Nitrous oxide emissions from a peatbog after thirteen years of experimental nitrogen deposition - Materials and methods

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1 Field site

Whim bog in the Scottish Borders (3°16' W, 55°46' N) represents a transition between a lowland raised bog and blanket bog, on 3-6m of deep peat. Mean temperatures of the air and soil (at 10-cm depth) were 8.6 °C and 7.7 °C respectively (2003-2009 means). The annual rainfall was 1092 mm (734-1462 mm range). On average, the water table was 10 cm below the surface of the peat in the hollows, i.e. relatively wet for most of the year. Hummocks were typically 20 cm higher than the hollows. The peat was very acidic, with pH 3.4 (3.27-3.91 in water). The vegetation was classified as a *Calluna vulgaris-Eriophorum vaginatum* blanket mire community (M19 in the UK National Vegetation Classification, **?**). Replicate plots were highly variable and dominated by unmanaged *Calluna* of variable age and stature occurring as mosaics containing *Calluna vulgaris* and *Sphagnum capillifolium* hummocks and hollows containing *S. fallax* and *S. papillosum*. Other common species included *Erica tetralix* and the mosses *Hypnum jutlandicum* and *Pleurozium schreberi*.

2 Experimental Design and Treatments

Nitrogen was applied to the site using two different treatment systems, for dry deposition of NH_3 gas, and wet deposition of NH_4^+ and NO_3^- in solution. Treatments commenced in June 2002 and continued all year round, except when temperatures were near freezing.

NH_3 deposition was manipulated using a free-air release system (Leith et al., 2004). NH_3 was supplied from a cylinder of pure liquid NH_3, diluted with ambient air and released from a perforated 10-m long pipe, 1 m off the ground. NH_3 was released only when the wind direction was in the south-west, between 180 and 215°, temperatures exceeded freezing and wind speed exceeded 2.5 m s^{-1}. This produced a sector downwind wherein NH_3 decreased with distance from the fumigation source. NH_3 concentrations were measured 0.1 m above the vegetation using passive ALPHA samplers (Tang et al., 2001) at 8, 12, 16, 20, 24, 32, 48 and 60 m from the source along the transect. A detailed profile was measured to capture the concentration gradients both vertically and horizontally (Leith et al., 2004). Ammonia deposition was calculated from the concentration measurements, using the method of Cape et al. (2008). The deposition at these locations was interpolated using ordinary kriging, as shown in Figure **??**, assuming the deposition velocity was spatially homogeneous.

Wet deposition of NH_4^+ and NO_3^- was experimentally increased in a number of replicated plots in a randomised block design, using a water sprayer system (Sheppard et al., 2004). Concentrated solutions of either NH_4Cl or $NaNO_3$ were diluted in rainwater, and transferred to each plot via 100-m lengths of 16-mm pipe. Each pipe terminated in a central sprayer with a 360°spinning disc that distributed the solution uniformly over the 12.8 m^2 plot. The volume of soulution applied to each plot was monitored using a water meter on each supply line. Three treatment levels were applied, aiming to provide total N deposition rates of 16, 32 and 64 kg N ha^{-1} y^{-1}, in addition to a control treatment which only received ambient N deposition (8 kg N ha^{-1} y^{-1}). The three treatment levels were achieved by applying either NH_4Cl or $NaNO_3$ solution at concentrations of 0.57, 1.71 or 4.0 mM. Wet treatments increased precipitation amounts by ca. 10%. Control plots receive the additional rainwater without any additional nitrogen. There were four blocks, with one treatment level in each, to give a total of 28 plots. The sprayer system was automatically triggered every 15 minutes, so long as there was sufficient rainwater in the collection tank, air temperature was above 0 °C and wind speed was above 5 m s^{-1}. This produced a realistic pattern of high frequency, extensive nitrogn deposition, with ca. 120 applications y^{-1}.

3 Collection methods - Soil Water Chemistry

Soil water samples were extracted from dipwells in all plots at the same time as gas flux measurements were made. Concentrations of soil water NH_4^+ and NO_3^- were measured by ion chromatography following filtration. The detection limits were 0.014 and 0.062 mg l^{-1} for NH_4^+-N and NO_3^--N respectively. The percent cover of each vegetation species was recorded within each chamber location every few years.

4 Collection methods - Greenhouse gas exchange

Nitrous oxide fluxes were measured by the static chamber method (Hutchinson and Mosier, 1981), typically on a monthly basis. Cylindrical PVC collars (38 cm in diameter and typically 25 cm high) were inserted into the peat within each plot. On each sampling occasion, a lid was sealed on top, and left in place for 30-40 minutes. Four 20-ml samples were removed by syringe through a 3-way tap or rubber septum, stored in vials or tedlar bags.

