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Nitrous oxide emissions from a peatbog after thirteen years of experimental nitrogen deposition

Sarah R. Leeson, Peter E. Levy, Netty van Dijk, Julia Drewer, Sophie Robinson, Matthew R. Jones, John Kentisbeer, Ian Washbourne, Mark A. Sutton, and Lucy J. Sheppard

Centre of Ecology and Hydrology, Edinburgh, UK

Correspondence to: Peter Levy (plevy@ceh.ac.uk)

Abstract.

Nitrogen deposition was experimentally increased on a Scottish peat bog over a period of thirteen years (2002-2015). Nitrogen was applied in three forms, NH_3 gas, NH_4^+ solution, and NO_3^- solution, at rates ranging from ambient (8) to 64 kg N ha^{-1} y^{-1}, and higher near the NH_3 fumigation source. An automated system was used to apply the nitrogen, such that the deposition was realistic in terms of rates and high frequency of deposition events. We measured the response of nitrous oxide (N_2O) flux to the increased nitrogen input. Prior expectations, based on the IPCC default emission factor, were that 1 % of the added nitrogen would be emitted as N_2O. In the plots treated with NH_4^+ and NO_3^- solution, no response was seen, and there was a tendency for N_2O fluxes to be reduced by additional nitrogen, though this was not significant. Areas subjected to high NH_3 emitted more N_2O than expected, up to 8.5 % of the added nitrogen. Differences in the response are related to the impact of the nitrogen treatments on the vegetation. In the NH_4^+ and NO_3^- treatments, all the additional nitrogen is effectively immobilised in the vegetation and top 10 cm of peat. In the NH_3 treatment, much of the vegetation was killed off by high doses of NH_3, and the nitrogen was presumably more available to denitrifying bacteria. The design of the wet and dry experimental treatments meant that they differed in statistical power, and we are less likely to detect an effect of the the NH_4^+ and NO_3^- treatments, though they avoid issues of pseudo-replication.

1 Introduction

Since the industrial revolution, peatlands have been subject to increased deposition of anthropogenic nitrogen (N), as a result of fossil fuel burning and agricultural use (Fowler et al., 2005). The overall consequences of enhanced N deposition in ombrotrophic peat bogs are poorly understood, but bogs are likely to be sensitive to enhanced N inputs, because they are adapted to conditions of very low N availability (Bobbink et al., 1998). When N deposition exceeds plant demand, the additional N may be used by soil microbes, and can result in the production of the greenhouse gas nitrous oxide (N_2O) via nitrification and denitrification (Regina et al., 1996; Bobbink et al., 1998; Silvan et al., 2005). Of the total N applied to agricultural land and arising from livestock waste which is subsequently deposited on semi-natural land, it it estimated that 1 % is re-emitted as N_2O (De Klein, 2006). This so-called "indirect" emission of N_2O is a large, but uncertain, term in the national inventory of

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greenhouse gas emissions. There have been relatively few experimental attempts to determine these emissions on peat bogs, and most information comes from Fenno-Scaninavian bogs (Regina et al., 1998; Nykanen et al., 2002; Lund et al., 2009).

N deposition may lead to changes to peat bog ecosystems which influence the emission of N_2O in complex ways, particularly via soil chemistry and vegetation composition (Simek and Cooper, 2002; Juutinen et al., 2010). For example, N deposition may affect soil pH, which affects the composition of the microbial community (Nicol et al., 2008), and affects the relative prevalence of the biochemical pathways by which denitrification produces N_2 or N_2O (Simek and Cooper, 2002). *Sphagnum* mosses can immobilise a significant proportion of the incoming N deposition (Curtis et al., 2005). If *Sphagnum* cover is reduced as a result of N deposition (Bobbink et al., 1998), more N may become available to denitrifying microbes, and result in greater emissions of N_2O (Lamers et al., 2000). The effects may also depend on the form of deposited N, whether reduced N (NH_x) coming predominantly from animal waste, or oxidised N (NO_x) coming from energy combustion, and whether deposited as a gas (NH_3) or in rainfall (NH_4^+ or NO_3^-).

This paper reports measurements of N_2O emissions, as part of a long-term experiment in which additional N has been deposited on a peatbog in central Scotland, for over thirteen years, in three different forms (as NH_3 gas, as NH_4^+ solution or NO_3^- solution). The automated experiment was designed to provide realistic N deposition, in terms of doses, frequency (>100 spray events y^{-1}) and exposure concentrations, reflecting the pollution climate experienced in the UK. Ambient N inputs at the site are relatively low, so that the responses should be representative of the more pristine northern European peat bogs. Previous results from the experiment have demonstrated that high doses of NH_3 reduces the cover of several plant species, but that the effects of NH_4^+ and NO_3^- on vegetation composition and cover are not large (Sheppard et al., 2008, 2011, 2014). Here, we examine the effects of the dose and form of N deposition on emissions of N_2O. Preliminary data on N_2O fluxes were reported by Sheppard et al. (2013), showing an increase with NH_3, but no effect of NH_4^+ and NO_3^-. Here, we analyse an additional five years of data collected at a wider range of locations, and with further time for any treatment effects to accumulate. The aims were to investigate (i) the extent to which N_2O emissions are stimulated by N deposition, and whether the 1 % emission factor used in IPCC inventories is accurate, (ii)whether the form of N deposition is important, and (iii) whether other changes induced by N deposition (e.g. on soil chemistry or vegetation) have an indirect effect on N_2O emissions.

