

Southern California Air Quality Study - Summer Phase

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ABSTRACT

A field study was performed as part of the Air Resources Board-sponsored Southern California Air Quality Study (SCAQS). Sampling was done at Long Beach Community College for eleven, 24-hr periods from within the period June 19 - September 4, 1987. Sampling focussed on measurements of airborne particulate acids. Two fine particulate samplers were operated, with one of the units preceded by an ammonia denuder. In addition, a semi-continuous particle sulfur monitor was employed, which was able to discriminate between sulfuric acid and ammonium sulfates. Concentrations of sulfur dioxide and ozone as well as relative humidity and temperature were also monitored continuously.

Strong acid concentrations observed were very low, ranging up to about $3 \mu\text{g}/\text{m}^3$, expressed as H_2SO_4 . Total particulate acid concentrations ranged up to $11 \mu\text{g}/\text{m}^3$, expressed as H_2SO_4 . The results for filter samplers with and without the ammonia denuder were not significantly different at these relatively low acid concentrations.

Acidic sulfates contributed no more than 20% of the strong acidity. Relatively strong organic acids (e.g. formic acid) are possibly important contributors to the particulate strong acids. Sulfuric acid concentrations with the particle S monitor were below detectable levels. Ammonium sulfate results with the S monitor showed moderate correlation with filter-collected sulfate ($r=0.82$) and averaged about 5% higher. Sulfur dioxide concentrations were usually ≤ 16 ppb but reached a one-hour average concentration of 35 ppb, coincident with the sulfate maximum, on 9/2/87, the day of highest photochemical smog intensity at Long Beach.

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I. SUMMARY AND CONCLUSIONS

A field study was performed as part of the Air Resources Board-sponsored Southern California Air Quality Study (SCAQS), summer phase. Sampling was done at Long Beach Community College for eleven, 24-hr periods selected by a study management team from within the time period June 19 - September 4, 1987. Our sampling focussed on measurements of airborne particulate acids. Two fine particulate samplers were operated using Teflon filters which were changed at the 4, 5 or 7 hour intervals established for other SCAQS samplers at Long Beach and elsewhere. One of the two samplers was preceded by an ammonia denuder to assess the influence of such a denuder on the concentration of recovered strong and total acid. In addition, a semi-continuous particle sulfur monitor was employed, which was able to discriminate between sulfuric acid and ammonium sulfates, if present at levels $\geq 2 \mu\text{g}/\text{m}^3$. In parallel with these measurements, concentrations of sulfur dioxide and ozone as well as relative humidity and temperature were monitored continuously to aid in data interpretation.

Strong acid concentrations, calculated from the pH of aqueous filter extracts, were very low, ranging up to about $3 \mu\text{g}/\text{m}^3$, expressed as H_2SO_4 . Total particulate acid concentrations, calculated from the volume of base required to titrate extracts to the pH of deionized water, ranged up to $11 \mu\text{g}/\text{m}^3$, expressed as H_2SO_4 . The ammonia-denuded samples exceeded the strong acid and total acid levels of the undenuded samples by, on average, 7% and 13%, respectively. Allowing for the scatter in the data, the results for samplers with and without the ammonia denuder are not considered to be significantly different for these relatively low acidity samples.

Comparing strong acidity to sulfate concentrations, acidic sulfates contributed no more than 20% of the strong acidity. Relatively strong organic acids (e.g. formic acid), are possibly important contributors to the particulate acid concentration. The contribution of nitric acid to particle-phase acidity was not assessed, however.

Consistent with the filter results, sulfuric acid concentrations were below detectable levels with the semi-continuous particle S monitor. Particulate sulfate results with the S monitor, ascribable to ammonium sulfates, showed moderate correlation ($r=0.82$) with filter-collected sulfate, with a ratio of mean results, S Monitor/Filter SO_4 , of 1.05.

Sulfur dioxide concentrations at the Long Beach site were generally ≤ 16 ppb, with ozone concentrations ≤ 100 ppb. However, on sampling day 10, 9/2-9/3/87, the maximum hourly average values for SO_2 and O_3 were 35 and 174 ppb, respectively. On this day, particulate sulfate, as measured with the continuous monitor, showed diurnal variations similar to that for SO_2 .

II. INTRODUCTION

A. Particulate Acidity

Our previous studies (1-3) have reviewed the problems associated with measurement of atmospheric particulate acidity and reported results of such measurements in the South Coast Air Basin and elsewhere. Sampling was carried out with a low volume (lo-vol) sampler employing Teflon filters preceded by a denuder intended to remove atmospheric ammonia. In addition, a high volume (hi-vol) sampler was used employing acid-washed quartz filters without such a denuder. Both samplers used cyclones to exclude particles larger than 2 or 3 micrometers. For samples collected in the South Coast Air Basin at Lennox, in September 1979, the total strong acid recovered with the lo-vol sampler was substantially higher than that with the hi-vol. One possible explanation of this result was a decrease in neutralization of acidic particles resulting from the use of the ammonia denuder. However, given the differences in filter medium, sampling times, and face velocities, the effectiveness of the denuder could not be assessed with confidence.

The present experiment was conducted as part of the Southern California Air Quality Study (SCAQS) in the Summer, 1987, to compare collection of atmospheric strong particulate acid and total particulate acidity using two fine-particulate lo-vol samplers, in which only one unit employed the ammonia denuder. Long Beach was selected as the sampling site in an effort to maximize the concentration of such species, because of the proximity of sulfur oxide emissions.

B. Semi-Continuous Sulfate and Sulfuric Acid Monitoring

Employing the benzaldehyde extraction technique, sulfuric acid concentrations up to $11 \mu\text{g}/\text{m}^3$ were measured at Lennox in July, 1979 (3). However, this procedure is laborious and subject to error caused by neutralization during and subsequent to filter collection. In assessing an alternative procedure potentially suitable for routine monitoring, our previous study (4) described the construction of a monitor for semi-continuous operation, its working principles, laboratory evaluation and results of atmospheric sampling at El Camino College, Torrance, CA. In Sept. 1986, during a period of relatively light air pollution, no sulfuric acid was detected. However, the particle-phase S measured with the device, representing total ammonium sulfates, agreed within about 20% with filter-collected, water soluble sulfate.

The monitor was operated in the Summer SCAQS program to assess the level of sulfuric acid at the Long Beach sampling site, and for comparison with particulate strong acid concentrations measured by filter-collection and titration procedures.

C. Supplemental Measurements

Sulfur dioxide concentrations were monitored continuously for comparison with continuous particulate S measurements. Ozone was monitored continuously to assess the level of photochemical smog at

the sampling site. Relative humidity and temperature were measured since both can be significant in influencing the rate of formation of particulate sulfate, especially by heterogeneous processes (5).

D. Sampling Design

Sampling was done at the Long Beach SCAQS site located at Long Beach Community College for a total of 11, 24-hr periods. Filter samples for acidity were operated for 4, 6 or 7 hour periods:

Period 1	0100 - 0600 Hours PDT
Period 2	0600 - 1000
Period 3	1000 - 1400
Period 4	1400 - 1800
Period 5	1800 - 0100

In addition to measuring strong H^+ and total H^+ , the filter extracts were analyzed for SO_4^{2-} . The sulfuric acid monitor operated continuously during the 11 intensive periods.

III. PARTICULATE ACIDITY WITH AND WITHOUT AN AMMONIA DENUDER

A. Experimental

Samples were collected on 47 mm, 2 μm pore size, Zefluor (PTFE Teflon) filters (Gelman Sciences Co.) mounted in Nuclepore filter holders, preceded by PFA Teflon-coated aluminum cyclones (6) to exclude particles larger than about 2.2 μm at 28 Lpm. With one unit, an ammonia denuder was placed between the cyclone and the filter holder. The denuder employed 24, 40-cm long, 6-mm I.D., HF-etched tubes coated with H_3PO_3 . Since the acid readily absorbs water and tends to run out of the tubes, the denuder was mounted nearly horizontally, with the downstream end slightly elevated to minimize transfer to the downstream filter. Analysis of field blanks and samples for PO_3^- showed no evidence of transfer of the denuder coating to the filter. The denuder tubes were replaced after completion of 6, 24-hr intensive periods.

Flow rates were checked against rotameters attached to the inlets as well as to the filter holders at the beginning and end of each sampling period. Mass flow controllers were employed to maintain constant flow rates. Flow rate changes experienced were negligible, as was leakage within the denuder and cyclones. Following completion of sampling, the filters in color-coded holders were rapidly transferred to a glove box, and the box purged with synthetic air. Filters were cut into strips and inserted into color-coded and prelabelled 15 mL polystyrene screw-cap test tubes in synthetic air, and these tubes transferred to plastic bags and stored over dry ice. Samples were transported to the laboratory for analysis over "Blue Ice", and stored at -10°C until ready for analysis. Filters were extracted by adding 10 mL deionized water to each tube, shaking the tube for 1 hour at room temperature on a platform shaker and for another hour on a Fisher RotoRack.

Strong acid in each filter extract was determined to the nearest 0.001 pH from the initial pH of the nitrogen-flushed solution measured with a Radiometer PHM 64 research pH meter. Total acidity was determined by titration with a Radiometer Autoburette AB12 and TTT 60 Titrator to the pH of nitrogen-flushed deionized water (6.5). Samples were arranged in sequence for analysis such that the corresponding denuded and undenuded samples were analyzed successively. This minimized the effects of day-to-day variations in the analytical method.

Field blanks were obtained midway through the sampling program by mounting filters in their holders, operating the units for 30 sec at 28 Lpm, with sample processing as described above. In addition to field blanks, laboratory blanks were obtained following the field program by mounting filters in a holder previously used with the denuded sampler, followed immediately by filter processing (i.e. the filters were not mounted and run in the sampler). Results for field and laboratory blanks are given in Table 1. Field blank results are means for 10 samples, including 5 obtained with the denuded and 5 with the undenuded sampler. The laboratory blank results are means for 5 determinations.

Table 1. Field and Laboratory Blank Values for Teflon Filters ($\mu\text{g}/47$ mm filter)

Field Blanks ^a			Laboratory Blanks ^b		
Strong H ⁺ (as H ₂ SO ₄)	Total H ⁺ (as H ₂ SO ₄)	SO ₄ ⁼	Strong H ⁺ (as H ₂ SO ₄)	Total H ⁺ (as H ₂ SO ₄)	SO ₄ ⁼
4.0 ± 1.5	16.8 ± 9.3	0.4 ± 0.4	1.4 ± 0.1	1.5 ± 0.4	0.9 ± 0.6

a. Results are mean ± 1 σ for 10 samples.

b. Results are mean ± 1 σ for 5 samples.

The field blanks were relatively high, much higher than obtained in prior work sampling at El Camino College (4). In the latter case, field blank results were similar to those obtained for laboratory blanks in the current program. Among possible causes, those ruled out include transfer of H_3PO_3 to the Teflon filters, elevated acidity for the batch of Teflon filters used, and contamination by the filter holder or during filter handling. The field blanks were used to correct all atmospheric data. Since the principle objective of this work was to assess differences between results with the denuded and undenuded sampler, the elevated blanks have reduced significance.

Atmospheric samples were coded with a 7-digit identifier, exemplified by the label: 02S012Z. The first two digits are the sampler number, S01 indicates sampling day 1, 2Z indicates sampling period 2 and filter type (Zefluor), respectively. The dates corresponding to sampling days S01 through S11 are given in Table 2.

