# Influence of land use on the emission of sulfur dioxide from acid sulfate soils

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## Abstract

Measurements of $SO_2$ emissions were conducted from four different land uses in acid sulfate soil environments, a growing sugar cane crop, a fallow cane block, remnant forest and pasture. Sulfur dioxide concentrations were measured using passive diffusion samplers. Estimations of population densities of the sulfur and iron oxidising bacterium *Acidithiobacillus ferrooxidans*, was conducted at each site using a most probable number count technique. In this preliminary study land use was found to be an influencing factor in the emission of $SO_2$ from acid sulfate soils. Precipitation and low air pressure conditions are probable drivers of the $SO_2$ system and soil physical characteristics, soil moisture and evaporation, also influence the emission of $SO_2$. Bacterial activity is also identified as a potential component in the generation and liberation of $SO_2$ in acid sulfate soil environments.

## Key words

Sulfur dioxide, Acid sulfate soils, Soil bacteria

## Introduction

The highly productive floodplain of the Tweed River valley is underlain by Holocene acid sulfate soils (ASS). This is common to many of the world's coastal floodplains because of the shared geomorphic evolution since the last glacial maximum. Subsequent sea level rise drowned coastal valleys and formed low energy estuaries (Roy 1984). These embayments facilitated development of ASS through the deposition of high sulfur-bearing fine grained marine and lacustrine sediments (Evangelou 1995; Lin *et al*. 1995; Melville *et al.* 1993; White *et al*. 1997). Anoxic conditions, labile organic carbon and dissolved sulfate within embayments produce an ideal environment for sulfate reducing bacteria (Morse 1987). These together with available iron, sourced from terrigenous sediment led to the formation of iron pyrite ($FeS_2$). Many coastal embayments over the last 16,000 years have in-filled with pyritic sediments and in some areas have been overlain by fluvial deposits or peats. A mature system of in-filled floodplains exists along the Australian coastline. Drainage of the coastal lowland sulphidic soils, through both natural and anthropogenic activities have led to the widespread oxidation of ASS (Sammut *et al.* 1994). Pyrite oxidation is accelerate by microbes especially *Acidithiobacillus ferrooxidans* in pH conditions <4.

Pyrite oxidation can lead to severe environmental degradation such as plant deaths, drastic declines in water quality through export of acidic drainage rich in dissolved metals, and massive gilled organism deaths in receiving waters (Easton 1989; Macdonald *et al.* 2002; 2004b). The main focus of research on ASS has been on understanding the geochemical and hydrological processes, environmental impacts, and in the development of appropriate management strategies. Two areas of research that require further investigation are gas emissions from ASS and soil microbial process in ASS. Macdonald *et al.* (2004a) have recently shown that ASS are an important source of $SO_{2.}$ Macdonald *et al.* (2004a) investigated one land use type. The aim of this study is to examine the influence of land use on the flux of $SO_2$ emissions. Four different land uses were examined on the Tweed River floodplain, northern NSW. A secondary aim is to relate variations in $SO_2$ emissions with microbiological populations within each land use.

## Methods

The fallow and sugarcane block and pasture sites chosen for this study were located at Blacks Drain near Murwillumbah, the forest site was located along Condong Creek near Kiel Vale. Study sites lie on modified drainage systems that are right bank tributaries of the Tweed River (28°S, 153° E). All sites

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have been modified by artificial drainage and flood mitigation works. Field measurements were conducted during the dry season in May and July 2003.

Passive diffusion samplers (ferm tubes) were used to measure atmospheric $SO_2$ concentrations above the soil. Ferm tubes have been widely used in long term passive emission monitoring, (Svensson and Ferm 1993; Ayers *et al.* 1998; Charmichael *et al.* 2003; Macdonald *et al* 2004a). Samplers were assembled in following the method developed by Ayers (1998) and the $SO_4$ content of the trapping paper was determined by high pressure liquid chromatography (Dionex column; Ferm 1991; Macdonald *et al.* 2004a). Here an attempt was made to use ferm tubes for daily flux measurements.

