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PLUME CHARACTERISTICS

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REA

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INTRODUCTION

Interest in the fate of sulfur dioxide, one of the major atmospheric pollutants, has recently been heightened by recognition that oxidation product sulfate is a serious health hazard. The major source of urban sulfur dioxide arises from combustion of coal and decisions affecting the operation and location of power plants will be strongly influenced by our understanding the nature of sulfate formation and its dispersion from the source. Furthermore, power plant plumes are convenient vehicles for studying the oxidation of atmospheric sulfur dioxide. Although they have been studied extensively there is still considerable disagreement concerning the rate and mechanism of atmospheric sulfate formation from sulfur dioxide, and the relative importance of meteorological parameters.

In previous papers[1,2] we reported on sulfur-dioxide conversion (oxidation to sulfate) in both oil- and coal-fired power plant plumes. Samples were obtained by fixed-wing aircraft and analyzed for SO_2 and particulate sulfate content as well as stable sulfur isotope ratios. A mechanism was proposed for the oxidation which involved the dissolution of a small fraction of the SO_2 in the water associated with the particulates, followed by a fast catalytic formation of sulfate, permitting more SO_2 to dissolve. Maximum conversion reached 20% in the oil-fired plume, whereas it seldom exceeded 5% in the coal-fired plume. The difference was attributed to the particulate loading and the catalytic nature of the particulates in the respective plumes. This investigation we have extended our observations to four additional coal-fired plants.

EXPERIMENTAL

SAMPLING:

Samples of the power plant plumes were obtained with a single-engine Cessna 182 by means of a 8 x 10" high-volume filter assembly containing a glass-fiber particulate filter (Whatman 81) for sulfate collection followed by two KOH-triethanolamine impregnated cellulose papers (Schleicher and Schuell Fast Flow No. 2W) to absorb SO_2. In some runs this was replaced with a 4" diameter filter pack. Details of the equipment have been described previously.[1,3] Pallflex Tissuequartz filters, pretreated to neutralize alkaline sites was sometimes used as the prefilter. This modification made possible chemical speciation of plume sulfate particulates with emphasis upon measurement of sulfuric acid. Pretreatment of the quartz filters consisted of first heating overnight at 700-750°C, subsequently rinsing with 2-3 l of distilled water using suction, drying at 110°C, soaking in hot 85% H_3PO_4 at steam bath temperatures for 30 min., rinsing thoroughly with 10-15 l distilled water using suction, and then drying.

ANALYSIS:

Analyses for the amount of SO_2 and SO_4^{2-} collected on the filter pack were performed by a procedure which utilizes silver (110).[4] Briefly, the collected sulfur compounds were reduced to H_2S, distilled over into cadmium acetate to precipitate the sulfide, and metathesized with $AgNO_3$ containing tracer ^{110}Ag to form Ag_2S which was separated and counted. When isotope ratios (^{34}S:^{32}S) were desired, the Ag_2S was converted to SO_2 by combustion with oxygen and the isotope ratios measured with a mass spectrometer.[4]

OBSERVATIONS

GENERAL:

The major effort focused upon Union Electric Company's Labadie, Missouri, plant in conjunction with the RAPS (Regional Air Pollution Study) Program. Other experiments, of somewhat smaller dimensions, were performed at the Portage des Sioux plant of Union Electric Company at West Alton, Missouri; at the Muscle Shoals, Alabama, plant of the Tennessee Valley Authority; and the Kyger Creek plant of Ohio Valley Electric Company, situated near Charleston, West Virginia. Upwind background measurements of SO_2 and SO_4^{2-} concentrations were made for all runs and were subtracted from plume concentrations accordingly (no background corrections were made at Muscle Shoals). Background SO_2 concentrations at plume height for Labadie and Sioux locations averaged at 0.028 ppm with values ranging from 0.003 ppm to 0.082 ppm. Plume SO_2 concentrations were generally an order of magnitude or more greater than background, so that the subtractive correction for background seldom exceeded 10%. Particulate sulfate background ranged over a factor of ~50, from 1.1 μg m^{-3} to 56 μg m^{-3}, averaging at 12.9 μg m^{-3}. Corrections applied to plume SO_4^{2-} ranged generally from 5 to 30%. The background corrections fell well within the considerations of plume variability and any uncertainties attached to their measurement have a minimal effect upon calculated conversion rates. Upon several occasions particulate sulfate within the plume reached 100 μg m^{-3} at distances of 16 to 48 km and twice were as high as 200 μg m^{-3} at 16 km. However, even when the SO_4^{2-} was as high as 200 μg m^{-3} it only represented 3 to 4% of the total sulfur.