2 Materials and methods

2.1 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 peat surface, i.e. relatively wet for most of the year. 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, Rodwell, 1998). 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.*

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fallax and *S. papillosum*. Other common species included *Erica tetralix* and the mosses *Hypnum jutlandicum* and *Pleurozium schreberi*.

2.2 Experimental 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 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 1.

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}.

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. Vegetation species composition was surveyed in all plots every few years, and the percent cover recorded within each chamber location.

2.3 Greenhouse gas exchange

Nitrous oxide fluxes were measured by the static chamber method (Hutchinson and Mosier, 1981). Cylindrical PVC collars (38 cm in diameter and typically 25 cm high) were inserted into the peat at the locations shown by green circles in Figure 1.

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

2.4 Statistical analysis

The data were first analysed using a linear mixed-effects model (Pinheiro and Bates, 2006), 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}, 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 $\mathrm{Z_{i,j}}$ to account for the repeated measures on each chamber location, *j*, nested within each experimental block, *i* :

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

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

The data were also analysed using a general additive mixed-effects model (Wood, 2006), with the same fixed- and random effect terms, but allowing for non-linearity in the fixed-effect responses. To analyse the relationship between N_2O flux and vegetation species composition, we used a multivariate approach, partial least squares regression (PLS, Mevik and Wehrens, 2007). The approach is an extension of principal components analysis (PCA), but whereas PCA focuses on the variance in a matrix of variables, $\mathbf{X}$, PLS computes the scores and loadings in such a way to describe the covariance between $\mathbf{X}$ and a response variable or matrix, $\mathbf{Y}$. In this context, we have a matrix consisting of the percent cover of each plant species in each chamber, and the response variable is the N_2O flux. PLS should perform better than PCA in situations where an infrequent species (contributing little to the variance in $\mathbf{X}$) is highly correlated with $\mathbf{Y}$. In PLS, such a component would automatically be present in the first component, but would be a minor component in PCA.

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3 Results

Figure 1 shows the spatial distribution of N deposition in the dry and wet deposition treatments. Deposition of NH_3 peaks at around 100 kg N ha^{-1} y^{-1} just downwind of the fumigation source. NH_3 deposition decreases with downwind and cross-wind distance from the fumigation source, and approximates a Gaussian plume pattern expected from micrometeorological theory. The plume is aligned slightly to the east of the boardwalk transect, although there is some uncertainty in the interpolation berween NH_3 samplers. Deposition of NH_4^+ and NO_3^- on the wet deposition plots are shown on the same colour scale. These are known with much greater certainty, as no modelling step is required.

Figure 2 shows the time series of nitrogen deposition in the NH_4^+ and NO_3^- treatments, and on the NH_3 transect at 16 m, where annual deposition was similar to that in the NH_4^+ and NO_3^- treatments. Distribution of deposition events over time is similar in both treatments. Deposition events were spread over most days of the year, with only no deposition in a short period in mid-winter. NH_3 deposition is calculated as a function of stomatal conductance (Cape et al., 2008), so rates are higher in daytime and in the summer.

Whilst there is considerable scatter in the response of N_2O fluxes to mean annual nitrogen deposition, an increase in N_2O flux with NH_3 deposition was apparent (Figure 3). No trend with NH_4^+ or NO_3^- deposition was obvious. In many of the flux measurements, the magnitude of N_2O fluxes was close to the measurement error in the static chamber method. In both the NH_4^+ and NO_3^- treatments, only 9% of fluxes (respectively) had 95 % confidence limits which did not include zero. Detecting a clear response is inevitably difficult when measurement noise contributes substantially to the variability in the data. By contrast, in the NH_3 treatment, 40 % of fluxes had confidence limits which did not include zero.

The output from the linear mixed model analysis is shown in Table 1, with the coefficients representing the response to the fixed factors. As well as showing significant responses to temperature and water table depth, N_2O fluxes responded to NH_3 deposition (Figure 3). This response was greater than the default 1 % IPCC emission factor, and comes close to 8.5 % (with the appropriate unit conversion). The relationship may not be linear (Philibert et al., 2012), and the general additive mixed model (GAMM) was fitted to allow for non-linearity in the fixed effects. However, the exact form of the response to NH_3 deposition was not well constrained by the data, especially at the lower values, and a simple linear fit was justified (Figure 4). The modelled effect of NH_4^+ and NO_3^- deposition was slightly negative on average, although positive and negative slopes are both plausible (Table 1,Figure 4).

NH_4^+ concentrations in the soil water were elevated in the high NH_4^+ deposition treatment, by around 1 mg N dm^{-3} on average (Figure 5). By contrast, the high NO_3^- deposition treatment had no clear effect on NO_3^- concentrations in the soil water. On the NH_3 deposition transect, there was a clear trend in soil water concentrations of both NH_4^+ and NO_3^- with NH_3 deposition (Figure 5), right-hand plots). At the equivalent level of NH_3 deposition, NH_4^+ concentrations in the soil water were elevated by a similar amount to that in the high NH_4^+ deposition treatment. There were weak relationships between N_2O flux and NH_4^+ and NO_3^- concentrations in the dry treatment, but no clear relationship in the wet treatment.

