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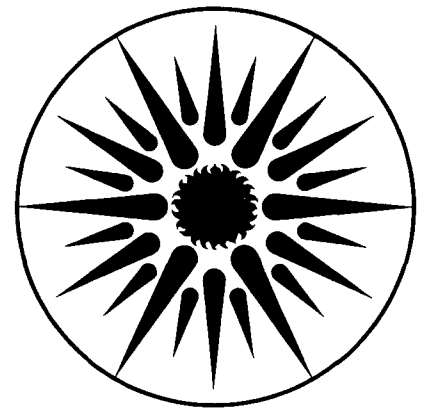
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IN LJUBLJANA, YUGOSLAVIA

M. Bizjak, V. Hudnik, A.D.A. Hansen,  
and T. Novakov

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EVIDENCE FOR HETEROGENEOUS SO<sub>2</sub> OXIDATION  
IN LJUBLJANA, YUGOSLAVIA†

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*Abstract*

The results of analyses of 24-hr wintertime aerosol samples collected during the 1981/82 and 1983/84 sampling periods demonstrate that the highest sulfate formation is observed during periods of high relative humidity and persistent subzero temperatures. Such conditions are conducive to formation of liquid water droplets. The existence of an aqueous mechanism is corroborated by the observed aerosol chloride loss during high sulfate episodes and by the fact that most aerosol sulfate is confined to a particle size range between 0.3 and 2  $\mu\text{m}$ . Soot particles are found in the same size range, indicating the association of aerosol sulfate with combustion products. Under favorable meteorological conditions, up to 20% of the SO<sub>2</sub> may be oxidized to sulfate by heterogeneous mechanisms in winter.

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## *Introduction*

Most previous research on sulfate aerosols was devoted either to  $\text{SO}_2$  conversion during long-range transport or to sulfate formation in urban atmospheres where, because of the high degree of environmental regulations and controls, the pollutant concentrations are relatively low. Much less is known about sulfate chemistry in highly polluted source-dominated urban atmospheres, where scattered, uncontrolled, and usually inefficient small furnaces are major sources of pollutants. Such atmospheres, because of high concentrations of both particles and gases, are more likely to provide conditions for heterogeneous reactions and therefore a greater probability for demonstrating their occurrence and inferring the contributions of local sources to aerosol sulfates.

The research described in this paper deals with certain aspects of heterogeneous formation of aerosol sulfate in Ljubljana, Yugoslavia. This city, located in a valley, is well suited for such a study because of high pollutant concentrations, especially during winter. Winter concentrations of both primary ( $\text{SO}_2$  and soot) and secondary (sulfate) species may be up to 30 times higher than average summer values. Twenty-four hour average values of  $600 \mu\text{g m}^{-3}$   $\text{SO}_2$ ,  $100 \mu\text{g m}^{-3}$  sulfate, and  $120 \mu\text{g m}^{-3}$  particulate carbon are commonly measured (Bizjak et al., 1984). The pattern of energy use accounts for the maximum pollution in winter. While transportation and industrial emissions are approximately constant throughout the year, space heating emissions are strongly seasonally modulated. Space heating, in a large number of dispersed individual furnaces and a few larger central heating plants, is the principal source of  $\text{SO}_2$  during the winter. During the relatively cold winters, inversions with characteristic pollution-related urban fog occur almost daily. The combination of topography and temperature inversion serves to confine and concentrate emissions from local city sources. During summer, the inversions are rare; emissions are decreased; and because of increased wind speed, the pollutants are readily dispersed. Based on such considerations, in principle the local source emissions could be differentiated from those originating from distant sources. Further-

more, because the highest sulfate concentrations occur in winter when photochemical activity is at a minimum, nonphotochemical SO<sub>2</sub> oxidation processes should be easier to identify.

This paper discusses our results from the 1981/82 and 1983/84 sampling periods. These results demonstrate that wintertime sulfates are related to local sources and produced by aqueous heterogeneous processes. The conditions favoring maximum sulfate formation are high relative humidity and low ambient temperatures under stagnant atmospheric conditions.

### *Experimental*

Two kinds of 24-hr ground-level aerosol filter samples were collected. Total samples, i.e., without size segregation, were collected during the 1981/82 sampling period. Size segregated 24-hr filter samples corresponding to cutoffs of  $< 0.3 \mu\text{m}$  and  $2.0 \mu\text{m}$  were collected during the 1983/84 period.

The total aerosol samples were collected with a low-volume sampler. Two filters of 47-mm diameter were exposed in parallel for different analyses. The filter materials used were quartz fiber (Pallflex type 2500 QAO, pre-fired for 6 hr at 700° C to remove combustible carbon) and cellulose membrane (Millipore type RATF, 1.2- $\mu\text{m}$  pore size). The flow rates used were 6.7  $\mu\text{pm}$  for both filters. Samples were normally collected for 24 hours from 8 a.m., giving a flow of 1 m<sup>3</sup> of air per 1 cm<sup>2</sup> of exposed filter area per 24-hr sample. The sampler has 1-mm mesh insect screen on the inlet and was located under a weather protection roof. The air inlet chamber (of approximately 10  $\mu\text{l}$  capacity) was slightly heated to prevent condensation.

