

Oxidation Rate of Sulphite on Decomposing Leaf Litter

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Received 12.06.1996

Abstract

Sulphite (SO_3^{2-}), the major solution product of SO_2 , has been shown to inhibit leaf litter decomposition at concentrations occurring in urban rainfall. The rate of oxidation of SO_3^{2-} on leaf litter is a major factor in determining the effect of this inhibition and this study investigated the oxidation rate of SO_3^{2-} to sulphate (SO_4^{2-}) when applied to decomposing Scots pine (*Pinus sylvestris* L.) needle litter under laboratory conditions. Measurements showed that SO_2 has a short life under atmospheric conditions and oxidises very quickly in the presence of metal ions and in alkaline conditions. After addition of sulphite (0.1 mM SO_3^{2-}) to Scots pine litter, about 80% of the SO_3^{2-} oxidised in 5 h, and SO_3^{2-} was not detected after 24 h. The time period over which SO_3^{2-} underwent oxidation at environmentally-realistic concentrations was sufficient to affect microbial decomposition processes in soil and leaf litter.

Key Words: Leaf Litter, Scots Pine, Sulphite Measurement, Sulphite Oxidation.

Sülfitin Parçalanın Yaprak Döküntüleri Üzerindeki Oksitlenme Hızı

Özet

Kükürt dioksidin suda çözünmüş en önemli ürünü sülfıt (SO_3^{2-}), yerleşim yerleri civarında yağmur suyunda ölçülen konsantrasyonlarda yaprak döküntülerinin parçalanmasını etkilemektedir. Bu etki mekanizmasında sülfidin oksidasyon hızı önemlidir. Bu almada laboratuvar şartlarında dekompozite olmakta olan sarı çam yaprak döküntüleri üzerine ilave edilen suda çözünmüş SO_3^{2-} 'in sülfata (SO_4^{2-}) oksitlenme hızı araştırıldı. ölçümler SO_2 'nin atmosferik şartlarda Çok çabuk oksitlendiğini göstermiştir. Sülfıtın (0.1 mM SO_3^{2-}) sarı çam yaprak döküntüleri üzerine ilavelerinden yarım saat sonra yaklaşık % 80'inin oksitlendiği ve 24 saat sonra hiç sülfıt kalmadığı bulunmuştur. Çevre şartlarında ölçülebilecek konsantrasyondaki sülfıtın oksitlenmesi için bulunan süre toprak ve yaprak döküntülerinin parçalanmasında rol oynayan mikroorganizmaları etkileyebilmektedir.

Anahtar Sözcükler: Yaprak Döküntüsü, Sarı Çam, Sülfıt Analizi, Sülfıt Oksidasyonu.

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Introduction

Most sulphur pollution enters the atmosphere as SO₂ and, despite large scale reductions in recent years, concentrations of SO₂ around industrialized areas of Europe are still high (Anon., 1993; WMO, 1994). Sulphur dioxide is oxidised rapidly to SO₄²⁻ and the oxidation rate is important in relation to microbial decomposition processes since SO₄²⁻ does not generally inhibit CO₂ evolution from decomposing plant litter, and in some circumstances may even stimulate fungal respiration (Dursun *et al.*, 1993 & 1996a). There have been several investigations of the oxidation of elemental sulphur by microorganisms (Wainwright, 1978; Wainwright & Killham, 1980; Janzen & Bettany, 1987; Watkinson, 1989), but there have been few investigations of the oxidation of SO₃²⁻. Littlejohn *et al.*, (1993) investigated the effect of NO₂ on the oxidation of aqueous SO₃²⁻ in distilled water (*i.e.* in the absence of other materials) but the oxidation rate on decomposing leaf litter has not been addressed. Lett1 (1982) applied high concentrations of SO₃²⁻ (127.2 mg S in 5 ml) to thin soil layers and measured SO₃²⁻ concentration. However, the concentrations used were considerably in excess of those encountered in the natural environment, and there is currently no information on oxidation rates in the litter layers of soils. In this investigation, oxidation of an environmentally-realistic concentration of SO₃²⁻ was investigated over time, and a reaction equation derived. A concentration of 0.1 mM (100 µeq L⁻¹) SO₃²⁻ solution was used in the experiments described here, this being the highest concentration found in precipitation (Davies, 1976).

