Conference or Workshop Item (Refereed)

Sheppard, L. J.; Leith, I. D.; Field, C.; van Dijk, N.; Rung, M.; Skiba, U.. 2008 Effects of different nitrogen forms, ammonia gas and wet deposited ammonium and nitrate, on methane and nitrous oxide emissions from an ombrotrophic bog, Whim Moss, in the Scottish Borders. [Lecture] In: *After Wise Use - The future of peatlands, Tullamore, Ireland, 8-13 June 2008*. Finland, International peat society, 628-632.

Paper presentation

EFFECTS OF DIFFERENT NITROGEN FORMS, AMMONIA GAS AND WET DEPOSITED AMMONIUM AND NITRATE, ON METHANE AND NITROUS OXIDE EMISSIONS FROM AN OMBROTROPHIC BOG, WHIM MOSS, IN THE SCOTTISH BORDERS.

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Enhanced reactive nitrogen deposition may compromise the sustainability and functioning of bogs, with respect to carbon sequestration and greenhouse gas production. Since 2002, three N forms have been applied to an ombrotrophic bog growing *Calluna, Sphagnum capillifolium* and *Eriophorum vaginatum* in order to test this. Significant changes in species cover and soil chemistry, especially in response to elevated ammonia concentrations, have been recorded. Ammonia deposition has also increased nitrous oxide emissions, while the same N dose as ammonium or nitrate had a far smaller effect. Methane emissions were increased by nitrate additions, although fluxes were equally responsive to water table and temperature. The significance of N form, and 'natural' drivers, is discussed.

KEY WORDS
Bogs, methane, nitrous oxide, sustainability, reactive nitrogen

INTRODUCTION

Peat lands and bogs represent an important conservation resource and potential carbon sink. The ability of these organic soils to sequester C is fundamental to their existence, arising because C assimilation rates exceed those of decomposition. However, anthropogenic activities can challenge these systems' ability to fulfil this requirement (Gunnarsson and Rydin 2000), especially where change influences the drivers that control C and N cycling. Changes in water-table through drainage, climate or species composition, changes often observed in response to N eutrophication (Berendse *et al.* 2001), are particularly likely to influence C exchange, both via the uptake of CO_2 and the release of methane (CH_4). Increases in anthropogenic N deposition can affect both the assimilation and release of C through decomposition and N cycling and these ecosystems are highly sensitive to enhanced N inputs because they are constrained by low N availability, which arguably maintains the *status quo*. When N deposition exceeds plant demand N the additional mineral N may be used by soil microbes, which via nitrification and denitrification can lead to emissions of the greenhouse gas nitrous oxide (N_2O). Enhanced pore water mineral N concentrations can also potentially affect the production of CH_4 both, because NO_3^- can act as an alternative electron acceptor, and *via* effects on plants which transport CH_4 to the atmosphere and exude labile C sources. Both CO_2 and especially CH_4 are greenhouse gases, with large radiative forcing properties that contribute to global warming. Methane is produced in the anaerobic, waterlogged portions of the peat, and oxidised in the aerated zone, the acrotelm. The net flux to the atmosphere represents the balance between production and consumption rates. Methane production and

oxidation rates depend on substrate (acetate, CO_2 and H_2) availability, the presence of alternative electron acceptors that compete for substrate with methanogenesis, anoxic conditions temperature and bacterial activity (Segers 1998).

Despite the obvious potential for N to significantly affect the basic ecosystem services that peat lands provide, there have been few *in situ* experiments to quantify such changes, especially with respect to the different N forms. This paper reports the effects of five years of unique experimental N additions, as dry ammonia gas (NH_3), wet reduced NH_4^+ or wet oxidised NO_3^-, on greenhouse gas emissions. The objectives of the study were to establish whether the major ecosystem service of C sequestration in peat bogs is at risk from enhanced N addition, and if so whether the form of N addition was important.