Twenty-four-hour size-segregated samples were collected on the quartz afterfilters of two single-stage impactors. Two such units were used, producing one filter sample from which all particles of effective diameter greater than 0.3  $\mu\text{m}$  have been excluded and another representing particles smaller than 2  $\mu\text{m}$ . The impaction surfaces were greased to minimize particle bounce. The impactors operated at a flowrate of 8.5  $\mu\text{pm}$ .

The sampling was performed at the Hydrometeorological Institute in central Ljubljana. Meteorological data consisting of wind speed and direction, temperature, and relative humidity were collected at the site, as well as 24-hr average  $\text{SO}_2$  concentrations by a conventional titration method.

The exposed quartz filters were analyzed for total carbon and sulfur by combustion followed by relative conductometric determination of  $\text{SO}_2$  and  $\text{CO}_2$  (with the relative conductometric C and S analyzer manufactured by Wösthoff Co.) at the B. Kidrič Institute in Ljubljana. Portions of the same filters were also analyzed for total carbon at Lawrence Berkeley Laboratory by a combustion technique with coulometric  $\text{CO}_2$  detection (Huffman, 1977). Millipore filters were analyzed for sulfur and trace elements by x-ray fluorescence (XRF) using an energy dispersive spectrometer (Giauque, 1979). Aerosol sulfur data used in this study are those determined by combustion. These were judged to be more accurate than the XRF data because of the self-absorption of sulfur x-rays in these heavily loaded samples. The combustion sulfur results agreed within  $\pm 5\%$  with water-soluble sulfate as determined by ion chromatography.

### *Results and Discussion*

The seasonal pattern of pollutants in Ljubljana is illustrated in Fig. 1a and b, where biweekly  $\text{SO}_2$  and particulate sulfur,  $S_p$ , concentrations are plotted as a function of time during the 1981/82 sampling season. The particulate sulfur to gaseous sulfur ratios,  $S_p/S_g$ , for this period are shown in Fig. 1c. This ratio, which can be viewed as a measure of  $\text{SO}_2$ -to-sulfate conversion, is about four times higher in the summer (~ 0.4) than in the winter (~ 0.1), indicating a different chemistry during the two seasons.

In the analysis of the data, we will also make use of another ratio: particulate sulfur to particulate carbon,  $S_p/C_p$ . In Ljubljana, as previously demonstrated (Bizjak et al., 1984), total particulate carbon and soot concentrations are approximately equivalent. As a primary combustion-generated particulate pollutant, soot can be used as a conservative tracer for the products of incomplete combustion (Novakov, 1981). The  $S_p/C_p$

ratio can therefore be used to infer the relationship between secondary sulfates and primary source emissions. The  $S_p/C_p$  ratios for the 1981/82 sampling period are shown in Fig. 1d. The variations of these ratios are qualitatively similar to the variations of  $S_p/S_g$  ratios but with less pronounced maxima. Furthermore, there seems to be a clear difference in these ratios between Nov./Dec. and Jan./Feb., with the latter period having higher values. Another way of presenting the differences in the sulfate chemistry for these two periods is shown in Fig. 2. In this figure, 24-hr particulate sulfur concentrations are plotted against  $SO_2$  and particulate carbon concentrations for Nov.-Dec. 1981 and Jan.-Feb. 1982. Distinct differences are seen for these two periods. During Nov.-Dec. a very good correlation with carbon (Fig. 2b) is seen, but there is essentially no correlation with  $SO_2$  (Fig. 2a). The situation is reversed during Jan.-Feb., when a good correlation is observed with  $SO_2$  (Fig. 2c) but not with carbon (Fig. 2d). Note, however, that the line corresponding to the fit to the Nov.-Dec. data also represents the lower limit for  $S_p/C_p$  ratios in the subsequent period, indicating enhanced sulfate formation during the latter part of the winter.

In the remainder of this section, we will provide arguments that the enhanced sulfate formation occurs when the atmospheric conditions are most favorable for heterogeneous aqueous  $SO_2$  oxidation. Ozone concentrations were negligible during both the Nov.-Dec. and the Jan.-Feb. periods. Therefore, it is unlikely that the differences between these periods could be attributed to the differences in photochemical activity. The data in Table I imply that the differences in sulfur chemistry are not directly related to concentrations of  $SO_2$  and catalytically active species. Here the average concentrations of  $SO_2$  and aerosol carbon, sulfur, and other elements are listed for three periods: 9-18 Nov. 1981, 23-20 Dec. 1981, and 15-21 Jan. 1982. These three periods are characterized by increasing  $S_p/C_p$  and  $S_p/S_g$  ratios. Table I shows that there are no significant differences in concentrations of catalytically active species, such as C, Mn, V, and Fe, corresponding to periods of low and high  $S_p/C_p$  ratios.



The most significant changes in trace element concentrations were observed for chlorine. Its concentration decreased drastically as the sulfate concentration (and  $S_p/C_p$  and  $S_p/S_g$  ratios) increased. To a much lesser degree, a similar trend was also observed for bromine. This apparent loss of chlorine could be indicative of an aqueous chloride + acid reaction resulting in the formation of volatile HCl as originally proposed by Robbins et al. (1959). This observation is one of the indications that the enhanced sulfate formation in the Jan.-Feb. period is caused by a heterogeneous mechanism involving liquid water droplets or wet aerosol particles.