Materials and Methods

Preparation of litter for sulphite treatment

Scots pine (*Pinus sylvestris* L.) litter was collected from Grizedale Forest, Cumbria, U.K. (Nat. Grid Ref.: SD 333957), and cut into 2 cm lengths after drying for 1 wk in the laboratory. Two grams of non-sterile litter were placed in each of thirty-three 100 ml capacity Erlenmeyer flasks and wetted with 2 ml distilled water per gram of litter, and the flasks were shaken well for 5 min. Immediately before use, SO₃²⁻ solution (0.1 mM Na₂SO₃ L⁻¹ deionised water) was freshly prepared, and 1 ml of solution was added to each flask containing 2 g wetted litter. Three replicates were prepared for the SO₃²⁻ measurement with each sampling.

Determination of sulphite by the spectrophotometric method

The method of West & Gaeke (1956) was used for the determination of SO₃²⁻ concentration, as modified by Scaringelli *et al.* (1967), Dasgupta *et al.* (1980) and Irgum & Lindgren (1985). The following solutions were prepared with deionised water:

Sulphite stock solution for calibration (40 µg ml⁻¹): 0.1 g of anhydrous sodium sulphite was dissolved in 250 ml recently boiled deionised water. The solution was standardised by titration with standard 0.01 N I₂, with starch as the indicator (Terraglio & Manganelli, 1962). This solution was further diluted ten times to obtain 40 µg ml⁻¹ sodium sulphite: it was always freshly prepared and standardised.

Sodium tetrachloromercurate (TCM; 0.1 M): 0.1 mole mercury (II) chloride and 0.2 mole of NaCl were dissolved in water and diluted to 1 L.

Pararosaniline hydrochloride (0.04%): pararosaniline hydrochloride was purified by the method of Scaringelli *et al.* (1967), and obtained as a 0.3% solution in 1 M HCl. This solution (113.9 ml) plus concentrated HCl (133.3 ml) was diluted to 1 L for the working reagent.

Other solutions were *Formaldehyde* (0.2%), *Starch solution* (0.25%) and *Standard iodine solution* (0.005 M).

A calibration curve of absorbance measurements against SO₃²⁻ concentrations was obtained as follows. A series of 50 ml capacity volumetric flasks containing 40 ml TCM solution were prepared, and 0.125, 0.25, 0.4, 0.5, 0.75 and 1.0 ml of SO₃²⁻ stock solution (40 µg ml⁻¹) were added. Then, to each flask, 2 ml each of para-rosaniline reagent and formaldehyde solution were added, and diluted to 50 ml with water. After 35 min, the optical density of the solutions was measured at 548 nm in a UV-visible spectrophotometer (Cecil Instruments Ltd., Cambridge) against a blank reagent solution.

The SO₃²⁻ concentration in the samples was determined as follows: At 0.08, 0.5, 1.0, 1.6, 2.0, 3.0, 4.0, 5.0, 6.0, 12.0, and 19.0 h after addition of SO₃²⁻ to the litters, 40 ml of TCM solution was added to each of the three SO₃²⁻ treated litters. The solutions were filtered separately through a nylon mesh (0.04 mm mesh size), and centrifuged at 1800 g for 1 min. Decanted solutions were poured into a 50 ml volumetric flask and a procedure was followed similar to that employed for constructing a calibration

graph. The absorbances of the solutions were then measured, and the concentration of SO_3^{2-} estimated from the calibration curve. Concentrations of SO_3^{2-} were plotted against time (Figure 1).