(1)Daily measurements (fallow cane block only). Three ferm tubes were suspended daily from a mast at heights of 1.5 m and 0.5 m above ground surface over a period of 13 days.

(2) Closed chamber measurements (A). Closed chambers were used to measure emissions from the four different land uses. Three chambers containing two passive diffusion samplers were randomly placed over the ground surface on the different land use sites for periods of two hours.

(3) Closed chamber measurements (B). Following rainfall (140mm/day on the 16-05-2003) Three chambers were placed in transect on the fallow cane block 09:30 to 15:30 EST each day over a two-day period. At each change-over of samplers, chambers were moved onto un-sampled soil to measure emissions from the drying soil.

**Soil Sampling and Population assessment of Acidithiobacillus ferrooxidans**
Soil samples were collected at 0.1 m depth intervals using a bucket auger and soil gouge. Soil pH was measured (Ionode Intermediate junction pH probe and Redox probed coupled to a TPS FLMV 90 field-meter), soil profile descriptions were taken. Bacterial analysis was carried out in the oxidised soil horizon. Population counts of the bacterium *Acidithiobacillus ferrooxidans* was undertaken using a most probable number technique (MPN). Three repetitions of a four series dilution were prepared within 24 hours of sampling. Dilutions were inoculated in a selective Colmer media (ferrous sulfate media, pH 2.5) and incubated at $25^{o}$C for 30 days prior to analysis (Alexander 1977).

**Results and Discussion**
(1)Daily measurements. Ambient $SO_2$ atmospheric concentration within the fallow cane block has large daily variability (see Figure 1). Typically no $SO_2$ emission was recorded on most days, but occasional $SO_2$ was detected. On most days the upper mast (1.5m) ferm tubes measured a slightly higher content that the lower (0.5m) ferm tubes on most days, except on 14/05/2003. A decreasing $SO_2$ gradient away from the soil surface is indicative of sulfur dioxide emission from the ground surface.

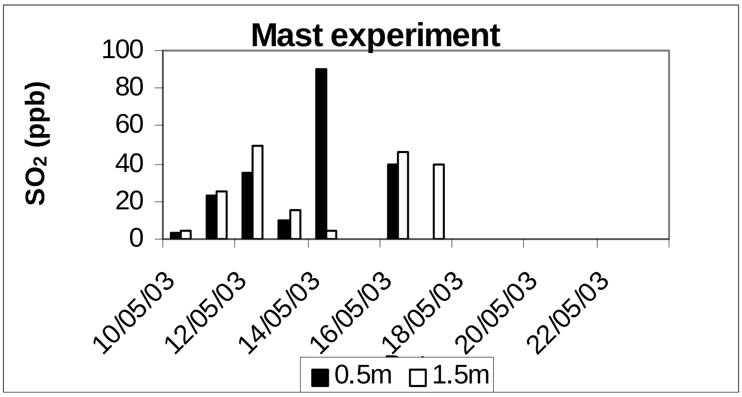


**Figure 1. Daily emission of $SO_2$ from fallow cane block.**

(2) Closed chamber measurements (A). Ambient $SO_2$ concentration from the chambers showed variation over the different land uses (Figure 2). The greatest net emitter of $SO_2$ was the pasture site, followed by the fallow cane, forest and growing cane. After rainfall, ambient $SO_2$ fluxes from the pasture, fallow and forest sites increased relative to the fluxes before the rainfall.

