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Spatial and temporal variability in CH_4 and N_2O fluxes from a Scottish ombrotrophic peatland; implications for modelling and upscaling

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Abstract

Peatlands typically exhibit significant spatial heterogeneity which can lead to large uncertainties when catchment scale greenhouse gas fluxes are extrapolated from chamber measurements (generally <1 m^2). Here we examined the underlying environmental and vegetation characteristics which led to within-site variability in both CH_4 and N_2O emissions and the importance of such variability in up-scaling. We also consider within-site variation in the controls of temporal dynamics. Net annual emissions (and coefficients of variation) for CH_4 and N_2O were 1.06 kg ha^{-1} y^{-1} (300%) and 0.02 kg ha^{-1} y^{-1} (410%), respectively. The riparian zone was a significant CH_4 hotspot contributing ~12% of the total catchment emissions whilst covering only ~0.5% of the catchment area. In contrast to many other studies we found smaller CH_4 emissions and greater uptake in chambers containing either sedges or rushes. We also found clear differences in the drivers of temporal CH_4 dynamics across the site, e.g. water table was important only in chambers which did not contain aerenchymous plants. We suggest that depending on the heterogeneity of the site, flux models could be improved by incorporating a number of spatially distinct sub-models, rather than a single model parameterized using whole-catchment averages.

Greenhouse Gases, Variability, Peatlands, Microtopography, Vegetation

1. Introduction

Northern peatlands are currently thought to act as net sinks of CO_2 (Gorham, 1991). However, due to the prevalence of waterlogged conditions, they represent a significant net source of CH_4 (Bartlett and Harriss, 1993; Huttunen et al., 2003) and in some cases a net source of N_2O (Regina et al., 1996; Huttunen et al., 2002). In order to calculate a realistic global warming potential for peatland systems, all three of the aforementioned gases need to be accurately quantified and upscaled. It is also becoming increasingly important to understand what drives variability in the sink/source strength of the various greenhouse gases (GHG), in order to predict the biospheric feedback of peatlands in response to changes in peatland management and global climate.

The availability of micrometeorological techniques has greatly improved our understanding of the temporal variability in CO_2 emissions, revealing significant patterns in annual and inter-annual emissions (Lafleur et al., 2003; Lund et al., 2007). Furthermore, the availability of near-continuous datasets has led to a much greater understanding of the drivers of CO_2 emission and uptake, allowing emission predictions to be made under different climate change scenarios (Griffis and Rouse, 2001). Similar micrometeorological techniques for the measurement of CH_4 and N_2O are not widely used, with most current flux estimates from peatlands based on a series of enclosed chamber measurements (e.g. MacDonald et al., 1998; Whalen and Reeburgh, 2000; Laine et al., 2007; Roulet et al., 2007). However, with many studies repeatedly reporting high variability in fluxes both within and between sites (Bartlett and Harriss, 1993; Bubier et al., 1993; Waddington and Roulet, 1996), the uncertainty associated with up-scaling chamber measurements to annual catchment budget

64 estimates is often extremely large. Furthermore, such high uncertainty leads to
65 difficulties in identifying the primary drivers of temporal variability and hence
66 predicting future emissions under different climate change scenarios or management
67 regimes.

68 The hummock/hollow microtopography typical of many peatlands can cause
69 significant variation in soil environmental conditions at scales not picked up by single
70 chamber measurements (Nungesser, 2003). The preferential colonisation of
71 hummocks or hollows by distinct plant communities reinforces differences due to
72 topography alone by influencing the quantity and quality of soil organic substrate, and
73 altering the aerobic capacity of the peat by transporting O_2 to the rhizosphere. Plants
74 containing aerenchymous tissue can also provide a direct pathway for many GHGs to
75 the atmosphere, bypassing the aerobic peat horizon, and greatly increasing soil-
76 atmosphere fluxes (Whiting and Chanton, 1996; Ström et al., 2003; Minkkinen and
77 Laine, 2006). A clear understanding of the major sources of variation within a site is
78 essential both during the set-up of a study, when choosing where to place individual
79 chambers, and during the up-scaling process so that individual chamber fluxes can be
80 correctly weighted in the final estimate. Knowledge of expected variability is also
81 required when deciding how many chambers are needed to achieve a specific level of
82 confidence in the results; however this statistically ideal number is often not met due
83 to time constraints on both field sampling and analysis.

84 Although both temperature and water table have repeatedly been shown to be
85 strong drivers of temporal variability in surface CH_4 and N_2O fluxes, studies often
86 disagree as to their relative importance (Daulat and Clymo, 1998; Hargreaves and
87 Fowler, 1998; Updegraff et al., 2001). It is likely, given the degree of within-site

variability often observed, that the primary drivers of temporal variability are not consistent across typical peatland sites. By examining how these drivers vary spatially this study aims to improve our understanding of the underlying processes that control surface emissions, and aid the design of future chamber studies to achieve the best possible up-scaled emission estimates.

2. Materials and Methods

2.1. Site description

Auchencorth Moss is a relatively flat, low lying, acid peatland, located approximately 17 km south of Edinburgh, Scotland (55º47'34 N; 3º14'35 W). The site is designated as a 'supersite' under the 'European Monitoring and Evaluation Programme' (EMEP) and a 'level-3' site under the 'NitroEurope' project. Total nitrogen and sulphur deposition rates at the site are16.5 kg N ha^{-1} y^{-1} and 6.9 kg S ha^{-1} y^{-1}, respectively (Smith, personal communication, 2008). The land-use is primarily low-intensity sheep grazing with an area of peat extraction at the western edge of the catchment. Histosols (peats) cover approximately 85% of the catchment with areas of Gleysol (9%), Humic Gleysol (3%) and Cambisol (3%) occurring at the catchment margins; peat depth ranges from <0.5 m to >5 m (Billett et al., 2004). Mean annual rainfall (1995-2006) at the site is 1016 mm (Coyle, unpublished data, 2008); maximum and minimum monthly mean temperatures (1971-2000) are 19ºC in July and 0.7ºC in January, respectively (www.metoffice.gov.uk). The vegetation consists of a patchy mix of grasses, sedges and soft rush covering a base layer of moss on a typical peatland hummock/hollow microtopography. The dominant vascular species include *Deschampsia flexuosa*, *Molinia caerulea*, *Festuca ovina*, *Eriophorum*

angustifolium, *Eriophorum vaginatum*, *Juncus effusus*, *Juncus squarrosus* and *Calluna vulgaris*; bryophytes are dominated by *Sphagnum* and *Polytrichum* species.