PREFERENTIAL SULFATE DROPOUT:

In previous studies of the plume of the Keystone plant in Pennsylvania[2] it appeared that a significant amount of sulfate was dropping out of the plume. A test was performed at Labadie to evaluate this possibility. A sample was taken 8 km downwind at an elevation of 120 meters directly below the plume which was at a 220 meter elevation. The results were compared with a background sample taken at plume elevation upwind of the stack. Although SO_2 concentrations were approximately equal in both cases, 0.061 ppm for background and 0.056 ppm beneath the plume, the SO_4^{2-} level under the plume, 13.6 μg m^{-3}, was 60% higher than the background value of 8.4 μg m^{-3}. The 5 μg m^{-3} increase above background probably represents only 10% of the plume SO_4^{2-} in this instance. However, one must be aware that at times plume dropout could become significant, resulting in a measured oxidation rate which is lower than the true rate. In future experiments more attention should be paid to measuring the extent of plume dropout of sulfate.

REPRODUCIBILITY:

Controlled experiments within the laboratory and of ambient samples at ground level defining precision of analyses and reproducibility of data have inspired confidence that our measurement techniques are good to approximately 20%.[3,4] It would be highly unreasonable though to extrapolate these results as an indication of plume data reproducibility. There are intermittent changes constantly occurring in plant operating conditions affecting total S emissions and SO_4^{2-}/SO_2 ratios and in the natural environment affecting plume behavior, such as wind speed and direction, temperature, humidity, and solar radiation. Consequently, even under the most stable conditions, one should anticipate significant variability in plume data within the time frame of an experimental run. Therefore, an experiment was conducted to define plume variability more precisely. Samples were taken at 1.6, 4.8, and 16 km downwind from the stack. After a 30 min. interval for background sampling, the plane returned to the respective locations for a second series of samples. The results indicate that there can be changes in the percent of sulfur present as SO_4^{2-} by as much as a factor of two between sampling periods. These differences could be due to any of the above delineated but difficult to quantitate reasons. What should be recognized, however, is that it will be most difficult without a sufficient number of runs to interpret differences in measured oxidations of less than a factor of two.

FLIGHT PATTERNS:

Two basic approaches to flight patterns can be taken. The first assumes that the extent of reaction at a given distance is independent of the position within the plume (fringe vs. center). This necessitates that only a concentration ratio of SO_4^{2-} to SO_2 be obtained to measure the extent of oxidation. The second approach assumes that there might be differences in the extent of oxidation depending on the position within the plume; to determine the average extent of oxidation, integrated samples of each species need be obtained across a complete plane of the plume. In practice this is not possible so that a number of transects (usually three) are taken at different elevations and an integration performed by deriving plume dimensions and then using wind fields to determine plume fluxes.[5] We believe that the second approach is necessary only when one is studying fast reactions such as NO oxidation but is not required for slow reactions such as we believe the case to be with SO_2. Nevertheless, we decided to test our premise as to whether there are differences to be seen depending on the sampling flight pattern.

Our usual flight pattern consisted of starting at the closest location to the stack and progressing downwind. Whenever possible, the plane flew in tight circles within the plume to facilitate obtaining the maximum amount of sample within the available time. At closer distances where the narrow plume prohibited this type of operation, the plane flew back and forth across the plume until adequate sample was collected. In both cases, elevation was maintained as close as possible to the vertical center line.

To establish the interchangeability of both procedures, a comparison was made of particulate sulfur to total sulfur ratios on samples obtained by cross plume and circular within plume samples. Four pairs of cross and circular plume samples were taken at 8 km from the stack; the experiment was repeated again with two pairs. Both sets of data indicate that no trend in either direction exists and that reproducibility falls within the realm of plume variability.

