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Management Effects on Greenhouse Gas Dynamics in Fen Ditches

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Abstract

Globally, large areas of peatland have been drained through the digging of ditches, generally to increase agricultural production. By lowering the water table it is often assumed that drainage reduces landscape-scale emissions of methane (CH_4) into the atmosphere to negligible levels. However, drainage ditches themselves are known to be sources of CH_4 and other greenhouse gases (GHGs), but emissions data are scarce, particularly for carbon dioxide (CO_2) and nitrous oxide (N_2O), and show high spatial and temporal variability. Here, we report dissolved GHGs and diffusive fluxes of CH_4 and CO_2 from ditches at three UK lowland fens under different management; semi-natural fen, cropland, and cropland restored to low-intensity grassland. Ditches at all three fens emitted GHGs to the atmosphere, but both fluxes and dissolved GHGs showed extensive variation both seasonally and within-site. CH_4 fluxes were particularly large, with medians peaking at all three sites in August at 120-230 mg m^{-2} d^{-1}. Significant between site differences were detected between the cropland and the other two sites for CO_2 flux and all three dissolved GHGs, suggested that intensive agriculture has major effects on ditch biogeochemistry. Multiple regression models using environmental and water chemistry data were able to explain 29-59% of observed variation in dissolved GHGs. Annual CH_4 fluxes from the ditches were 37.8, 18.3 and 27.2 g CH_4 m^{-2} yr^{-1} for the semi-natural, grassland and cropland, and annual CO_2 fluxes were similar (1100 to 1440 g CO_2 m^{-2} yr^{-1}) among sites. We suggest that fen ditches are important contributors to landscape-scale GHG emissions, particularly for CH_4. Ditch emissions should be included in GHG budgets of human modified fens, particularly where drainage has removed the original terrestrial CH_4 source, e.g. agricultural peatlands.

Keywords: peatland, carbon dioxide, methane, nitrous oxide, ditch flux, restoration

1. Introduction

Northern peatlands store approximately 547 Pg of carbon (Yu *et al.*, 2010) and contribute to the global atmospheric balance of GHGs through the release and uptake of carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O). Intact peatlands are typically net sinks for CO_2, and sources of CH_4 and N_2O (Freeman *et al*., 1993, Nykänen *et al*., 1995, Smith *et al*., 2004, Kirschke *et al*., 2013). On a 100-year timescale CH_4 and N_2O have global warming potentials (GWP) of 28 and 298, respectively, relative to CO_2 (IPCC, 2013). Insights into biogeochemical cycling in peatlands are therefore important in developing understanding of global GHG dynamics and future climate change.

Globally, peatlands have been extensively drained for conversion to agriculture, forestry and peat extraction. Drained lowland fens, such as those of Eastern England, the Netherlands and the Southern Baltic coast are extremely fertile, and are therefore principally converted to intensive agricultural use (Morris *et al*., 2000). Conversion to agricultural use often includes strict hydrological management, such as the use of subsurface irrigation and, in part due to the long-term subsidence which is an inevitable consequence of peat drainage, the active pumping of water around fields (e.g. Morrison *et al*., 2013). There is now growing interest in the restoration of agricultural fens to wetlands (e.g. Höll *et al*., 2009, Peh *et al*., 2014), although there are strong commercial factors, as well as food security considerations, that favour their continued agricultural use (Glenk *et al*., 2014).

Drainage and conversion of fens to agricultural use has the capacity to alter the cycling of GHGs. It is generally considered that peatland drainage leads to a decrease in CH_4 emissions (to near-zero values), but increases in CO_2 and N_2O emissions (Glenn *et al*., 1993, Martikainen *et al*., 1995, Alm *et al.,* 1999, Haddaway *et al*., 2014). Upon draining, peatlands therefore become a diminishing carbon reservoir, releasing carbon into the atmosphere that was fixed over thousands of years.

CH_4 fluxes from drained peatlands were previously assumed to be insignificant (IPCC, 2006). However, a number of studies have shown that the ditches created during drainage can themselves be significant CH_4 sources (Best & Jacobs, 1997, Sundh *et al.,* 2000,

Minkkinen & Laine, 2006, Hendriks *et al.*, 2007, Hyvönen *et al.*, 2013), contributing 60-70% of total CH_4 emissions in one study (Schrier-Uijl *et al.*, 2010), over 84% in another (Teh *et al.*, 2011) and with measured fluxes as high as 366 mg CH_4 m^{-2} hr^{-1} (Schrier-Uijl *et al.*, 2010). Where the space between ditches is small, drainage could in theory actually result in a net increase in landscape-scale CH_4 fluxes compared to undrained sites (Roulet & Moore, 1995).

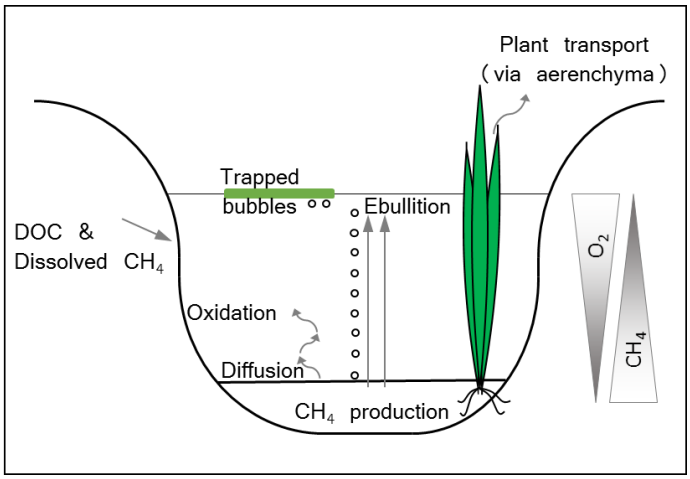


Figure 1. Schematic of methane transport pathways within ditch systems and surrounding peat.

Large ditch CH_4 fluxes are usually associated with productive, high-nutrient, sites with low water flow and high labile carbon inputs (e.g. agricultural grasslands; Best & Jacobs, 1997). Conversely, faster-flowing ditches in nutrient-poor upland bogs typically have small fluxes; Cooper *et al*. (2014) recorded an annual mean CH_4 flux of 59.7 kg CH_4 ha^{-2} y^{-1} from an open ditch in a blanket bog, and Sirin *et al*. (2012) measured a growing season flux of 9.9 mg CH_4 m^2 d^{-1} from ditches in a forested bog. A recent review found mean fluxes for different peat/land-use types varied from approximately 30 g CH_4 m^{-2} yr^{-1} in forest/semi-natural peatlands, to 200 g CH_4 m^{-2} yr^{-1} in tropical deforested peatlands (Evans et al., 2016a). It is important to recognise that methane emissions can occur via different pathways, and the rates of flux via these pathways will have different controls (fig.1). Diffusive/steady emissions result from the CH_4 concentration differential between the ditch and the atmosphere. Wetland plant aerenchyma may provide a chimney through which oxygen is transported into sediment and CH_4 escapes to the atmosphere. Finally, steady emissions may be punctuated by temporally and spatially heterogeneous ebullition, which can contribute significantly to net CH_4 fluxes (Vermaat *et al*., 2011). The importance of ditches in GHG cycling has therefore been recognised by the IPCC and incorporated into their guidelines (IPCC, 2014).