2.2. Experimental design

The full study area was separated into 3 sites approximately 0.6 km apart to cover the full range of soil-plant conditions; site 1 was located in the west of the catchment where drainage was better and patches of *Calluna vulgaris* were present; site 2 was located roughly in the middle of the catchment with an even mix of hummocks dominated by grasses and sedges, hummocks dominated by *J. effusus* and hollows; site 3 was located in the riparian zone dominated by *J. effusus*. Site 3 is often referred to as the 'riparian zone' throughout the text. In total, measurements were made from 21 chambers; 9 within site 1, 9 within site 2, and 3 within site 3.

The full study area was also separated into distinct microtopographic/vegetative classes: plots dominated by *C. vulgaris* (Calluna), hummocks dominated by sedges and grasses (Sedge/Hummock), hummocks dominated by *J. effusus* (Juncus/Hummock), and hollows dominated by mosses (Hollow). Within site 1, 3 chambers were positioned on each of Calluna, Sedge/Hummock, and Juncus/Hummock; within site 2, 3 chambers were positioned on each of Sedge/Hummock, Juncus/Hummock and Hollow; the 3 chambers within site 3 were all placed upon Juncus/Hummocks.

Flux measurements were made on all 21 chambers monthly from April 2006 until October 2007. An additional monthly measurement was made from each of the 9 chambers within site 2 from August 2006 until October 2007, leading to a fortnightly sampling frequency on 9 of the total 21 chambers, thus providing a better resolution

for examining temporal variability. Alongside flux measurements, soil temperature, moisture, water table depth and soil respiration were recorded and samples of soil atmosphere and soil water collected. Soil samples were collected monthly, though not on the same day as flux measurements.

2.3. Flux measurements

Flux measurements were made using the static chamber method described in Livingston and Hutchinson (1995). Polypropylene chamber bases were inserted into the soil to a depth of approximately 5 cm; the chamber bases remained *in situ* for the duration of the study. Lids consisted of a flexible, transparent, dome of polyethylene affixed to a polypropylene flange which could be securely attached to the chamber base during measurements (Clayton et al., 1994; MacDonald et al., 1996). The total enclosed volume was approximately 30 litres for chambers containing *J. effusus* and approximately 17 litres for all other chambers. Enclosure time generally ranged between 1-2 hours. As fluxes tended to be low, and direct sunlight or high temperatures rarely a problem at the site, up to 2 hours were required to collect gas at a sufficiently high concentration for accurate analysis. No significant levelling off of emissions was observed in the chambers with the highest recorded fluxes. Ambient air samples were collected at time zero with a further two samples of chamber air collected at the mid-point and end of the enclosure period. Air samples were stored in tedlar bags for up to one week prior to analysis using an HP5890 Series II gas chromatograph (detection limits: CO_2 < 199 μl l^{-1} (ppmv), CH_4 < 1.26 μl l^{-1}, N_2O < 0.2 μl l^{-1}) with electron capture (ECD) and flame ionisation detectors (FID) for N_2O and CH_4, respectively. Fluxes were calculated as the observed rate of concentration change times the enclosure volume to ground surface area ratio.

158 *2.4. Auxiliary measurements*

159 Soil temperature and moisture (mean of three theta probe readings) were
160 recorded adjacent to each chamber during flux measurements. Soil respiration
161 measurements were also made adjacent to each flux chamber using a PP-systems
162 SCR-1 respiration chamber attached to an EGM-4 infra-red gas analyser. The
163 chamber was attached to a plastic collar inserted ~5 cm into the soil to achieve an
164 airtight seal and allow repeated measurements to be made in the same place. Soil
165 atmosphere wells were created by inserting Accurel© water tight, gas permeable
166 tubing (Gut et al., 1998) into the soil from 10 to 40 cm depth adjacent to each
167 individual chamber before the study began. Air samples were then drawn from the
168 Accurel each time chamber measurements were made and analysed for CO_2, CH_4 and
169 N_2O; CO_2 was measured on the same gas chromatograph as CH_4 and N_2O using the
170 FID with attached methanizer. Water table depth was measured and water samples
171 collected from dip wells consisting of perforated pipes (4 cm diameter) inserted
172 adjacent to each chamber. Water samples were analysed for DOC and DIC on a
173 Rosemount-Dohrmann DC-80 total organic carbon analyser (detection range 0.1 to
174 4000 mg l^{-1}), using ultraviolet oxidation and sparging with N_2 to remove acidified
175 inorganic carbon; NO_3 and NH_4 were analysed on a dual channel CHEMLAB
176 continuous flow colorimetric analyser (detection range NH_4-N: 0.25 to 3.0 mg l^{-1};
177 NO_3-N: 0.25 to 5.0 mg l^{-1}).

178 Soil was collected from approximately 5 to 30 cm depth using a soil auger; 3
179 samples from within 0.5 m of each chamber were combined. A sub-sample of soil was
180 analysed for pH and the remainder frozen within 24 hours of collection for later
181 extraction with KCl and water for NO_3, NH_4 and DOC. Extracts were analysed

182 alongside the soil solution samples. Percent moss, grass, sedge and rush were visually
183 estimated for each individual chamber at the end of the study period.

184 In addition to the above manual measurements, continuous measurements of
185 air temperature, soil temperature at 5, 10, 20 and 40 cm depth, air pressure (mb),
186 photosynthetically active radiation (PAR, μmol m^{-2} s^{-1}) and net radiation (W m^{-2}),
187 were measured in the catchment at the EMEP flux tower site (Coyle, unpublished
188 data, 2008) and utilised in temporal regression models.

189 *2.5. Statistical analysis*

190 Monthly measurements of all 21 chambers (plus auxiliary data) were used in
191 the analyses of spatial variability. The data was separated prior to analysis into 3
192 periods: growing season 2006, winter period 2006-2007 and growing season 2007
193 (Figure 1). The growing season was from April until October. Mean daily CH_4 and
194 N_2O fluxes were calculated by integration over each season. The seasonal arithmetic
195 mean was used to describe temperature, soil respiration, pH, water table depth, soil
196 moisture and soil extractable NO_3, NH_4 and DOC. However, due to the skewed
197 distribution of the data, the geometric mean was used to describe soil solution NO_3,
198 NH_4, DOC and DIC, and soil atmosphere CO_2, CH_4 and N_2O concentrations. Where
199 mean values are quoted, ± refers to the standard error of the mean unless otherwise
200 stated.