5 Laboratory Instrumentation

Gas samples were analysed on a gas chromatograph (5890 series II, Hewlett Packard), together with replicates of three or four standard gases with known concentrations.

6 Calibration steps and values

Samples run on the gas chromatograph were converted to mole fractions using a 4 point calibration, see Table 1 for standard mole fractions, with standards run approximately every 20 samples.

Standard no.	N_2O (μ mol mol^{-1})
1	0.199
2	0.285
3	0.490
4	0.975

Table 1. Nitrous oxide mole fractions of standards used in calibrating gas samples from chambers on the gas chromatograph.

7 Analytical methods and Quality Control

For each sequence of gas samples from a chamber, the flux was calculated as:

$$F = \frac{\mathrm{d}C}{\mathrm{d}t_0} \cdot \frac{\rho V}{A} \tag{1}$$

Where F is gas flux from the soil (μmol m^{-2} s^{-1}), $\mathrm{d}C/\mathrm{d}t_0$ is the initial rate of change in concentration with time in μmol mol^{-1} s^{-1}, ρ is the density of air in mol m^{-3}, V is the volume of the chamber in m^3 and A is the ground area enclosed by the chamber in m^2.

The parameter $\mathrm{d}C/\mathrm{d}t_0$ was calculated using linear and non-linear asymptotic regression methods Levy et al. (2011). Using a mixture of goodness-of-fit statistics and visual inspection, the regression method that provided the best fit for the time series of concentration was chosen for each individual measurement. With this method of flux calculation, any non-linearity should be accounted for as far as possible. However, the time resolution (approximately 10 minutes) limits the detectable degree of non-linearity in the initial concentration change, so there remains some potential for underestimation of fluxes Cowan et al. (2014).

8 Statistical analysis

The data were first analysed using a linear mixed-effects model (Pinheiro and Bates, 2006). There were 729 flux measurements in total, after removing four outlying measurements above 10 nmol m^{-2} s^{-1} and two below -2 nmol m^{-2} s^{-1}. We fitted fixed-effect terms for soil temperature, T_{soil}, water table height, z_{water} (negative values indicate depth below the surface), ammonia-N deposition rate, $F_{\mathrm{N-NH_3}}$, ammonium-N deposition rate, $F_{\mathrm{N-NH_4}}$, and nitrate-N deposition rate, $F_{\mathrm{N-NO_3}}$, and random-effect terms with a design matrix $\mathrm{Z}_{\mathrm{i,j}}$ to account for the repeated measures on each chamber location, *j*, nested within each experimental block, *i* :

$$F_{\mathrm{N_2O,ij}} = \beta_0 + \beta_1 \cdot T_{\mathrm{soil,ij}} + \beta_2 \cdot z_{\mathrm{water,ij}} + \beta_3 \cdot F_{\mathrm{NH_3,ij}} + \beta_4 \cdot F_{\mathrm{NH_4,ij}} + \beta_5 \cdot F_{\mathrm{NO_3,ij}} + b_i \cdot \mathrm{Z_{i,j}} + b_{ij} \cdot \mathrm{Z_{ij}} + \epsilon_{ij} \quad (2)$$

$$b_i \sim N(0,\sigma_1^2)\; b_{ij} \sim N(0,\sigma_2^2)\; \epsilon_{ij} \sim N(0,\sigma_3^2).$$

9 Nature and Units of recorded values

The following tables list the variables in each of the files in the data set.

Variable name	Units	Description
ChamberID	na	Unique ID for each chamber, 1-72
chamberCode	na	Code consisting of PlotNumber and SubPlotNumber
chamberID-4dig	na	Four-digit chamber code
ExperimentalGrid	na	"Wet", "Dry", or "Ozone"
form	na	Form of N deposition - "Wet" or "Dry"
BlockID	na	ID for each experimental block - see Figure 1
PlotNumber	na	ID for each experimental plot - see Figure 1
SubPlotNumber	na	ID for each experimental sub-plot - see Figure 1
lon	degrees	Longitude of each chamber
lat	degrees	Longitude of each chamber
Fnh3	kg N $\mathrm{ha^{-1}\ y^{-1}}$	Flux of NH_3 to each chamber
Fnh4	kg N $\mathrm{ha^{-1}\ y^{-1}}$	Flux of NH_4 to each chamber
Fno3	kg N $\mathrm{ha^{-1}\ y^{-1}}$	Flux of NO_3 to each chamber
Ndep-total	kg N $\mathrm{ha^{-1}\ y^{-1}}$	Total flux of N to each chamber