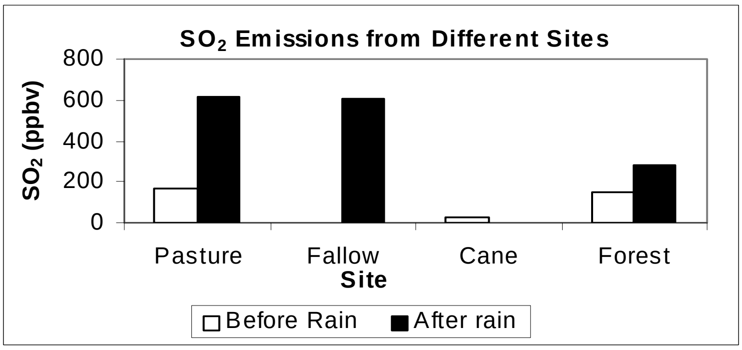


**Figure 2. $SO_2$ measurements (A) from different land uses before and after rainfall.**

(3) Closed chamber experiment (B). Measurements of $SO_2$ taken in the fallow cane block after rainfall showed an increase in abient flux of $SO_2$ peaking more than 48 hours after precipitation before declining rapidly (Figure 3).

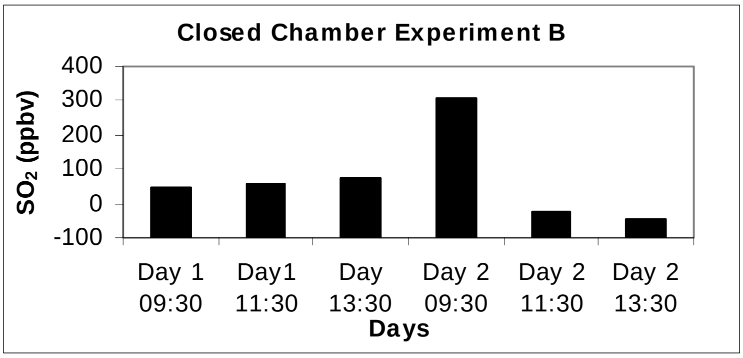


**Figure 3. Ambient $SO_2$ concentrations in the chambers in the fallow cane block following rainfall.**

**Model of $SO_2$ formation and emission from acid sulfate soils**

Measurements of $SO_2$ fluxes from the different sites differ markedly before and after rainfall (Figure 2). Soil water content and soil evaporation seems intrinsically linked to $SO_2$ evolution from soils (Farwell *et al.* 1979; Macdonald *et al.* 2004a). It appears that a soil moisture threshold exists for the release of $SO_2$, beyond which $SO_2$ is probably converted to aqueous products such $H_2SO_4$.

Soil moisture evaporation has been recently correlated to the emission of $SO_2$ from ASS (Macdonald *et al.* 2004). The drying of wetted fallow sugarcane soil released greater amounts of $SO_2$ than dry soils (Figure 3). This agrees with other studies of ammonia emission from soils (Roelle and Aneja 2002). Canopy cover and vegetation density influence soil evaporation through uptake of water and decreasing direct radiation to the soil surface (Denmead *et al.* 2000). Results here indicate that canopy cover decreases the emission of $SO_2$, as demonstrated by the contrasting measurements between the fallow and growing cane block sites, both on almost identical soil profiles.

It was also observed during the study that there was an increase in emissions following the drop in air pressure accompanying rainfall (Figure 4). Air pressure has previously been identified as an important factor in the emission of methane from landfills (Czpiel *et al.* 2003) and could also be an important factor causing the emission of $SO_2$ for ASS. Figure 5 shows a conceptual model for the flux of $SO_2$ from ASS.