This hypothesis is supported by an examination of the relative humidity and ambient temperature data. The average 24-hr relative humidity was high, usually exceeding 80%, and the wind speed was generally low ( $< 1 \text{ m sec}^{-1}$ ) during both the Nov.-Dec. and Jan.-Feb. periods. The only drastic difference in meteorology corresponding to low and high  $S_p/C_p$  ratios was the ambient temperature. This is seen from Fig. 3, where  $S_p/C_p$  ratios, average daily relative humidity, and temperature are plotted for December 1981 and January 1982. This figure shows that the high  $S_p/C_p$  ratios during January correspond to periods with high humidity and persistent subzero temperatures.

In our view, this observation represents the manifestation of a heterogeneous liquid-phase mechanism of  $\text{SO}_2$  oxidation. Under conditions of high humidity and low wind speed, subzero temperatures would enhance condensation of water droplets on combustion nuclei and increase the solubility of  $\text{SO}_2$ . Such conditions are known to favor the formation of urban fog, consisting of supercooled droplets.

Further evidence for heterogeneous  $\text{SO}_2$  oxidation was obtained from the analysis of size-segregated samples. Particles with diameters  $< 0.3 \mu\text{m}$  and  $< 2 \mu\text{m}$  were collected. Twenty-four-hour particulate sulfur and carbon concentrations corresponding to these two size cuts collected during the winter of 1983/84 are shown in Fig. 4. This figure shows that most particulate sulfur is found in the size range greater than  $0.3 \mu\text{m}$ , especially during high sulfur concentrations when approximately 70% of particulate sul-

fur is in this size range. Similar observations are also valid for particulate carbon. The fact that sulfur is predominantly found in the size fraction larger than  $0.3 \mu\text{m}$  suggests that aerosol sulfate is formed by aqueous heterogeneous reactions, based on the arguments of McMurry and Wilson (1983). The possible involvement of combustion-derived particles, in sulfate formation is suggested by the similarity between the size-segregated carbon and sulfur concentration patterns.

The effect of high humidity and low ambient temperatures on enhanced sulfur formation observed from 1981/82 data has been confirmed during the winter of 1983/84 with size-segregated sampling. This is illustrated in Fig. 5, where  $S_p/C_p$ ,  $S_p/S_g$  ratios (for particle diameters  $< 2 \mu\text{m}$ ), average temperature, relative humidity, and  $\text{SO}_2$  concentrations for February 1984 are shown. The second half of the month showed a pronounced increase in the  $S_p/C_p$  and  $S_p/S_g$  ratios. It is clear from the figure that during this period the average daily temperatures were consistently below  $0^\circ\text{C}$  and that the increase in the  $S_p/C_p$  and  $S_p/S_g$  ratios occurred after the relative humidity exceeded approximately 65%. Such dependence on relative humidity has been shown to be characteristic of heterogeneous reactions. (McMurry and Wilson, 1983). It should be noted that during this period, the  $\text{SO}_2$  concentration remained approximately constant, and therefore the apparent increase of the sulfate production is related entirely to the physical changes in the atmosphere, i.e., the liquid water content.

The observations described thus far can be qualitatively explained as follows: Water may condense on soot (or other) particles in a plume, forming a layer of liquid water on the particle. The  $\text{SO}_2$  in the plume will be dissolved in this layer and oxidized to sulfate by one or more oxidation mechanisms. If the ambient conditions, such as relative humidity and temperature, do not favor additional water condensation during transport to the receptor site, the entire oxidation would occur, possibly in the first phases of plume development. The resulting sulfate concentration would be related to the volume of the original layer of condensed water and hence to soot concentration. However, if

conditions favor additional condensation (e.g., high relative humidity and low temperature), particle-associated liquid water and its S(IV) content would continue to exist both in the plume and during transport, resulting in a  $S_p/C_p$  ratio greater than in conditions of low humidity. This scenario may also explain the differences in sulfate-SO<sub>2</sub> correlations. Good correlations with SO<sub>2</sub> are more likely to be found when the liquid water content is high and droplet lifetime long because the dissolved S(IV) concentration would be more proportional to the ambient SO<sub>2</sub> concentrations.

Several oxidation processes potentially capable of explaining wintertime observations can be identified. The first possibility is that local sulfates are primary, i.e., produced by high-temperature SO<sub>2</sub> oxidation to SO<sub>3</sub> in flames. This explanation may be in qualitative agreement with the observed correlations between sulfate and primary combustion-generated species during dry periods, but not with the observed inverse temperature dependence. Furthermore, the sulfate, even on days with low  $S_p/C_p$  ratios, composes close to 10% of the total airborne sulfur. This value is too high to be accounted for by primary sulfates because it was reported that only about 1% of the fuel sulfur is converted to primary sulfates. (For power plant results, see Dietz and Wieser, 1983.)

