

TRANSPORT AND OXIDATION OF SO₂ IN A STAGNANT FOGGY VALLEY

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Abstract—The fate of SO₂ emitted in the San Joaquin Valley of California under stagnant foggy conditions was determined by the release of an inert tracer and the concurrent monitoring of SO₂ and SO₄²⁻ concentrations. At night, SO₂ was found to be trapped in a dense fog layer below a strong and persistent inversion based a few hundred meters above the valley floor. This lack of ventilation led to the accumulation of SO₂ and SO₄²⁻ over a major SO₂ source region in the valley. The rate of oxidation of SO₂ to SO₄²⁻ in fog was estimated at $3 \pm 2\% \text{ h}^{-1}$. Production of acidity from the oxidation of SO₂ fully titrated the NH₃ (g) present before the fog, and led to a progressive drop of the fogwater pH over the course of the night. In the afternoon, the valley was found to be efficiently ventilated by a buoyant upslope flow through the inversion. The tracer data indicated that about 40% of the air transported upslope in the afternoon was returned to the valley in the night-time drainage flow. The fates of SO₂ and SO₄²⁻ in the valley during extended high-inversion episodes appear to depend considerably on the presence of fog or stratus, and on the extent of daytime insolation.

INTRODUCTION

Sulfur dioxide emitted from the combustion of fossil fuels is oxidized to H₂SO₄ in the atmosphere. The deleterious effects of SO₄²⁻ aerosols on visibility, deposition, and public health are well established (Appel *et al.*, 1985; Gmur *et al.*, 1983; Evans *et al.*, 1984). Atmospheric oxidation of SO₂ can be greatly facilitated by the presence of fog, because SO₂ is absorbed by the fog droplets and is rapidly oxidized in the aqueous phase (Jacob and Hoffmann, 1983; Seigneur and Saxena, 1984). Fogs are usually associated with stagnant weather conditions, which can then lead to very high SO₄²⁻ concentrations in SO₂ source regions. In the Los Angeles basin, for example, it has been observed that days with high SO₄²⁻ concentrations are generally preceded by foggy nights (Zeldin *et al.*, 1976; Cass, 1977).

Sulfate air pollution is a major problem in the San Joaquin Valley of California. The southern end of the valley is the site of important oil recovery by steam injection, and large amounts of SO₂ are emitted about 15 m above ground level by steam generators burning crude oil (Fig. 1). Stagnation high-inversion episodes

are frequent in the wintertime, as mesoscale subsidence over the valley due to high pressure aloft produces a strong and persistent temperature inversion based a few hundred meters above the valley floor. Radiative cooling of the moist air trapped below the inversion leads to widespread fog and stratus within the valley. Fog typically forms shortly after sunset, and may not dissipate until the following afternoon. High-inversion episodes persisting for over a week have been documented (Holets and Swanson, 1981).

The ventilation of the valley is severely restricted during high-inversion episodes, because the base of the temperature inversion lies below the mountain ridges surrounding the valley on three sides. Reible (1982) has estimated residence times of the order of 2 days for air parcels in the southern end of the valley under these conditions. Such long residence times, combined with the persistent fog or stratus, favor the oxidation of SO₂ and the subsequent accumulation of SO₄²⁻ aerosol within the valley. In January 1984, our research group conducted an extensive aerosol field study in the San Joaquin Valley during a high-inversion episode with low stratus (Jacob *et al.*, 1986). We observed a steady rise in SO₄²⁻ aerosol concentrations at all valley sites over 4 days of stagnation, and estimated a rate of SO₂ oxidation of 0.4–1.1% h⁻¹ in the overcast mixed layer. We suggested that most of the SO₂ oxidation took place in the stratus cloud which occupied the upper portion of the mixed layer.

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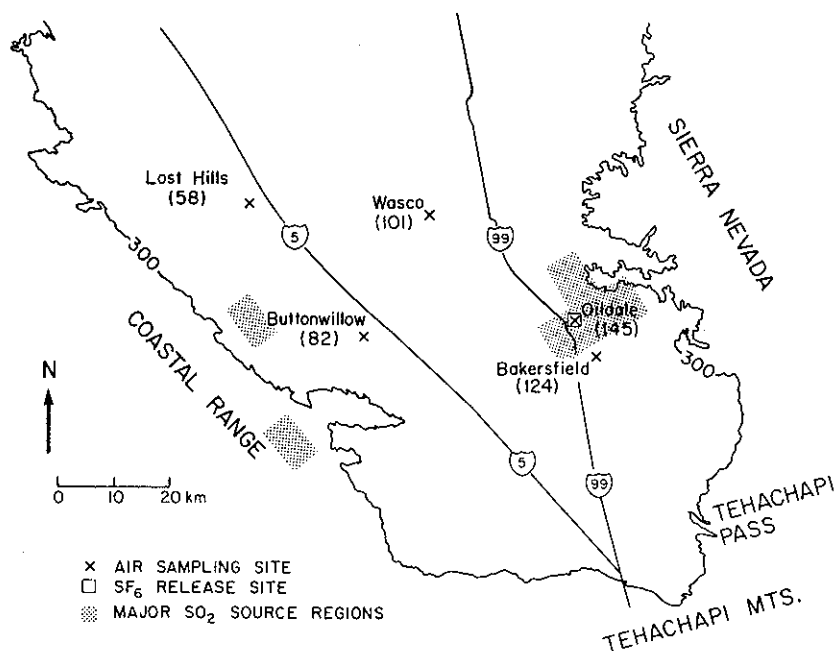


Fig. 1. Sampling sites in the San Joaquin Valley of California. Shaded areas represent major SO_2 source regions ($0.3\text{--}0.7$ tons $\text{SO}_2 \text{ km}^{-2} \text{ day}^{-1}$; Aerovironment Inc., 1984). Altitudes are in m MSL. The edge of the valley is defined by the 300 m MSL contour.