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Vegetation composition provided reasonably good explanatory power for N_2O flux, and the PLS regression explained 56 % of the variance in N_2O flux (Figure 6). The first two components explained 27 % of the variance, and gave an interpretable ordination of the chambers (Figure 7). The chambers high on the first axis were dominated by *Eriophorum vaginatum*, often damaged by NH_3, with little or no moss cover, and had hign fluxes. The chambers low on the first axis had high cover of *Sphagnum capillifolium*, and had low fluxes. The second axis differentiates hummock and hollow vegetation, and a soil moisture difference. The drier hummocks with *Calluna vulgaris* and *Deschampsia flexuosa* had lower fluxes than the hollows, dominated by *Sphagnum capillifolium*.

4 Discussion

Our results confirm the early findings of (Sheppard et al., 2013), that there was no clear response of N_2O flux to deposition of NH_4^+ or NO_3, whereas high doses of NH_3 reduced the cover of *Calluna vulgaris* and *Sphagnum* species, and increased N_2O flux. Other results in the literature show a range of responses of N_2O emission to experimental N addition, from no response to substantial increases. Lund et al. (2009) found no effect of experimental N addition (NH_4NO_3) on N_2O emissions from two Swedish bogs, and peak fluxes were less than 1 nmol $m^{-2}\,s^{-1}$, when 40 kg N $ha^{-1}\,y^{-1}$ was applied in only three relatively large doses. Nykanen et al. (2002) found no response of N_2O emission to additions of up to 100 kg N $ha^{-1}\,y^{-1}$ ($NH_4^+NO_3$) to a *Sphagnum fuscum* pine bog in Finland, over a six-year study. Following nitrate addition to *ex situ* peat cores from Polish sedge fen, Roobroeck et al. (2010) observed no increase in N_2O emissions from cores from vegetated tussocks or unvegetated hollows, except for an increase of 0.15 nmol $m^{-2}\,s^{-1}$ at their low nitrate (KNO_3) addition rate.

Some clearer positive responses have been observed where bogs have been drained, or where very high levels of nitrogen have been applied. Regina et al. (1998) found that N_2O emissions were increased by up to 0.8 nmol $m^{-2}\,s^{-1}$ for around nine months after a single experimental N addition of 100 kg N $ha^{-1}\,y^{-1}$ on a drained and forested peatland in Finland. Here, KNO_3, NH_4Cl, and urea gave a similar range of responses. Zhang et al. (2007) observed an increase of 0.3 nmol $m^{-2}\,s^{-1}$ with the application of 240 kg N $ha^{-1}\,y^{-1}$ (NH_4NO_3) to a freshwater marsh in China, bi-weekly over the summer growing season. Clear responses can, however, be very short-lived. For example, Gao et al. (2014, 2015) found a short-term response of N_2O efflux to NH_4NO_3 addition in an *in vivo* study of soil from an alpine peatland in Tibet, but differences from the control lasted less than ten days.

A response of N_2O emissions to nitrogen addition is more often detectable in laboratory incubations, where there are fewer feedbacks and interactions. Field studies commonly show complex interactions with other variables, resulting in no effect in the field, or making interpretation of results complicated. In a Finnish spruce swamp buffer zone, Saari et al. (2013) found that nitrogen addition increased N_2O efflux in laboratory incubations, but *in situ* N_2O effluxes were low and unresponsive. Regina et al. (1996) found that N_2O fluxes were positively correlated with the numbers of nitrite oxidizers, nitrification potential, N, P and Ca and pH of the soil and negatively with the level of water table and K content of the soil. In a study by Silvan et al. (2005) on a restored peatland in Finland, N_2O emissions showed an asymptotic increase with nitrate concentration, and

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an exponential decrease with *E. vaginatum* cover. The interpretation was that N_2O emission was the outcome of resource competition for nitrate between denitrifying bacteria and (*E. vaginatum*) roots, but both have limited capacities for uptake.

We can intrepret our results similarily in terms of resource competition for nitrate. The wet deposition of NO_3^- did not increase concentrations of NO_3^- in the soil water. Data in (Sheppard et al., 2013, Figure 7) suggest that all the additional N deposited on the wet treatment plots accumulated in the top 10 cm of the peat and below-ground vegetation. It was thereby immobilised, and not available to soil microbes, and was not denitrified to N_2O. The wet deposition of NH_4^+ did increase concentrations of NH_4^+ in the soil water, but NH_4^+ is less directly related to the microbial production of N_2O. In the dry deposition treatment at high levels of NH_3 deposition, although there was similar accumulation of the deposited N in the peat, much of the vegetation cover was killed, leaving only a sparse cover dominated by *E. vaginatum*. The deposited N was therefore more available to soil microbes because there was less competition with plants, and could be denitrified to N_2O.

The multivariate analysis of the vegetation provided the best means for explaining the variation in N_2O fluxes. Shifts in the species composition appeared to be the clearest sign that N deposition was affecting the long-term outcome of resource competition for nitrate, and thereby influencing N_2O flux. A similar result was found in a multivariate analysis of vegetation in relation to methane flux in the UK ecosystems (Levy et al., 2012; Gray et al., 2013). Direct relationships between N_2O flux and nitrate and ammonium were poor, possibly because these are influenced by feedback from the flux itself.

The unique aspect of the experimental design, in providing a very realistic simulation of nitrogen deposition rates, in terms of frequency and exposure concentrations, makes detecting effects more difficult. Unlike measuring N_2O fluxes on agricultural land, where large peak emissions typically follow fertiliser applications, here we are measuring small, diffuse N_2O fluxes spread over the whole year, which is necessarily more difficult.