Other candidate mechanisms could be heterogeneous processes involving aqueous systems in the form of liquid water droplets and/or wetted particle surfaces. These processes will be limited by the available liquid water, surfaces, catalysts, and/or oxidants and could result, under similar meteorological conditions, in approximately constant sulfate-to-soot ratios. Because of the very high concentrations of combustion products in this atmosphere and because of the observed association of sulfates and primary particulate emissions, the involvement of reactive combustion products in SO<sub>2</sub> oxidation is a distinct possibility. These primary oxidants are in two categories: gaseous and surface-active carbonaceous species (Novakov, 1984). Gaseous primary oxidants including hydrogen peroxide were recently shown by laboratory experiments to be capable of SO<sub>2</sub>

oxidation in water droplets (Benner et al., 1985). Carbon-catalyzed oxidation could be important under the conditions of this study. For example, in a recent study Calvert et al. (1985) have concluded that for carbon catalysis to compete with  $\text{H}_2\text{O}_2$  in solution, its concentration must exceed  $0.1 \text{ g } \mu\text{L}^{-1}$ . The  $\text{H}_2\text{O}_2$  concentrations in these estimates were those expected under maximal photochemical activity. In our study, typical carbon concentrations are about  $100 \mu\text{g m}^{-3}$ . If these were associated with  $0.1 \text{ g m}^{-3}$  of fog water, the equivalent carbon concentrations in solution would be  $1 \text{ g } \mu\text{L}^{-1}$  or higher, i.e., well above the  $0.1 \text{ g } \mu\text{L}^{-1}$  limit.

Further credence for the heterogeneous  $\text{SO}_2$  oxidation by primary oxidants was provided by Eatough et al. (1984), who studied the conversion of  $\text{SO}_2$  to sulfate in the plume of an oil-fired power plant located on the Pacific Coast. During plume passage through a fog bank, the conversion rate was determined to be an order of magnitude faster than when the plume was not in the fog. The authors concluded that the conversion involves oxidation by co-emitted primary oxidants.

At this time, we cannot rule out other mechanisms potentially capable of explaining the field evidence discussed here. However, we feel that there are sufficient indications that products of incomplete combustion may play a possibly significant role in  $\text{SO}_2$  oxidation in heavily polluted areas.

### *Conclusions*

The principal conclusion reached as the result of this study is that winter aerosol sulfate is produced by heterogeneous, aqueous processes. The highest sulfate formation was observed during periods of high relative humidity and persistent subzero temperatures. Such conditions are conducive to formation of supercooled liquid water droplets. The existence of an aqueous mechanism is corroborated by the observed aerosol chloride loss during high sulfate episodes and by the fact that most aerosol sulfate is confined to a particle size range between  $0.3 \mu\text{m}$  and  $2 \mu\text{m}$ . Soot particles are found in the same size range, indicating the association of aerosol sulfate with combustion products from local

sources. Under favorable winter meteorological conditions, up to 20% of the SO<sub>2</sub> may be oxidized to sulfate by heterogeneous mechanisms.

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We thank D. Hrček and Z. Alatič-Rajh for providing the sampling site and the meteorological data used in this paper. We also acknowledge the contributions of R. Giauque and W.H. Benner, who performed x-ray fluorescence and ion chromatography analyses, and of R. Schmidt, who constructed the aerosol samplers.

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Table I. Average concentration of SO<sub>2</sub> and principal elements for three periods corresponding to increasing S<sub>p</sub>/C<sub>p</sub> and S<sub>p</sub>/S<sub>g</sub> ratios.

	<b>Concentrations (μg/m<sup>3</sup>)</b>		
	<b>9-18 Nov</b>	<b>23-30 Dec</b>	<b>15-21 Jan</b>
	<b>1981</b>	<b>1981</b>	<b>1982</b>
<b>SO<sub>2</sub></b>	<b>256</b>	<b>402</b>	<b>399</b>
<b>C</b>	<b>81</b>	<b>104</b>	<b>82</b>
<b>S</b>	<b>10.4</b>	<b>18.2</b>	<b>27</b>
<b>Cl</b>	<b>1.2</b>	<b>0.5</b>	<b>&lt;0.01</b>
<b>K</b>	<b>1.3</b>	<b>1.0</b>	<b>2.0</b>
<b>Ca</b>	<b>3.6</b>	<b>0.33</b>	<b>2.9</b>
<b>V</b>	<b>0.05</b>	<b>0.03</b>	<b>0.06</b>
<b>Mn</b>	<b>0.18</b>	<b>0.09</b>	<b>0.17</b>
<b>Fe</b>	<b>2.1</b>	<b>1.1</b>	<b>3.2</b>
<b>Se</b>	<b>&lt;0.01</b>	<b>&lt;0.01</b>	<b>&lt;0.01</b>
<b>Pb</b>	<b>1.9</b>	<b>1.3</b>	<b>1.2</b>
<b>Br</b>	<b>0.58</b>	<b>0.32</b>	<b>0.17</b>
	<b>Ratios</b>		
<b>S<sub>p</sub>/C<sub>p</sub></b>	<b>0.13</b>	<b>0.17</b>	<b>0.34</b>
<b>S<sub>p</sub>/S<sub>g</sub></b>	<b>0.08</b>	<b>0.09</b>	<b>0.14</b>