201 As the CH_4 fluxes from Juncus/Hummock chambers in the riparian zone (site
202 3) were highly and significantly different from the Juncus/Hummock chambers in
203 both site 1 and site 2 ($F = 18.6$, $P < 0.01$), they were separated into a distinct class
204 (Riparian). Chamber types (Calluna, Hollow, Sedge/Hummock, Juncus/Hummock

and Riparian) were then compared using ANOVA tests after transformation to fit the normal distribution. Quoted test results refer to Pillai's test statistic (Townend, 2002) unless otherwise stated. Correlations were tested using Spearman's rank correlation. A combination of best subsets and backward selection stepwise regression was used to model CH_4 and N_2O fluxes using the full list of auxiliary data. Log transformations were performed to normalise positively skewed data; an arcsine transformation was applied to soil moisture values. Variables with $P > 0.05$ were allowed to remain in the final model if their exclusion resulted in a significant rise in the full-model *P*-value.

Fortnightly measurements of the 9 chambers within site 2 (plus auxiliary data) were used for the analysis of temporal variability. The data were separated, prior to analysis, by chamber type (Hollow, Sedge/Hummock, Juncus/Hummock). As before, best-fit models for both CH_4 and N_2O emissions were created using a combination of best-subsets and backward selection stepwise regression.

3. Results

Over the full study period the mean of the integrated CH_4 fluxes within the groups Calluna, Hollow, Sedge/Hummock, Juncus/Hummock and Riparian were 8.12, 20.61, 2.30, 4.73 and 586 $\mu g\ m^{-2}\ h^{-1}$, respectively (Table 1). Mean N_2O fluxes across the same groups were 1.52, -1.18, 2.02, -0.68 and 3.87 $\mu g\ m^{-2}\ h^{-1}$, respectively (Table 1). Overall group was not a significant factor explaining either CH_4 or N_2O flux variability, however significant differences between specific groups are considered in more detail below.

3.1. Spatial variability

Influence of microtopographic/vegetative group

The mean CH_4 flux from all chambers was 89.8 μg m^{-2} h^{-1}; the median, maximum and minimum were 0.72, 990 and -25.6 μg m^{-2} h^{-1}, respectively. The coefficient of variation in integrated means across the 21 individual chambers was 300%. However, the distribution of the CH_4 flux data was heavily skewed towards 2 chambers in the riparian zone with means an order of magnitude higher than the rest of the chambers. As well as containing the 2 highest integrated means, the 3 chambers situated within the riparian zone also contained the minimum integrated mean value. Excluding the 3 chambers in the riparian zone (site 3), the new mean, median, maximum and minimum were 7.13, -0.98, 69.2 and -12.7 μg m^{-2} h^{-1}, respectively. However, by excluding the riparian zone chambers, the coefficient of variation was only reduced to 284%. The N_2O fluxes were much smaller and more variable than the CH_4 fluxes, and followed a more normal distribution. The mean, median, maximum and minimum N_2O fluxes across all chambers were 0.99, -0.36, 9.91 and -4.25 μg m^{-2} h^{-1}, respectively. The coefficient of variation in integrated means was 410%.

Variables which showed significant ($P < 0.05$) or near-significant ($P < 0.10$) differences across microtopographic/vegetative groups included pH, water table depth, soil extractable NH_4 and DOC, soil solution DOC, NO_3 and NH_4 and soil atmosphere CH_4, CO_2 and N_2O concentrations (Table 1). The Riparian chambers in particular showed characteristics distinct from the other groups (Table 2), of which the greatest difference was in pH; the mean pH across Riparian chambers was 5.83 compared to a mean of 4.18 for all other groups combined.

Over the full study period, only the Riparian chambers, when compared to each alternative group separately, showed significantly different CH_4 fluxes ($P < 0.01$). CH_4 fluxes from the riparian zone were consistently higher, with a mean more

252 than an order of magnitude greater than the other groups (Table 1). A similar pattern
253 was observed in below ground CH_4 concentrations, with concentrations increasing in
254 the order Sedge/Hummock < Juncus/Hummock < Hollow < Calluna < Riparian
255 (Table 1). When the full dataset was considered collectively, the Spearman's rank
256 correlation between emissions and below-ground concentrations was not significant at
257 the 95% confidence limit ($t = 2.54$, $P = 0.08$). However, when separated by season the
258 results were significant in all cases (growing season 2006: $t = 3.29$, $P < 0.01$; winter
259 season: $t = 2.20$, $P < 0.05$; growing season 2007: $t = 2.45$, $P < 0.05$). During growing
260 season 2006, only the Riparian group had a net CH_4 emission; however, due to high
261 within group variability the difference from the other groups was not statistically
262 significant. Net uptake was greatest in the Juncus/Hummock group followed by the
263 Sedge/Hummock, Hollow and finally the Calluna chambers (Figure 2a). During the
264 winter season, both the Hollow and Riparian chambers were statistically similar,
265 showing much greater fluxes than the other groups (Figure 2b). In contrast to growing
266 season 2006, when all but the Riparian chambers displayed a net uptake, net
267 emissions were measured from all chambers during growing season 2007; again
268 Riparian fluxes were significantly higher than fluxes from the other chamber types.

269 A series of ANOVA tests were carried out comparing the conditions in the
270 Riparian group (site 3) with all other chambers combined into a single group (Table
271 2). Apart from high CH_4 concentrations and emissions, the riparian zone was
272 characterized by high soil respiration, pH and soil solution DIC concentrations
273 relative to the rest of the sites. With the exception of the Juncus/Hummock group, the
274 Riparian soil also contained significantly less extractable DOC than the other chamber
275 types (Table 1).

The N_2O fluxes were more variable and approximately one order of magnitude lower than CH_4 fluxes. No significant differences were observed between groups when the full dataset was used. Again, no significant group effect was evident during the 2006 growing season (Figure 3a), with standard error bars crossing the x-axis in all but the Hollow and Juncus/Hummock groups, which both showed net N_2O uptake. During the winter season (Figure 3b) a net uptake was measured in the Hollow chambers, in contrast to the net emissions measured in both the Sedge/Hummock and Juncus/Hummock groups. All groups displayed a net emission during growing season 2007 (Figure 3c) with emissions from the Riparian chambers significantly greater than any other group.

