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CONVERSION RATES IN POWER PLANT PLUMES BASED ON FILTER PACK DATA

Part I - The Coal-Fired Cumberland Plume

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Abstract

The TVA Cumberland Steam Plant plume was monitored during the August 1978 Tennessee Plume Study of Project STATE. Samples were obtained by employing a triple screen high-volume assembly which contained 1) a quartz filter for collecting particulate SO_4^{2-}, NO_3^- and NH_4^+, 2) two NaCl-impregnated cellulose filters for collecting gaseous nitrate, and 3) two K_2CO_3-impregnated cellulose filters for collecting SO_2. Formation rates of sulfate and nitrate in the atmosphere were calculated by using total sulfur as a conservative tracer.

Conversion of SO_2 to SO_4^{2-} varied from $\sim$0.1-0.8% h^{-1} during night and early morning hours; late morning and afternoon rates ranged from $\sim$1-4% h^{-1}. Rate of formation of NO_3^- from NO was $\sim$0.1-3% h^{-1} and $\sim$3-12% h^{-1} for similar time periods. Particulate NH_4^+ concentrations generally increased with plume age, but rates of formation varied widely. Mole ratios of NH_4^+/SO_4^{2-} fell within 1-3.

INTRODUCTION

Damage to the ecology and human health by sulfur dioxide, a major anthropogenic atmospheric pollutant, has long been recognized. More recently, the oxidation product sulfate has been indited as potentially more detrimental to health than its precursor (Lave and Seskin, 1977). Efforts to reduce atmospheric sulfur oxide concentrations by legislating SO_2 emission standards have not been completely successful; although SO_2 levels have generally decreased a parallel reduction in sulfate levels has not been observed (Altshuller, 1977). To a large extent, this phenomenon is being attributed to the transport and transformation of emissions from large industrialized areas and power plants over wide geographical areas hundreds of kilometers downwind. (Husar et al, 1978, Gillani et al, 1978). The acid rain which has lowered the pH of virtually all the lakes in the Adirondack region of New York State, for example, may have its origin in acid-forming pollutants from industrialized areas distantly located to the west and south of their ultimate destination (E.P.A., 1979, Galvin et al, 1978). Also of increasing interest during the past few years has been the role of nitric acid and nitrates as contributors to air pollution. More effective control of atmosphere sulfate and nitrate is dependent upon a broader knowledge of sulfur and nitrogen oxide transformation rates.

Although laboratory experiments have made major contributions to reaction rate information, meaningful determinations of these rates under varying meteorological conditions requires studying parcels of air as they are transported during long time periods. Power plant plumes, as convenient vehicles for these measurements, have been utilized by investigators at BNL and many other places (Forrest et al, 1979, Forrest and Newman, 1977, Husar et al, 1978, Lusis et al, 1978, Meagher et al, 1978). A review of recent investigations has been presented (Newman, 1980). Samples taken by fixed-winged aircraft in a plume as it progresses downwind and analyzed for SO_2 and particulate sulfate content reveal the extent of conversion. In previous papers (Newman et al, 1975a and b; Forrest and Newman, 1977; Forrest et al, 1979) we reported on our observations in both oil and coal-fired power plant plumes whereby oxidation of SO_2 to sulfate ranged predominantly from 1 - 4% within a time frame of up to 100 min and 50 km distance. No explicit correlation has been discerned that can clearly associate the extent of oxidation with any meteorological parameter (Newman, 1980). Plumes were tracked primarily in morning or early evening hours during inversion conditions, until they became undistinguishable from the background, which generally occurred in less than 50 km. There remained a special need to obtain more information during midday high sunlight conditions when homogeneous gaseous reactions might predominate, and certainly it would be advantageous to follow the plume for greater distances. Such an opportunity was realized by our participation in Project STATE (Sulfur Transport and Transformation in the Environment), an EPA-sponsored study aimed at investigating the processes affecting the spatial and temporal distributions, as well as properties of, gaseous and particulate sulfur.

During August 1978, BNL's Islander aircraft assisted in the Tennessee Plume Study under Project STATE to characterize the transport and transformation of sulfur in the plume of the coal-fired Cumberland Steam Plant of TVA. Recent development of a modified filter pack containing NaCl-impregnated filters to absorb HNO_3 enabled us to monitor total inorganic nitrate (Forrest et al, 1980) in addition to other constituents. Consequently, among the instruments carried on board the aircraft was a high volume sampler and filter pack assembly which enabled us to measure particulate and gaseous sulfur, particulate ammonium, and total inorganic nitrate (gaseous plus particulate). In this paper, we report on formation rates for sulfate and nitrate which were calculated by using total sulfur as a conservative tracer.

EXPERIMENTAL

Plant description

The Cumberland Steam Plant of TVA is located along Lake Berkley (Cumberland River) in Stewart County, Tenn. Power is generated by two 1300 MW boilers using horizontally opposed burners fueled by western Kentucky coal containing 3 - 5% S. Particles are removed from combustion gases by electrostatic precipitators which generally operate at 99+% efficiency. The gases are emitted via two 305 m stacks.

Sampling

Samples were obtained by means of a 12.5 cm diam. high-volume multi-filter assembly consisting of a quartz prefilter for particulate matter, sodium chloride-impregnated cellulose filters for collecting nitric acid, and potassium carbonate-impregnated cellulose filters for retaining SO_2 (Forrest et al, 1980). Flow rates were set through the assembly at $\sim 0.4\ m^3\ min^{-1}$.

Pallflex Tissuquartz prefilters were prepared by firing to remove binder and then treating with hot phosphoric acid as previously described (Tanner et al, 1977). Potassium carbonate filters were prepared from Schleicher and Schuell Fast Flow 2W papers by a pretreatment consisting of a soaking in 20% (W/V) KOH solution, draining excess liquid, and then drying for 2.5 h at 100°C. The filters were rinsed free of KOH, dried overnight in a vacuum desiccator, and the drying completed by heating at 100°C for 10 - 15 min. Finally a 25% (W/V)

K_2CO_3 - 10% (V/V) glycerol solution was used for impregnation. The excess liquid was removed by a wringer assembly and the filters dried for 5 min at 100°C. The NaCl filter circles were also prepared from Schleicher and Schuell Fast Flow 2W papers by prewashing the filters in distilled deionized water, drying at 110°C and then immersing in 5% (W/V) NaCl. The excess solution was drained off and the filters heated at 100°C to incipient dryness.

Besides the integrating high-volume filter pack, additional equipment on board the BNL aircraft included instrumentation for measuring in real-time SO_2, SO_4^{2-}, O_3, b_{scat}, SF_6, temperature, relative humidity, and total radiation. Flight supervision was under the direction of the STATE Mission Control Center based at Fort Campbell, KY. Plumes were tracked by means of tetroons released near the stacks and followed by radar. Also assisting in tracking were mobile pibal crews and a mobile lidar system (Stanford Research Institute). The major sampling events consisted of crosswind plume traverses, flights in background air, and vertical spirals (not included in this paper). Stack release time and corresponding plume age were calculated from average wind speeds at plume height supplied by pibal measurements (Tennessee Valley Authority) taken at approximately 1/2 hr intervals. Solar radiation data were obtained from the Cumberland plant 1 m tower.

Analysis

The potassium carbonate-impregnated filters were analyzed for collected SO_2 by extracting in dilute peroxide and measuring the resultant sulfate with a Dionex Model 10 Ion Chromatograph (Small et al, 1975). The various anionic species in the sample were separated on an anion exchange column using $NaHCO_3$-Na_2CO_3 as eluent and the eluted sulfate monitored by a conductivity cell.

Particulate sulfate collected on the quartz filter was extracted ultrasonically into water and analyzed by an automated technique (Technicon Instruments Corp., Tarrytown, NY). After removal of heavy metals by ion exchange, sulfate was precipitated by addition of barium chloride in the presence of methylthymol blue. Unreacted barium forms a chelate with the dye and the excess methylthymol blue remaining was measured spectrophotometrically (Adamski and Villard, 1975). Cross-check analyses were performed periodically by ion chromatography.

