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Author

Novakov, T.

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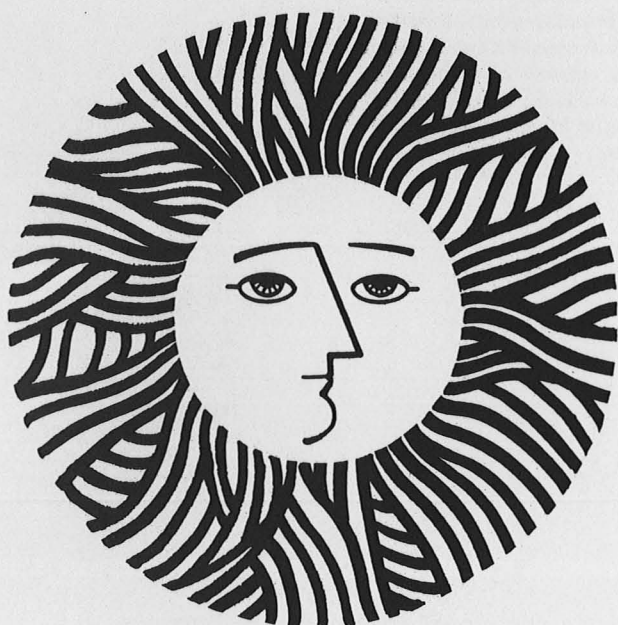
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T. Novakov

Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

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In this discussion contribution, we present evidence for significant local sulfate formation, postulate the existence of a chemical link between ambient sulfate and organic particulate material, and describe a new SO_2 oxidation process by a reaction between organic products of incomplete combustion and SO_2 . Specifically, we discuss results of field studies on the relationship among sulfate, SO_2 , and carbonaceous particles; speciation of sulfate and nitrogenous species; and laboratory results on certain aspects of SO_2 oxidation.

The principal conclusions reached from these studies are:

1. In highly polluted atmospheres, large concentrations of ambient sulfate can be produced by conversion of locally emitted SO_2 by a process that is largely independent of SO_2 but proportional to soot concentration.
2. Ambient sulfate from many locations is found as "anomalous" ammonium sulfate where charged organic nitrogen complexes substitute for ammonium ions. Such sulfate is found when the aerosol is rich in organic constituents.
3. The reaction between pyrolysis products of hydrocarbon fuels and SO_2 is an efficient mechanism for sulfate ion formation. This reaction is strongly dependent on combustion conditions.

Ambient observations. To gain a better insight into the relationship between carbonaceous and sulfate components of the aerosol particles, a field sampling program (involving 24-hr sampling) was initiated in Ljubljana, Yugoslavia.¹ This location was chosen because of high winter concentrations of particulate carbon, SO_2 , and sulfate. Further characteristics of this site during winter are that particulate carbon is $\approx 100\%$ primary carbon (i.e., soot) and that particulate carbon can therefore be used as a tracer for primary emissions. The sampling was done during winter, so it is essentially without photochemical atmospheric chemical processes.

The findings can be summarized as follows:

1. Most of particulate carbon is primary soot.
2. The particulate sulfur to gaseous sulfur ratio varies between 5 and 20%.
3. The sulfate to carbon ratio is approximately constant and independent of ambient SO_2 concentrations (up to ≈ 450 ppb).
4. On days when the SO_2 concentrations are similar, the sulfate levels are proportional to the particulate carbon concentration.
5. On days with similar carbon concentrations, the sulfate levels are

independent of SO_2 concentrations.

The interpretation of these findings suggests that sulfate is produced from locally emitted SO_2 by a relatively fast conversion mechanism. Because photochemical activity is negligible during the winter months at that location and because there are high particle concentrations, heterogeneous processes could play an important role. The empirically obtained relation $[\text{SO}_4^{=}] = k[\text{C}][\text{SO}_2]^0$ strongly suggests that soot-catalyzed SO_2 oxidation is responsible for most of the sulfate. Such a relationship has been established for soot-catalyzed reactions in laboratory studies for relatively high SO_2 concentrations.²

Speciation of ambient sulfate. It is commonly assumed that NO_3^- and NH_4^+ , present as NH_4NO_3 , NH_4HSO_4 , and $(\text{NH}_4)_2\text{SO}_4$, are the only significant nitrogenous species in atmospheric particles. This view was challenged about 10 years ago by results obtained with photoelectron spectroscopy (ESCA). According to these results,³ a significant fraction (as much as 50%) of the total reduced nitrogen is not present as ammonium but as amines, amides, and heterocyclic nitrogen compounds.⁴ Until recently there was no direct confirmation of this finding by another analytical method. Thermal evolved gas analysis (EGA) was applied to filter-collected ambient samples, and this application has resulted in confirmation and quantitation of these species.⁵ In general, two distinctly different situations are observed: sulfate appears as stoichiometric ammonium sulfate and as an "anomalous" ammonium sulfate, where a charged organic nitrogen complex substitutes for some of the ammonium ions. The first situation exists when the sulfate/organic ratio is high, while the second is found when this ratio is low. These results strongly suggest a direct link between aerosol organics and species such as sulfates that are traditionally classified as inorganic materials. This anomalous ammonium sulfate could be produced in the process of neutralization of acidic sulfates in the presence of both high concentrations of organic vapors and ammonia. Conversely, in atmospheres with low organic concentrations (An extreme example is the stratosphere), the sulfates are present as pure stoichiometric ammonium sulfate. Organic vapors and certain condensed particulate organics may also be directly involved in the SO_2 oxidation (see below). Here, the organic sulfur-containing reaction product may react with ammonia to form anomalous ammonium sulfate.

Reaction of organic combustion products with SO_2 . We have previously observed that when SO_2 diluted with air is brought into contact with effluents

of, for example, a propane flame, the apparent concentration of SO_2 is dramatically reduced.⁶ The effect is large, with SO_2 concentrations dropping from 1 ppm to ~ 0.2 ppm within a few seconds. A new series of experiments on this effect has been performed⁷; and, based on these, we have established that incomplete combustion or pyrolysis of hydrocarbon fuels produces reactive organic species that react with SO_2 to produce an organic sulfur compound that yields sulfate ions when dissolved in water. This reaction can occur in the gas phase or on particles, depending on whether the reactive organic species are condensable under the experimental conditions employed.

There are several interesting features of this SO_2 oxidation process. For a given flow of fuel, the magnitude of the effect depends on the combustion conditions. The effect is most pronounced with diffusion flames and diminishes with an increasing air to fuel ratio. The effect is completely absent when a stoichiometric premixed fuel and oxygen flame is used. Such flames produce only H_2O and CO_2 , which do not cause any change in the SO_2 concentration. Similarly, combustion of H_2 and CO does not affect the SO_2 concentration. The effect can be further enhanced by inducing turbulence into the flame by turning the flame off and on at intervals of a few seconds.

The reaction product produces sulfate ions in solution. It is likely that when reacted with gaseous ammonia, this reaction product may produce sulfate species similar to those described at the beginning of this abstract, i.e., sulfate linked to organic matter. This would help to explain the similarity in the diurnal behavior of sulfate, organics, and SO_2 in locations such as Los Angeles, where ambient hydrocarbons are high and SO_2 is relatively low.

References

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