*Figure Captions*

Figure 1. Biweekly concentrations of  $\text{SO}_2$ , particulate sulfur ( $S_p$ ), particulate to gaseous sulfur ratios ( $S_p/S_g$ ), and particulate sulfur to particulate carbon ratios ( $S_p/C_p$ ) for the 1981-1982 sampling season. (XBL 8411-8924A)

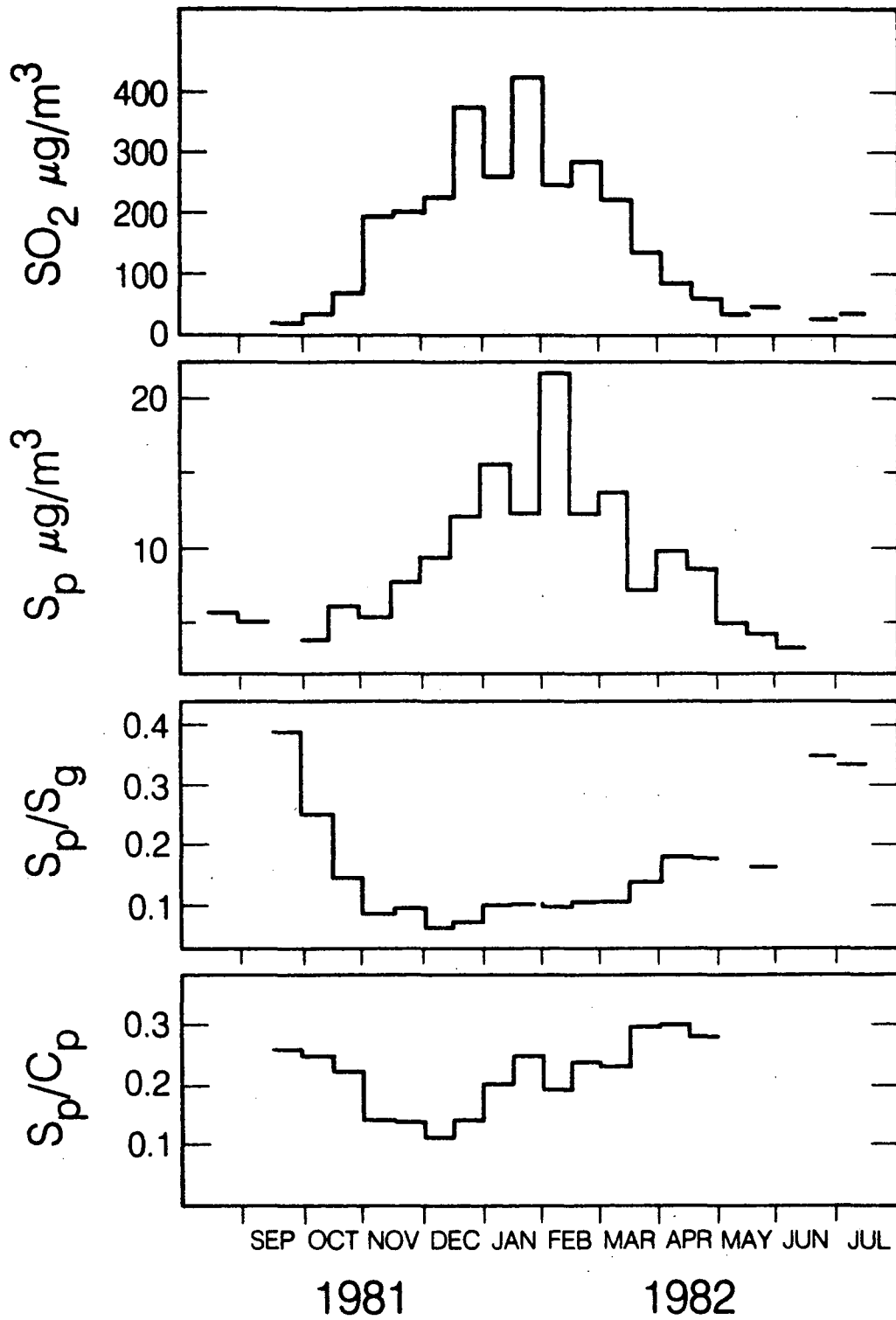
Figure 2. Correlations of particulate sulfur ( $S_p$ ) with  $\text{SO}_2$  and particulate carbon ( $C_p$ ) for the November-December 1982 and January-February 1982 periods. (XBL 8411-8922)

Figure 3. Dependence of the particulate sulfur to carbon ratio on mean relative humidity and ambient temperature. (XBL 859-12125)

Figure 4. Twenty-four-hour concentrations of particulate sulfur ( $S_p$ ) and carbon ( $C_p$ ) corresponding to particle size cuts of  $< 2 \mu\text{m}$  (solid line) and  $< 0.3 \mu\text{m}$  (dashed line) for the period December 1983 through March 1984. (XBL 859-12126)