A major source of uncertainty in the study of Jacob *et al.* (1986) was the difficulty in characterizing SO_2 transport under stagnant conditions. This transport is very complex because of the frequent wind reversals associated with mountain-valley breezes (Reible, 1982). Transport of SO_2 emitted from the Oildale oil field (Fig. 1) is of particular importance, because that source is responsible for most of the SO_2 emitted in the San Joaquin Valley (Aerovironment Inc., 1984). We present here the results of a study conducted the following year (January, 1985), which was aimed at determining the fate of the Oildale SO_2 plume. The plume was tagged with an inert tracer (SF_6) during a high-inversion stagnation episode, and the tracer was followed in the valley and aloft. We concurrently monitored the concentration of SO_2 , the composition of aerosol and fogwater, and the SO_4^{2-} deposition fluxes. From these measurements, we will estimate the rate of SO_2 oxidation in fog.

EXPERIMENTAL

A continuous 23-h release of SF_6 was conducted from Oildale between 1800 LST on 4 January and 1700 LST on 5 January 1985 (LST is local standard time). The SF_6 release rate was 23.4 kg h^{-1} , for a total of 538 kg SF_6 released. Grab samples of air were collected hourly at a number of fixed sites in the southern end of the valley. Networks of automobile traverses were also operated, in which grab samples were collected every mile. Two series of aircraft spirals collected samples at altitudes up to 1220 m MSL. The samples were analyzed by electron capture gas chromatography, which can

detect SF_6 concentrations down to 1 ppt. The analytical procedure, and the instrument calibration procedures, have been described by Lamb (1978).

An extensive air sampling network was operated in the San Joaquin Valley during December 1984 and January 1985 (Fig. 1). The complete data sets have been reported by Waldman (1986), along with detailed descriptions of sampling techniques and quality assurance tests. Aerosol samples were collected on open-faced Teflon filters, and fogwater samples were collected with a rotating arm collector (Jacob *et al.*, 1984). The fogwater pH was determined immediately upon sample collection with a Radiometer PHM82 meter and Radiometer GK2320C combination electrode. The analysis of aerosol and fogwater samples followed the protocol of Munger *et al.* (1983), except for fogwater anion analysis which followed the protocol of Jacob *et al.* (1986). The protocol of Jacob *et al.* (1986) makes possible the separate determinations of SO_4^{2-} and S(IV) in the fog sample. Concentrations of $\text{NH}_3(\text{g})$ were determined by a dual filter method (Russell, 1983). Concentrations of SO_2 were monitored at Oildale by Texaco. Deposition fluxes of aerosol and fog droplets were measured by Waldman (1986), using polystyrene Petri dish collectors. The fog liquid water content was determined from the collection rate of the rotating arm collector, assuming a collection efficiency of 60% (Jacob *et al.*, 1984). This method has been found to agree fairly well with other liquid water content measurement methods (Waldman, 1986).

Surface winds in the valley were determined at several sites by Texaco and West Side Operators. A tethered sonde was launched above Buttonwillow at intervals of 4–8 h, and recorded vertical profiles of temperature, relative humidity, wind speed, and wind direction from 100 to 500 m MSL. Upper air wind data were provided daily by Edwards Air Force Base, located in the Mojave desert on the other side of the Tehachapi mountains. Additional weather data were available from pilot reports and from the National Weather Service station at Oildale.

TRANSPORT OF SF₆ RELEASED FROM OILDALE

1. Weather pattern

The SF₆ release was conducted during a typical extended high-inversion episode associated with stationary high pressure over S Idaho and N Nevada (Great Basin High). Strong high pressure was observed over the valley between 1 and 5 January, and produced a persistent subsidence inversion based at 300–400 m MSL. Dense widespread fog filled the mixed layer below the inversion every night; the fog set in shortly after sunset and dissipated late in the following morning, giving way to hazy afternoon sunshine. We show in Fig. 2 some vertical profiles of temperature and relative humidity measured over Buttonwillow during 4–6 January. The inversion was very strong at night and in the morning, but weakened substantially in the afternoon because of solar heating. On the night of 5–6 January no fog was observed in the valley, and the temperature was higher than on the preceding nights; the high pressure had begun to decay. High clouds moved over the valley during that night, and rain began on the afternoon of 6 January. The inversion lifted during the afternoon of 6 January, and unstable conditions prevailed for the next few days.

