2.7 \pm .8$, suggests a $1.6 \mu\text{g}/\text{m}^3$ $\text{SO}_4^{=}$ enrichment due to the plume.** In the afternoon, ground level $\text{SO}_4^{=}$ ranged from 3.3 to 7.7 $\mu\text{g}/\text{m}^3$ (mean value $5.5 \pm 1.4 \mu\text{g}/\text{m}^3$). The highest $\text{SO}_4^{=}$ levels 7.6 and 7.7 $\mu\text{g}/\text{m}^3$ correspond to the center line of the plume at ground level, as defined by the SF_6 tracer. A comparison of mean $\text{SO}_4^{=}$ levels inside (7.04 ± 1.1) and outside ($4.8 \pm 0.9 \mu\text{g}/\text{m}^3$) the plume indicates that about $2.2 \mu\text{g}/\text{m}^3$ can be ascribed to the plume at ground level.***

A more detailed perspective on the origin of particulate pollutants at Moss Landing may be obtained from figures 6 to 12. They compare the diurnal variations of SF_6 , sulfate and nitrate at the different sampling sites. We note that for September 11, 1974 at all Moss Landing sites, nitrate concentrations peak in the morning and those for sulfate, in the afternoon regardless of the diurnal variations of SF_6 . The high diurnal maximum SF_6 values occurred at stations 2 and 7 (> 250 ppt) and station 9 (~ 100 ppt). At these, as well as the other sites, diurnal variations for nitrate and SF_6 showed no similarity on this day. However, at these 3 sites sulfate and SF_6 , while not tracking precisely, did show similar variations. Comparing the $\text{SO}_4^{=}$ levels during the SF_6 peak period at sites 2, 7 and 9 with the $\text{SO}_4^{=}$ levels for the remaining sites at this time period indicates about $2.3 \mu\text{g}/\text{m}^3$ $\text{SO}_4^{=}$ ascribable to the Moss Landing Plant. This is consistent with the 1.6 and $2.2 \mu\text{g}/\text{m}^3$ estimates calculated above by different techniques.

B. Data Analysis - Southern California Sites

1. The Relation between Sulfate, Oxidant and Meteorological Variables

Sampling in Southern California was done on 7 days in October - November of 1974. Table 4 lists maximum hourly average concentra-

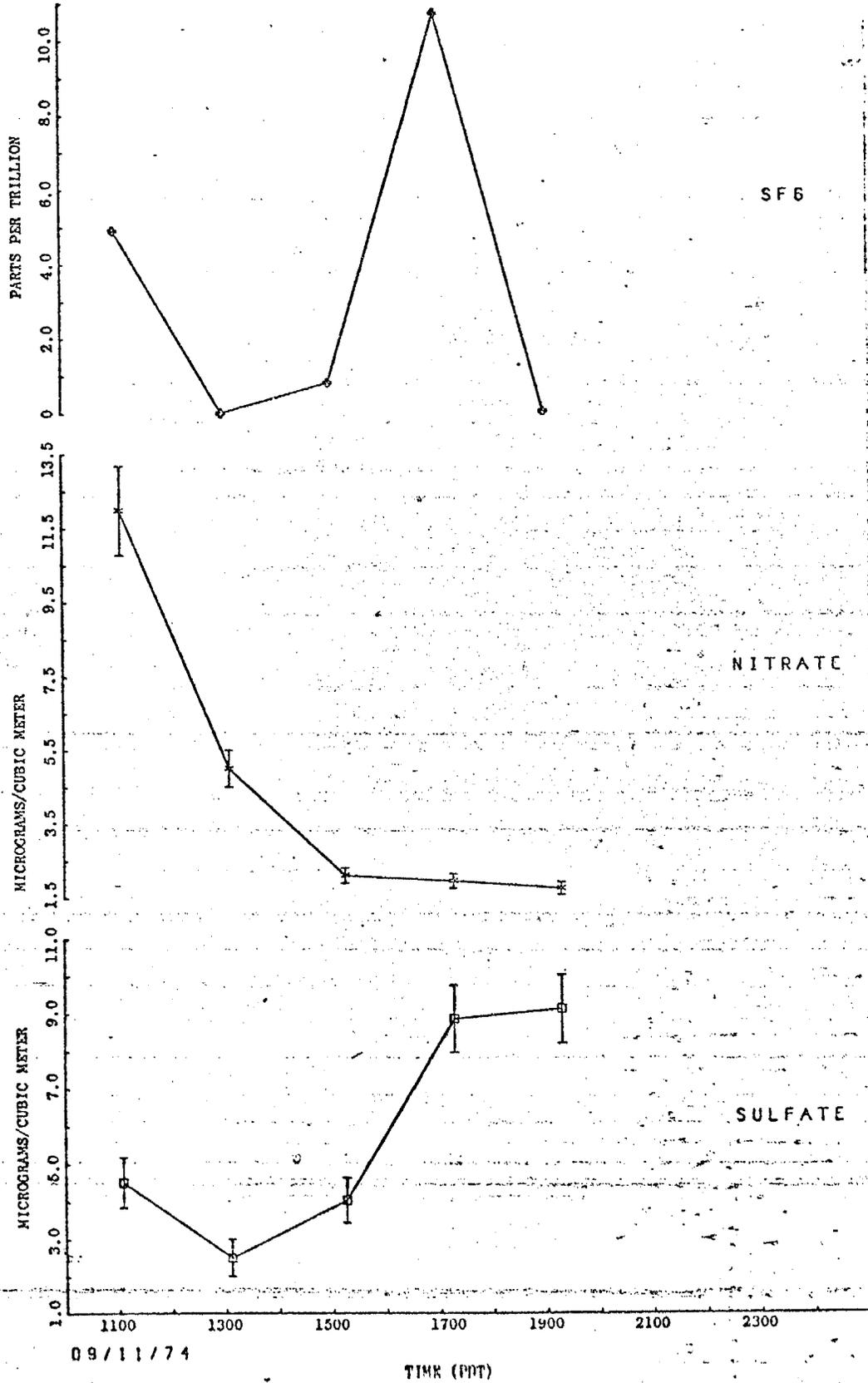
*Wilcoxon two sample rank test $\alpha = 0.54$ (not significantly different at 95% level).

**Wilcoxon two sample rank test $\alpha = .003$. This indicates the difference in concentrations between inside and outside the plume is > 0 at the 99% confidence level. The 2.9 value at Hollister was not included in calculating the difference of the means.

***Wilcoxon two sample rank test $\alpha \sim 0.0$

Figure 6

DIURNAL PATTERN OF SULFATE, NITRATE, AND SF6
SEPTEMBER 11, 1974
STATION 1
MOSS LANDING (Fuel Oil)



09/11/74

TIME (PDT)

Figure 7

DIURNAL PATTERN OF SULFATE, NITRATE, AND SF6
SEPTEMBER 11, 1974
STATION 2
MOSS LANDING (Fuel Oil)

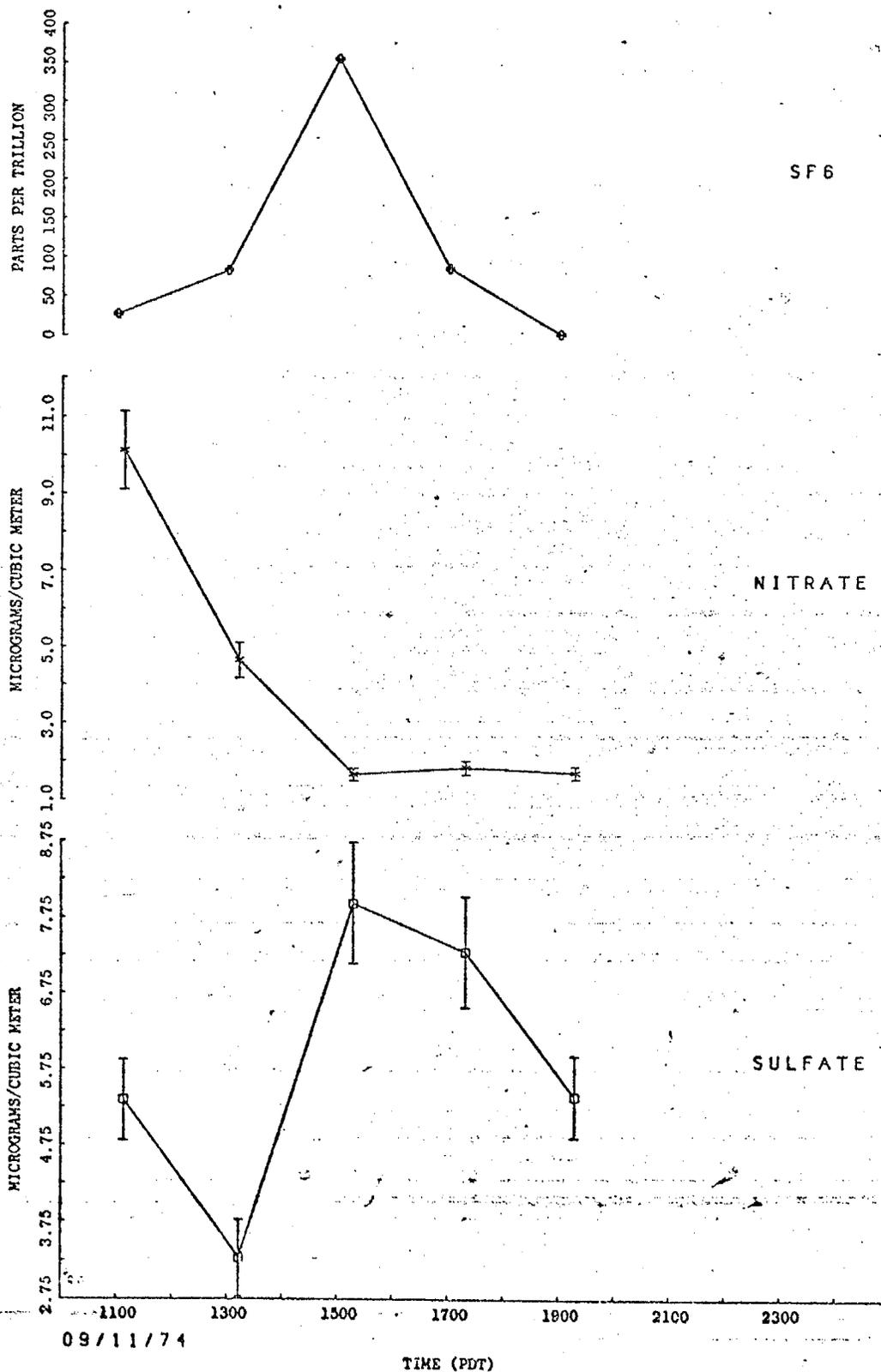


Figure 8

DIURNAL PATTERN OF SULFATE, NITRATE, AND SF6
SEPTEMBER 11, 1974
STATION 3
MOSS LANDING (Fuel Oil)

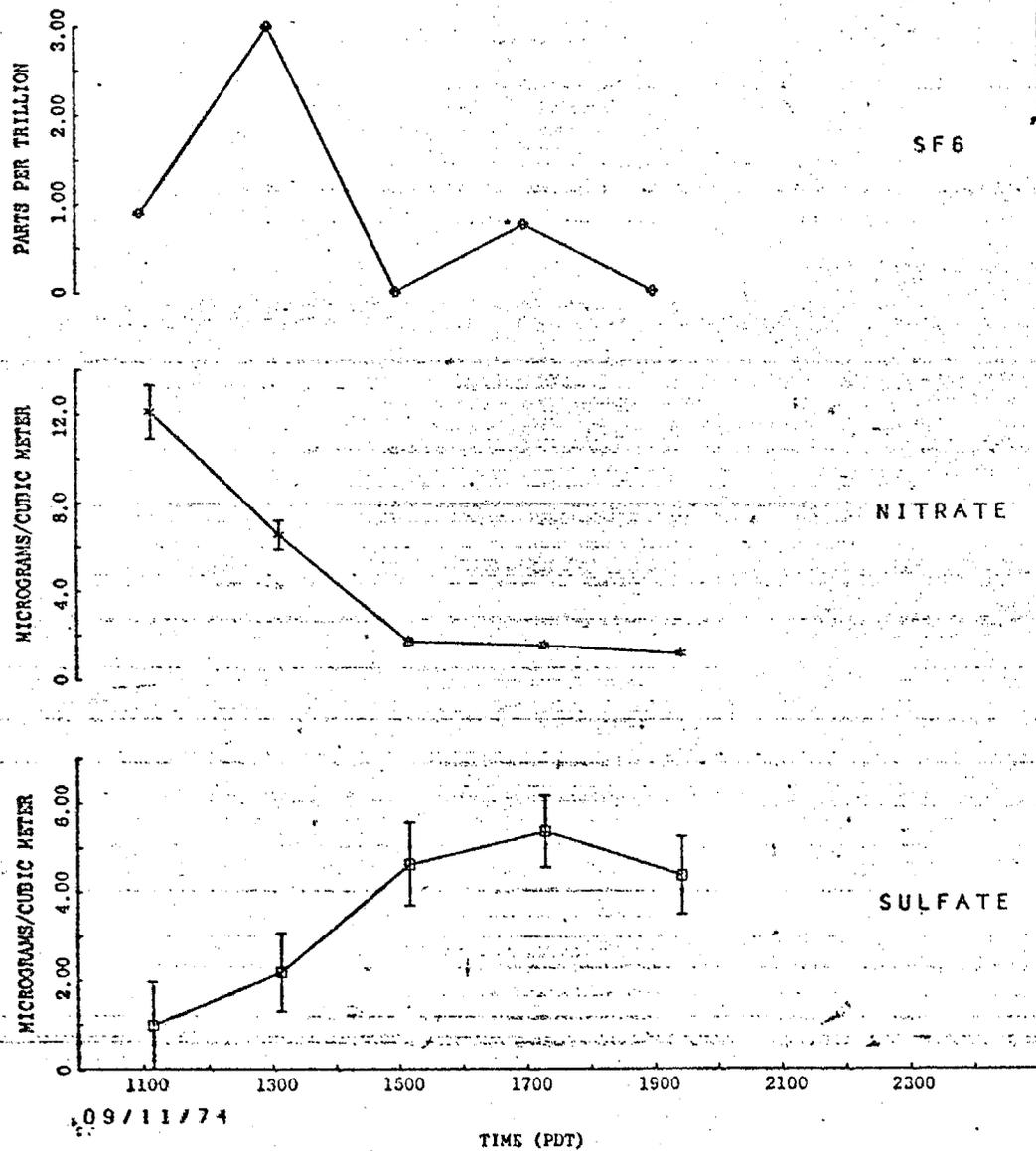


Figure 9

DIURNAL PATTERN OF SULFATE, NITRATE, AND SF6
SEPTEMBER 11, 1974
STATION 4
MOSS LANDING (Fuel Oil)

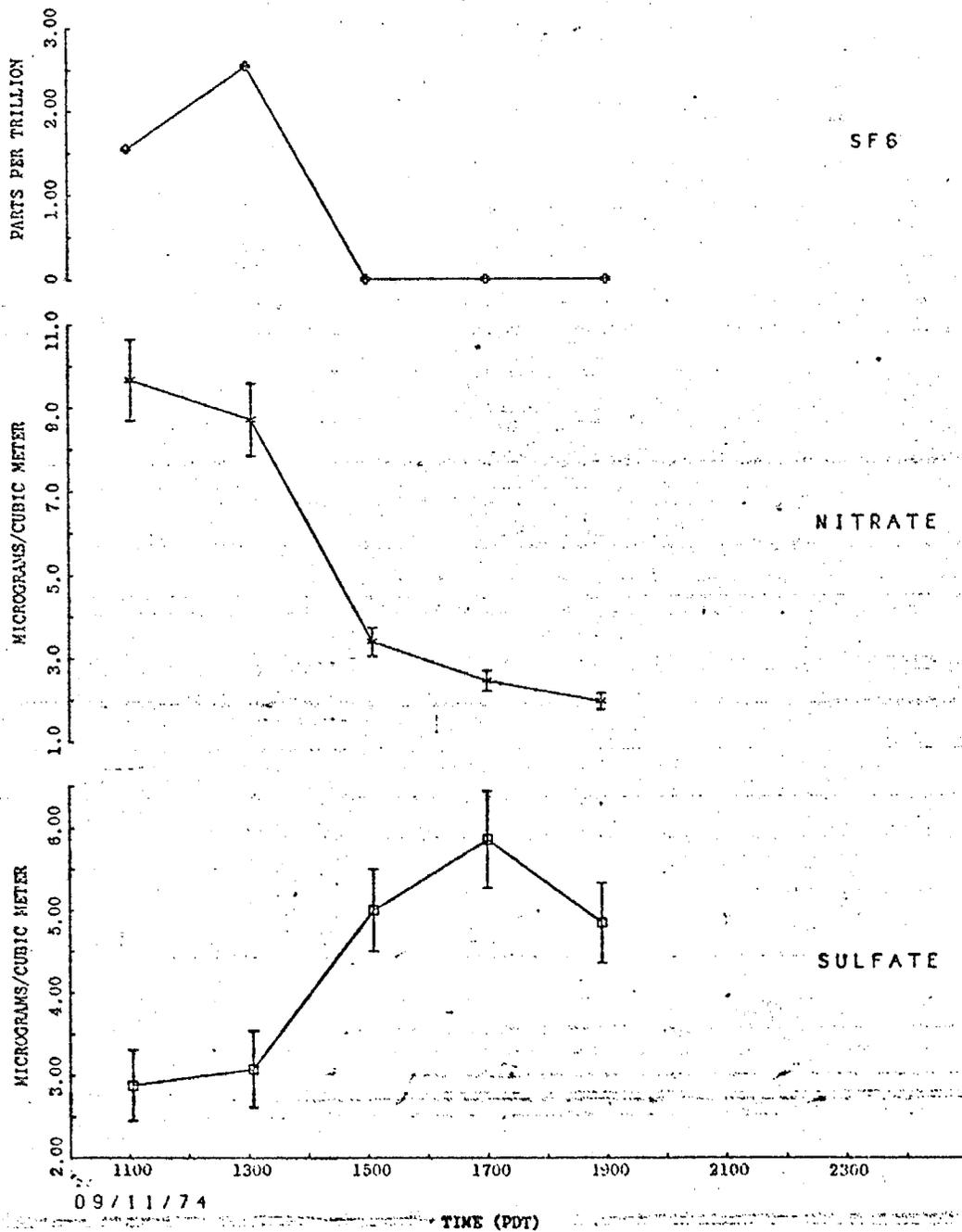


Figure 10

DIURNAL PATTERN OF SULFATE, NITRATE, AND SF6
SEPTEMBER 11, 1974
STATION 5
MOSS LANDING (Fuel Oil)

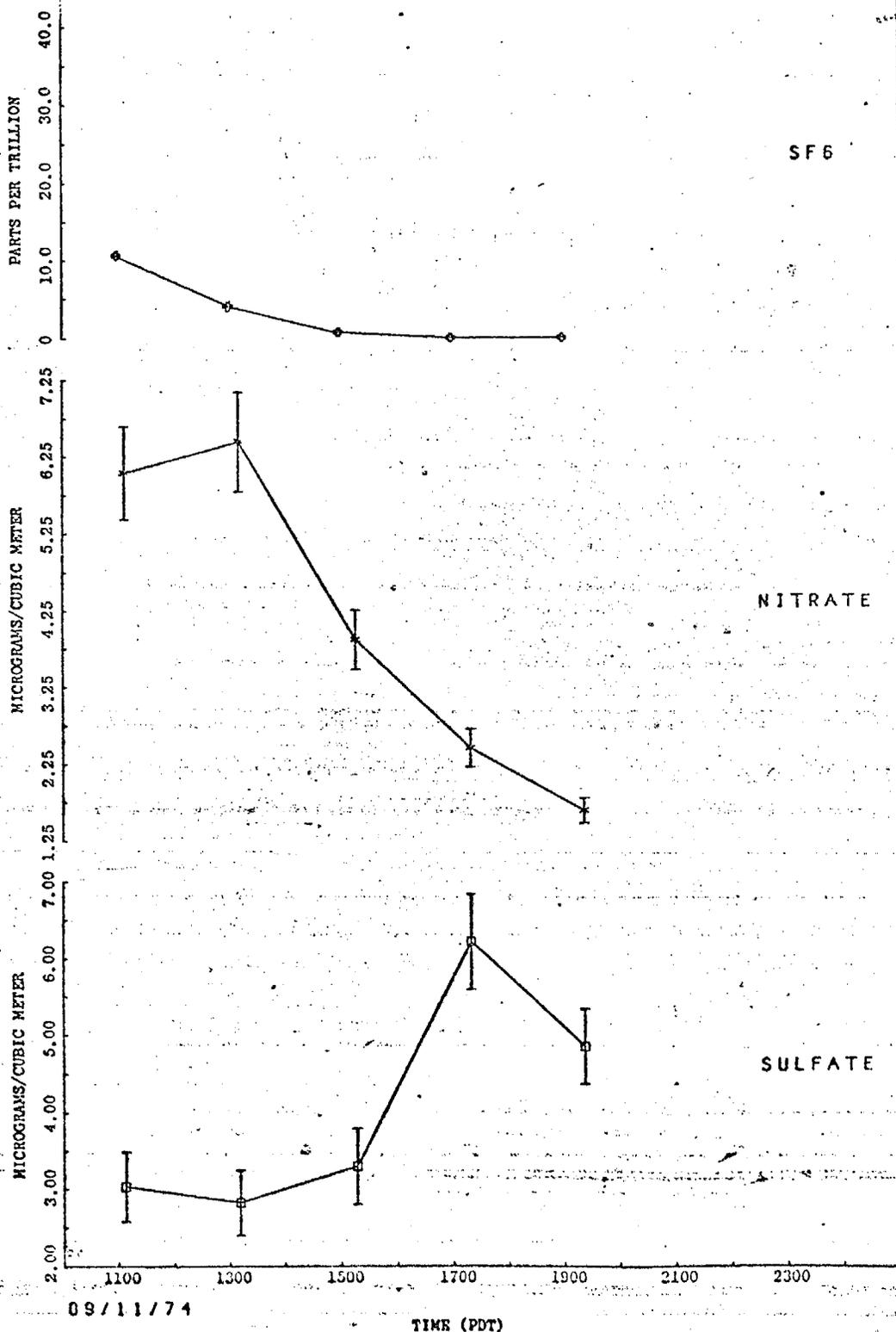


Figure 11
 DIURNAL PATTERN OF SULFATE, NITRATE, AND SF6
 SEPTEMBER 11, 1974
 STATION 7
 MOSS LANDING (Fuel Oil)

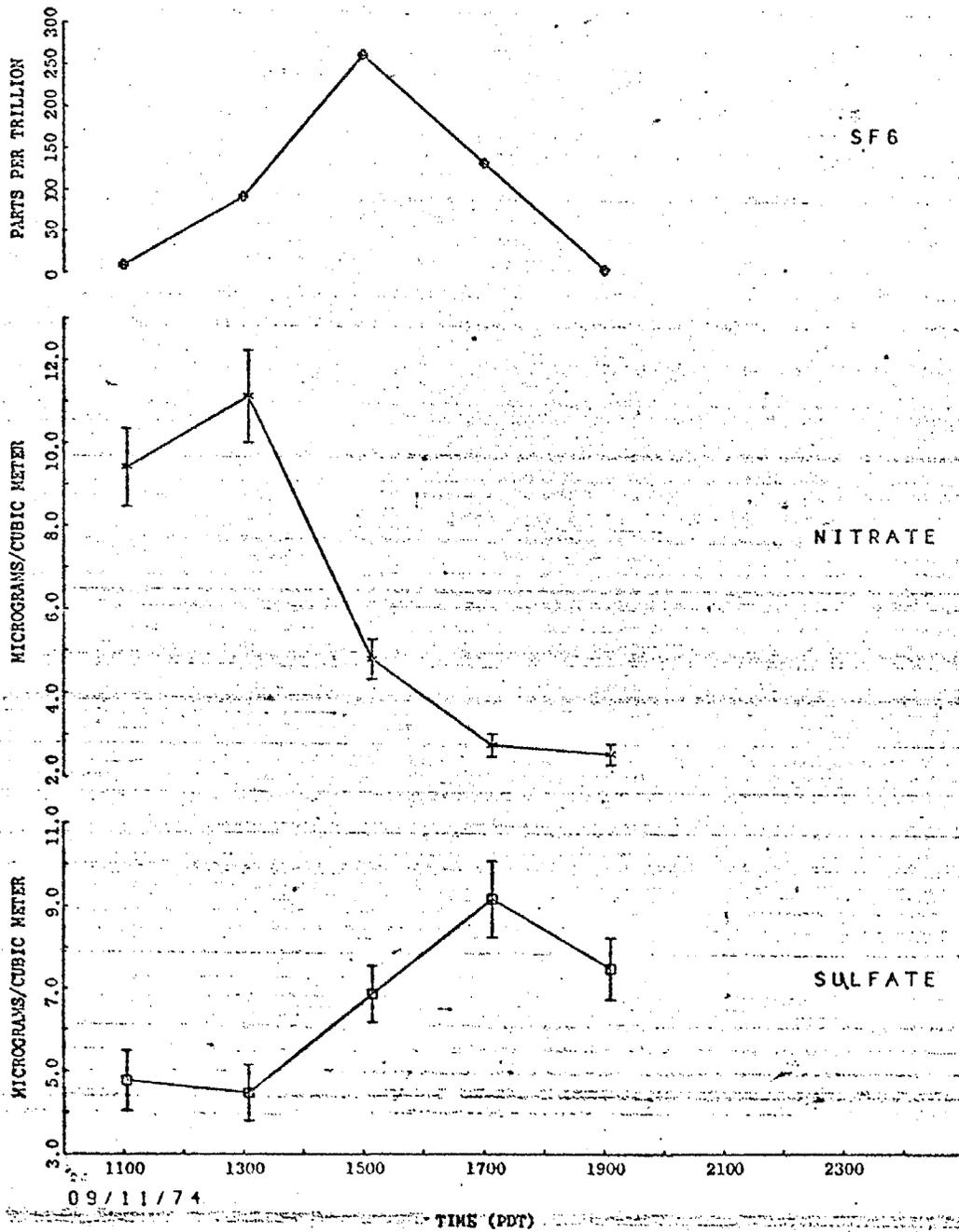
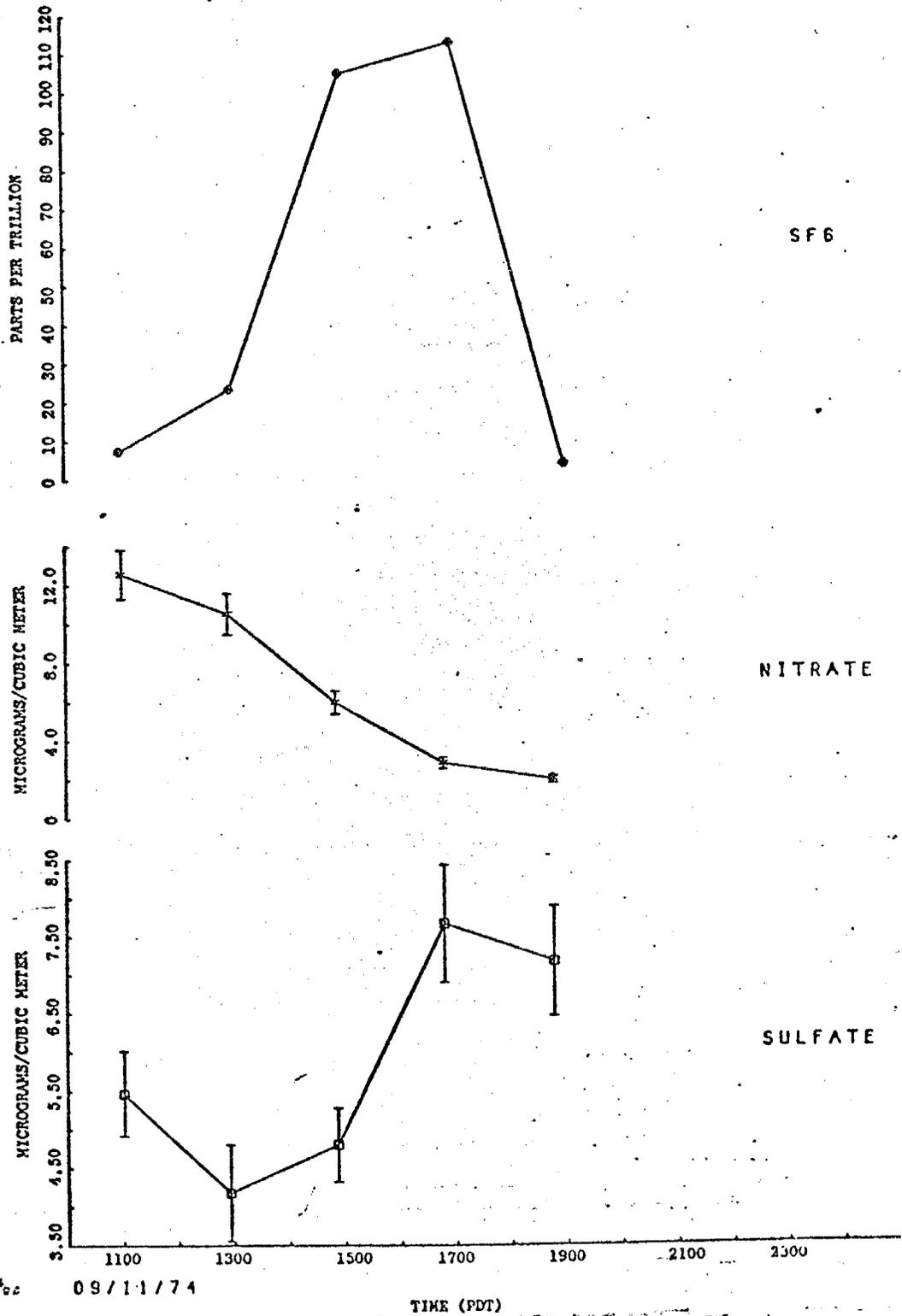


Figure 12

DIURNAL PATTERN OF SULFATE, NITRATE, AND SF6
SEPTEMBER 11, 1974
STATION 9
MOSS LANDING (Fuel Oil)



tions of relevant gaseous pollutants at several LAAPCD and Orange County monitoring stations and inversion-wind speed values for downtown Los Angeles. The monitoring sites selected are those considered most relevant to the impact zones of the Haynes-Edison plume. Data are shown for 3 additional days to provide additional background information. As noted in the table, photochemical smog levels on the sampling days remained generally light, at least over the first 40 km of the plume trajectory. The maximum oxidant value shown for a sampling day is 0.16 ppm at Pomona on October 1st. Thus the potential for plume contents to mix with oxidant was limited.