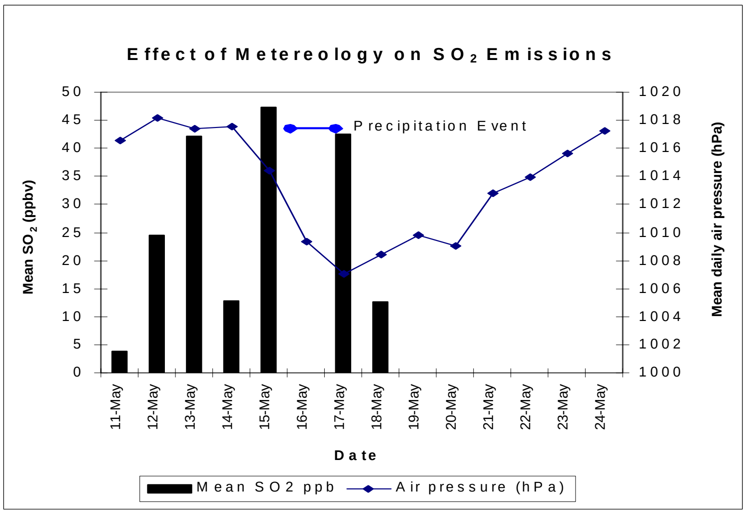
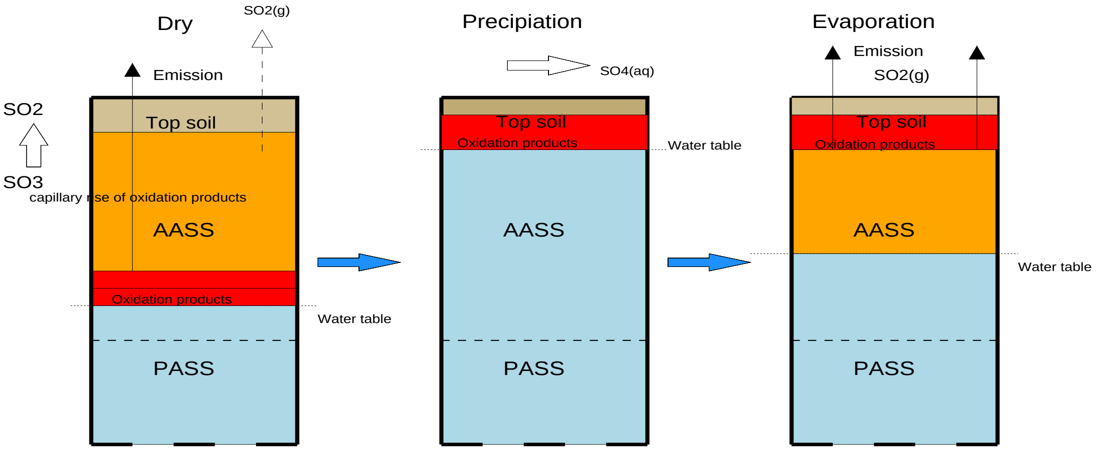


**Figure 4. Air pressure and ambient $SO_2$ from the fallow cane block.**



AASS (actual acid sulfate soil)
PASS (potential acid sulfate soil)

*Dry conditions:*
Oxidation products travel though soil profile via capillary rise
$SO_3$ transformed to $SO_2$ and released
Depth of oxidation controlled by on-site drainage and vegetation

*Effect of precipitation:*
Water table rises from increased recharge and the drop in air pressure
Oxidation products mobilised as aqueous products and moved up through the profile ($SO_2$ is highly soluble)

*Evaporation:*
Water table recession oxidation products left in upper layers of profile, source of $SO_3$
evaporation of soil moisture
$SO_2$ emission

**Figure 5. Factors affecting the formation and emission of $SO_2$.**

## Population assessment of Acidithiobacillus ferrooxidans

Microbiological population assessments were conducted for the purpose of comparative analysis between the sites. Results must be considered qualitative rather than quantitative due to the low number of survey points used within each site and absence of data from the bottom of the oxidising profile in the forest. Although this dataset is merely an attempt to link the chemical and biological soil conditions, population assessment of *Acidithiobacillus ferrooxidans* revealed variation between land uses, shown in Figure 6. Populations also varied within the soil profile. The pasture site contained the highest populations of *A. ferrooxidans*, with population counts exceeding the four series dilution. Populations of *A. ferrooxidans* in the growing cane block were minimal, with some bacteria present in the top of the oxic profile, and absence of *A. ferrooxidans* in the bottom of the profile.

