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INCOMPLETE COMBUSTION

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HETEROGENEOUS SO_2 OXIDATION AND INCOMPLETE COMBUSTION*

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Most previous work on sulfate aerosols was devoted either to 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 combustion 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. However, source-dominated atmospheres exhibit large spatial and temporal variations in pollutant concentrations. Such atmospheres cannot be represented as well-mixed reactors and are therefore not amenable to conventional modeling techniques. A first step toward eventual understanding of heterogeneous processes in source-dominated regions is an empirical characterization of pollutant behavior.

In this paper empirical evidence for heterogeneous SO_2 oxidation in several heavily polluted urban atmospheres is presented. This evidence, complemented by laboratory experiments, points to a link between sulfate production

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and products of incomplete combustion. The amount of SO_2 oxidized depends critically on the physical properties of the atmosphere, being highest when the atmospheric conditions favor the formation of liquid droplets.

Two sites were selected for field studies — one in Ljubljana, Yugoslavia (15), and the other in Beijing, China (2). These locations are well suited for such a study because of high pollutant concentrations, especially during winter. Space heating, in a large number of dispersed individual furnaces and a few larger central heating plants, is the principal source of SO_2 during the winter. Because relatively low-grade coal is burned in inefficient combustors, large soot concentrations are observed in the winter. Ljubljana in the winter is characterized by relatively cold temperatures and high relative humidities. Because of the humidity, low wind speeds and temperature inversions, characteristic pollution-induced urban fogs occur almost daily. In contrast, the Beijing winters are generally dry with average relative humidities below approximately 50%.

In Ljubljana, 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 μm and 2.0 μm were collected during the 1983/84 sampling period. The filter substrate materials used were quartz fiber (Pallflex type 2500 QAO) and cellulose fiber (Millipore type RATF).

Daily 24-hr filter samples of ambient aerosol particles were also collected in a densely populated part of Beijing, using a sampler designed for the simultaneous collection of two low-volume samples on 47-mm diameter filters. One filter was Pallflex 2500 QAO quartz fiber; the other was Millipore cellulose ester. The sampling program in Beijing was arranged to cover approximately three seasons — spring, summer, and winter. The spring samples were collected from March through the beginning of May, 1983. Summer samples were gathered

during July 1983; and the winter samples, from the end of October 1983 through February 1984.

The quartz filters were used for combustion analyses for C and S, and the cellulose filters were used for XRF analyses. Meteorological data consisting of wind speed and direction, temperature, and relative humidity were collected at the sites, as well as 24-hr average SO_2 concentrations. Most samples were also analyzed by thermal evolved gas analysis (EGA)(3,4) to determine their primary carbon or soot content. Results from these analyses, together with meteorological information and SO_2 concentrations, constitute the data base. An evaluation of this data base has enabled us to draw descriptive conclusions about the SO_2 to $SO_4^=$ conversion processes.

In the analysis of the data, we make extensive use of the particulate sulfur to particulate carbon ratio, S_p/C_p. Because at these locations total particulate carbon is equivalent to primary combustion-generated soot, the S_p/C_p ratio can be used to infer the relationship between secondary sulfates and primary source emissions. The ratios of particulate to gaseous sulfur, S_p/S_g, were also used in the interpretation of the data.

At the Ljubljana site (1), these ratios during the winter period are approximately constant during periods with similar meteorological conditions. The highest S_p/C_p ratios, i.e., the highest sulfate formation, were 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 μm. 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_2 may be oxidized to sulfate by heterogeneous mechanisms.

In Beijing (2), similar to Ljubljana, the total particulate carbon concentrations are relatively low and approximately constant during spring and summer. Starting in October, however, much larger carbon concentrations are seen. The maximum carbon concentration reached about 400 $\mu g/m^3$ in the beginning of December. Particulate sulfur (sulfate) concentrations, like the carbon concentrations, are relatively constant during April, May, and July. However, during cold periods, large sulfate concentration peaks are observed on many days. When the daily S_p/S_c ratios are computed, different seasonal patterns are observed. During July, large scatter is seen; in the winter, S_p/C_p ratios are nearly constant but lower than in the summer. The summer aerosol (and to a lesser degree the spring aerosol) is therefore enriched in sulfate with respect to the soot tracer. The winter aerosol, however, seems to be directly related to the emissions from, most likely, local sources.