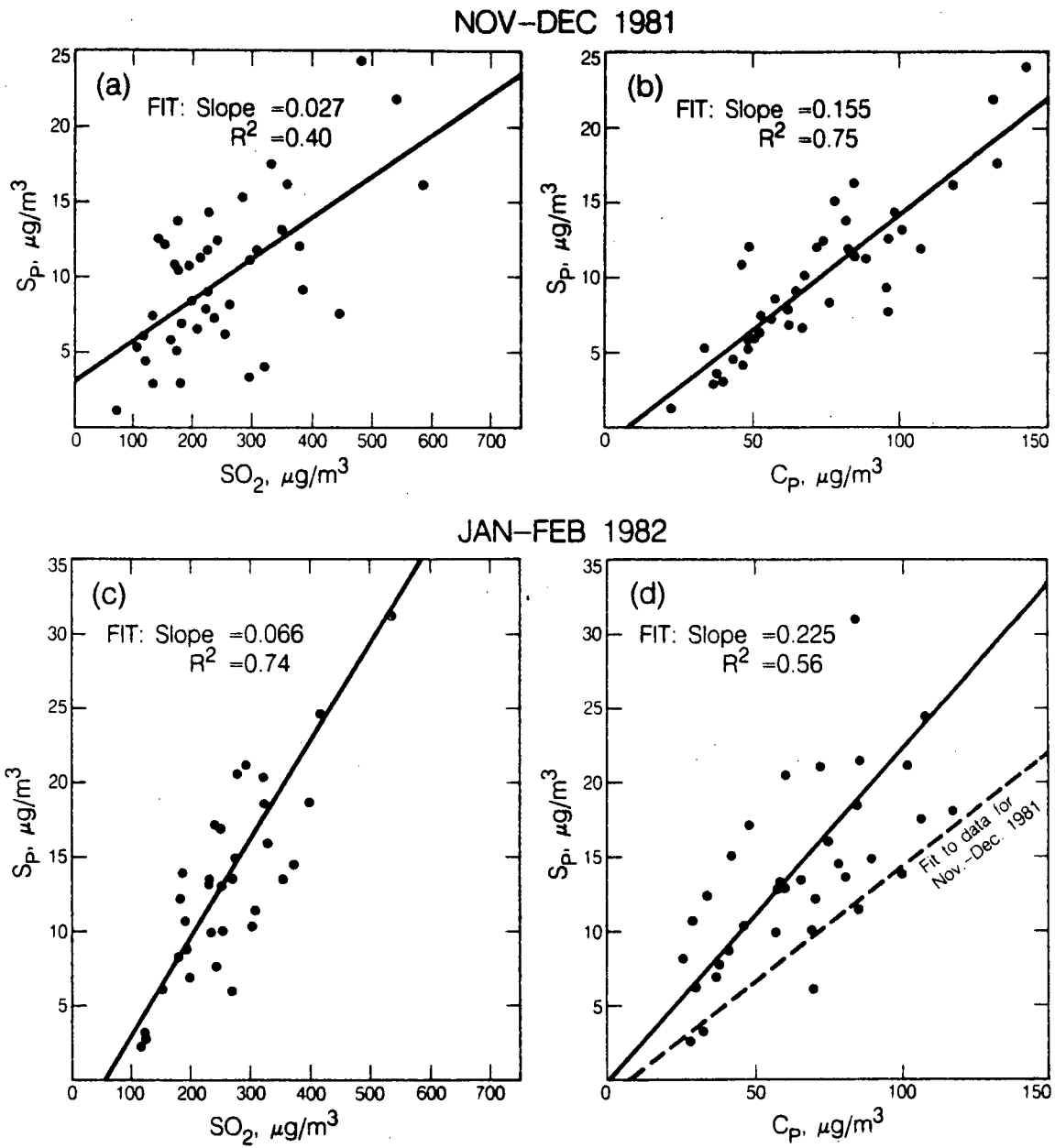
Figure 5. Dependence of particulate sulfur ( $S_p$ ) to particulate carbon ( $C_p$ ) and gaseous sulfur ( $S_g$ ) ratios on mean daily relative humidity, temperature, and  $\text{SO}_2$  concentration for February 1984. The data are for the  $< 2\text{-}\mu\text{m}$  size cut. An increase in  $S/C_p$  and  $S_p/S_g$  ratios is seen when the temperature is below  $0^\circ\text{C}$  and the relative humidity exceeds 60%. (XBL 859-12124)





