

Conversion of SO₂ to Sulfur Particulate in the Los Angeles Atmosphere

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Gas phase and particulate phase sulfur have been measured at various locations in the Los Angeles basin to determine atmospheric conversion rates and mechanisms. A new technique was developed for the measurement of particulate sulfur. From measurements of the particulate to gas phase sulfur ratio near the major stationary sources and far downstream and from estimates of travel times determined by air trajectory analysis, it is possible to estimate gas-to-particle conversion rates for sulfur. Such calculations show that automobiles presently contribute a major part of the total sulfur as measured at a receptor site such as Pasadena, while contributing only a small amount to the particulate sulfur loading. The introduction of oxidation catalyst-equipped vehicles may add significantly to the particulate sulfur at downwind receptor sites; predictions of particulate sulfur concentrations near freeways show substantial increases due to such vehicles.

Introduction

There have been many laboratory studies of SO₂ to aerosol sulfur conversion (1) but data on the actual rate and/or conversion mechanisms in an urban atmosphere are scanty. Most of the atmospheric studies to date have been made in power plant plumes (2). In this paper, we report the results of measurements of the particulate to gas sulfur ratio near sources and far downstream. From estimates of travel times based on air trajectory analyses, rates for conversion of gas to particulate sulfur can be calculated. These calculations show that the automobile presently contributes relatively little to the particulate sulfur loading; however, the

additional particulate sulfur resulting from catalytic conversion in automobile reactors may add significantly to the aerosol sulfur burden at local and downwind receptor sites.

Model Development

In Los Angeles, the major stationary sources of SO₂ are power plants and refineries located along the coast. When a stable marine wind is established during the late morning, sulfur oxides are transported from these sources to downwind receptor sites. Additional quantities of sulfur oxides are emitted from industrial and automobile sources along the trajectory.

For a detailed understanding of the time and emission history of aerosol samples taken at a receptor site, it is convenient to use an air trajectory technique such as that

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suggested by White, Husar, and Friedlander (3). From such an analysis, it is possible to determine the average position-time history of that air parcel and to calculate pollutant inputs during movements of the air from major source to receptor site. Once this has been done, such data can be used in the Eulerian diffusion model which will be developed next.

First, we write the diffusion equation for both SO_2 and total sulfur (S_T) in an Eulerian system [eqs. (1) and (2)], where we have assumed zero wind in the y and z directions and have neglected dispersion in the direction of transport. Here, SO_2 where we have assumed zero wind in the y and z directions and have neglected dispersion in the direction of transport. Here, SO_2 and S_T are both concentrations expressed as sulfur, u is the steady wind in the x direction, W_{SO_2} and W_{S_T} are the area source emission terms for SO_2 and total sulfur, H is the mixing height, and K_y and K_z are the eddy diffusivities. Also, k is the pseudo first-order rate term for the SO_2 to aerosol sulfur con-

version, v_g is the deposition velocity for loss of SO_2 to the ground, and v_a is the deposition velocity for loss of aerosol sulfur to the ground. The area source emission is assumed to become uniformly mixed in the vertical direction quickly and is thus treated as a volume source term. Likewise the gas and aerosol sulfur ground loss terms are treated as volume loss terms.

Georgii (4) has shown that the SO_2/S_T ratio is not a function of z at low altitudes. Assuming also that $\text{SO}_2/S_T = g(x)$, we can carry out the substitution of eq. (3).

On substituting into eqs. (1) and (2) and rearranging, the result is eq. (4): Setting the travel time $T = x/u$ and integrating along a known trajectory yields eq. (5): For area automobile emissions, we denote the aerosol sulfur to total sulfur ratio as $f = (W'_{S_T} - W'_{\text{SO}_2})/W'_{S_T}$, where W'_{S_T} and W'_{SO_2} are the area source terms for the automobile only. Then eq. (5) can be rewritten as eq. (6).

$$\frac{\partial \text{SO}_2}{\partial t} + u \frac{\partial \text{SO}_2}{\partial x} = \frac{\partial}{\partial y} (K_y \frac{\partial \text{SO}_2}{\partial y}) + \frac{\partial}{\partial z} (K_z \frac{\partial \text{SO}_2}{\partial z}) - k \text{SO}_2 + \frac{W_{\text{SO}_2}}{H} - v_g \frac{\text{SO}_2}{H} \quad (1)$$

$$\frac{\partial S_T}{\partial t} + u \frac{\partial S_T}{\partial x} = \frac{\partial}{\partial y} (K_y \frac{\partial S_T}{\partial y}) + \frac{\partial}{\partial z} (K_z \frac{\partial S_T}{\partial z}) + \frac{W_{S_T}}{H} - v_g \frac{\text{SO}_2}{H} + \frac{v_a (S_T - \text{SO}_2)}{H} \quad (2)$$