In spite of the generally low smog levels on the sampling days, two episodes, October 1 and October 11, yielded markedly higher sulfate levels than the others. Sulfate concentrations in the range 30-40 $\mu\text{g}/\text{m}^3$ were observed at most of the ground level sampling sites for these days compared to values $< 10 \mu\text{g}/\text{m}^3$ generally seen on the other sampling days.

October 1st is notable in that it follows two successive days of moderate smog. Furthermore a calculated inversion height of 2100-2200 feet at downtown Los Angeles (DOLA) persisted for the September 29 - October 1st period. October 11th does not, however, follow a day of elevated smog levels and the calculated maximum inversion height is substantially higher (3300 feet). Based on these observations an additional parameter was sought to rationalize the high sulfate levels on these two days.

The oxidation of SO_2 to sulfate can occur much more rapidly in aqueous phase than by strictly gas phase mechanisms.³ In aqueous phase a number of soluble metal salts have been shown to catalyze the oxidation. This suggests that relative humidity should be an important parameter influencing sulfate formation.

Indeed, J. Freiberg reported⁴ a rate expression for the Fe^{+3} catalyzed oxidation of SO_2 to sulfate:

$$\text{Rate of } \text{SO}_2 \text{ disappearance} = \frac{\text{constant}}{(1-\text{R.H.})^3} (\text{SO}_2)^2 (\text{Fe}^{+3})(\text{NH}_3)^3$$

A change from 80 to 90% relative humidity would be expected to increase the sulfate formation rate by a factor of 8. Accordingly in addition to the pollution data given in Table 4, relative humidity values at hourly intervals were obtained for Long Beach Airport. These values, compiled in Table 5, do suggest a correlation between early morning high relative humidity and high sulfate levels; the periods 9/29-10/1/74 and 10/10-10/11/74 are the only days in which relative humidities exceeded 85%.

TABLE 4

Meteorological Data and Maximum Hourly Average Concentrations of
Pollutants at Selected ARB Stations During Sampling Periods at
Haynes-Edison Power Plants (September - October - November, 1974) ppm^a

Place and Contaminant	Day of Month									
	9/29 ^b	9/30 ^b	10/1	10/4	10/10 ^b	10/11	10/17	10/25	10/30	11/7
Los Alamitos										
ozone	.22	.19	.09	.04	.08	.13	.12	.05	.06	.07
sulfur dioxide	.10	.07	.14	.02	.05	.03	.01	.03	.07	.01
Anaheim										
oxidant	.20	.18	.05	.03	.06	.07	.09	.03	.02	.02
sulfur dioxide	—	.06	—	.00	.01	.02	.02	.04	.00	.01
oxides of nitrogen	.16	.23	.10	.12	.24	.16	.42	.28	.18	.25
Whittier										
oxidant	.17	.21	.03	.03	.06	.07	.07	.02	.03	.04
sulfur dioxide	.06	.06	.06	.03	.03	.03	.05	.04	.04	.03
oxides of nitrogen	.11	.18	.10	.06	.27	.21	.36	.35	.27	.38
Pomona										
oxidant	.24	.27	.16	.04	.10	.13	.10	.08	.03	.04
sulfur dioxide	.05	.05	.05	.01	.03	.03	.05	.02	.04	.02
oxides of nitrogen	.23	.34	.18	.13	.26	.29	.40	.46	.35	.35
Inversion Ht (Wind Speed) at DOLA ^c	22(3.8)	21(4.3)	22(5.5)	37(4.3)	39(4.0)	33(3.0)	42(4.2)	29(4.3)	99(4.2)	99(3.5)

- a Abstracted from "California Air Quality Data, California Air Resources Board", Vol. VI, without corrections to ozone (or oxidant) values.
- b Sampling of Power Plant Plume not done on this day.
- c Calculated maximum inversion height, hundreds of feet above MSL, based on a 0600 sounding at LAX. Wind speed in mph. Data from "Air Quality and Meteorology", Air Pollution Control District, County of Los Angeles. "99" = > 5,000

Table 5

Hourly Relative Humidity Values at Long Beach Airport.
During the Period September - November 1974

Date:	9/29	9/30	10/1	10/4	10/10	10/11	10/17	10/25	10/30	11/7
Time (pst)										
0600	90	100	87	76	83	89	69	75	66	51
0700	90	100	87	81	86	87	63	72	64	44
0800	90	100	87	81	84	87	46	69	61	42
0900	87	97	81	78	78	81	41	65	62	27
1000	81	81	81	76	76	78	32	61	56	20
1100	76	73	76	70	73	76	27	63	52	17
1200	69	76	73	64	70	73	31	53	52	15
1300	71	64	71	66	68	70	26	48	54	15
1400	64	58	62	66	70	70	23	46	56	15
1500	62	58	64	63	70	68	32	49	58	20
1600	66	69	66	73	68	73	47	49	58	19
1700	76	68	70	76	70	78	60	60	60	22
1800	84	73	78	81	78	78	70	63	60	44
1900	87	84	81	84	84	81	78	56	60	38

Based upon the rate expression given above and the presumption that SO_2 loss is equivalent to $\text{SO}_4^{=}$ formation, this equation predicts a linear relationship between the logs of the sulfate concentration and $\frac{1}{1-\text{RH}}$ with a slope of 3.

This relationship is tested in Figure 13. The relative humidity data are for 0800 hours PDT (at the Long Beach Airport) while the sulfate values are the average of results for sites 0 and 1 for either 0900-1100 or 1000-1200 PDT for all the sampling days.* The correlation coefficient is 0.96 and the slope, 1.9. To our knowledge this is the first demonstration of such a correlation for the South Coast Basin.

2. Contribution of Haynes-Edison Plants to Ground Level Sulfate

As noted previously, the October 1st episode was chosen for detailed evaluation because 1) the sulfate levels were especially high, and 2) the plume impact area was well defined and typical of most of the sampling episodes. In addition the November 7th episode was studied since it was the only episode in which evidence was found for plume impact in the Santa Ana Canyon where many of the particulate samplers were located.²⁾***

Figures 14 and 15 show comparisons of $\text{SO}_4^{=}$ and SF_6 for the Haynes-Edison power plants for the study conducted on October 1, 1974 when the plume touchdown was away from the majority of the particulate samplers. Comparing sites within and outside the plume defined by the 10^{-6} SF_6 isopleth, the mean sulfate values within the plume was $35.6 \pm 4.0 \mu\text{g}/\text{m}^3$ compared to $33.0 \pm 4.3 \mu\text{g}/\text{m}^3$ outside the plume during the midday period and 21.0 ± 4.5 vs. $22.1 \pm 5.5 \mu\text{g}/\text{m}^3$ outside during the afternoon. In neither case was the $\text{SO}_4^{=}$ level within the plume touchdown area significantly different from levels outside.**

Diurnal variations for sulfate and nitrate are compared to that for SF_6 for this October 1st episode in Figures 16 through 21. As in Moss Landing, the diurnal maximum for nitrate occurred in the morning hours. In contrast to Moss Landing, however, the sulfate maximum occurred between 1000 - 1400 hours making its pattern similar to that for nitrate. From the data available, in only one case, Station 0, was the SF_6 concentration maximum for this day

*The presumption is made that early morning sulfate formation near Long Beach under high humidity conditions influences sulfate concentrations in the late morning at Fullerton, about 20 km northeast.

**Wilcoxon two sample rank test $\alpha \geq 0.13$

***A recent reanalysis of these data¹⁾ suggests that even in this case plume touchdown is insignificant.

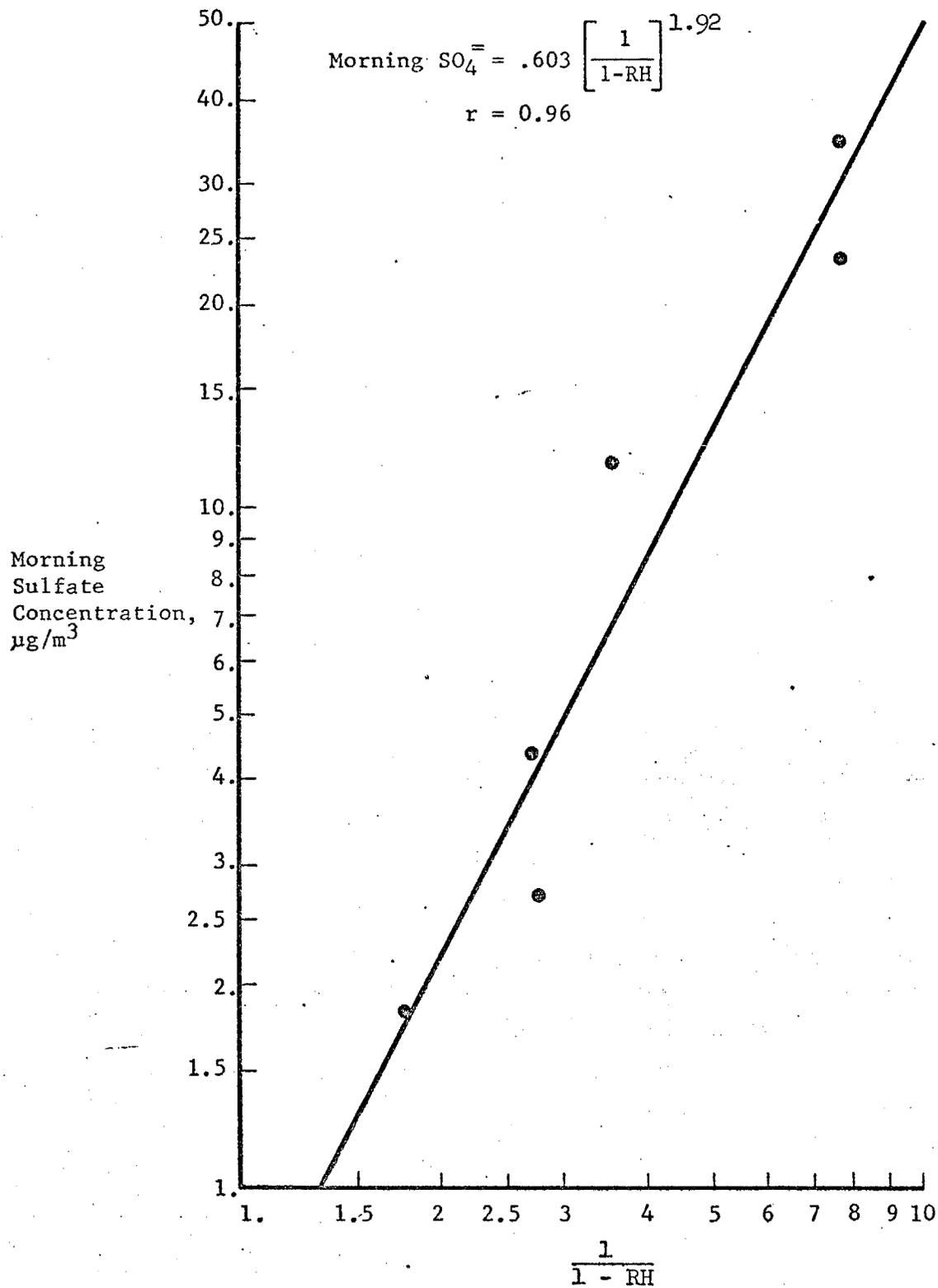
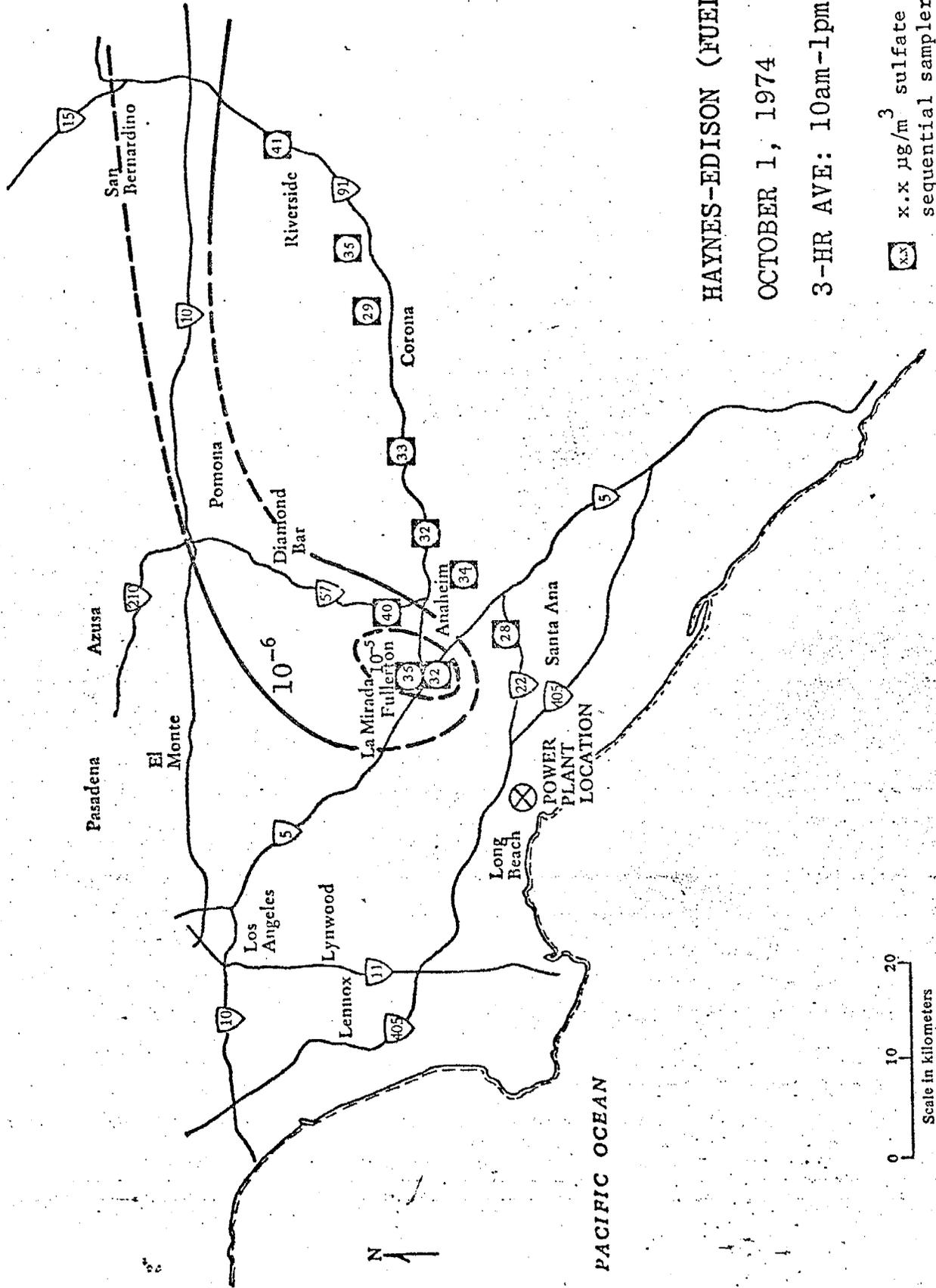


Figure 13. Sulfate Concentrations (0900-1200 PST) Averaged for Sites 0 and 1, Haynes-Edison Plant Episodes, V.S. 0700 PST Relative Humidity at Long Beach Airport.

Figure 14. GROUND LEVEL DISTRIBUTION OF SF₆* AND CORRESPONDING SULFATE LEVELS.



HAYNES-EDISON (FUEL OIL)

OCTOBER 1, 1974

3-HR AVE: 10am-1pm

x.x µg/m³ sulfate at sequential sampler location

* SF₆ isopleth levels expressed as fraction of original stack concentration
Dashed lines indicate approximate contours

Figure 16

DIURNAL VARIATION OF SULFATE, NITRATE, AND SF6
OCTOBER 1, 1974
STATION 0
HAYNES-EDISON (Fuel Oil)

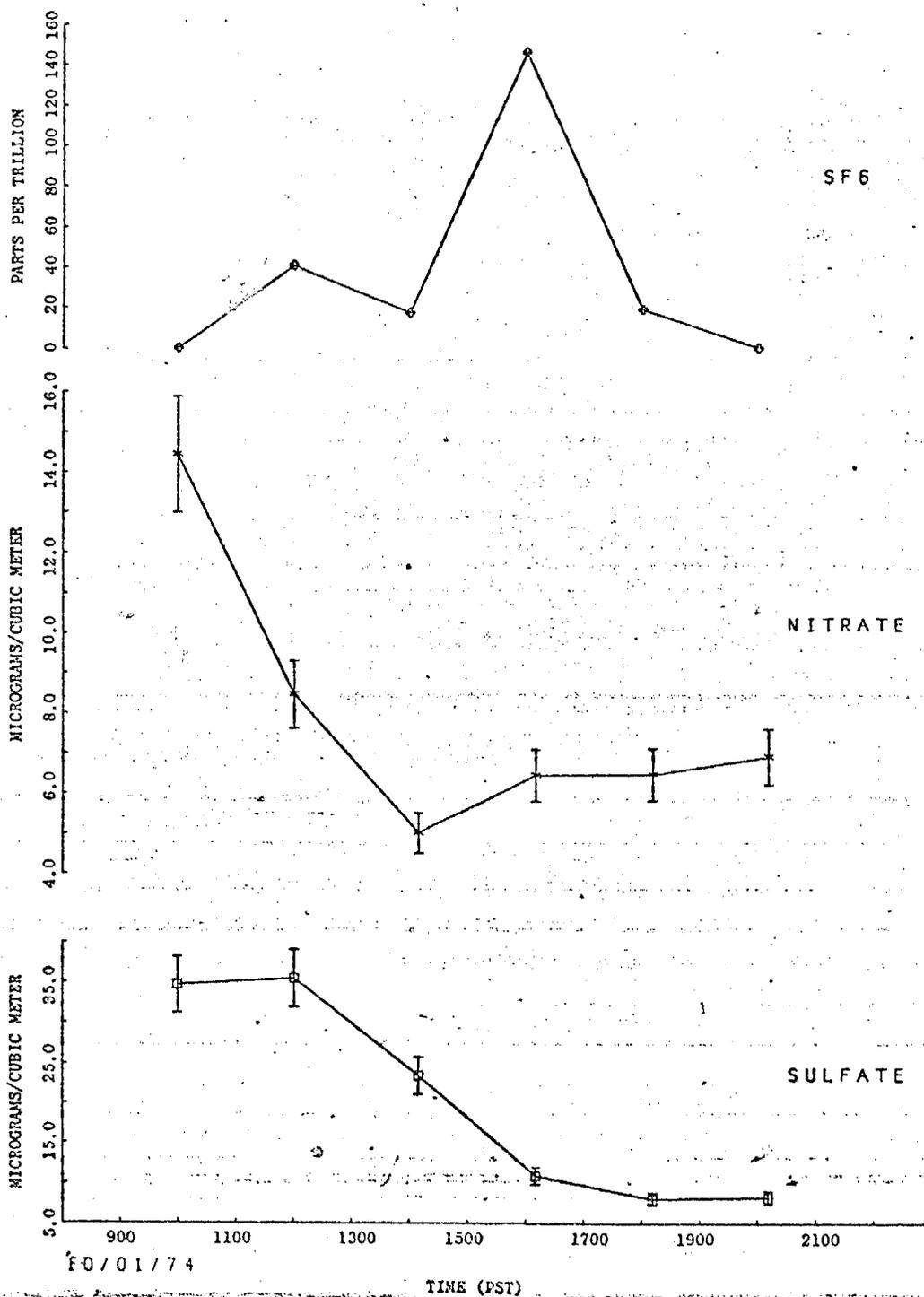


Figure 17

DIURNAL PATTERN OF SULFATE, NITRATE, AND SF6
OCTOBER 1, 1974
STATION 3
HAYNES-EDISON (Fuel Oil)

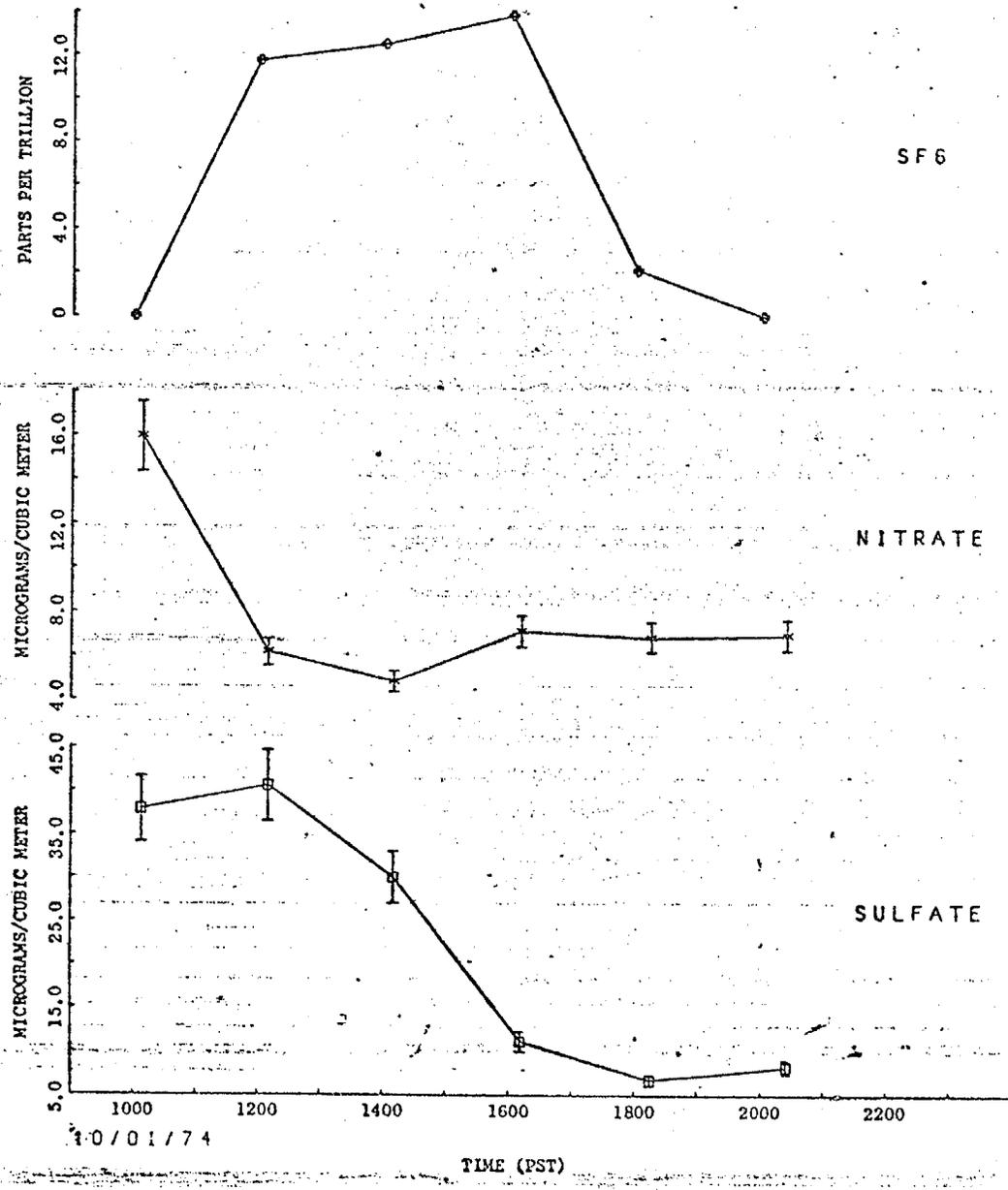


Figure 18

DIURNAL PATTERN OF SULFATE, NITRATE, AND SF6
OCTOBER 1, 1974
STATION 5
HAYNES-EDISON (Fuel Oil)

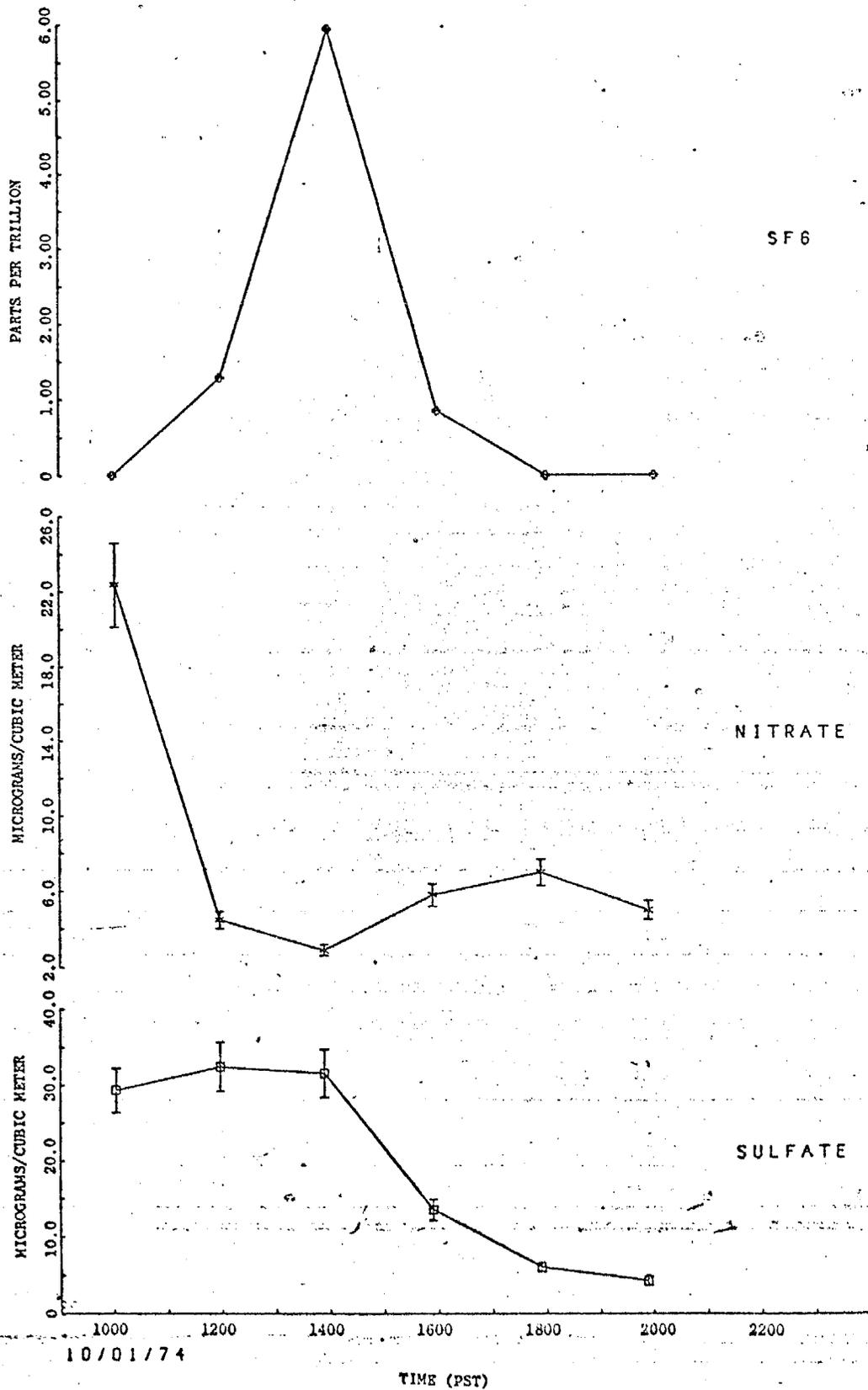


Figure 19

DIURNAL PATTERN OF SULFATE, NITRATE, AND SF6
OCTOBER 1, 1974
STATION 6
HAYNES-EDISON (Red Oil)

