Gas emissions from the interaction of iron, sulfur and nitrogen cycles in acid sulfate soils

Ben Macdonald[A], Ian White[A] and Tom Denmead[B]

[A] The Fenner School of Environment and Society, Australian National University, Canberra, ACT Email ben.macdonald@anu.edu.au
[B] Land and Water, CSIRO, Canberra, ACT

Abstract

Nitrous oxide is a powerful greenhouse gas, 298 times more potent than CO_2. Coastal lowland acid sulfate soils (~18,000 ha; ASS) constitute only about 5% of Australia's sugarcane soils, but could contribute about 1/4 of the national N_2O emissions from sugarcane. It has been proposed by a number of authors that the large differences between the N-gas emissions from ASS and non-ASS is that in ASS nitrate oxidises reduced iron in the soil producing nitrous oxide and other N-gases. Here we report on laboratory studies that investigate the geochemical pathways that cause these gas emissions. The presence of pyrite enhanced gaseous nitrogen and SO_2 emissions and the flux was also dependent on sample moisture content. This chemical de-nitrification pathway needs to be considered in fertiliser management and other crop nutrient models. Most of the gas evolution reactions are favoured by acid conditions and it is suggested that increasing surface soil pH and controlling water logging may decrease N-gas emissions.

Key Words

Pyrite, chemo-denitrification, nitrous oxide, nitrogen oxides, ammonia, sulfur dioxide, hydrogen sulphide.

Introduction

Acid sulfate soils used for sugarcane production relative emit large quantities of NO_x and N_2O (Denmead *et al.* 2005; 2007; 2006; 2008) relative to other cropping soils as well as SO_2 and H_2S (Kinsela 2007; Macdonald *et al.* 2004). These acid soils are wet and have high organic carbon and clay contents, and either have high natural mineral N content or have significant quantities of N fertiliser, up to 160kg N/ha added at the start of each growing season. Such conditions favour the production of NO (see Serça *et al.* 1994; Blackmer and Cerrato 1986) and NO_2 (Slemr and Seiler 1984), collectively known as NOx as well as N_2O. While NO_2 can be formed by the photochemical reaction of NO and O_2 in the atmosphere (Akyama and Tsuruta, 2003), it is also possible for NO_2 and NO to be formed in the surface layers of the soil (Slemr and Seiler 1984). N_2O can also be produced during both nitrification and denitrification (eqns 2 and 5). It is noted that many of the N gas evolution reactions (eqns 2-5, 7-9) appear favoured by acid soil conditions.

In agricultural soils the full range of redox reactions for N fertiliser species are possible. This includes:

nitrification:

$$NH_4^+ + 2O_2 \rightarrow NO_3^- + H_2O + 2H^+ \quad [1]$$

$$NH_4^+ + O_2 \rightarrow 0.5\,N_2O + 1.5H_2O + H^+ \quad [2]$$

denitrification:

$$NO_3^- + 1.25c + H^+ \rightarrow 0.5N_2(g) + 1.75H_2O + 1.25CO_2\,(g) \quad [3]$$

$$NO_3^- + 0.75\{CH_20\} + H^+ \rightarrow NO(g) + 1.25H_2O + 0.75CO_2\,(g) \quad [4]$$

$$NO_3^- + \{CH_20\} + H^+ \rightarrow 0.5\,N_2O\,(g) + 1.5\,H_2O + CO_2\,(g) \quad [5]$$

and reduction:

$$2NO_3^- + 2\{CH_2O\} + 8H^+ \rightarrow N_2 + 6H_2O + CO_2(g) \quad [6]$$

From eqns [3] to [6], acidic soils with high organic carbon content, favour denitrification, releasing N_2, NO and N_2O and possibly CO_2, provided soil water conditions are favourable. In acid sulfate soils, nitrate can also oxidise underlying sulfides producing further denitrification:

$$NO_3^- + 0.7S^- + .03H^+ \rightarrow 0.5N_2(g) + 0.7SO_4^{2-} + 0.1H_2O \quad [7]$$

$$NO_3^- + 0.4S^- + 0.6H^+ \rightarrow NO(g) + 0.4SO_4^{2-} + 0.3H_2O \quad [8]$$

$$NO_3^- + 0.6S^- + 0.4H^+ \rightarrow 0.5N_2O(g) + 0.6SO_4^{2-} + 0.2H_2O \quad [9]$$