Quartz filter extracts were also analyzed for particulate nitrate and ammonium by automated techniques. Nitrate was measured spectrophotometrically by reduction with hydrazine to nitrite, diazotization with sulfanilamide and formation of the reddish purplish azo dye by coupling with N-(1-naphthyl) ethylenediamine (Mullin and Riley, 1955). Ammonium was determined colorimetrically by the blue colored compound resulting from the addition of sodium phenoxide and alkaline sodium hydroxide (Bolleter et al, 1961).

Inorganic gaseous nitrate collected on the NaCl-impregnated filters was extracted ultrasonically in water at 40°C and measured for nitrate as above.

Prior to analysis, the sampled filter packs were loaded on a high-volume sampler in the laboratory and room air at 50°C was drawn through the assembly for 5 min to desorb any HNO_3 possibly retained by the quartz filter. As a precaution against introducing extraneous particulate matter, a clean quartz filter was placed upstream of the assembled pack.

OBSERVATIONS

General

Included in this report is a summary of 12 flights made from 18 - 28 August. Samples were taken at distances of 11 to 200 km from the Cumberland plant and the plume ages ranged from 0.8 to 9 hr. Background measurements were taken during all runs and were subtracted accordingly from plume concentrations. The SO_2 background averaged 7.8 $\mu g\ m^{-3}$, ranging from nondetectable levels to 21.9 $\mu g\ m^{-3}$. Corrections to apparent plume concentrations seldom exceeded 20% and averaged $\sim$2%. Particulate sulfate background levels were 1.1 to 27.6 $\mu g\ m^{-3}$ averaging 12.5 $\mu g\ m^{-3}$ as SO_4^{2-}. The background SO_4^{2-} was appreciable and the corrections applied to the plume sulfate measurements could be quite high and averaged $\sim$45%. Inorganic nitrate (particulate plus gaseous) background ranged from 0.7-4.6 $\mu g\ m^{-3}$ with an average of 2.5 $\mu g\ m^{-3}$. Nitrate corrections were also significant, averaging $\sim$38%. The background NH_4^+ ranged from 1.1 to 8.3 $\mu g\ m^{-3}$ and averaged 3.7 $\mu g\ m^{-3}$, but the relatively low plume concentrations led to an average correction to plume particulate NH_4^+ of $\sim$50%.

Oxidation of sulfur dioxide

Conversion of SO_2 to sulfate was calculated by ratioing plume particulate sulfur concentrations to total sulfur after applying corrections due to sulfate formed as a result of the combustion process. Possible introduction of error to these measurements through plume losses by dry deposition have been discussed (Forrest et al, 1979). From both box model calculations with assumed deposition velocities for SO_2 and SO_4^{2-} (Forrest et al, 1979), and also by experimentally observed removal rates at the Portage des Sioux power plant (Husar et al, 1978), errors from this source have been estimated at from 0 to 3.5% h^{-1} of the total sulfur and remain within acceptable limits. Furthermore, since we can anticipate SO_2 deposition to be more rapid than particulate sulfate, the direction of any error from this effect would only be a slight increase of the apparent rate of SO_2 to sulfate conversion.

Nitrate formation

Nitrogen oxides are emitted in power plant plumes almost totally as NO which converts to NO_2 as atmospheric O_3 diffuses into the plume. By measuring plume NO_2/NO ratios, Hegg et al (1977) have demonstrated the variable rate of this reaction in plumes. Oxidation of NO_2 to nitric acid may then proceed by reaction with OH, HO_2 or O_3. Davis et al (1979) have measured OH concentrations in the vicinity of a power plant plume and have assigned an average midday value of 9.5×10^6 cm^{-3}. For the reaction:

$$OH + NO_2 + M \rightarrow HNO_3 + M \ (M = N_2, O_2)$$

they have postulated conversion rates as a function of plume age, plume mixing, moisture, and time of day (solar flux).

Only total nitrate results ($HNO_3 + NH_4NO_3$) are discussed in this paper since filter techniques are subject to potential errors in distinguishing between particulate and gaseous nitrate. The lack of distinguishability arises from the potential for transferral of the collected ammonium nitrate through evaporation and/or topochemical reactions between acidic sulfate and nitrates. The resulting nitrate measurements were normalized by ratioing them to total sulfur as a conservative tracer.

Formation of ammonium

Many investigators have observed (Tanner et al, 1977; Brosset et al, 1975; Charlson et al, 1974) that well-aged atmospheric sulfate aerosols, either rural or urban are predominantly ammonium sulfate or bisulfate. Initially, however, the homogeneous oxidation product of plume SO_2 is sulfuric acid. If neutralization proceeds by diffusion of background NH_3 into the plume at a reasonable rate, analysis of the quartz filter for NH_4^+ should permit us to follow this reaction as the plume is transported downwind from the stack. Consequently, the aqueous extracts from the quartz filters were analyzed for NH_4^+ and the results presented as ratios to total sulfur.

RESULTS

Formation of sulfate

A compilation of the data obtained from all the runs is shown in Table 1. The time of emission is back calculated utilizing average wind speeds at plume height obtained from pilot balloon measurements made at approximately half-hour intervals. Plume age represents the interval between time of emission and the midpoint in time during which traverses were made at each location. The integrated solar radiation to which the plume was subjected during its lifetime was determined from the hourly readings at the Cumberland plant's 1 m tower. Readings were unavailable for 8/18 AM but estimates were made from corresponding time spans for several days prior to and after 8/18. The data presented in the penultimate column are corrected for the backround values taken during each flight, with the exception of 8/27 PM for which an estimate had to be made. Primary sulfate emission was found to be 0.60 ± 0.12% of the total sulfur, obtained from 13 flue gas measurements taken over a period of several days (Dietz and

Garber, 1979). This value was subtracted from particulate sulfur prior to calculating the ratios. Average SO_2 conversion rates from emission to sampling time for each flight are tabulated in the final column.

In Figure 1, the ratios of particulate to total sulfur as a function of plume age are displayed. There is a general increase in the ratio of sulfate with time but a great variability in the rate, with early morning runs generally showing lower oxidation rates than was observed during late morning and afternoon. As a possible indication of photochemical activity, the percentage of total plume sulfur in particulate form is plotted as a function of total solar radiation in Figure 2. The data seems to indicate that solar radiation plays a significant role in the formation of sulfate although the involvement of other rate-controlling parameters such as turbulence, which generally parallels the increase in solar radiation is a distinct possibility. The high conversion at the 25 km location on 8/24 appears to be an anomaly for which we have no explanation. Following the suggestion of Husar et al (1978) we explore by the plot shown in Figure 3 the possible significance of time of day as an indicator of photochemical activity. Points to the left of each bar are plume emission times and to the right, the time of sampling. The dotted line is a plot of typical solar radiation obtained from 8/20. Conversion of SO_2 to SO_4^{2-} varied from $\sim$0.1-0.8% h^{-1} during night and early morning hours, with one measurement at 1.5% h^{-1}. Late morning and afternoon rates ranged from 1-4% h^{-1} with one measurement (8/24, 25 km) at 7% h^{-1}.

Nitric oxide conversion to nitrate

Employing real-time instrumentation for NO and NO_2, several investigators have succeeded in making experimental observations of the rate of reaction

$NO \rightarrow NO_2$ (Hegg et al, 1977, O'Brien et al, 1976). Rates of NO_x transformation/removal measured in the urban plumes of Phoenix, Ariz. and Boston, Mass. were <5% h^{-1} and 14-24% h^{-1} respectively (Spicer, 1980). A lower bound for the yearly average removal rate of NO_x during daylight hours in the Los Angeles Basin was found to be 4% h^{-1}, with a similar daytime rate prevailing during the summer months at West Covina and St. Louis (Chang et al, 1979). The present lack of real-time instrumentation for NO_3^- has limited the determination of the rate of reaction $NO \rightarrow NO_3^-$. Our modified filter pack enabled us to take integrated plume NO_3^- samples and relate them to total sulfur as a means of estimating overall $NO \rightarrow NO_3^-$ kinetics.