Modelling spatial variability

Using best subset multiple regression on the full dataset (n = 21), spatial variability in CH_4 fluxes could be modelled with an r^2 of 0.81 ($P < 0.01$) using the variables soil moisture and soil CH_4 concentration. When separated by season, soil CH_4 concentration was the major variable evident in all models (data not shown). However, the model was highly influenced by the chambers situated in the riparian zone and therefore not applicable to the rest of the catchment. Model fitting was repeated after excluding the 3 chambers in the riparian zone (Table 3). Over the full study period an r^2 of 0.46 was achieved using the variables percent sedge cover, pH, water extractable DOC, soil solution DIC and soil moisture. The variability in CH_4 flux during growing season 2006 was well modelled ($r^2 = 0.80$), with emissions increasing in response to a lower proportion of rushes, a decrease in the depth of the water table and concentration of soil NO_3, and an increase in soil moisture, soil solution DOC and below-ground CH_4 concentration (Table 3b). Variability in CH_4

300 emissions during the winter season was modeled ($r^2 = 0.36$, $P = 0.05$), with negative
301 correlations between CH_4 emission and soil respiration and soil solution DIC, and
302 positive correlations with percent moss cover and below-ground CH_4 concentration
303 (Table 3c). Lastly, the best model for emissions during growing season 2007 ($r^2 =$
304 0.45, $P = 0.02$) included percent sedge cover (negative) and soil pH (positive) (Table
305 3d).

306 Although water table position appeared only in the 2006 growing season
307 model (Table 3b), the maximum CH_4 emissions recorded on each sampling occasion
308 often occurred where the water table was closest to the surface. Within all 21
309 chambers 3 chambers repeatedly ranked in the top 3 CH_4 emitters, the same 3
310 chambers repeatedly ranked among the 3 highest water tables and 3 highest soil
311 moisture contents. For example, one of the chambers within the riparian zone ranked
312 within the top 3 CH_4 emitters on 94% of sampling occasions, the same chamber
313 ranked among the top 3 highest water tables on 89% of sampling occasions.

314 Spatial variability in N_2O emissions amongst all chambers over the full study
315 period, was best modeled using only soil respiration ($r^2 = 0.28$, $P < 0.01$). Excluding
316 the riparian chambers from the analysis, soil respiration was no longer significant and
317 the best model ($r^2 = 0.25$, $P = 0.05$) was achieved by including a negative correlation
318 with pH and a positive correlation with below-ground N_2O concentration (Table 3a);
319 however neither pH nor below-ground N_2O concentration was individually significant
320 at the 95% confidence limit. Other variables which appeared in the seasonal models
321 included soil CO_2 concentration (winter season: $t = -3.66$, $P < 0.01$) and soil solution
322 DOC (growing season 2007: $t = 2.27$, $P < 0.05$).

323 *3.2. Temporal variability (Site 2)*

Temporal variability in CH_4 emissions from all 9 chambers at site 2 was best modeled ($r^2 = 0.55$, $P < 0.01$) using the variables soil moisture and soil temperature at 40 cm depth (Table 4a). The mean (± SE) Q_{10} across all 9 chambers was 4.16 ± 0.96. Having separated the chambers by group, both the Hollows ($r^2 = 0.68$, $P < 0.01$) and Juncus/Hummocks ($r^2 = 0.41$, $P < 0.01$) responded negatively to soil respiration (Table 4b and d). However, in the Hollow group water table depth and soil temperature were also important. The primary drivers of emissions in the Sedge/Hummock plots appeared to be soil moisture and again soil temperature (Table 4c). Neither the Sedge/Hummock nor the Juncus/Hummock plots appeared to be affected by changes in water table depth.

Temporal variability in N_2O emissions across all plots (Table 4a) was poorly captured; the best achievable model gave $r^2 = 0.18$ ($P < 0.05$). Again both soil respiration, to which emissions were negatively correlated, and soil temperature at 40 cm depth appeared as primary variables using both the full 9 chambers and the Juncus/Hummock group alone. The mean (± SE) Q_{10} across the 9 chambers was 7.12 ± 1.25. Variability in emissions was best captured in the Hollow chambers where water table depth and soil moisture, in addition to soil respiration, were significant factors (Table 4b); N_2O emissions increased in response to near-surface water tables and increasing soil moisture contents. Soil moisture was again significant in the Sedge/Hummock plots (Table 4c). Although soil temperature alone was not significant, its exclusion from the model increased the overall model *P*-value above 0.05 and was therefore included.

4. Discussion

4.1. Importance of emission hotspots and spatial variability to up-scaling

348 Using an unsupervised, ground-truthed, classification of a Quickbird satellite
349 image taken in May 2006 (Dinsmore, data not shown, 2008), and assuming a riparian
350 zone spanning approximately 3 m either side of the Black Burn stream, the percent
351 cover within the catchment of Calluna, Hollow, Sedge/Hummock, Juncus/Hummock
352 and Riparian zone were estimated as 10%, 29%, 29%, 28% and 0.6%, respectively.
353 Weighting the above means accordingly, and assuming values are representative of
354 the mean daily emission, the mean catchment fluxes of CH_4 and N_2O from April 2006
355 until October 2007 were 291 and 5.12 $\mu g\ m^{-2}\ d^{-1}$, or 1.06 and 0.019 $kg\ ha^{-1}\ y^{-1}$,
356 respectively. Ignoring the different groups and treating the chambers as replicates
357 gave mean fluxes for CH_4 and N_2O of 2156 and 23.6 $\mu g\ m^{-2}\ d^{-1}$, respectively, or 171
358 and 12.1 $\mu g\ m^{-2}\ d^{-1}$ if the riparian chambers were excluded. With the riparian
359 chambers included, treating the chambers as replicates significantly overestimated
360 CH_4 emissions, whilst excluding them led to an underestimation of emissions. N_2O
361 emissions were overestimated with or without the riparian chambers included. Both
362 CH_4 and N_2O fluxes calculated in this study are at the low end of literature values for
363 peatland systems (Regina et al., 1996; MacDonald et al., 1997; Hargreaves and
364 Fowler, 1998; Laine et al., 2007; McNamara et al., 2008). This is most likely due to
365 the relatively shallow peat layer underlying the chambers limiting CH_4 production and
366 low nitrate availability restricting denitrification.