An experiment was devised to explore the possibility that conversion rates could be greater in the fringes of the plume than in the center. Cross-plume samples were taken at approximately 5 and 16 km. from the emission source by flying at three discrete vertical levels of the plume representing the top, center, and bottom sections. Should more reaction occur at the fringes, one should expect a greater conversion of SO_2 to particulate S at the upper and lower levels. No significant differences were found to exist exceeding those anticipated from plume variability. The question that was raised[6] suggesting that our cross-plume center elevation sampling approach gives erroneous results compared with a flux-measuring-sampling approach, does not appear to be justified.

RESULTS

A typical set of data collected at Labadie is shown in Table I. Both SO_2 and SO_4^{2-} concentrations have been corrected for background contributions. The last column, % SO_2 converted to particulate sulfur, is calculated from the ratio of particulate S to total S, including sulfate formed during the combustion process and emitted from the stack. No attempt was made to correct the data for primary sulfate production. However, this value is estimated at ~1% based upon our previous experiments at another coal fired plant.[2] The main feature shown in this data is that essentially all of the observed oxidation occurs within the first few kilometers of the stack. There is some indication of possible plume dropout of sulfate with distance (decreasing % conversion) but one should consider that the reproducibility of plume measurements might be no better than a factor of two.

A composite plot of % SO_2 converted as a function of distance from the source is presented in figure 1. Each run is shown by drawing a straight line to connect the points between succeeding distances in the run. Most runs went out to 15 km and with decreasing frequency to as far as 50 km. This plot clearly demonstrates the rather narrow envelope, between 0.5 and 4%, in which the bulk of the data fall. In only two runs were oxidations observed which reached significantly higher levels.

Examination of the envelope of the composite plot again indicates there is no significant increase in the extent of oxidation with increasing distance. No significant change in the general structure of the curves resulted by considering time as determined from wind speeds instead of the measured distances.

In Table II are presented the results taken at Sioux. The essential features are the same as those which are observed at Labadie. The data from four runs, made at Muscle Shoals are presented in Table III. Included are the measured SO_2 ^{34}S:^{32}S isotope ratios presented as del values defined as

$$\text{del}\ ^{34}S = \left[\frac{^{34}S/^{32}S\ \text{(Sample)}}{^{34}S/^{32}S\ \text{(Standard)}} - 1\right] X\ 1000\ . \qquad (1)$$

No specific trend in del vs. distance was observed. In fact, variations were close to the analytical precision anticipated for sample preparation and mass spectrometry. The lack of any trend for the isotope ratio measurements parallels the similar lack of any trend with distance of the % converted as determined from concentration measurements. The correspondence in the two methods assures that the low oxidation rates do not arise from a spurious aspect of either technique.

Results of the two flights made at Kyger Creek are displayed in Table IV. The ^{34}S:^{32}S isotopic ratios which have been corrected for background are again essentially invariant with distance, indicating very little oxidation in this plume. Calculations of % conversion based upon concentration measurements support this contention.

DISCUSSION

The most significant conclusion one can deduce from an overview of the data, is that the overall extent of oxidation is comparatively low, seldom exceeding 5% over the distances (as much as 50 km) and the times (as long as 2 hrs) encompassed by these experiments. Completely absent is the appearance of any sort of trend. There is certainly no general indication, as suggested by others[5,6] there is at first a very slow reaction followed by a sharply increasing rate at some distinct distance downwind. In fact, quite the contrary is observed in the present studies. All the oxidation that does take place occurs prior to or within the first few kilometers and then the reaction seems to be turned off during the rest of the time scale during which the plume can be followed.