MATERIALS and METHODS

Site description

Whim bog, an ombrotrophic bog, NVC classification M19 (Rodwell 1991) in the Scottish Borders at 282 m a.s.l. represents a transition between upland blanket bog and lowland raised bog. The experimental site is on the edge of the bog, where peat has been extracted since 1978, separated by a 2 m deep ditch > 30 m SW of the site. No major drainage ditches have been formed across the site since 1800 and minimal influence on water table draw down, acidification and oxidation from the deep ditch is expected. The site, grazed by rabbits, has not been burned and the *Calluna* is degenerate. *Sphagnum capillifolium* together with *Eriophorum vaginatum* are the main peat forming species. *S. papillosum, S. fallax,* and *S. magellanicum* grow in wetter areas and there is no exposed peat. The micro-topography, of hummocks and hollows, where the elevation difference and hence the immediate water table, can vary by up to 0.5 m repeats in a mosaic over a 0.5 to 3 m scale. The fibrous peat varies between 3 and 6 m, overlying boulder clay and mounds of sand and gravel.

Experimental treatments

In 2002 an automated N manipulation experiment was established, comprising an ammonia fumigation (Leith *et al.* 2004) simulating ~ 24,000 broiler hens (Sheppard *et al.* 2008), and a wet spray system supplying oxidised or reduced N (Sheppard *et al.* 2004). Annually ~ 120 kg y^{-1} of gaseous NH_3 is released from a 10 m perforated pipe, 1 m above the vegetation over a ~ 65 m (L) x 10 m (W) transect when the wind direction is in the 180^o-215^o quadrant and wind speed exceeds 2.5 m s^{-1}. The NH_3 concentration gradient declines exponentially from a maximum 4 year mean of ~ 180 µg m^{-3} measured 8 m from the line source, down to the background NH_3 concentration of 0.3 - 0.5 µg m^{-3} ~ 100 m from the NH_3 source. Equivalent N doses to those applied to the wet treatments, (8, 24 and 56 kg N $ha^{-1}y^{-1}$) were estimated to deposit at 8, 16 and 32 m from the NH_3 source (Cape *pers comm*.). A revolving sprayer head in the centre of each of four replicate12.5 m^{-2} treatment plots, provides the wet treatments, as either sodium nitrate or ammonium chloride at three N doses: 8, 24 and 56 kg N $ha^{-1}y^{-1}$, over and above the 8-10 kg N $ha^{-1}y^{-1}$ background, at a maximum N concentration of 4 mM. A water only control is included to assess the effects of the additional 10 % precipitation. Wet treatments are applied in precipitation collected on site, and thus rainfall patterns govern treatment amount and frequency, no rain no treatment. Treatments are applied throughout the year, except when the temperature is < 0 ^oC, as and when meteorological conditions permit. Wind direction and wind speed control the NH_3 release and wet spraying.

Measurements

Meteorological variables are logged as 1 or 15 minute averages, for wind direction, wind speed, solar radiation, rainfall, surface wetness, mean air temperature, soil temperature (10

and 20 cm) and water-table (Leith *et al* 2004). Trace gas measurements are made using permanent static chambers with an expandable lid, one per plot, (~40 cm d * 20 cm h of varying volume due to the unevenness of the ground and unavoidable differences in species composition). Dip wells were installed adjacent to each chamber and are read simultaneously with trace gas sampling and soil temperature, 0-5 cm depth. Chambers are enclosed for up to 60 min and air samples withdrawn in to Tedlar bags by syringe, at varying intervals after pumping the system to mix the air and measured by ECD and FID gas chromatography for N_2O and CH_4 respectively. Only the control, ambient, 5 kg NH_3 at 60 m, 56 kg N NH_3 at 8 m and 56 kg N plots are reported. Soil and pore water (Rhizon soil moisture samplers 5cm of porous (0.45µm) length) are sampled monthly from 0-10 cm depth for pH (1:2 mass to volume in water) and DOC (Thermalux TC analyser), NO_3^- and NH_4^+ (DIONEX).