As well as CH_4, drainage ditches emit N_2O (Reay *et al*., 2003, Teh *et al.*, 2011, Hyvönen *et al*., 2013). Some ditches have been found to emit CO_2 (Best & Jacobs, 1997, Sundh *et al*., 2000, Teh *et al.*, 2011, Hyvönen *et al*., 2013), which others with emergent vegetation have sometimes been observed to fix CO_2 (e.g. Vermaat *et al*., 2011). However, whilst ditches appear to be consistent hotspots for CH_4 emissions, CO_2 and N_2O fluxes are of a considerably smaller magnitude in terms of their overall contribution to GHG emissions, and are typically more similar to fluxes from drained peat adjacent to ditches (Evans *et al*., 2016a). For example, Hyvönen *et al*. (2013) found ditches in a boreal cutaway peatland being used to cultivate *Phalaris arundinacea* contributed just 1% and 5% of total ecosystem emission of N_2O and CO_2.

Internationally, there is a lack of information on GHG emissions from drainage ditches; in a recent review of published studies, a total of just 19 studies were identified in which peatland CH_4 emissions had been reported, for a total of 69 individual peatland sites where CH_4 was measured (Evans et al., 2016a). The same analysis suggested that studies of CO_2 and N_2O are still too few to allow the data to be collated in a meaningful way. Just two studies to date have reported CH_4 fluxes from ditches in the UK. In contrast to this dearth of information on ditches, numerous studies have looked at GHG emissions associated with other freshwaters. For instance, Cole *et al*. (2007) noted that carbon emissions from lakes and rivers could be approximately 0.8 Pg C y^{-1}; enough to exert effects on regional budgets, despite these features occupying small areas. Similarly, Bastviken *et al*. (2011) suggested that CH_4 emissions from inland waters have the capacity to offset 25% of the terrestrial carbon sink, whilst Deemer et al. (2016) calculate that reservoirs emit 1.5% of global anthropogenic CO_2-equivalent emissions from CO_2, CH_4 and N_2O. Considering N_2O, rivers and estuaries could account for 20% of global anthropogenic emissions (Seitzinger & Kroeze, 1998).

To help address this knowledge gap, we carried out seasonal fieldwork for one year in ditches at three lowland fens in East Anglia, England. Each site was under a different management regime: 1) a semi-natural fen under conservation management; 2) former cropland that has been restored to extensive grassland, and; 3) intensive deep-drained cropland. We measured dissolved GHGs within ditches, diffusive fluxes of CO_2 and CH_4 from ditches, and a variety of physical ditch attributes and water chemistry determinands. Our

aim was to quantify the differences in GHGs between and within sites, and across seasons, and to attempt to elucidate the drivers behind GHG dynamics.

2. Materials and methods

2.1. Field sites

All three field sites were located in East Anglia, in Eastern England. This region was once the largest area of lowland fen peatland in the UK, covering several thousand square kilometres. Since the 17th century, drainage of the land resulted in the loss of most of the natural fenland, with only a handful of intact fragments remaining. The principal land use of the drained areas is intensive arable and horticultural agriculture. The drainage and conversion of the fens has resulted in extensive peat wastage, with much of the original deep peat area now reduced to a dense, thin intermixed organic and mineral layer (Hutchinson, 1980, Burton and Hodgson, 1987). The altitude of the land is close to (and in many areas below) sea level. Mean annual rainfall in the area is 574 mm, and mean annual temperature is 10.1 °C (data from UK Met Office station in Mepal, within 30 km of all study sites). The sites were:

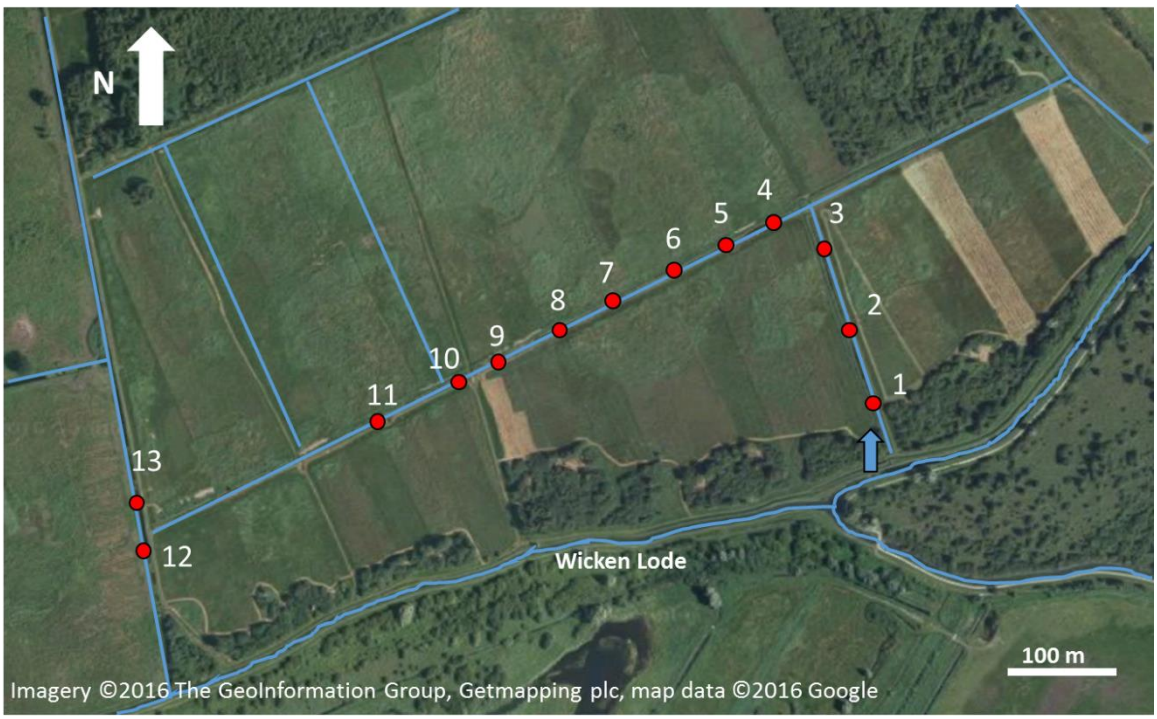
1. Sedge Fen (semi-natural fen). 52.31 N, 0.28 E. Area = 61 ha. Sedge Fen is part of the Wicken Fen National Nature Reserve. Peat depth is 3.8 m, bulk density is 0.37 g cm^{-3}, C/N is 15.8 (Evans *et al*., 2016b). Vegetation comprises reedbeds dominated by *Cladium mariscus* and *Phragmites australis*, with some *Phalaris arundinacea* and *Calamagrostis canescens* (Eades, 2016), as well as areas of fen carr dominated by *Rhamnus cathartica* and *Frangula alnus* (Rowell, 1986). The fen cannot be considered to be 'pristine' as it contains numerous internal ditches, and the reedbeds are cut on a three year rotation. However, the site contains vegetation and peat that is characteristic of an intact site, and has never been converted to other land-uses.

