Links between emissions of nitrogen and sulfur gases from acid sulfate soils: field evidence

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Abstract
Field scale emissions of nitrous oxide, nitrogen oxides and sulphur dioxide, measured by micrometeorological techniques, were examined to investigate a suggestion from laboratory studies that reduction of nitrate by pyrite could explain the very large emissions of nitrogen gases and sulphur dioxide from acid sulphate soils (ASS). All three of the target gases were emitted simultaneously from a bare ASS in the field, as they were in laboratory experiments in which nitrate solutions were added to pyrite or pyritic soil. However, the presence of a crop made it difficult to decide if chemodenitrification was at work in the field because of effects on soil evaporation and possible foliar absorption of emitted gases. The possibility remains that reaction between nitrate and pyrite might contribute to very high N2O emissions from ASS. More work on bare field soils is needed.

Key Words
Nitrous oxide, sulphur dioxide, nitrification, denitrification.

Introduction
In a whole-of-season study of emissions of greenhouse gases from an acid sulfate soil (ASS), Denmead et al. (2009) found that emissions of nitrous oxide (N2O) were extraordinarily large and prolonged. For the whole year they were the equivalent of 21% of the 160 kg of nitrogen (N) applied to the crop as fertiliser. The authors suggested that the porosity and high carbon content of the ASS at their experimental site coupled with frequent rainfall leading to high water filled pore space (WFPS) were important drivers of the large emissions, but also suggested that alternative mechanisms be explored. Macdonald et al. (2004) demonstrated that ASS also can be significant sources of SO2, perhaps accounting for about 3% of known anthropogenic emissions of sulfur (S). The SO2 emissions seemed coupled to evaporation of soil water containing sulfite. In a companion paper to this Congress, Macdonald et al. (2010) report laboratory studies which indicate that interactions between iron and nitrogen cycles also might explain the large emissions of SO2 from ASS. They suggest that in ASS, nitrate interacts with reduced iron in the soil profile, producing nitrous oxide (N2O) and oxides of nitrogen (NOx) as well as sulfur dioxide (SO2). Here, we report field studies on an ASS of the simultaneous emissions of these three gases, which, while not conclusive, confirm at least some of the laboratory findings.

Methods
Site
The experimental sites were in sugarcane fields on the farm of W. Stainlay on coastal lowlands near Murwillumbah, NSW. Soils in the region are sulfuric and are classified formally as Sulfaquets and Humaquets (Soil Survey Staff 1998), commonly referred to as ASS. During periods of high rainfall, they are often inundated. They are characterised by a surface organic horizon 0.2-0.3 m deep (a clay loam with 10% organic carbon and pH ~5), a strongly acidic A2 horizon (pH < 4) extending to around 0.5 m, a reduced B horizon and often, a water table at depths of 0.5-0.7 m. The acidic A2 horizon is formed from the oxidation of pyrite.

Studies
All three target gases were measured simultaneously in 3 campaigns, the first in 2003 and the last in 2007. The first campaign was conducted in a fallow sugarcane field, and the second and third were in a sugarcane crop at different stages of its growth. The field where the crop was growing was within 200 m of the first
The first measurements were made when the crop was starting to ratoon after harvest and was between 0.4 and 0.9 m high and the second were made 11 months later, shortly before the crop was due for harvest again and was 4 m high. Rain occurred in all 3 campaigns. Particularly heavy falls occurred during the first and second campaign and persistent rain in the third. The rainfalls and the water filled pore space and temperature of the top 10 cm of soil along with evaporation rates are shown in Figure 1a.

**Emission measurements**

Micrometeorological techniques were employed to measure gas emissions using a flux-gradient technique in which fluxes were calculated as the product of a transfer coefficient derived from aerodynamic theory and the difference in gas concentration between two heights above the soil surface (Denmead 2008). The necessary measurements to derive the transfer coefficient were the wind speeds and air temperatures at the two heights in the first campaign and turbulence statistics provided by a 3D sonic anemometer in the other two. The concentrations of N$_2$O were measured with a Fourier transform infrared (FTIR) spectrometer, those of SO$_2$ by a pulsed fluorescence SO$_2$ analyser (Monitor Labs 9850), and those of NO$_x$ by a chemiluminescence gas analyser (Monitor Labs 9851), all instruments measuring on-line in the field and returning one-minute averaged concentrations. Temperatures and moisture contents of the soil down to a depth of 20 cm were measured as well. All measurements were processed as ½-h means. The first campaign was conducted between 27 November and 14 December, 2003. Urea fertiliser was drilled into the soil at a rate equivalent to 50 kg N/ha mid-way through the observation period on October 8. The 2nd campaign was conducted between 18 October 2005 and 2 November 2005 and the 3rd conducted in the same cropped field between 13 and 19 September 2006. Urea fertilizer at 160 kg N/ha was applied to the field on 18 October 2005. Some results of these campaigns, but not all, have been included in previous conference proceedings, but as reports of individual gas emissions and not in the context of exploring links between sulfur and nitrogen processes in ASS.