Experimental designs of the wet and dry deposition experiments were quite different, because of the logistics of applying gases and liquids to ecosystems. This may partly explain why the effect of NH_3 was easier to detect. NH_3 was applied on a larger spatial scale, with very high rates of deposition adjacent to the fumigation outlet. Implicitly, we assume that differences with distance are effects of NH_3, as there was no true replication (i.e. there was only one transect). Given this assumption, we take n to be 60 in the NH_3 experiment. The probability of detecting an effect size of +0.068 nmol m^{-2} s^{-1} (= 1 % of 60 kg N ha^{-1} y^{-1}) is reasonably high (p = 0.97), from a standard power analysis (Cohen, 1988), given the typical measurement error in static chamber data (and ignoring between-plot variability). In the case of the wet depostion experiment, there were true replicate plots in a randomised block design, but sample size was small (4 plots per treatment). The probability of detecting the same effect size with $n = 4$ is rather low (p = 0.14).

In our experimental results, neither NH_4^+ nor NO_3^- deposition increased fluxes of N_2O (indeed the mean effect of both was negative), and all the deposited N appeared to be retained in the peat and below-ground vegetation. However, we need to be careful before concluding that the true effect was zero (or negative), given that the effect size we were looking for was small. An emission factor of 1 % is not inconsistent with the data, given the between-plot variability, measurement precision and small sample size. If this were the true emission factor, we can estimate the N_2O emission resulting from N deposition over peatlands in the UK. Combined deposition rates of NH_4^+ and NO_3^- are generally less than 10 kg N ha^{-1} y^{-1} on UK peatbogs (Department for Environment, Food and Rural Affairs, 2016). With a 1 % emission factor, this would imply a mean emission

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of 11 pmol m^{-2} s^{-1} or 1.3 g C - CO_2 eq m^{-2} y^{-1}. (To express N_2O flux in units of C - CO_2 equivalents, we convert to a mass of N_2O and multiply by 298 (the global warming potential of N_2O over a 100-year time period including carbon cycle feedbacks, IPCC, 2013), and report only the mass of carbon in the CO_2 equivalents i.e. 12/44.) This compares with contemporary net ecosystem carbon balance measurements in the range of 28-50 g C - CO_2 equivalents in UK peatlands (Helfter et al., 2014; Levy and Gray, 2015).

NH_3 has a different spatial distribution, being deposited much closer to its sources, so with high "hotspots", but with lower overall mean deposition rates (<5 kg N ha^{-1} y^{-1}). In the immediate vicinity of a large agricultural source, high mean emissions would be predicted, in the order of 0.58 nmol m^{-2} s^{-1} or 65 g C - CO_2 eq m^{-2} y^{-1} (i.e. 8.5 % of 60 kg N ha^{-1} y^{-1}), but over relatively small areas. This approaches the large values observed by Repo et al. (2009) in Arctic bare peat circles (averaging 0.86 nmol m^{-2} s^{-1} or 97 g C - CO_2 eq m^{-2} y^{-1}), but upscaling these emissions to national scale is challenging.

Author contributions. LS and MS designed the experiment. SL, MJ and LS maintained the experiment. SL collected the bulk of the flux data, with additional data collected by JD, SR, JK and IW. NvD collected vegetation data and analysed the soil chemistry data. PL performed the statistical analysis and wrote the manuscript.

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	DF	F.value	p.value	Coefficient
Intercept	391	23.88	0.000	-0.1655
T_{soil}	391	14.10	0.000	0.0527
z_{water}	391	25.36	0.000	0.0181
$F_{\mathrm{NH_3}}$	40	29.89	0.000	0.0092
$F_{\mathrm{NH_4}}$	40	1.27	0.267	-0.0046
$F_{\mathrm{NO_3}}$	40	1.74	0.194	-0.0041

Table 1. Results of fitting the linear mixed-effects model (Equation 2) to the data by maximizing the restricted log-likelihood. Columns show the denominator degrees of freedom, F-values, p-values from Wald tests for each term, and the β coefficients in Equation 2.