$$\frac{\partial}{\partial y} (K_y \frac{\partial \text{SO}_2}{\partial y}) + \frac{\partial}{\partial z} (K_z \frac{\partial \text{SO}_2}{\partial z}) - \frac{\partial \text{SO}_2}{\partial t} = g(x) \left[\frac{\partial}{\partial y} (K_y \frac{\partial S_T}{\partial y}) + \frac{\partial}{\partial z} (K_z \frac{\partial S_T}{\partial z}) - \frac{\partial S_T}{\partial t} \right] \quad (3)$$

$$u \frac{dg}{dx} = -kg + \frac{g}{H} \left[\frac{W_{\text{SO}_2}}{\text{SO}_2} - \frac{W_{S_T}}{S_T} + \frac{S_T - \text{SO}_2}{S_T} (v_a - v_g) \right] \quad (4)$$

$$k = \frac{1}{\Delta T} \left\{ \ln \frac{\text{SO}_2}{S_T} \right|_{\text{end}}^{\text{start}} + \int_{\text{start}}^{\text{end}} \frac{1}{H} \left[\frac{W_{\text{SO}_2}}{\text{SO}_2} - \frac{W_{S_T}}{S_T} + \frac{S_T - \text{SO}_2}{S_T} (v_a - v_g) \right] dT \right\} \quad (5)$$

$$k = \frac{1}{\Delta T} \left\{ \ln \frac{\text{SO}_2}{S_T} \right|_{\text{end}}^{\text{start}} + \int_{\text{start}}^{\text{end}} \left[\left(1 - \frac{\text{SO}_2}{S_T} \right) \left(\frac{v_a - v_g}{H} + \frac{W_{S_T}}{H S_T} \right) - \frac{f W'_{S_T}}{H \text{SO}_2} \right] dT \right\} \quad (6)$$

$$\left. \frac{\text{SO}_2}{S_T} \right|_{i+1} = \left. \frac{\text{SO}_2}{S_T} \right|_i \exp \left\{ (\Delta T) \left[-k + \left(1 - \left. \frac{\text{SO}_2}{S_T} \right|_i \right) \left(\frac{v_a - v_g}{H} + \frac{W'_{s_T}}{H \text{SO}_2} \right) \left| \frac{fW_{s_T}}{H \text{SO}_2} \right| \right] \right\} \quad (7)$$

Because we do not know the value of S_T along the trajectory, eq. (6) must be solved by a trial-and-error iterative process. A value for k is chosen and then, for hourly intervals along the trajectory, each successive SO_2/S_T ratio is calculated by eq. (7).

where i and $i + 1$ are the beginning and the end of the interval, and \bar{H} and $\bar{\text{SO}_2}$ are the average values during that hourly period. The value of k is adjusted until the SO_2/S_T ratio at the end of the trajectory matches the measured value. The SO_2/S_T ratio at the beginning and end of the trajectory and the values of W_{SO_2} , W_{s_T} , H , and SO_2 as a function of time (or distance) along the trajectory are necessary for solution of eq. (6).

Average values for each hour along a known trajectory were determined by using Los Angeles APCD monitoring data for H and SO_2 . The contribution of stationary sources to W_{SO_2} along the trajectory path was calculated by using emission inventory data supplied by the LAAPCD (5). The automobile contribution to W_{s_T} was calculated by updating (to summer 1973) the average miles driven as a function of time of day and position in the Los Angeles basin (6) and using the average sulfur content of Los Angeles area gasoline, 0.075 wt-% sulfur (7). Values of $v_g = 0.7$ cm/sec (8) and $v_a = 0.03$ cm/sec (9) were used in eq. (7).

Experimental

Total filter and cascade impactor aerosol samples of 1 hr duration were taken at Pasadena in July 1973 and at California State University at Dominguez Hills in October 1973 and analyzed for sulfur. Sulfur gas and other parameters were also measured at both sites. Because of the many possible trajectory starting locations, it is difficult to sample at both ends of the same trajectory. Therefore, 5-days were spent at the Dominguez Hills

location to determine the near-source SO_2/S_T ratio and its variability. This ratio was found to range from 0.88 to 0.98, depending on the type of source in the downwind direction.