**Results and discussion**

**N$_2$O**

Average daily emission rates in the 3 campaigns are shown in Figure 1b. These exhibit a classical dependence on available soil N and the WFPS. In the first campaign, they virtually doubled after 8 December when recent rain had increased the WFPS from around 40% to the critical level for nitrification and N$_2$O production of 60% (Davidson and Schimmel 1995). In the 2nd campaign, the WFPS was always between 60 and 80%, available N was plentiful, and N$_2$O emission occurred at an increasing rate throughout. In the 3rd campaign, the WFPS was close to saturation level at which N$_2$O is produced through denitrification, and significant amounts of the gas were emitted. Since the supply of fertiliser N was exhausted by then (Wang et al. 2008), N$_2$O production may have been augmented by reaction between nitrate and pyrite in the ASS. This possibility exists for the other campaigns as well since the rates of N$_2$O emission in all of them were much greater than typical literature values. The default emission factor for soils in many greenhouse gas inventories, including the Australian inventory is 1.25%, whereas that for only 3 days after fertilisation in the 1st campaign was 2.6% and for the whole growing season in 2005-2006 was 21%.

**SO$_2$**

Average daily emission rates are shown in Figure1c. Macdonald et al. (2004) noted that SO$_2$ emission was coupled to evaporation, but also that emissions were higher from a drying soil than a wet one, presumably because the gas stayed in solution until the wet soil had dried sufficiently. This was observed in the laboratory studies by Macdonald et al. (2010) and was very clear in the field studies reported here. For instance, in the 1st campaign, SO$_2$ emissions were twice as large when the soil was dry before 63 mm of rain fell as they were afterwards. This behaviour says nothing about the mechanism of SO$_2$ production, however, but it does mask any link between N$_2$O and SO$_2$ production because N$_2$O is not highly soluble and its production appears to be linked positively with soil wetness. We note that the data presented in Figure 1c confirm the early observations of SO$_2$ production in ASS by Macdonald et al. (2004). In the present study, the soil was a source rather than a sink on 28 of the 32 days of data available.
Figure 1. (a) Rainfall, water filled pore space and temperature in surface soil, and daily evaporation during 3 campaigns; (b) Average daily rates of emission of N$_2$O; (c) Average daily rates of emission of SO$_2$; (d) Average daily rates of emission of NO$_x$. 

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1 – 6 August 2010, Brisbane, Australia. Published on DVD.
Average daily emission rates are shown in Figure 1d. Macdonald et al. (2010) found that NO\textsubscript{x} was emitted in all their laboratory studies. This was also the case in the study on the fallowed field (1\textsuperscript{st} campaign) reported here. Emission rates were a substantial fraction of those measured for N\textsubscript{2}O and were highest after rain and fertiliser application. However, they were much smaller and sometimes negative in the 2\textsuperscript{nd} campaign when a crop cover was present. Plants are known to act as sinks for NO\textsubscript{x} (and SO\textsubscript{2} also), particularly when the foliage is wet. Again, this is a complicating factor in linking N and S emissions.

Conclusions
Field measurements of emissions of N\textsubscript{2}O, SO\textsubscript{2} and NO\textsubscript{x} from an ASS substantiate the laboratory findings of Macdonald et al. (2010) in confected systems combining nitrate solutions and pyrite or pyritic soils in as much as they demonstrate that all 3 gases can be produced and emitted simultaneously. This was seen most clearly in a field campaign on bare soil. However, the presence of a crop makes it difficult to demonstrate links between N and S production, not only because it influences evaporation from the bare soil, but also because the foliage can absorb both SO\textsubscript{2} and NO\textsubscript{x} as they diffuse through the crop canopy to the atmosphere. Not all the production of the N gases can be attributed to reduction of nitrate by pyrite because their production appears to occur mostly during nitrification, the process of nitrate formation. However, it is possible for chemodenitrification through nitrate reduction by pyrite in ASS to augment the formation of N\textsubscript{2}O through classical pathways. Certainly the extraordinarily large emissions of N\textsubscript{2}O from ASS warrant further research along these lines.

References


Macdonald BCT, White I, Denmead OT (2010) Gas emissions caused by the interaction of iron and nitrogen cycles within acid sulphate soils. (This Congress)