Total nitrate concentrations, obtained by summing particulate and gaseous nitrates from the quartz and NaCl filters, are listed in Table 2 along with total sulfur. Calculation of the conversion rate required the introduction of several assumptions. First, no ground removal of plume constituents occurs and consequently one could assume that total flux of SO_x and NO_x remained constant. Errors introduced by dry deposition would be minimal in any case by virtue of low loss rates (Forrest et al, 1979). Second, assume no NO_3^- in the stack effluent. An estimate of nitrate production can consequently be made as follows, defining NO_x as all oxides of nitrogen including nitrate: If in the stack gas we allow

$$\frac{NO_x^{\bullet}}{S_{total}} = C$$

and in plumes

$$\frac{NO_3^-}{S_{total}} = M$$

then plume

$$\frac{NO_3^-}{NO_x} = \frac{M}{C}$$

Column 5 lists the measured molar NO_3^-/Total S ratios. Calculations for column 6 were based on an average flue gas SO_2 concentration of 2400 ppm as found by Dietz and Garber (1979) and an estimate of $\sim$480 ppm for NO from an assumed emission ratio of 0.2. Utilizing plume ages from Table 1, the average conversion rates are calculated and tabulated in the final column.

Nitrate as a percentage of total NO_x vs plume age is plotted in Figure 4. As with SO_4^{2-}, a general increase in the amount formed with time is indicated, but once again nighttime and early morning rates are much lower than those of late morning and afternoon. Similarly, an apparent correlation of nitrate formation with solar radiation is perceived from Figure 5, with the 8/24-25 km location again seemingly anonymously high. Figure 6 displays NO → NO_3^- conversion rate as a function of time of day. This is not dissimilar to the sulfate data but a somewhat random scatter in the diurnal rate pattern suggests the probable involvement of parameters other than insolation.

Ammonium particulates

Neutralization of H_2SO_4 or HNO_3 by NH_3 and/or reaction of SO_2 with NH_3 to form ammonium particulate compounds was followed by analyzing the quartz filters for NH_4^+ aerosols. In Table 3 are presented the concentrations of NH_4^+ normalized for plume dispersion by expressing them as a ratio to total sulfur. The data in column 5 indicates a trend toward increasing NH_4^+/Total S ratios

7 where the NH_4^+/Total S ratios are plotted against plume age. Since ambient $NH_3(g)$ concentrations were not monitored, it is difficult to quantify plume-NH_3 reactions.

The last column in Table 3 presents on a molar basis the NH_4^+ to SO_4^{2-} ratios. Of the 15 values listed, 11 ratios are <2 indicating the existence of acidic sulfate (bisulfate), while 3 ratios are >2, suggesting the presence of ammonium sulfate along with other ammonium compounds (e.g. NH_4NO_3). The anomaly for 8/23, 77km is probably an analytical error.

DISCUSSION

In previous field studies limitations of instrumental and supportive capabilities restricted our ability to track plumes to a maximum of ∼50 km with a corresponding plume age of ∼1.6 hrs. With the assistance of the STATE Mission Control Center during these experiments, our measurements were extended to plumes 200 km downwind with travel times as much as 9 hrs. from the power plant. Moreover, whereas most of our previous observations were made during early morning or dusk hours under atmospherically stable conditions, we now report data obtained during midday.

During the past several years evidence has pointed toward relatively slow SO_2 oxidation rates as compared to the rather high rates found in some earlier studies (Newman, 1980). The present work introduces further evidence for the relatively slow oxidation rate of sulfur dioxide to sulfate, and to a large extent parallels the diurnal cycle displayed at Labadie (Husar et al, 1978, and Gillani et al, 1978). Late morning and afternoon rates ranged from 1-5% h^{-1} with an average of ∼3% h^{-1} and with but one measurement at 7% h^{-1}. Conversion during night and early morning hours was 0.1-0.8% h^{-1} with an average of ∼0.5%

h^{-1} and with one value at 1.5% h^{-1}. Deposition losses were not considered in these calculations, but their inclusion would not significantly alter the results. If we assume an equal number of insolation and non-insolation hours during the day at this time of the year, the average diurnal rate at Cumberland during the summer was $\sim$2% h^{-1}.

The data presented show a correspondence of oxidation with time of day and solar radiation, and might be taken as evidence for photochemistry as the primary mechanisms. Radical species, especially OH, which are produced by photolysis of ozone, have been postulated as the principal intermediates in a homogeneous mechanism. Conversion rates for seven daytime periods based upon the reaction of SO_2 with experimentally measured and diurnally extrapolated values of ambient OH have been published by Davis et al, 1979. Their data suggest that during midday summertime conditions, SO_2 conversion rates in power plant plumes of 1-2% h^{-1} (possibly 4-6% h^{-1} under favorable conditions) could easily be explained in terms of an OH induced oxidation of SO_2. As an indication of photochemical activity in the Cumberland plume, we have observed above-background ozone levels during many distant plume traverses, (Figure 8) suggesting the existence of free radicals capable of reacting with SO_2.

Another rate-controlling mechanism which must be considered is the rate of introduction of background air into the plume. The importance of ambient trace constituents in relationship to reactivity of plume constituents has been suggested by the observation of increased levels of Aitken nuclei (Wilson et al, 1976) and of aerosol production via b_{scat} measurements (White, 1979) at the plume fringes. Unstable atmospheric conditions would tend to accelerate mixing of the plume with background air and increase reaction rates. Lack of turbulence data available to us precluded a quantitative evaluation of this parameter in the present study.

The temptation to advocate homogeneous mechanisms as an explanation for SO_2 oxidation should be tempered by consideration of other possibilities. Increased solar radiation causes increased mixing of the plume with background particles which may serve as surfaces for heterogeneous reactions. Rigorous models for heterogeneous mechanisms are difficult to construct because of the complexity of the reactions; nonetheless, one can conclude that reactivity could be great enough to satisfy the observed measurements. The importance of heterogeneous reactions to sulfate formation is underlined by McMurray's (1979) study of aerosol dynamics. In addition, an explanation for the lack of concomitant decreases in sulfate levels with lower ambient SO_2 concentrations (Altshuller, 1977; Judeikas et al, 1978) suggest the controlling mechanism to be the atmospheric particle burden via a heterogeneous path.

It appears that although experimentally measured SO_2 oxidation rates fall into a somewhat coherent pattern, elucidation of the oxidative process still requires further information. Real time instrumentation, including sulfate-measuring capability, to closely define plume structure may provide the key in unraveling the relative significance of the proposed mechanisms.

The data in Table 2 indicate that rates for $NO \rightarrow NO_3^-$ conversion were $\sim$0.1-3% h^{-1} for nighttime and early morning with one measurement at $\sim$6% h^{-1}. Late morning and afternoon rates were $\sim$3-12% h^{-1} with outlying values at 0.6 and 22% h^{-1}.

Since the reactions

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad (1)$$

and

$$NO_2 + OH \rightarrow HNO_3 \qquad (2)$$

are governed by the availability of photochemically-derived reactants, the observed correlation of NO → HNO_3 reaction rate with solar intensity is not unexpected. However, other parameters are also involved. Both Davis et al (1974) and O'Brien et al (1976) observed a greater fraction of conversion of NO to NO_2 at the fringes of the plume, where the supply of O_3 was more plentiful, than at the center. Hegg et al (1977) found, in most cases, an inverse relationship between plume NO_2/NO ratios with the sum of their concentrations, and suggested this to be an indication of atmospheric turbulence. It seems clear that the macroscopic reaction rate for (1) is controlled by the rate of mixing of the plume with ambient air, as well as solar insolation. We would anticipate the same limitation would apply to reaction (2), and to the overall $NO \rightarrow NO_3^-$ rate.