Again reactions [7] to [9] seem favoured by acidic conditions. In acid sulphate soils conditions appear optimum for the conversion of fertiliser N to gaseous N provided there is sufficient soil N, organic matter and water.

It is also possible for NO_3^- to interact with the iron cycle and under reducing conditions directly oxidise iron minerals or dissolved aqueous species.

$$2FeS_2 + 6NO_3^- \rightarrow 3N_2 + 2FeOOH + 4SO_4^{2-} + 2H^+ \qquad [10]$$

Reaction 10 proceeds through complex pathways with various nitrogen intermediates produced i.e. NO_2^-, NO, N_2, N_2O. For example nitrite, NO_2^- can be produced by denitrifying or nitrifying micro-organisms; nitrite may then react with ferrous iron to produce gaseous N compounds

$$Fe^{2+} + 2NO_2^- + 3H^+ \rightarrow FeOOH + N_2O + H_2O \qquad [11]$$

In acid sulfate soils there is a possibility for enhanced emissions of nitrogen gases due to the oxidation and reduction potential of ferrous and ferric iron present in the soil, and the presence of organic carbon and when the water filled pore space (WFPS) is greater than 60 %. Soil emissions could be generated during the reduction of ferric and the oxidation of ammonia (Clément *et al.* 2005) and/or by the reduction of NO_3^- by the operation of the "ferrous wheel" (see Davidson *et al.* 2003) and the direct oxidation of reduced iron by NO_3^- (see Postma *et al.* 1991). Our hypothesise is that the interaction of nitrate and iron sulfide minerals can cause emissions of nitrogen and sulfur gases. This paper aims to test this hypothesis using both a pure chemical system and a more complex soil incubation system.

Methods

Experimental apparatus

A reaction vessel (Figure 1) was constructed from quick-fit glass ware and Teflon tubing. The 3 necked reaction flask was connected to industrial air stream (6 L/min; BOC Australia), temperature in and mass of the vesselwere measured every 10 seconds using thermocouples and a balance and the 1 minute average values recorded using a Campbell Scientific CR1000 logger. The air stream from the reaction vessel was then sent to a manifold and the air stream split; 1 L/min was sent to an ADC Nitrous Oxide Analyser and 5 L/min was sent to an ECOTECH Trace Gas Analyser Station. The ECOTECH Trace Gas Analyser Station consisted of 4 gas analysers, Sulfur Dioxide Analyser EC9850T; Hydrosulfide Analyser EC9850T with convertor; Ammonia Analyser EC9842 and NOx Analyser EC9841T. Gas concentrations in the air stream were recorded at one minute intervals.

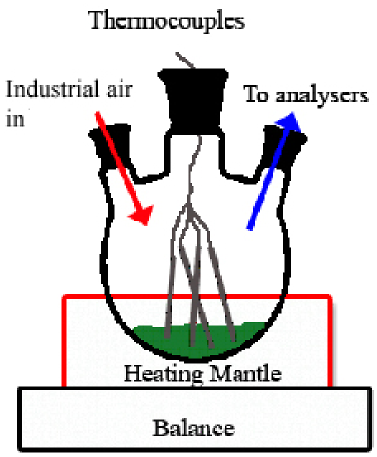

Figure 1. Experimental Apparatus.