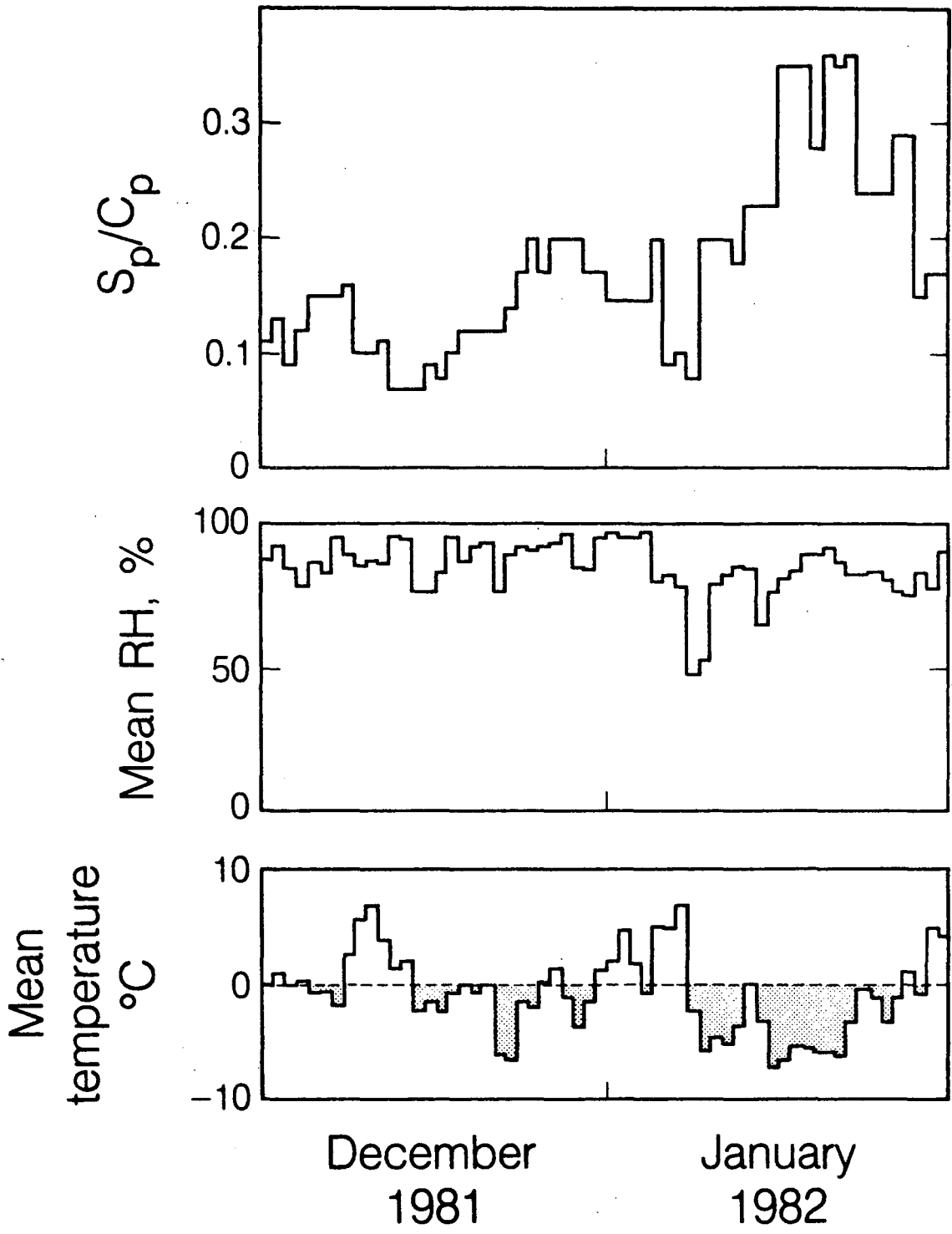
XBL 8411-8924A

Figure 1.



XBL 8411-8922

Figure 2.



XBL 859-12125

Figure 3.