Based upon their measurements of the OH radical in the vicinity of a power plant plume and assuming complete mixing of ambient air with the plume, Davis et al (1979) predicted reaction (2) to be faster than the oxidation rate of SO_2 by an order of magnitude. Our data indicate a rate difference of 2-4 times between $NO \rightarrow NO_3^-$ and $SO_2 \rightarrow SO_4^{2-}$, but lacking information on $NO \rightarrow NO_2$ rates, we are unable to verify their predictions. Conceivably, nitrate formation was limited by the relatively slow diffusion controlling reaction (1), and ultimately reaction (2) may indeed occur at a much greater rate than 2-4 times that of SO_2 oxidation. Future studies should include the monitoring of all oxides of nitrogen in a manner capable of interpretation so as to delineate the intermediate reaction and thus make possible a more comprehensive picture of plume nitrogen chemistry.

CONCLUSIONS

1. Conversion of SO_2 to particulate sulfate averaged 0.5% h^{-1} (range 0.1-0.8) during night and early morning hours, and 3% h^{-1} (range 1-4) during late morning and afternoon. Plumes were tracked to distances of 200 km and 9 hrs duration.
2. Formation rates of total inorganic nitrate (gaseous plus particulate) from NO averaged 2% h^{-1} for nighttime and early morning and 6% h^{-1} (range 3-12) for late morning and afternoon.
3. Both reactions were positively correlated with total solar radiation.
4. Particulate ammonium concentrations generally increased with plume age, but rates varied widely. Mole ratios of NH_4^+/SO_4^{2-} fell within 1-3.

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LIST OF FIGURES

Table 1. Conversion of SO_2 to SO_4^{2-} in the Cumberland plume

Date	Distance (km)	Plume emission time (CDT)	Plume age (hrs)	Integrated solar radiation (gm-cal cm^{-2})	$\frac{\text{Partic. S(a)}}{\text{Total S(a,d)}}$ (%)	Conversion rate (% hr^{-1})
8/18 AM	35	0642	1.4	8(b)	2.0	1.5
	60	0715	2.8	55(b)	0.80	0.3
8/18 PM	200	0820	8.5	(c)	27	3.2
8/20	90	1034	3.6	238	3.8	1.1
	114	1115	5.0	357	9.3	1.9
	188	1025	9.0	495	15.2	1.7
8/22 AM	11	0530	0.76	0	0.2	0.2
	40	0445	2.8	0.04	0.3	0.1
8/22 PM	17	1252	1.6	119	4.4	2.8
	34	1153	3.6	268	5.7	1.6
8/23	77	0800	3.6	126	0.6	0.2
	106	0650	5.6	184	6.6	1.2
8/24	15	1506	2.2	123	6.6	3.0
	25	1554	2.6	98	18.2	7.0
8/25	17	1113	1.9	123(b)	8.9	4.7
	25	1129	3.3	213(b)	12.8	3.9
8/26	19	1532	2.4	94	9.0	3.8
8/27 AM	92	0321	4.3	3.7	1.6	0.4
	104	0423	4.6	31	3.8	0.8
8/27 PM	90	1629	3.6	57	11.3(b)	3.1(b)
8/28	107	1208	4.3	282	13.8	3.2

(a) Corrected for background and primary SO_4^{2-} (0.6%).

(b) Estimated.

(c) Not available.

(d) Corrected for background SO_2

Table 2. Conversion of NO_x to NO_3^- in the Cumberland plume

Date	Distance (km)	Total S (a) (μg m^{-3})	Total NO_3^- (a) (μg m^{-3})	$\frac{\text{Total } NO_3^-}{\text{Total S}}$ (mole %)	NO converted to NO_3^-(b) (%)	Conversion rate (% hr^{-1})
8/18	35	132	4.05	1.6	8.0	5.9
	60	653	5.24	0.41	2.1	0.75
8/20	90	55.6	2.18	2.1	10.5	2.9
	114	45.6	3.04	3.5	17.5	3.5
	188	25.4	3.01	6.2	31	3.4
8/22 AM	11	1138	11.0	0.51	2.6	3.4
	40	277	4.3	0.82	4.1	1.5
8/22 PM	17	114	3.38	1.5	7.5	4.7
	34	31.8	2.69	4.4	22	6.1
8/23	77	112	0.99	0.46	2.3	0.6
	106	51.5	4.92	5.0	25	4.5
8/24	15	43.7	5.32	5.4	27	12.3
	25	27.3	6.0	11.5	58	22
8/25	17	69.4	4.83	3.6	18	9.5
	25	38.7	3.12	4.2	21	6.4
8/26	19	30.5	1.51	2.6	13	5.4
8/27 AM	92	508	0.56	0.06	0.3	0.07
	104	123	2.41	1.0	5.0	1.1

(a) Corrected for background.

(b) Calculated from ratios of measured NO_3^-/S and emitted NO/S.

Table 3. Particulate NH_4^+ in the Cumberland plume

Date	Distance km	Plume age (hrs)	NH_4^+ conc. ($\mu g\ m^{-3}$)	NH_4^+/Tot. S (moles)	NH_4^+/SO_4^{2-} (moles)
8/18	35	1.4	2.5	0.034	1.3
	60	2.8	5.9	0.016	1.2
8/20	90	3.6	1.6	0.05	1.2
	114	5.0	2.8	0.11	1.2
	188	9.0	2.5	0.18	1.2
8/22	11	0.76	5.5	0.009	1.1
	40	2.8	1.6	0.011	1.2
	17	1.6	4.8	0.07	1.6
	34	3.6	3.0	0.19	2.9
8/23	77	3.6	5.8	0.09	11.1
	106	5.6	3.5	0.12	1.7
8/24	15	2.2	4.1	0.19	2.6
	25	2.6	5.5	0.29	1.5
8/25	17	1.9	0.71	0.018	0.2
	25	3.3	6.9	0.36	2.7