The Oildale wind data for 4–6 January are summarized in Fig. 3. At night, winds were very weak and frequently shifted in direction. In the daytime, however, a well-defined upslope flow was observed, due to heating of the mountain slopes (Reible, 1982). The upslope flow set in shortly after sunrise, but remained weak until midday. Afternoon insolation of the valley floor following dissipation of the fog strengthened the

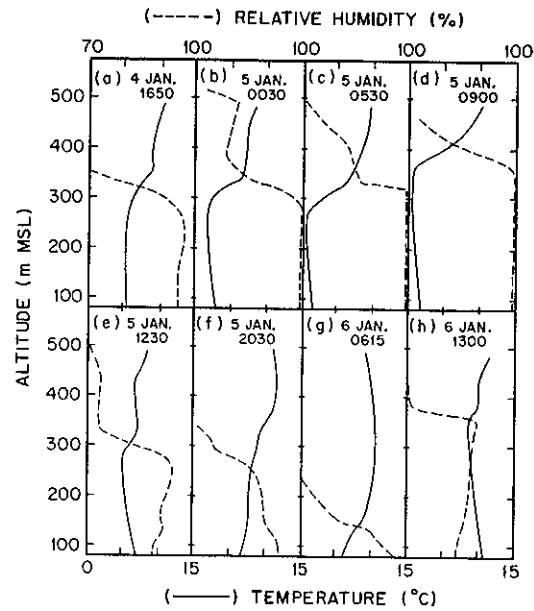


Fig. 2. Vertical profiles of temperature and relative humidity over Buttonwillow. Times are LST.

upslope flow considerably, and wind velocities of 10–20 km h⁻¹ were measured at Oildale in the mid-afternoon. Surface winds in the valley were decoupled from the winds aloft; persistent and strong E winds were observed above the inversion, reflecting the circulation around the Great Basin High.

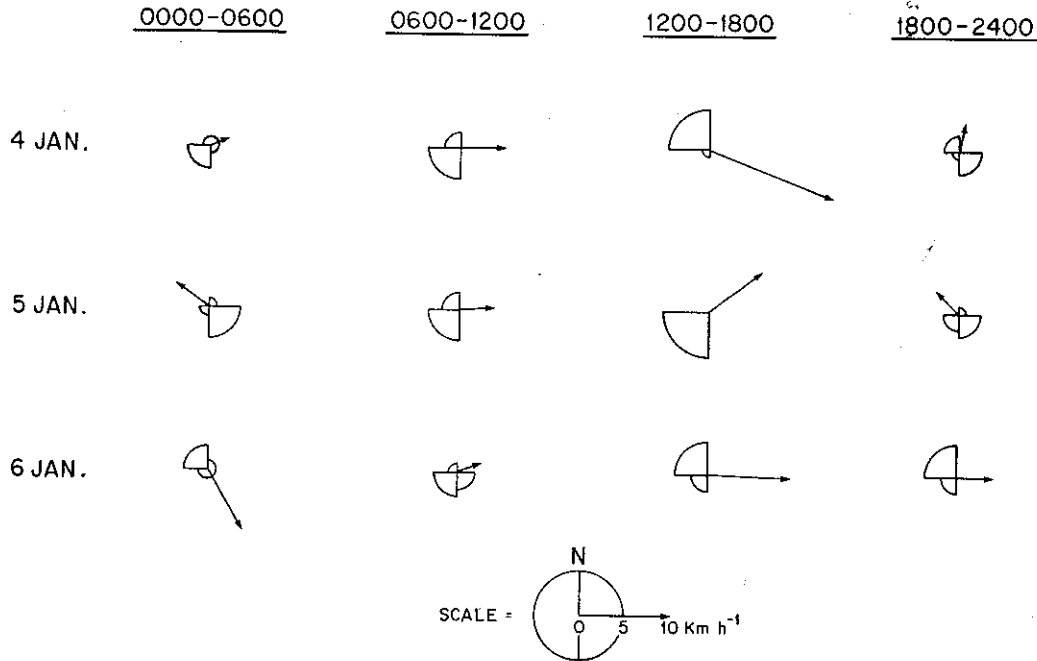


Fig. 3. Surface winds at Oildale. The arrows indicate the mean resultant winds averaged over 6-h periods. The wind roses give the relative frequencies of the different wind directions. Times are LST.