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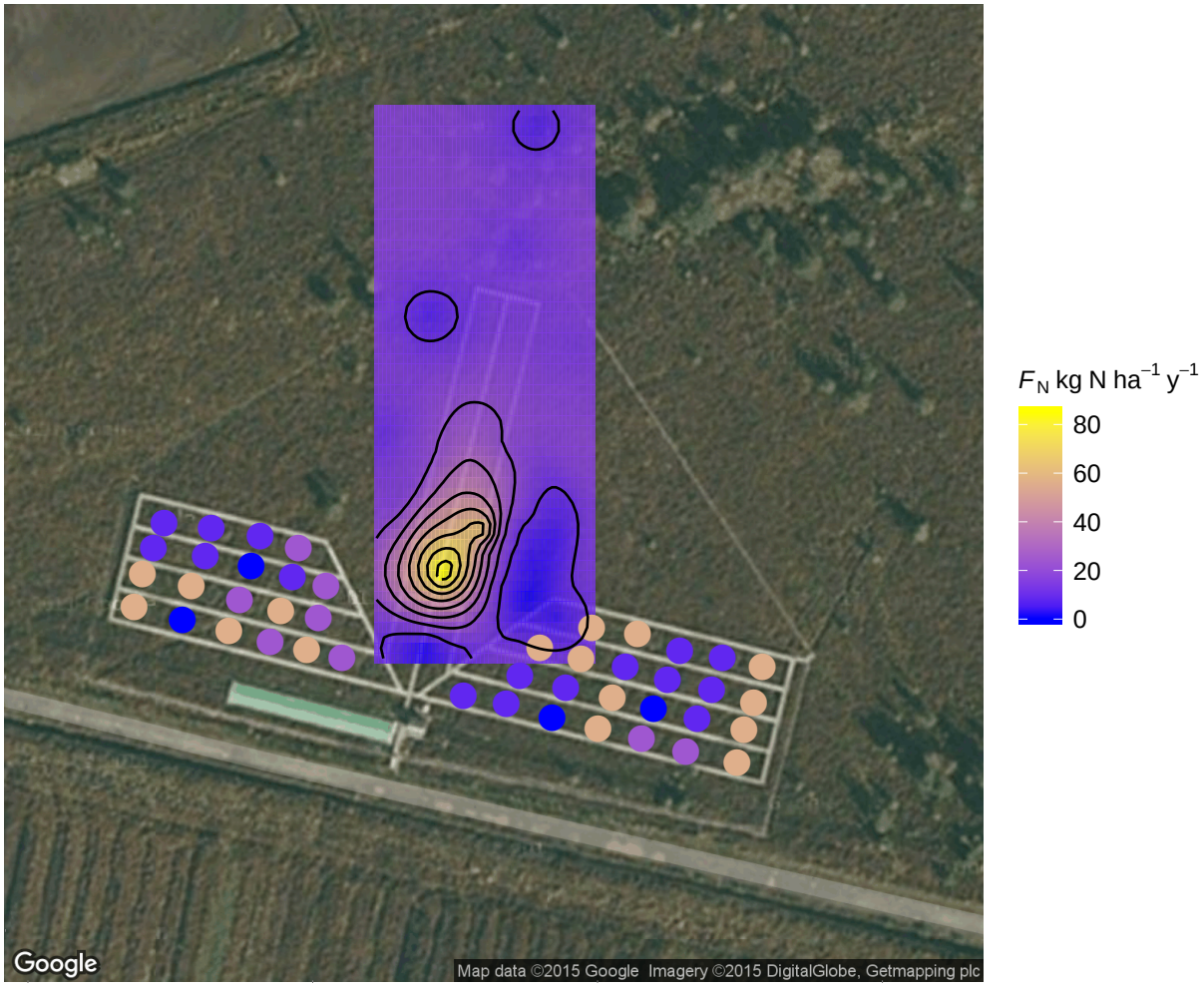

Figure 1. Spatial distribution of N deposition in the Whim experiment. The ammonia release system was located at the centre of the boardwalk structure in the middle of the image. Ammonia deposition was calculated from concentration measurements downwind of the ammonia source using the method of Cape et al. (2008), and interpolated across the central rectangular area of the image using ordinary kriging. In the wet deposition plots (circles in the lower part of the image), the nitrogen solution applied was sprayed evenly across the whole 12.8 m^2plot.

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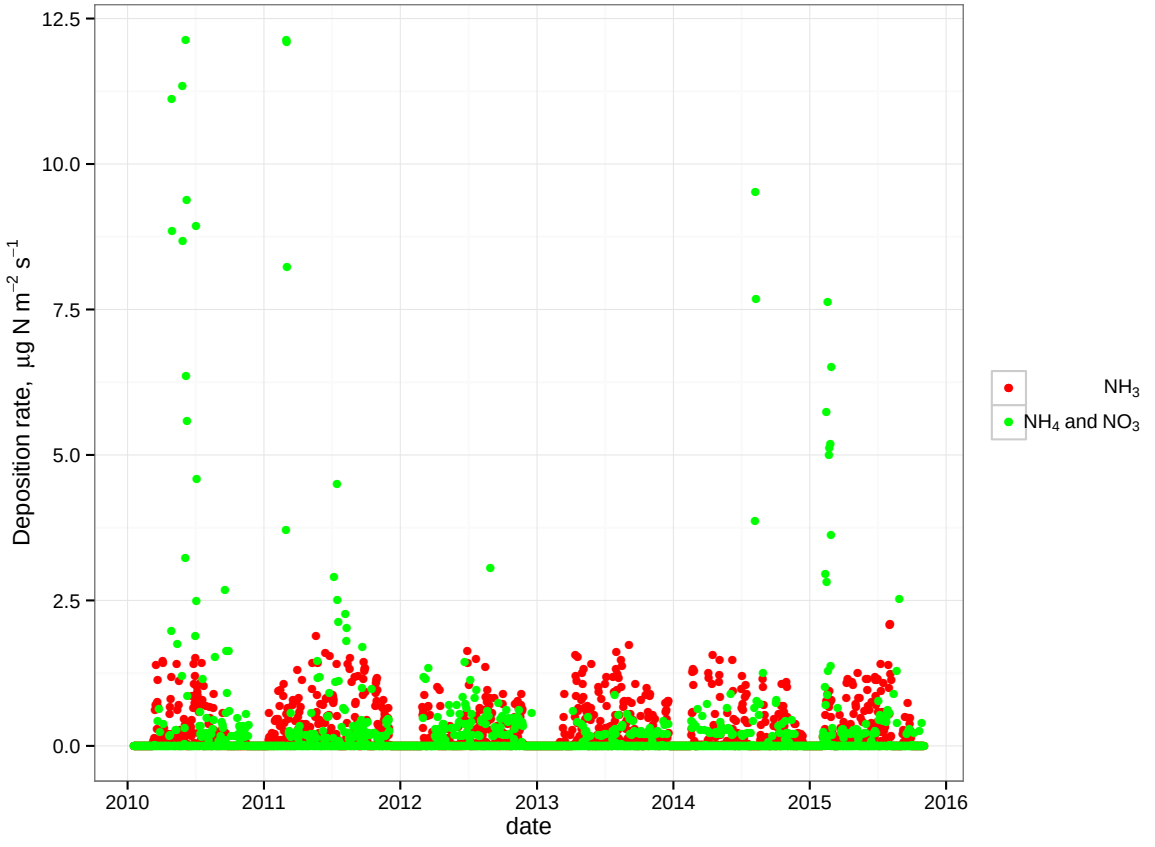