B. Results

The results for the denuded (Sampler 2) and undenuded sampler (Sampler 3) are tabulated in Tables 3 and 4, respectively. Previous studies (e.g. at El Camino College, September 1986, Ref. 4) have demonstrated that sulfate particles are not significantly removed in passing through the ammonia denuder employed in the current work; sulfate concentrations measured with and without such a denuder differed by, on average, <5%. However, in the current study, 14 of the 55 paired sulfate results differed by factors ranging from 1.5 to 3. Errors due to flow measurements are highly unlikely. Since the water extracts were completely consumed in analyses for acidity as well as for sulfate, the possibility that the extractions into deionized water were incomplete cannot be discounted. Based on the prior studies, the results for these 14 samples were discarded for comparing strong acid and total acidity values with and without the denuder. Figure 1 shows the scatter diagram for the sulfate values, with and without the ammonia denuder, for the remaining 41 data pairs. These results indicate high correlation and excellent agreement. The strong acid values, with and without the denuder, for these 41 paired samples are compared in Figure 2. For strong acid concentrations below $3 \mu\text{g}/\text{m}^3$ (as H_2SO_4), the difference in concentrations with and without an ammonia denuder was small. Based on ratios of means, the denuded samples averaged only 7% higher. A similar comparison of total acidity results is shown in Figure 3. Again, the difference in average results between the samplers was small. Based on ratios of means, the denuded samples averaged 13% higher. Allowing for the considerable scatter in the data, the differences are probably not statistically significant. Thus, at least at such low levels of particulate phase acidity, an ammonia denuder provided little, if any, enhancement in acid recovery.

Figure 4 is a scatter diagram of strong acidity (as H_2SO_4) against SO_4^- (as H_2SO_4). The results suggest that acidic sulfates, on average, contributed no more than 20% of the strong acidity.

Table 2. Sampling Dates for Summer SCAQS

<u>Sampling Days</u>	
<u>Code</u>	<u>Date</u>
S01	6/19-6/20/87
S02	6/24-6/25/87
S03	6/25-6/26/87
S04	7/13-7/14/87
S05	7/14-7/15/87
S06	7/15-7/16/87
S07	8/27-8/28/87
S08	8/28-8/29/87
S09	8/29-8/30/87
S10	9/2-9/3/87
S11	9/3-9/4/87

Table 3.

Listing of Strong Acid, Total Acid and Sulfate, as Sulfuric Acid with an Ammonia Derider

FILTER ID	START DATE (PDT)	TIME (MS)	TOTAL VOLUME (UG)	TOTAL ACID (UG/M3)	TOTAL ACID (UG/M3)	STRONG ACID H+ (UG/FILTER)	STRONG ACID H2SO4 (UG/M3)	S04= UG/SAMP.	S04= UG/M3 (AS H2SO4)
02S0112	6-19	1 5	8.24	59	5.12	11.00	.65	13	1.94
02S0122	6-19	6 0	6.63	42	3.80	8.00	.60	31	4.68
02S0132	6-19	9 52	6.91	62	6.54	15.00	1.59	40	5.79
02S0142	6-19	13 53	7.42	64	6.36	11.00	.94	33	4.45
02S0152	6-19	13 3	12.09	62	3.74	14.00	.83	53	4.38
02S0212	6-24	1 0	6.81	88	8.08	25.00	2.36	97	11.01
02S0222	6-24	5 57	7.21	78	6.49	21.00	2.36	88	12.21
* 02S0232	6-24	9 59	7.01	68	7.30	13.00	1.28	26	3.71
* 02S0242	6-24	14 0	6.95	57	5.78	10.00	.86	14	2.01
02S0252	6-24	18 0	12.02	80	5.26	20.00	1.33	95	7.90
02S0312	6-25	1 0	8.44	87	8.32	22.00	2.13	83	9.83
02S0327	6-25	5 52	6.88	66	7.15	14.00	1.45	64	9.30
02S0332	6-25	9 53	7.06	61	6.26	13.00	1.27	39	5.52
02S0342	6-25	13 57	6.79	56	5.77	9.00	.74	11	1.62
02S0352	6-25	17 59	11.95	66	4.12	17.00	1.09	92	7.70
02S0412	7-13	1 2	8.18	49	3.94	14.00	1.22	24	2.93
02S0422	7-13	5 53	6.98	63	7.36	12.00	1.15	28	4.02
02S0432	7-13	9 53	6.80	77	6.85	15.00	1.62	47	6.91
02S0442	7-13	14 13	6.11	73	9.20	13.00	1.47	43	7.04
02S0452	7-13	17 51	11.77	62	3.84	12.00	.68	55	4.67
02S0512	7-14	0 59	8.19	59	5.15	15.00	1.34	71	8.67
02S0522	7-14	5 55	6.74	94	11.45	22.00	2.67	82	12.17
02S0532	7-14	9 56	6.82	73	8.24	16.00	1.76	80	11.73
02S0542	7-14	13 56	6.49	74	8.81	15.00	1.69	66	10.17
02S0552	7-14	17 58	13.19	66	3.73	17.00	.99	66	6.52
02S0612	7-15	1 53	6.53	49	4.93	12.00	1.23	42	6.43
02S0622	7-15	5 53	6.53	46	4.47	13.00	1.33	43	6.58
02S0632	7-15	9 54	6.12	40	3.79	10.00	.98	28	4.58
02S0642	7-15	13 57	6.59	33	2.46	9.00	.76	20	3.03
02S0652	7-15	18 4	11.35	47	2.66	26.00	1.94	77	6.78
02S0712	8-27	1 8	7.79	55	4.90	9.40	.69	18	2.31
02S0722	8-27	6 0	6.34	73	8.46	12.00	1.20	22	3.31
02S0732	8-27	9 59	6.73	65	7.16	14.00	1.49	46	6.84
* 02S0742	8-27	14 4	6.22	65	7.75	14.60	1.70	48	7.72
* 02S0752	8-27	17 59	9.48	62	4.77	14.00	1.05	87	9.18
* 02S0812	8-28	1 5	7.93	43	3.30	9.60	.73	31	3.91
* 02S0822	8-28	6 5	6.37	33	2.54	7.90	.61	39	6.12
* 02S0832	8-28	9 59	6.47	40	3.59	11.10	1.10	67	10.36
02S0842	8-28	13 56	6.71	71	8.08	19.00	2.24	115	17.14
02S0852	8-28	17 57	11.90	72	4.64	21.00	1.43	102	8.57
* 02S0912	8-29	1 11	7.79	37	2.59	16.10	1.55	66	8.47
* 02S0922	8-29	5 56	6.72	23	.92	7.30	.49	28	4.17
* 02S0932	8-29	9 59	6.54	59	6.45	46.00	6.42	108	16.51
* 02S0942	8-29	13 54	6.69	42	3.77	11.40	1.11	28	4.19
02S0952	8-29	17 54	11.66	47	2.59	12.90	.76	76	6.52
02S1012	9-2	1 2	8.18	39	2.71	8.10	.50	7.6	.93
* 02S1022	9-2	6 2	6.73	45	4.19	8.00	.59	38	5.65
* 02S1032	9-2	9 59	6.63	35	2.75	7.80	.57	44	6.64
02S1042	9-2	13 59	6.57	59	6.42	10.20	.94	34	5.18
02S1052	9-2	17 57	11.22	42	2.25	8.50	.40	56	4.99
02S1112	9-3	1 0	8.21	69	6.36	14.40	1.27	19.5	2.38
02S1122	9-3	6 0	6.59	48	4.73	11.40	1.12	55	8.35
02S1132	9-3	9 57	6.56	39	3.38	10.90	1.05	48	7.32
02S1142	9-3	14 34	5.65	46	5.17	13.20	1.63	41	7.26
02S1152	9-3	17 58	11.57	40	2.01	13.20	.80	54	4.67

* Poor agreement for sampler 2 and 3 sulfate. Results suspect.

Table 4.

Listing of Strong Acid, Total Acid and Sulfate, as Sulfuric Acid Without an Ammonia Denuder

FILTER ID	START DATE	TIME (PDT)	TOTAL VOLUME (M3)	TOTAL ACID (UG)	TOTAL ACID (UG/M3)	STRONG ACID H+ AS H2SO4 UG/FILTER	STRONG ACID H+ AS H2SO4 UG/M3	SO4= UG/MP	SO4= UG/M3 (AS H2SO4)
03S0112	6-19	1 8	8.15	39	2.72	9.00	.61	16	1.96
03S0122	6-19	5 56	6.84	56	5.73	10.00	.88	31	4.53
03S0132	6-19	9 53	6.88	46	4.24	9.00	.73	40	5.61
03S0142	6-19	13 54	7.30	49	4.41	12.00	1.10	31	4.25
03S0152	6-19	18 7	11.64	43	2.21	9.00	.34	51	4.31
03S0212	6-24	1 1	8.61	90	8.50	20.00	2.79	96	11.15
03S0222	6-24	5 55	7.13	92	10.55	23.00	2.66	87	12.20
* 03S0232	6-24	10 1	7.04	75	8.27	16.00	1.70	59	8.33
* 03S0242	6-24	14 2	6.98	72	7.91	13.00	1.29	48	6.88
03S0252	6-24	18 1	12.06	74	4.74	20.00	1.33	89	7.33
03S0312	6-25	1 5	8.19	70	6.60	20.00	1.75	82	10.01
03S0322	6-25	5 50	6.91	64	2.83	14.00	1.45	63	9.12
03S0332	6-25	9 55	7.07	48	4.41	9.00	.71	32	4.53
03S0342	6-25	13 59	6.74	28	1.66	5.00	.15	9	1.34
03S0352	6-25	17 58	12.09	55	3.15	17.00	1.08	94	7.78
03S0412	7-13	1 1	8.09	61	5.46	12.00	.99	23	2.84
03S0422	7-13	5 54	6.86	60	6.30	18.00	2.04	29	4.23
03S0432	7-13	9 55	6.77	81	9.48	15.00	1.62	48	7.09
03S0442	7-13	14 13	6.18	66	7.96	13.00	1.46	40	6.47
03S0452	7-13	17 53	11.74	52	3.00	13.00	.77	54	4.60
03S0512	7-14	1 0	8.63	75	6.74	18.00	1.62	72	8.34
03S0522	7-14	5 56	6.75	63	6.64	16.00	1.78	81	12.00
03S0532	7-14	9 57	6.65	76	3.90	16.00	1.80	78	11.73
03S0542	7-14	13 56	6.71	48	4.65	10.00	.89	29	4.32
03S0552	7-14	18 0	11.29	57	3.56	16.00	1.06	78	6.91
03S0612	7-15	0 48	8.34	40	2.78	13.00	1.08	49	5.88
03S0622	7-15	5 56	6.52	43	4.02	10.00	.92	42	6.44
03S0632	7-15	9 56	6.15	35	2.96	9.00	.81	25	4.07
03S0642	7-15	13 59	6.56	31	2.16	8.00	.61	19	2.90
03S0652	7-15	18 5	11.36	41	2.13	22.00	1.58	77	6.78
03S0712	8-27	1 10	7.78	64	6.07	10.20	.80	28	3.60
03S0722	8-27	6 8	6.24	63	7.40	11.10	1.14	20	3.21
03S0732	8-27	9 57	6.79	63	6.80	12.60	1.27	40	5.89
* 03S0742	8-27	14 8	6.19	52	5.69	12.30	1.34	30	4.85
03S0752	8-27	18 2	11.20	63	4.13	14.00	.89	84	7.50
* 03S0812	8-28	1 7	7.98	48	3.91	11.50	.94	20	2.51
* 03S0822	8-28	6 7	6.31	29	1.93	6.60	.41	34	5.39
* 03S0832	8-28	10 3	6.46	34	2.66	6.50	.39	24	3.72
03S0842	8-28	14 0	6.69	55	5.71	14.70	1.60	117	17.49
03S0852	8-28	17 59	11.92	47	2.53	19.60	1.31	101	8.47
* 03S0912	8-29	1 13	7.78	64	6.07	33.50	3.79	110	14.14
* 03S0922	8-29	5 58	6.77	34	2.54	16.10	1.79	72	10.64
* 03S0932	8-29	10 1	6.65	13	1.57	7.30	.50	25	3.76
* 03S0942	8-29	13 56	6.72	50	4.94	17.20	1.96	85	12.65
03S0952	8-29	17 56	11.74	88	6.06	48.00	3.75	89	7.58
03S1012	9-2	1 4	8.26	41	2.93	8.00	.48	13.3	1.61
* 03S1022	9-2	6 4	6.58	47	4.59	8.80	.73	21.2	3.22
* 03S1032	9-2	9 57	6.66	75	8.74	15.40	1.71	63	9.46
03S1042	9-2	14 2	6.61	64	7.14	10.50	.98	33	4.99
03S1052	9-2	18 0	11.58	37	1.74	7.80	.33	57	4.92
03S1112	9-3	1 2	8.31	41	2.91	6.20	.26	18.6	2.24
03S1122	9-3	6 2	6.67	59	6.33	11.90	1.18	66	9.90
03S1132	9-3	9 58	6.58	48	4.74	10.90	1.05	59	8.97
03S1142	9-3	14 32	5.76	31	2.47	9.60	.97	41	7.12
03S1152	9-3	18 2	11.55	24	.62	9.00	.43	54	4.68

* Poor agreement for sampler 2 and 3 sulfate. Results suspect.