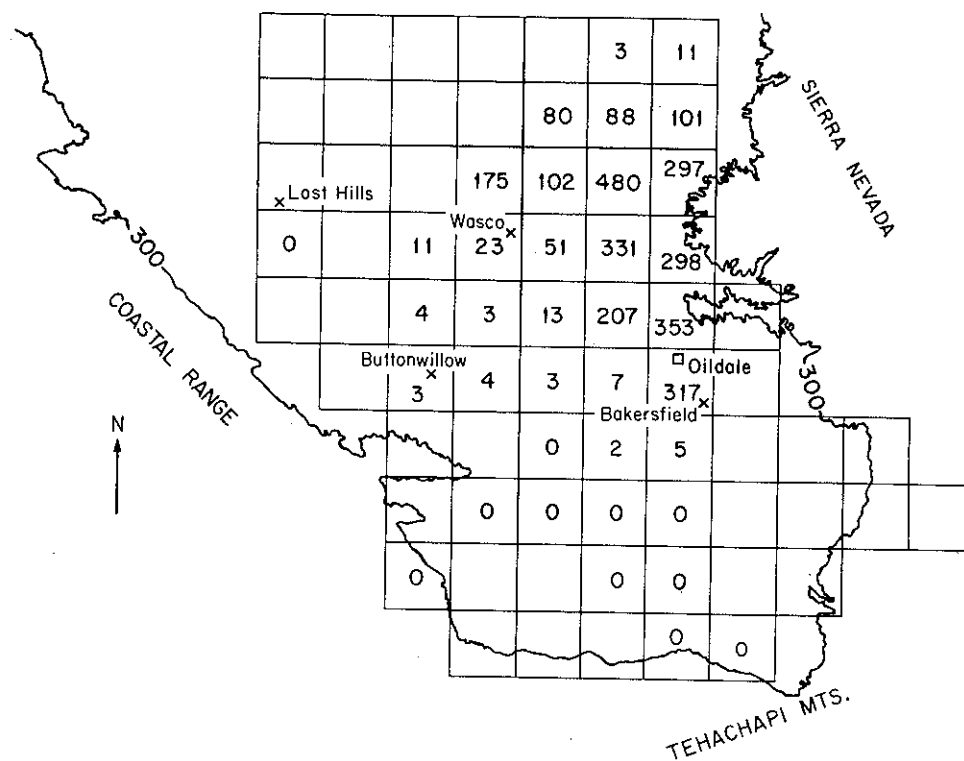


Fig. 4. Surface concentrations of SF₆ (ppt) at 1000–1200 LST on 5 January. The data are averaged over a 10 km × 10 km grid.

2. Transport of SF₆

A first network of automobile traverses was operated in the southern end of the valley between 1000 and 1200 LST on 5 January, immediately after the fog had dissipated. The tracer had been released for 16–18 h by that time, and was still being continuously released. The observed concentrations of SF₆, averaged over a 10 km × 10 km grid, are shown in Fig. 4. A mass balance calculation assuming vertical mixing of SF₆ up to the base of the inversion accounted for 91% of the SF₆ released. This demonstrates the lack of ventilation of the valley during the night and morning; almost all of the SF₆ released during the night was trapped within the mixed layer. The SF₆ plume extended about 40 km N of the release site, and spread laterally over about 20 km. This extent of northward transport is consistent with the net weak S–SE winds (2–3 km h⁻¹) observed at Oildale during the night. Concentrations of SF₆ S and W of the release site were very low.

A second network of automobile traverses was operated in the valley during the mid-afternoon of 5 January, but they failed to find the SF₆ plume. The plume had apparently been transported eastward through the inversion by the upslope flow. An aircraft spiral over Oildale at 1530 LST on 5 January indicated the presence of SF₆ within the inversion layer up to at least 1200 m MSL (Fig. 5). The concentration of SF₆ did not decrease progressively with height, as would have been expected from general penetration of SF₆

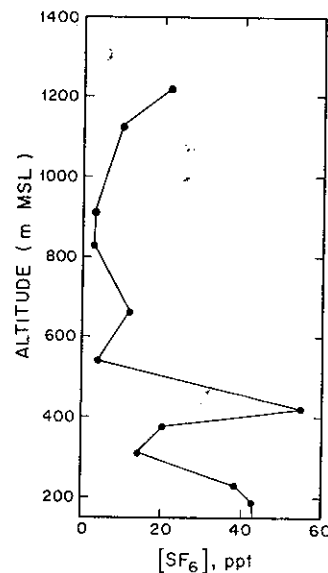


Fig. 5. Vertical profile of SF₆ concentrations over Oildale at 1530 LST on 5 January.

through the weakened afternoon inversion. Instead, a layer of high SF₆ concentrations was observed at 1200 m MSL, which was also observed in aircraft spirals conducted over other valley sites during the same period. We conclude that SF₆ was transported

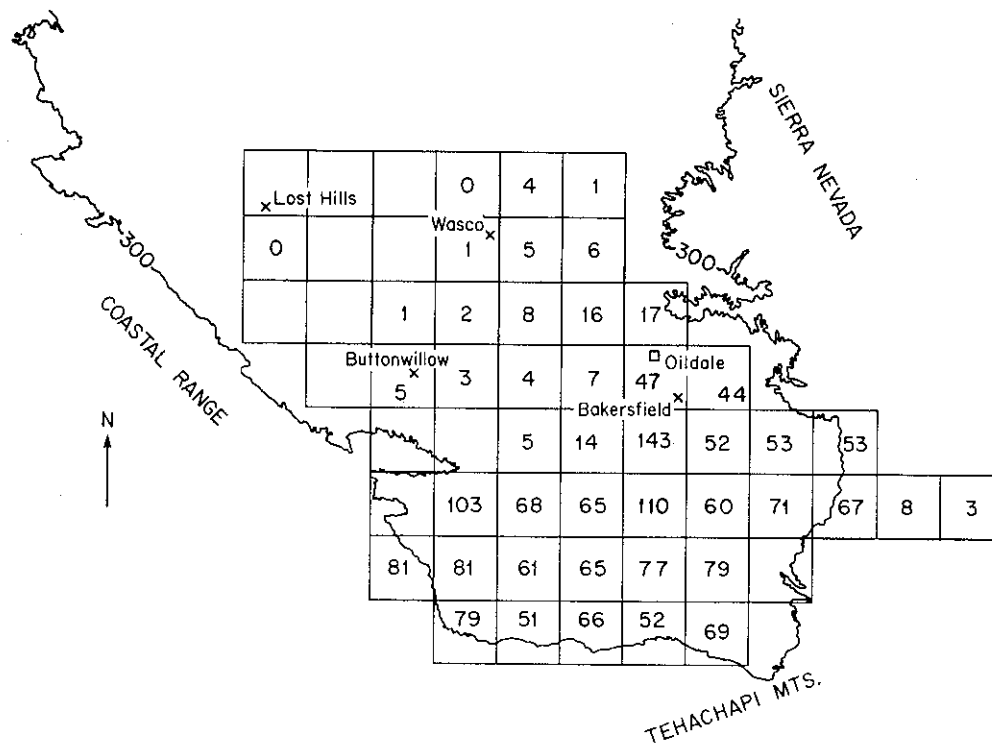


Fig. 6. Surface concentrations of SF₆ (ppt) at 1100–1400 LST on 6 January. The data are averaged over a 10 km × 10 km grid.