2. Baker's Fen (extensive grassland). 52.30 N, 0.29 E. Area = 56 ha. Baker's Fen is part of the wider Wicken Fen area. Historically, the fen was drained and used for arable agriculture, resulting in extensive peat wastage and loss of organic soil. Soil depth is now less than 50 cm, bulk density is 1.06 g cm^{-3}, C/N is 19.7 (Evans *et al*., 2016b), and organic content is low (measured as 13-18 % loss on ignition by Stroh *et al*., 2013). The site was removed from

153 arable use and re-seeded with an unknown "grass mixture" in 1995 and 1996, and is
154 undergoing "open-ended" restoration (Hughes *et al*., 2011); river water is pumped onto the
155 site in autumn and winter to inundate it, and highland cattle and wild horses graze it. Much
156 of the fen consists of species-poor, flood-plain pasture. Plant species vary across the site
157 according to variations in hydrology and nutrient status, but include *Carex otrubae,*
158 *Arrhenatherum elatius, Agrostis stolonifera, Cirsium arvense*, *Poa trivialis* and several *Juncus*
159 species (Eades, 2016). *C. mariscus* and *P. australis* occur in some of the ditches.
160
161 3. Rosedene (cropland). 52.52 N, 0.49 E. Field area = 8.7 ha. The cropland site consists of
162 ditches that surround a field near Methwold Hythe. The field is part of a much larger area (~
163 90 km^2) of drained fen that is now under intensive arable cultivation, and is bounded by
164 rivers and canals. Peat depth is 1 m, bulk density is 0.32 g cm^{-3}, and C/N is 15 (Evans *et al*.,
165 2016b). The hydrology of the site is highly managed; the fields contain subsurface pipes at 1
166 m depth to aid irrigation and drainage, and water is actively pumped round field perimeter
167 ditches in order to maintain water levels within the field, removing water during wet
168 periods and providing irrigation water during dry periods. During 2015, the study site was
169 used to cultivate celery (*Apium graveolens*). This site is 28 km from the other two sites.
170
171 All three sites formed part of a larger study of GHG emissions from a total of fifteen lowland
172 peatland sites at located across six regions of England and Wales, which included a broad
173 suite of eddy covariance and static chamber gas flux, hydrological and water quality
174 measurements. The results of this large-scale study are reported elsewhere (Evans et al.,
175 2016b).
176
177 *2.2. Sampling*
178 The sites were visited on four occasions in 2015 in March, May, August and October.
179 Because of proximity, the intact and restored site could be visited on the same day, whilst
180 the agricultural site was visited within three days. The sampling dates were as follows: 11th
181 March – semi-natural/grassland, 12th March – cropland; 5th May – semi-natural/grassland,
182 6th May – cropland; 17th August – cropland, 20th August – semi-natural/grassland; 12th
183 October – cropland, 15th October – semi-natural/grassland. At each site, ditch sampling
184 locations were selected with the aim of covering a large area, and were selected on a non-

random basis according to where measurements from the ditch could easily be taken. For the semi-natural site, we sampled along a 910 m length of ditch network (i.e. all sampling points were hydrologically connected) and then onto a ditch that bounded the edge of the fen (fig. 2). Similarly, all ditch locations at the grassland site were hydrologically connected, with a ditch distance of 1200 m between farthest sampling points. At the cropland site the ditch ran continuously round a field, with junctions connecting to other ditches at field corners. The sampling locations here ran for 1200 m. The number of sampling locations for each site was: semi-natural = 13, grassland = 11, cropland = 10. The same sampling locations were used for each of the four seasonal visits.

A range of measurements were taken at each sampling location. Environmental and physical measurements were: air temperature, water temperature, atmospheric pressure, and water depth. A 50 ml water sample for water chemistry analysis was collected in a polypropylene vial. A sample for dissolved GHG analysis was collected using the headspace method (Hope *et al*., 2004); 30 ml of ditch water was collected in a 60 ml plastic syringe and equilibrated with 30 ml of ambient air by shaking for approximately 60 seconds, and 12 ml of headspace was then collected in a 12 ml borosilicate glass vial. Fluxes of CH_4 and CO_2 were measured in real time in the field using a floating chamber (0.6 x 0.6 x 0.3 m) that was shrouded to exclude light. Buoyancy for the chamber was provided by two 2 l plastic bottles filled with air, and the chamber was placed carefully on the water to minimise disturbance. Emergent vegetation was excluded (e.g. *P. australis*), but some sampling points contained floating algae that will have contributed to fluxes. The chamber was connected to a Los Gatos Ultraportable Greenhouse Gas Analyzer. The chamber was deployed until a linear flux was observed, and this was typically 1-5 minutes. Whilst there has been some criticism of the use of floating chambers, flow rates in the ditches we studied where either extremely low or absent (i.e. chambers did not drift away) and therefore our measurements are likely to be robust (see Lorke *et al*., 2015).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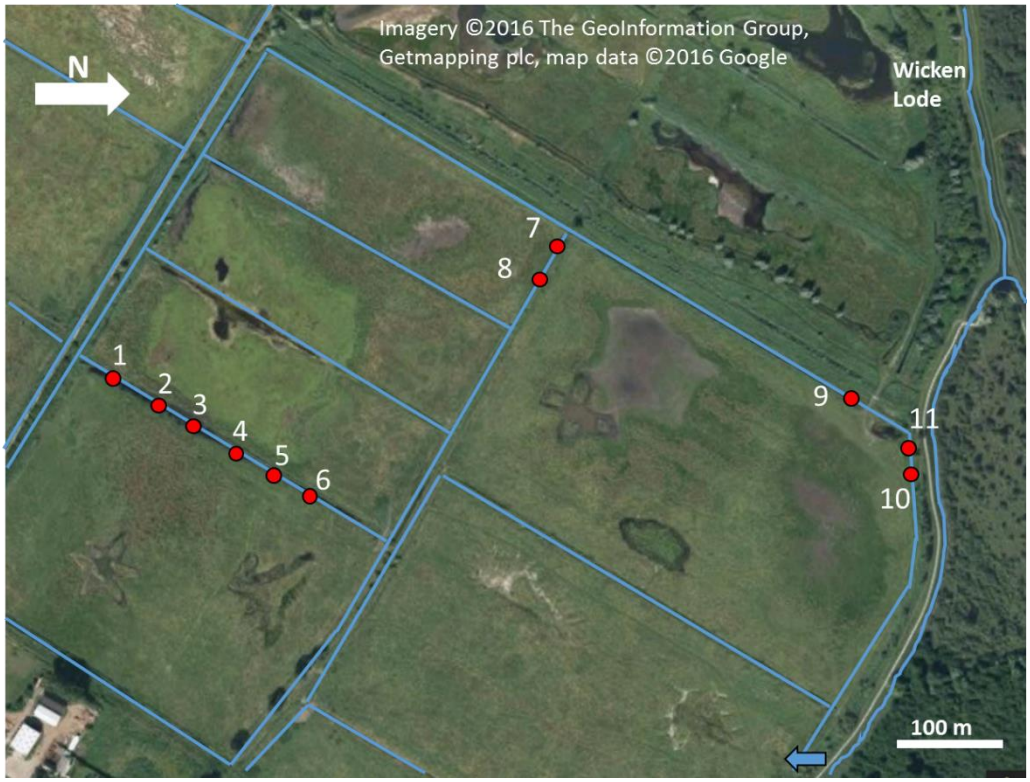
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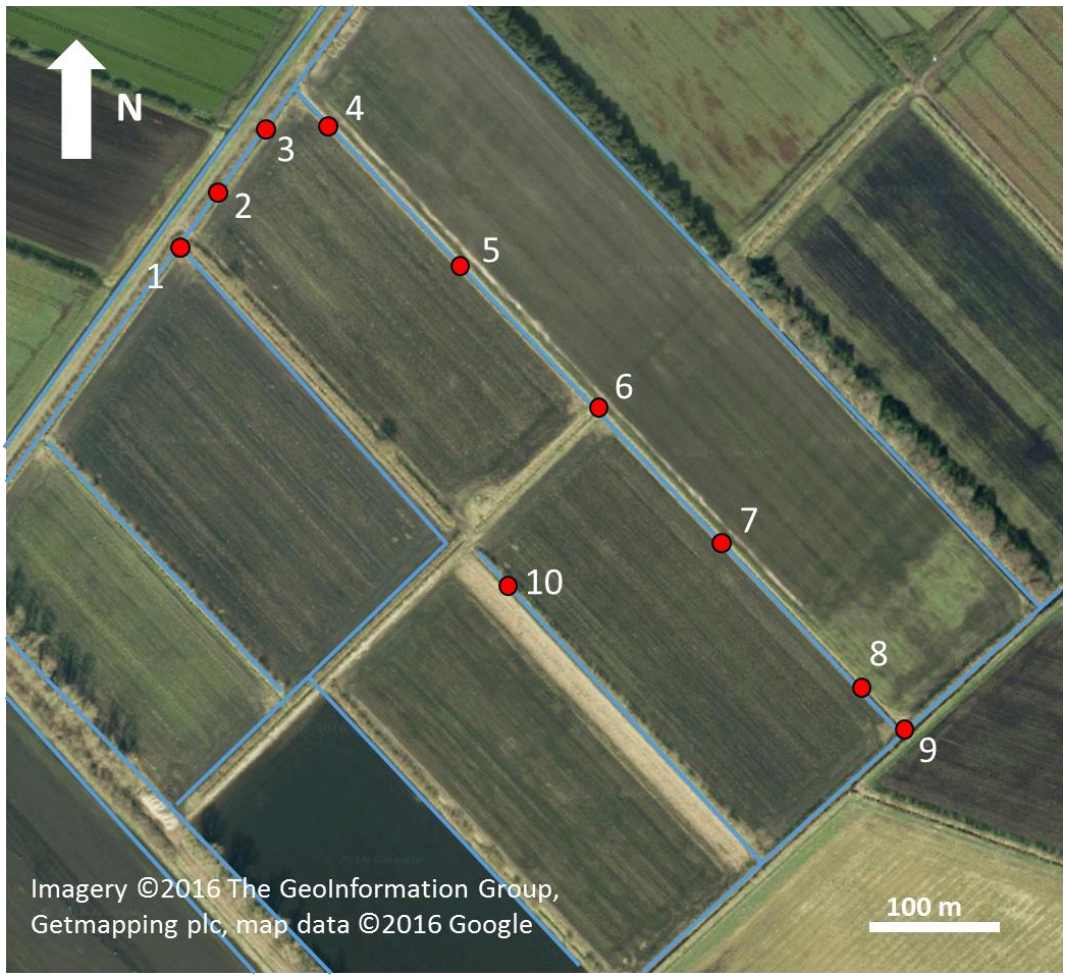