367 The riparian zone alone contributed ~12% of the total catchment CH_4
368 emission, highlighting the importance of identifying and including emission hotspots
369 in catchment budgets even if they cover only a small proportion of the overall area, a
370 result also found by McNamara et al. (2008). Even after separating the chambers into
371 groups to minimize spatial variability, the uncertainty within each group was still
372 large. Furthermore, the exact weight given to each group in the final catchment

calculation has significant uncertainties. By sequentially changing the percent cover estimates by plus or minus 10% and evenly distributing the difference among the remaining groups, the total catchment CH_4 and N_2O means varied by up to 36% and up to 38% respectively. Despite the large measured fluxes, due to the relatively small area of the riparian zone, a 10% error in its relative size altered the final catchment mean by the least amount (CH_4 2.86%, N_2O 0.97%).

4.2. Controls on spatial variation

Clear differences in CH_4 emissions were observed both between the growing seasons and the winter season, and between the growing seasons in 2006 and 2007, respectively (Figure 2). The differences were less pronounced for N_2O fluxes, primarily due to the very large variation seen across all chamber types within seasons (Figure 3). The most striking difference between groups was the consistently large CH_4 emissions and below-ground CH_4 concentrations measured in the riparian chambers. Although DOC, often quoted as the primary substrate for methanogenic bacteria (Segers, 1998), was low in the riparian zone (247 μg C g^{-1}) compared to the rest of the catchment (386 μg C g^{-1}), the pH was significantly higher (Riparian 5.83, Catchment 4.81), hence closer to the methanogenic optima of ~7 (Segers, 1998). Studies have repeatedly reported an increase in potential CH_4 production in response to increased pH (Yavitt et al., 1987; Dunfield et al., 1993; Valentine et al., 1994). The depth of the water table at the riparian site was not significantly higher than the rest of the catchment due to extremely high variability among the 3 riparian chambers. However, in 2 of the 3 riparian chambers water table was repeatedly in the top 3 highest. In particular, one of the chambers, which was also in the top 3 highest CH_4 emitters on 94% of sampling occasions, had the highest water table on 89% of

occasions. Even during the relatively dry summer of 2006 when catchment water tables were drawn down to an average of almost 50 cm below the soil surface, the water table at this chamber remained within 18 cm of the surface.

Among the variables included in the CH_4 flux spatial variation models (Table 3) were pH, DOC, water table depth and soil moisture. The correlation with water table depth has been well documented in previous studies (Moore and Dalva, 1993; Aerts and Ludwig, 1997; Hargreaves and Fowler, 1998; MacDonald et al., 1998; Dinsmore et al., in press). Soil moisture is strongly linked to water table depth and may act as an indication of not only current but also antecedent water levels. Therefore in some cases soil moisture represents a better indicator of CH_4 emission than an instantaneous water table measurement. The effect of water table depth on CH_4 emissions was only significant during growing season 2006, when it ranged from approximately 5 to 50 cm below the peat surface. Similarly Shannon and White (1994) found that water table was only important in one of 3 annual cycles, corresponding to the year with the greatest range of water table depths (15cm – 50 cm). Soil respiration represents a measure of aerobic microbial activity and thus is likely to correlate strongly with rates of CH_4 oxidation, hence the negative correlation with emissions during the winter season.

During the growing seasons CH_4 emissions were negatively correlated to the frequency of either rushes or sedges inside the chambers (Table 3b and d). Although contrary to much of the current literature which suggests the presence of aerenchyma containing vegetation (i.e. rushes and sedges) increases emissions (Shannon et al., 1996; Yu et al., 1997; Greenup et al., 2000), a similar result to that observed here was found in an earlier study with mesocosms collected from Auchencorth Moss

421 (Dinsmore et al., in press). As well as providing a source of readily available organic
422 substrate, plants containing aerenchymous tissue can provide a direct pathway for
423 many greenhouse gases to the atmosphere, bypassing the aerobic surface horizon and
424 therefore reducing the potential for oxidation (Bartlett and Harriss, 1993; Minkkinen
425 and Laine, 2006). However, studies have also shown that aerenchyma can transport
426 O_2 into the rhizosphere and can significantly alter the redox state of the surrounding
427 peat (Visser et al., 2000; Wiebner et al., 2002). Similarly, Arah and Stephen (1998)
428 found that increasing root-mediated transport in a CH_4 flux model led to a decrease in
429 simulated CH_4 emissions, due to the increase in oxidation outweighing the positive
430 influence of increased CH_4 transport.

431 For emissions to increase via plant-mediated transport, roots must penetrate
432 areas of high CH_4 production, thought to occur ~15-20 cm below the water table
433 (Daulat and Clymo, 1998; Kettunen et al., 1999), and bypass the surface oxidizing
434 peat layer. As the water table was drawn down to almost 50 cm during much of the
435 2006 growing season, and repeatedly to similar low levels during 2007, it is likely that
436 no significant reservoir of CH_4 was present in the shallow peat for plant roots to tap
437 into. Roura-Carol and Freeman (1999) suggest that the radial loss of O_2 from plant
438 roots is likely to be dependent on photosynthetic activity. Rhizospheric oxidation is
439 therefore likely to be minimal during the winter when plants are relatively inactive,
440 and this may explain the lack of an aerenchymous vegetation variable in our winter
441 season model (Table 3c). In the riparian zone where water table levels remained high
442 throughout the growing season and high below-ground CH_4 concentrations were
443 evident, the effect of plant-mediated transport may outweigh rhizospheric oxidation.
444 However, this could not be tested in this study as all our riparian chambers included *J.*
445 *effusus*.

446 N_2O emissions were negatively correlated ($P < 0.1$) with soil pH in both the
447 full study period and the growing season 2006 models (Table 3a and b).The optimum
448 pH from denitrifiers is often thought to be between approximately 6.5-8.0 (Knowles,
449 1981; Šimek and Cooper, 2002), therefore any increase above the mean catchment pH
450 of 4.18 should theoretically increase N_2O production. However the partitioning of
451 N_2O and N_2 is also influenced by pH with a higher proportion of N_2O in more acid
452 conditions (Šimek et al., 2002). Soil pH was also strongly negatively correlated with
453 both soil extractable NO_3 ($r = -0.61$, $P < 0.001$) and soil extractable NH_4 ($r = -0.75$, P
454 < 0.01) concentrations over the same period. Therefore the reduction of N_2O
455 emissions at higher pH values could also have occurred as an indirect response to low
456 soil nitrogen availability.