The aerosol sulfur analyses were performed by using an aerosol vaporization technique developed in this laboratory. The method, a modification of gas evolution analysis, measures the total sulfur mass in the aerosol of all sulfur compounds which either vaporize (e.g., H_2SO_4) or decompose [e.g., $(\text{NH}_4)_2\text{SO}_4$] below approximately 1100°C. The aerosol is vaporized in an all glass-Teflon system into a stream of clean air flowing directly into a flame photometric detector (Melay SA-160) for total sulfur (see Fig. 1). Electronic integration of the sulfur peak results in the mass of sulfur vaporized from the sample. Standardization is accomplished by using known volumes of doubly distilled water solutions containing 5–500 ng sulfur as H_2SO_4 , $(\text{NH}_4)_2\text{SO}_4$, and Na_2SO_4 . Such compounds are included among the major sulfur compounds existing in urban aerosols (10).

The method depends upon the resistance heating of a thin stainless steel strip (0.001 in. \times 0.25 in. \times 0.80 in.) to about 1100°C by a capacitor discharge through the strip. The analysis of impactor samples collected directly on such strips is accomplished by mounting the strip in the glass system and

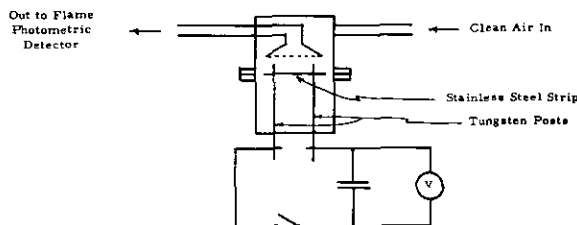


FIGURE 1. Schematic diagram of vaporization apparatus.

subsequent capacitor discharge. More than 95% of the sulfur placed on such a strip for standardization is recovered after a single heating. In order to analyze filter samples, a small disk cut from a glass fiber filter is placed between two stainless steel strips and heated by a capacitor discharge of approximately twice the energy as that used for a single strip. It is necessary to heat such samples twice in order to recover more than 95% of the measurable sulfur. Replicate analysis is possible for filter samples. Any punch size less than $\frac{1}{4}$ in. diameter can be used, depending on the quantity of sulfur aerosol on the filter. Total filter analysis is also possible by water extraction of a filter medium, placement of an aliquot of the extract on a clean single strip and heating. The stainless steel strips are prepared for use by heating at 900°C for about 2 hr. The glass fiber filters (Gelman type A) are prepared by heating at 450°C for about 8 hr. These preparation methods reduce background sulfur to less than 1 ng per single strip and 4 ng per disk.

Results

Table 1 shows the calculated k for 3 days in July and the general starting location of the trajectories. The Alamitos Bay sources consist of two large power plants, and the El Segundo sources of two power plants plus a refinery. An initial value of 0.97 was used for the SO_2/S_T ratios from such sources. The calculated rate constants vary significantly, indicating dependence on parameters (such as O_3 , free radicals, olefins, relative humidity) involved in the complex photochemistry occurring in the Los Angeles atmosphere.

An estimate of the contribution of automobile emitted sulfur to the aerosol sulfur at Pasadena can be made by substituting the rate constants shown in Table 1 into eq. (6) and eliminating the area automobile source (W for industrial sources only) to determine the resulting SO_2/S_T ratio at Pasadena. Comparison of this ratio with that

Table 1. Pseudo first-order rate constants for sulfur in the Los Angeles Basin [eq. (1)].

Date (1973)	Time of arrival at Pasadena (PST)	k , %/hr	Starting location
July 10	1300	1.2	El Segundo
	1400	3.0	" "
	1500	9.0	" "
	1600	13.0	" "
July 25	1400	12.8	Alamitos Bay
	1500	8.2	El Segundo
	1600	8.8	" "
July 26	1200	4.3	Alamitos Bay
	1300	5.6	" "
	1400	7.6	" "
	1500	4.7	" "

actually found results in the aerosol sulfur presently due to the automobile. Such calculations for the samples shown in Table 1 indicate 2–11% of the aerosol sulfur measured at Pasadena resulted from conversion of auto-emitted SO_2 . However, 20–70% of the total sulfur at Pasadena resulted from SO_2 emissions from the automobile (calculated for the samples shown in Table 1 by using the CO concentration at Pasadena as a tracer). This results because the automobile emits only about 15% of the SO_2 emitted in the Los Angeles basin, but that emission can occur anywhere along the trajectory. Any SO_2 emitted late in the trajectory is given heavier weight than earlier emissions in determination of the total sulfur at a receptor site, but smaller weight in determination of the aerosol sulfur.