upward along the slopes by the buoyant afternoon upslope flow, and was spread out horizontally aloft by the strong upper-level E winds. A rough mass balance, which was based on the aircraft data and dependent on the assumption that SF₆ mixed horizontally aloft over the southern end of the valley, indicated that about 40% of the total SF₆ released was present by mid-afternoon within the inversion layer between 400 and 1200 m MSL. Clearly, the buoyant afternoon upslope flow removed a large fraction of the tracer from the mixed layer below the inversion.

The upslope flow ceased at sunset, and a net weak downslope flow developed in the evening. Winds from the N were observed during the early hours of 6 January, but gave way to weak and inconsistent winds later in the morning (Fig. 3). A network of automobile traverses was operated on 6 January between 1100 and 1400 LST (Fig. 6); high concentrations of SF₆ were found throughout the southern end of the valley. A mass balance calculation from Fig. 6, again assuming vertical mixing up to the base of the inversion, accounted for 37% of the total amount of SF₆ released. Therefore, an important fraction of the SF₆ carried upslope during the afternoon of 5 January was returned to the valley floor in the evening, and was then transported to the southern end of the valley during the night. An aircraft spiral over Oildale at 1220 LST on 6 January (Fig. 7) again showed substantial SF₆ concentrations within the inversion layer.

During the afternoon of 6 January, the upslope flow again transported SF₆ eastward out of the valley. An

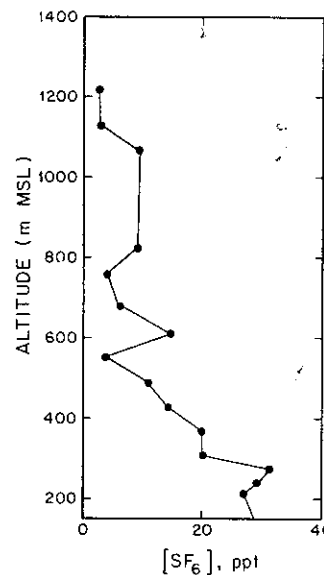


Fig. 7. Vertical profile of SF₆ concentrations over Oildale at 1220 LST on 6 January.

automobile traverse was conducted in the late afternoon over the Tehachapi pass (1200 m) in the SE end of the valley. Significant SF₆ concentrations (5–20 ppt) were found over the pass and in the Mojave desert on the other side of the mountains. No SF₆ was found to

return in the valley on 7 January, probably because of the unstable weather conditions.

TRANSPORT AND OXIDATION OF SO₂

Atmospheric concentrations measured at Oildale during 4–5 January are shown in Fig. 8. Concentrations of SO₂ were very low during the afternoon of 4 January, because of the strong upslope flow carrying SO₂ aloft. After the upslope flow gave way to stagnant conditions in the evening, the SO₂ concentration started to rise and attained a stable value of 40 ppb at midnight. The concentration of SO₂ remained at about 40 ppb from midnight until 1100 LST the following morning, and then dropped rapidly following ventilation of the valley by the upslope flow.

The high night-time SO₂ concentration, combined with the foggy conditions, led to a substantial increase in aerosol SO₄²⁻ concentrations at Oildale. No such increases were observed at Wasco or Buttonwillow, which were both out of the SO₂ plume. Fog set in at Oildale at 2000 LST on 4 January, and persisted until 0900 LST the following morning. The liquid water content of the fog was very stable, and averaged 0.20 g m⁻³. Most of the aerosol SO₄²⁻ in the fog was incorporated into fog droplets (Waldman, 1986). The fogwater SO₄²⁻ concentration increased during the early hours of fog, and stabilized after midnight to an average value of 1100 µeq ℓ⁻¹. The pH of the fogwater progressively dropped over the course of the night, from 6.26 to 3.75. The acidification of the fogwater resulted in the total depletion of NH₃ (g).

The SO₂ sources around Oildale are spread over an area *A* of about 200 km² (shaded area in Fig. 1). We assume that this SO₂ source region can be modeled under stagnant conditions as a stirred tank of characteristic length *L* = 15 km and height *h* = 130 m (mixing height over Oildale), slowly ventilated by a steady wind of velocity *U*. The stable concentrations of SO₂ (40 ppb) and fogwater SO₄²⁻ (1100 µeq ℓ⁻¹) observed at Oildale between 0000 and 0700 LST then correspond to the attainment of a steady state between sources and sinks within the stirred tank. We assume that SO₂ oxidation in fog can be represented by a pseudo first-order rate expression:

$$\frac{d(\text{SO}_2)}{dt} = -k(\text{SO}_2). \quad (1)$$

The major sinks of SO₄²⁻ within the source region are (1) ventilation (wind velocity *U*), and (2) fogwater deposition (deposition velocity *V_d*). The steady-state fogwater SO₄²⁻ concentration in the source region is then given by:

$$\langle [\text{SO}_4^{2-}] \rangle = \frac{\frac{2}{WRT} k \langle (\text{SO}_2) \rangle + \frac{U}{L} \frac{W_0}{W} [\text{SO}_4^{2-}]_0}{\frac{U}{L} + \frac{V_d}{h}} \quad (2)$$

where *W* is the liquid water content of the fog (v/v), *R*

is the universal gas constant, *T* is temperature, $\langle (\text{SO}_2) \rangle$ is the steady-state SO₂ partial pressure, and the subscript 0 refers to fog upwind from the source region. From Fig. 3, the average wind velocity, *U*, was between 0000 and 0600 was 4 km h⁻¹, so that ventilation provided a loss rate of about 27% h⁻¹. Waldman (1986) measured an average fogwater deposition velocity *V_d* = 1 cm s⁻¹ at Oildale during the night of 4–5 January, corresponding to a deposition rate of 28% h⁻¹. Therefore, the total rate of SO₄²⁻ removal from the source region (ventilation + deposition) was 55% h⁻¹. The fogwater composition upwind from the source region can be estimated from fogwater samples collected at Buttonwillow simultaneously with the Oildale samples (Waldman, 1986); these samples contained SO₄²⁻ concentrations averaging 300 µeq ℓ⁻¹ for a liquid water content averaging 1.4 × 10⁻⁷ v/v. Based on *W* = 2.0 × 10⁻⁷ v/v, $\langle [\text{SO}_4^{2-}] \rangle = 1100 \text{ eq } \ell^{-1}$, *W*₀ = 1.4 × 10⁻⁷ v/v, [SO₄²⁻]₀ = 300 µeq ℓ⁻¹, and $\langle (\text{SO}_2) \rangle = 40 \text{ ppb}$, we calculate *k* = 3% h⁻¹. An uncertainty of ± 2% h⁻¹ on this value is estimated from the individual uncertainties on the variables in Equation (2).

DISCUSSION

1. SO₂ oxidation mechanism

The oxidation of SO₂ to H₂SO₄ can proceed by a number of pathways. Jacob and Hoffmann (1983) and Seigneur and Saxena (1984) have modeled the chemical behavior of night-time fogs in polluted atmospheres, and discussed the relative importances of the major SO₂ oxidation pathways. They predict that SO₂ is rapidly oxidized in the initial stage of a fog by the aqueous-phase reaction of S(IV) with H₂O₂ (aq), but that this reaction cannot be sustained because of the depletion of H₂O₂ by SO₂ present in large excess. They find that the main contributor to SO₂ oxidation in the mature stage of the fog is the autoxidation of S(IV) catalyzed by Fe(III) and Mn(II).

These model simulations considered very acidic fogs typical of the Los Angeles coastline (pH 2–4); in our study, however, the fogwater pH remained mostly between 4 and 6, and this can lead to important differences in the rates of SO₂ oxidation. Above pH 4, Fe(III) precipitates, and therefore is not a suitable catalyst for S(IV) autoxidation (Hoffmann and Jacob, 1984). The autoxidation reaction can still be catalyzed by Mn(II), which was present in the Oildale fog samples at concentrations ranging from 0.4 to 0.8 µeq ℓ⁻¹ (Waldman, 1986). Assuming a Mn²⁺ concentration of 0.6 µeq ℓ⁻¹, an average pH of 5.1, *W* = 2.0 × 10⁻⁷ v/v, and using the rate expression proposed by Hoffmann and Calvert (1985) with the appropriate temperature correction (*T* = 278 K), we estimate that the SO₂ conversion rate by Mn(II)-catalyzed autoxidation was 0.5% h⁻¹. This reaction appears to be too slow to fully account for the observed rate.