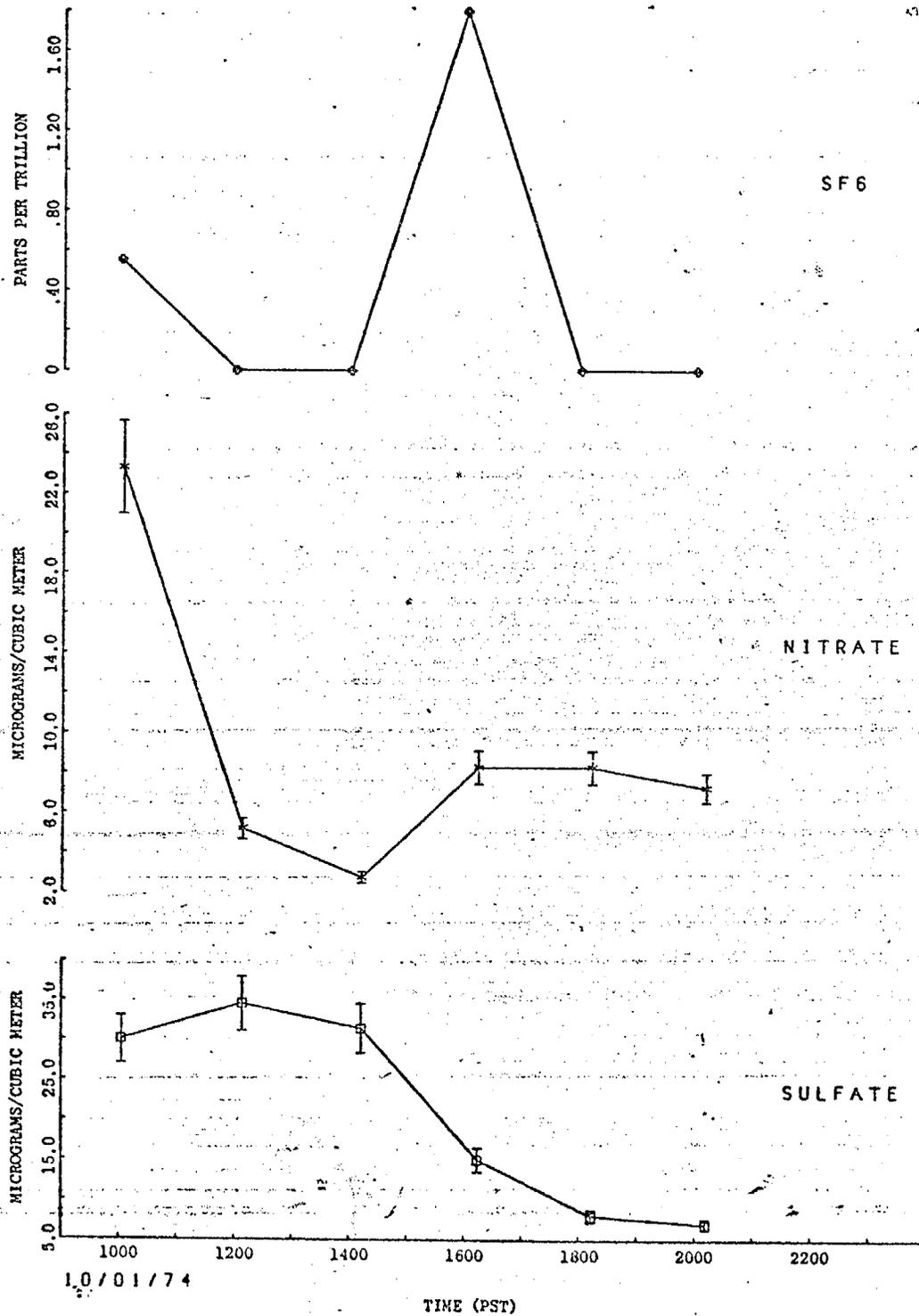
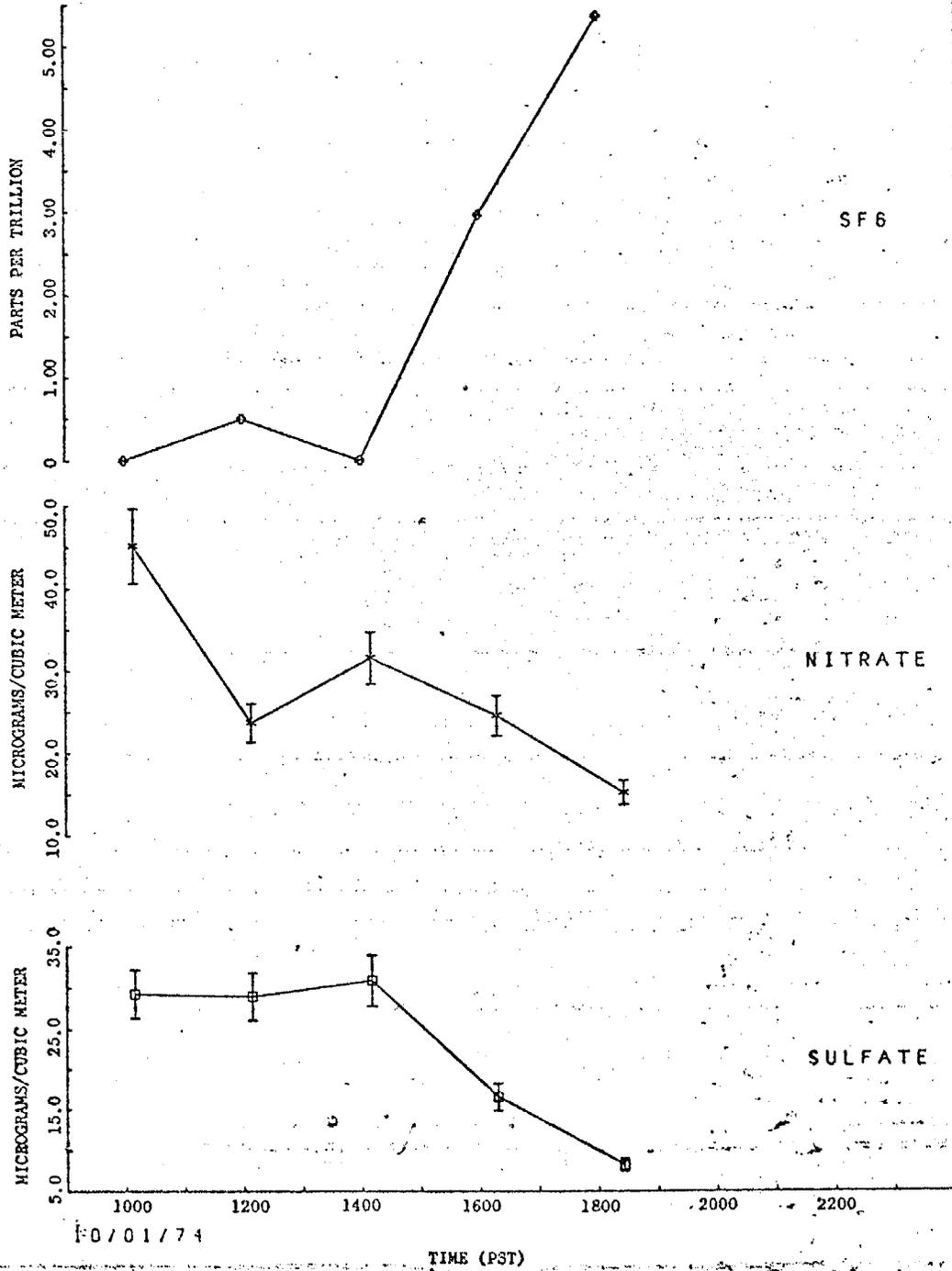


Figure 20

DIURNAL PATTERN OF SULFATE, NITRATE, AND SF6
OCTOBER 1, 1974
STATION 7
HAYNES-EDISON (Fuel Oil)



similar in magnitude to the maximum values observed in Moss Landing.* There was no obvious parallel at this or any other site between SF₆ concentrations and those for nitrate and sulfate on this day. Thus the plume contributions of nitrate and sulfate at the sampling sites are small relative to those from other sources.

It is interesting that at many sites on October 1st, an afternoon maximum in nitrate was observed of lesser magnitude than the morning values, consistent with findings in the Aerosol Characterization Experiment⁵ for the South Coast Air Basin.

Figures 22 and 23 relate to the November 7, 1974 episode at the Haynes-Edison complex for midday and afternoon periods, respectively. Compared to the October 1st episode the sulfate values are much lower here. Considering the midday period (Figure 22), the mean SO₄²⁻ value within the 10⁻⁶ isopleth was 2.7 ± 0.6 µg/m³ which was not significantly different from 1.7 ± 1.0 µg/m³ for stations outside the plume.**

Since, according to the data analysis of Dr. Shair and co-workers,² the plume is more diffuse during the afternoon period and generally includes all sampling sites, we have compared the mean of SO₄²⁻ values within the 10⁻⁵ SF₆ isopleth (7.2 ± 0.8 µg/m³) to the mean of all values outside this isopleth (4.0 ± 1.4 µg/m³). These data suggest about 3 µg/m³ as a minimum contribution from the Haynes-Edison plume.***

Figures 24 to 29 show diurnal variations for the November 7, 1974 episode. In this case SF₆ concentrations reached at least intermediate levels (e.g. 100 ppt) at stations 0 and 1 for the sampling period 1400-1600 PST. At station 0 and 1 there is a marked parallel between sulfate and SF₆, which is absent at the other locations. Nitrate failed to correlate well with either sulfate or SF₆ at any of the stations. Unlike sulfate, which exhibited a single peak in the late afternoon hours, nitrate levels often reached two diurnal peaks. The larger nitrate peak occurs after the maxima in sulfate.

*SF₆ data were not obtained at site 1 on this day. This site would also be expected to display high SF₆ concentrations (see Figure 14).

**Wilcoxon two sample rank test $\alpha \approx 0.13$

***Wilcoxon two sample test $\alpha = 0.0$ - A recent reanalysis of the SF₆ data¹⁾ suggests that the plume does not include the sampling sites in the Santa Ana Canyon area.

Figure 21

DIURNAL PATTERN OF SULFATE, NITRATE, AND SF6
OCTOBER 1, 1974
STATION 9
HAYNES-EDISON (Fuel Oil)

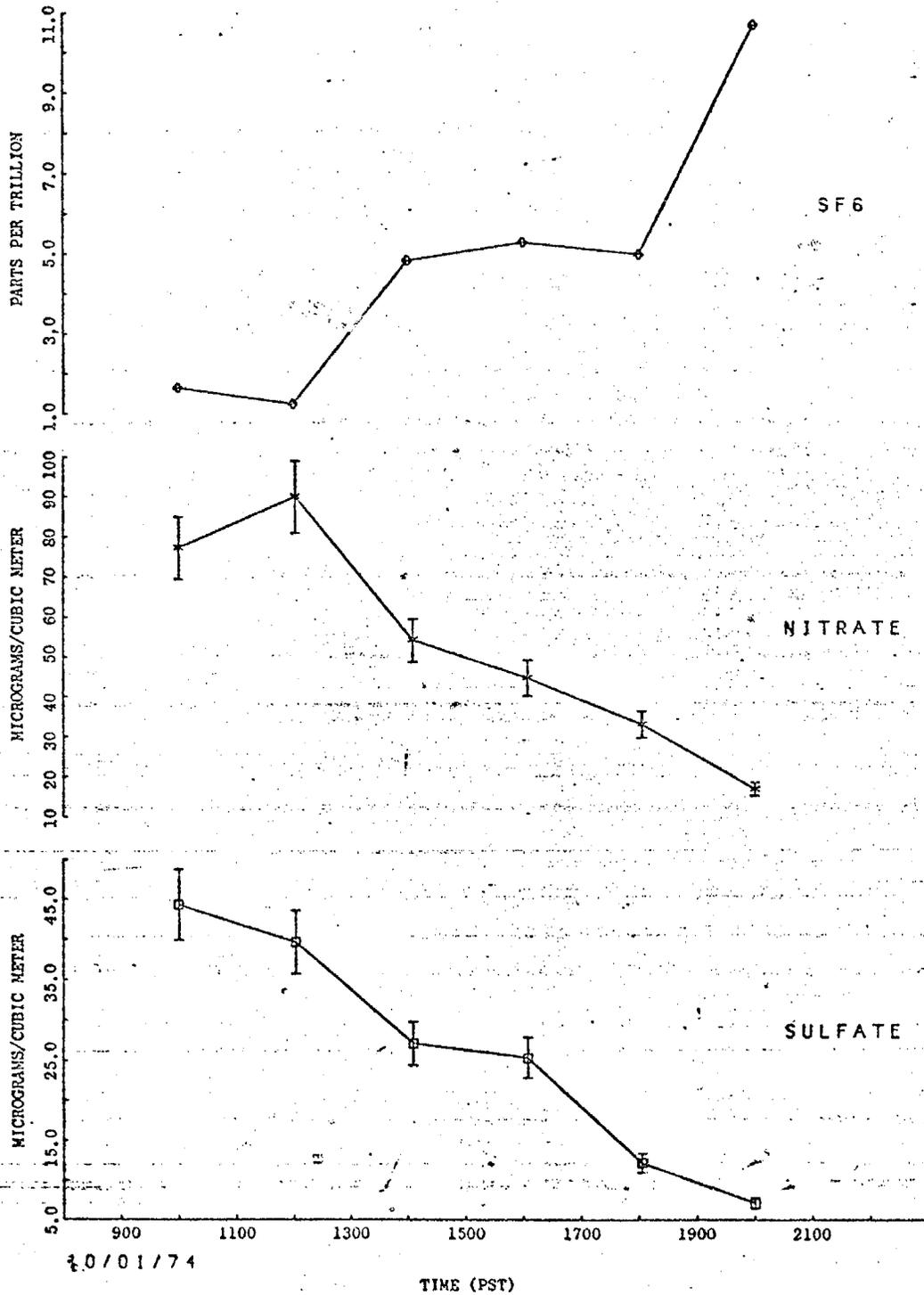
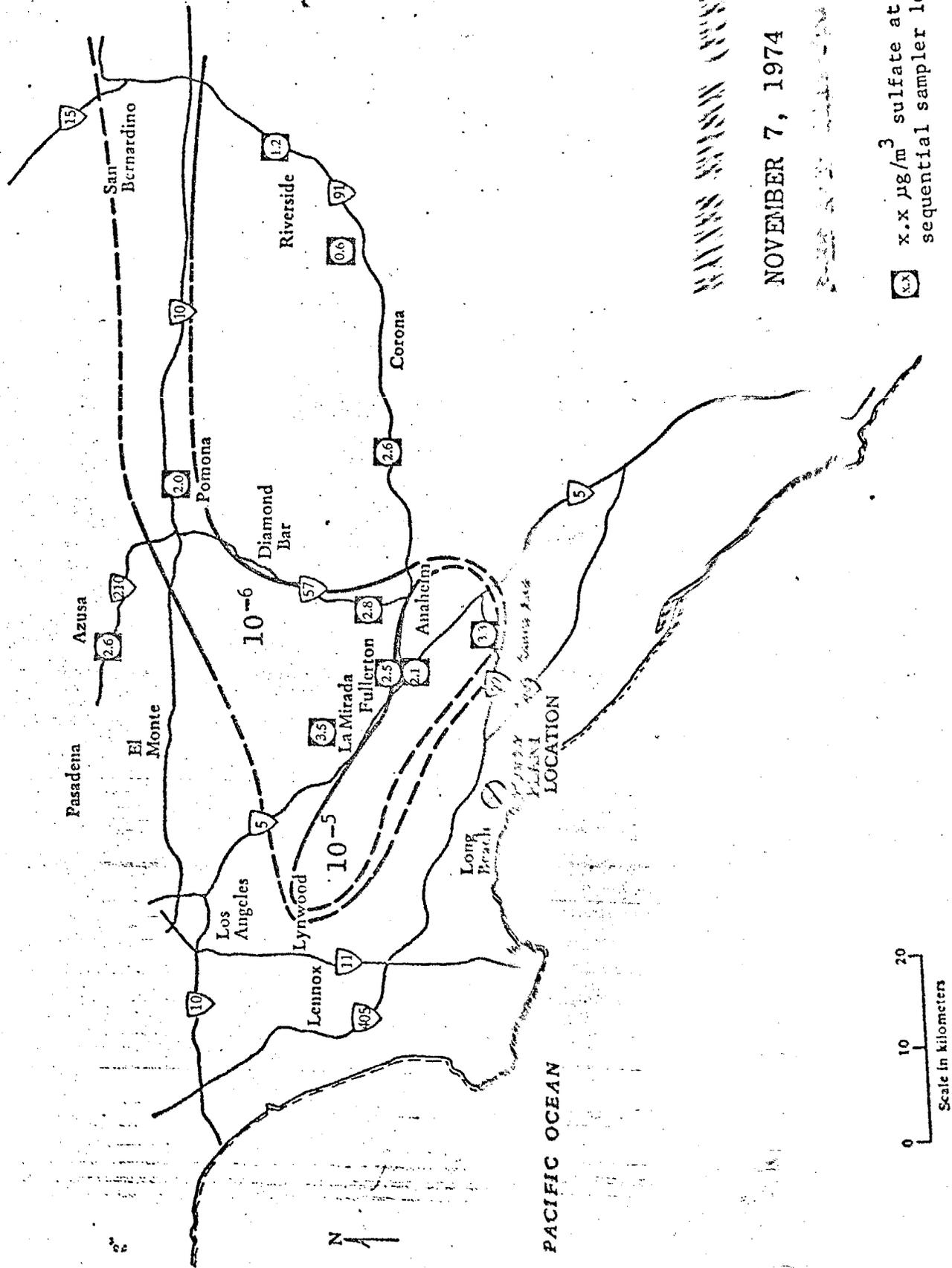


Figure 22. GROUND LEVEL DISTRIBUTION OF SF₆* AND CORRESPONDING SULFATE LEVELS.



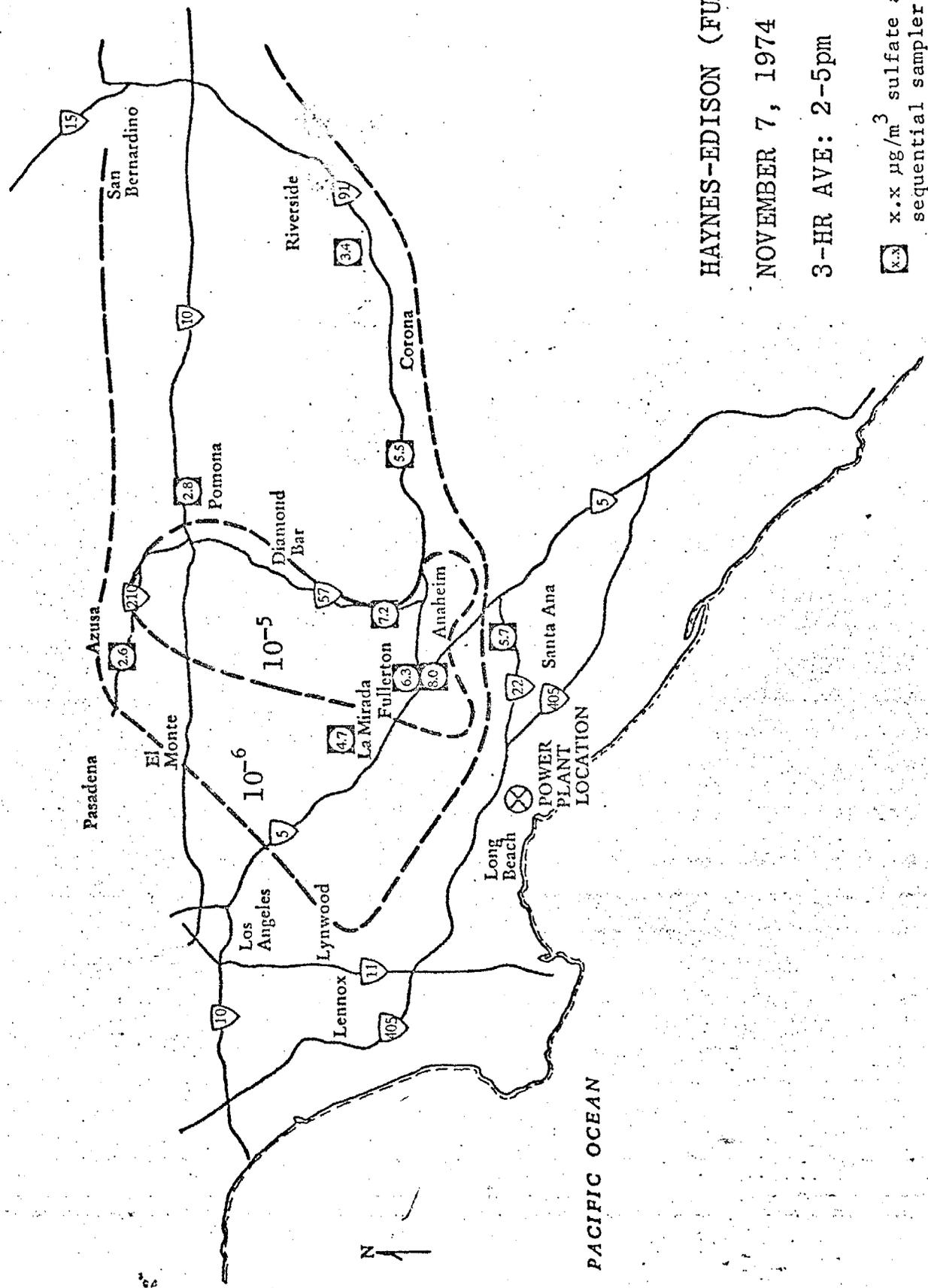
WATSON WATSON (WWSL 011)

NOVEMBER 7, 1974

x.x µg/m³ sulfate at sequential sampler location

* SF₆ isopleth levels expressed as fraction of original stack concentration

Figure 23. GROUND LEVEL DISTRIBUTION OF SF₆* AND CORRESPONDING SULFATE LEVELS.



HAYNES-EDISON (FUEL OIL)
 NOVEMBER 7, 1974
 3-HR AVE: 2-5pm

☐ x.x μg/m³ sulfate at sequential sampler location

* SF₆ isopleth levels expressed as fraction of original stack concentration
 Dashed lines indicate approximate contours

Figure 24
 DIURNAL PATTERN OF SULFATE, NITRATE, AND SF6
 NOVEMBER 7, 1974
 STATION 0
 HAYNES-REASON (Fuel Oil)

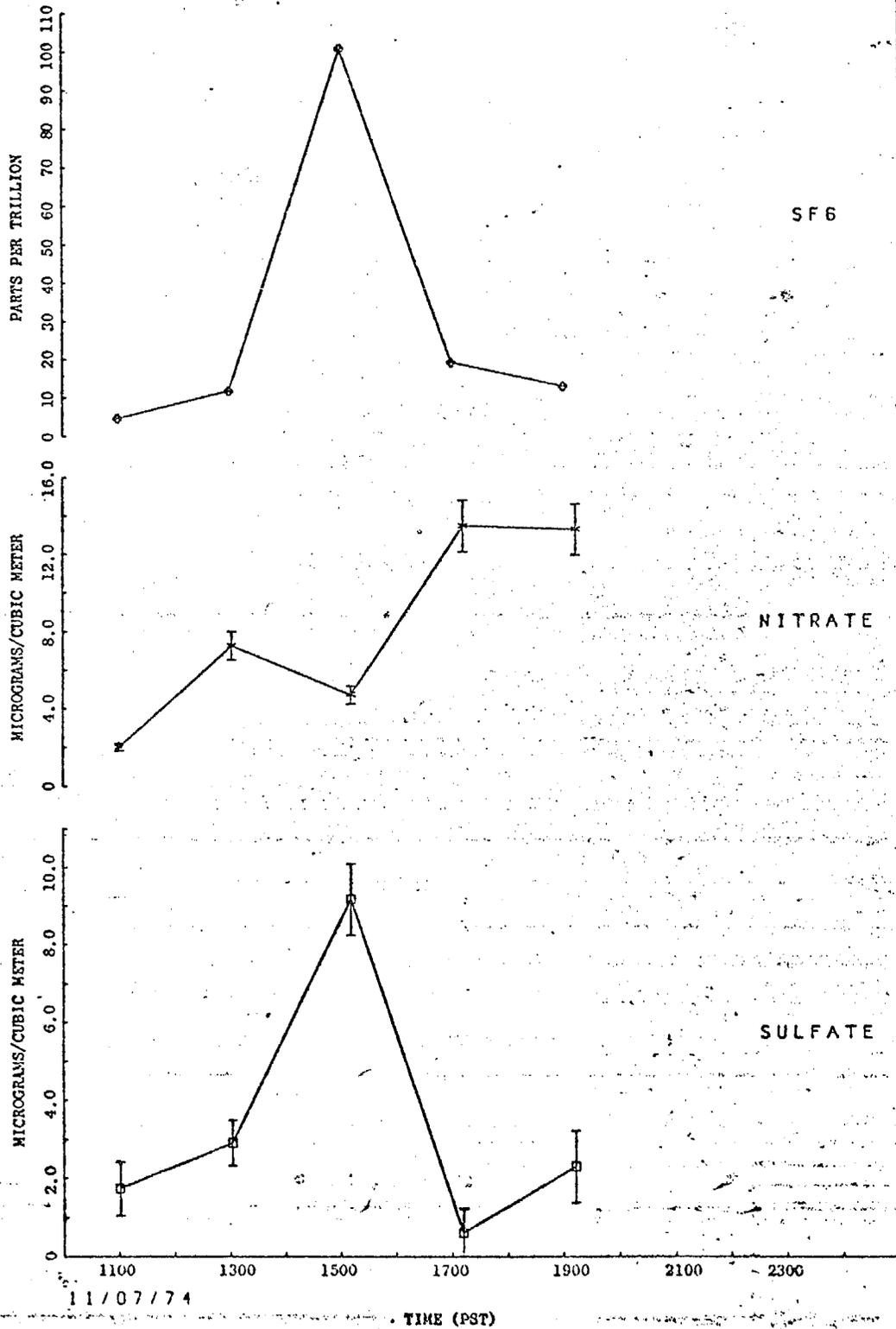
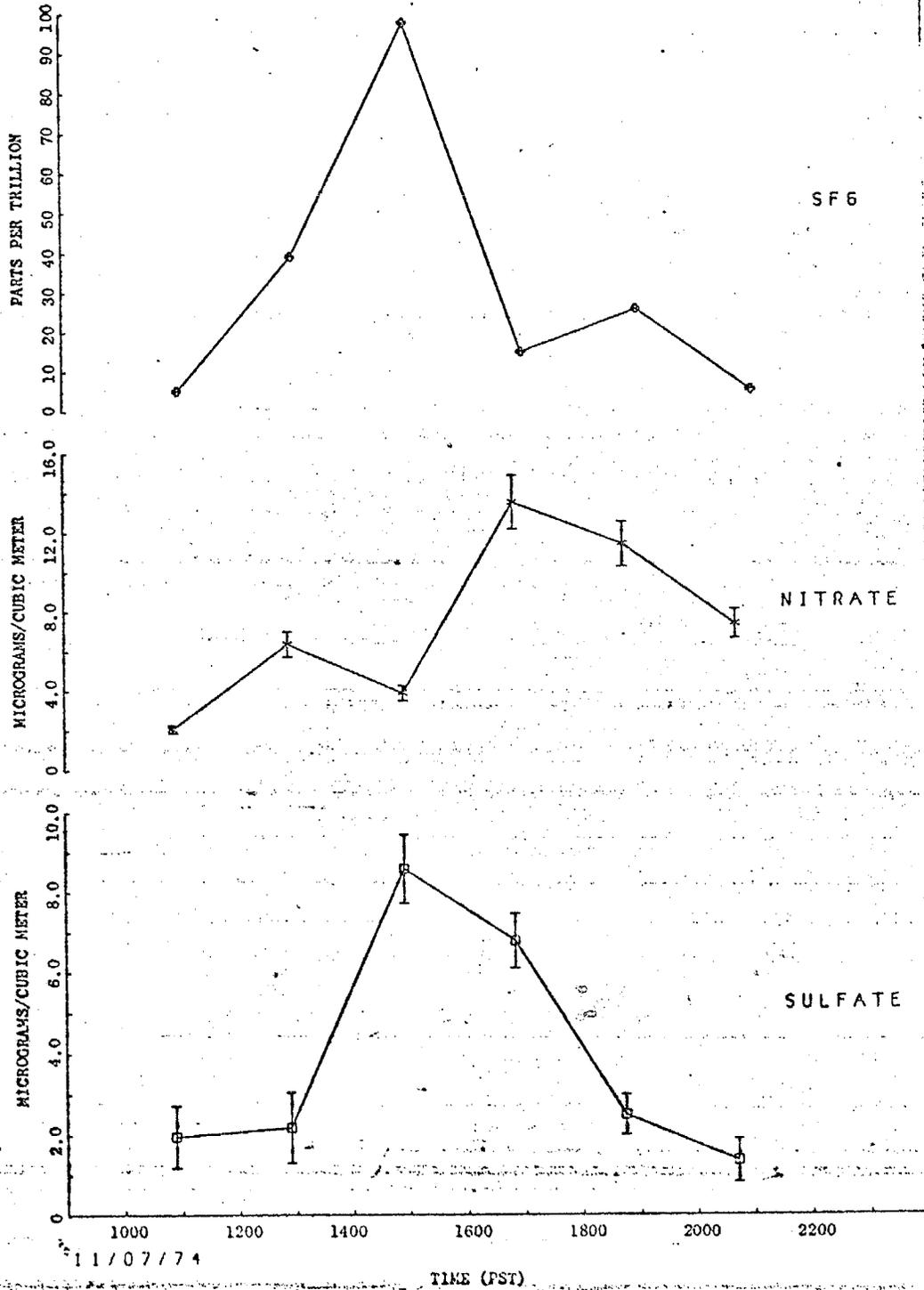


Figure 25

DIURNAL PATTERN OF SULFATE, NITRATE, AND SF6
NOVEMBER 7, 1974
STATION 1
HAYNES-EDISON (Fuel Oil)