Figure 1

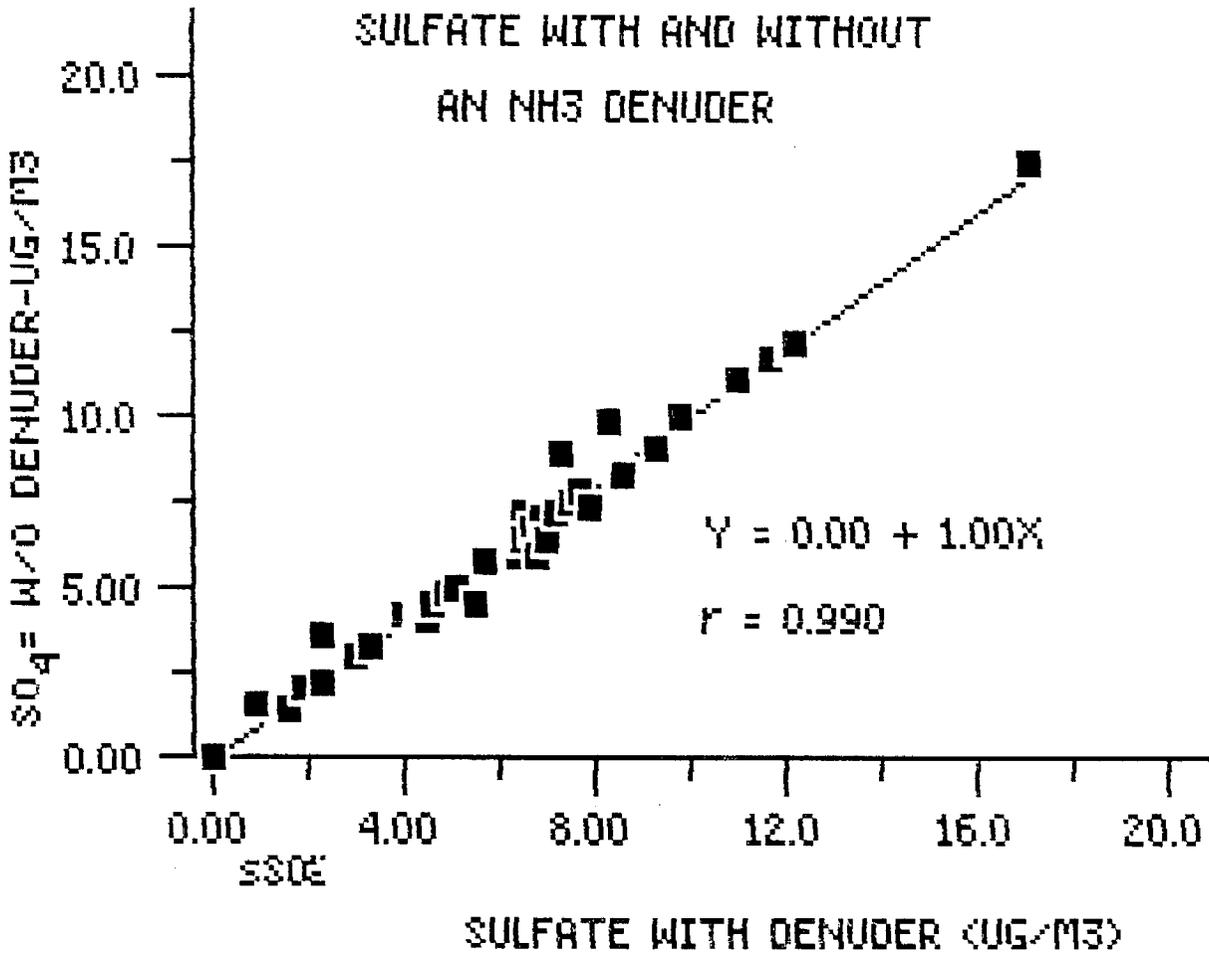


Figure 2

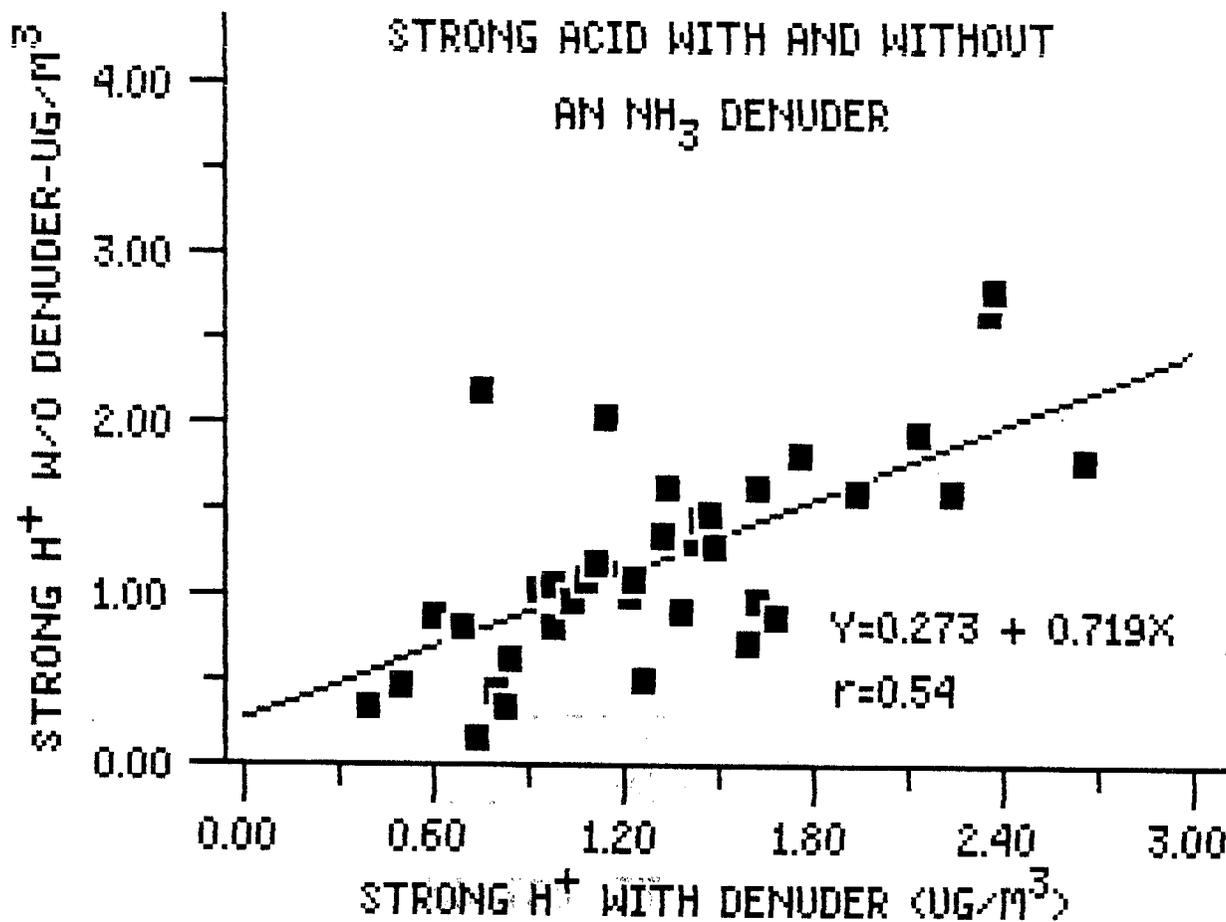


Figure 3

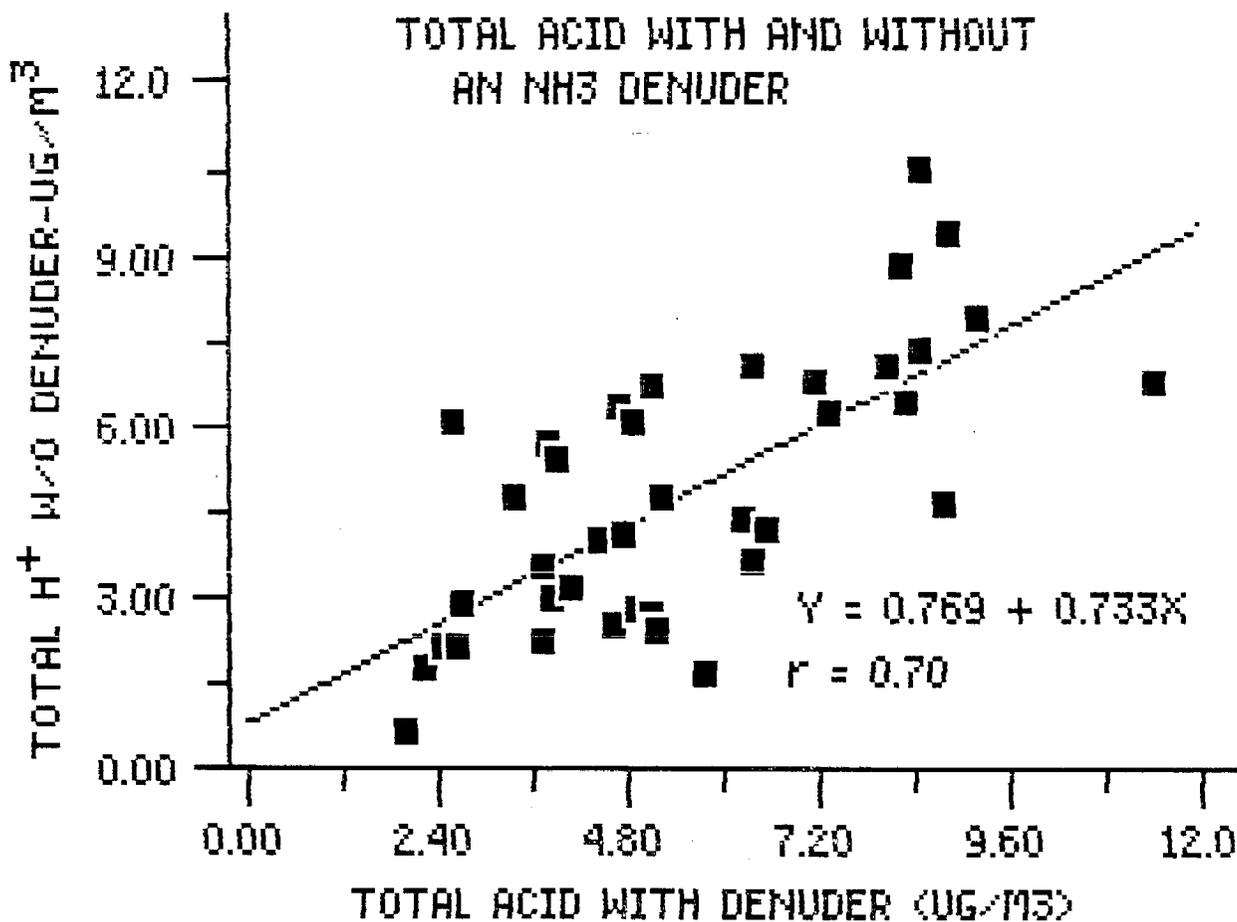
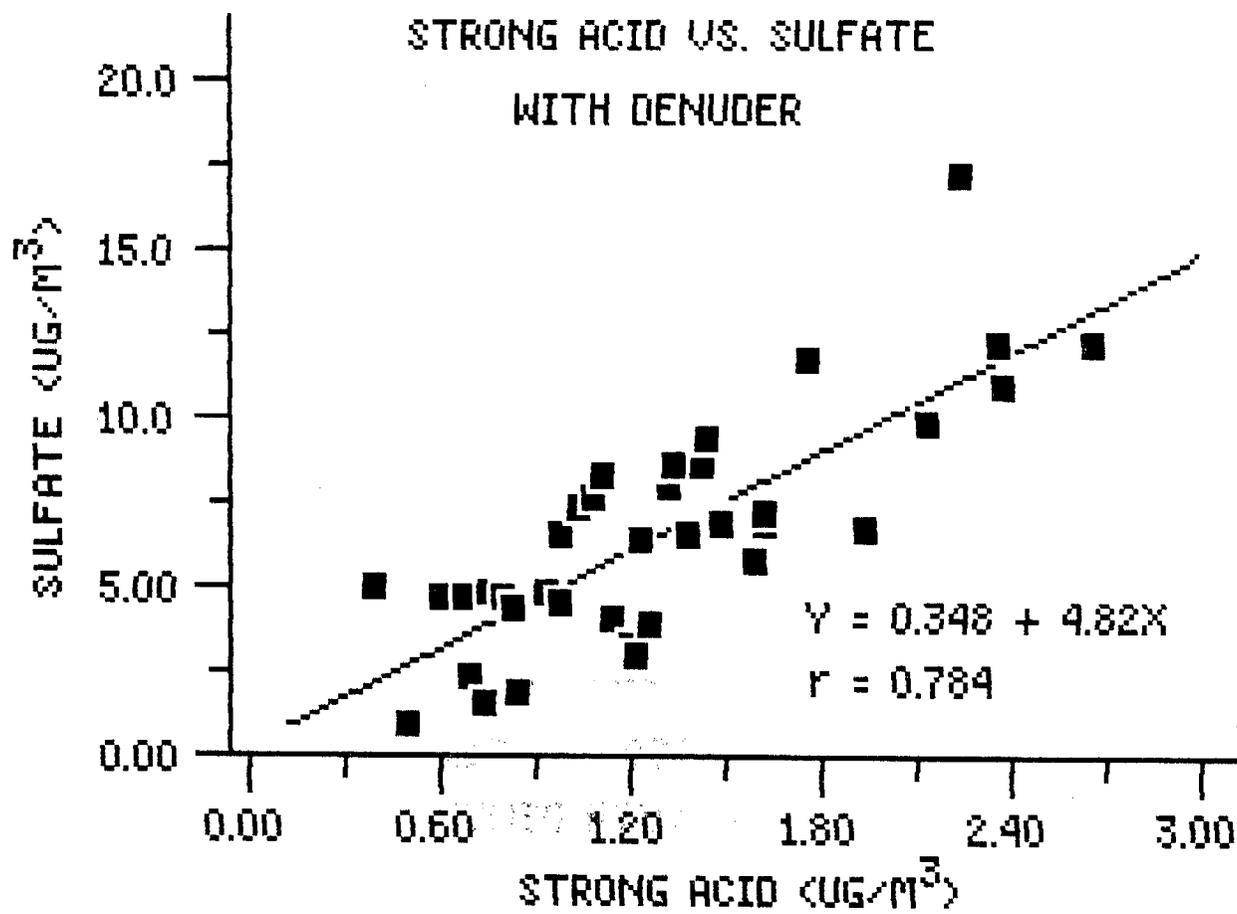