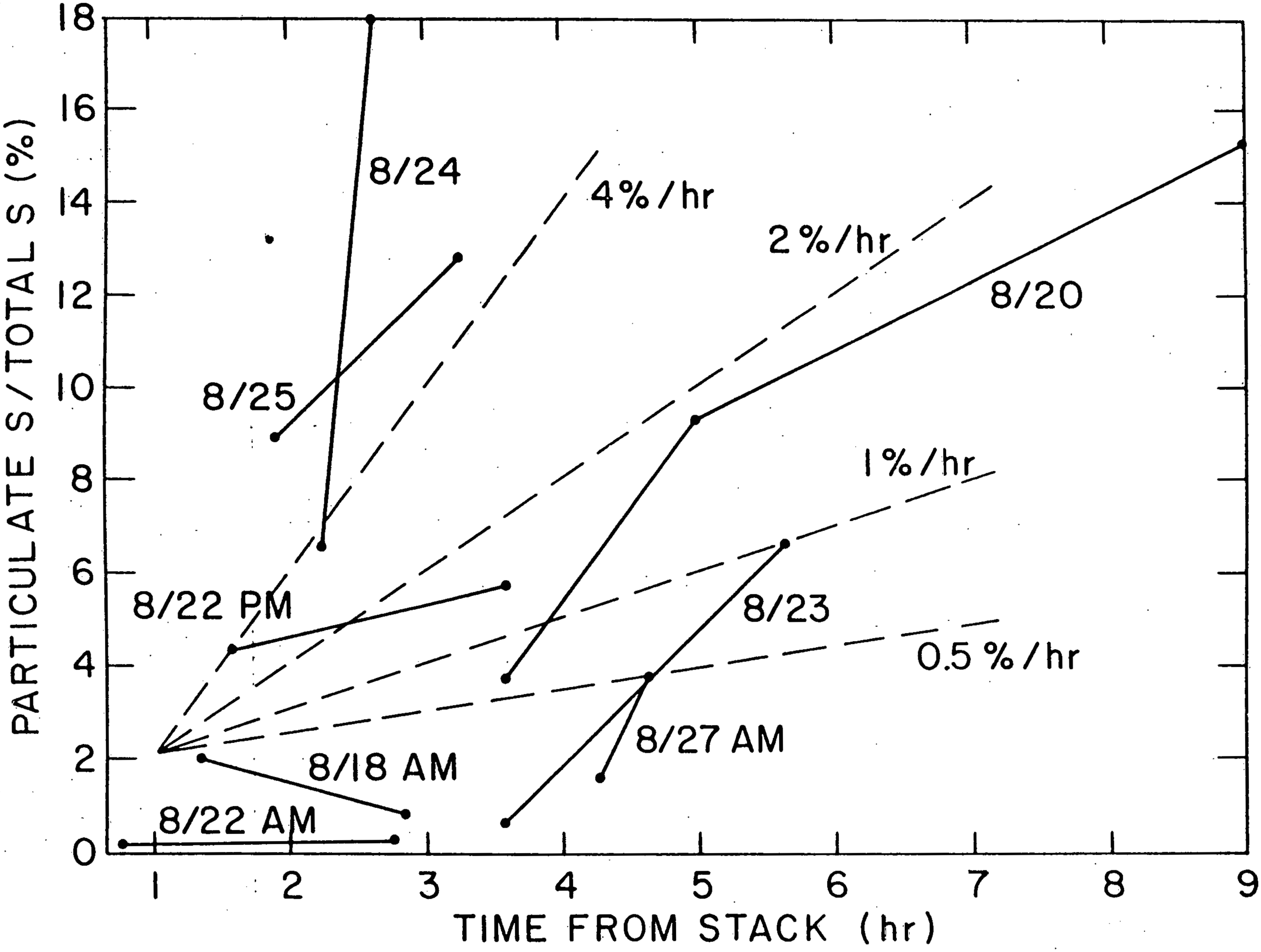
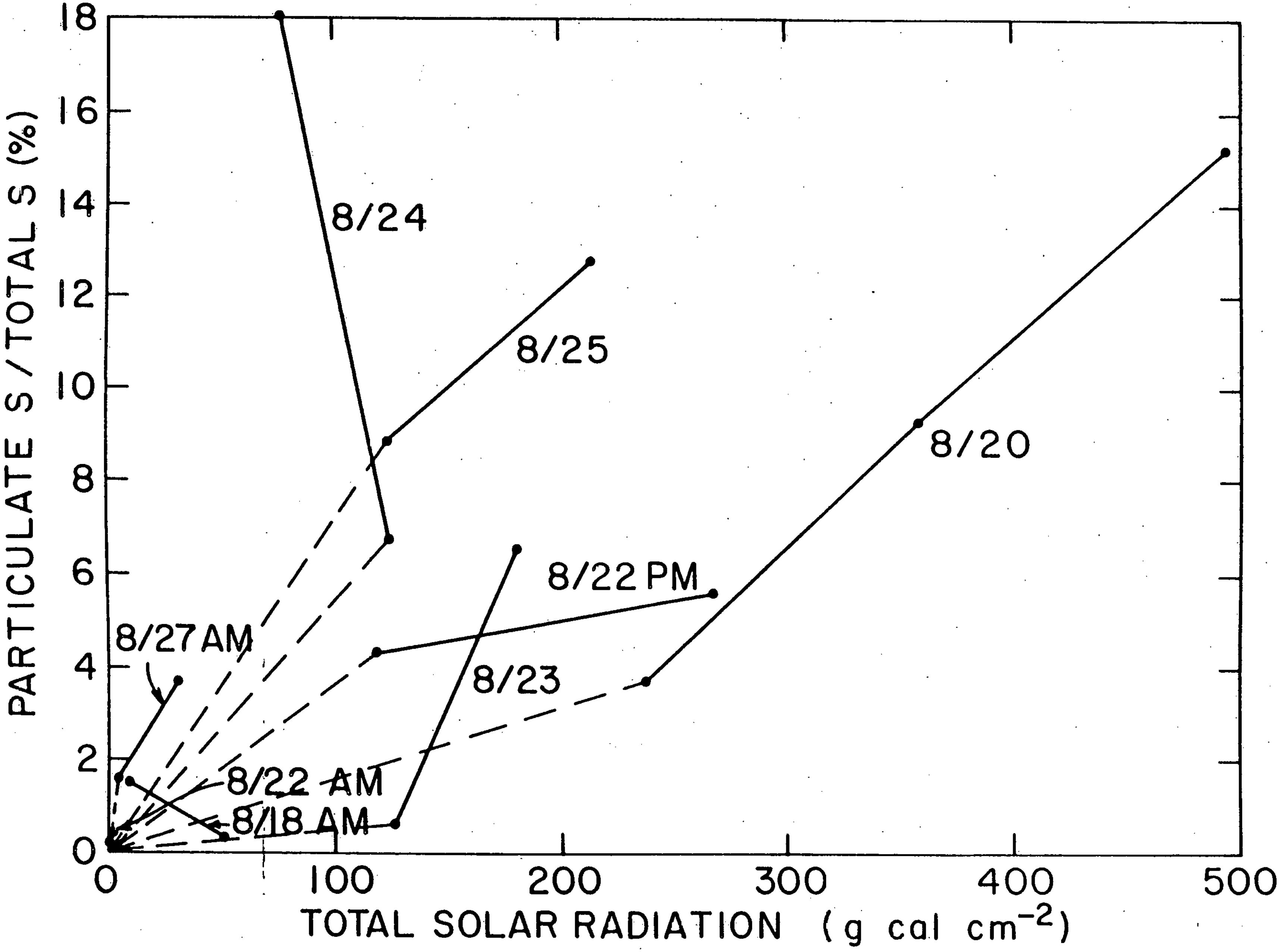

PARTICULATE S / TOTAL S (%)
TIME FROM STACK (hr)
0
2
4
6
8
10
12
14
16
18
1
2
3
4
5
6
7
8
9
8/24
8/25
4%/hr
2%/hr
8/20
1%/hr
8/22 PM
8/23
0.5%/hr
8/27 AM
8/18 AM
8/22 AM

Figure 1.



PARTICULATE S / TOTAL S (%)
TOTAL SOLAR RADIATION (g cal cm^{-2})
0
2
4
6
8
10
12
14
16
18
0
100
200
300
400
500
8/24
8/25
8/20
8/22 PM
8/23
8/27 AM
8/22 AM
8/18 AM

Figure 2.