11/07/74

TIME (PST)

Figure 26

DIURNAL PATTERN OF SULFATE, NITRATE, AND SF6
NOVEMBER 7, 1974
STATION 2
HAYNES-EDISON (Fuel Oil)

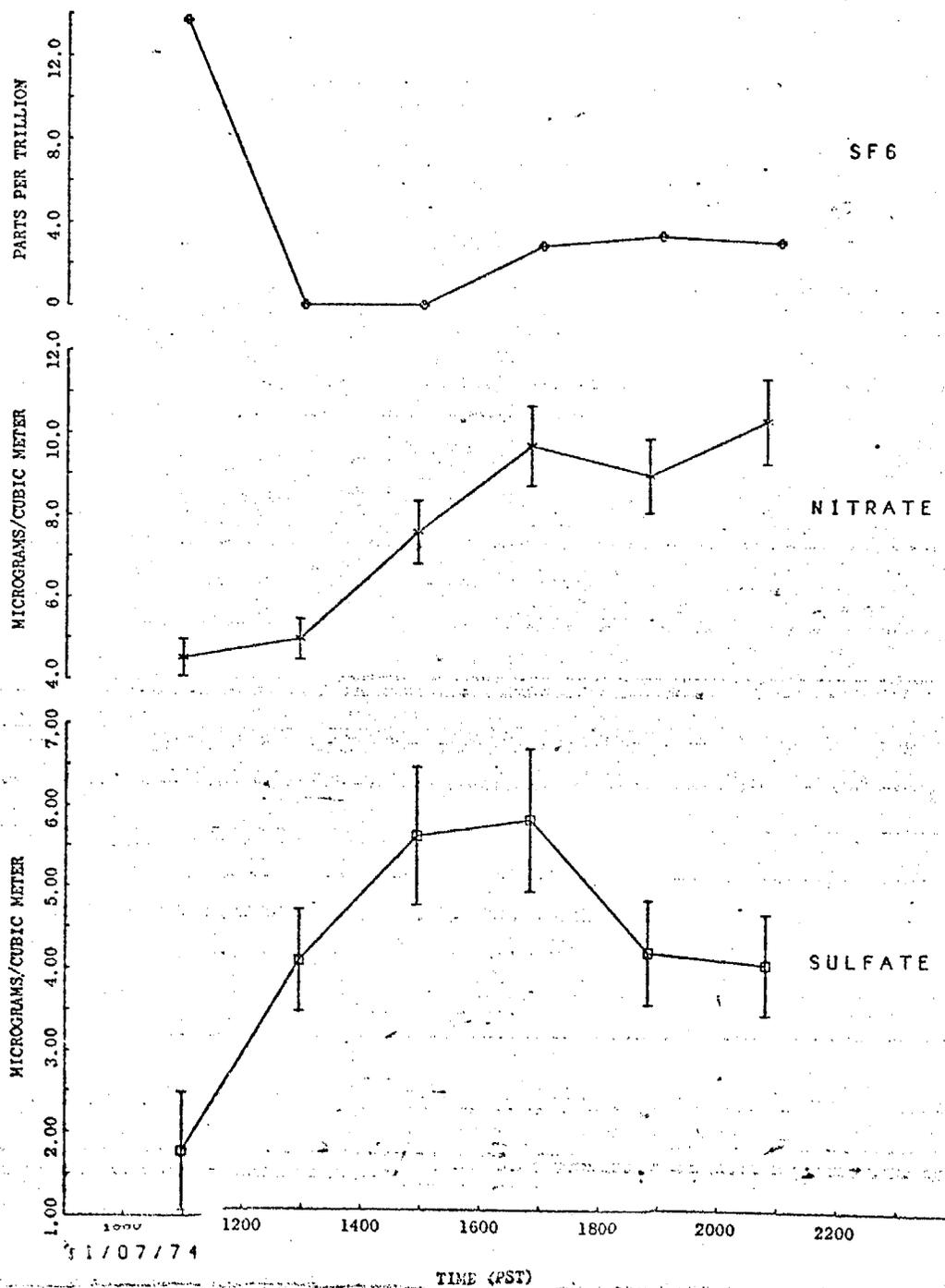


Figure 27

DIURNAL PATTERN OF SULFATE, NITRATE, AND SF6
NOVEMBER 7, 1974
STATION 4
HAYNES-EDISON (Fuel Oil)

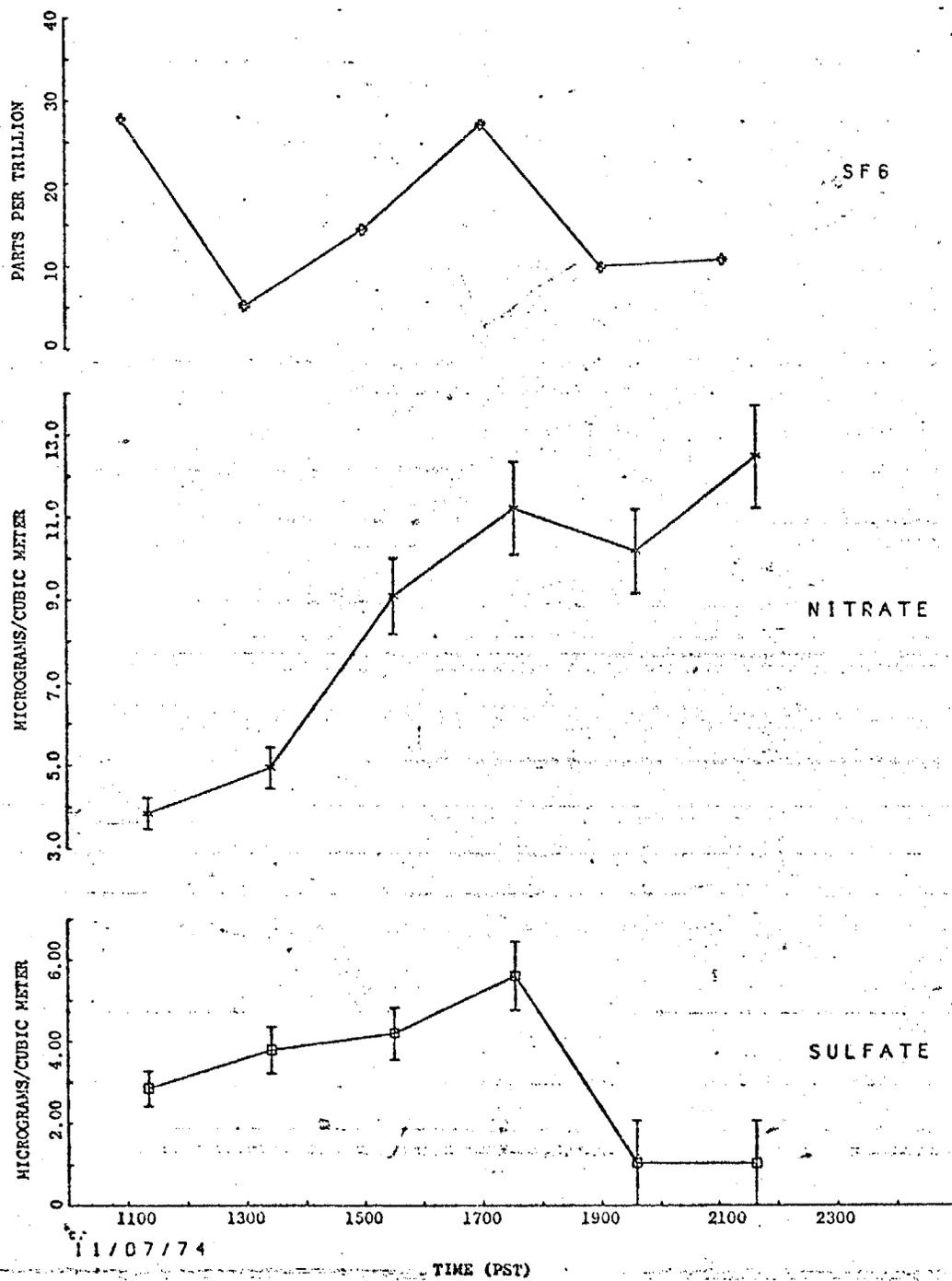


Figure 28

DIURNAL PATTERN OF SULFATE, NITRATE, AND SF6
NOVEMBER 7, 1974
STATION 5
HAYNES-EDISON (Fuel Oil)

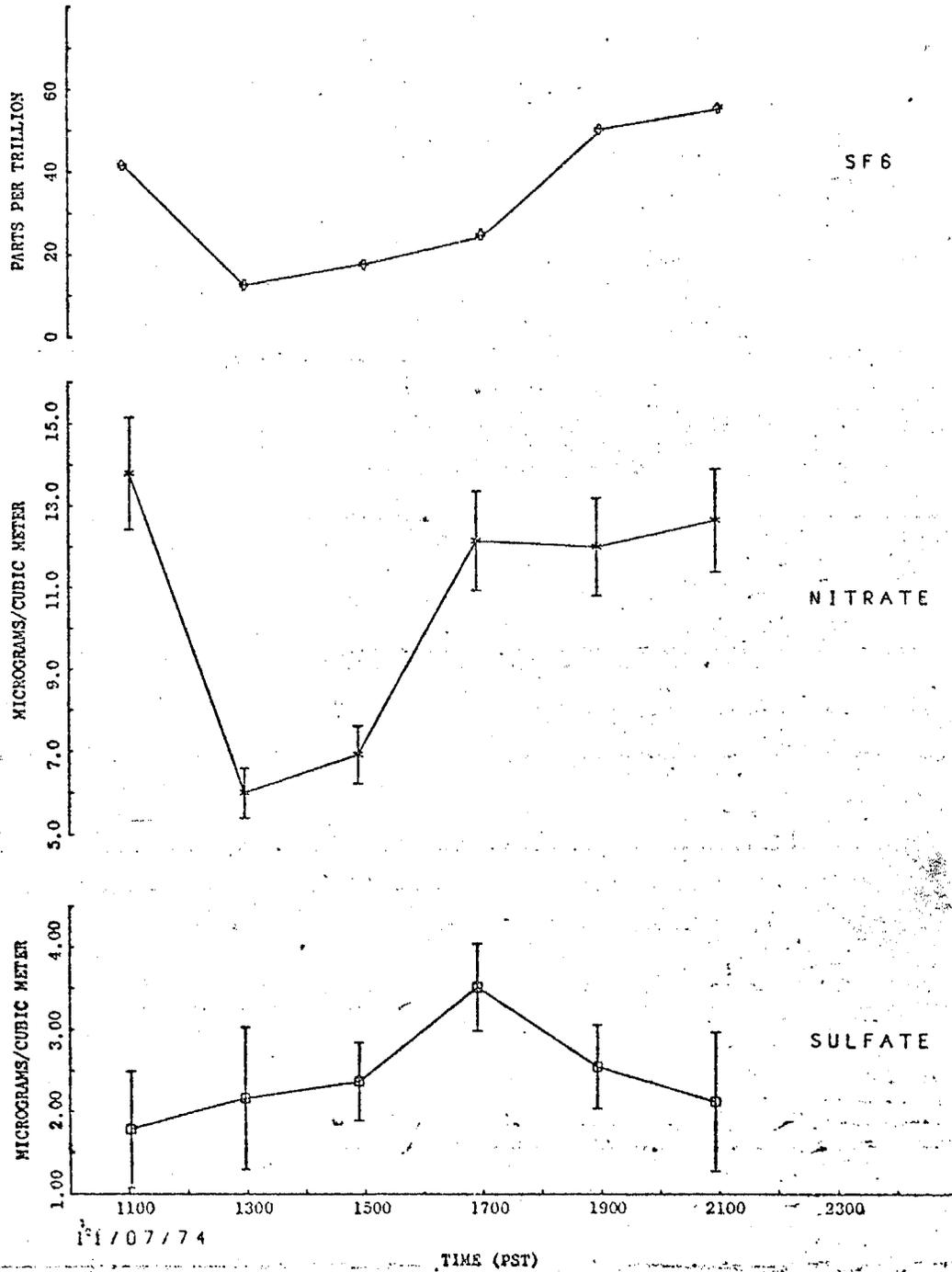
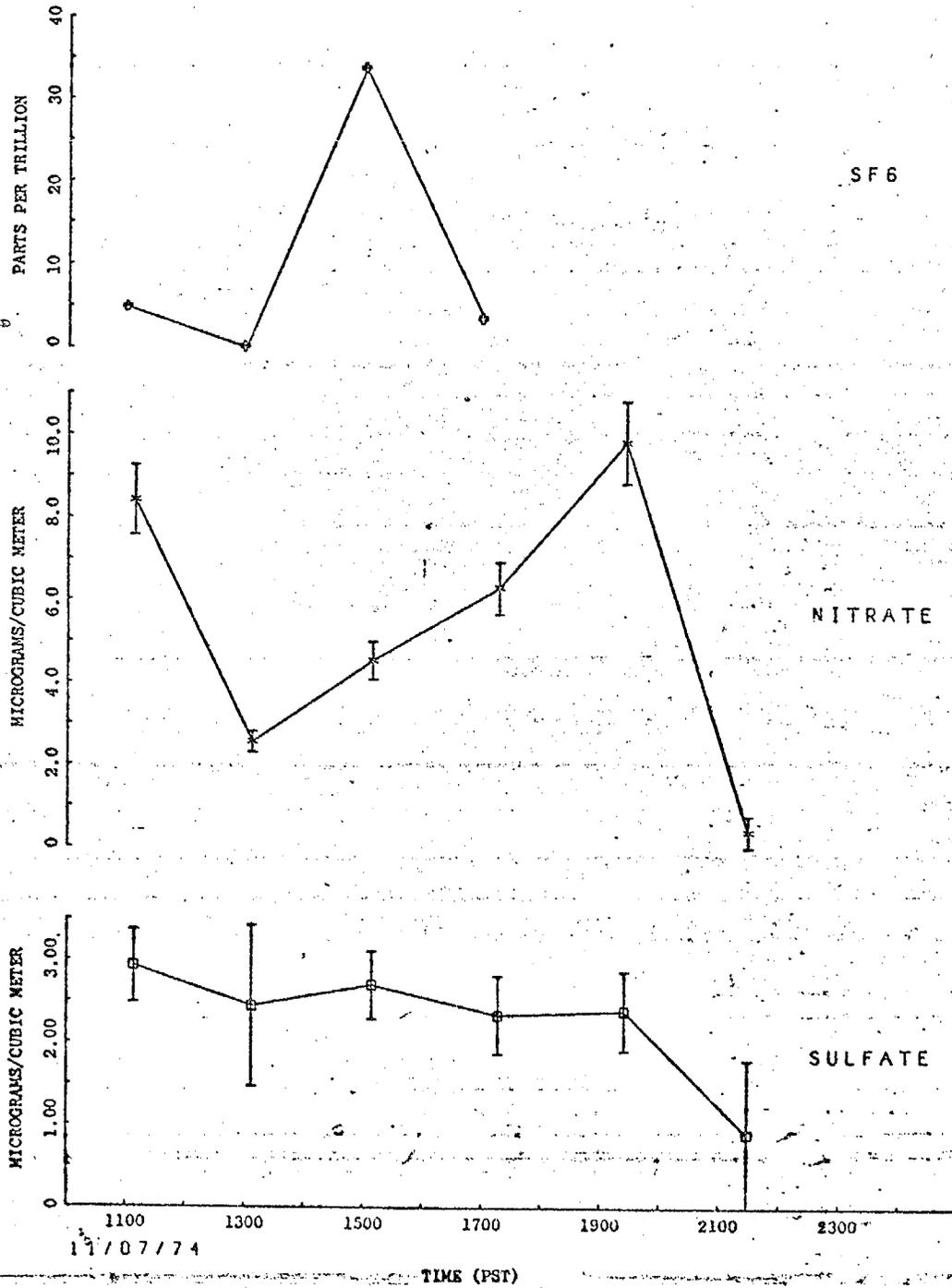


Figure 29

DIURNAL PATTERN OF SULFATE, NITRATE, AND SF6
NOVEMBER 7, 1974
STATION 7
HAYNES-EDISON (Fuel Oil)



The mean sulfate for sites 0 and 1 at the time of the SF₆ maximum was 8.9 ± 0.41 . For the remaining sites the mean maximum observed sulfate was $3.7 \pm 1.5 \mu\text{g}/\text{m}^3$. This suggests that at the 2 sites receiving the greatest impact from the Haynes - Edison plants plume, the sulfate contribution due to the plume was about $5.2 \pm 1.6 \mu\text{g}/\text{m}^3$.

Thus for the four time periods examined in detail here, 3 failed to reveal significant contribution of sulfate, relatable to the Haynes - Edison complex, within the plume impact area. For the fourth, the afternoon of November 7th, a contribution of from 3 to 5 $\mu\text{g}/\text{m}^3$ sulfate can be seen. This compares to the value $2.3 \mu\text{g}/\text{m}^3$ obtained for Moss Landing. The results are sufficiently varied and imprecise such that no inferences can be drawn from these data about possible differences in sulfate contributions from the power plants for the Moss Landing and Southern California sites.

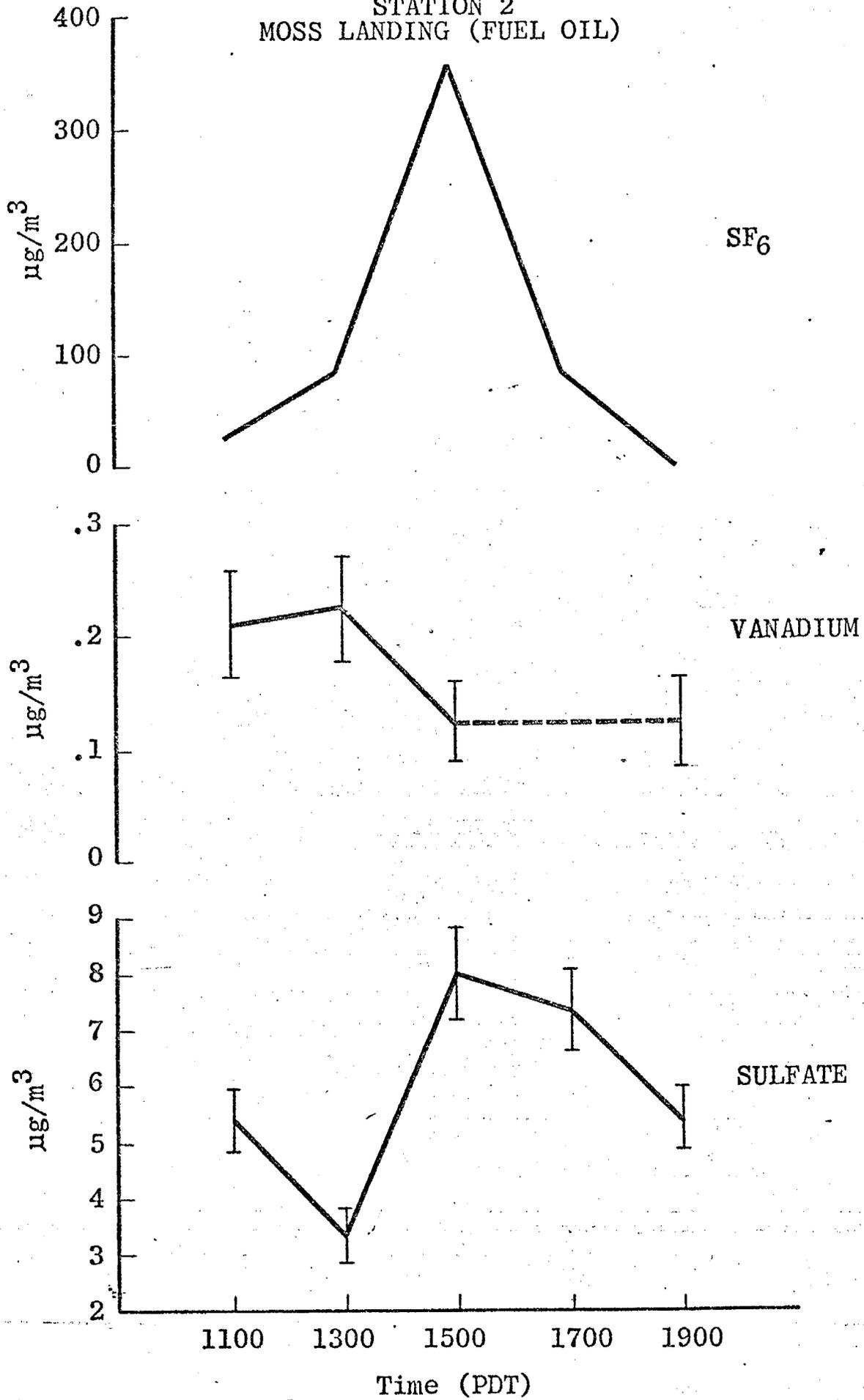
C. Elemental Data Analysis

Besides the wet chemical analyses carried out at AIHL, each of the ground level samples was analyzed by the Crocker Nuclear Laboratory (CNL) by α -particle induced x-ray fluorescence (AIXE) for total sulfur as well as approximately 15 other elements. In the following section on Quality Assurance, a comparison between total sulfur and wet chemical sulfate is included.

The extensive AIXE data set will not be discussed in detail here but is included, together with wet chemical and mass results in the data tape and listing accompanying this report.

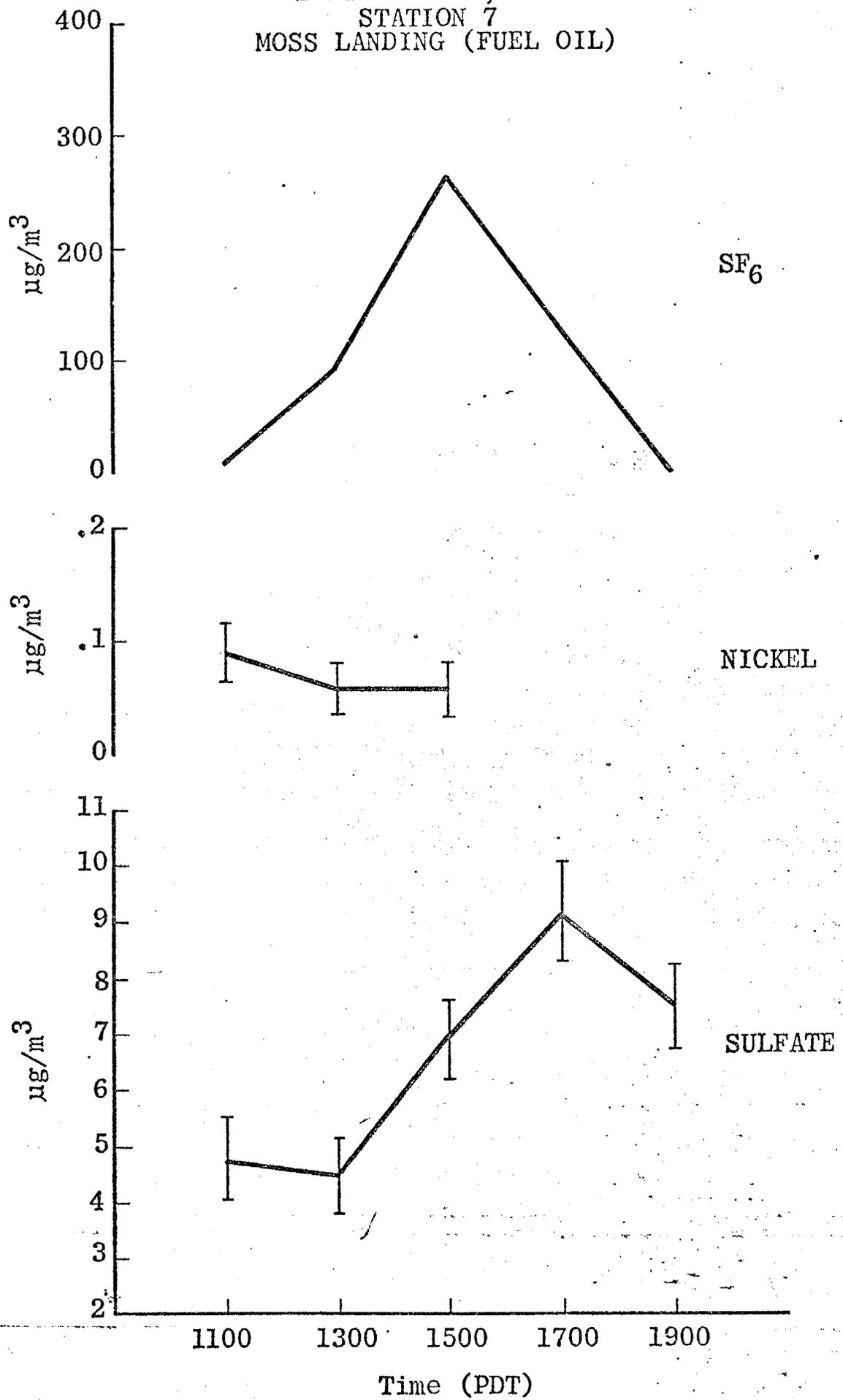
Aside from sulfur, vanadium and nickel are the elements of greatest interest obtained by AIXE since they can serve as a natural tracer for fuel oil combustion.⁶ However, the relatively low concentrations of these elements and the rather poor sensitivity of this method for vanadium limited the usefulness of this approach. All of the AIXE results were examined for cases in which sufficient data (above detection limits) were obtained to permit inspection of diurnal patterns. In the case of vanadium, only two such cases were found: the September 11th episode, station 2 and the October 1st episode, station 9. In both cases vanadium concentrations were in the range $0.1-0.2 \mu\text{g}/\text{m}^3$. In the October 1st episode the SF₆ level at station 9 remained low (< 12 ppt) indicating little impact of the labelled plume. Not surprising, therefore, there were no similarities in the diurnal patterns of SF₆ and vanadium in this case. The September 11th example did occur at a site which received substantial fumigation from the plume as evidenced by SF₆ concentrations up to 350 ppt. Figure 30 compares the diurnal patterns of vanadium, SF₆ and sulfate. The results suggests that even in this case much of the vanadium resulted from sources other than the labelled plume.

DIURNAL PATTERN OF VANADIUM, SF₆ AND SULFATE
SEPTEMBER 11, 1974
STATION 2
MOSS LANDING (FUEL OIL)



For nickel, again only two cases were found in which diurnal patterns could be drawn, September 11th at station 7 and October 1st at station 3. In these cases nickel concentrations ranged from 0.05 to 0.15 $\mu\text{g}/\text{m}^3$. Again, only in the September 11th episode was the SF_6 level substantial at this site. Figure 31 shows the diurnal patterns of nickel, SF_6 and sulfate. As with vanadium, nickel does not correlate with either SF_6 or sulfate.

Figure 31
DIURNAL PATTERN OF NICKEL, SF₆ AND SULFATE
SEPTEMBER 11, 1974
STATION 7
MOSS LANDING (FUEL OIL)



III. Aerial Collection and Analysis of Samples for Sulfate

A. Sampling Medium and Sampling Strategy

Samples were collected in the MRI instrumented aircraft sampling at about 20 l/minute. The aircraft collected samples while flying back and forth across plumes generated by the Moss Landing, Haynes and Edison Power Plants. By sampling at varying distances from the stack it was hoped to gain information on rates of conversion of SO₂ to sulfate. To aid in interpretation of these results SF₆ tracer, NO_x, SO₂ and O₃ levels were also monitored on board the aircraft.

Samples for analysis were collected on 1" diameter Gelman A glass fiber filters which had been acid washed in an effort to reduce the sulfate blank and to minimize artifact sulfate formation. The pre-treatment used was that developed at Brookhaven National Laboratory by Dr. L. Newman and co-workers and is given in Table 6.

It was not assumed, however, that artifact sulfate formation by SO₂-filter interaction would be eliminated by this pre-treatment. Instead, a sampling protocol was adopted in which a second or backup filter sampled in series. SO₂ sampled must pass through both filters except for a small percentage which is converted to sulfate on both filters due to SO₂-filter interaction. Using the observed sulfate on the backup filter as a "blank" to correct the sulfate value observed on the front filter should, to a good approximation, correct for artifact sulfate formation from this source. Unfortunately it cannot correct for possible sulfate formation on the front filter which involved interactions between SO₂ and oxidation-promoting particulate matter constituents.

The samples collected were obtained at 3 or 4 distances from the stack, in the range 0.8 to 40 kilometers (0.5 to 25 miles) downwind. The total air volume sampled within the plumes ranged from 0.1 to 1.1 m³.

B. Results of Sulfate Analysis

The samples were analyzed by flash vaporization-flame photometric detection as developed by Roberts and Friedlander and modified by Husar. The equipment and procedures are detailed in Appendix B.

Table 7 summarizes the apparent sulfate values, in µg/m³, calculated using the total sampling times and flows provided by MRI. Such values range from about 1 to 15 µg/m³ SO₄⁼ at the distances from the stack indicated.

Application of results of aerial sampling to calculate conversions of SO₂ in the plume requires that the plume under study be the only source of the sulfate, SO₂ and the conservative tracer, SF₆. Under such conditions an increase in sulfate levels in the plume beyond that ascribable

to dilution may reasonably be considered the result of oxidation of the labelled plume's SO₂.

Such conditions are much more likely to exist on the Moss Landing area than in Southern California because of the multiplicity of SO₂ sources in the South Coast Air Basin.