Figure 4



Relatively strong organic acids (e.g. formic acid) are implicated as important contributors. However, previous work at Lennox suggested that nitric acid may be contributing to the strong particle acidity (4). Measurement of HNO_3 was beyond the scope of the current effort and, therefore, its contribution in the present study cannot be assessed.

IV. CONTINUOUS SULFURIC ACID AND SULFATE MEASUREMENTS

A. Experimental

A continuous monitor for particulate S was constructed and evaluated in a prior study (4). It employs a denuder to remove S-containing gases and S compounds volatilized by heating after entry to the sampler. A flame photometric detector is used to detect particulate S, with its response enhanced by addition of SF₆ to the H₂ fuel. Speciation is based primarily on selective volatilization with a heater tube ahead of the S denuder, permitting, in the absence of interferents, measurement of H₂SO₄ discretely, but leaving the various ammonium sulfates unresolved. To discriminate between H₂SO₄ and organosulfur, particle phase materials, the unit was programmed to introduce NH₃ into the sample stream. Sulfuric acid was equated with a particulate S species volatilized at 125°C which reacts with NH₃ forming a S species not volatilized at that temperature. Ammonium sulfates (e.g. (NH₄)₂SO₄ and NH₄HSO₄) were equated with particulate S species not volatilized at 125°C but volatilized at 300°C.

For the SCAQS, the S monitor sampled ambient air through a 2 meter length of 0.25 inch I.D. stainless steel tubing extending outside of the mobile laboratory in which the monitor was mounted. The monitor was calibrated at the sampling site by introducing a known concentration of SO₂ at the entrance to the sampler inlet, as employed during atmospheric sampling. Figure 5 is a log-log plot of instrument responses against SO₂ concentrations. The regression equation shown was used for reducing all S results. Based on the instrumental noise experienced, we estimate the lower limit for reliable quantitation of H₂SO₄ and for ammonium sulfates at 2 µg/m³.

The sampler was operated for 20 minute cycles, yielding three determinations per hour. An APPLE ISAAC data system provided concentrations each 20 minutes for the the species H₂SO₄, and NH₄HSO₄ + (NH₄)₂SO₄. As detailed in a preceding report (4), the presence of H₂SO₄ was tested both by its volatility behavior and its reaction with NH₃ to form a non-volatile sulfur compound at 125°C.

B. Results

A sulfur species exhibiting the volatility of H₂SO₄ was observed in only isolated instances, three cycles of the 792 cycles measured for the 11 intensive days. The apparent H₂SO₄ in these cases was several µg/m³. In no case, however, was the presence of the acid supported by reactivity with ammonia.

Particulate sulfate results with the S monitor are compared to those from filter sampling in Table 5 and Figure 6. Results show moderate correlation (r=0.82) with a ratio of mean results, S Monitor/Filter SO₄²⁻, of 1.05.

Figure 5

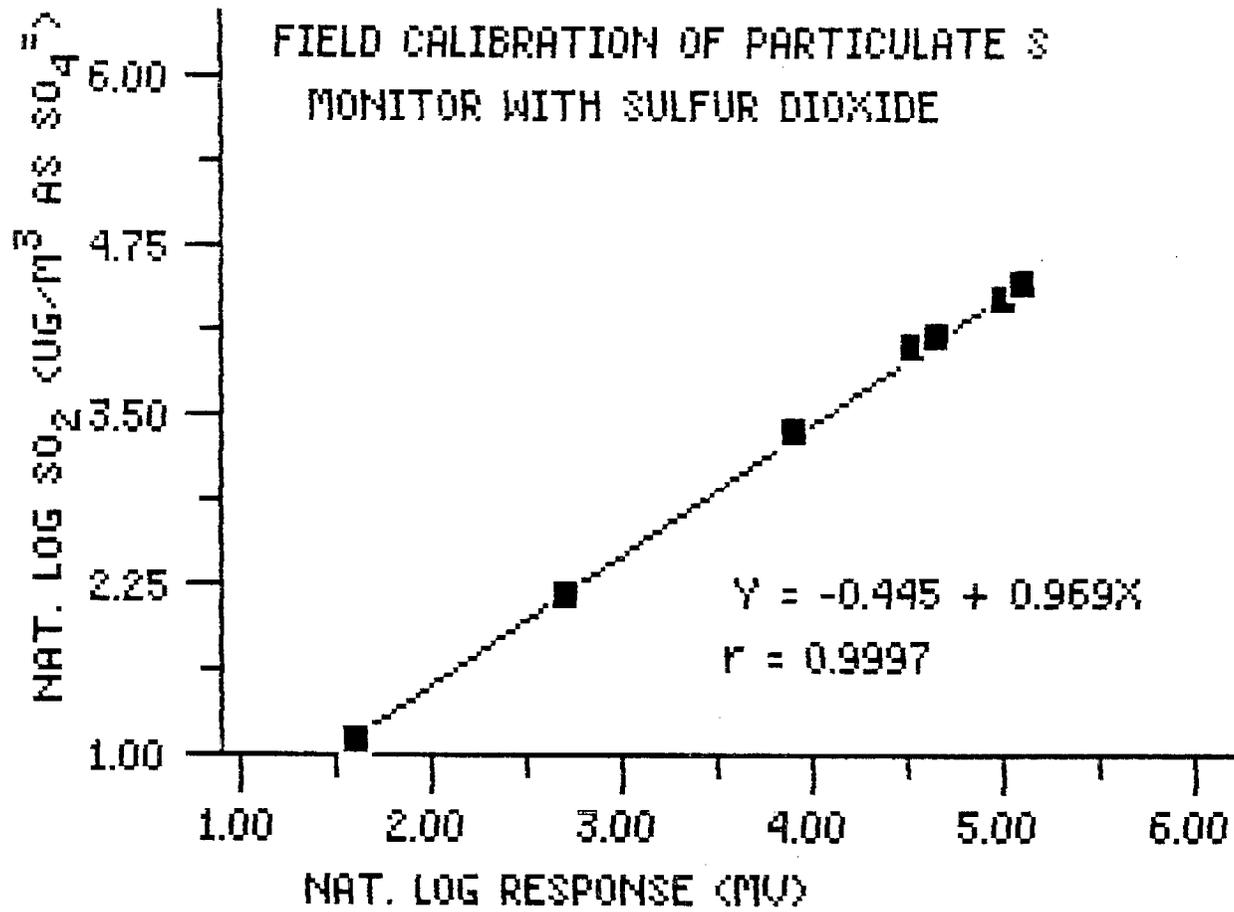
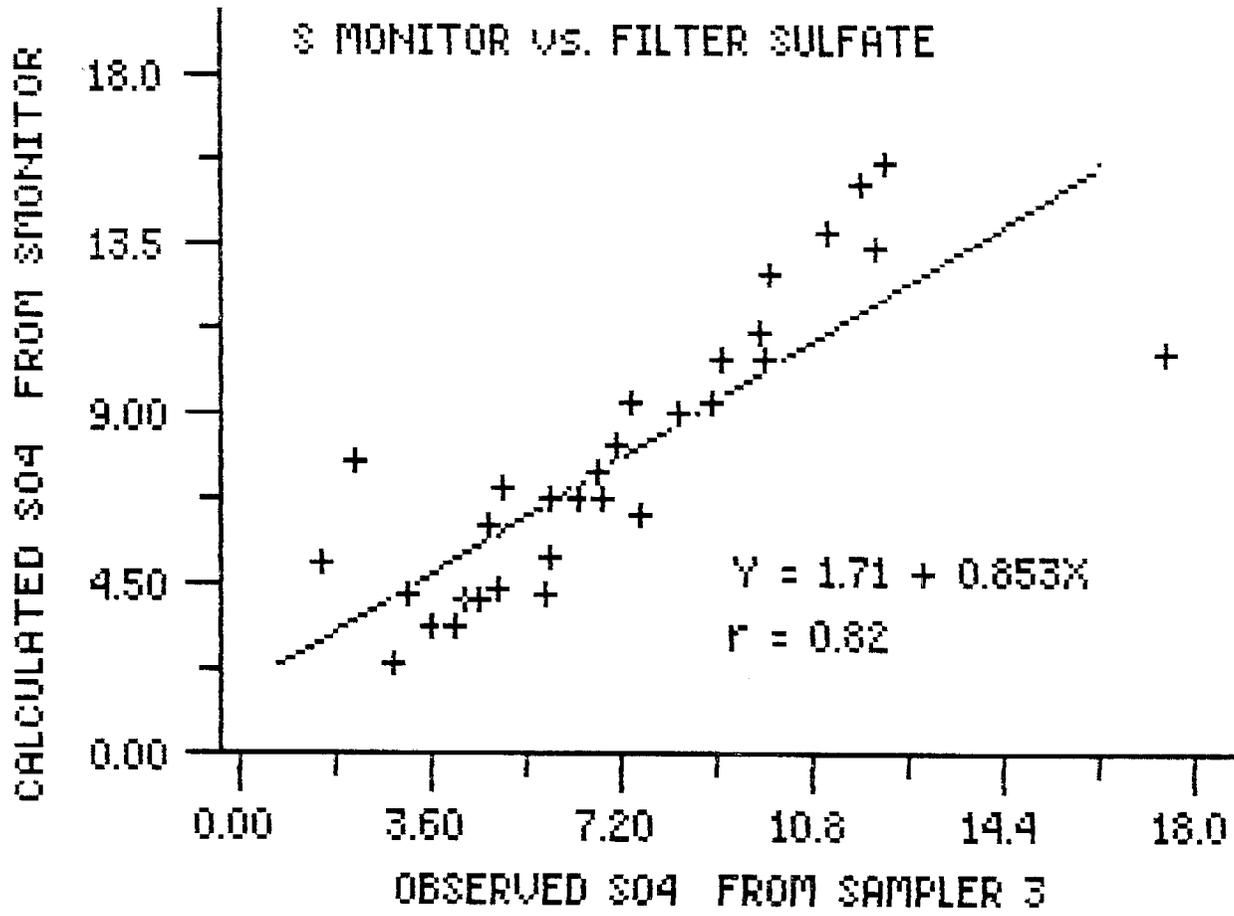