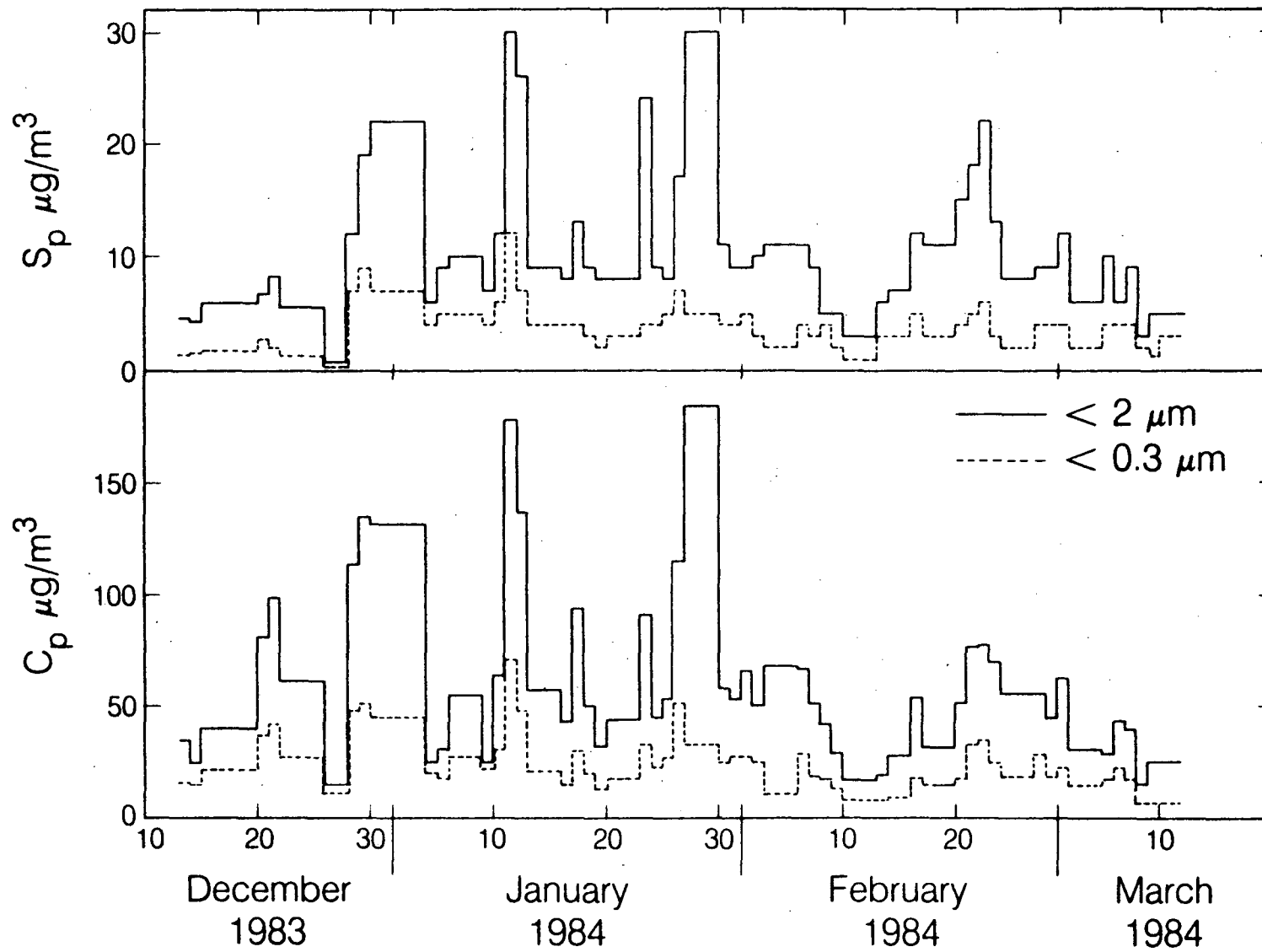
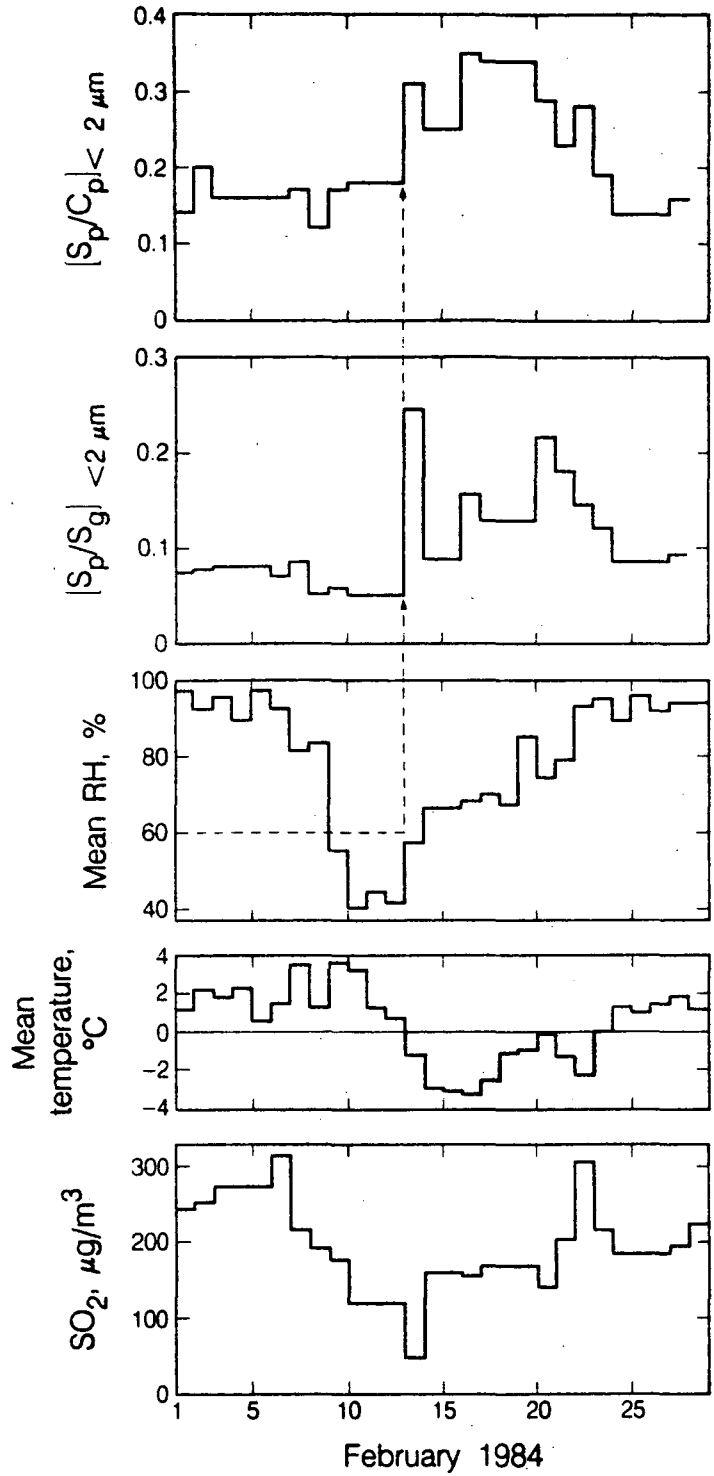


Figure 4.

XBL 859-12126



XBL 859-12124

Figure 5.

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