In the current aerial sampling program the MRI aircraft sampled the plume at several distances from the stacks. Sampling of particulates continued both within and outside the plume as the airplane traversed back and forth thereby further complicating interpretation of results. The fraction of the total air volume sampled which was inside the plume defined by the SO₂ and/or NO_x monitors was as small as 12%. Calculation of plume concentrations of sulfate at a given distance could be done if the sulfate concentration outside the plume were either zero or some known value:

$$\text{Plume Sulfate } (\mu\text{g}/\text{m}^3) = \frac{E_T}{E_P} \times (\text{SO}_4^{=})_{\text{apparent}} - \frac{E_B}{E_P} \times (\text{SO}_4^{=})_{\text{background}} \quad (1)$$

Where

- E_T = Total time sample collected for n passes
- E_P = Total time spent in plume for n passes
(determined from real time SO₂ and NO_x analyzers)
- E_B = Total time spent sampling background air

Regrettably, the sampling protocol developed jointly by MRI and AIHL did not include monitoring of the surrounding airspace to obtain "background" sulfate levels. Thus correction of the measured (or apparent) values to plume concentrations cannot be done with confidence.

Since estimation of the aerial background may yet prove feasible we have compiled in Table 7 the fraction of the total sampling time spent in the plume.

C. Technique for Calculating Fractional Conversion of SO₂ to Sulfate in the Plume

While the present sulfate data appear inadequate to permit calculation of conversion in the plume, we compile here the other necessary data and present a procedure which may be useful with future data sets.

Table 6 WASHING PROCEDURE FOR GLASS FIBER FILTERS^a

1. Wash three 8 x 10" filters^b with 1-1/2 l distilled H₂O.
2. Dry at 475°C (for 2 hours).
3. Rewash as above.
4. Cover with 0.5 N HCl. Let stand for 2 minutes. Remove all possible water by suction.
5. Dry at 110°C overnight.

- a. Developed by L. Newman et al, Brookhaven National Laboratory for use with Whatman GF81 (glassfiber) filters.
- b. The equivalent filter area with 1" diameter filters was employed in the present work.

TABLE 7 SULFATE CONCENTRATIONS IN POWER PLANT PLUMES

SAMPLE	DATE	TIME ^a (PST)	DISTANCE FROM STACK		APPARENT SULFATE, ^{b,c} µg/m ³	FRACTION OF TIME IN PLUME ^d
			Kilometers	Miles		
XA0340TV	9/10/74	1039-1142	1.6	1 (circle)	< 3.1	0.13
XA0342TV	9/10/74	1310-1333	1.6	1	6.1 ± 4.5	0.16
YA0344TV	9/10/74	1348-1431	8	5	4.0 ± 1.6	0.13
ZA0346TV	9/10/74	1452-1536	16	10	6.3 ± 1.9	0.09
XB0348TV	9/11/74	1026-1051	1.6	1 (circle)	< 1.1	0.14
XC0312TV	9/12/74	1508-1542	1.6	1	< 3.0	0.18
YC0310TV	9/12/74	1430-1448	16	10	2.0 ± 0.4	N.D.
ZC0306TV	9/12/74	1345-1427	24	15	11.4 ± 2.7	N.D.
XD0370TV	10/1/74	1409-1421	1.2	0.75	14.9 ± 9.3	0.25
YD0372TV	10/1/74	1433-1513	3.2-4.8	2-3	8.9 ± 3.0	0.06
ZD0374TV	10/1/74	1550-1614	32-40	20-25	4.1 ± 3.9	N.D.
WF0467TV	10/11/74	1331-1405	0.8	0.5	14.4 ± 2.5	0.12
XF0469TV	10/11/74	1423-1443	4.8	3	14.4 ± 2.2	0.38
YF0473TV	10/11/74	1448-1524	9.6	6	14.3 ± 1.9	0.38
ZF0475TV	10/11/74	1533-1607	32	20	8.9 ± 1.3	N.D.
XG0483TV	10/17/74	1459-1507	0.8	0.5	N.D.	N.D.
YG0485TV	10/17/74	1512-1526	4.8	3	1.3 ± 0.8	N.D.
ZG0487TV	10/17/74	1542-1613	9.6	6	0.9 ± 0.5	N.D.
WG0489TV	10/17/74	1622-1705	24	15	1.9 ± 0.3	N.D.
XH0515TV	10/25/74	1322-1403	1.6	1	2.2 ± 0.8	0.10
YH0517TV	10/25/74	1417-1442	4.8	3	4.6 ± 1.2	0.17
ZH0519TV	10/25/74	1456-1642	16	10	2.9 ± 0.6	N.D.
WH0521TV	10/25/74	1752-1813	32	20	3.5 ± 1.3	N.D.
XI0525TV	10/30/74	1250-1318	1.6	1	4.5 ± 1.7	0.12
YI0527TV	10/30/74	1323-1420	4.8	3	2.1 ± 0.4	0.20
ZI0529TV	10/30/74	1434-1539	16	10	1.6 ± 0.3	0.25
WI0499TV	10/30/74	1644-1705	32	20	0.8 ± 0.3	N.D.
WJ0501TV	11/7/74	1248-1324	1.6	1	2.6 ± 0.4	0.29
XJ0503TV	11/7/74	1348-1430	4.8	3	1.8 ± 0.3	N.D.
YJ0509TV	11/7/74	1439-1540	16	10	3.2 ± 0.4	N.D.
ZJ0511TV	11/7/74	1631-1712	16	10	1.8 ± 0.3	N.D.

- a. Includes the complete time interval for sampling both within and outside the plume.
- b. All values corrected for filter blanks using the backup filter.
- c. Analysis by AIHL by flash volatilization with flame photometric detection.
- d. Equals E_p/E_T as defined for equation 1 (see text).

Calculation of the apparent conversion of SO₂ to sulfate in the power plant plume can be done using the equation:

$$\beta \frac{\left[\left(\frac{\text{SO}_4^{=}}{\text{SF}_6} \right)_{D_2} - \left(\frac{\text{SO}_4^{=}}{\text{SF}_6} \right)_{D_1} \right]}{\left(\frac{\text{SO}_2}{\text{SF}_6} \right)_{D_1}} \times 100 = \% \text{ SO}_2 \text{ Conversion}$$

where

D₁ and D₂ refer to distance 1 and 2 respectively, with D₂ > D₁.

β is a constant = $\frac{\text{molecular weight of SO}_2}{\text{molecular weight of SO}_4^{-2}} = \frac{64}{96}$

Accordingly, in addition to sulfate concentration in the plume at a given distance from the stack, corresponding mean SO₂ and SF₆ data are needed. SF₆ results from samples collected by MRI and analyzed by F. Shair and co-workers were obtained from MRI. MRI also supplied a limited set of SO₂ results.

As with sulfate, SF₆ samples were obtained by sampling which proceeded both before and after the airplane sampled the plume. SF₆ results for each pass were corrected by the MRI staff to relate only to the time period spent in the plume. For example if a single pass lasted 140 seconds of which only 65 seconds was spent in the plume then the measured SF₆ result was multiplied by 140/65 = 2.15.

Typically 8-10 passes were used to collect a single particulate sample. To relate SO₄⁼ levels to SF₆ and SO₂, the concentrations of SF₆ and SO₂ per pass (corrected values for case of SF₆) are averaged. Table 8 lists the relevant information based on information available from MRI.

TABLE 8. SO₂ AND SF₆ CONCENTRATIONS IN POWER PLANT PLUMES

DATE	TIME (PST)	DISTANCE FROM STACK		Arith. ^a Mean SF ₆ (ppt)	Arith. Mean SO ₂ ^b	
		Kilometers	Miles		PPM	UG/m ³
9/10/74	1039-1142	1.6	1 (circle)	3960	-	-
9/10/74	1310-1333	1.6	1	5626	.082	215
9/10/74	1348-1431	8	5	141	.065	170
9/10/74	1452-1536	16	10	~ 35	.048	126
9/11/74	1026-1051	1.6	1 (circle)	1603		
9/12/74	1508-1542	1.6	1	599		
9/12/74	1430-1448	16	10	ND		
9/12/74	1345-1427	24	15	ND		
10/1/74	1409-1421	1.2	0.75	367		
10/1/74	1433-1513	32-4.8	2-3	425		
10/1/74	1550-1614	32-40	20-25	ND		
10/11/74	1331-1405	0.8	0.5	688	.045	118
10/11/74	1423-1443	4.8	3	208	.027	70.7
10/11/74	1448-1524	9.6	6	149	.016	42
10/11/74	1533-1607	32	20	ND	-	
10/17/74	1459-1507	0.8	0.5	ND		
10/17/74	1512-1526	4.8	3	ND		
10/17/74	1542-1613	9.6	6	ND		
10/17/74	1622-1705	24	15	ND		
10/25/74	1322-1403	1.6	1	1888	.034	89
10/25/74	1417-1442	4.8	3	379	.024	63
10/25/74	1456-1607	16	10	~105	.005	13.1
10/25/74	1752-1813	32	20	ND	.003	7.9
10/30/74	1250-1318	1.6	1	1114		
10/30/74	1323-1420	4.8	3	220		
10/30/74	1434-1531	16	10	115		
10/30/74	1644-1705	32	20	ND		
11/7/74	1248-1324	1.6	1	751		
11/7/74	1348-1430	4.8	3	584		
11/7/74	1439-1540	16	10	ND		
11/7/74	1631-1710	16	10	ND		

a. Data for single passes supplied by F. Shair et al, CIT and W. White, MRI
 b. Data for single passes supplied by W. White, MRI.

IV. Quality Assurance

A. General

Flow calibration of the ground level particulate samplers was done by RI and for the aerial particulate sampler, by MRI.

AIHL provided detailed written instructions to RI and MRI personnel covering the recording of filter sampling data in log books also furnished by AIHL.

The Gelman GA-1 filters used for ground level sampling were prewashed with twice distilled water dried in a laminar flow "clean bench" equilibrated at 44% R.H. to constant weight, and weighed on a Cahn 4100 electrobalance. A "control filter" technique was employed to allow for weight variation caused by humidity changes. The reproducibility in reweighing these filters after several months was established to be $\pm 5 \mu\text{g}$.

B. Interlaboratory Comparison for Elemental Data

Prior to analysis of the majority of samples by the Crocker Nuclear Laboratory (CNL) by α -particle induced x-ray fluorescence analysis (AIXE) an interlaboratory comparison with the Lawrence Berkeley Laboratory (LBL), was run on 20 Gelman GA-1 membrane filter samples. LBL employed x-ray induced x-ray fluorescence analysis (XRFA). Both laboratories use energy dispersive systems.

The results of the interlab comparison are shown for three elements, Pb, Fe and S in Figures 32, 33 and 34. This comparison revealed agreement within 5% for Pb and Fe but a systematic discrepancy of about 20% for S. These statistical evaluations were supplied to both laboratories. Mr. Robert Eldred of CNL discovered a necessary correction factor needed to allow for partial penetration of sulfur species into the Gelman membrane filter matrix. With this correction results for sulfur agreed within 5% without altering agreement previously obtained for other elements.

C. Interlaboratory Comparison of Sulfur and Sulfate Data

A comparison between LBL XRFA sulfur values and AIHL SO_4^{m} determinations was obtained as part of Phase II of the ACHEX study.⁷ Employing about 400 Gelman GA-1 filters average agreement was within 4%. Since CNL and LBL sulfur results agreed within 5%, good agreement between CNL and AIHL wet chemical results was expected.

Following wet chemical sulfate and AIXE of all samples at CNL, the results were compared. This comparison, shown in Table 9 is by episode, each episode consisting of approximately 70 filters. Wet chemical

Figure 32

INTERLABORATORY COMPARISON OF X-RAY FLUORESCENCE RESULTS FOR LEAD
 LAWRENCE BERKELEY LABORATORY (LBL) AND CROCKER NUCLEAR LABORATORY (CNL)
 Moss Landing Samples
 September 10, 11, 1974

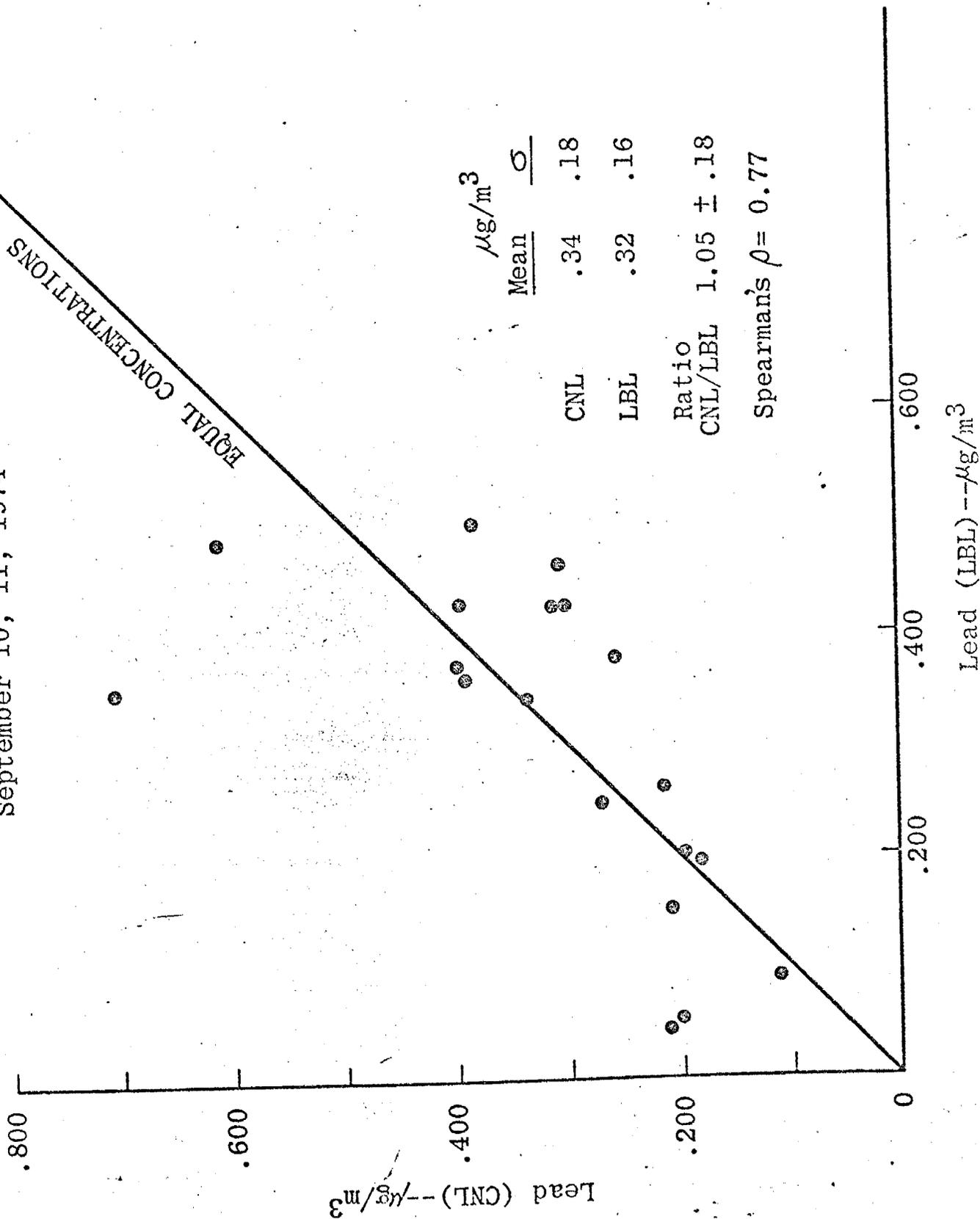


Figure 33

INTERLABORATORY COMPARISON OF X-RAY FLUORESCENCE RESULTS FOR IRON
 LAWRENCE BERKELEY LABORATORY (LBL) AND CROCKER NUCLEAR LABORATORY (CNL)
 Moss Landing Samples
 September 10, 11, 1974

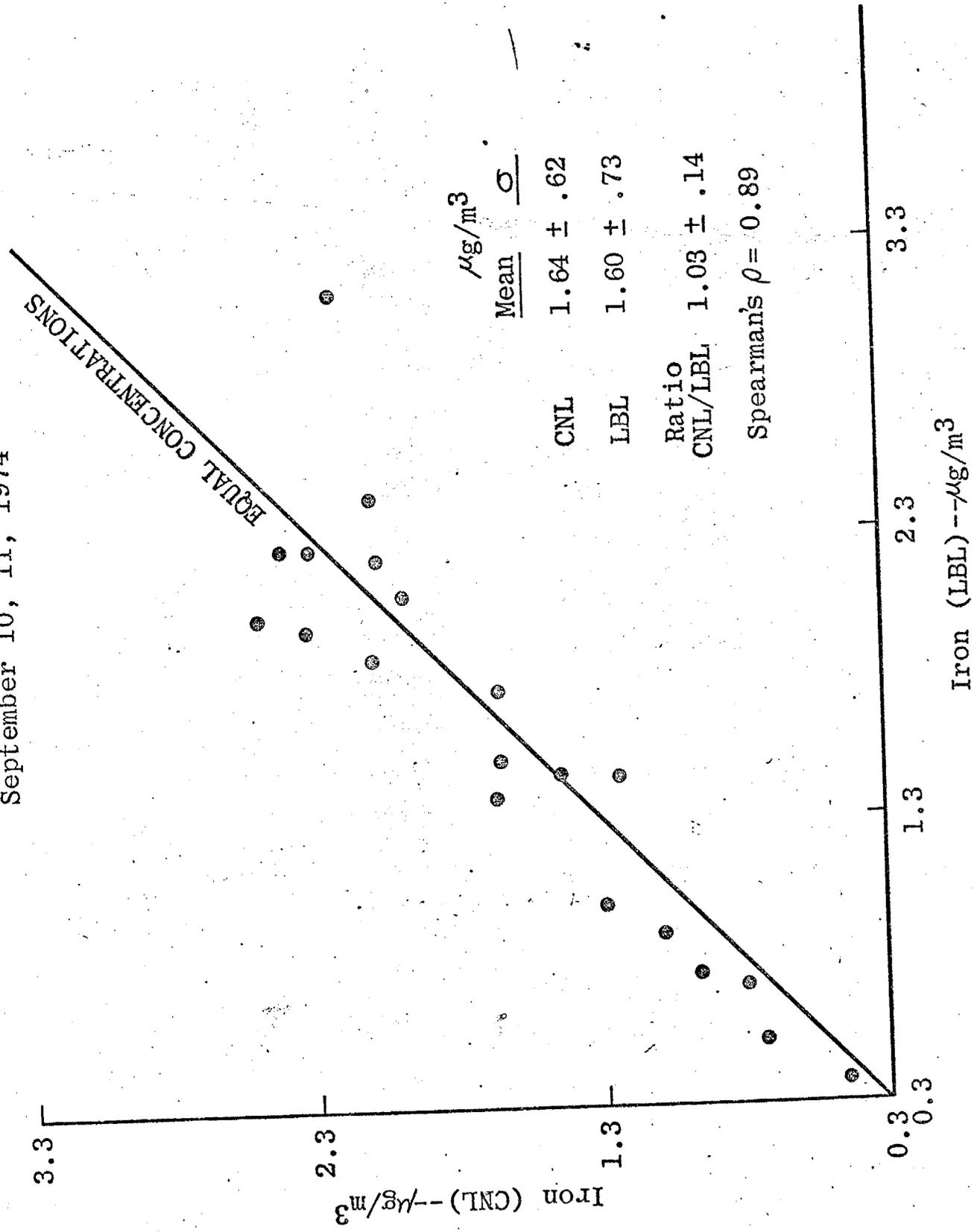


Figure 34

INTERLABORATORY COMPARISON OF X-RAY FLUORESCENCE RESULTS FOR SULFUR
 LAWRENCE BERKELEY LABORATORY (LBL) AND CROCKER NUCLEAR LABORATORY (CNL)
 Moss Landing Samples
 September 10, 11, 1974

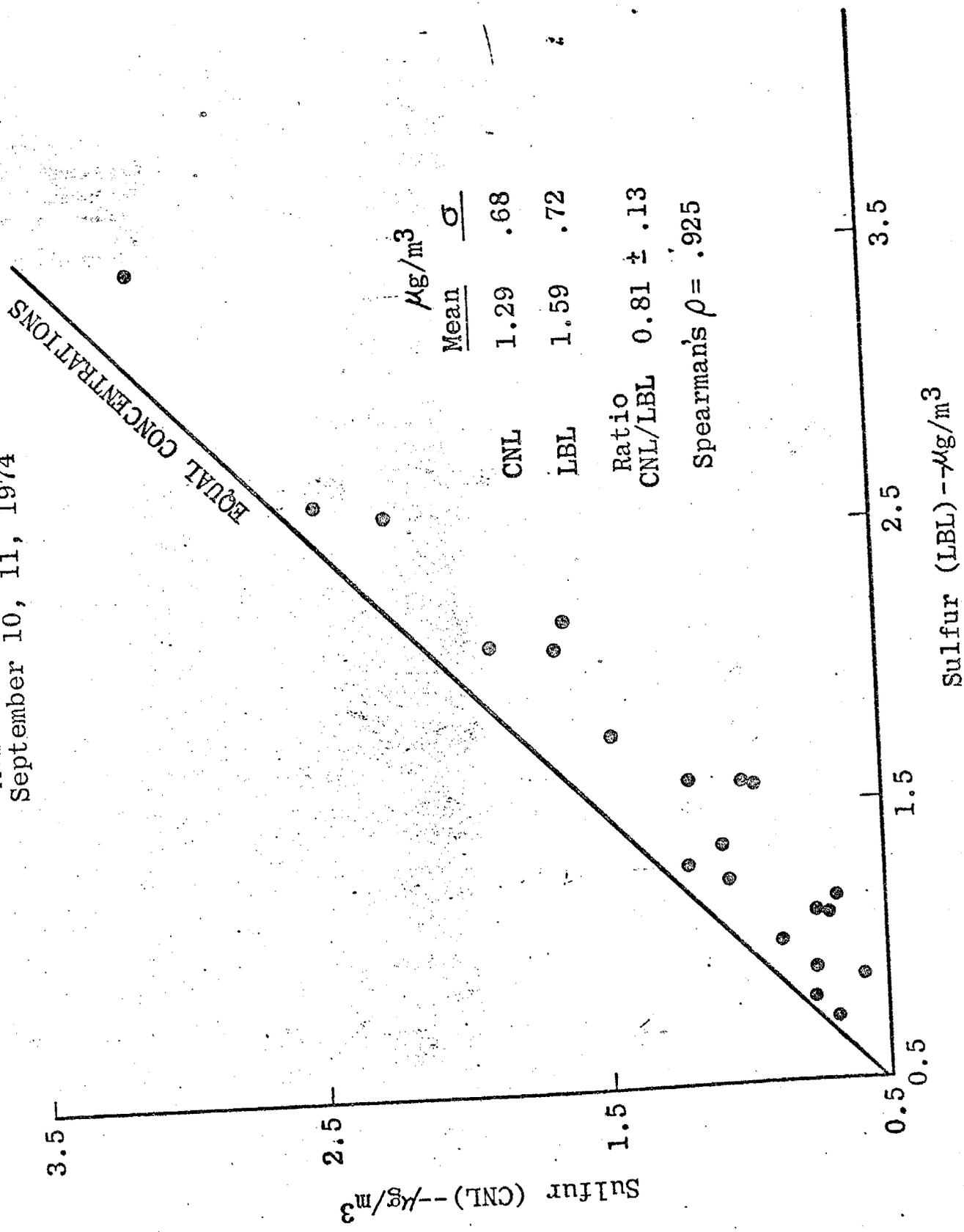


Table 9.

COMPARISON OF WET CHEMICAL SULFATE AND TOTAL SULFUR BY
 α -INDUCED X-RAY FLUORESCENCE (AIXE)

<u>Episode</u>	<u>Mean Ratio $\text{SO}_4^{=}$/AIXE S as $\text{SO}_4^{=}$</u>
A	0.920 \pm .038
B	1.07 \pm .030
C	0.940 \pm .028
D	0.971 \pm .022
F	1.15 \pm .027
G	1.26 \pm .058
H	1.31 \pm .052
I	1.45 \pm .108
J	0.884 \pm .050
Overall	1.07 \pm .013

sulfate values (as sulfur) exceeded AIXE total sulfur values by an average of 7% but, for individual episodes wet chemical results were higher by up to 45%. These findings are similar to those from the intermethod comparison done for ACHEX.

An additional perspective on intermethod comparison is obtained by comparing the results as a function of sulfate concentration. Figure 35 examines the frequency distribution of the ration of AIHL $\text{SO}_4^{=}$ to total S as $\text{SO}_4^{=}$ by AIXE for all the filters analyzed for this study. Dashed lines indicate that one or both determinations for a filter were below the limit of detection (ca. $1 \mu\text{g}/\text{m}^3$ as $\text{SO}_4^{=}$ for both methods). The results suggest an approximately Gaussian distribution about the ratio 1.0 with some positive skewness.

Figures 36-51 provide similar data for individual ranges of sulfate (taking the AIHL value to define the range). In Figure 35 ($0.5-1.0 \mu\text{g}/\text{m}^3$) all of the results are below detection limits yielding erratic ratios. Similarly in Figure 36, with values just above the limit of detection for the AIHL method, the results indicate poor agreement. At $1.5 \mu\text{g}/\text{m}^3 \text{SO}_4^{=}$ (Figure 37) the results begin to approach a symmetric distribution about the ratio 1.0. The best agreement was achieved in the range $4.5-5.0 \mu\text{g}/\text{m}^3 \text{SO}_4^{=}$ (Figure 43). Above this range results are often skewed toward higher ratios (i.e. greater apparent sulfate sulfur than total sulfur).

Based upon these results, all samples with a ratio of AIHL sulfate/AIXE S as $\text{SO}_4^{=} > 2.5$ (total of 15 or about 2% of the samples) were reanalyzed by AIXE. The results, summarized in Table 10 indicated marked improvement in agreement for the 5 heavily loaded filters ($\text{SO}_4^{=} \geq 13 \mu\text{g}/\text{m}^3$). With more lightly loaded samples ($\text{SO}_4^{=} \leq 8 \mu\text{g}/\text{m}^3$) the discrepancy usually increased. Table 9 and Figures 33 to 48 were not corrected for these changes following reanalysis.

The source of some if not all, of the problems with these samples by AIXE is thought to relate to a combination of absorption corrections for sulfur simultaneously with a similar correction for the M x-ray of lead in cases where Pb is present in relatively high concentrations. The following statement by Prof. Cahill⁸ details the problem:

"Fine aerosols (less than about 1 micron) penetrate deeply into most filter media. Soft x-rays, such as that of sulfur, are strongly absorbed passing through such filter, and therefore corrections have to be applied. One value reported for this correction for sulfur was about 30%, and these corrections are routinely done for all elements

"The problem becomes compounded when a second element is present that interferes with a primary element. This occurs with the M transitions of lead. Since lead has energetic lines, it can be

Table 10. Comparison of Wet Chemical Sulfate and AIXE S as Sulfate Before And After Reanalysis of "Outliers".

Sample ID	AIHL SO ₄ ⁼ μg/m ³	SO ₄ ⁼ /S as SO ₄ ⁼	
		Initial	After reanalysis by AIXE
5B1700TF	3.04± .46	2.53	> 3.8
5B1702TF	3.30± .50	2.91	3.24
4F1626TF	13.2 ±1.98	2.70	1.12
5F1463TF	22.7 ±3.41	2.76	0.93
7F1660TF	26.5 ±5.31	3.41	1.15
7F1661TF	33.4 ±6.67	3.14	1.43
7F1666TF	13.6 ±1.36	2.91	1.99
1G1977TF*	4.47± .67	2.81	> 6.80
3H1940TF	4.09± .61	2.53	2.13
6H2013TF	8.27± .12	2.68	3.69
8H1854TF	3.44± .52	3.64	2.51
3I2021TF	2.80± .56	2.83	1.63
3I2025TF*	3.50± .53	3.88	> 5.98
3I2026TF*	3.15± .63	0.905	< 4.27
4I2064TF	3.09± .46	3.00	1.03

*Prof. Cahill indicates large error likely in S by AIXE because of high Pb concentration.