Table 5. Comparison of S Monitor and Filter Sulfate Measurements During the SCAQS at Long Beach ($\mu\text{g}/\text{m}^3$)

<u>Sampling Day and Period</u>	<u>Filter $\text{SO}_4^{=}$</u>	<u>S Monitor (as $\text{SO}_4^{=}$)</u>
S012	4.53	4.01
S013	5.81	4.26
S014	4.25	4.02
S021	11.15	13.8
S022	12.2	15.6
S025	7.38	9.34
S031	10.0	12.6
S032	9.12	10.4
S051	8.34	9.06
S052	12.0	13.3
S053	11.7	15.1
S054	9.84	11.14
S055	6.91	6.72
S061	5.88	6.69
S062	6.44	6.68
S063	4.07	3.36
S064	2.90	2.37
S065	6.78	7.47
S071	3.60	3.41
S072	3.21	4.21
S073	5.89	5.25
S075	7.50	6.30
S084	17.5	10.5
S095	7.58	6.35
S101	1.61	5.05
S104	4.99	7.00
S105	4.92	4.33
S111	2.24	7.76
S112	9.90	10.4
S113	8.97	9.34
S114	7.12	8.12
S115	4.68	6.04

a. S01 through S11 indicate sampling day. The final digit is the sampling period. See Table 2.

Figure 6



Figures 7 through 16 show diurnal changes in one-hour average concentrations of SO_4 for sampling days 1 through 11, excepting day 3 from 1200 to 0100, and on day 4, on which the data system malfunctioned. Sulfate levels on that day ranged from 2 to 10 $\mu\text{g}/\text{m}^3$, with the diurnal maximum at around 1300 hours.

Concentrations of SO_2 during the 11 sampling days generally remained <16 ppb. However, on sampling day 10 SO_2 one-hour average concentrations reached 35 ppb. The diurnal variations of SO_2 are shown for this day compared in Figure 17. Comparing Figures 15 and 17, both sulfate and SO_2 experienced their maxima during the period 1400-1500 hours (PDT). Ozone levels for this day were also the highest encountered; the maximum hourly average was 0.17 ppm at 1300-1400 hours.