Figure 2. Maps of the semi-natural site (top panel), extensive grassland site (middle panel) and cropland site (bottom panel). Red dots mark numbered sampling locations, blue lines mark ditches/watercourses. For the semi-natural and extensive grassland sites, blue arrows mark where water is pumped onto site from Wicken Lode.

2.3 Analysis

Electrical conductivity (EC) and pH were measured on the 50 ml water sample. The sample was then passed through a nylon filter at 0.45 µm for further analysis. Dissolved organic carbon (DOC) and inorganic carbon (DIC) were analysed using a Shimadzu TOC Analyzer. DOC was measured as non-purgeable organic carbon (NPOC). Absorbance was measured at 280 nm using a Thermo Spectronic Helios Gamma Spectrophotometer. This was normalised against DOC concentration to give the specific ultraviolet absorbance (SUVA). SUVA is commonly measured at 254 nm, although high nitrate (NO_3^-) concentrations can interfere at wavelengths < 250 nm (Wang & Hsieh, 2001). Considering

229 the potential for high NO_3^- concentrations in surface waters in areas of intensive agriculture
230 a SUVA wavelength of 280 nm was selected. NO_3^- was measured using a NICO 2000 ion-
231 selective electrode and appropriate standards. Dissolved CH_4 and CO_2 were analysed using
232 a Los Gatos Ultraportable Greenhouse Gas Analyzer equipped with a sampling loop (Baird *et*
233 *al*., 2010). Dissolved N_2O was analysed on an Ai Cambridge GC94 equipped with an Electron
234 Capture Detector (ECD).

235 Floating chamber fluxes of CH_4 and CO_2 fluxes were calculated according to
236 Denmead (2008), using the modified formula:

237 $$F_g = \frac{1}{A}\frac{dg_m}{dt}$$

238 where F_g is the flux of CH_4 or CO_2 (M L^{-2} T^{-1} – mg m^{-2} day^{-1}), A is the area inside the
239 chamber (L^2 – m^2), gm is the mass of gas in the chamber (M – mg), and t is time (T – days).
240 Fluxes were calculated using a linear regression between time and chamber gas mass, and
241 accepted if this regression was significant ($p \leq 0.05$). Fluxes that were not significant were
242 assumed to be zero. Although it is usual to specify a cut-off value for the R^2 of the flux
243 regression (below which value fluxes are rejected) we did not take this approach, because
244 the high-frequency measurements provided by the analyser allowed detection of small but
245 clearly non-zero (significant) fluxes despite high short-term scatter (low R^2). However, of
246 the 253 fluxes that were significant, only 12 had an R^2 under 0.7. Fluxes were corrected for
247 atmospheric pressure and temperature measured during each individual chamber
248 deployment. Because of the short deployment time we assumed that pressure and
249 temperature remained steady during flux measurement. Piston velocity was calculated
250 using the standard formula (e.g. Gålfalk *et al*., 2013):

251 $$F = k\ x\ (C_{aq} - C_{eq})$$

252 where F is the CH_4 flux, k is the piston velocity, C_{aq} is the dissolved concentration of
253 CH_4, and C_{eq} is the theoretical dissolved concentration if the water is in equilibrium with the
254 air (calculated via Henry's Law). The formula was rearranged to give k.

255

256 *2.4 Statistics*

257 Statistical analysis was carried out in SPSS to determine if differences in GHGs and
258 piston velocity (CH_4 and CO_2 flux, and dissolved concentrations of CH_4, CO_2 and N_2O) were
259 present between sites. All six variables failed Levene's test for homogeneity of variance.

Kolmogorov-Smirnov tests were used to check for normal distributions. All six variables were not normally distributed, so transformations were sought to resolve this. CO_2 flux was transformed by square root transformation, and dissolved CO_2 was normalised by cube root transformation. Remaining variables could not be transformed to fit normal distributions. As such, a linear mixed model was used to test for differences between sites, using time as a repeated measure, and with Bonferroni correction for pairwise comparisons. Stepwise regression analysis was used as an exploratory test to look for relationships between dissolved CH_4 and CO_2 and the following variables: ditch water temperature, ditch depth, EC, absorbance at 280 nm, NO_3^-, DOC, SUVA, DIC, peat depth of the terrestrial fen, C:N, and water table in the terrestrial fen at the time of sampling (data for this was taken from Evans *et al*., 2016b). For the dissolved CO_2 model, pH was not used as an explanatory variable due to the fact that dissolved CO_2 and pH are interlinked (e.g. Abril *et al*., 2015). Differences were considered significant when $p \leq 0.05$.