RESULTS

Site characteristics

The acid (pH 3.8, 1:5 water) peat has low base saturation (10%), low available P and (43 and 90 mg kg^{-1}), and a C:N ratio of 33. In 2007, when the trace gas measurements were made, the mean annual water-table was 8.4 cm below the surface, following 1239 mm of rain, almost twice the rainfall of the drought year, 2003. Mean soil temperature was 7.8 ^oC.

Trace gas emissions

Fig 1

Methane concentrations were spatially and temporally highly variable and although linked to water there were simple relationships with either water-table or the timing of treatment. Throughout May CH_4 emissions/uptake were insignificant, < 0.1 mg CH_4 m^{-2} h^{-1}(Fig.1) coinciding with a dry period from the end of March through to the end of April when the water table hovered 20 cm below the surface. Methane uptake dominated during this dry spell. The largest emissions in August, 27-29 mg CH_4 m^{-2} h^{-1}, coincided with the warmest temperatures and a site water table barely 5 cm below the surface. With increasing rainfall from May onwards CH_4 emissions increased from all plots and uptake, CH_4 oxidation, was minimal. Highest emissions were measured from the ambient plots whereas the control, rainfall only wet plots produced very little CH_4. Among the high N treatments, only plots receiving oxidised N emitted significant amounts of CH_4. Reasonably high, > 12mg CH_4 m^{-2} h^{-1}emission rates were maintained through to December from these high emitting plots.

Fig 2

N_2O concentrations likewise were highly variable, not linked to water table or treatment in a simple manner and were generally small < 50 µg N_2O m^{-2} h^{-1}, except in the high ammonia (Amm56) treatment (Fig. 2) where emissions reached 400 µg N_2O m^{-2} h^{-1} .The site was generally an emitter, ~20 µg N_2O m^{-2} h^{-1} with small amounts of uptake measured over the summer. Annual N losses (incomplete year, 11 assessments) as N_2O from the Amm56 plots were ~3 kg N $ha^{-1}y^{-1}$ compared to 0.3 kg N $ha^{-1}y^{-1}$ from the wet N treatments and ~0.15 kg N $ha^{-1}y^{-1}$ in the low/no N treatments.

Soil pH and Pore water chemistry
Fig 3 a and b

Soil pH was significantly affected by the N treatments: NH_3 deposition increased pH by 0.5 units, NO_3^- by ~0.3 whereas the addition of NH_4^+ had no effect (Fig.3). Pore water ambient N concentrations were low < 0.5 ppm and DOC was ~35 ppm (Fig. 3). The high NH_3 treatment significantly enhanced both N forms and even the low NH_3-N treatment enhanced soluble N compared with the wet N treatments (Fig. 3). DOC followed the change in NO_3^- and concentrations were positively correlated in a logarithmic manner $R^2 = 0.71$.

DISCUSSION

The literature suggests the main drivers for N and especially C exchange will be the coupling between water table, peat temperature and species. On Whim bog the role of water table in determining CH_4 emissions was shown conclusively by the comparison between the control and ambient N deposition plots which were often waterlogged, and had large emissions, signifying a deeper anaerobic zone and less opportunity for CH_4 oxidation (Sundh *et al.* 1995). Partially independent of the water-table driver, the addition of oxidised N also

significantly stimulated CH_4 emissions, although neither of the wet or dry reduced N forms had any noticeable effect, despite no real differences in water table among these plots (data not shown). This positive effect of NO_3^- on CH_4 emissions is counter intuitive as NO_3^- can act as an alternative electron acceptor, which should suppress methanogenesis (Segers 1998). A comparison of these CH_4 emissions with other bogs, nutrient rich fens (Bubier *et al.* 1995) suggests that, even at relatively high N doses, 56 kg N $ha^{-1}y^{-1}$, neither wet nor dry N deposition significantly increase CH_4 emissions in the short-term.