This observation is substantiated by averaging the % SO_2 converted in figure 1 at each of nine discrete distances. The averaging involves interpolation between actual data points, from which the "pooled" curve of figure 2 was obtained. The data summarized in this manner indicate that on average there is a 1 to 2% oxidation of SO_2 to SO_4^{2-} during the initial stages of the plume, and that this value does not increase with distance or time. This characteristic is in general agreement with that observed at Keystone[2] where the extent of reaction was possibly 3 to 4%. In a recent publication we discuss that the rate of plume expansion is shown to exert a controlling influence upon reactions that are higher than first order in plume constituents and that quenching of reaction is exhibited at high expansion rates. In this instance we believe the reaction is a second order heterogeneous reaction involving particulates. However, since the apparent quenching occurs so soon after the emission we do not believe that plume dilution is responsible in this instance but rather that the catalytic activity of the particulates is consumed by the formation of sulfate.

The data were examined to see if relative humidity, temperature, atmospheric stability, or early morning vs. early evening had any significant effect on the extent of oxidation. No strong effects were observed. As an example of such considerations, we present in figure 3 the data obtained at Labadie at a distance of 5 km from the source. The plot shows the percent oxidized vs. relative humidity. The morning and evening points are delineated and the data are grouped into three temperature regimes. No correlations or groupings can be observed.

A more detailed presentation and analysis of the data will be presented elsewhere.[8]

CONCLUSIONS

(1) Under a variety of parameters, within the limits of plume detection, SO_2 conversion in coal-fired plumes is of the order of a few percent, usually significantly less than 5% and only occasionally exceeding this level.

(2) Within the range of 10-25°C and 32-85% relative humidity, no correlation has been found between these parameters and extent of oxidation.

(3) Similarly, distance, travel time, and time of day seem to have no effect upon SO_2 oxidation.

(4) Within experimental error, no evidence was found for the existence of plume fringe effects in accelerating SO_2 conversion.

(5) Reproducibility measurements have shown the plume can vary from moment to moment by as much as a factor of two in percentage of total S as particulate S.

(6) Further investigations should include studies of the effect of high humidity, low temperature, total darkness, atmospheric stability, and the significance of plume dropout.

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TABLE I

Results of a Typical Run at Labadie

Source of Sample Distance (km)	Concentrations SO_2 (ppm)	$SO_4^=$ (μg m^{-3})	%SO_2 Converted to Particulate S
Background	0.026	5.1	
1.6	2.14	210	2.4
4.8	1.58	248	3.9
16	0.93	97	2.6
32	0.83	91	2.8
56	0.42	29	1.8

TABLE II

Results of runs at Sioux

Source of sample, distance (km)	Concentrations SO_2 (ppm)	SO_4^{2-} ($\mu g\ m^{-3}$)	% SO_2 Converted to Particulate S
Background	0.008	15	
1.6	1.19	96	1.6
4.8	0.55	43	1.3
16	0.21	40	3.1
40	0.13	16	0.2
64	0.13	17	0.5
Background	0.026	8.6	
1.6	0.59	41	1.4
4.8	0.46	31	1.2
Background	0.016	21	
1.6	1.28	66	0.9
4.8	0.82	201	5.2
16	0.43	61	2.3
32	0.27	33	1.1

TABLE III

Results of runs at Muscle Shoals

Source of sample, distance (km)	Concentrations SO_2 (ppm)	SO_4^{2-} ($\mu g\ m^{-3}$)	Del Values of SO_2	% SO converted based on conc.
1	5.97	1878	- 0.2	6.8
20	0.85	75	- 0.2	2.0
1	8.90	392	0.0	1.0
5	6.83	259	0.2	0.9
20	2.37	167	0.7	1.6
1	4.22	401	- 0.6	2.2
5	0.71	55	- 0.7	1.8
10	0.46	30	- 0.3	1.5
20	0.34	17	- 0.9	1.2
1	2.92	200	- 0.3	1.6
5	0.97	61	- 0.5	1.5
20	0.27	22	- 0.8	1.9

TABLE IV

Results of runs at Kyger Creek

Source of Sample, Distance (km)	Concentrations SO_2 (ppm)	SO_4^{2-} ($\mu g\ m^{-3}$)	Del Values of SO_2	% SO_2 Converted To Particulate S
Background	0.004	8.6	- 2.5	
1.6	2.79	166	5.3	1.5
3.2	1.56	100	5.4	1.7
4.8	0.89	33	5.5	0.9
8	0.66	23	5.3	0.9
16	0.31	7.7	5.1	0.6
Background	0.012	8.1	1.6	
1.6	4.35	259	4.8	1.5
3.2	4.41	182	5.0	1.0
4.8	2.90	120	5.2	1.0
8	1.62	77	4.9	1.2
16	1.31	45	5.0	0.9