457 *4.3. Drivers of temporal variation (site 2)*

458 Considering all 9 plots within site 2 where measurements were made
459 fortnightly, the main drivers of temporal variability in CH_4 emissions appeared to be
460 soil moisture and soil temperature (Table 4a). The temporal response in CH_4
461 emissions to variations in temperature is consistent with previous studies (Frolking
462 and Crill, 1994; Shannon and White, 1994; Laine et al., 2007) and the mean Q_{10} of
463 4.16 is similar to values previously reported for a different Scottish peatland
464 (MacDonald et al., 1998). Soil temperature was also an important driver of temporal
465 N_2O dynamics with a very high Q_{10} of 7.12, and an apparent switch from
466 consumption to production at approximately 8ºC (data not shown). A very similar
467 result was observed by Dinsmore et al. (in press) in mesocosms collected from
468 Auchencorth Moss, where a switch from consumption to production was recorded
469 between approximately 7.5 and 8.5ºC. However, as was also the case in Dinsmore et

al. (in press), N_2O fluxes are low and variability high, so further work is required to assess the significance of this switch.

Net CH_4 flux is dependent on the balance between oxidation and production processes. As the temperature response in methanogens is generally greater than that of methanotrophs (Segers, 1998), the overall effect on net emissions is positive. Where temperature is a significant driver of variability, as in both Hollow and Sedge/Hummock chambers, it suggests that variability is due primarily to changes in methanogen activity rather than oxidation. However the primary correlate with net emissions in the Juncus/Hummock plots was soil respiration, itself likely to be an indicator of aerobic microbial activity, and as such linked to potential oxidation. The dominance of oxidation in controlling emission variability in the Juncus/Hummock plots may be due to potential methanogenesis being limited by lower substrate availability, possibly reflected in the lower concentrations of extractable DOC in the Juncus/Hummock chambers (Table 1). Hence the controls on temporal changes in CH_4 emissions appear to be variable across the site.

Although significant changes in water table depth (e.g. drainage or drain blocking) have repeatedly been shown to strongly influence CH_4 emissions (Alm et al., 1999; Strack et al., 2004), a much weaker relationship is often observed with temporal water table variability in the field (Frolking and Crill, 1994; Shannon and White, 1994). In our study water table was a significant correlate only in the Hollow chambers, although soil moisture, which may provide a better measure of both current and antecedent soil water conditions, was also included in the Sedge/Hummock model. The presence of aerenchyma containing vegetation in the Sedge/Hummock and Juncus/Hummock chambers might have partially off-set any increase in CH_4

emissions associated with a rise in water table by increasing oxidation in the rhizosphere. Again the drivers of temporal variability do not appear consistent across the site; hence differences between studies in the importance of water table as a driver of variability may be caused in part by differences in site-specific vegetation cover.

4.4. Conclusions

CH_4 emissions varied considerably across the catchment, with the riparian zone representing a significant hotspot. High emissions also appeared to be linked to areas with consistently near-surface water tables. Contrary to many previous studies, the presence of either sedges or rushes containing aerenchymous tissue decreased net CH_4 emissions during the 2 growing seasons. Upscaling the calculated fluxes using vegetation cover estimates from a satellite image, gave mean catchment CH_4 and N_2O emissions of 291 μg CH_4 m^{-2} d^{-1} and 5.12 μg N_2O m^{-2} d^{-1}, although these values are extremely sensitive to error in the cover estimates. Hence it is important when planning future studies to identify the presence of significant emission hotspots, such as the riparian zone or areas with a consistently near-surface water table, prior to experimental set-up.

The drivers of temporal variability were not consistent across the study site. The within-site differences in drivers found at Auchencorth Moss, possibly linked in this case to vegetation and substrate availability, may partially explain the discrepancies between previous studies. Depending on the heterogeneity of the site, creating a number of spatially distinct integrated models which are parameterized independently, may be more accurate than using a single model based on averaged catchment values.

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664

665 **Table 1** Mean ± SE of data from full study period, separated by chamber type. *P*-
666 values from ANOVA's testing for significant between group differences are indicated
667 by asterisks where * and ** refer to $P < 0.05$ and $P < 0.01$, respectively; † indicates that
668 the result was not significant but had $P < 0.10$.

	Calluna	Hollow	Sedge/Hummock	Juncus/Hummock	Riparian
CH_4 (μg m^{-2} h^{-1})	8.12 ± 5.77	20.6 ± 24.3	2.30 ± 6.47	4.73 ± 6.52	586 ± 311
N_2O (μg m^{-2} h^{-1})	1.52 ± 3.34	-1.18 ± 1.49	2.02 ± 1.97	-0.68 ± 1.36	3.87 ± 1.35
Soil respiration (g m^{-2} h^{-1})	0.29 ± 0.04	0.24 ± 0.01	0.28 ± 0.02	0.37 ± 0.11	0.45 ± 0.06
Soil pH **	3.74 ± 0.01	4.54 ± 0.09	4.03 ± 0.12	4.41 ± 0.07	5.83 ± 0.28
Water table depth (cm) †	-20.7 ± 0.89	-18.5 ± 2.65	-27.2 ± 2.25	-27.8 ± 2.88	-23.4 ± 8.1
Soil moisture (m^3 m^{-3})	0.85 ± 0.04	0.88 ± 0.02	0.85 ± 0.02	0.85 ± 0.02	0.88 ± 0.04
Soil extractable NO_3 (μg N g^{-1})	5.08 ± 0.90	3.14 ± 1.05	4.38 ± 0.91	3.61 ± 0.45	4.57 ± 2.41
Soil extractable NH_4 (μg N g^{-1}) **	42.9 ± 0.95	18.0 ± 3.31	21.7 ± 2.76	18.9 ± 0.73	24.8 ± 10.5
Soil extractable DOC(μg C g^{-1}) *	595 ± 56	301 ± 57	410 ± 59	239 ± 11	247 ± 154
Soil solution NO_3 (mg N l^{-1}) †	0.17± 0.02	0.12 ± 0.02	0.12 ± 0.01	0.14 ± 0.01	0.15 ± 0.04
Soil solution NH_4 (mg N l^{-1}) **	0.58 ± 0.17	0.08 ± 0.01	0.23 ± 0.03	0.17 ± 0.03	0.14 ± 0.04
Soil solution DOC (mg C l^{-1}) *	33.0 ± 5.67	17.0 ± 0.92	23.8 ± 2.09	22.6 ± 2.84	17.3 ± 1.38
Soil solution DIC (mg C l^{-1})	2.24 ± 0.20	2.59 ± 0.51	2.76 ± 0.28	2.70 ± 0.31	3.88 ± 1.06
Soil CH_4 concentration (μl l^{-1}) **	9.35 ± 5.27	5.52 ± 1.13	2.73 ± 0.29	3.13 ± 0.41	48.2 ± 31.7
Soil CO_2 concentration (μl l^{-1}) *	4490 ± 894	3850 ± 802	2680 ± 411	3150 ± 535	2890 ± 538
Soil N_2O concentration (μl l^{-1})	0.35 ± 0.01	0.36 ± 0.02	0.44 ± 0.05	0.44 ± 0.03	0.37 ± 0.04

669

Table 2 Results from ANOVA tests describing variables which make Riparian chambers distinct from all other groups combined. Arrows indicate whether variable is higher or lower in Riparian chambers.