However, N_2O emissions were significantly affected when 56 kg N $ha^{-1}y^{-1}$ was deposited, in a simulation of an adjacent intensive livestock unit, to the bog in the form of NH_3. Ammonia is an alkaline gas and its deposition significantly increased soil pH by 0.5 units, probably accounting for the enhanced soluble NO_3^-, via increased nitrification rates, and DOC concentrations. The significantly elevated NH_3 concentrations also caused the death of keystone species on this bog, *Calluna* and *S. capillifolium*, probably reducing the sink source for N, increasing the amount of mineral N available for nitrifying and denitrifying bacteria. These observations suggest that elevated NH_3 concentrations, such as found in the vicinity of intensive livestock units, will have significant implications for the release of the greenhouse gas N_2O from bogs.

ACKNOWLEDGEMENTS

Sinclair Horticulture for site access, NERC (GANE) for establishment, CEH, Defra (CPEA 18) and NITROEUROPE. C. Field, MMU/CEH studentship, M. Rung, NERC studentship.

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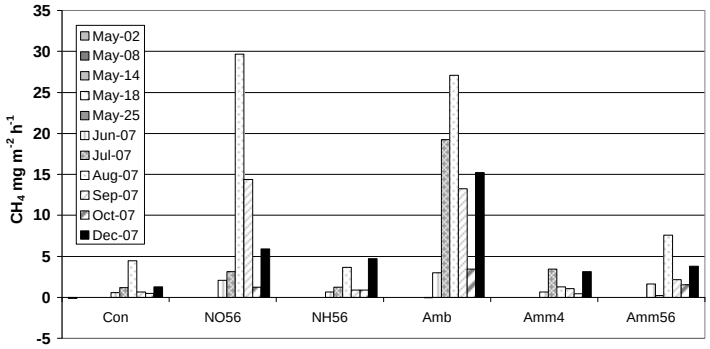

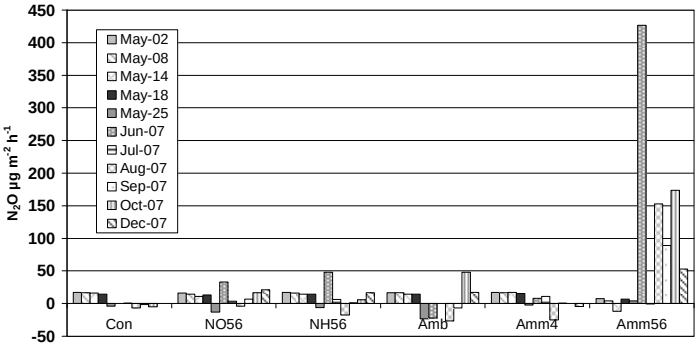

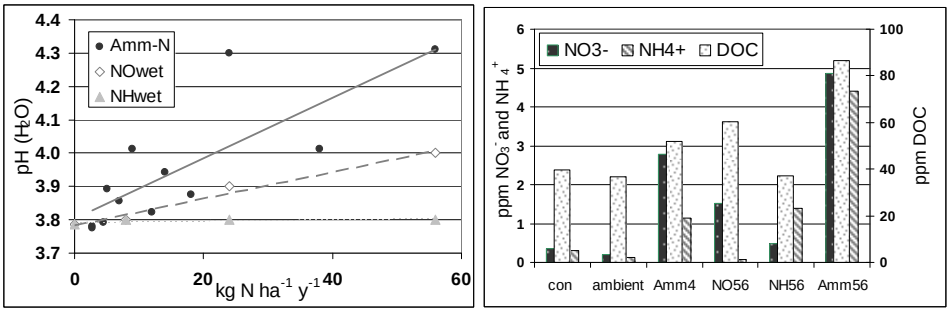

Fig. 1 CH_4 emissions from an ombrotrophic bog, with and without 5 years of 56 kg N $ha^{-1}y^{-1}$ additions as dry NH_3-N or wet NO_3-N or NH_4-N, between May and December 2007, (n=4).
Fig. 2 N_2O emissions from an ombrotrophic bog, with and without 5 years of 56 kg N $ha^{-1}y^{-1}$ additions as dry NH_3-N or wet NO_3-N or NH_4-N, between May and December 2007, (n=4).
Fig. 3 Mean pH in response to N dose as NH_3 or wet oxidised and reduced N and N effects on pore water mean NO_3^-, NH_4^+ and DOC (n=4).