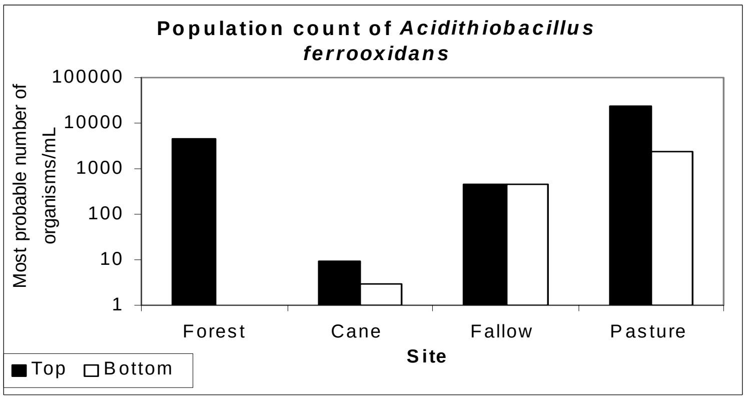


**Figure 6. Most probable number of *Acidithiobacillus ferrooxidans*.**

Acidithiobacillus ferrooxidans is an important catalyst in the oxidation of pyrite under low pH conditions. Results of the population assessments of A. ferrooxidans indicate a potential relationship between bacterial populations and $SO_2$ emission. This suggests that bacterial activity is a driver of the $SO_2$ system in ASS. Low populations of A. ferrooxidans coincide with low emissions of $SO_2$. A notable characteristic of the population of A. ferrooxidans was that the bacterial populations of all sites were higher at the top of the oxidising profile than at the bottom of the oxidising profile.

The temporal dynamics of nutrients and soil pH are important factors for microbial populations. Both of the sandy loam sites (fallow and growing cane blocks) were commercially cropped. The application of industrial fertiliser, (urea) and lime is a standard management practice. The nutrient levels of the soil should be measured, in future studies, to elucidate their influence on bacterial populations.

Acidithiobacillus ferrooxidans is a strictly autotrophic bacterium. In previous studies, populations of A. ferrooxidans have not tolerated media containing sugars (Rawlings 2001). This may account for the low population density recorded in both the fallow and growing cane blocks. The presence of sugar in the soils of these sites, through root exudates, may decrease populations of A. ferrooxidans, reducing oxidation rates in areas under sugar cane production.

Application of industrial lime can also be considered a constraint on populations of A. ferrooxidans, which are acidophilic, with a niche pH range of 1 – 4 (Johnson 1998). Treatment of soil with lime can be considered an inhibitor of bacterial catalysed oxidation. Maintenance of soil pH above 4 would provide a control on bacterial populations and therefore oxidation rates. Application of lime has previously been recommended to retard bacterial catalysed oxidation (Evangelou 1995).

## Methodological issues

High levels of background interference in $SO_2$ measurements were recorded during the study. This phenomenon has not been recorded in past uses of this apparatus. The source of interference was not identified in this study. Ferm tubes, originally designed for long term measurements of atmospheric gas concentrations are not sensitive enough for use in daily measurements from soils.
Ideally all experiments would have been continued over a longer period of time with increased repetition. Accuracy of the datasets is reduced due to limited experimental repetition. Statistically intra site variations such as spatial variability cannot be accounted for (Smith *et al.* 2003; Husson *et al*. 2000).

## Conclusion

The evolution of $SO_2$ from ASS is complex. This preliminary work has demonstrated that Ferm tubes, designed for use over long periods are too insensitive for daily measurements. Different land uses appear to result in differing fluxes of $SO_2$, with cane production giving the lowest flux and pasture the highest flux. As soil dries following rainfall, the evolution of $SO_2$ increases. Low pressures also appear to increase gas fluxes. We have shown there appears to be a correlation between the population numbers of *Acidithiobacillus ferrooxidans* in soil and the evolution of $SO_2$. This work demonstrates the continued need for additional research in this area.

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