Table 2. `ancilliaryData-byChamber.csv`. The file contains ancilliary data for each chamber. The four-digit chamber code is formatted EPPS, where E is the experiment, PP is the two-digit PlotNumber and S is the SubPlotNumber

Variable name	Units	Description
chamberCodeinFile	na	Code used for chamber in GC raw data file
gasName	na	"N2O" only
filename	na	File name for raw GC data
fullpathname	na	File name for raw GC data including path
date	dd/mm/YYYY	Date of measurement
chamberID$_4dig$	na	see Table 2
lon	degrees	see Table 2
lat	degrees	see Table 3
BlockID	kg N ha^{-1} y^{-1}	see Table 2
PlotID	kg N ha^{-1} y^{-1}	see Table 2
form	kg N ha^{-1} y^{-1}	see Table 2
Fnh3	kg N ha^{-1} y^{-1}	see Table 2
Fnh4	kg N ha^{-1} y^{-1}	see Table 2
Fno3	kg N ha^{-1} y^{-1}	see Table 2
Ndep-total	kg N ha^{-1} y^{-1}	see Table 2
Tair-degC	degrees C	Air temperature in chamber
Tsoil-degC	degrees C	Soil temperature in chamber
WTdepth-cm	cm	Water table depth below the surface

Table 3. `ancilliaryData-byChamber-byDate.csv`. The file contains ancilliary data which vary by chamber and by date.

Variable name	Units	Description
filename	na	File name for raw GC data
fullpathname	na	File name for raw GC data including path
flux linear	nmol N_2O m^{-2} s^{-1}	Flux calculated by linear model
flux quadratic	nmol N_2O m^{-2} s^{-1}	Flux calculated by quadratic model
flux linear2nd	nmol N_2O m^{-2} s^{-1}	Flux calculated by linear model
flux quadratic2nd	nmol N_2O m^{-2} s^{-1}	Flux calculated by linear model
flux asymptotic	nmol N_2O m^{-2} s^{-1}	Flux calculated by asymptotic model
flux HMR	nmol N_2O m^{-2} s^{-1}	Flux calculated by HMR model
flux bestfit	nmol N_2O m^{-2} s^{-1}	Flux calculated by best-fitting model
ci95lo linear	nmol N_2O m^{-2} s^{-1}	Lower 95 % confidence interval on linear model estimate
ci95hi linear	nmol N_2O m^{-2} s^{-1}	Upper 95 % confidence interval on linear model estimate
ci95lo bestfit	nmol N_2O m^{-2} s^{-1}	Lower 95 % confidence interval on best-fitting model estimate
ci95hi bestfit	nmol N_2O m^{-2} s^{-1}	Upper 95 % confidence interval on best-fitting model estimate
adjr2 linear	nmol N_2O m^{-2} s^{-1}	Adjusted r2 for linear model estimate
adjr2 quadratic	nmol N_2O m^{-2} s^{-1}	Adjusted r2 for quadratic model estimate
bestFitMethod	nmol N_2O m^{-2} s^{-1}	Integer code for method that gives the best-fit
chamberCodeinFile	na	see Table 3

Table 4. `RCfluxOutput.csv`. The file contains fluxes of N2O calculated by the RCflux program.

Variable name	Units	Description
chamberID$_4dig$	na	see Table 2
BlockID	na	see Table 2
PlotID	na	see Table 2
form	na	see Table 2
Calluna vulgaris	Percent cover	Percentage of area in chamber covered by *Calluna vulgaris*
... for each species	Percent cover	Percentage of area in chamber covered by each species

Table 5. `vegetation-speciesPercentCover-Whim-byChamber.csv`. The file contains percent cover data for each species in each chamber.

Variable name	Units	Description
chamberID$_4dig$	na	see Table 2
BlockID	na	see Table 2
PlotID	na	see Table 2
form	na	see Table 2
Jun$_2010$	mg N per litre	Ammonium concentration in soil water in June 2010
… for each month	mg N per litre	Ammonium concentration in soil water for each month

Table 6. `chemistry-NH4mgNperl-Whim-byChamber-byDate.csv`. The file contains soil water ammonium concentrations for each chamber and date.