Experimental Approach

Three different experimental runs were undertaken, using 5 mL 1 M KNO_3, 1 g of reagent grade pyrite, or 1 g of pyritic soil. The pyritic soil was collected from McLeods Creek, on the Tweed River, Northern New South Wales Australia. This site is well characterised (see Smith and Melville 2004; White *et al.* 1996; Wilson *et al.* 1999) and the soils are classified as acid sulfate soils, which have 5-10% organic carbon in the surface soil and 3-5 % pyrite below the oxidation front at depths of 0.8 to 1.5m. The collected pyritic soil was placed in an insulated container, returned to the laboratory, freeze-dried and stored in a freezer until use. The gas analysers and hot-plate were switched on and allowed to warm up for 1 hour prior to the start of an experiment. The experimental apparatus was assembled and a background was run for 15 minutes, after which the sample was sealed in the reaction chamber and left for further 15 minutes. 5 mL of 1 M KNO_3 were then mixed with the sample within the sealed chamber and the experiment proceeded until all of the solution had evaporated.

Results

Small gas concentrations were detected during background runs (Figure 2a). The presence of reduced iron, in the pyrite greatly enhanced the emissions of NOx and NH_3 in the model system (Figure 2b). The interaction of NO_3 with the pyrite and the resulting de-nitrification must provide various nitrogen intermediates that result in NOx formation. The enhance NH_3 emissions that also occur during the NOx emission peak are possible due to ammonification caused by the ferric iron, acidity and evaporation. There is also enhanced emission of SO_2 from the ideal system during the final phases of evaporation. Macdonald *et al*. (2004) found that field emissions of SO_2 from acid sulfate soils were strongly correlated to evaporation.

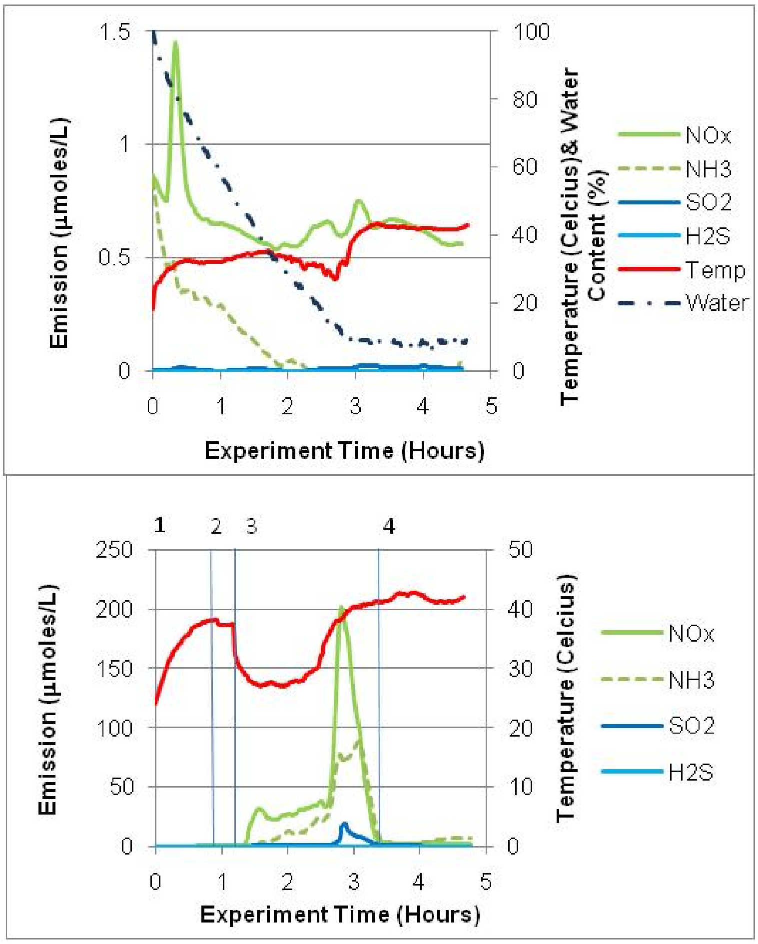

Figure 2. a. 5 ml 1 M KNO_3 b. Nitrogen and sulfur gas emissions from pyrite bathed in 5ml 1 M KNO_3 Period 1 represents the background emission, Period 2 is the emission when the pyrite is added. Period 3 is when the nitrate is added to the reaction vessel and Period 4 is the point where there is no more solution visible in the reaction vessel.