Variable		F	*P*-value
CH_4 flux	↑	18.55	< 0.01
Soil respiration	↑	3.94	< 0.01
pH	↑	52	< 0.01
Soil extracted DOC	↓	3.51	0.08
Soil solution DIC	↑	5.33	0.03
Soil CH_4 concentration	↑	13.30	< 0.01

673 **Table 3** Results from best subset multiple regression model describing the spatial
674 variation in CH_4 and N_2O fluxes with the riparian chambers excluded across a) the
675 full dataset, b) growing season 2006, c) the winter season 2006-07 and d) growing
676 season 2007.

CH_4 flux			N_2O flux		
Variable	t	*P*	Variable	t	*P*
a) Full study period					
(r^2 = 0.46; *P* = 0.03)			(r^2 = 0.25; *P* = 0.05)		
Intercept	---	---	Intercept	---	---
Sedges (%)	-1.37	0.10	pH	-1.94	0.07
pH	2.39	0.03	Soil N_2O concentration	1.81	0.09
Extractable DOC	2.22	0.05			
Soil solution DIC	-2.50	0.03			
Soil moisture	1.92	0.08			
b) Growing season 2006					
(r^2 = 0.80; *P* < 0.01)			(r^2 = 0.14; *P* = 0.07)		
Intercept	---	---	Intercept	---	---
Rushes (%)	-4.04	< 0.01	pH	-1.93	0.07
Water table depth	-2.52	0.03			
Soil moisture	6.04	< 0.01			
Extractable NO_3	-3.54	< 0.01			
Soil solution DOC	2.65	0.02			
Soil CH_4 concentration	2.48	0.03			
c) Winter season 2006-07					
(r^2 = 0.36; *P* = 0.05)			(r^2 = 0.44; *P* < 0.01)		
Intercept	---	---	Intercept	---	---
Soil respiration	-2.28	0.04	Soil CO_2 concentration	-3.66	< 0.01
Soil solution DIC	-2.65	0.02			
Soil CH_4 concentration	2.70	0.02			
Mosses (%)	2.36	0.04			
d) Growing season 2007					
(r^2 = 0.45; *P* = 0.02)			(r^2 = 0.65; *P* < 0.01)		
Intercept	---	---	Intercept	---	---
Sedges (%)	-2.07	0.06	pH	2.58	0.02
pH	2.07	0.02	Soil solution DOC	2.27	0.04
			Soil N_2O concentration	1.69	0.12

677 **Table 4** Results from best subset multiple regression model describing the temporal
678 variation in CH_4 and N_2O fluxes across a) all chambers within site 2 (n = 9), b)
679 Hollow chambers within site 2 (n = 3), c) Sedge/Hummock chambers within site 2 (n
680 = 3) and d) Juncus/Hummock chambers within site 2 (n = 3)

CH_4 flux			N_2O flux		
Variable	t	*P*	Variable	t	*P*
a) All chambers					
($r^2 = 0.55$; $P < 0.01$)			($r^2 = 0.18$; $P = 0.03$)		
Intercept	---	---	Intercept	---	---
Soil moisture	5.85	< 0.01	Soil respiration	-2.67	0.01
Soil temperature (40 cm)	3.45	< 0.01	Soil temperature (40 cm)	1.76	0.09
b) Hollow					
($r^2 = 0.68$; $P < 0.01$)			($r^2 = 0.45$; $P < 0.01$)		
Intercept	---	---	Intercept	---	---
Soil respiration	-2.09	0.05	Soil respiration	-1.98	0.06
Water table depth	-6.13	< 0.01	Soil moisture	2.00	0.06
Soil temperature (5 cm)	4.59	< 0.01	Water table depth	-4.43	< 0.01
c) Sedge/Hummock					
($r^2 = 0.50$; $P < 0.01$)			($r^2 = 0.25$; $P = 0.01$)		
Intercept	---	---	Intercept	---	---
Soil moisture	5.13	< 0.01	Soil moisture	3.28	< 0.01
Soil temperature (40 cm)	3.85	< 0.01	Soil temperature (40 cm)	1.55	0.13
d) Juncus/Hummock					
($r^2 = 0.41$; $P < 0.01$)			($r^2 = 0.16$; $P = 0.04$)		
Intercept	---	---	Intercept	---	---
Soil respiration	-4.40	< 0.01	Soil respiration	-2.24	0.03
			Soil temperature (40 cm)	2.07	0.05