Variable name	Units	Description
chamberID$_4dig$	na	see Table 2
BlockID	na	see Table 2
PlotID	na	see Table 2
form	na	see Table 2
Jun$_2010$	mg N per litre	Nitrate concentration in soil water in June 2010
… for each month	mg N per litre	Nitrate concentration in soil water for each month

Table 7. `chemistry-NO3mgNperl-Whim-byChamber-byDate.csv`. The file contains soil water nitrate concentrations for each chamber and date.

Variable name	Units	Description
chamberID$_4dig$	na	see Table 2
BlockID	na	see Table 2
PlotID	na	see Table 2
form	na	see Table 2
Jun$_2010$	pH	pH in soil water in June 2010
… for each month	pH	pH in soil water for each month

Table 8. `chemistry-pH-Whim-byChamber-byDate.csv`. The file contains soil water pH concentrations for each chamber and date.

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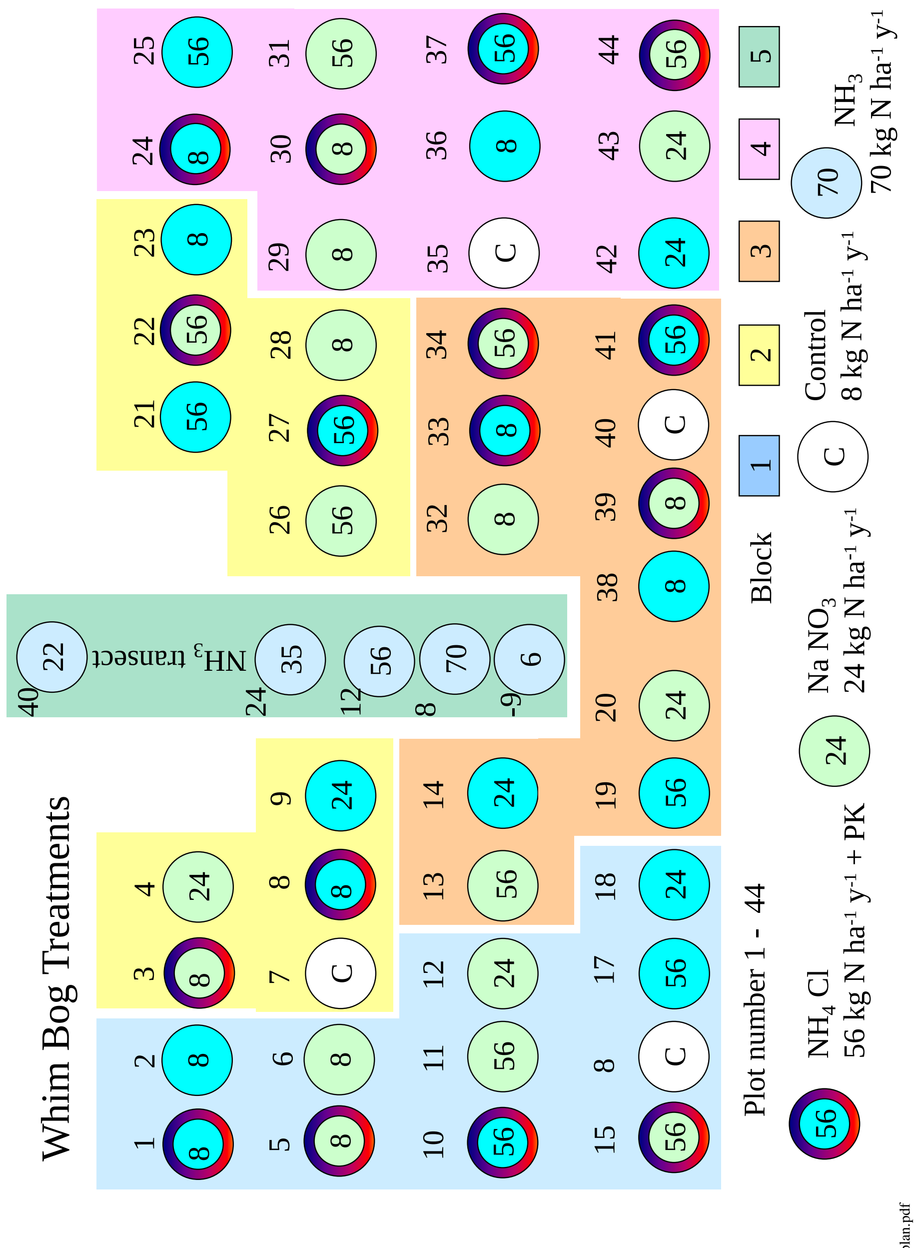

Figure 1. Layout of N deposition plots in the Whim experiment.