3. Results

3.1. Water chemistry, ditch depths and environmental data

Table 1 displays a range of environmental and biogeochemical/physical data for the three sites through the year. Ditch water depths at the semi-natural site were consistently deep through the year (60 cm and above). Depths at the grassland site were generally shallow (~ 20cm), as were those at the cropland site, except during August when the mean was 60 cm. For all sites water and air temperature was highest during August. Mean ditch pH at all three sites was between 7.2 and 8.0, but EC was more variable both seasonally and between sites (intact < agricultural < restored). NO_3^- concentrations peaked in May at the cropland site (18 mg l^{-1}), presumably due to the use of fertilisers. At the grassland site NO_3^- was low (≤ 5 mg l^{-1}) except in March when the mean was 19 mg l^{-1}. The fen is rewetted during autumn and winter using high- NO_3^- river water, and the high concentration in March is a legacy of this rewetting. DOC concentrations were moderately high at the semi-natural and grassland sites (mean ~ 30 mg l^{-1}), but were lower by a third at the cropland.

3.2. Differences in ditch fluxes between and within sites

There was no significant difference in CH_4 flux between sites, but a significant ($p < 0.001$) difference was found for CO_2 flux between the cropland and other two sites (fig.3).

Median CH_4 fluxes were relatively low in March (≤ 10.5 mg m^{-2} d^{-1}). Fluxes stayed low in May at the grassland and cropland fens, but were higher (80 mg m^{-2} d^{-1}) at the semi-natural fen. Median CH_4 fluxes peaked in August at all three sites, at 120-230 mg m^{-2} d^{-1}. Highest individual fluxes at each site were: 3650, 25400 and 7430 mg m^{-2} d^{-1} for the semi-natural (May), grassland (August) and cropland (August) site respectively. CO_2 flux was relatively stable at the semi-natural site at 2050-3250 mg m^{-2} d^{-1}, but fluctuated at the other two sites, peaking at 6600 mg m^{-2} d^{-1} in August at the grassland site, and at 4760 mg m^{-2} d^{-1} in October at the cropland site. Highest individual fluxes at each site were: 9580, 16800 and 13800 mg m^{-2} d^{-1} for the semi-natural, grassland and cropland sites respectively, and were all recorded in August. Differences were also apparent within sites, and median fluxes for each individual sampling location are shown in fig.4.

There was considerable variation apparent in piston velocities between sites and months, but none of these differences was significant (table 2).

3.3. Annual ditch fluxes

To calculate annual mean fluxes for 2014, a simple time-weighted median approach was used, using the medians from fig.3. For CH_4, these produced estimates of 37.8, 18.3 and 27.2 g CH_4 $m^{-2}yr^{-1}$ for the semi-natural, grassland and cropland sites respectively, with respective standard errors of 74.6, 244, and 97.3 g CH_4 $m^{-2}yr^{-1}$. For CO_2 the annual fluxes were 1100, 1170 and 1440 g CO_2 m^{-2} yr^{-1} for the semi-natural, grassland and cropland sites respectively, with respective SEs of 225, 340 and 312 g CO_2 m^{-2} yr^{-1}.

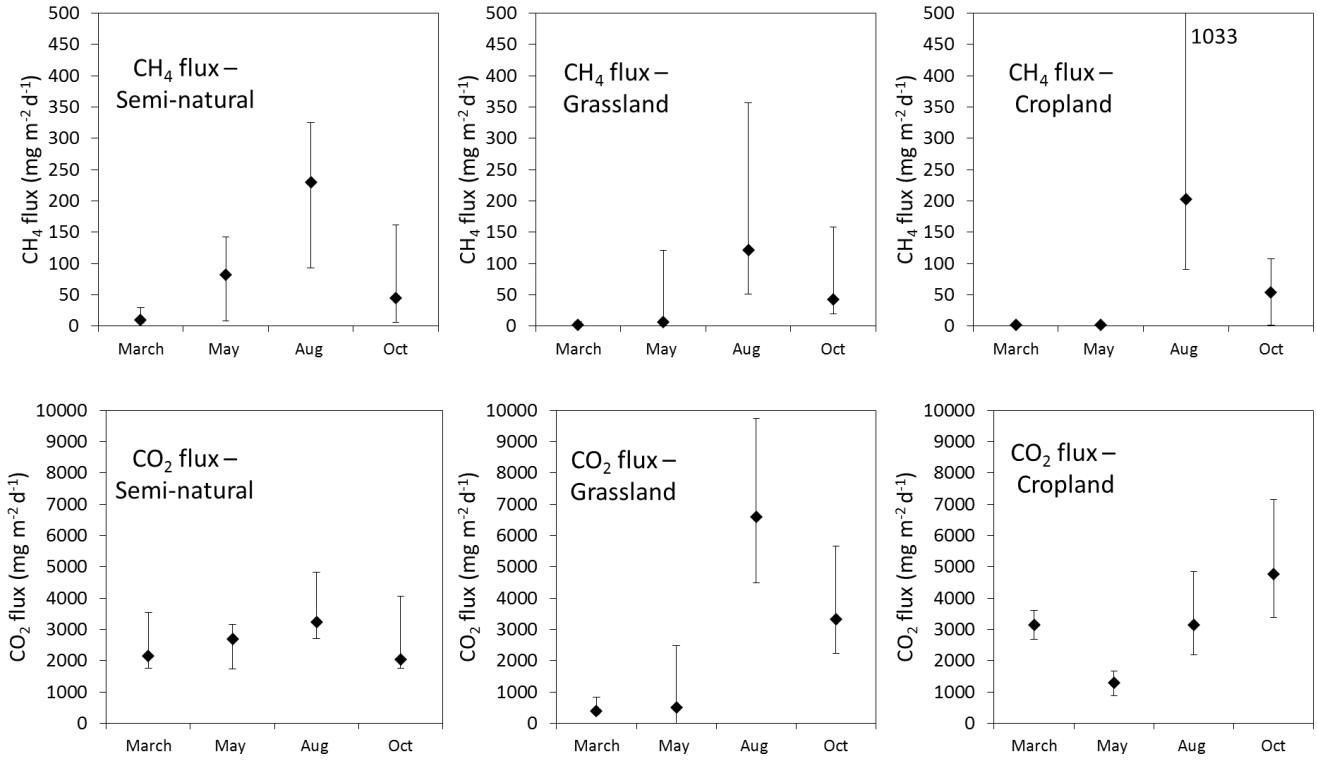

Figure 3. Median ditch fluxes of CH_4 and CO_2 measured using floating chambers at the three sites. Error bars represent first and third quartiles. . Note that the error bar for CH_4 in August at the cropland site exceeds the scale. There was a significant difference ($p \leq 0.001$) for CO_2 fluxes between the cropland and other two sites.