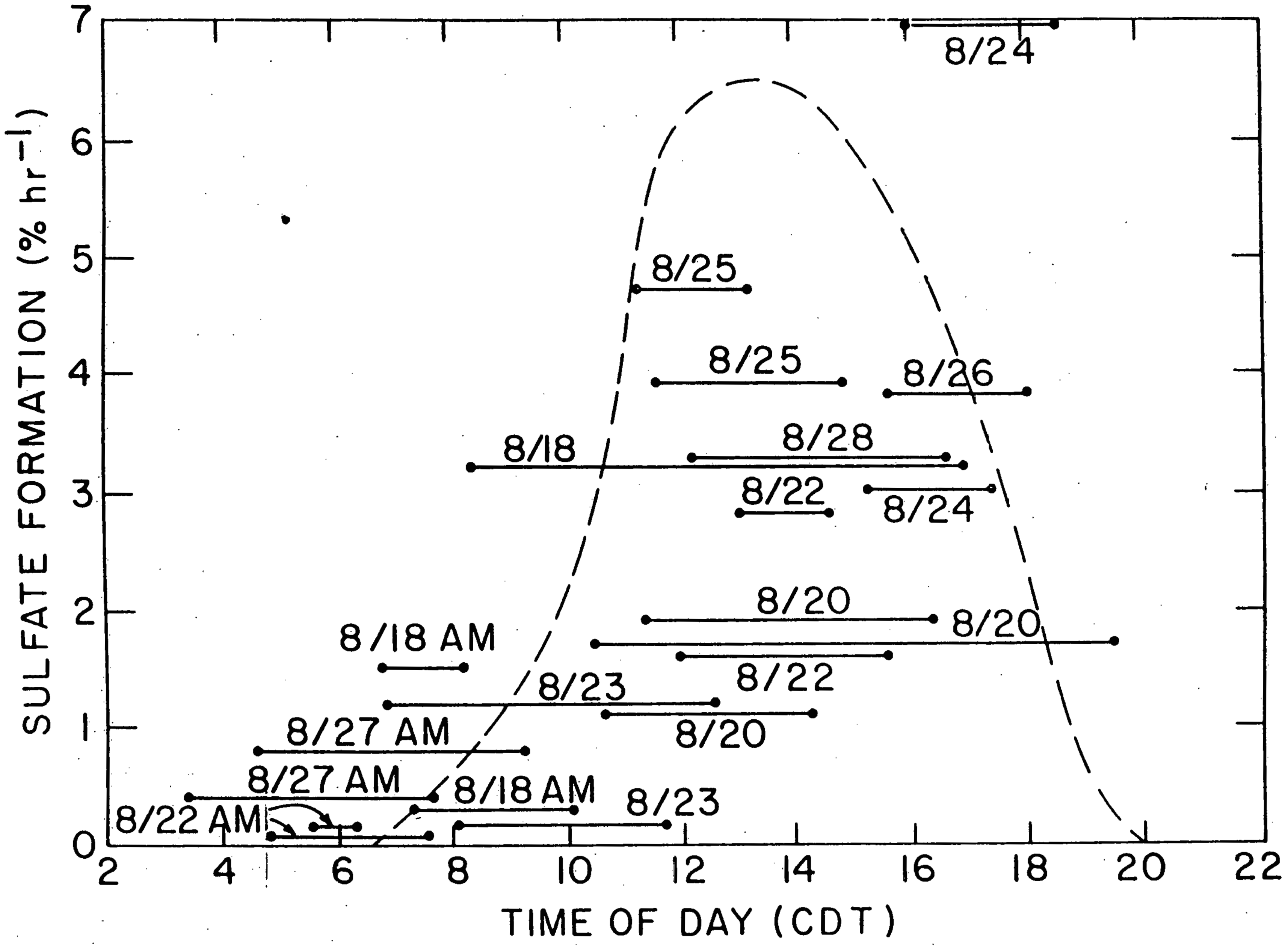
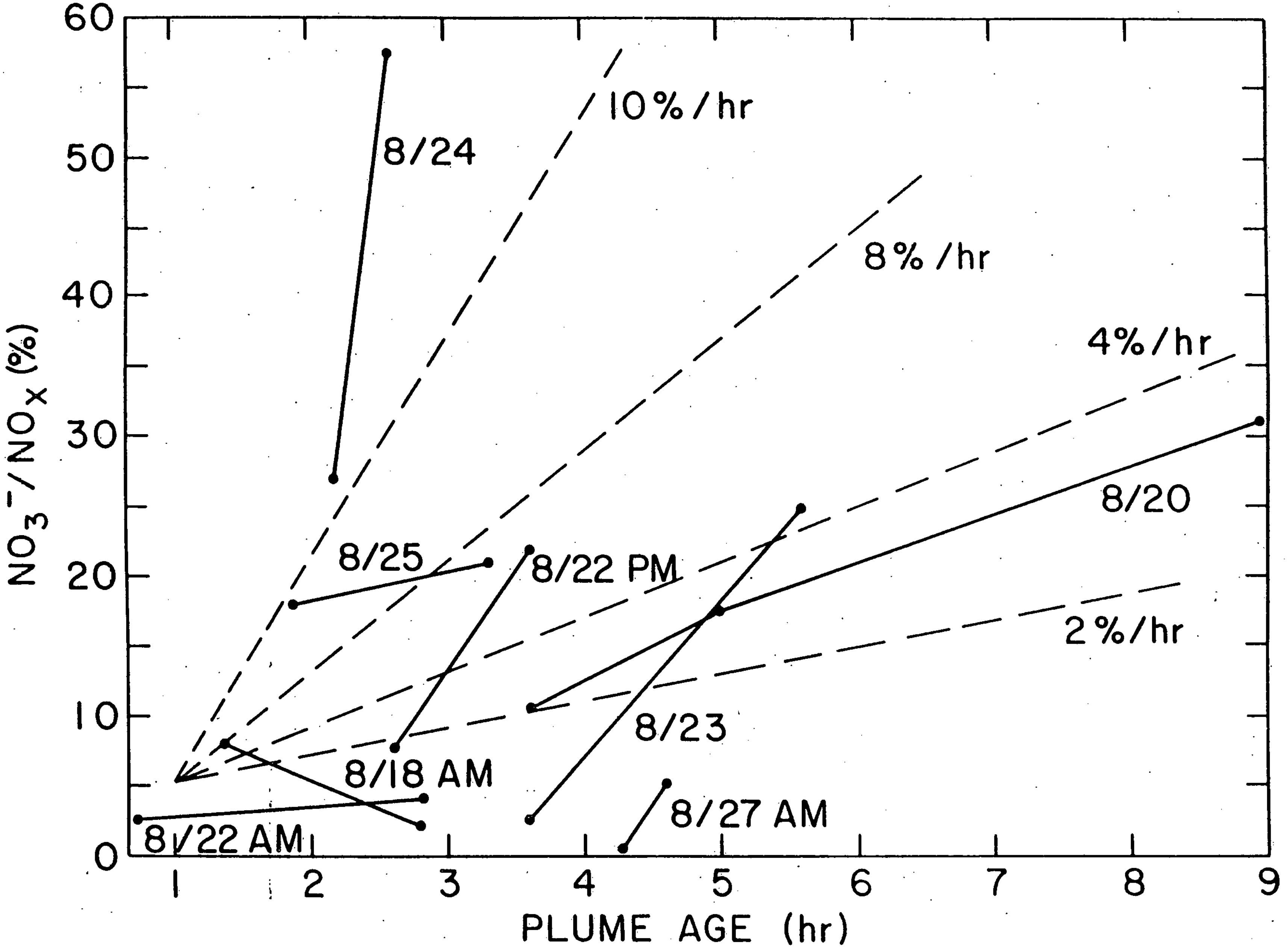
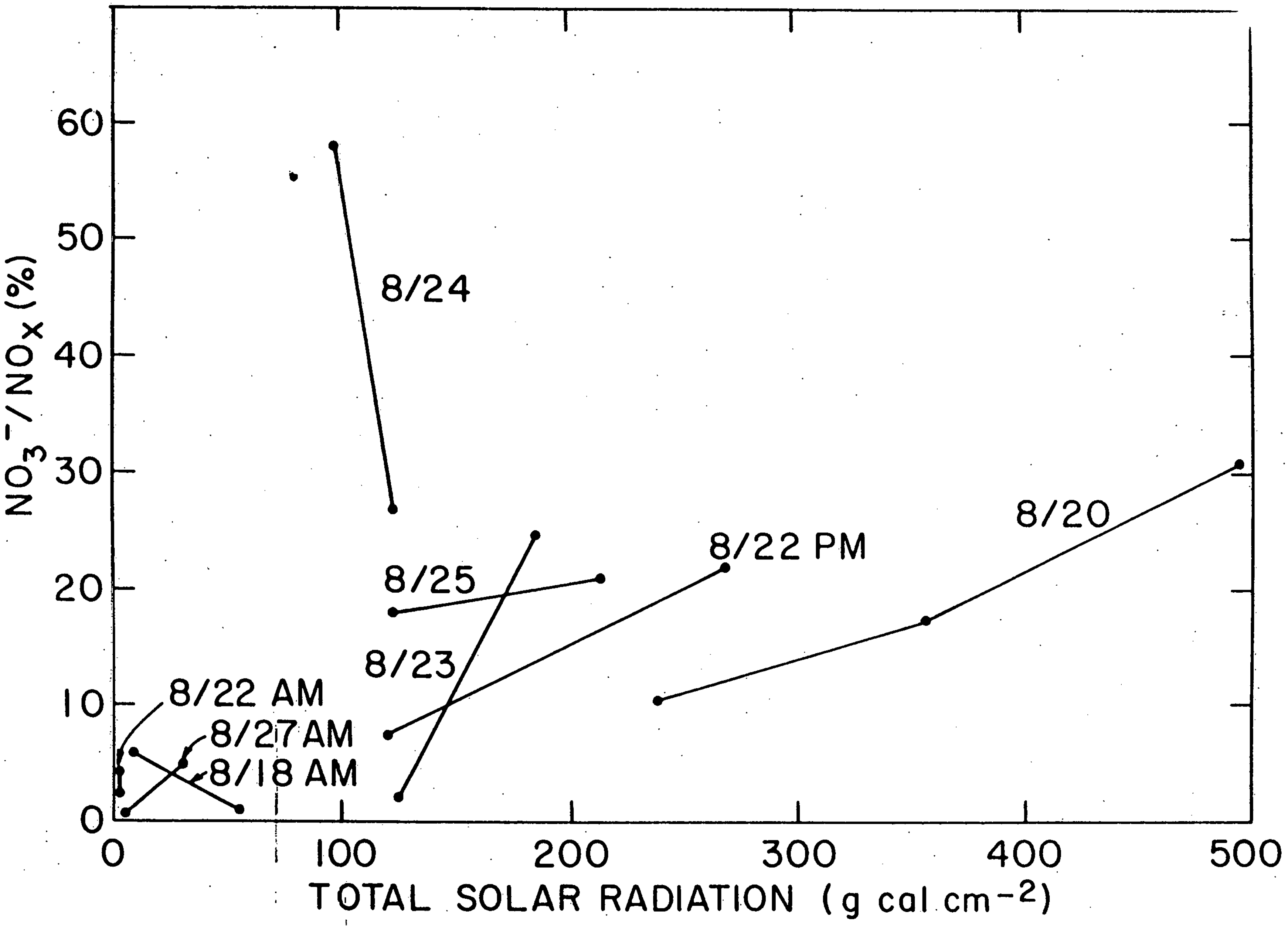