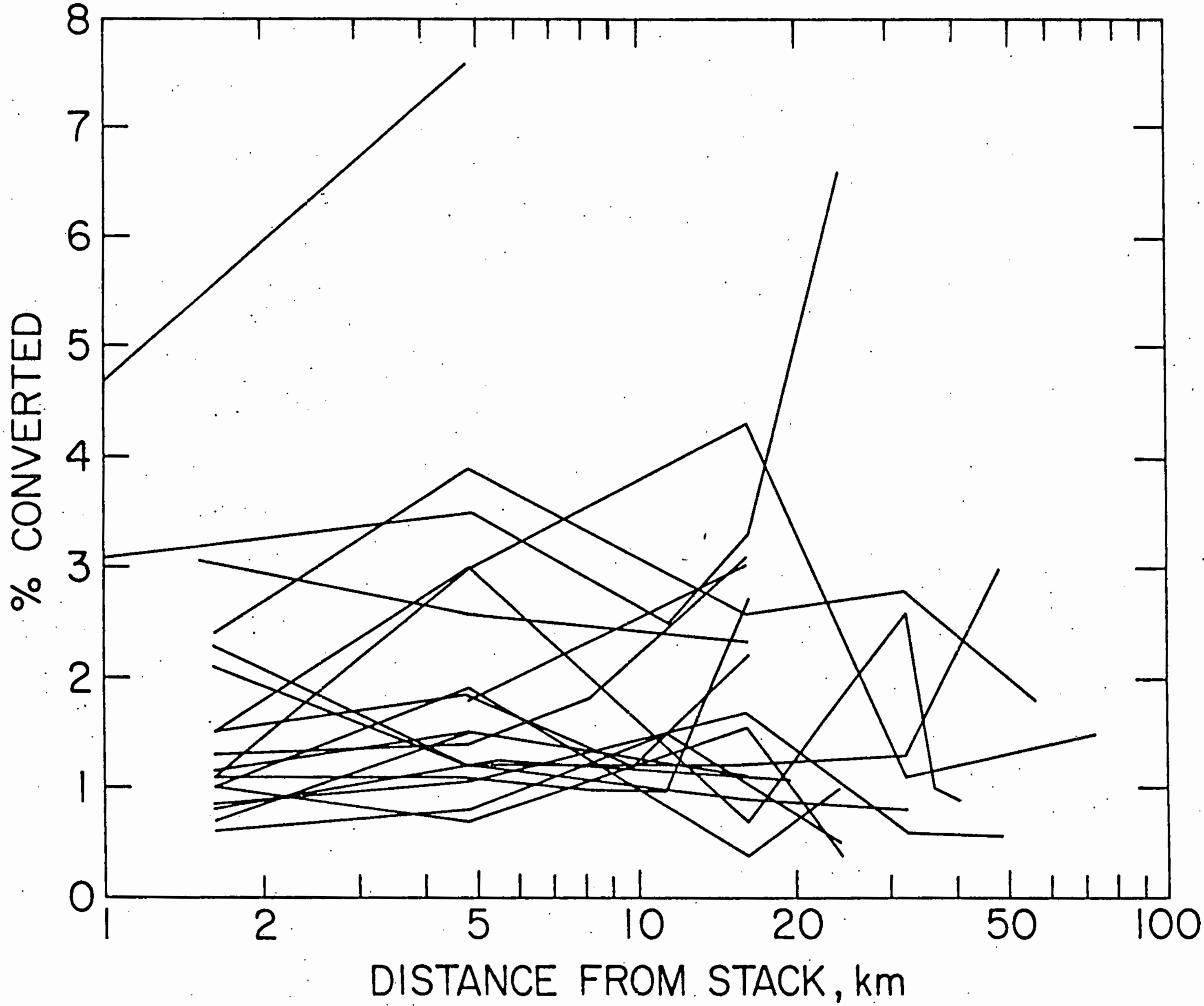

Figure 1

Conversion of SO_2 with distance.