ALL FILTERS

n = 537
L = 75

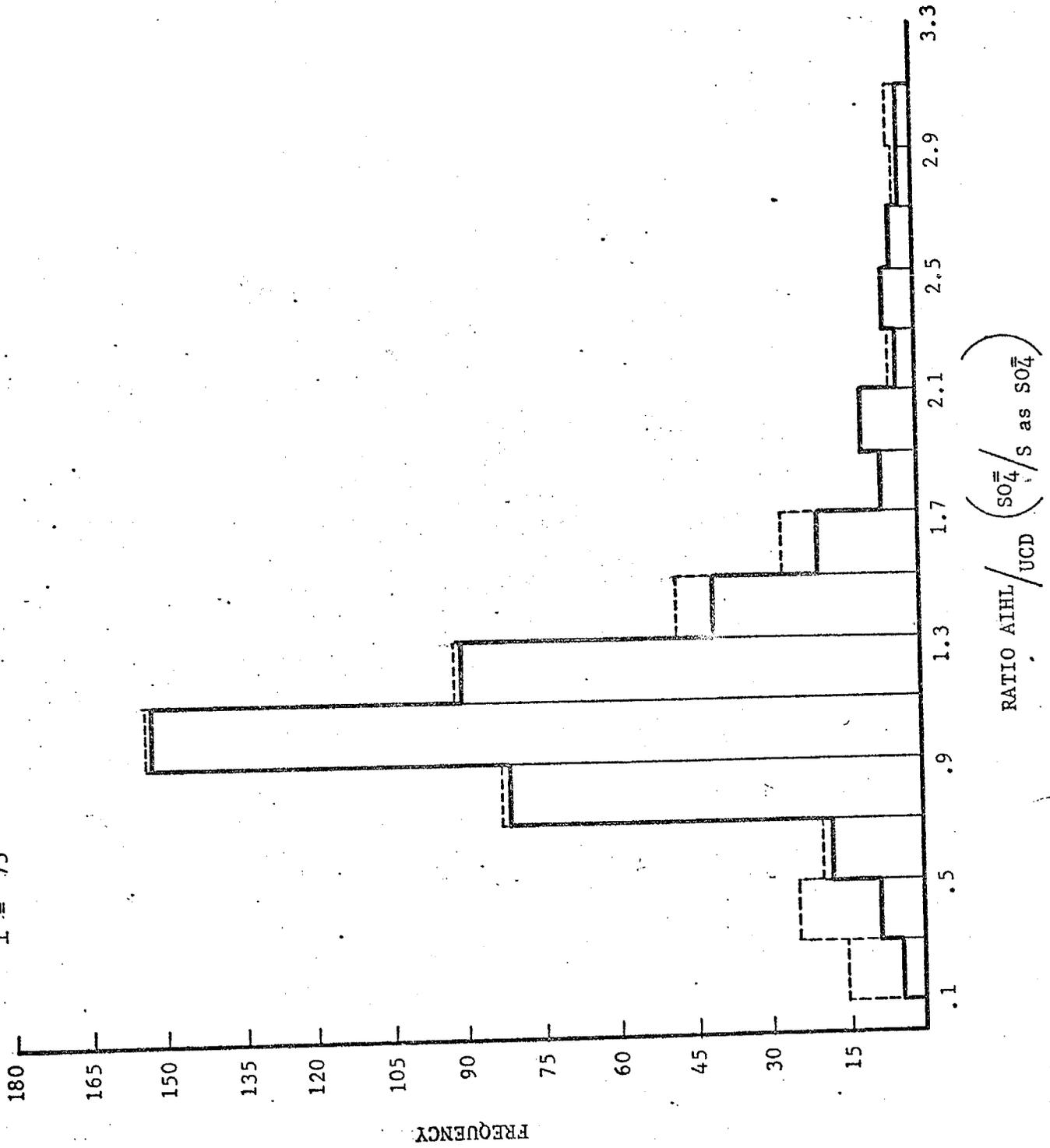


Figure 35

Range: 0.51-1.00ug/m³ SO₄⁻²

n = 23
l = 23

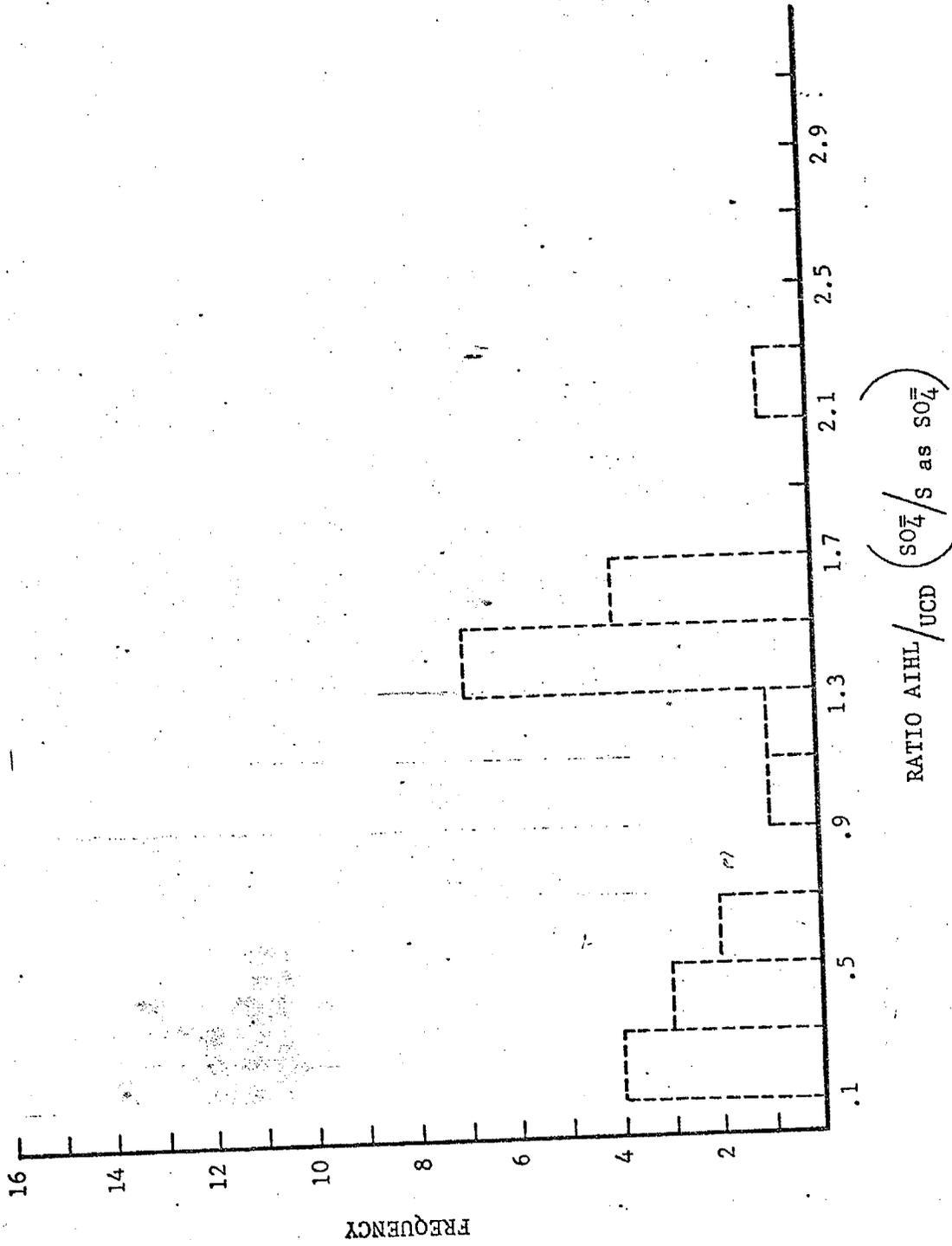


Figure 36

Range: 1.01-1.50 $\mu\text{g}/\text{m}^3$ SO_4

n = 32
l = 16

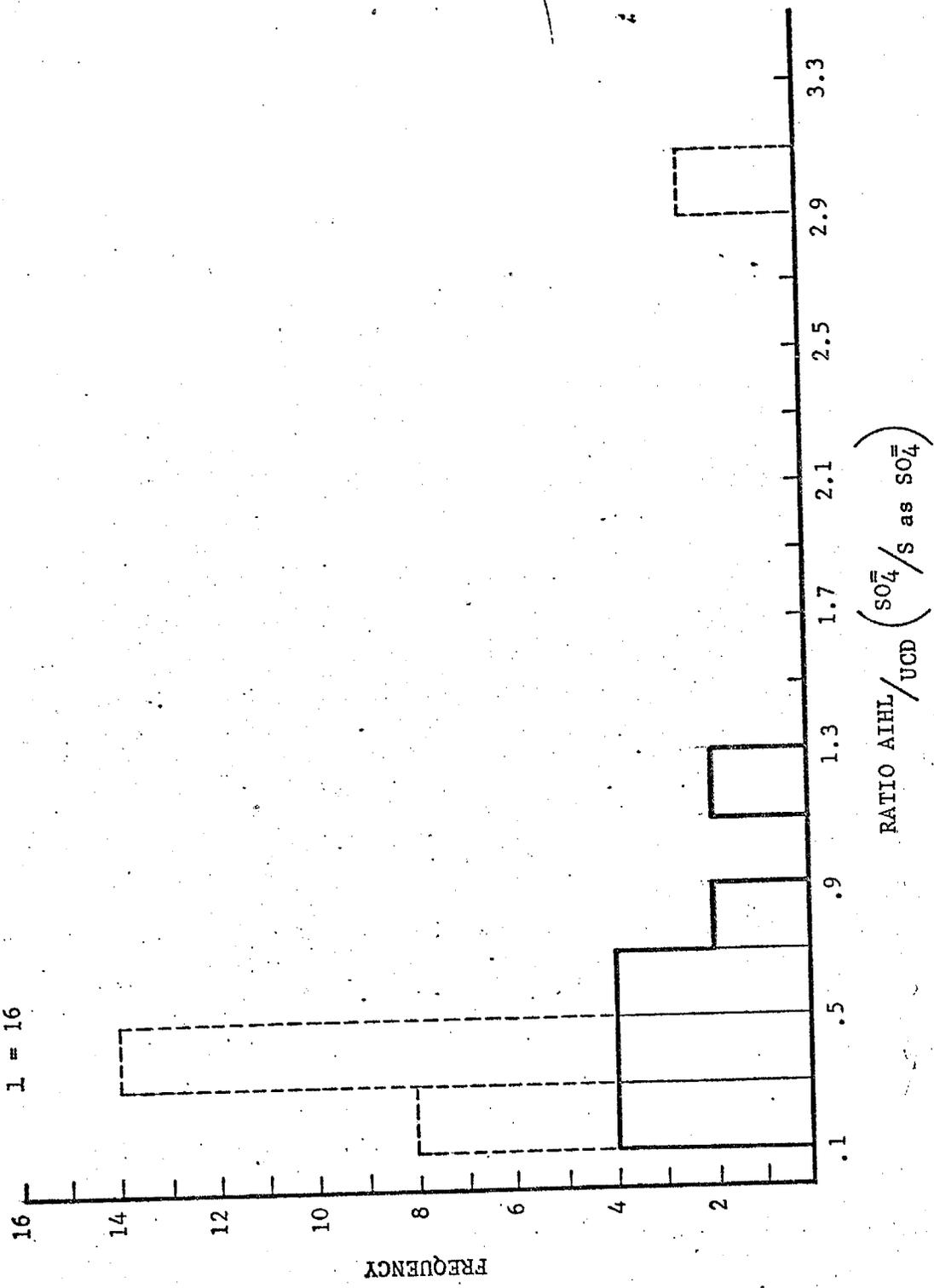


Figure 37

Range: 1.51-2.00 $\mu\text{g}/\text{m}^3 \text{SO}_4^-$

n = 32

l = 9

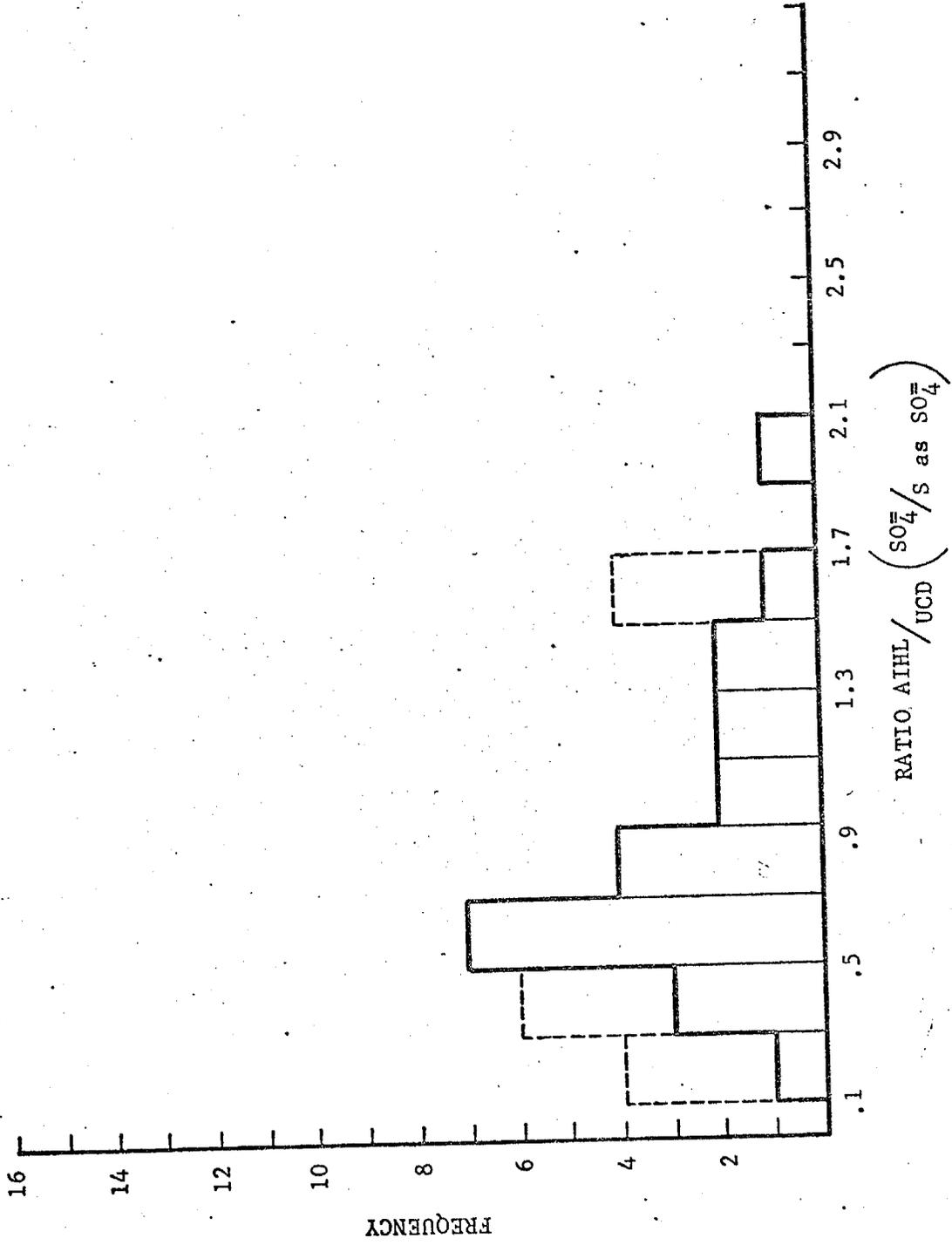


Figure 38

Range: 2.01-2.50 $\mu\text{g}/\text{m}^3 \text{SO}_4^-$

n = 32

l = 1

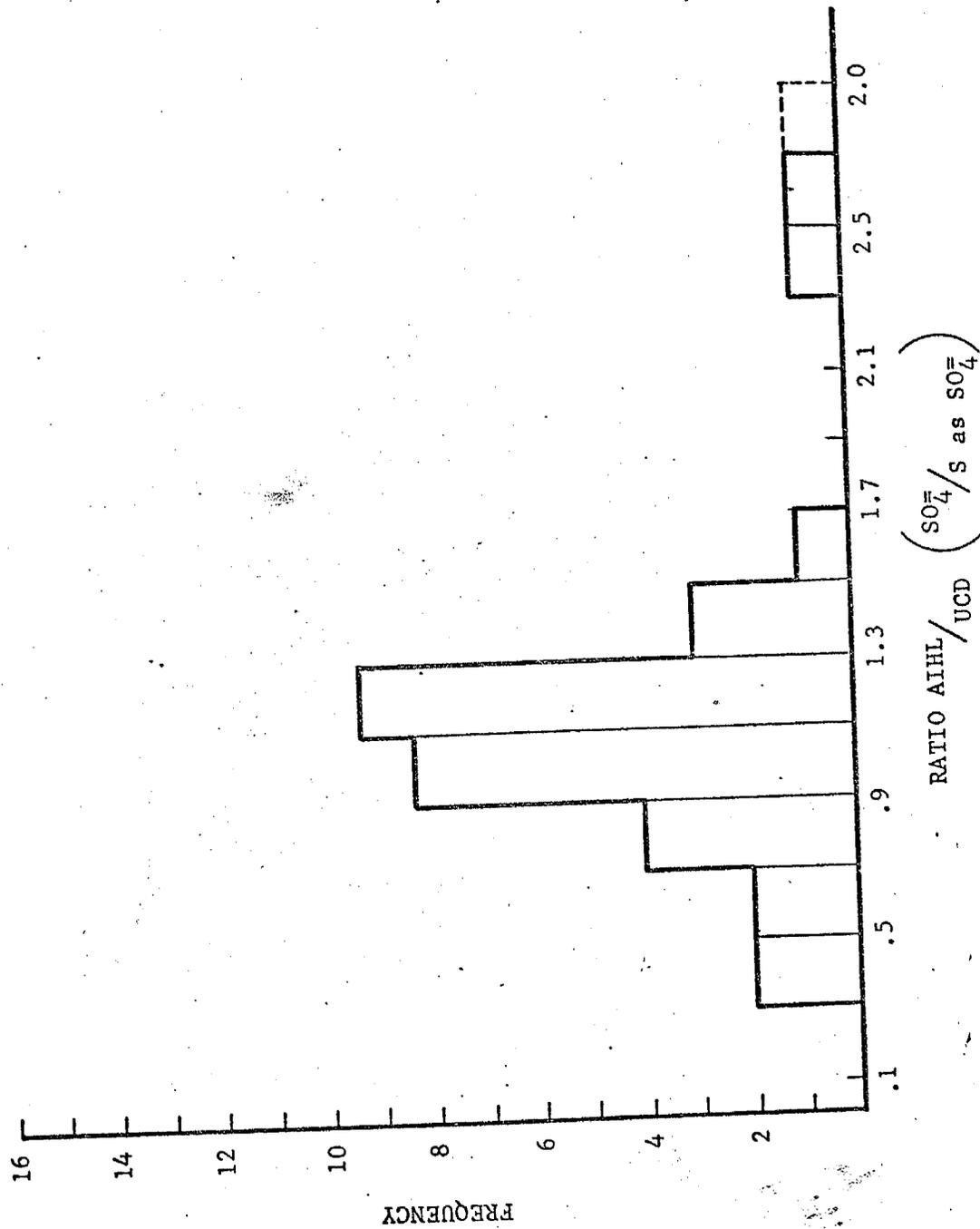


Figure 39

Range: 2.51-3.00 $\mu\text{g}/\text{m}^3\text{SO}_4^-$
n = 35

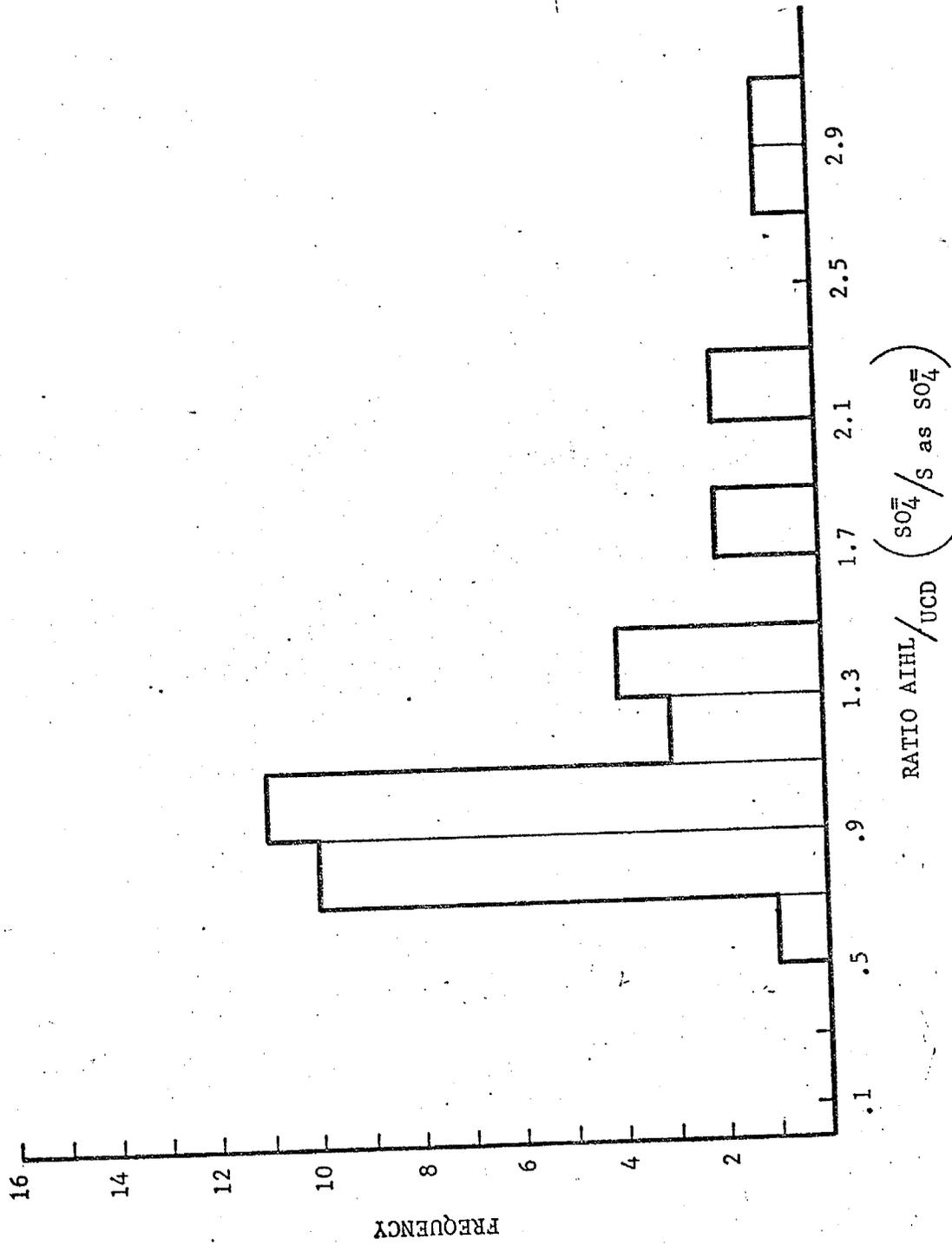


Figure 40

Range: 3.01-3.50 $\mu\text{g}/\text{m}^3$ SO_4^-

n = 29

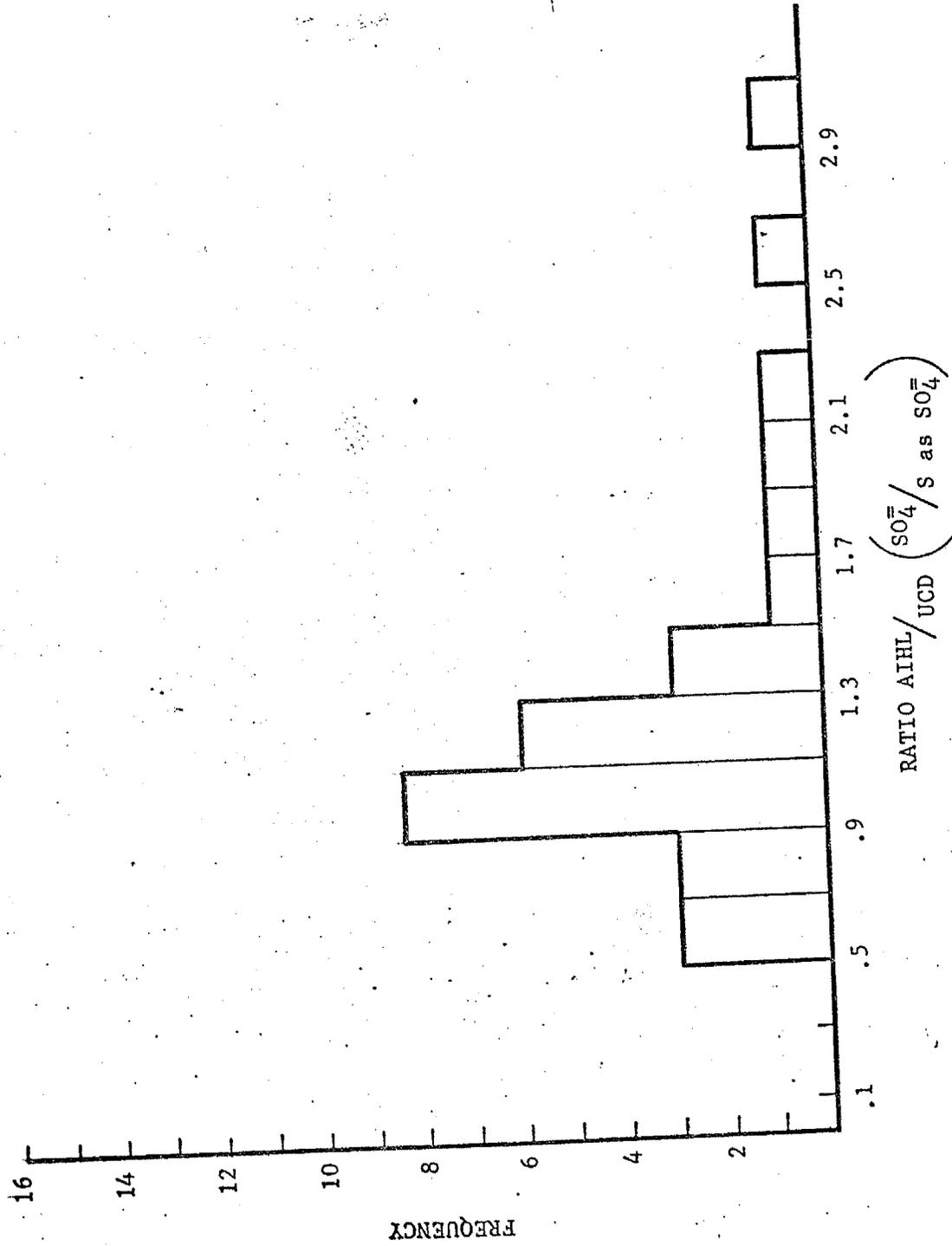


Figure 41

Range: 3.51-4.00 $\mu\text{g}/\text{m}^3 \text{SO}_4^-$

$n = 32$
 $l = 1$

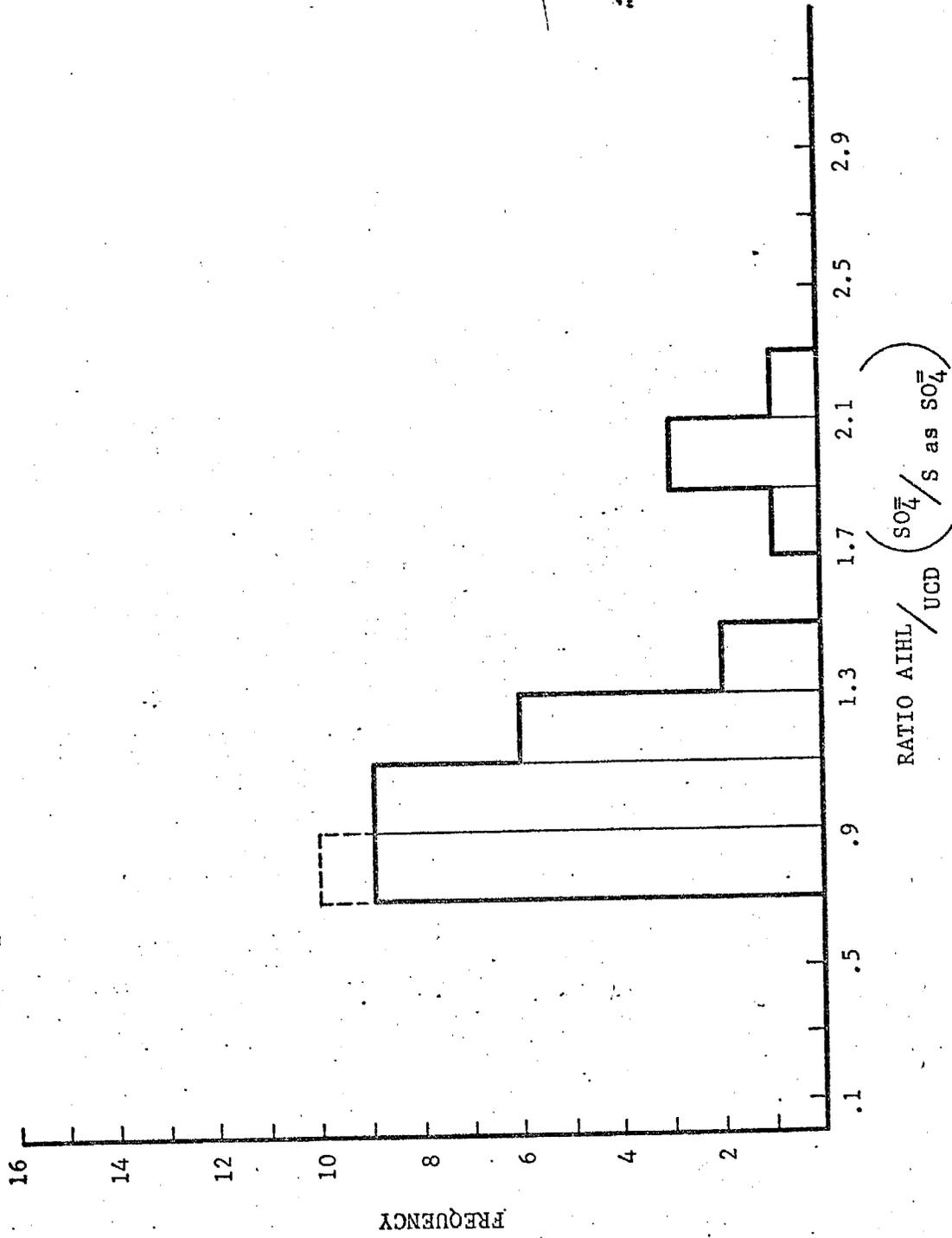


Figure 42

Range: 4-01-4.50 $\mu\text{g}/\text{m}^3 \text{SO}_4^-$

n = 42

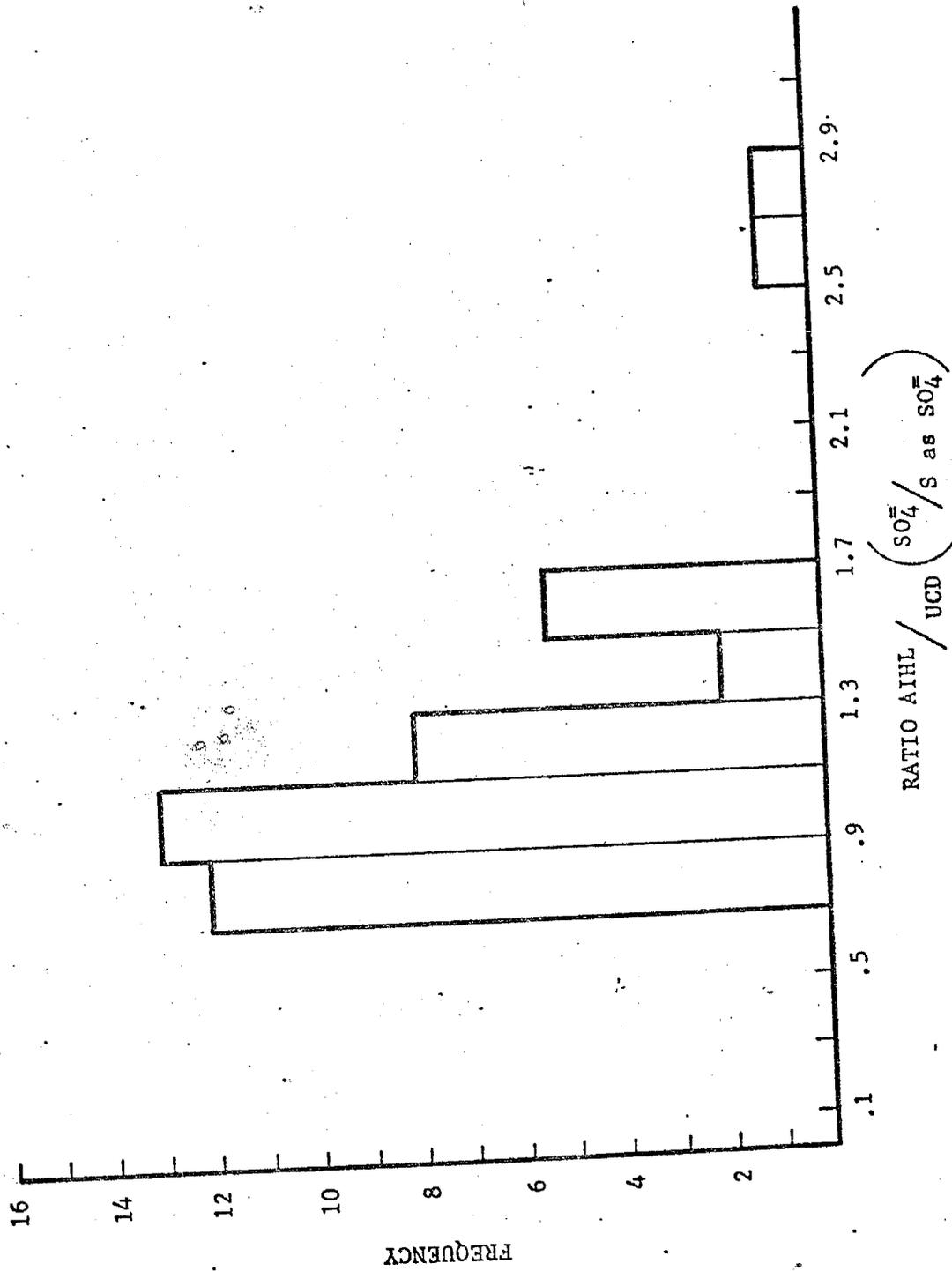


Figure 43

Range: 4.51-5.00 $\mu\text{g}/\text{m}^3 \text{SO}_4^-$

$n = 28$

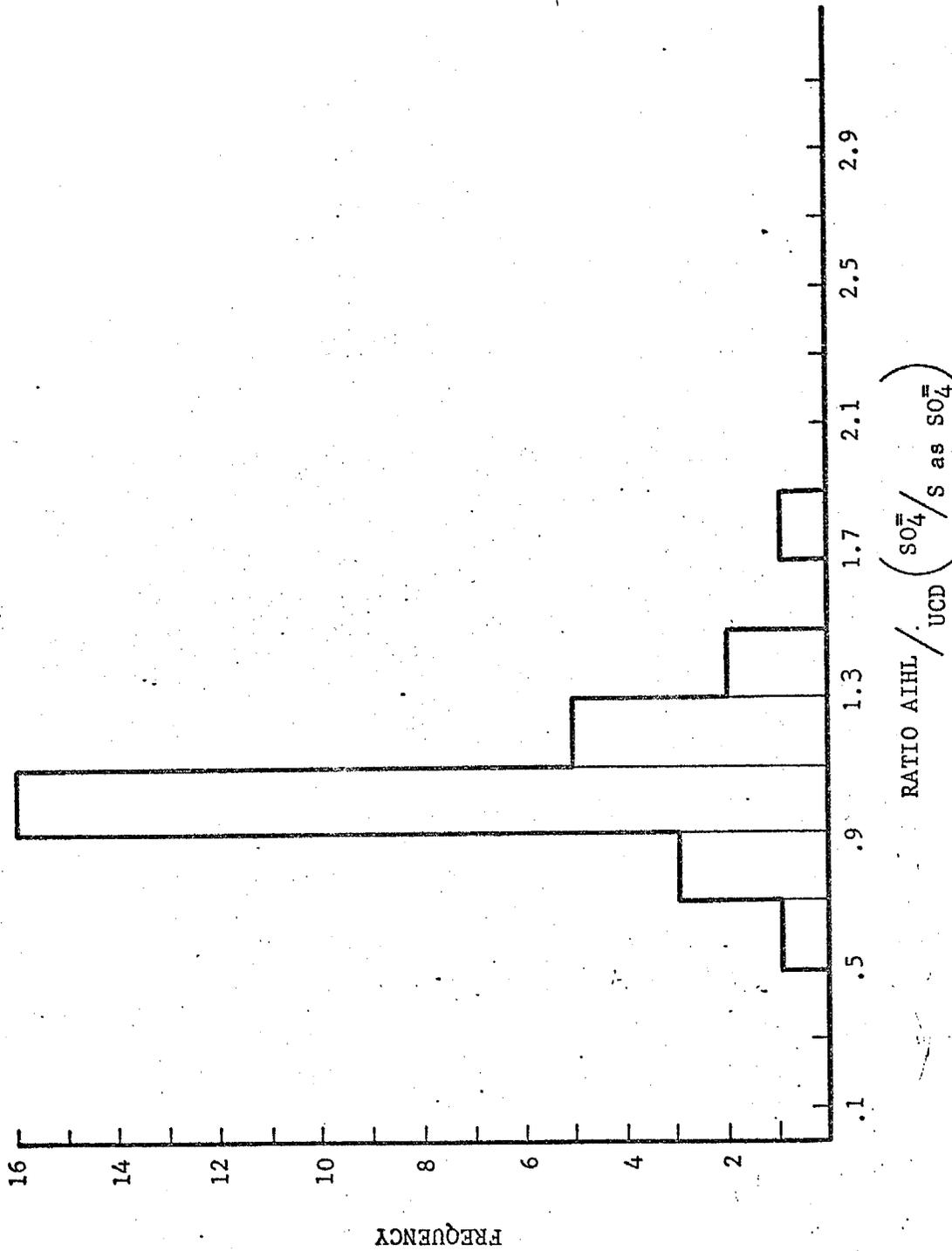


Figure 44

Range: 5.01-6.00 $\mu\text{g}/\text{m}^3 \text{SO}_4^-$

n = 35

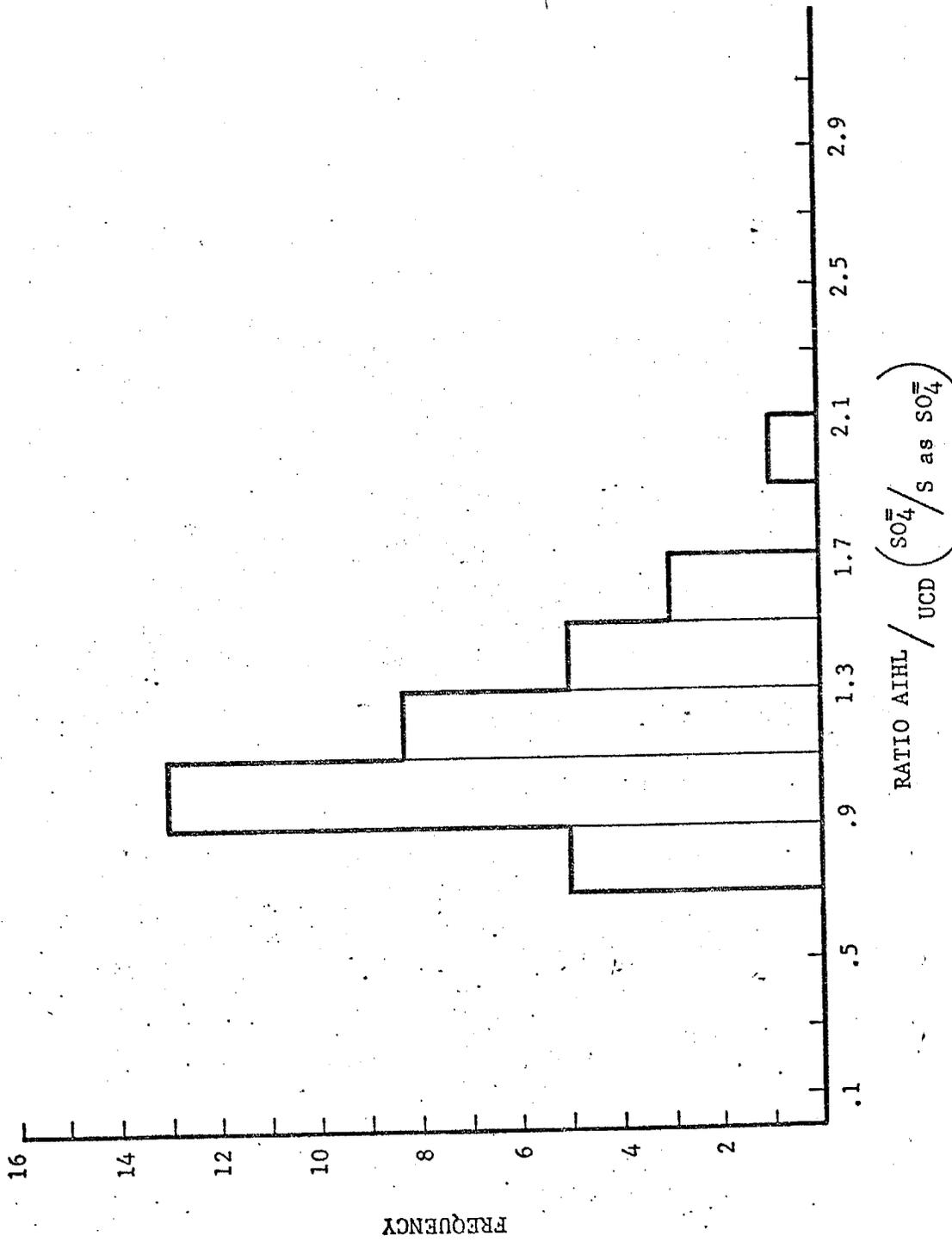


Figure 45

Range: 6.01-7.50 $\mu\text{g}/\text{m}^3\text{SO}_4^-$

n = 31

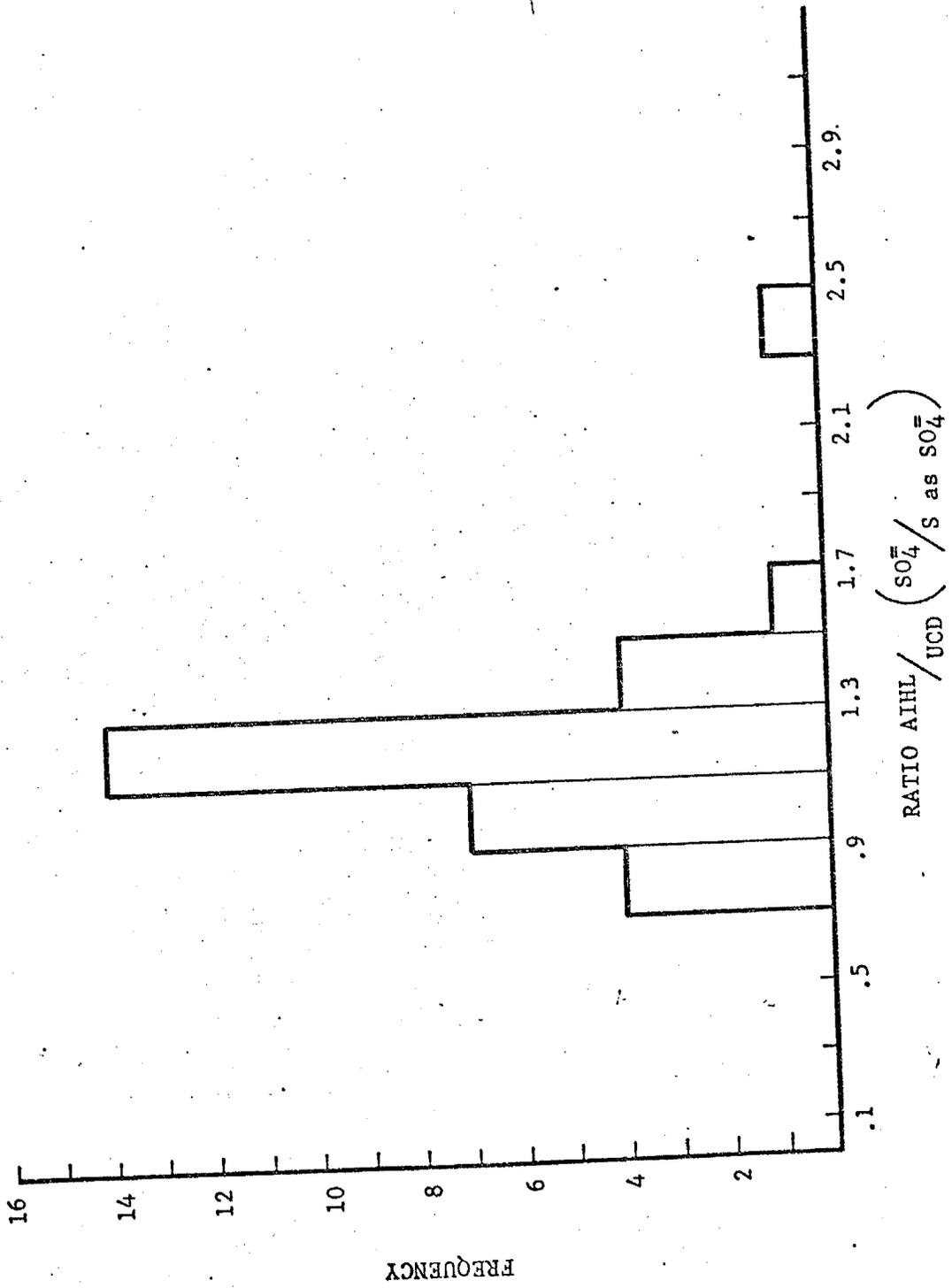


Figure 46

Range: 7.51-9.00 $\mu\text{g}/\text{m}^3 \text{SO}_4^-$

n = 35

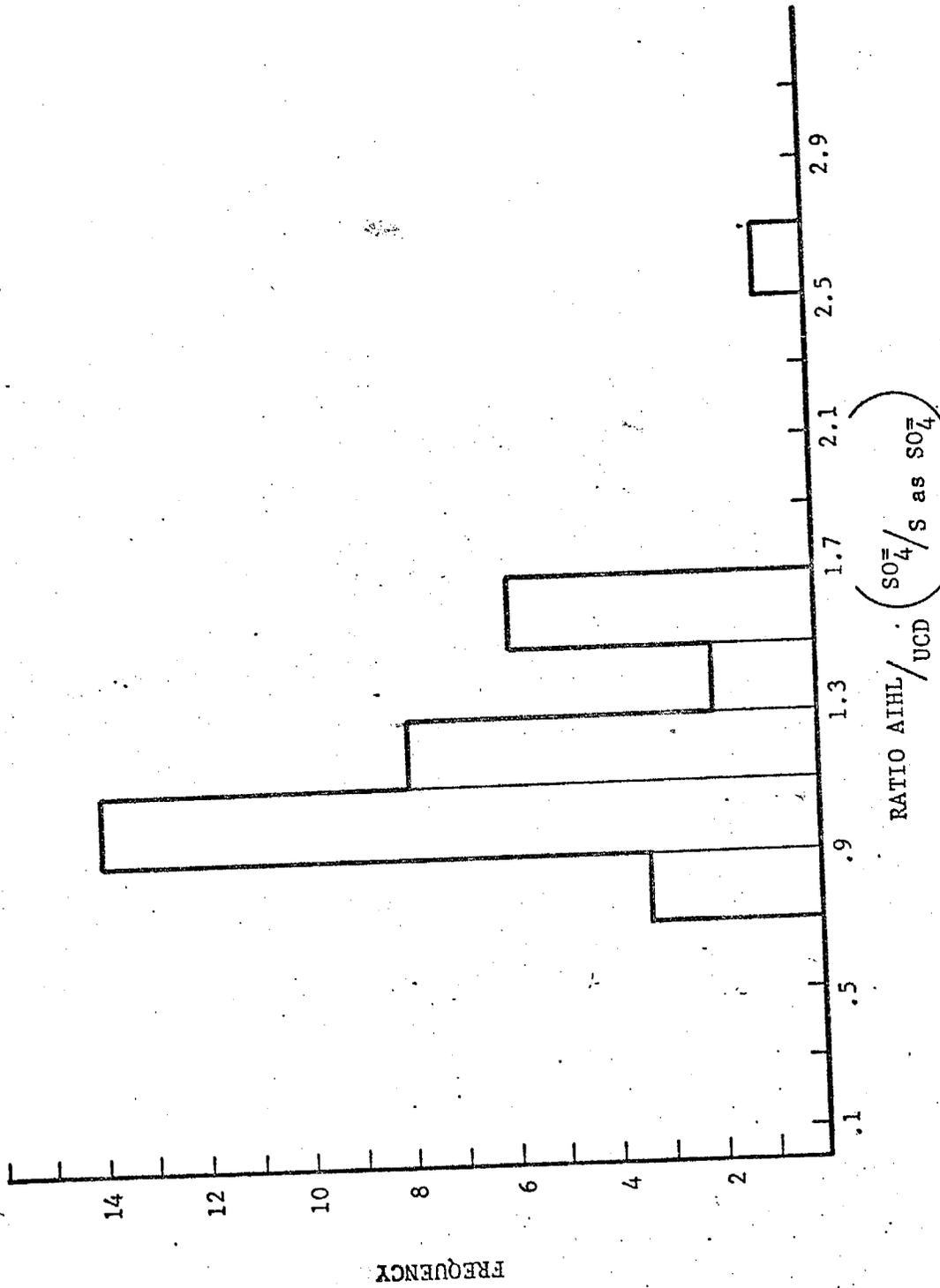


Figure 47

Range: 9.01-13.00 $\mu\text{g}/\text{m}^3 \text{SO}_4^-$

n = 32

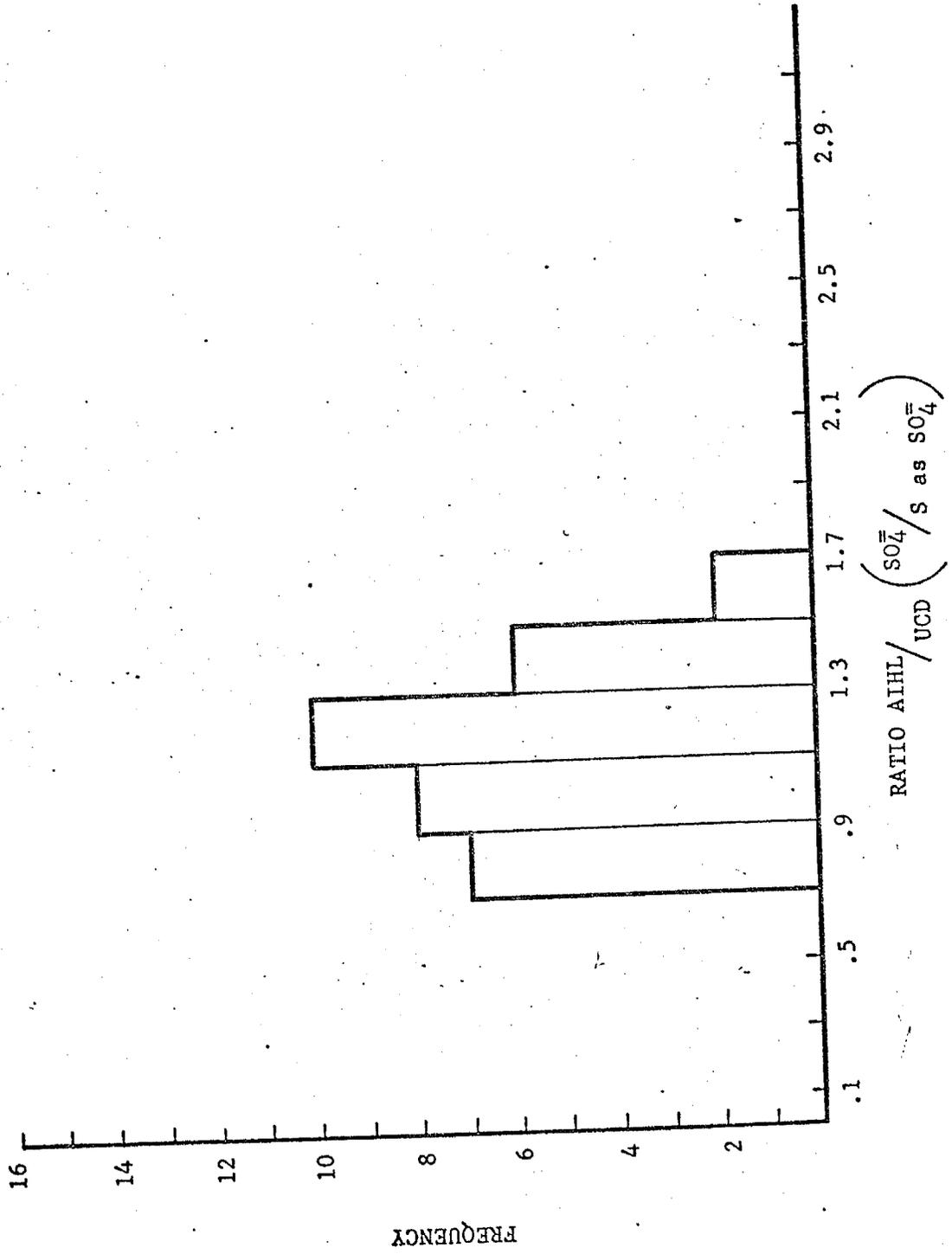


Figure 48

Range: 13.01-22.50 $\mu\text{g}/\text{m}^3 \text{SO}_4$

n = 32

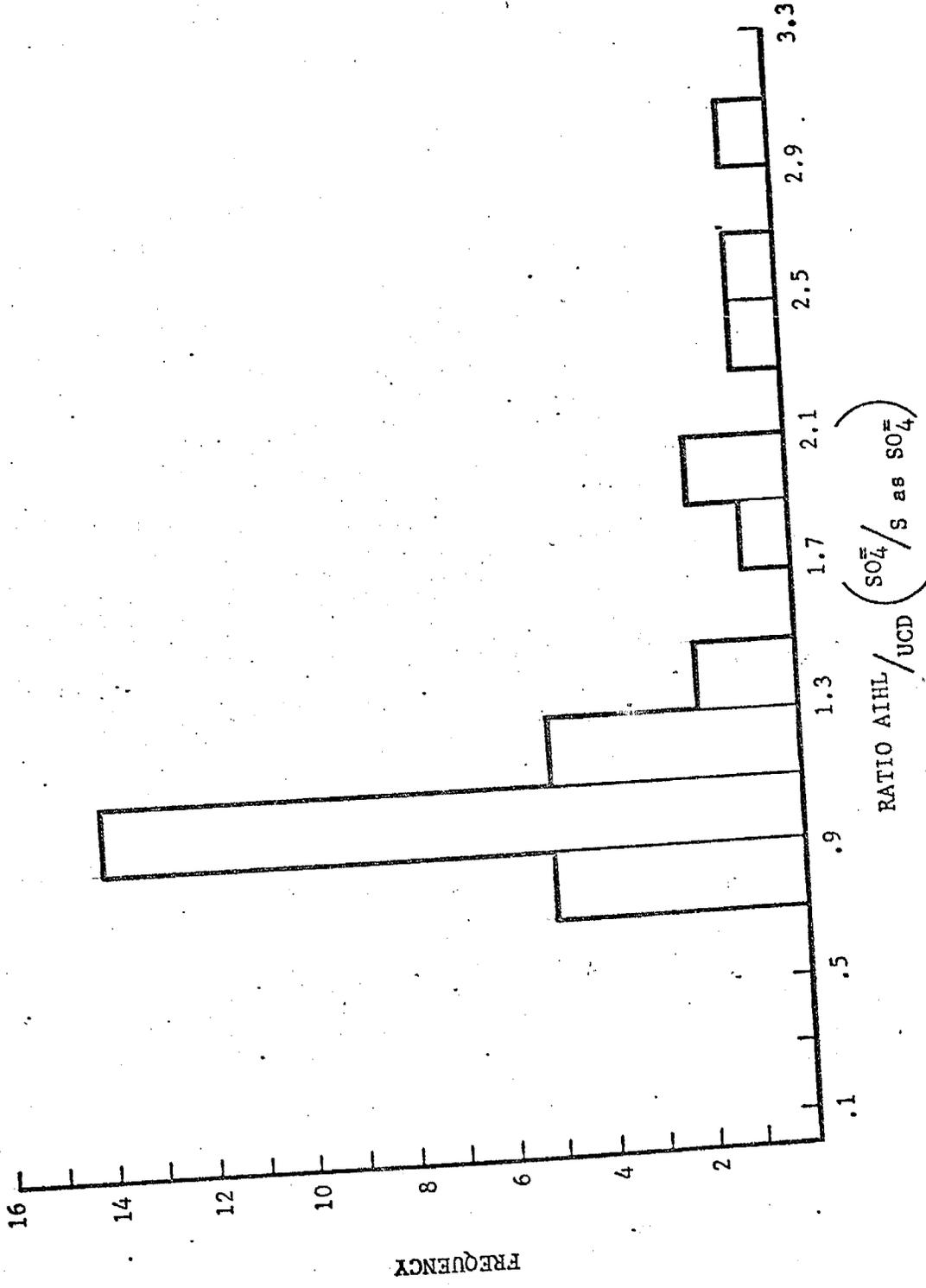


Figure 49

Range: 22.51-29.50 $\mu\text{g}/\text{m}^3 \text{SO}_4^-$

n = 31

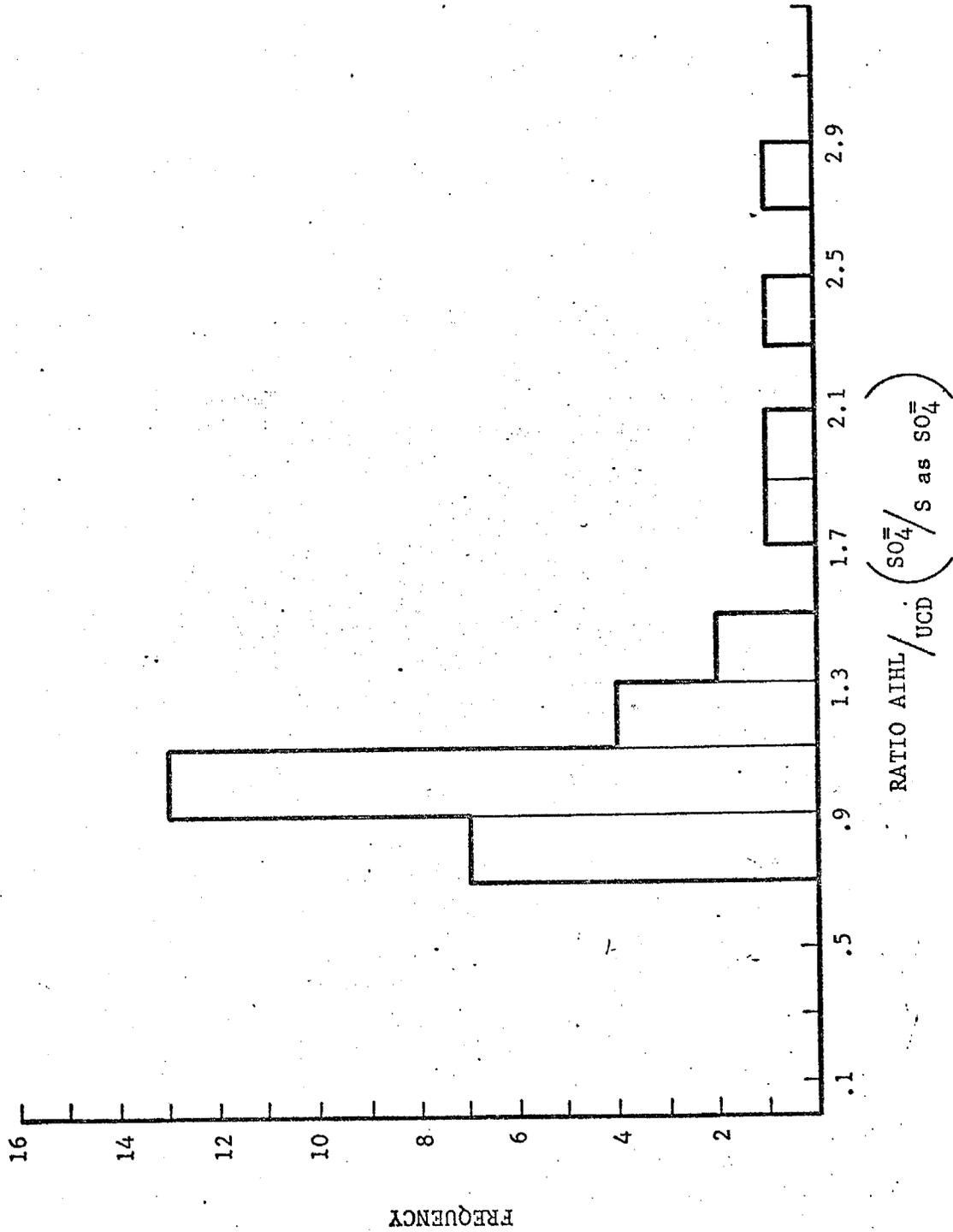


Figure 50

Range: 29.51-40.00 $\mu\text{g}/\text{m}^3 \text{SO}_4^-$

n = 25

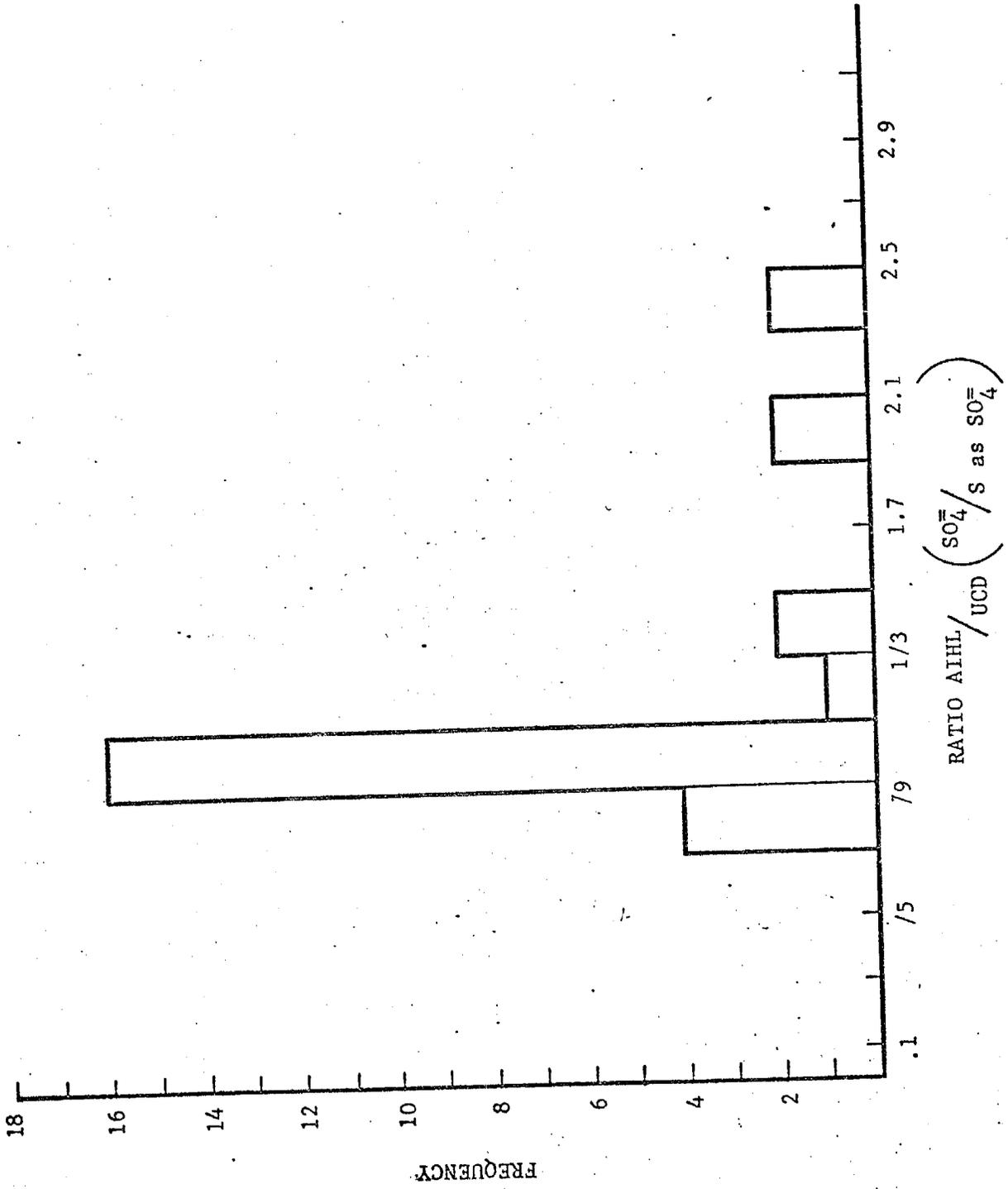


Figure 51

measured in such filters with very small uncertainties due to matrix corrections. However, the M x-ray has the same penetration correction as sulfur, and these must be applied to these lead x-rays before the interference can be resolved

"The problem becomes even more troublesome due to the fact that, while lead occurs almost entirely in very fine particles at all sites away from smelters and industrial sources, sulfur has been found in two size ranges: one similar to that of lead, and one much larger, around 1 micron. These can vary independently from site to site and day to day. Thus, the correction for the Pb/S interference depends quite strongly on how deeply the sulfur penetrates into the filter, which is a function of the size. The same statement goes for the lead, although the uncertainty in size is less. Therefore, with large amounts of lead present on moderately thick (4 mg/cm^2) filters (except for Nuclepore), corrections for S are quite uncertain, and must be viewed with caution."

In addition to the problems detailed above, the possibility of volatilization of the sulfur-containing species in the vacuum during AIXE must be considered. Filter samples undergo substantial heating during α -particle bombardment. The lower AIXE results on re-analysis of the lightly loaded samples may be indicative of such losses.

D. Wet Chemical Analyses

Sulfate was determined by the AIHL microchemical method.⁹ This method was shown to have a coefficient of variation of $< 5\%$ with atmospheric samples. Accuracy with optimal concentrations of sulfate was established to be within 4% by standard additions to extracts from atmospheric samples.¹⁰

Nitrate was determined with the Technicon Industrial Method 100-70W. The reproducibility of this method was found to be within 1% .¹¹

V. Summary and Conclusions

As planned, sampling of the plume from the Moss Landing power plant was conducted during a period of minimal photochemical oxidant. It was determined that ground level sulfate concentrations were not enhanced above background when natural gas was the power plant fuel, consistent with the negligible sulfur content of this fuel. When the Moss Landing plant burned fuel oil containing 0.4% sulfur, a statistically significant enhancement of 1.6-2.3 $\mu\text{g}/\text{m}^3$ sulfate within the plume touchdown region was observed.

In Southern California sampling was generally done under light smog conditions limiting the potential for studying oxidant-induced sulfate formation. Nevertheless two of the sampling days exhibited high sulfate levels. For all sampling days, late morning sulfate concentrations in the Fullerton area were found to correlate with the function $1/1-\text{Rel. Humidity}$ using early morning humidity data from Long Beach airport. This is consistent with a formation mechanism involving oxidation in suspended water droplets or water absorbed on other particulate matter. To our knowledge this is the first such correlation reported for the So. Coast Basin.

No significant difference in sulfate levels inside and outside of the labeled plume could be detected when ground level sulfate concentrations were high ($> 30 \mu\text{g}/\text{m}^3$). However when background levels were low ($< 10 \mu\text{g}/\text{m}^3$), for one of the two such periods examined in detail, a statistically significant enhancement in sulfate of 3-5 $\mu\text{g}/\text{m}^3$ was found, ascribable to the Haynes-Edison plume.

Nitrate levels at both the Moss Landing and the Southern California ground level sampling sites displayed no apparent relationship to the power plant plume.

Employing airplane-collected samples, plume sulfate concentrations, with coefficients of variation ranging from 13 to 75%, were obtained employing a flash vaporization-flame photometric analytical technique. The large C.V. values in some cases reflected primarily the high blank values of the filter medium employed, acid-washed Gelman A glass fiber.*