Figure 7

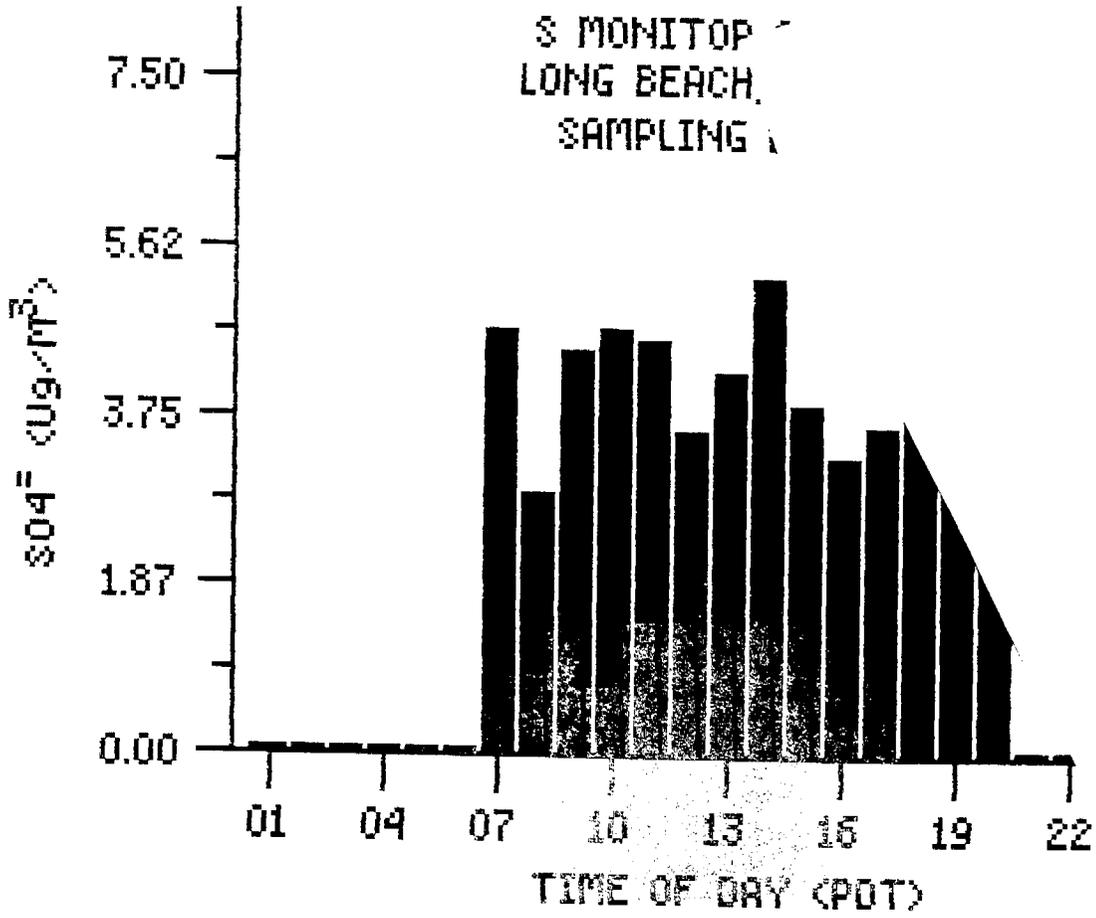


Figure 8

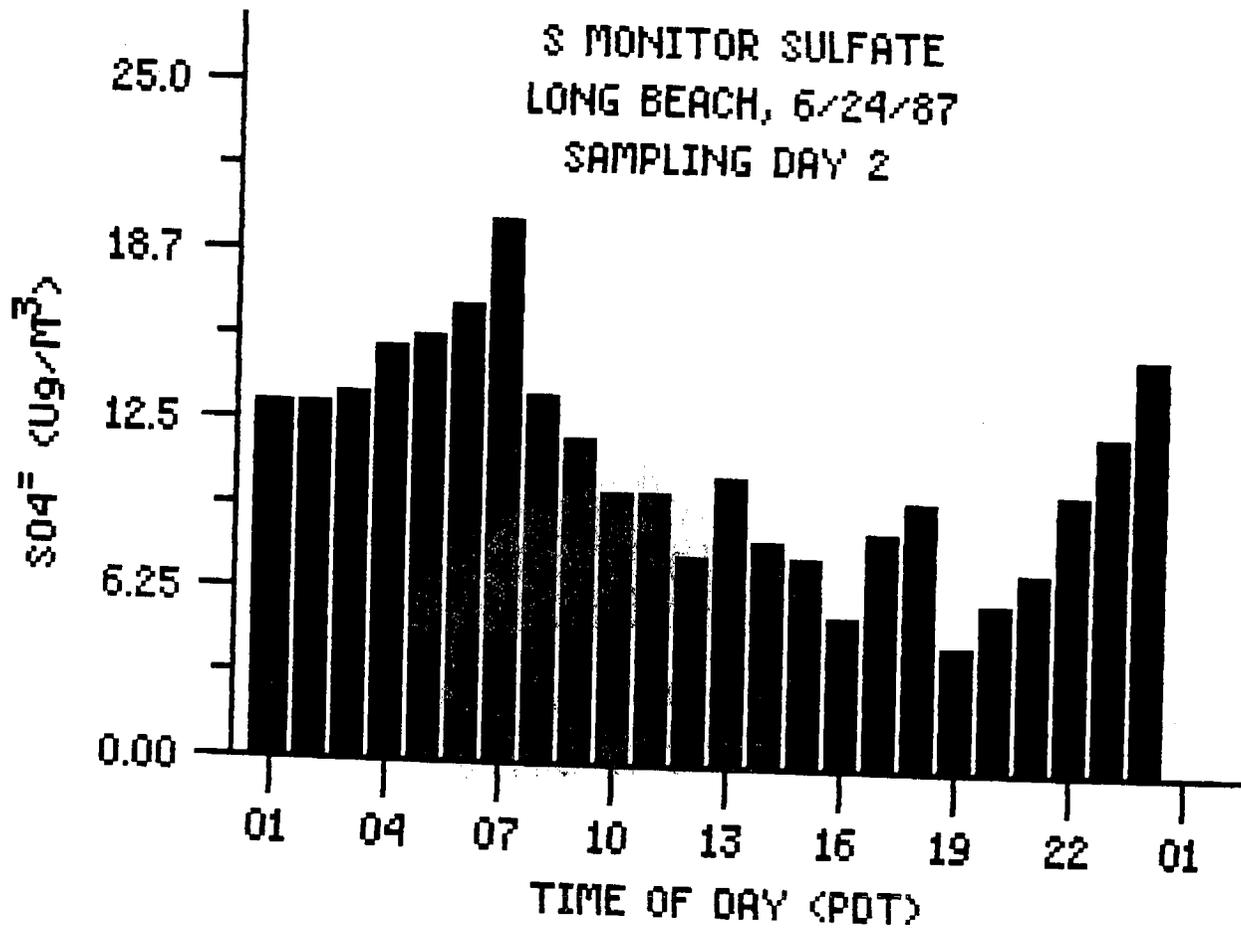


Figure 9

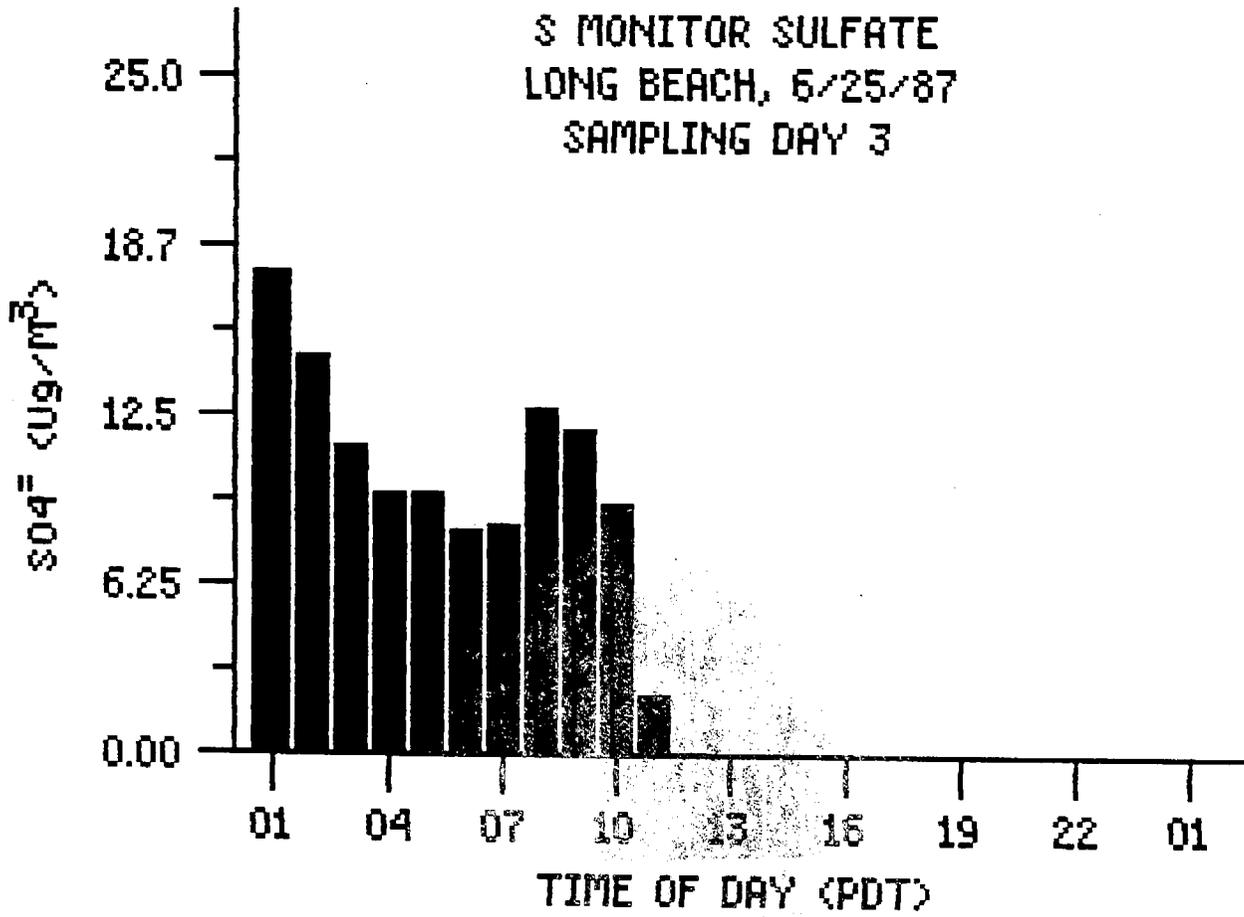


Figure 10

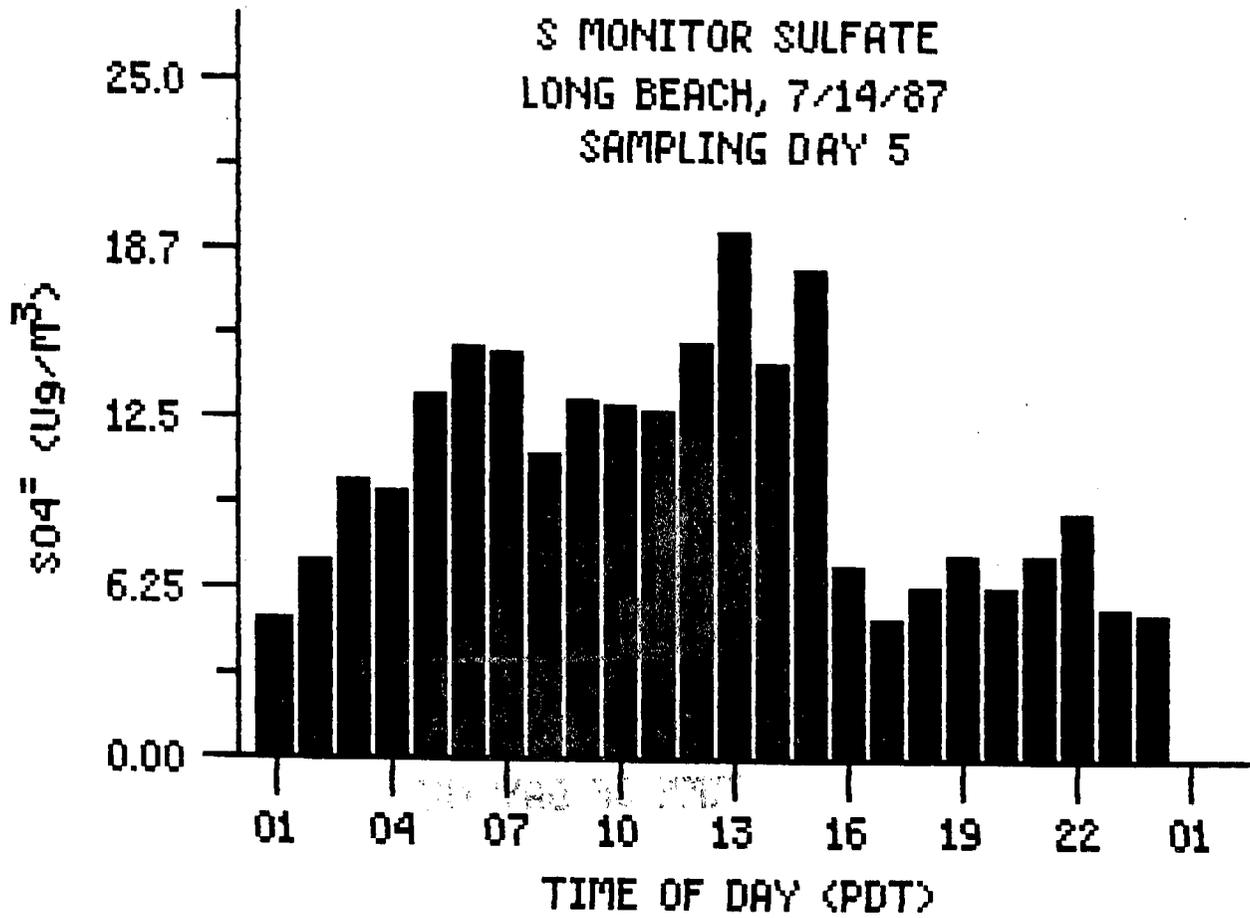


Figure 11

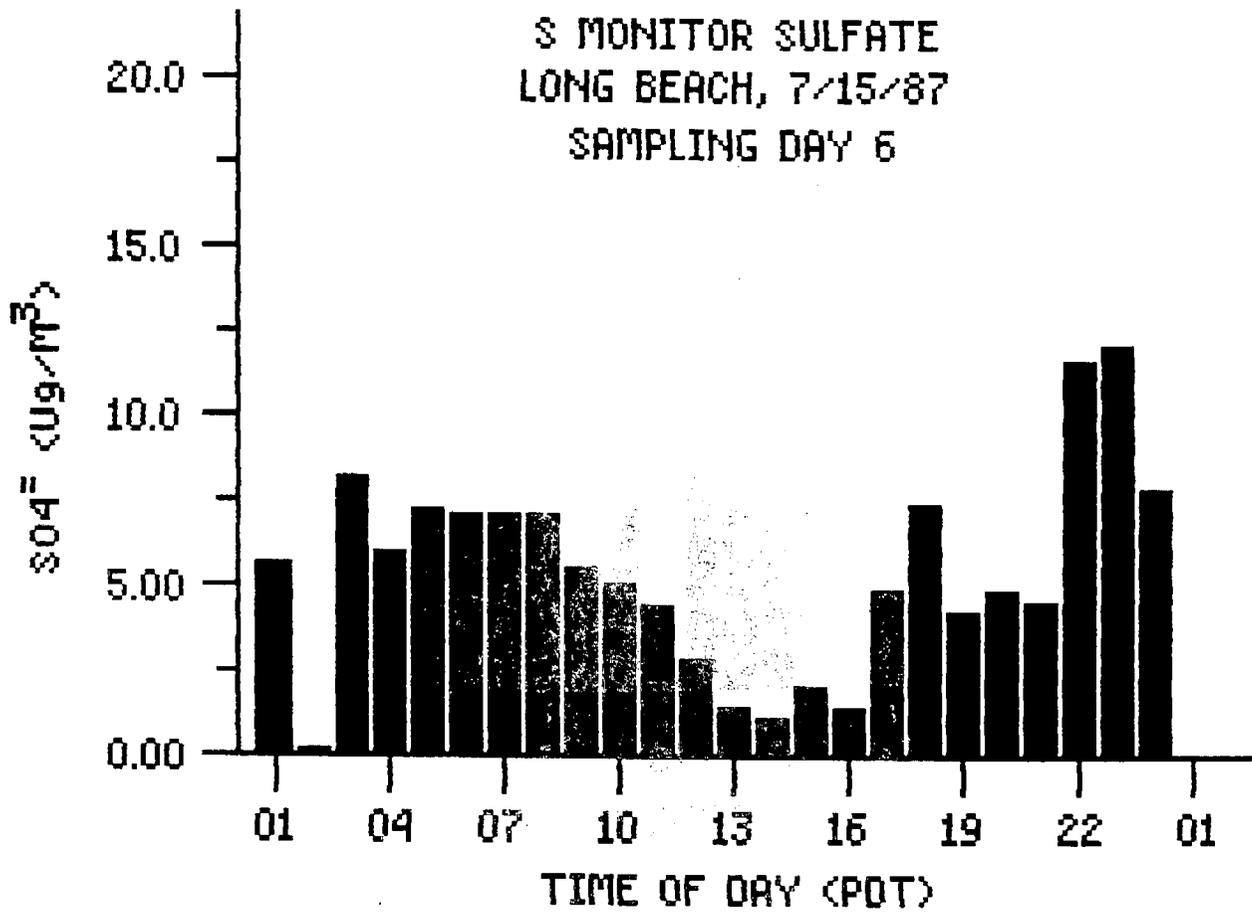


Figure 12

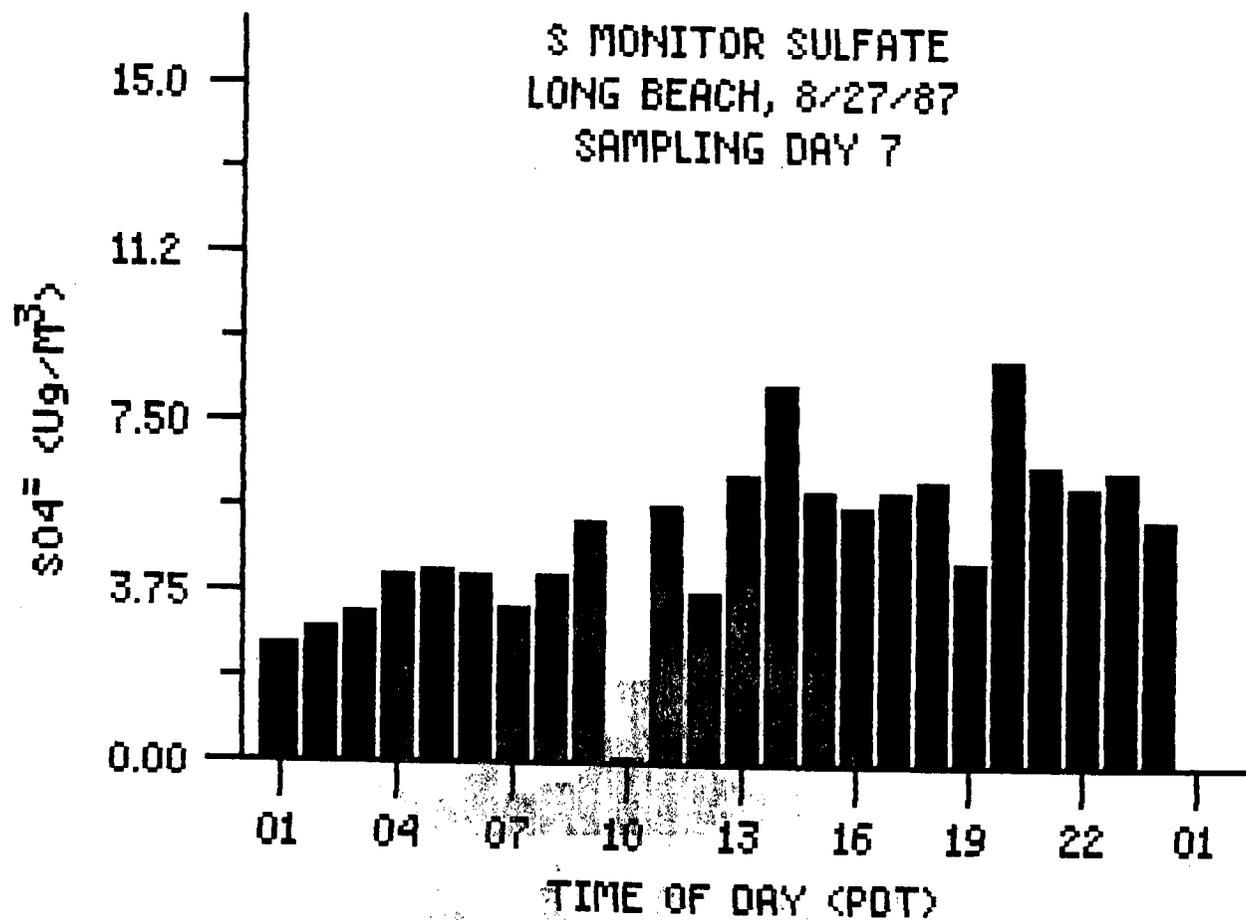
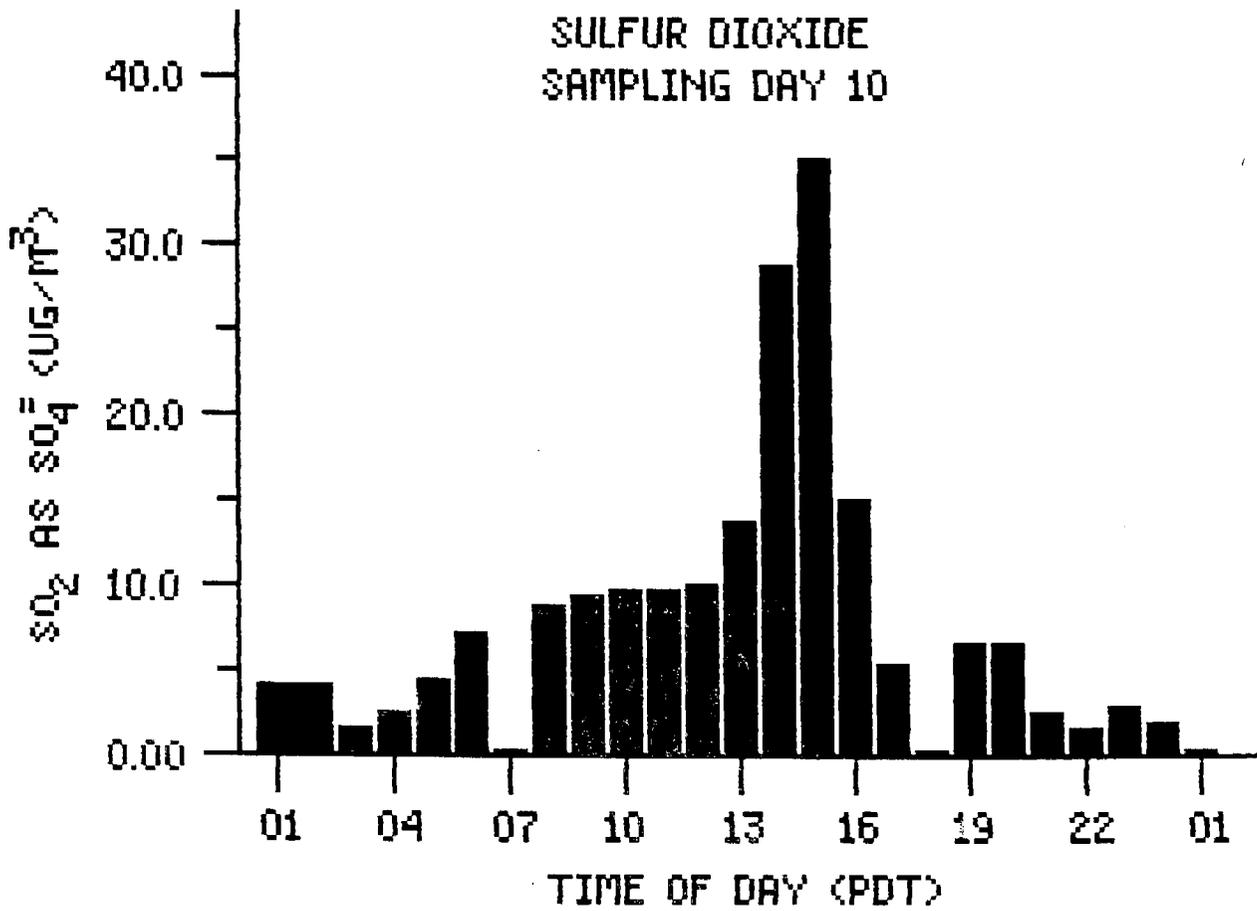


Figure 17



V. SUPPLEMENTAL MEASUREMENTS

A. Sulfur Dioxide

Sulfur dioxide was measured continuously with a TECO Model 43 pulsed fluorescence analyzer. The unit was calibrated at the sampling site with a Scott cylinder of SO₂ in N₂ whose concentration was established relative to a permeation tube traceable to NBS. One hour average values were calculated and printed with a Kaye Digistrip III data system. Maximum hourly average SO₂ concentrations for the study are given in Table 6. Except for sampling day 3, during which extensive power outages occurred, all one-hour average values for SO₂ are listed in Appendix A, which is a portion of the Digistrip printout.

B. Ozone

Ozone was monitored continuously with a Dasibi Model 1003 UV analyzer. The unit was calibrated against a transfer standard Dasibi unit, which, in turn, had been calibrated against a UV photometer maintained at the California Institute of Technology. Data acquisition and averaging were done as with SO₂. Maximum hourly average O₃ concentrations for the study are given in Table 7. All one-hour averages are listed in Appendix A.

C. Relative Humidity and Temperature

Relative humidity and temperature were monitored continuously with an EG&G Model 911 digital humidity analyzer, calibrated at the factory. Data acquisition and averaging were done as with SO₂. One-hour averages are listed in Appendix A. Data for Day 7 and a portion of Day 8 are excluded because of an instrument malfunction.

Table 6. Maximum Hourly Average SO₂ Concentrations

<u>Sampling Day</u>	<u>Date</u>	<u>Period (PDT)</u>	<u>SO₂ (ppb)</u>
1	6/19-6/20/87	1900-2000	6
2	6/24-6/25/87	1800-1900	11
3	6/25-6/26/87	-	Not Determined
4	7/13-7/14/87	1600-1700	13
5	7/14-7/15/87	1900-2000	16
6	7/15-7/16/87	1800-1900	5
7	8/27-8/28/87	1800-1900	7
8	8/28-8/29/87	1800-1900	10
9	8/29-8/30/87	1700-1800	2
10	9/2-9/3/87	1400-1500	35
11	9/3-9/4/87	-	ca. 0

Table 7. Maximum Hourly Average Ozone Concentrations

<u>Sampling Day</u>	<u>Date</u>	<u>Period (PDT)</u>	<u>O₃ (ppb)</u>
1	6/19-6/20/87	1400-1500	57
2	6/24-6/25/87	1300-1400	90
3	6/25-6/26/87	-	Not Determined
4	7/13-7/14/87	1200-1300	40
5	7/14-7/15/87	1500-1600	81
6	7/15-7/16/87	1500-1600	82
7	8/27-8/28/87	1300-1400	75
8	8/28-8/29/87	1300-1400	102
9	8/29-8/30/87	1300-1400	90
10	9/2-9/3/87	1300-1400	174
11	9/3-9/4/87	1400-1500	52

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APPENDIX A^a

Listing of One-Hour Average Values for
SO₂, O₃, Relative Humidity and Temperature

Sampling Day 1 (6/19-6/20/87)

	01 TEMP(C)	02 DEWPOINT	03 R.H.	04	05 O ₃ (PPB)	06	07 SO ₂ (PPB)
02:01:00	16.13	11.59	75.10		8.44		-0.85
03:01:00	15.80	11.72	77.46		2.21		-1.07
04:01:00	15.51	12.88	85.30		9.15		-1.67
05:01:00	15.89	13.34	85.80		26.26		-2.42
06:01:00	16.32	12.90	81.03		31.65		-2.20
07:01:00	16.41	12.35	77.63		35.36		-2.48