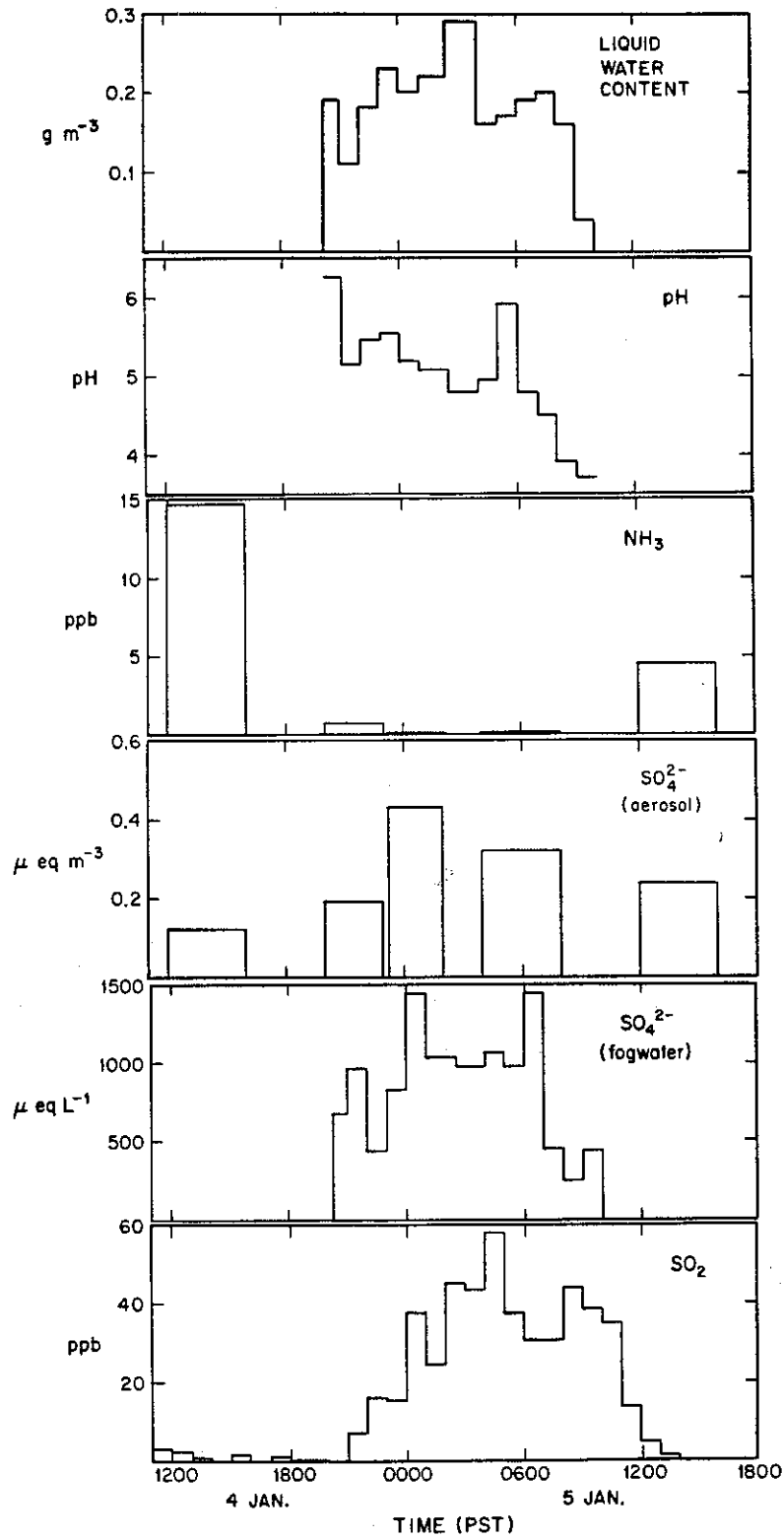


Fig. 8. Atmospheric concentrations measured at Oildale on 4-5 January. Aerosol SO₄²⁻ concentrations are in units of microequivalents m⁻³ of air, and fogwater SO₄²⁻ concentrations are in units of microequivalents per liter of fogwater.

The persistence of a high SO_2 concentration throughout the fog indicates a total depletion of H_2O_2 and organic peroxides, which would otherwise rapidly oxidize SO_2 (Lind *et al.*, 1987); Daum *et al.* (1984) have noted that SO_2 and H_2O_2 appear to be mutually exclusive in clouds. A more important SO_2 oxidation pathway is likely to be the aqueous-phase reaction of S(IV) with O_3 (Hoffmann, 1986), which proceeds rapidly at high pH. Under night-time stagnant conditions in the San Joaquin Valley, O_3 is rapidly depleted in the mixed layer by large excesses of NO (Jacob *et al.*, 1986). However, O_3 concentrations aloft are likely to be higher than at ground level, and O_3 would diffuse to some extent from the inversion layer down into the mixed layer. The O_3 monitoring instrument at Oildale had a detection limit of 10 ppb, and did not measure detectable O_3 concentrations during the night of 4–5 January; however, more sensitive instruments on the west side of the valley reported O_3 concentrations up to 2 ppb. The rate of oxidation of S(IV) by O_3 (aq) in fog droplets is limited at high pH by the rate of aqueous-phase diffusion of O_3 (aq) within the droplets (Schwartz and Freiberg, 1981; Martin, 1983; Jacob, 1986). If we assume an O_3 concentration of 2 ppb at Oildale, a droplet radius of 10 μm , fogwater pH and W as above, and the kinetic expression of Hoigne *et al.* (1985) with the mass transfer correction of Schwartz and Freiberg (1981), we find an oxidation rate for SO_2 by O_3 (aq) of $2\% \text{ h}^{-1}$ (with $T = 278 \text{ K}$). This reaction could possibly be an important contributor to S(IV) oxidation in the San Joaquin Valley.

2. Sulfur budget

We have shown that the near-totality of SF_6 released between 1800 LST on 4 January and 1100 LST on 5 January (or a period of 17 h) remained trapped within the mixed layer below the inversion. The deposition velocity of SO_2 over grass is about 0.5 cm s^{-1} under stable conditions (Sehmel, 1980); based on $h = 130 \text{ m}$ at Oildale, the SO_2 deposition rate in the valley during the night of 4–5 January was about $14\% \text{ h}^{-1}$. In comparison, the SO_2 oxidation rate in fog was previously estimated at $3\% \text{ h}^{-1}$. We find from the above loss rates that 33% of the SO_2 released over that 17-h period remained as SO_2 in the mixed layer, 55% was deposited on the valley floor, and the remaining 12% was converted to SO_4^{2-} . Due to the slow rate of SO_4^{2-} production, the maximum SO_4^{2-} concentration in the valley was probably not at Oildale but more likely about 20 km downwind (to the N). Most of the SO_4^{2-} produced was removed to the valley floor by rapid deposition of the fog droplets. The importance of SO_4^{2-} deposition in fogs has been discussed in detail by Waldman (1986).