The observed sulfate levels ranged from < 1.1 to $14.9 \mu\text{g}/\text{m}^3$. Since aerial sampling continued both within and outside the plume it was necessary to correct the observed sulfate levels to plume concentrations. The present data appear insufficient to permit this calculation. A procedure was detailed for calculating the percent SO_2 conversion to SO_4 in the plume

*Subsequent to the field work for this program other filter media have been evaluated which should permit substantial improvement in analytical precision and lower limits of detection for sulfate for future programs.

which should be useful to future studies. Such studies would be greatly assisted by particulate sampling devices which could operate only while in the labelled plume and by a separate monitoring of aerial sulfate levels outside the plume.

Because of the inherently greater error associated with plume sampling and analysis relative to ground level studies it is doubtful whether such plume sulfate $-SO_2-SF_6$ results may be used to find differences in the SO_2 conversion rate within plumes between clean and polluted air. However, it may be useful to repeat this experiment in Southern California during the summer months since the present study was hampered by the lack of photochemical oxidant on the days sampled.

Finally, other available short term sulfate data such as those from ACHEX should be re-evaluated for correlations with relative humidity as detailed herein.

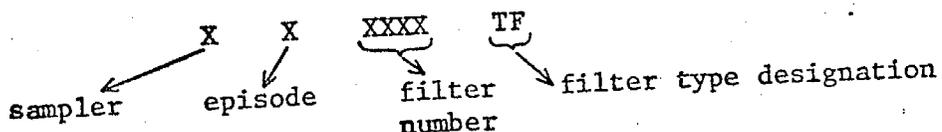
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11. B. R. Appel and J. J. Wesolowski, "Impact of Motor Vehicle Exhaust Catalysts on Air Quality," Final Report, Contract No. ARB 3-985.

Appendix A

Filter Coding

All filters are coded with an eight digit (or letter) code. Those for ground level samples are as follows:



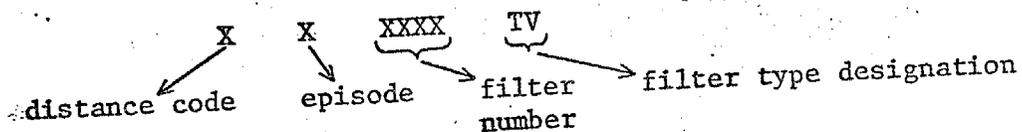
Sampler - refers to the sequential filter sampler numbered 0-9. The 10 samplers are coded in increasing number running from left to right (when viewed looking east from the stacks) and with increasing distance from the stacks.

Episode - coded consecutively from A-J with one day's sampling termed an episode.

Filter number - for AIHL use.

TF - indicates a total filter, Gelman GA-1 cellulose acetate membrane filter (5 μ m pore size), 47 mm diameter.

For aerial samples, filter identification was as follows:



Distance Code - X, Y, Z refer to successively greater sampling distances from the stack. The actual distance corresponding to X, Y or Z varied from episode to episode and supplementary information is necessary for interpretation.

Episode - Episodes were coded successively A through J. Episodes A-C refer to sampling of the Moss Landing plume and D-J, the Haynes and/or Edison plumes.

Filter Type - "TV" refers to a total filter, Gelman A glass fiber, 25 mm diameter. The designation "TVB" indicates a backup filter used for blank correction of the sulfate collected on the front filter.

Appendix B

The analyses of Sulfate by Flash Vaporization and Flame Photometric Detection (The Roberts-Friedlander Technique)

Introduction

The determination of particulate sulfate usually involves trapping of the particles on a filter and subsequent analysis. For analyzing these sulfates, a number of methods are available. Listed below are four methods in current use along with their approximate working ranges.

<u>Procedure</u>	<u>Approximate Working Range ($\mu\text{g}/\text{ml}$)</u>
1. BaCl_2 Turbidimetric	10-100
2. Methylthymol Blue	6-60
3. Ba-Thorin Exchange Reaction (Brosset)	2-12
4. Ba-Dinitrosulfanazo III Exchange Reaction (AIHL Micro)	6-15

To collect sufficient atmospheric sulfate for analysis by any of these techniques requires that large volumes (e.g. $> 10 \text{ m}^3$) of air must be sampled. At ground level sampling sites, the requisite volumes can be collected by large volume rates and/or long term sampling. For studying sulfate in elevated plumes, however, the samplers are generally installed in airplanes and helicopters. Due to the speed of these vehicles, the residence time in the plume is extremely short (seconds or minutes) and the sampling rates relatively low due to power limitations in the aircraft. For example if the airplane collects a one m^3 air sample containing $5 \mu\text{g}/\text{m}^3$ sulfate and the resulting filter is extracted in 5 ml of water, the sulfate concentration is $1 \mu\text{g}/\text{ml}$. This is below the useful working ranges of the wet chemical methods in current use.

While extractions in smaller volumes of water may be useful, many samples will still be below the range of reliable quantitation. Accordingly a new concept providing improved analytical sensitivity was clearly needed.

Such a technique was developed by P. Roberts and S.K. Friedlander relying on the flame photometric detector (FPD) for the improved sensitivity (limit of detection $5-10 \text{ ng SO}_4^{=}$).^{*} Introduction of particle phase sulfates into the FPD was accomplished by flash heating of the sample, still supported on a glass fiber filter. A recent modification of this procedure by J. D.

^{*}P. Roberts, Ph.D. Thesis, Calif. Inst. of Tech., 1974.

Husar et al* employed aqueous extracts of the filter samples, thereby eliminating possible high temperature interactions of sulfate with the filter or other aerosol constituents. The Roberts-Friedlander procedure as modified by Husar was technique employed for analysis of plume sulfate samples collected in the present study.

In brief, 1 inch disc filter samples were extracted in one ml of water. Aliquots of the sample were placed on a metal boat and dried. The dried residue was then volatilized by a capacitor discharge through the boat which momentarily raised the boat temperature to red heat ($\sim 1100^{\circ}\text{C}$). Sulfur in the gaseous decomposition products was swept into a flame photometric sulfur analyzer and detected.

Apparatus