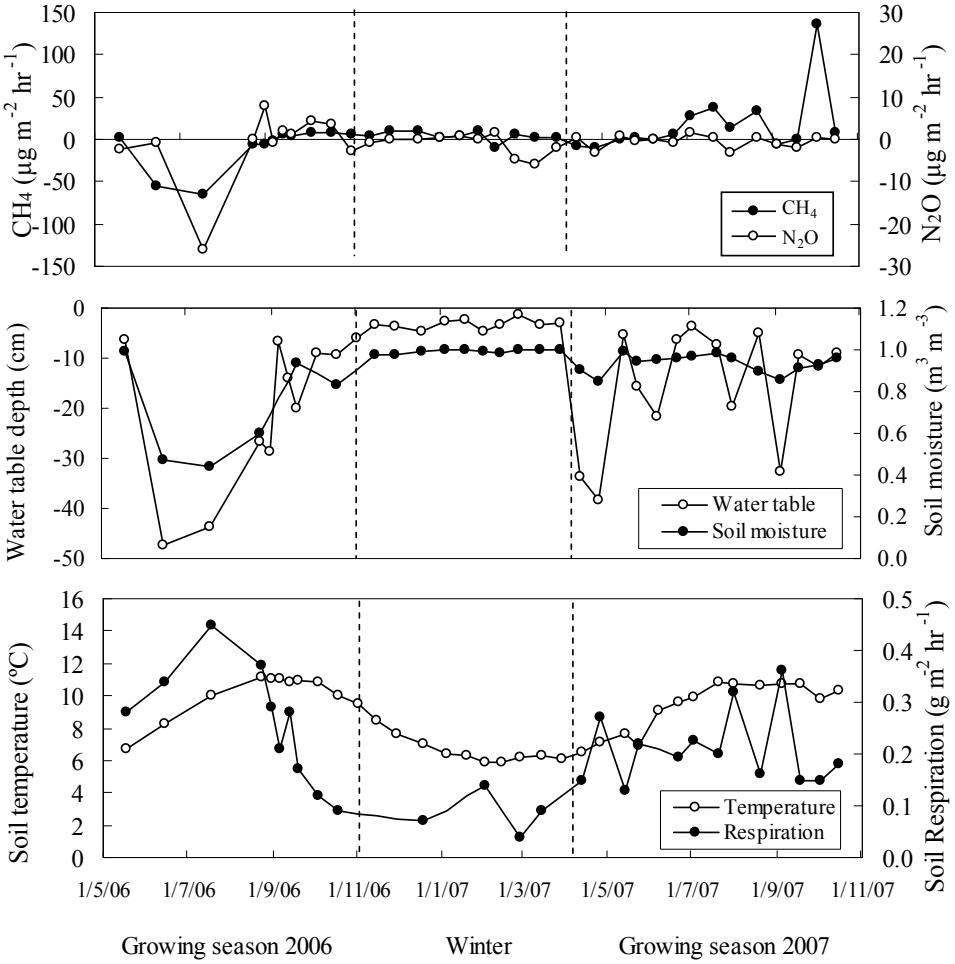
Figure Legends

Figure 1 Time series of a) median CH_4 and N_2O fluxes from 9 chambers at site 2, b) water table depth and soil moisture and c) soil temperature and respiration over the study period. The dashed lines separate the study into growing season 2006, winter period 2006-07 and growing season 2007, respectively

Figure 2 Mean integrated CH_4 flux during a) growing season 2006, b) the winter period and c) growing season 2007, separated by microtopographic/vegetative group. Error bars represent the standard error of the mean. Common letters indicate statistically similar fluxes ($P < 0.05$)

Figure 3 Mean integrated N_2O flux during a) growing season 2006, b) winter period 2006-07 and c) growing season 2007, separated by microtopographic/vegetative group. Error bars represent the standard error of the mean. Common letters indicate statistically similar fluxes ($P < 0.10$)

694 Figure 1



695

696 Figure 2
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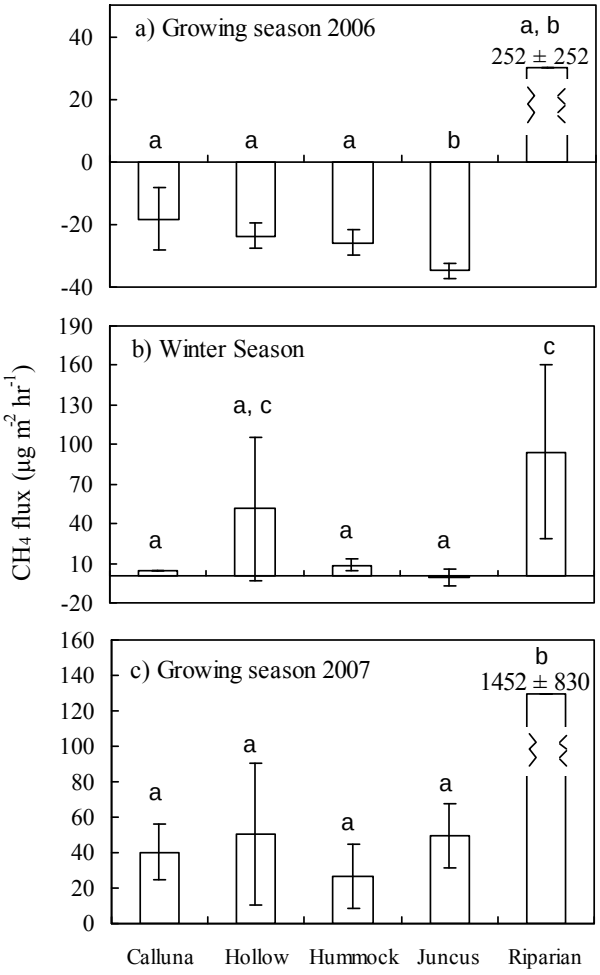

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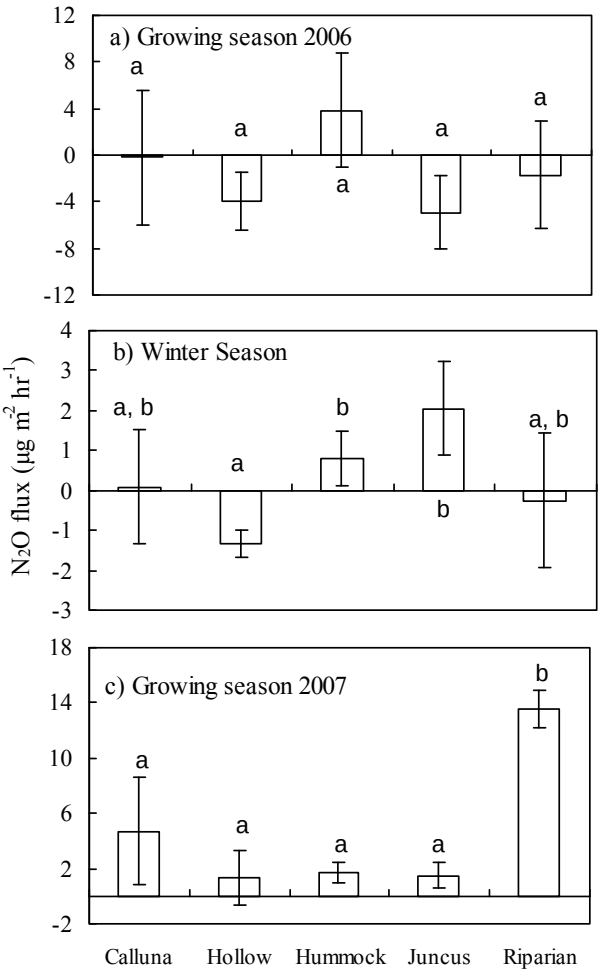
699 Figure 3



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