SULFATE FORMATION (% hr⁻¹)
TIME OF DAY (CDT)
0
1
2
3
4
5
6
7
2
4
6
8
10
12
14
16
18
20
22
8/24
8/25
8/25
8/26
8/18
8/28
8/22
8/24
8/20
8/20
8/18 AM
8/22
8/23
8/20
8/27 AM
8/27 AM
8/18 AM
8/23
8/22 AM

Figure 3.



60
50
40
30
20
10
0
NO3⁻/NOx (%)
1
2
3
4
5
6
7
8
9
PLUME AGE (hr)
10%/hr
8%/hr
4%/hr
2%/hr
8/24
8/25
8/22 PM
8/20
8/23
8/18 AM
8/22 AM
8/27 AM

Figure 4.



60
50
40
30
20
10
0
NO_3^-/NO_x (%)
0
100
200
300
400
500
TOTAL SOLAR RADIATION (g cal cm^{-2})
8/24
8/25
8/23
8/22 PM
8/20
8/22 AM
8/27 AM
8/18 AM

Figure 5.

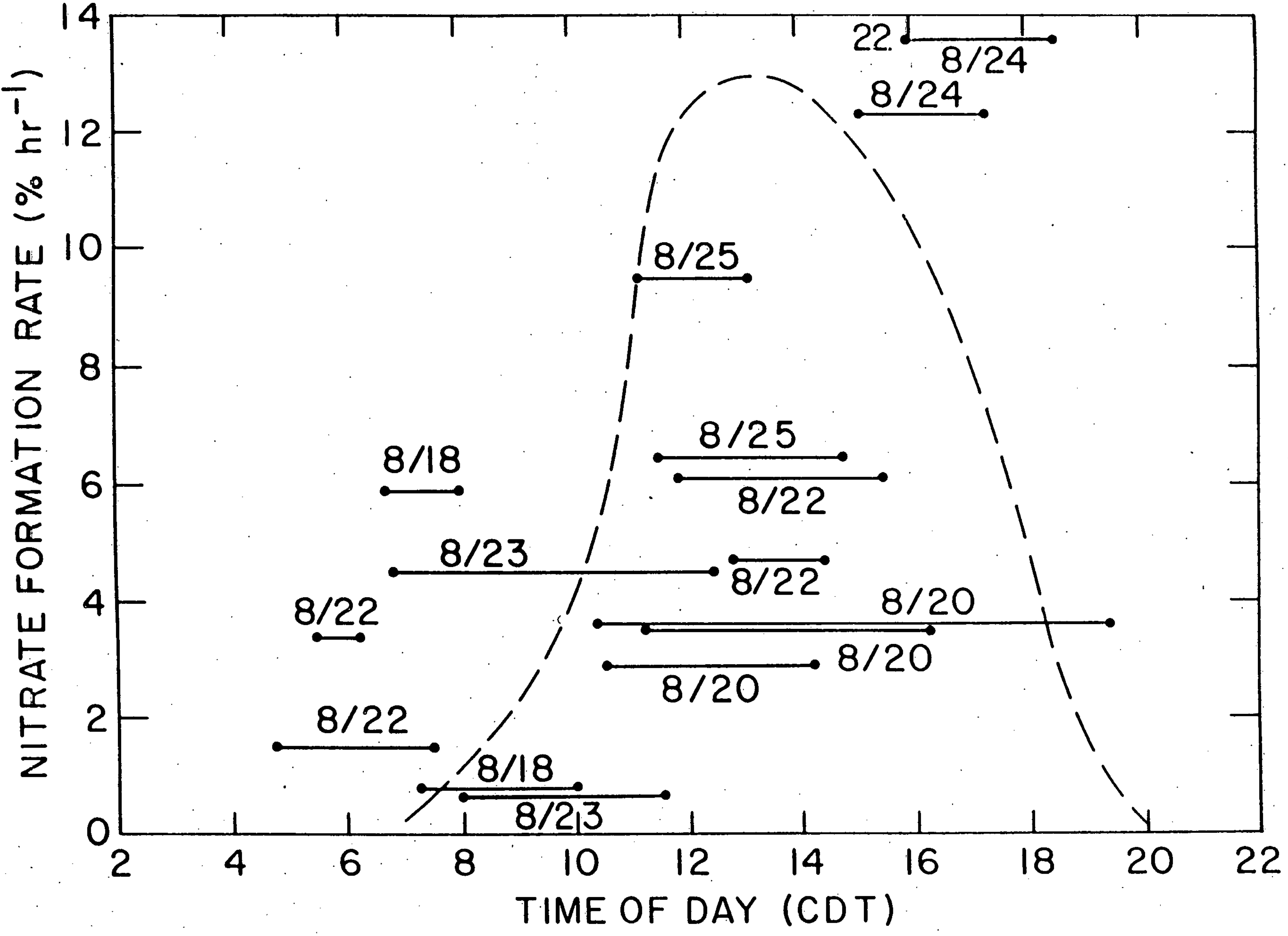
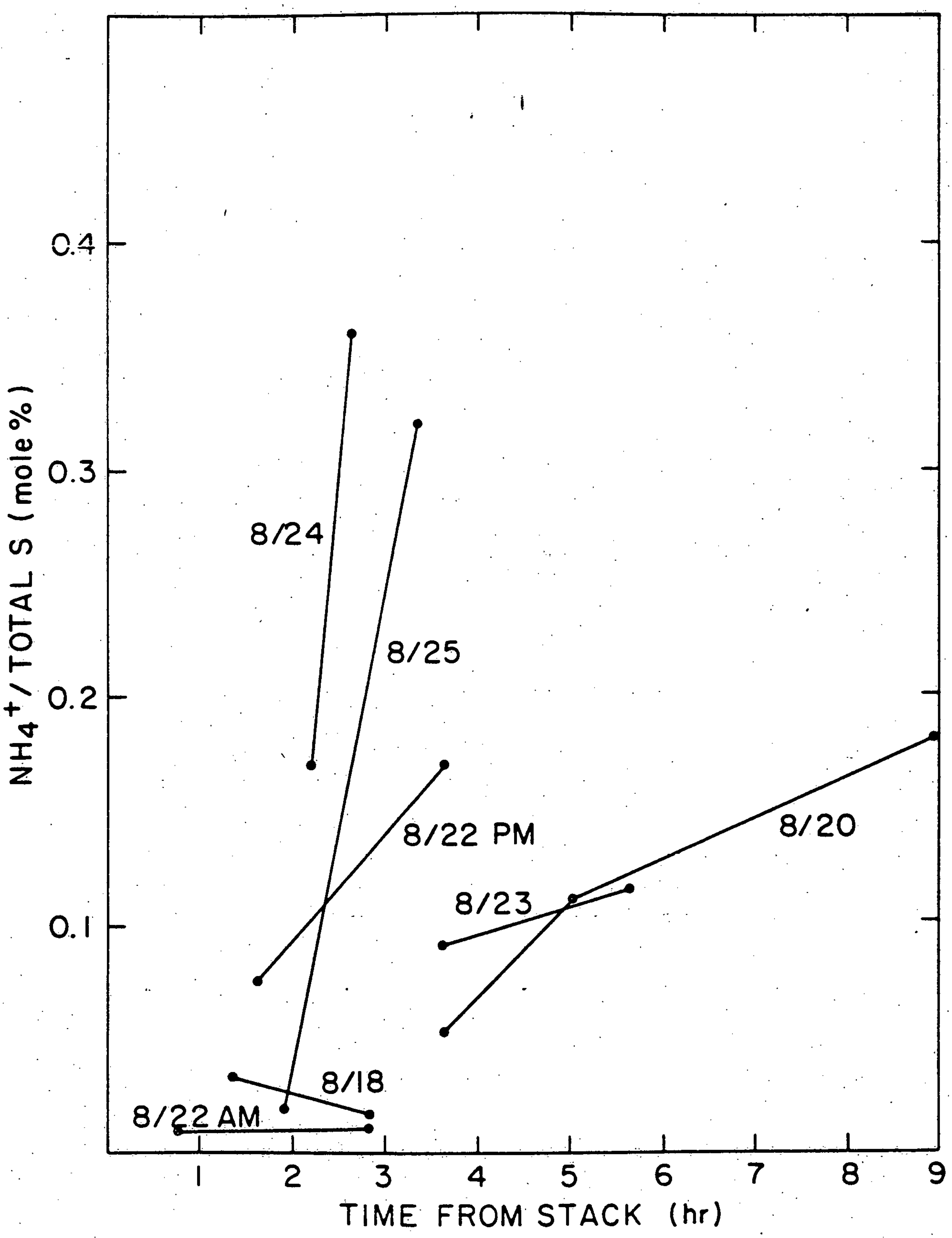