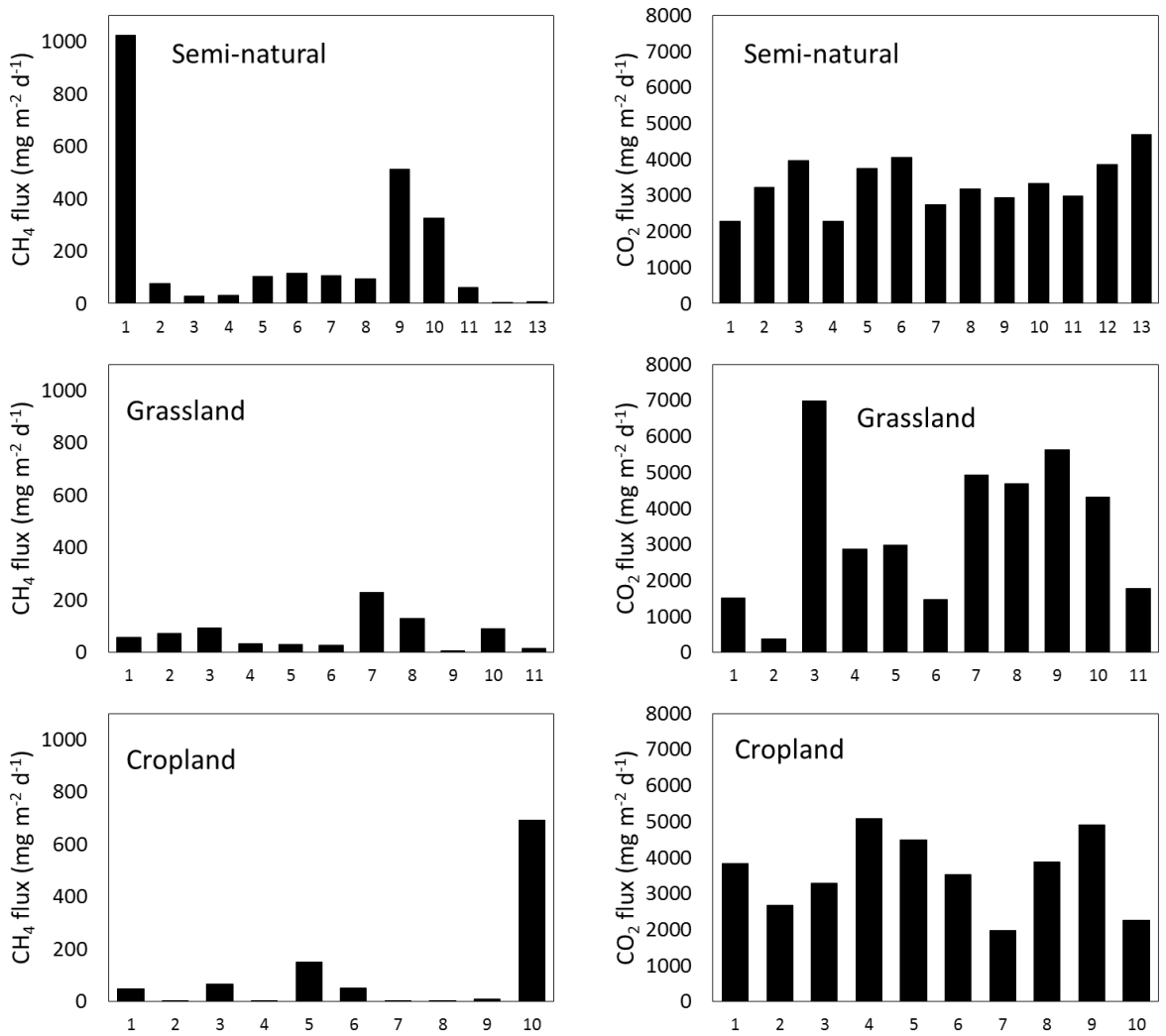

Figure 4. Median CH_4 (left) and CO_2 (right) fluxes for each individual numbered sampling point, grouped by site. Fig.2 displays numbered sampling points on site maps.

3.4. Differences in dissolved gases between sites

Significant differences were observed for dissolved CO_2 between the cropland and other two sites ($p < 0.001$). For dissolved CH_4, significant differences were found between the cropland and semi-natural fen ($p < 0.01$) and the cropland and grassland ($p < 0.05$). For N_2O, a significant difference was found between the cropland and other two sites ($p < 0.001$) (fig.5). Median CH_4 concentrations were below 0.1 mg l^{-1}, except for a spike of 0.43 mg l^{-1} at the cropland site in August. Median dissolved CO_2 at the semi-natural site showed no obvious seasonal variation (range 4.8-9.0 mg l^{-1}), whilst there was an increase through the year at the grassland site (1.7-7.5 mg l^{-1}). Dissolved CO_2 at the cropland site also peaked later in the year (15 mg l^{-1} in August and October). Median N_2O concentrations were under

1.5 µg l^{-1} at the semi-natural and grassland sites. At the cropland site N_2O concentrations were generally higher. Differences were apparent within sites, and median concentrations for each individual sampling location are shown in fig.6.