Figure 2. Daily mean nitrogen deposition rates in the NH_4^+ and NO_3^- treatments and at 16 m downwind on the NH_3 transect. NH_4^+ and NO_3^- deposition was calculated from the duration of spraying events each day, multiplied by the NH_4^+ and NO_3^- concentration in the solution, and accounting for the area covered by the spray. NH_3 deposition was calculated from the duration of fumigation events each day, measurements of NH_3 concentration, and meteorological data, using the method of Cape et al. (2008).

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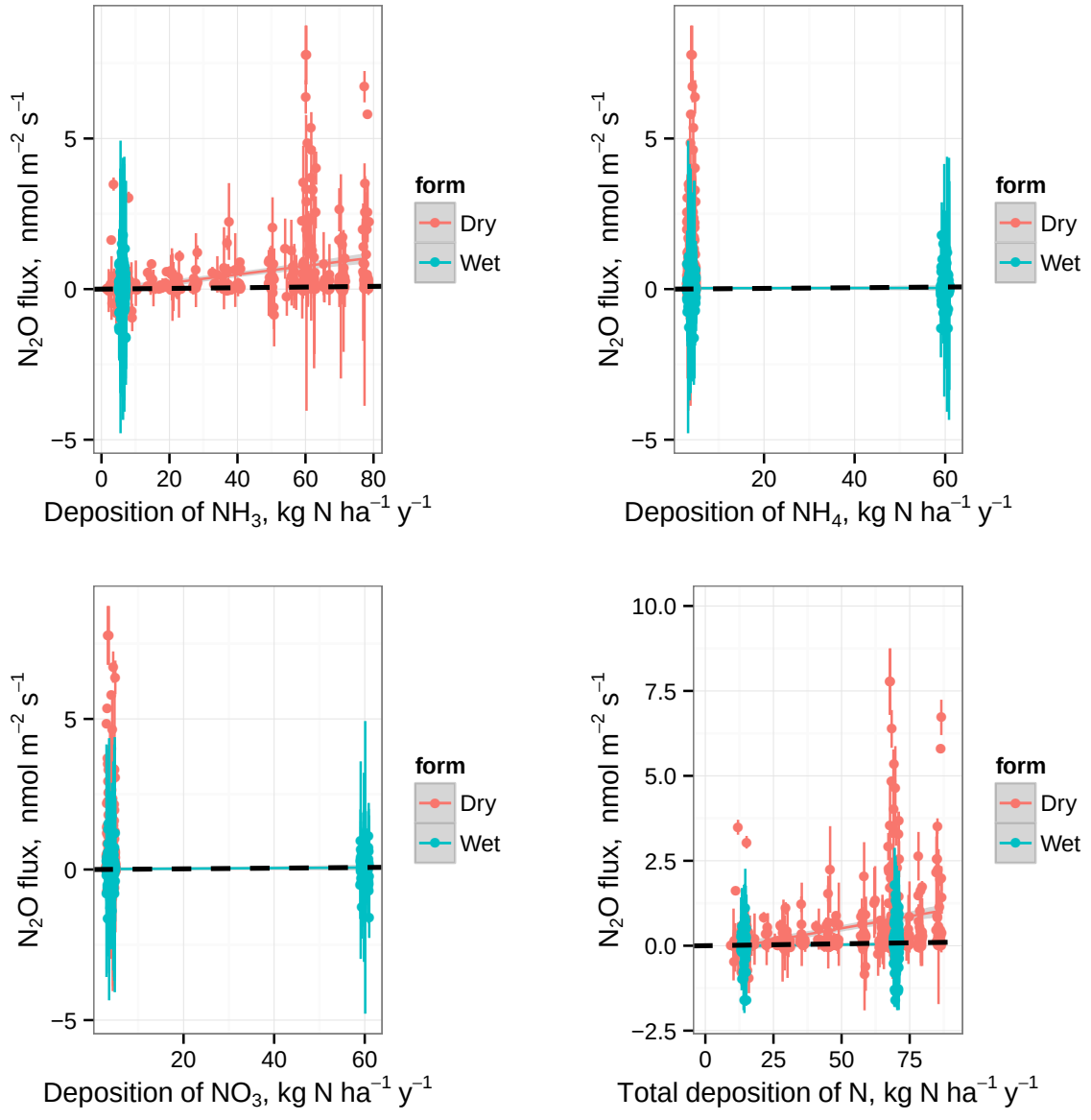

Figure 3. Response of N_2O flux to deposition of NH_3, NH_4, NO_3, and total N deposition. Error bars show the 95 % confidence interval, based on the regression slope for each flux measurement. Dotted lines show the emission predicted with the IPCC default emission factor, as 1 % of the deposited N.