NITRATE FORMATION RATE (% hr^{-1})
TIME OF DAY (CDT)
0
2
4
6
8
10
12
14
2
4
6
8
10
12
14
16
18
20
22
22
8/24
8/24
8/25
8/25
8/22
8/18
8/23
8/22
8/22
8/20
8/20
8/20
8/22
8/18
8/23

Figure 6.



NH4+/ TOTAL S (mole %)
0.4
0.3
0.2
0.1
1
2
3
4
5
6
7
8
9
TIME FROM STACK (hr)
8/24
8/25
8/22 PM
8/20
8/23
8/18
8/22 AM

Figure 7.

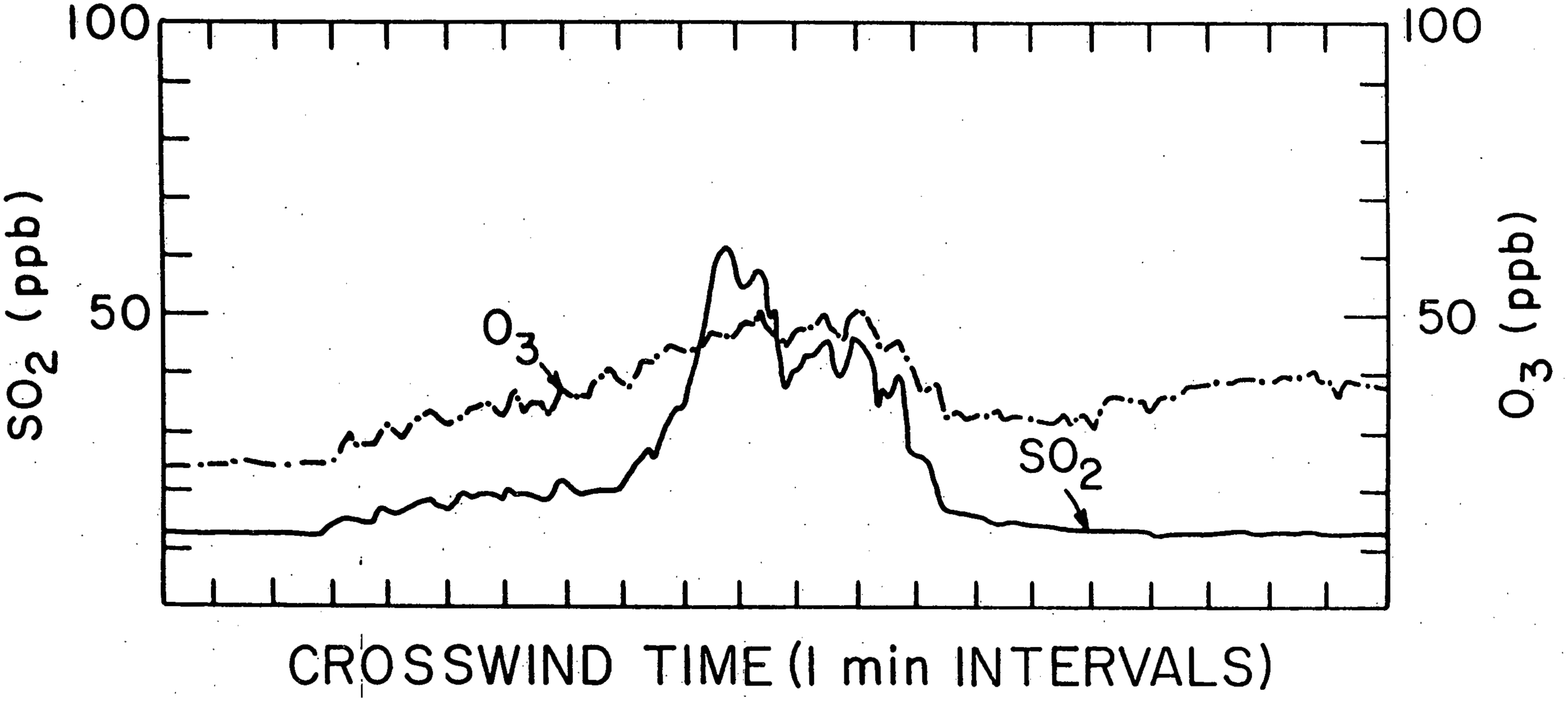

100
50
SO2 (ppb)
100
50
O3 (ppb)
O3
SO2
CROSSWIND TIME (1 min INTERVALS)

Figure 8