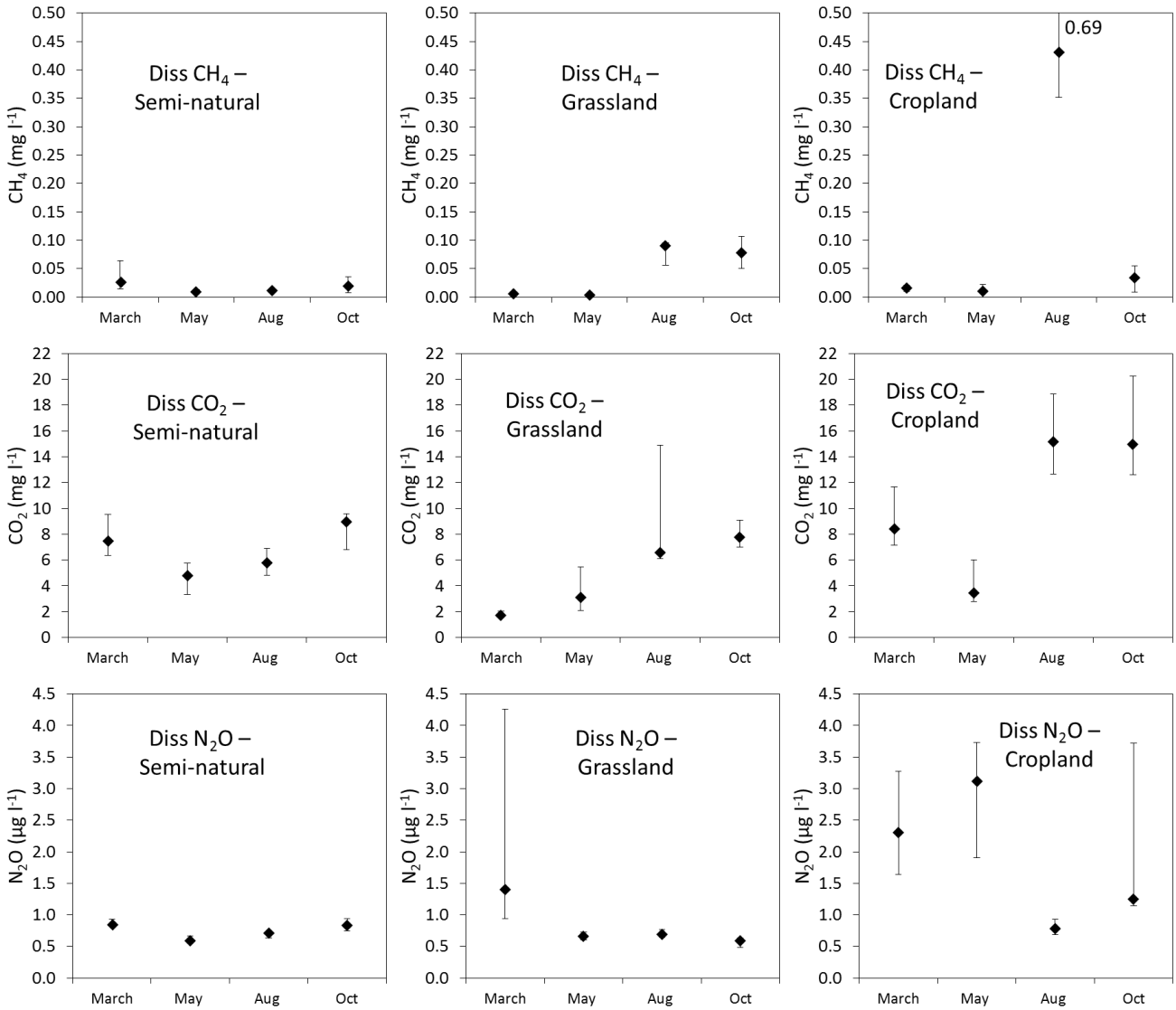

Figure 5. Median ditch dissolved concentrations of CH_4, CO_2 and N_2O at the three sites. Error bars represent first and third quartiles.. Note that the error bar for CH_4 in August at the cropland site exceeds the scale. There were significant differences between the cropland and other two sites for CO_2 ($p < 0.001$) CH_4 (cropland vs semi-natural $p < 0.01$, cropland vs grassland $p < 0.05$) and N_2O ($p < 0.001$).

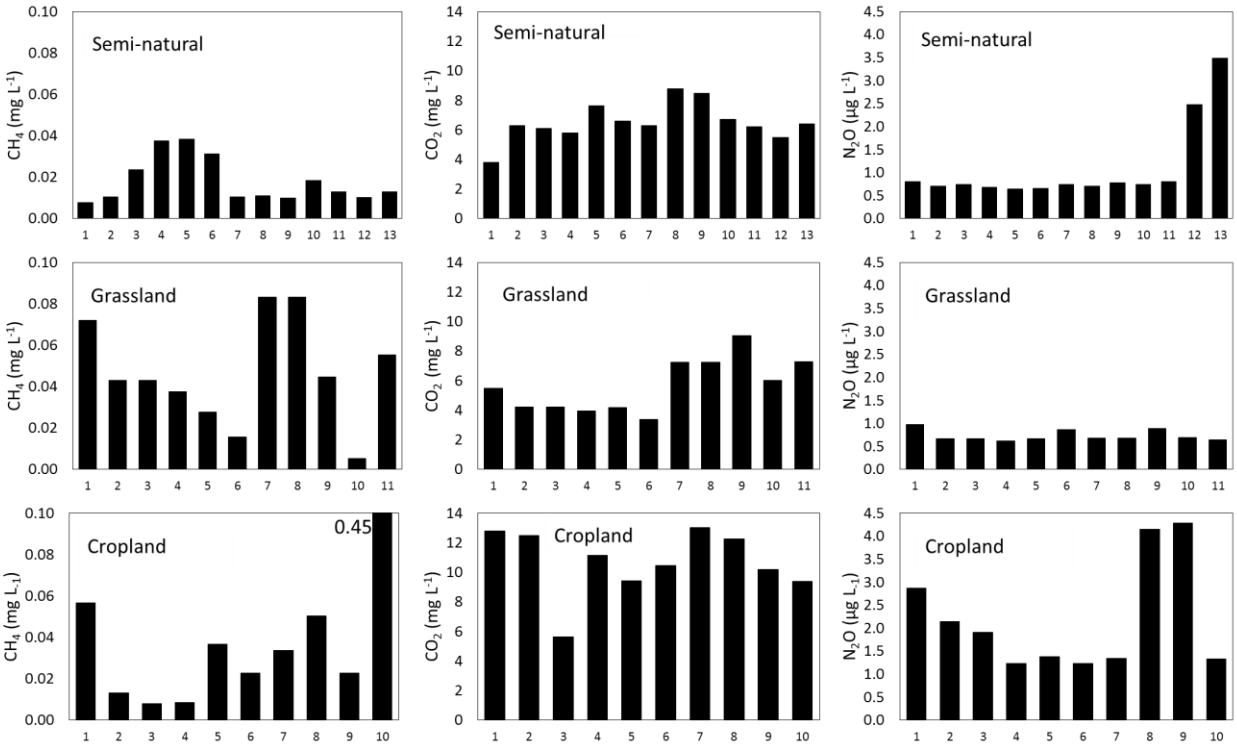

Figure 6. Median CH_4 (left) CO_2 (middle) and N_2O (right) concentrations for each individual numbered sampling point, grouped by site. Fig.2 displays numbered sampling points on site maps.

3.5. Drivers of dissolved GHGs

Significant regression models were produced for both dissolved CH_4 and CO_2, with respective R^2 values of 0.29 and 0.50. Table 3 displays the p values and slope coefficients used in each model.

There was a significant positive linear relationship between dissolved N_2O concentrations and NO_3^- ($p < 0.001$, $R^2 = 0.33$) but an improved fit was found between dissolved N_2O and the DOC:NO_3^- ratio, with N_2O concentrations increasing as the ratio decreased (fig.7). Apart from three clear outliers (which were not removed from the analysis), dissolved N_2O concentration did not rise above 1.5 µg l^{-1} until DOC:NO_3^- fell below 5. This relationship was consistent across all three sites.

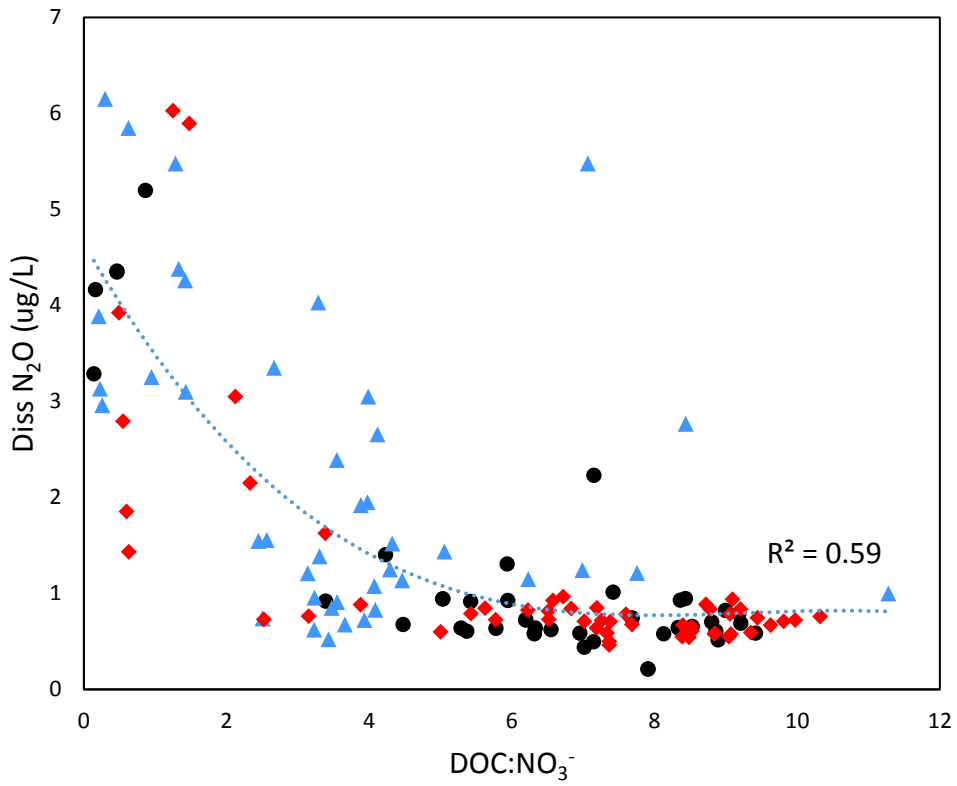

Figure 7. Relationship between dissolved N_2O and DOC:NO_3^- ratio for all individual samples. Red diamonds = semi-natural fen, black circles = grassland, blue triangles = cropland. Trend line is 3rd order polynomial.