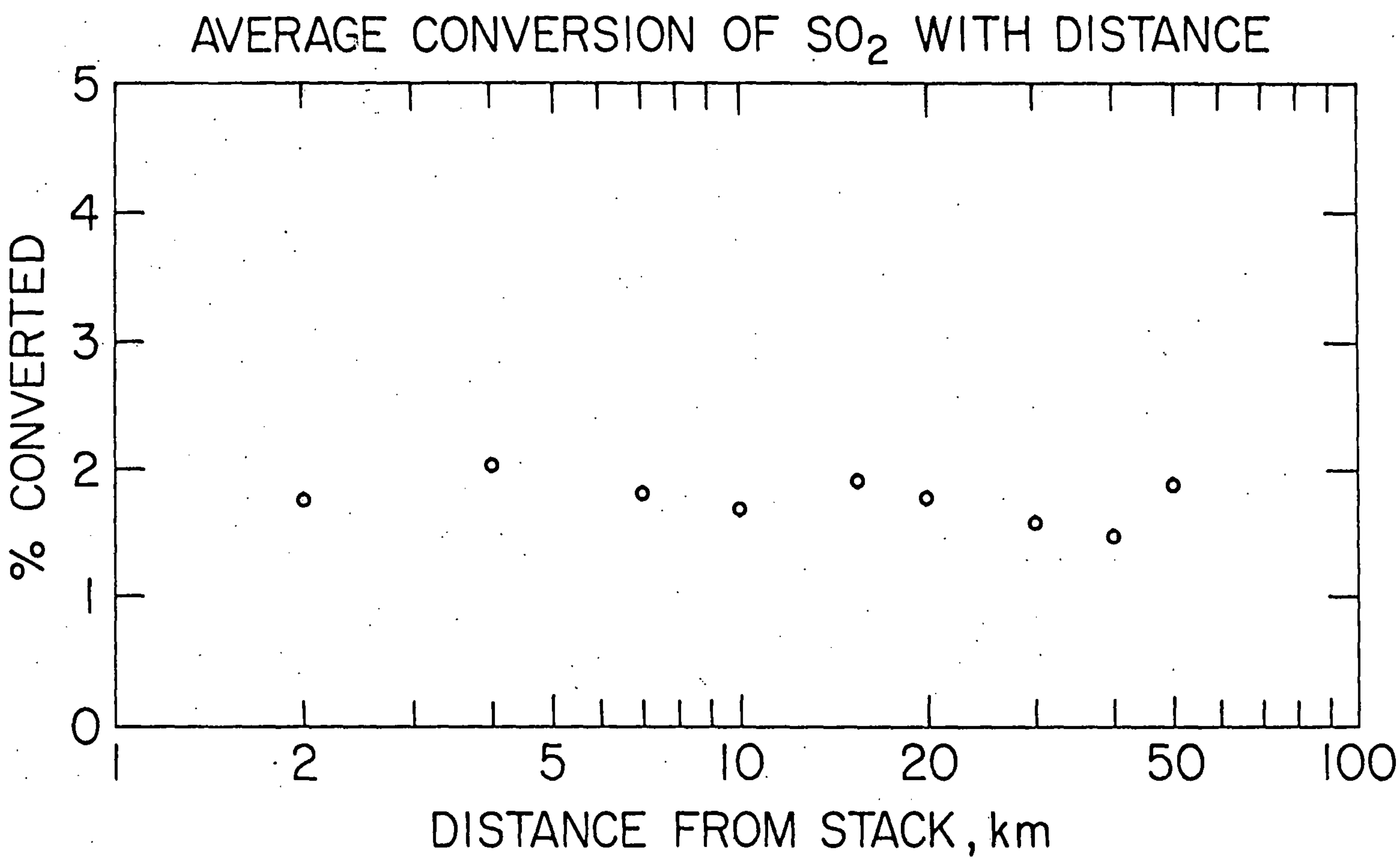

Figure 2

Average conversion of SO_2 with distance.

Figure 3

Evaluating relative humidity, time of day, and temperature on conversion of SO_2 at 5 km.