08:01:00	16.64	12.13	75.33		29.56		-2.45
09:01:00	17.46	11.76	69.69		33.61		-2.70
10:01:00	19.02	11.77	63.16		34.00		-2.44
11:01:00	20.06	12.12	60.58		44.80		-2.81
12:01:00	21.00	12.05	56.83		50.00		-2.98
12:05:13	21.00	12.05	56.83		50.00		-2.98
13:01:00	21.65	11.69	53.26		56.69		-2.99
14:01:00	22.56	11.18	48.78		57.22		-3.45
15:01:00	22.72	11.82	50.52		52.47		-2.65
16:01:00	22.79	12.41	52.20		48.59		-2.68
17:01:00	22.75	12.35	52.13		42.10		-2.18
18:01:00	22.66	12.55	52.95		43.00		-0.03
19:01:00	21.19	12.91	59.53		36.11		1.64
20:01:00	18.99	12.91	68.41		20.46		3.54
21:01:00	17.69	11.92	69.48		15.25		3.07
22:01:00	16.97	11.55	71.23		9.59		1.66
23:01:00	16.76	11.95	73.82		5.65		2.63
00:01:00	16.60	11.53	72.60		14.47		-0.58
01:01:00	16.48	11.17	71.49		13.34		2.27

a. Significant figures shown do not reflect precision, which was unmeasured. Ozone and SO₂ results should be rounded to the nearest ppb before use. Relative humidity values should be rounded to the nearest percent, and temperature to the nearest °C.

Sampling Day 2 (6/24-6/25/87)

	01 TEMP(C)	02 DEWPOINT	03 R.H.	04	05 O ₃ (PPB)	06	07 SO ₂ (PPB)
02:00:00	17.58	14.18	80.95		49.98		6.31
03:00:00	17.13	14.08	83.29		45.70		6.20
04:00:00	17.24	14.19	82.74		44.32		6.35
05:00:00	17.89	14.26	80.18		41.77		7.06
06:00:00	17.97	14.21	79.57		36.94		6.25
07:00:00	18.01	14.25	79.53		32.95		6.97
08:00:00	18.48	14.33	77.46		29.77		7.60
09:00:00	18.73	14.50	77.37		34.39		6.34
10:00:00	19.53	14.53	73.87		38.50		5.92
11:00:00	20.52	14.43	69.07		50.16		5.74
12:00:00	21.84	14.44	63.24		61.92		5.33
13:00:00	22.63	14.46	60.51		77.65		4.80
13:46:37	23.50	14.61	57.84		88.56		5.21
14:00:00	23.75	14.66	57.13		90.92		5.64
15:00:00	23.98	14.72	56.47		87.92		7.19
16:00:00	23.89	14.98	57.97		82.89		6.86
17:00:00	24.28	15.44	58.37		74.91		7.56
18:00:00	23.72	15.31	59.85		69.94		9.02
19:00:00	22.27	15.16	65.04		57.73		10.88
20:00:00	19.95	15.05	74.12		62.58		6.47
21:00:00	18.65	14.95	79.93		63.29		6.01
22:00:00	18.59	14.86	80.17		62.98		6.32
23:00:00	18.66	14.96	79.84		61.67		6.52
00:00:00	18.63	14.97	80.41		63.39		5.98
01:00:00	18.60	15.06	80.20		56.63		5.40

Sampling Day 4 (7/13-7/14/87)

	01 TEMP(C)	02 DEWPOINT	03 R.H.	04	05 O ₃ (PPB)	06	07 SO ₂ (PPB)
02:00:00	18.00	24.00	99.89		8.05		3.35
03:00:00	17.03	20.30	99.30		6.96		3.25
04:00:00	16.75	19.77	98.78		8.32		3.55
05:00:00	16.29	19.29	99.00		8.61		3.51
06:00:00	16.22	19.25	98.20		9.06		4.23
07:00:00	16.87	19.45	98.45		9.71		5.29
08:00:00	18.52	19.60	98.21		11.75		5.69
09:00:00	20.18	20.04	98.21		16.24		6.76
10:00:00	22.11	20.38	91.78		23.77		7.61
11:00:00	23.12	20.77	87.95		25.34		5.57
12:00:00	23.75	20.71	83.45		32.99		6.82
13:00:00	24.98	20.66	76.98		39.56		10.33
14:00:00	24.72	20.27	75.96		37.06		10.79
15:00:00	24.57	20.06	75.83		31.37		11.54
16:00:00	24.64	16.39	59.21		34.79		10.02
17:00:00	24.40	14.26	52.67		24.15		13.13
18:00:00	23.51	14.24	55.46		20.05		8.27
19:00:00	22.01	14.86	63.56		16.15		7.13
20:00:00	20.08	14.83	71.86		14.33		7.23
21:00:00	18.82	14.24	74.10		16.14		4.39
22:00:00	18.25	14.84	80.13		13.55		4.56
23:00:00	17.92	15.01	82.76		14.66		6.27
00:00:00	17.67	14.80	83.27		13.93		6.73
01:00:00	17.54	14.70	83.26		15.07		5.74