The summertime sulfate formation mechanism is also more efficient, as evidenced by higher particulate to gaseous sulfur ratios. These differences could be interpreted as a result of a photochemical SO_2 oxidation mechanism that predominates during the summer, possibly occurring during long-range transport, while a less efficient mechanism predominates during the winter. An examination of supplementary meteorological information indicates that there may be a substantial increase in the S_p/C_p ratio during the summer when relative humidity exceeds 60%, suggesting that an aqueous process is involved in the oxidation of SO_2 during the summer. Similar behavior has been observed in some United States data by McMurry and Wilson (5). During winter the relative humidity was consistently low (below 60%), a fact that is reflected in relatively low but constant S_p/C_p ratios.

Several generalizations could be made from these observations. An

examination of the average temperatures suggests that at both sites the wintertime increase in soot concentrations is related to space heating. (Both sites rely heavily on coal as the principal fuel for space heating.) The high concentrations of ambient soot suggest that its sources are local. Because of the excellent sulfate-soot correlations, an inference could be made that the sulfates are also derived from local sources in the winter. Further examination of the data also suggests that wintertime sulfate is formed rapidly. This conclusion is reached by examining periods of air stagnation that can last for several days. It is plausible, therefore, that during such episodes the average residence of pollutants in the air differs from day to day, allowing more sulfate to be formed during stagnant periods. This should result in systematically increasing S_p/S_g and S_p/C_p ratios, which were not observed, however. These remained approximately constant for periods of similar meteorology. During winter periods, the only factor identified as influencing the S_p/S_g and S_p/C_p ratios is the meteorology. These ratios are highest when the relative humidity is high and especially when ambient temperatures are low.

Several oxidation processes potentially capable of explaining wintertime observations can be identified: (1) primary sulfate emissions, (2) oxidation by primary oxidants in the liquid phase, and (3) catalytic oxidation by carbon particles or metals within droplets. There could be other mechanisms as well as synergistic effects, not yet identified, that involve several oxidants and catalysts.

The first possibility is that local sulfates are primary, that is, produced by high-temperature SO_2 oxidation to SO_3 in flames. Such SO_3 will react with water vapor and ammonia to form suspended sulfate. 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/C ratios, composes about 10% of the total airborne sulfur (gas and aerosol). This value is too high to be accounted for by primary sulfates because it is believed that only about 1% of the fuel sulfur is converted to SO_3 in the combustion process (6,7).

All other candidate mechanisms are 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 in approximately constant sulfate to soot ratios. Sulfates formed by such mechanisms will behave like "quasi-primary" species.

Primary oxidants and their role in SO_2 oxidation were recently demonstrated (8) with the help of a simple fog chamber connected to a burner in which gaseous fuels could be combusted under different air/fuel ratios. Fog droplets produced by nucleation of combustion water on combustion nuclei were formed by cooling the effluent below the dew point of the incoming combustion gas. Either fog droplets or residual particles obtained after drying the fog droplets were collected for chemical analyses.

These experiments have also clearly demonstrated the role of liquid water in aerosol sulfate formation. The highest concentrations of particulate sulfate were produced when conditions for aqueous reactions were present. Sulfate production was greatest when visible fog was observed; however, even in the absence of visible fog, sulfate was formed while the temperature was at or below the dew point. At these temperatures, a relatively thin layer of water could condense on combustion particles, which was sufficient to enable the aqueous SO_2 oxidation reactions to occur. However, essentially no sulfate was detected when sampled directly from the chimney, i.e., when the temperature was

above the dew point.

The primary oxidant mechanism may help to explain the observed systematic sulfate-soot correlation, especially under winter conditions, because soot is also a product of incomplete combustion and is co-emitted with primary oxidants. Soot, besides being a tracer, is also a catalyst for SO_2 oxidation; and sulfate may be produced in part by its catalytic action. It is thus possible that both gaseous and particulate products of incomplete combustion play a role in atmospheric SO_2 oxidation.

A recent study by Eatough et al. (9) has demonstrated oxidation of SO_2 by primary combustion products under field conditions. These authors have studied the conversion of SO_2 to sulfate in the plume of an oil-fired power plant located on the Pacific Coast. The plume of this power plant was frequently in a marine fog for the first 30-60 min of plume transport. The conversion process during daylight hours when the plume was not in the fog bank was first order in SO_2 with a rate of 2-4% $SO_2(g)/h$. However, during plume passage through a fog bank, the conversion rate was determined to be about 30% $SO_2(g)/h$, i.e., an order of magnitude faster. These authors concluded that the conversion process occurring in the fog bank probably involves oxidation of SO_2 by co-emitted primary oxidants.

At this time, we cannot rule out other mechanisms potentially capable of explaining the field evidence discussed in this section. However, we feel that there are sufficient indications that combustion products play a possibly significant role in SO_2 oxidation in source-dominated regions, particularly during winter.

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