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Suppression of the Oxidation of S(IV) in Rain Water

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The combustion of fossil fuels containing sulfur compounds injects SO_2 [S(IV)] into the troposphere. The most stable oxidation state of combined sulfur under aerobic conditions is S(VI). S(IV) is rapidly oxidized, principally by the OH radical, in aerosols, clouds, or individual rain droplets. Oxidation rates of S(IV) as high as $30\% \text{ h}^{-1}$ have been observed (Finlayson-Pitts and Pitts, 1986). Although the presence of organics and transition metal ions can promote higher concentrations of S(IV) in aerosols, clouds, and rain droplets than would be expected from equilibrium considerations (Huie and Peterson, 1983; Eatough and Hanson, 1983), one would normally expect to find very high S(VI)/S(IV) ratios in rainwater.

However the presence of aldehydes, particularly HCHO, can result in the slow formation of S(IV) adducts that are stable toward oxidation (Munger et al., 1984). Under such conditions, S(IV) may have concentrations above the limit of detectability.

Should reducing conditions prevail in isolated regions of a water sample, the S(VI) may be reduced. It is known from the study of soil waters that bacterial reduction is possible in localized anaerobic regions of waterlogged soils (Greenland and Hayes, 1981). However, the product of the reduction is S(-II) rather than S(IV). Thus, if significant amounts of S(IV) are observed in a rainwater sample, it is probably due to a decrease in the rate of oxidation of S(IV).

The rainfall sampling site was in a residential area of the central part of the city of Jonesboro, Arkansas. The collector was located at the center of a 100 m^2 area free of overhead obstacles. Tree and structure density in the surrounding area was typical of an older residential section. There was no problem with wind carried debris except when wind velocity exceeded 40 km h^{-1} nor was the problem of rainwater rebounding from trees or structures ever observed.

The rainwater was collected using a 25 cm diameter polycarbonate funnel placed at a height of approximately 1 m above the ground. The rainwater was immediately transferred to a 250 mL polyethylene bottle. For the event described herein, the collector was washed to remove dry precipitate within 5 h of the onset of rainfall so that contamination from this source was minimized.

Rainwater was collected as sequential fractions within each event. The fractions were equivalent to 2-6 mm of

rainfall. Immediately upon collection, the pH of all water samples was determined, and the water was stored in polycarbonate bottles and refrigerated at 5°C .

Within 24 h of collection the rainfall samples were filtered through a pre-weighed combination of Whatman 40 paper and $0.45 \mu\text{m}$ membrane filter. The filtrate was returned to that bottle and placed back in refrigeration until anion analysis was completed.

Analysis of the concentrations of the major anions was performed using a Varian 5000 liquid chromatograph equipped with a Wescan 269-001 anion column and using an elutant of 1mM phthalic acid adjusted to a pH of 4.8-5.0. The presence of nitrite ion was confirmed by using the standard sulfanilamide-NED colorimetric method (Franzen, 1980). The mass of suspended solids was determined by weighing the filters after drying in air and then a desiccator. Other species were also determined by standard methods: phosphate by the ascorbic acid method; and the major metal cations by atomic absorption.

This report deals only with the rainfall of 13 April 1987. All but the last of the five fractions collected during this rainfall were noticeably colored by the inclusion of large amounts of soil-like solids. The color varied from the first fraction's deep tan to the fourth's faint yellow. The first fraction, after filtration and sitting for ten days, became cloudy and then a fibrous precipitate formed. The analyses for this fraction were quite unusual with very high concentrations of solids and the phosphate and K(I) ions.

The ion chromatogram of the first fraction, summarized in Table 1 (where RT = retention time of the anion and α = separation factor of the anion with respect to sulfate), exhibited a peak not observed in any of the 283 samples from 61 other events studied during this time. Neither did this peak (peak 3 in Table 1) appear in chromatograms of later fractions. This peak has been attributed to sulfite ion on the basis of its α value which corresponds well to that found for a solution of NaHSO_3 . The α value in question does not come close to those of the anions commonly found in rainwater.

A third peak (peak 2), rarely observed in 62 rainfalls, was tentatively identified from its α value as due to the nitrite ion. The presence of nitrite was confirmed by colorimetric analysis. By that time, however, the nitrite concentration had decreased to $4 \mu\text{equiv/L}$. The initial con-

centration was estimated to have been approximately 150 μ equiv/L using a standard chromatogram of nitrite ion run eleven days after the fraction's chromatogram. Neither the first or second fraction contained any nitrate ion.

Table 1. Summary of retention times (RT) and separation factors (α) of peaks in sample and standard chromatograms.

Peak No.	13 Apr Sample		April Standard		Sulfite Standard	
	RT (min)	α	RT (min)	α	RT (min)	α
1 (c1)	2.012 ± 0.001	0.187 ± 0.001	2.074 ± 0.004	0.199 ± 0.002		
2 (NO ₂)	2.368 ± 0.004	0.253 ± 0.001	2.398 ± 0.001	0.259 ± 0.002		
3 (SO ₃ ²⁻)	5.610 ± 0.021	0.848 ± 0.003			7.731 ± 0.025	0.833 ± 0.006
4 (SO ₄ ²⁻)	6.447 ± 0.015	----	6.431 ± 0.021	----	9.083 ± 0.018	----
Solvent	0.991 ± 0.001	----	0.992 ± 0.006	----	0.984 ± 0.006	----
NO ₃			2.627 ± 0.010	0.301 ± 0.003		

It is hypothesized that rainwater samples from this event incorporated significant amounts of airborne soil during aerosol or droplet formation. The airborne soil may have been a result of the preparation of agricultural fields for Spring planting. The coloration due to soil-like solids and the presence of high concentrations of ions found in commercial fertilizers support this inference (Hooper and Peters, 1989).

Since S(IV) cannot be the product of the reduction of S(VI), it must be concluded that the oxidation of S(IV) that had dissolved in the aerosol or droplets after their formation was suppressed by the presence of large amounts of soil and the organic material associated with it. The S(VI) observed probably resulted from the incorporation of particulate metallic sulfates during droplet formation.

However, the incorporation of metallic nitrates would also be expected. But it is possible that any N(V) initially present was consumed before the analysis. Nitrate has been observed to be consumed by reduction in rain water (Mahendrappa, 1985; de Pena et al., 1985); N(III) is an intermediate in this process.

It is also of interest to note the co-existence of N(III)

and S(IV). In aqueous solutions containing only these species, the N(III) would be reduced to N(-III) while S(VI) would be formed. The reducing conditions induced by the presence of the soil carried impurities stabilized the N(III) and S(IV).

Thus, it is believed that a rare occurrence (in 1 out of 62 events sampled), the interrupted oxidation of S(IV) to S(VI), was observed in this 13 April 1987 sample which contained large amounts of soil and organic matter.

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