Sampling Day 5 (7/14-7/15/87)

	01 TEMP(C)	02 DEWPOINT	03 R.H.	04	05 O ₃ (PPB)	06	07 SO ₂ (PPB)
02:00:00	17.17	14.46	83.62		13.76		5.40
03:08:33	17.10	14.32	84.53		15.17		4.73
03:08:51	17.10	14.32	84.53		15.17		4.73
03:09:00	17.22	14.35	83.94		15.86		4.82
05:44:25	18.75	14.65	77.03		18.75		4.31
05:46:59	18.75	14.65	77.03		18.75		4.31
05:47:09	18.40	14.60	78.54		15.94		4.74
06:02:00	18.05	14.55	79.98		13.38		5.05
06:39:00	17.92	14.46	80.10		13.31		6.17
07:39:00	18.00	14.57	79.61		14.43		6.20
08:00:00	18.20	14.56	78.37		13.29		5.94
09:00:00	18.58	14.65	77.35		13.48		5.27
10:00:00	18.99	14.66	75.75		18.66		4.21
11:00:00	19.97	14.55	70.72		21.99		3.74
12:00:00	22.03	14.50	62.71		26.13		3.74
13:00:00	23.65	14.74	57.15		63.97		8.47
14:00:00	24.33	14.91	55.26		73.95		10.97
15:00:00	24.85	15.26	55.04		75.25		11.51
16:00:00	24.92	15.52	55.81		81.18		8.22
17:00:00	24.23	15.31	57.04		47.28		11.22
18:00:00	22.92	15.07	60.71		45.70		13.82
19:00:00	21.39	15.24	68.07		38.22		9.86
20:00:00	19.25	15.16	77.01		44.27		15.56
21:00:00	18.12	14.91	81.28		46.82		6.68
22:00:00	18.52	14.85	79.57		38.45		6.27
23:00:00	18.52	15.02	79.00		29.30		4.99
00:00:00	18.69	14.88	78.00		40.19		4.11
01:00:00	18.05	14.56	79.66		48.82		1.84

Sampling Day 6 (7/15-7/16/87)

	01 TEMP(C)	02 DEWPOINT	03 R.H.	04	05 O ₃ (PPB)	06	07 SO ₂ (PPB)
02:00:00	17.77	14.69	81.91		46.10		0.82
03:00:00	17.53	14.89	84.35		45.92		1.85
04:00:00	17.83	14.76	82.44		49.04		1.87
05:00:00	19.32	14.84	75.51		50.94		-0.30
06:00:00	18.74	14.75	77.38		43.34		-0.94
07:00:00	18.05	14.65	80.22		29.84		1.07
08:00:00	17.69	14.73	82.35		34.71		2.14
09:00:00	17.58	15.08	83.63		39.68		2.91
10:00:00	17.98	14.76	81.53		40.61		3.85
11:00:00	18.33	14.96	79.04		42.72		3.37
12:00:00	18.53	14.79	78.92		44.14		3.03
13:00:00	18.98	14.78	76.40		42.87		3.19
14:00:00	19.43	14.84	74.09		45.81		3.28
15:00:00	20.50	14.52	68.65		51.08		3.75
16:00:00	21.06	14.50	66.14		57.64		3.78
17:00:00	21.44	14.55	64.72		55.65		3.90
18:00:00	21.10	14.73	66.75		53.66		4.32
19:00:00	20.54	14.92	70.23		51.22		4.47
20:00:00	19.07	14.92	76.86		42.17		3.93
21:00:00	18.17	14.92	81.04		45.47		2.42
22:00:00	18.30	14.79	80.26		47.53		2.50
23:00:00	18.24	14.66	80.61		49.81		2.70
00:00:00	18.19	14.82	80.79		51.73		2.68
01:00:00	17.94	14.96	82.04		46.28		2.19

Sampling Day 7 (8/27-8/28/87)

	01 TEMP(C)	02 DEWPOINT	03 R.H.	04	05 O ₃ (PPB)	06	07 SO ₂ (PPB)
02:01:00	19.16				12.00		-1.64
03:01:00	20.27				12.53		-1.38
04:01:00	20.87				13.66		-1.61
05:01:00	20.41				29.96		-1.60
06:01:00	19.22				3.47		-1.51
07:01:00	19.63				-0.60		-0.81
08:01:00	19.70				1.22		0.22
09:01:00	21.84				9.76		1.14
10:01:00	21.97				23.46		1.68
11:01:00	23.53				57.57		6.33
12:01:00	24.84				69.08		6.64
13:01:00	25.44				66.03		-0.37
14:01:00	25.70				75.54		4.16
15:01:00	24.79				69.53		7.32
16:01:00	24.16				62.47		5.38
17:01:00	23.44				40.17		6.12
18:01:00	22.38				31.47		7.99
18:57:18	21.19				28.02		7.46
18:59:00	20.83				25.39		4.88
19:00:00	20.47				24.02		2.74
20:00:00	19.55				15.06		4.44
21:00:00	18.89				11.03		8.34
22:00:00	18.78				1.91		2.83
23:00:00	18.75				1.48		1.06
00:00:00	18.74				4.93		1.00
01:00:00	19.28				24.60		0.01

Sampling Day 8 (8/28-8/29/87)

	01 TEMP(C)	02 DEWPOINT	03 R.H.	04	05 O ₃ (PPB)	06	07 SO ₂ (PPB)
02:00:00	19.39				26.86		1.23
03:00:00	19.22				37.85		-1.29
04:00:00	18.60				31.98		-1.70
05:00:00	17.86				12.59		-0.76
06:00:00	17.67				-0.47		1.19
07:00:00	18.17				0.53		4.43
08:00:00	19.20				3.79		7.32
09:00:00	20.13				11.31		7.14
10:00:00	20.44				15.68		5.64
11:00:00	21.55				33.47		5.05
12:00:00	23.61				71.50		5.09
13:00:00	25.04				86.46		5.57
14:00:00	25.41				102.32		5.36
15:00:00	24.87				100.40		1.78
16:00:00	24.88				76.02		1.53
17:00:00	24.55				54.80		1.29
18:00:00	23.32	15.23	59.64		72.79		0.67
19:00:00	22.33	15.49	65.58		40.27		9.93
20:00:00	20.46	15.44	73.16		35.28		2.01
21:00:00	18.84	15.26	79.96		49.69		-0.80
22:00:00	18.48	15.44	82.40		40.46		-1.48
23:00:00	18.32	15.52	83.40		42.11		-1.45
00:00:00	18.33	15.38	84.09		36.51		-1.30
01:00:00	18.44	15.48	84.46		29.08		-1.18

Sampling Day 9 (8/29-8/30/87)

	01	02	03	04	05	06	07
	TEMP(C)	DEWPOINT	R.H.		O ₃ (PPB)		SO ₂ (PPB)
02:00:00	18.56	15.69	84.84		47.27		-1.39
03:00:00	18.60	15.85	83.46		54.14		-1.54
04:00:00	18.52	15.84	81.26		45.77		-1.57
05:00:00	18.65	15.58	79.88		32.44		-1.30
06:00:00	18.98	15.53	77.95		24.83		-1.22
07:00:00	18.82	15.75	80.71		26.18		-1.28
08:00:00	19.03	15.64	77.46		25.02		-0.96
09:00:00	19.31	15.54	76.13		41.03		-1.75
10:00:00	19.53	15.24	73.56		42.51		-2.38
11:00:00	20.26	15.30	70.45		50.13		-1.90
12:00:00	20.77	15.29	67.93		61.62		-0.94
13:00:00	22.19	15.61	63.68		75.89		0.33
14:00:00	23.55	16.73	62.98		90.15		0.62
15:00:00	24.06	18.75	70.01		89.34		1.03
16:00:00	24.15	17.29	63.25		81.73		0.45
17:00:00	23.89	17.62	65.76		83.28		0.64
18:00:00	23.16	17.11	67.37		69.95		1.75
19:00:00	21.07	16.29	71.28		46.55		0.27
20:00:00	19.89	18.08	84.82		30.87		0.86
21:00:00	19.41	19.01	91.93		18.23		-0.24
22:00:00	18.94	17.32	87.69		13.49		-0.55
23:00:00	18.58	17.83	91.98		7.66		-0.55
00:00:00	18.57	18.09	93.08		7.17		-1.06
01:00:00	18.37	18.54	94.42		2.82		-0.85

Sampling Day 10 (9/2-9/3/87)

	01	02	03	04	05	06	07
	TEMP(C)	DEWPOINT	R.H.		O ₃ (PPB)		SO ₂ (PPB)
02:00:00	20.82	15.59	72.57		0.35		4.02
03:00:00	20.07	15.82	76.42		-0.98		1.59
04:00:00	20.37	15.84	74.76		-0.60		2.49
05:00:00	20.69	15.75	72.58		-0.52		4.39
06:00:00	20.33	15.41	74.48		0.28		7.21
08:00:00	21.92	16.22	69.88		2.75		8.73
09:00:00	25.27	16.25	56.52		9.37		9.52
10:00:00	27.17	15.81	48.90		25.47		9.72
11:00:00	29.46	15.38	41.80		70.52		9.57
12:00:00	31.10	16.36	40.48		88.38		10.13
13:00:00	30.29	15.33	39.50		145.96		13.61
14:00:00	32.51	15.40	35.17		174.07		28.04
15:00:00	30.03	14.87	39.45		46.62		35.01
15:18:40	29.51	14.45	39.58		45.26		15.00
16:00:00	29.09	14.05	39.38		49.94		5.32
17:00:00	28.35	13.90	40.51		55.59		0.41
18:00:00	27.52	12.91	39.55		40.26		1.73
19:00:00	27.08	11.57	36.79		41.97		6.54
20:00:00	23.28	14.64	57.53		12.53		6.57
21:00:00	20.30	16.95	79.52		16.96		2.41
22:00:00	19.59	16.87	82.84		18.90		1.61
23:00:00	19.64	16.35	80.27		12.93		2.68
00:00:00	19.88	17.18	83.26		18.40		1.81
01:00:00	19.75	17.18	84.22		18.71		0.41

Sampling Day 11 (9/3-9/4/87)

	01 TEMP(C)	02 DEWPOINT	03 R.H.	04	05 O ₃ (PPB)	06	07 SO ₂ (PPB)
02:00:00	19.70	16.99	83.36		30.52		-0.16
03:00:00	19.32	17.03	85.81		26.87		-0.47
04:00:00	19.93	17.08	82.75		25.91		-0.72
05:00:00	20.21	17.06	81.19		32.43		-1.02
06:00:00	20.53	16.92	78.66		35.66		-0.76
07:00:00	20.86	16.78	76.48		32.69		-0.86
08:00:00	20.31	16.59	77.72		31.89		-0.80
09:00:00	21.47	16.57	73.14		27.88		-0.15
10:00:00	22.94	16.70	66.75		34.08		0.16
11:00:00	24.72	16.84	60.64		38.53		0.39
12:00:00	25.11	16.65	58.82		44.64		-0.19
13:00:00	24.74	16.44	58.70		55.52		-0.49
14:00:00	23.76	16.33	61.70		53.21		-1.11
15:00:00	23.14	16.11	63.33		51.85		-0.85
16:00:00	22.72	15.65	63.68		49.94		-0.54
17:00:00	22.38	15.51	64.25		46.38		-0.12
18:00:00	21.62	15.52	67.73		41.54		0.08
19:00:00	20.20	15.46	73.39		35.50		0.00
20:00:00	19.35	15.45	76.97		37.82		-0.18
21:00:00	19.14	15.17	77.11		34.16		-0.04
22:00:00	19.22	14.92	75.11		37.75		-0.23
23:00:00	19.37	14.60	72.38		38.17		-0.60
00:00:00	20.03	14.56	70.63		37.04		-0.98
01:00:00	20.58	14.61	68.28		40.05		-1.99

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