Reaction kinetics of oxidising sulphite

The rate of this first order reaction (see Borderei *et al.*, 1990; Atkins, 1993) is directly proportional to the concentration of the reactants. If c is the concentration of a reacting substance at time t , and k is the proportionality of c with time, the rate can be expressed as:

$$\text{Rate of oxidation} \Rightarrow \frac{dc}{dt} = -kc, \quad (1)$$

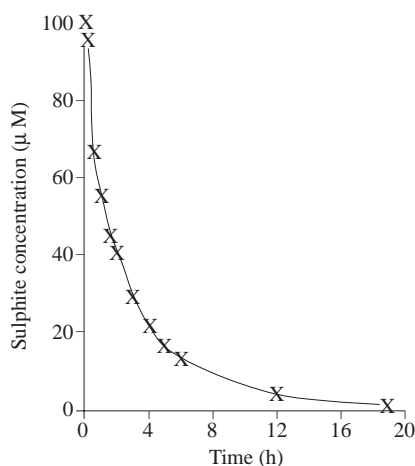


Figure 1. Oxidation of sulphite added to Scots pine leaf litter.

Results and Discussion

Dursun *et al.* (1993; 1996b) used four broad species and two conifer species whose leachate from Scots pine litter was strongly acidic. Respiration from the coniferous litter was strongly inhibited by SO_3^{2-} at low pH values, Scots pine being the most sensitive of the litters tested. Dursun *et al.* (1993) also tested the buffer capacity of six species and compared this with the effect of SO_3^{2-} on CO_2 evolution from decomposing leaf litters. Inhibition of SO_3^{2-} increased with decreasing buffer capacities of the litter with the result that the oxidation of SO_3^{2-} on Scots pine litter took longer than on angiospermous litter. For these reasons, a single species of litter was used in this investigation and the oxidation time was greater than those of other species. Similar experiments with

rearranging the equation (1),

$$\frac{d[\text{SO}_3^{2-}]}{[\text{SO}_3^{2-}]} = -kdt. \quad (2)$$

When integration is taken from time *zero* to t , the equation gives;

$$-kt = \ln[\text{SO}_3^{2-}]_t - \ln[\text{SO}_3^{2-}]_{t=0}. \quad (3)$$

A plot (Figure 2) of $\ln[\text{SO}_3^{2-}]_t$ against time, t , will give a straight line of slope k , reaction rate constant, and intercept of the initial concentration of SO_3^{2-} $\ln[\text{SO}_3^{2-}]_{t=0}$.

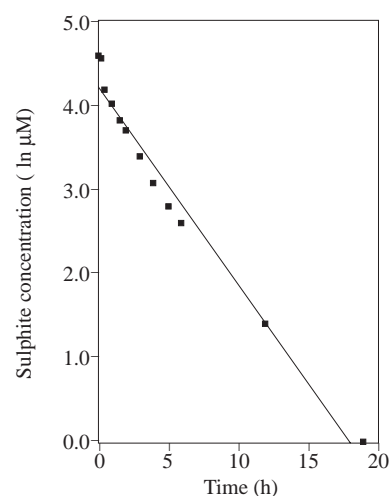


Figure 2. Plot of \ln sulphite concentration against time on Scots pine leaf litter.

the other leaf litters are still needed to determine the effect of leaf litter on SO_3^{2-} oxidation.

In the experiment reported here, 34% of the initial concentration of SO_3^{2-} was oxidised in 10 min and 83.5% in 5 h (Figure 1). After 12 h, the oxidation rate was very slow, with the concentration being very low at that time. There was an approximately linear relationship between $\ln[\text{SO}_3^{2-}]$ and time (Figure 2), implying that the oxidation was close to a first order reaction ($R^2 = 0.974$). On this assumption the following expression was obtained;

$$\ln[\text{SO}_3^{2-}] = 4.243 - 0.235t \quad R^2 = 0.974 \quad (4)$$

where t = time (h).