The fates of SO_2 and SO_4^{2-} determined in the present study differ considerably from those determined in our study of the previous year (Jacob *et al.*, 1986). Jacob *et al.* observed a steady accumulation of SO_2 and SO_4^{2-} over 4 days of stagnation, with no apparent ventilation of the valley and little SO_4^{2-}

deposition. In that study, fog did not form on the valley floor; instead, the valley remained overcast as a persistent stratus cloud occupied the upper part of the mixed layer. The overcast limited daytime insolation of the slopes, thereby preventing the upslope flow from ventilating the valley. Further, the deposition of SO_4^{2-} was very slow because of the lack of fog; deposition velocities of haze aerosol particles are over one order of magnitude lower than those of fog droplets (Waldman, 1986). We conclude that the fates of SO_2 and SO_4^{2-} in the San Joaquin Valley during high-inversion episodes depend to a considerable degree on whether or not the valley is insolated, and whether fog or stratus occur. The rate of in-fog SO_2 oxidation estimated in the present study is consistent with the value of $5\% \text{ h}^{-1}$ estimated in the study of Jacob *et al.* (1986) for SO_2 oxidation in the stratus cloud above the valley floor.

3. Fogwater and aerosol acidity

The atmosphere of the San Joaquin Valley usually contains excess alkalinity, due to the presence of important confined cattle feeding operations which discharge large amounts of NH_3 (Jacob *et al.*, 1986). On the afternoon of 4 January, the concentration of NH_3 (g) at Oildale was 15 ppb, and the pH of the first fog sample collected that evening was high (pH 6.26). However, the pH dropped progressively over the course of the fog, as the oxidation of SO_2 to H_2SO_4 produced acidity which titrated NH_3 (g). By 2300 LST, NH_3 (g) was fully titrated, and NH_3 (g) concentrations remained below our detection limit of 0.5 ppb until the following afternoon. High concentrations of NH_3 (g) were again observed on the afternoon of 5 January, following dissipation of the fog and transport of the acidic aerosol out of the valley.

The decrease in fogwater pH observed after midnight was much slower than that expected from the rate of H_2SO_4 production. The pH drop from 5.5 to 3.75 over 10 h of fog, with $W = 2 \times 10^{-7} \text{ v/v}$, is equivalent to the production of $4 \text{ neq H}^+ \text{ m}^{-3} \text{ h}^{-1}$; by comparison, oxidation of 40 ppb SO_2 at the rate of $3\% \text{ h}^{-1}$ produces $100 \text{ neq H}^+ \text{ m}^{-3} \text{ h}^{-1}$. It appears that most of the H_2SO_4 produced was neutralized by NH_3 , which was continuously being released from ground sources, and therefore that the H_2SO_4 and NH_3 source rates were in close balance.

Jacob *et al.* (1986) had previously reported a similar close balance between high acidic and alkaline emissions in the Southern San Joaquin Valley. Because of the precariousness of the present acid/base balance, relatively small fluctuations in either SO_2 or NH_3 emissions could have important implications for fogwater and aerosol acidity in the San Joaquin Valley. Both SO_2 and NH_3 emissions are currently decreasing in the valley, due to the increasing use of SO_2 scrubbers on steam generators and the decline of the cattle industry. Therefore, it is difficult to forecast whether or not the Southern San Joaquin Valley will be affected by acid fog in the years ahead. The occurrence of acid fog episodes in the valley could have major environmental

implications, in view of the rapidly increasing population and the important agricultural activity. In addition, our data indicate that upslope transport of the acidic aerosol produced in the valley during stagnation episodes affects the National Forests and National Parks on the west side of the Sierra Nevada. Acidic aerosols from the San Joaquin Valley could possibly be a contributing factor to the recent increase in tree necroses observed in Sequoia National Park at elevation 1000–1500 m MSL (California Air Resources Board, private communication, 1986). The possible role of acid fog in provoking pine needle necrosis has been previously discussed by Waldman *et al.* (1984).

CONCLUSIONS

An inert tracer, SF₆, was released from a major SO₂ source region in the San Joaquin Valley of California during an extended high-inversion episode. At night, the near-totality of the tracer was trapped below a strong and persistent subsidence inversion based 200–300 m above the valley floor. In the daytime, however, the upslope flow generated by the insolation of the mountain slopes was sufficiently buoyant to transport the tracer up through the inversion. About 40% of the tracer transported upslope in the afternoon was returned to the valley floor in the evening by the downslope drainage flow.

Considerable accumulation of SO₂ and SO₄²⁻ was observed at night in the stagnant foggy boundary layer. The production of acidity from the oxidation of SO₂ to SO₄²⁻ fully titrated the NH₃(g) present, and led to a progressive decrease of the fogwater pH over the course of the night. A stirred-tank approximation for the SO₂ source region was used to model the night-time sources and sinks of SO₂ and SO₄²⁻. From that model, the rate of oxidation of SO₂ to SO₄²⁻ in fog was estimated at $3 \pm 2\% \text{ h}^{-1}$. We suggest that SO₂ oxidation proceeded mainly in the fog droplets by reaction of S(IV) with O₂(aq) [catalyzed by Mn(II)] and O₃(aq). In the daytime, the upslope flow efficiently transported SO₂ and SO₄²⁻ out of the valley. By comparing the results of this study to those of a study conducted the previous year, we conclude that the fates of SO₂ and SO₄²⁻ during extended high-inversion episodes in the valley are considerably dependent on the presence of fog or stratus, and on the extent of daytime insolation.

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