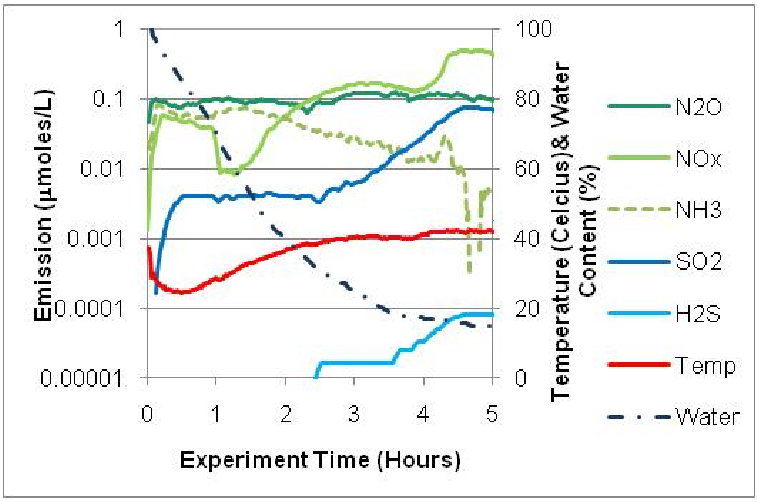

Figure 3. Gas emissions from pyrite sediments and 5 ml of 1 M KNO3

The production of the N_2O, NOx, NH_3 from the pyritic soil was not as clear cut as the model experiments but the general emission trends werere similar (Figure 3). The low concentrations of the emission were most likely due to the amount of pyrite that was present in the pyritic soil sample that was used in the experiment.

The average pyrite content of the sample was 5 % w/w, which means that only 0.05g pyrite was present in the reaction chamber. Despite this there was clear evidence of the interaction of the pyrite with the applied nitrate from the emission of SO_2 from the system. The emission of SO_2 indicates that the pyrite within the reaction vessel was oxidised. The SO_2 emission was strongly linked to evaporation and began when the water content reached 50%. The emission of NOx, had two periods of sustained emissions between hours 1-2 and at hour 4 these emissions were also correlated to changes in evaporation and water content.

Denmead *et al*. (2007, 2008) has shown that the emission factor for N_2O from fertilisers applied to acid sulfate soils is 29%. This is nearly 10 times greater than for non acid sulfate soils (Denmead *et al*. 2007, 2008). Results from the pyritic soil experiment shows that N_2O can be produced due to the interactions between nitrate and pyrite (Figure 3). While only 1.4 mg N_2O was produced, it is possible that the higher emissions that are seen in the field could be caused by the direct interactions of NO_3 and N intermediaries with iron-monosulfides or soluble ferrous iron.

Conclusion

The interaction of the iron, nitrogen and sulfur cycles may explain the large emissions of N_2O, NOx, NH_3 and SO_2 from acid sulfate soils. The laboratory experiments here clearly showed that the presence of pyrite increased the production of these gases relative to the control. The emission peaks were also clearly related to the water content of the reaction matrix. There were also clear emissions of N_2O and NOx from the pyrite soil sample but in future experiments the sample size will need to be increased by a factor of 10 to increase the pyrite content.

The oxidation of pyrite by NO_3 also caused the emission of SO_2. This emission, like the nitrogen, was strongly correlated to moisture content of the reaction matrix. These results indicate that chemical denitrification caused by the interaction of nitrogen with iron and sulfur is an important soil process. This process can occur under ambient temperatures very likely occur in the surface soils. It is possible that increasing surface soil pH and controlling surface water logging may reduce these emissions.

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