The sulfate analysis system used, shown schematically in Figure B-1, consisted of a flash vaporization unit, flame photometric sulfur analyzer, electronic integrator and strip chart recorder. The vaporization unit (Figure B-2) included the vaporizer vessel, power supply and a source of clean (charcoal-soda lime filtered) air.

The design of the vaporizer unit strongly influences the utility of the system. Several modifications were tried before settling on that shown in Figure B-3. This unit, designed to minimize loss of sulfate, was fabricated of quartz (upper shell) and brass (lower shell). The sample container for flash heating the sample was a tungsten boat (Ernst Fullam #1209) commonly used for vacuum depositing metal coatings on electron microscope specimens.

To increase sensitivity and system response, the effective vaporizer volume was reduced from the 80 cm^3 of the entire vessel to about 4 cm^3 using a quartz cone inverted over the boat and an axially adjustable quartz cup under the boat. Thus all of the vaporized sample entered the cone and was not dispersed into the larger volume. This is the same concept employed by Husar et al.

The vaporizer power supply consisted of two supplies, one for the preliminary heating and drying the sample (AC) and one for the flash vaporization of the sample (DC). The AC power was furnished by a variable (0 to 140 V) AC auto transformer. It was empirically determined that the application of 3.70 VAC to the tungsten boat was sufficient to dry $5\text{ }\mu\text{l}$ of aqueous sample in 12 ± 1 sec without significant loss ($< 2\%$) of sulfate. The power supply for the vaporization consisted of a bank of capacitors (total capacitance = 0.58 F). The capacitors were charged by a 0 to 15 V (0 to 0.5 A) adjustable DC power supply (Heath SP-18A). A 3-1/2 digit digital multimeter (Fluke 8000A) was used to monitor both the applied AC (for drying) and DC

*J. D. Husar, R. B. Husar and P. K. Stubits, Anal. Chem. 47 2062 (1975).

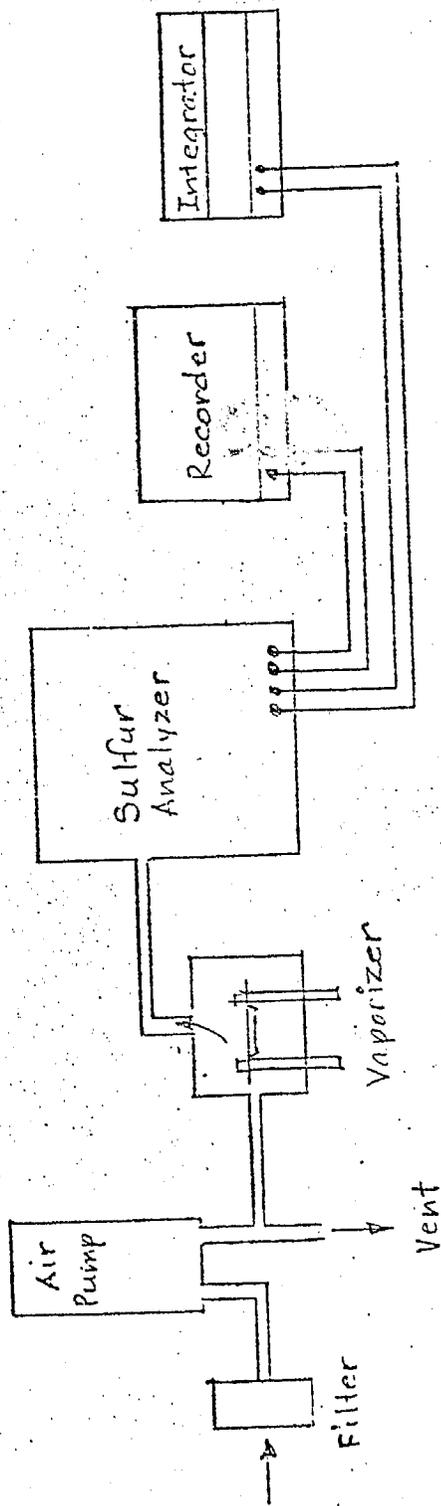


Figure B1

Block Diagram - Sulfate Analysis System

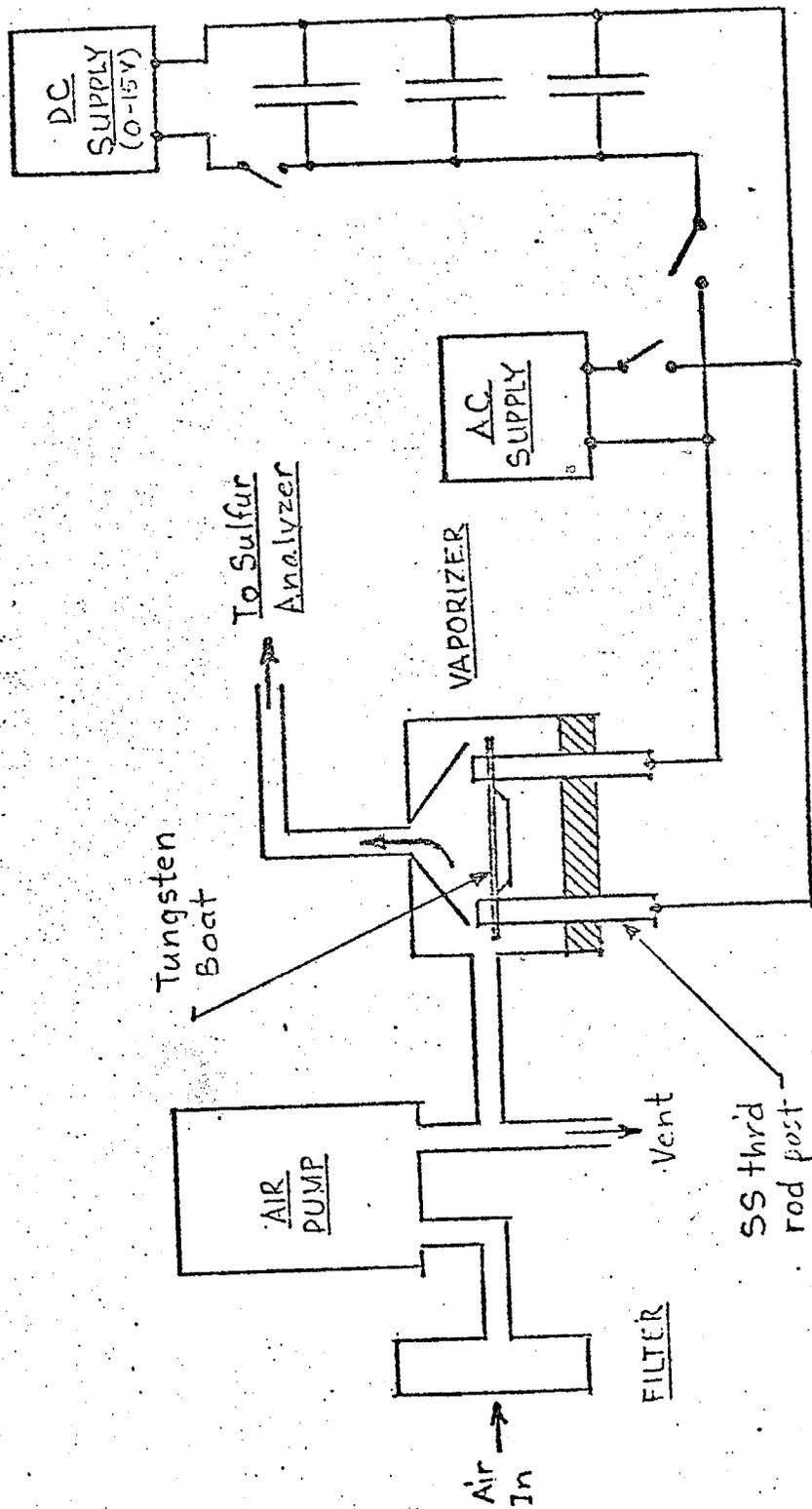


Figure B2
Schematic - Vaporization System

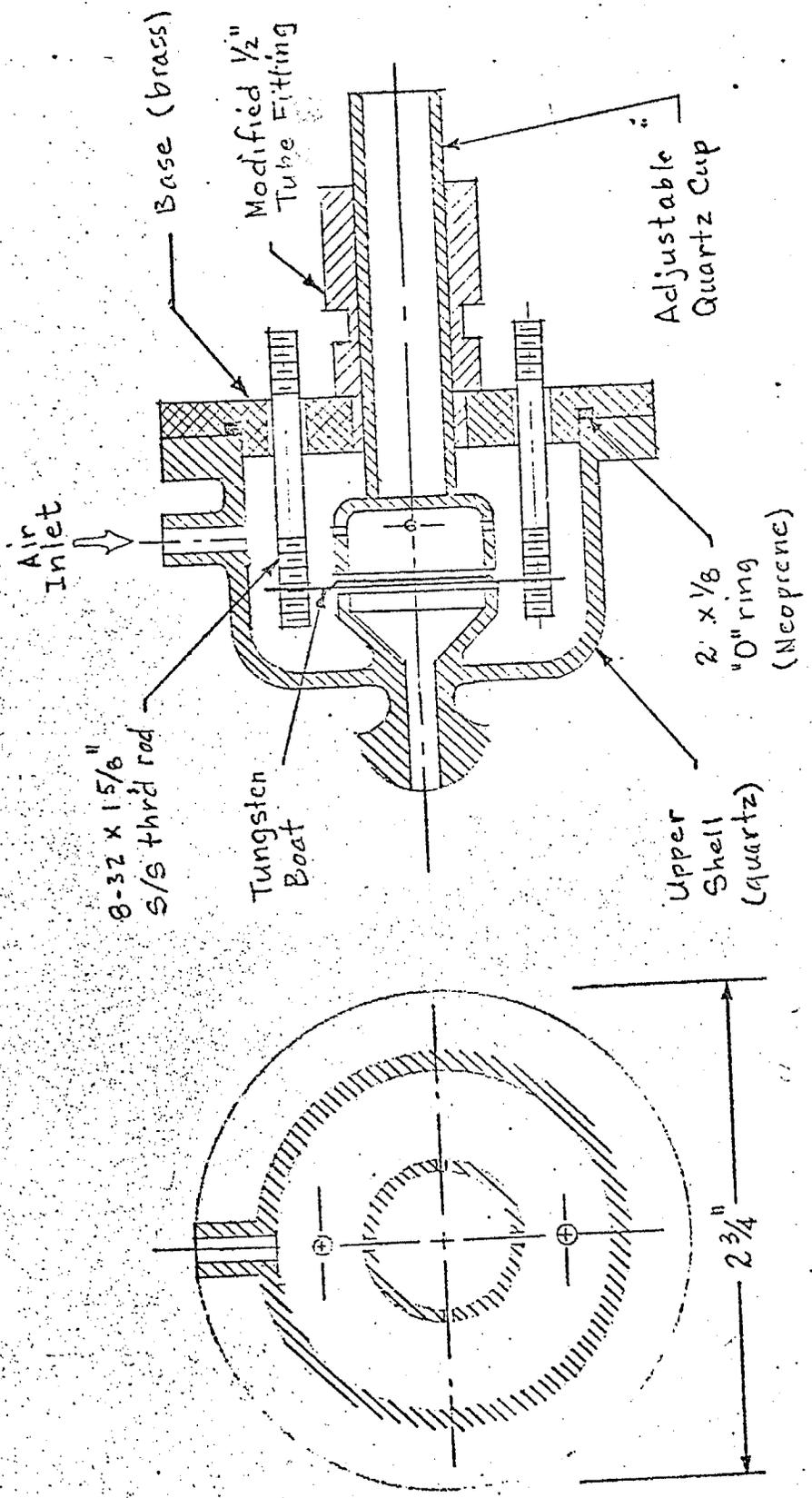


Figure B3
 Details of Vaporization Assembly

(vaporization) voltages. At maximum charging current; (i.e. 0.5 A), the capacitors required 12 ± 1 sec to charge after a discharge.

The sulfur analyzer used (Meloy Labs SA 160-2) operates on the principle of measuring the light emitted by sulfur species when passing through a hydrogen-rich flame. The analyzer log signal output was recorded on the strip chart recorder. The integrated area of the analyzer linear output, used for quantitation, was registered by a Spectra-Physics Minigrator.

Analytical Procedure

Filter samples were extracted by immersing the entire 1 inch diameter filter in 1.00 ml distilled H₂O at 80 to 82°C for two hours in 13 mm diameter screw cap culture tubes. A similar procedure involving 5 ml H₂O and 47 mm filters was demonstrated to extract 92% of the water extractable sulfate.* The extracts were then centrifuged to separate particles of filter medium that were released by the reflux operation. A volume (2.5 or 5.0 µl) of the sample extract was next transferred to the vaporizer boat with a 0-20 µl digital pipette and the boat heated (at 3.70 VAC) until the extract was dry (12±1 sec). The dry residue was then vaporized by discharging the capacitors through the boat. The resistance of the boat material raised the boat temperature momentarily to red heat (about 1100°C). The gaseous decomposition products were drawn by the stream of clean air into the analyzer detector at 200 ml/min through a 7 in. long 1/8 in. I.D. section of Teflon tubing.

The first discharge usually accounted for about 90% of the total sulfate measured. Adding a second discharge usually increased the recovery to more than 95%. Additional discharges (up to four) were used to recover 98 to 99%. The number of discharges required depended on the boat's history (number of samples previously analyzed) and increased with use.

Between each sample, 5 µl aliquots of distilled H₂O were introduced, dried and vaporized to reduce the carry-over of residual sulfate to the following sample to less than 1 ng. From two to four aliquots, with two to three discharges per aliquot, were required depending on the previous history of the boat.

The tungsten boats were replaced whenever the number of discharges required to recover 98% of the total sample exceeded six or whenever the number of H₂O aliquots needed to reduce the residual sulfate to less than 1 ng exceeded four.

*E. M. Hoffer and B. R. Appel, AIHL Report No. 181, "A Comparative Study of Extraction Methods for Sulfate and Nitrate from Atmospheric Particulate Matter".

Calibration

The analysis system response to sulfate was established by introducing 5 μl portions of standard H_2SO_4 (covering the range of 0 to 90 ng $\text{SO}_4^{=}$), drying and vaporizing as described in the procedure for analysis.

With new boats the first discharge accounted for more than 98% for the total sulfate. Two discharges recovered better than 99%. Also, two 5 μl portions of H_2O (with two discharges each) were sufficient to reduce the $\text{SO}_4^{=}$ carry-over to less than 1%.

With used boats, however, the number of discharges needed depended on the number and $\text{SO}_4^{=}$ concentrations of the samples previously analyzed. Concurrent with this increase in the number of discharges and H_2O aliquots required the system response tended to change (usually decrease). To determine the magnitude of this change and to permit correction of the analysis data, the system response was checked, when possible, at the beginning and end of each day's sample run with three replicates of the same H_2SO_4 standard (usually 80 ng $\text{SO}_4^{=}$). When the results indicated a shift of more than 10%, the three replicates were repeated at two other concentrations (usually 20 and 40 ng) so that the slope and intercept of the new response could be determined.