In closed systems, the oxidation process is likely to take longer than under ambient conditions, and in alkaline conditions the gas phase control of SO_2

dissolution can be assumed when considering the importance of this environment as a sink for SO₂. However, the same simplification cannot necessarily be made for the dissolution of the gas in leaf surface water, which is likely to be more acidic (Brimblecombe, 1978). In an experiment by Fowler & Unsworth (1974), SO₂ deposited on crops overnight was found to produce 260 μM S⁴⁺, and Brimblecombe (1978) found that at an atmospheric SO₂ concentration, 31 μg m⁻³ (10 nl L⁻¹), leaf surfaces saturated with deposited SO₂ contained 20 μM S⁴⁺.

There have been several reports of experiments designed to investigate the effects of **dissolved** SO₂ on plants and soil microorganisms (Neuvonen & Suomela, 1990; Dueck & Elderson, 1992; Dursun *et al.*, 1993; 1996c). Gases and particles may enter a solution by a number of different routes, but the most important is that whereby particles (formed by gas-phase oxidation of primary pollutants SO₂ and NO_x) act as condensation nuclei for water droplets (Fowler, 1980). Sulphur dioxide has high solubility in pure water, and the first product of dissolution is H₂SO₃. If rain or dew is alkaline, SO₂ solubility increases. Dissolved SO₂ is continuously removed or diluted and all the S⁴⁺ is eventually oxidised to sulphate or removed by volatilisation.

There is little information on SO₃²⁻ (S⁴⁺) concentrations in precipitation because of sample preservation problems, and most of the available data is from short-term measurements in which special sample-preservation practices were implemented. Typical SO₃²⁻ concentrations range between 0 and 40 μM in central England, with higher values occurring under conditions of high ambient SO₂ concentration (Davies, 1976).

In general, oxidation of SO₃²⁻ in soil is probably not microbial (Grant *et al.*, 1979), since the aforementioned studies have shown that biological oxidation is slow, but SO₃²⁻ still oxidises rapidly in soil (Ghiorse & Alexander, 1976; Lettl, 1982). The results given in Figure 2 are in accordance with these findings and suggest that, when SO₃²⁻ is added to leaf litter, oxidation is slower than in soil, which may be due to differences in the concentrations of other ions

(Littlejohn, *et al.*, 1993; Lettl, 1985). For example, Lettl (1985) applied 795 mM Na₂SO₃ solution to forest floor layers and found 90% sulphite oxidation in 30 min., which is clearly at a concentration far in excess of that ever observed under even highly polluted conditions. It was, therefore, decided to use 0.1 mM SO₃²⁻ in this laboratory experiment. The reaction rate of SO₃²⁻ oxidation is faster in the presence of metal-catalysts, O₂, O₃, H₂O₂, NO₂ and NH₃, and the rate increases with concentration (Clarke & Williams, 1983; Littlejohn, *et al.*, 1993).

Clark *et al.* (1990) performed a field study of the oxidation of SO₂ in clouds and demonstrated that the concentration of H₂O₂ and O₃ played a significant role in the oxidation process. When the SO₂ concentration was raised artificially to 15 nl L⁻¹, the concentration of H₂O₂ decreased from 25 μM to zero, and the H₂O₂ concentration was found to increase in clouds with decreasing SO₂ concentrations. Ozone is another oxidant responsible for sulphate production (Martin & Damschen, 1981; Maahs, 1983). There have been few investigations of the oxidation of SO₃²⁻ in soils. Lettl (1982) added 5 ml of a 795 mM solution onto a 2 mm soil layer from a spruce forest stand, measured the SO₃²⁻ concentrations and found less than 1% remaining SO₃²⁻ after 3 h. However, he used high concentrations, considerably in excess of those encountered in the natural environment. In our study, environmentally-realistic concentrations of SO₃²⁻ were used and the results showed that the oxidation timespan in natural conditions would be very short, so that on severely polluted sites microbial flora would be likely to be affected only immediately after precipitation.

Acknowledgements

We would like to thank the British Council for financial help with Dursun's visit to the U.K. during the preparation of this paper. We would also like to thank the I.T.E., Merlewood Research Station, for providing facilities. Phil Ineson would like to thank the U.K. Department of the Environment for funding aspects of the study.

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