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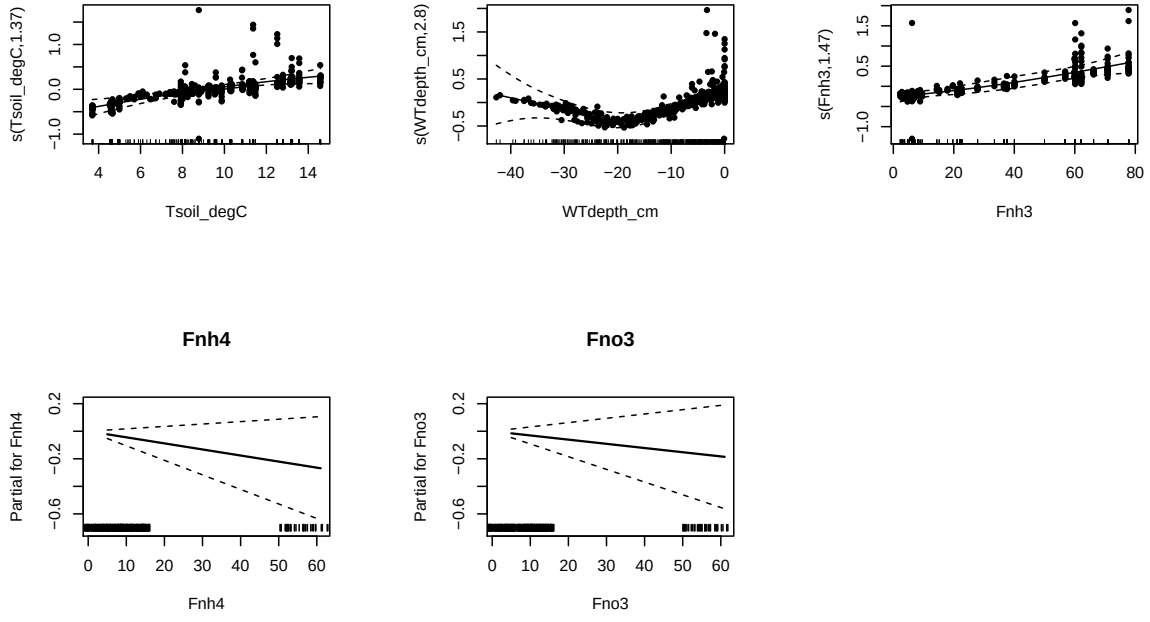

Figure 4. Fitted response of N_2O flux to soil temperature, water table height, and deposition of NH_3, NH_4^+ and NO_3, as estimated by the general additive mixed model. Partial residuals are shown for the smooth terms, which are the residuals that would be obtained by dropping the term concerned from the model, while leaving all other estimates fixed. NH_4^+ and NO_3 were treated as linear terms. Upper and lower lines show 2 standard errors above and below the fitted estimate.

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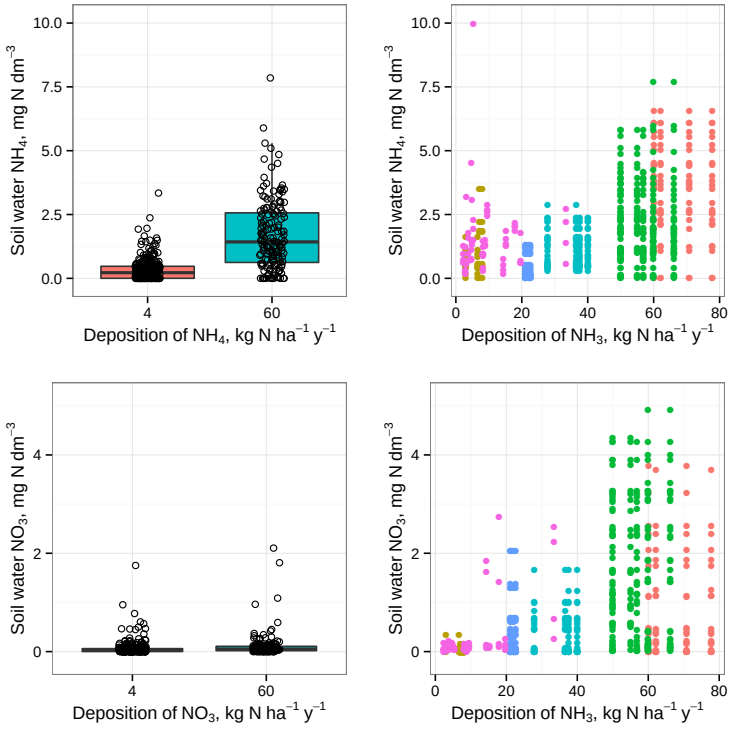

Figure 5. NH_4^+ and NO_3^- concentrations in the soil water in the experimental treatments. In the right-hand plots, colours show measurements grouped by distances downwind of the fumigation source.