Figures 2 and 3 show the estimated increase in aerosol sulfur at Pasadena due to the conversion of SO_2 to H_2SO_4 in automobile oxidation catalytic converters. It is assumed that such vehicles use an unleaded fuel of sulfur content 0.075 wt-%, a quantity typical of present Los Angeles gasoline. Figure 2 assumes all automobiles to have such converters and shows the increased sulfur aerosol (expressed as $\mu\text{g SO}_4/\text{m}^3$) as a function of the fraction converted in the automobile. This is accomplished by adjusting the parameter f in eq. (6). The middle curve indicates an average response of the eleven trajectories

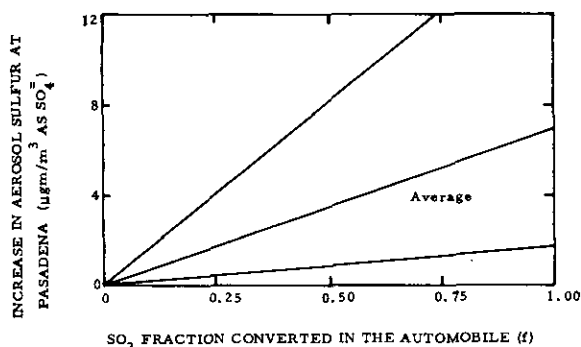


FIGURE 2. Increase in aerosol sulfur at Pasadena as a function of the amount of SO_2 converted in automobile reactors. All automobiles assumed equipped with catalytic converters. Sulfur content of gasoline assumed to be 0.075 wt.-%. Upper and lower curves show the range from the trajectory calculations in Table 1.

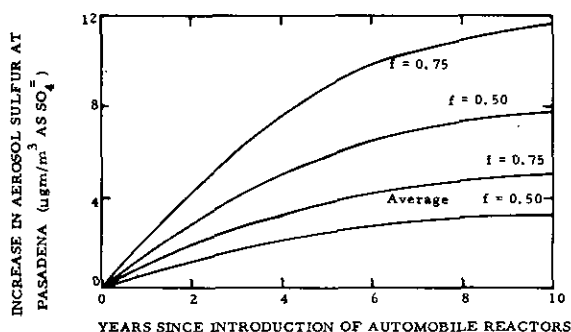


FIGURE 3. Increase in aerosol sulfur at Pasadena as a function of the fraction of SO_2 converted in automobile reactors with the replacement schedule reported by Lees et al. (12). Sulfur content of gasoline assumed to be 0.075 wt.-%. Upper curves show the maximum for the trajectory calculations in Table 1.

shown in Table 1. The other two curves indicate the range of response. The average sulfur aerosol concentration of $20 \mu\text{g}/\text{m}^3$ as sulfate results in a 20% increase in aerosol sulfur at Pasadena, assuming a 50% conversion before emission (11). Figure 3 shows the dynamic effect of replacement of older automobiles without catalytic converters by those with such devices for the average and higher curves in Figure 2 at two levels of the converted fraction ($f = 0.50$ and $f = 0.75$). This assumes the birth-death schedule and average mileage as a function of vehicle age for Los Angeles County as given by Lees et al. (12). These estimates indicate that the

Table 2. Estimated aerosol sulfur concentrations near roadways due to conversion of 50% of the automobile emitted SO_2 to aerosol in automobile reactors (all automobiles assumed equipped with such reactors).

[CO] level Los Angeles	[CO], ppm	Estimated [SO_4^{2-}], $\mu\text{g}/\text{m}^3$	
		(CO by 7- mode)	(CO by CVS)
Average, summer 1973	4	12	8
Average, winter 1972	6	18	12
Daily max average— winter 1972	17	51	33
Average near freeway at rush hour	25	76	48
APCD first stage alert for [CO]	50	151	97

introduction of oxidation catalytic converters will have little effect on the aerosol sulfur at downwind receptor sites such as Pasadena during the first few years; however, a significant effect is estimated to occur as the system approaches that of all automobiles having such catalytic converters.

Local receptor effects of the oxidation catalytic converters must be considered along with the downwind receptor effects estimated above. Table 2 shows sulfate concentrations due to the conversion of SO_2 to H_2SO_4 in automobile reactors estimated by using measured CO concentrations as a tracer for such emissions and on assuming all automobiles to have such reactors. These concentrations are in addition to other aerosol sulfate already existing in the air. Although they show some variance in the estimated sulfate concentrations, both the 7-mode and CVS emission factors result in a substantial addition to the aerosol sulfur burden close to high density automobile traffic.

Conclusions

Estimates have been made of the pseudo first-order rate term for SO_2 to aerosol sulfur conversion in the Los Angeles atmosphere. This rate appears to depend upon parameters such as O_3 , free radicals, olefins, and relative humidity which are involved in the complex photochemistry of the Los Angeles atmos-

phere. The calculation procedure outlined here has been used to estimate the dynamic and steady-state effect of the introduction of automobile oxidation catalytic converters on aerosol sulfur. This shows a significant increase in aerosol sulfur at a receptor site such as Pasadena and a much larger increase in aerosol sulfur at receptor sites near high-density automobile traffic.

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