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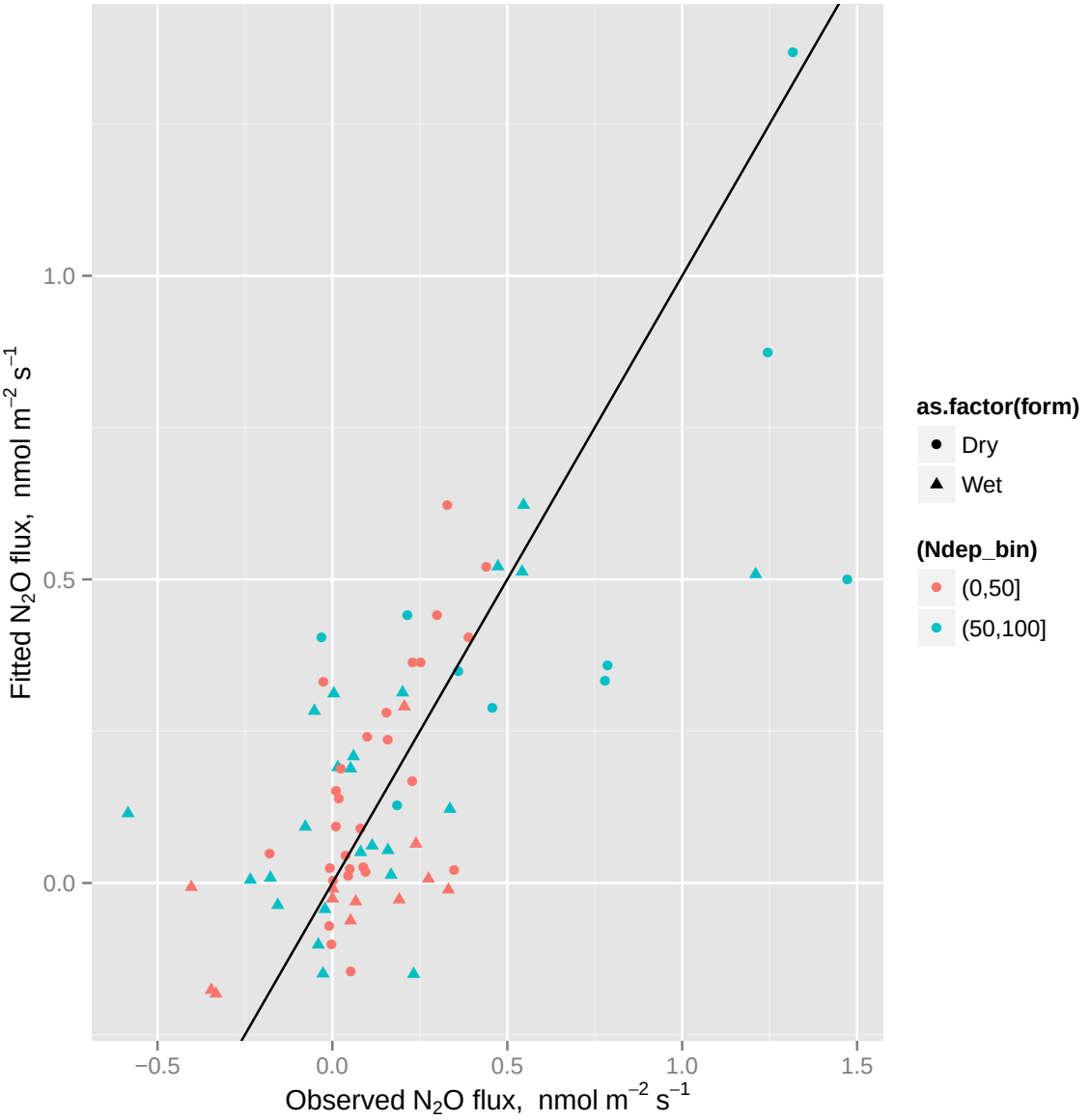

Figure 6. Mean N_2O flux at each chamber location fitted by the PLS model based on vegetation species composition plotted against observed mean fluxes. The data are grouped by nitrogen treatment form (symbol shape) and dose (symbol colour).

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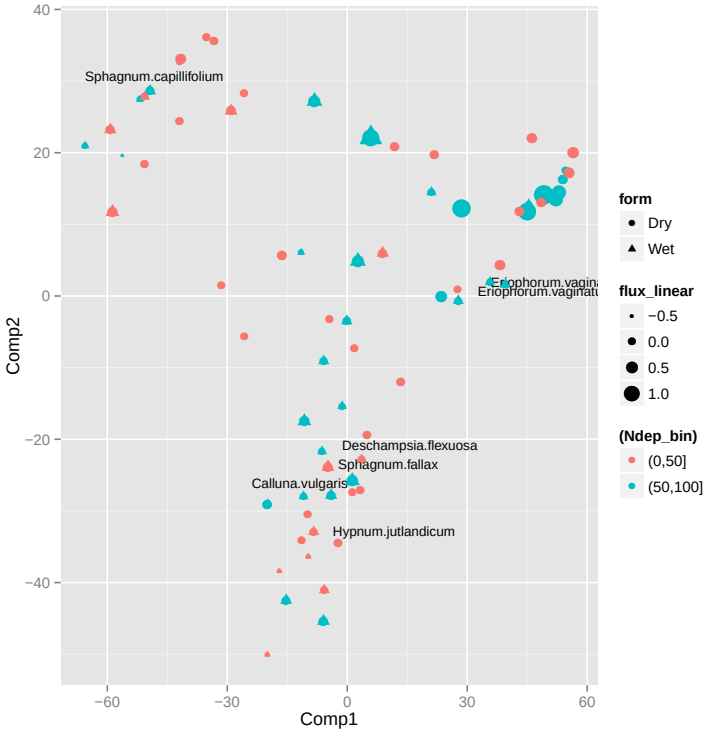

Figure 7. Biplot showing the scores for each chamber location for the first two PLS components. The first two PLS components represent the orthogonal indices of vegetation species composition which are the best linear predictors of mean N_2O flux at each chamber location. The loadings for the important plant species are superimposed, indicating which species contribute most to the components. The data are grouped by nitrogen treatment form (symbol shape) and dose (symbol colour); symbol size is proportional to the magnitude of the mean N_2O flux.