4. Discussion

4.1. Site characteristics

There were physical and biogeochemical differences in the ditches of the three fen sites. The ditches at the semi-natural site were deepest whilst those at the grassland site were shallowest, reflecting the difficulties in keeping this grassland site wet, as noted by Peh *et al*. (2014). Ditch water levels at the cropland site were also shallow, but were raised for irrigation during the peak of the growing season; this demonstrates the high degree of water management to maximise arable production (Morrison *et al*., 2013).

4.2. CO_2 and CH_4 fluxes

We no significant differences between sites for CH_4 fluxes, but fluxes were CO_2 fluxes were significantly higher at the cropland compared to the grassland and semi-natural sites.. There were seasonal patterns in fluxes of CH_4; emissions peaked at all three fens in August at which time they were not significantly different. It is likely that these high fluxes are due to the effect of summer temperatures on methanogenesis (Dunfield *et al*., 1993). There was

375 extensive within-site variation in gas fluxes, particularly for CH_4. For instance, at the semi-
376 natural fen, sample point 1 had CH_4 fluxes an order of magnitude higher than the adjacent
377 sample point 2. Sample point 1 was close to the wind pump that pumps river water onto
378 the fen, and it could be that the mixing between low DOC/high NO_3^- river water and high
379 DOC/low NO_3^- fen water produces a 'hotspot' of organic carbon processing resulting in CH_4
380 production (*sensu* Palmer *et al*., 2016). The lowest CH_4 fluxes were recorded at a ditch that
381 bounded the edge of the fen, which displayed lower DOC concentrations and higher NO_3^-
382 concentrations, suggesting that this ditch was connected to the river, and contained less
383 organic substrates for methanogenesis. At the grassland site, CH_4 fluxes were highest at
384 adjacent sample points 7 and 8 though this was not obviously related to any measured
385 variables, e.g. EC, DIC and DOC were not elevated at these locations. At the cropland site,
386 sample point 10 was extremely high compared to the other points. This ditch was shaded
387 by a dense cover of trees and was near to a dead-end in the ditch system. This point had
388 elevated levels of EC (25% higher compared to the mean of the other sample points) and
389 DOC (114% higher), and it is likely that standing water here leads to an accumulation of
390 organic matter and stagnation, and hence higher rates of methanogenesis (fig.1). This
391 hypothesis is supported by the fact that dissolved CH_4 concentrations at this location were
392 higher than any other sampling point at any site (fig. 6).
393 Although we only sampled four times within a year, our design featured large
394 numbers of sampling points per site, and different sites were sampled at the same times of
395 year. Calculated mean fluxes may not therefore be an accurate representation of the
396 annual values, but should provide a reasonable representation of between-site differences.
397 Mean CH_4 fluxes followed the order semi-natural>cropland>grassland. The mean flux for
398 the semi-natural fen, 38 g CH_4 m^{-2} yr^{-1}, falls within the range of other reported fluxes from
399 ditches in semi-natural peatlands; e.g. 12 g CH_4 m^{-2} yr^{-1} and 164 g CH_4 m^{-2} yr^{-1} from drained
400 boreal fens (Glagolev *et al*., 2008, Minkkinen & Laine, 2006). The only reported annual ditch
401 CH_4 flux from a temperate semi-natural site are 5.5 g CH_4 m^{-2} yr^{-1} from a UK upland blanket
402 bog (Cooper *et al*., 2014). The considerably higher flux reported from our semi-natural site
403 therefore shows the effect of nutrient status on ditch emissions. It has been suggested that
404 ditch CH_4 emissions increase as land-use intensity increases (Evans *et al*., 2016a) but our
405 data do not show this. The flux from our grassland site, 18 g CH_4 m^{-2} yr^{-1} is low compared to
406 values such as 43, 66, 77 and 70 g CH_4 m^{-2} yr^{-1} from other low-intensity grasslands (Schrier-

407 Uijl *et al*., 2010, Vermaat *et al*., 2011, McNamara, 2013, Hendricks *et al*., 2007), although
408 van den Pol-van Dasselaar *et al*. (1999) recorded an annual flux of just 11 g CH_4 m^{-2} yr^{-1}. To
409 our knowledge, our annual ditch flux calculation of 27 g CH_4 m^{-2} yr^{-1} for the cropland is, along
410 with the fluxes in our broader project report (Evans *et al*., 2016a), the first annual flux
411 estimate for a temperate peatland under agriculture. There are several possible reasons for
412 the highest annual flux being observed at the semi-natural site. Firstly, subsidence at our
413 grassland site has resulted in the loss of the majority of peat soil, and it may be that the low
414 organic content of the soil has led to a reduction in CH_4 production. This could be especially
415 relevant if CH_4 is produced in the saturated peat, then transported laterally and degassed
416 from ditches (e.g. fig.1); the grassland site dries out completely, presumably resulting in zero
417 methanogenesis, whilst the water table remains in the peat at a deep level at the cropland,
418 making this a plausible hypothesis. Secondly, the semi-natural site is likely to have a well-
419 established methanogenic community compared to the other two sites where severe
420 drainage and loss of peat (Stroh *et al*., 2013) may have disrupted the microbial communities
421 (Jerman *et al*., 2009). Thirdly, the ditches at the semi-natural site were relatively deep, and
422 depth fluctuations were minimal compared to the other two sites. This could lead to the
423 formation of anoxic conditions, thus stimulating CH_4 emissions and reducing oxidation in the
424 water column (O_2 measurements on future sampling campaigns would help to resolve this).
425 Finally, Vermaat *et al*. (2011) recorded more ebullition in ditches sheltered by reed beds. It
426 is therefore possible that steady ebullition contributed to the high fluxes at the semi-natural
427 fen, as well as being responsible for the individual high fluxes (e.g. 25400 and 7430 mg m^{-2} d^{-}
428 ^{1}) that were observed at the grassland and cropland. Ebullition from ditches in a Finnish
429 mire measured using bubble traps was 3-37 mg m^{-2} d^{-1}, and was negligible (0.2-2.3%
430 compared to diffusive emissions) in flowing ditches but substantial in ditches with standing
431 water (10-22% of diffusive flux) (Minkkinen *et al*., 1997, 2006). Vermaat *et al*. (2011)
432 calculated ditch ebullition by interpreting steep, short-term increases in CH_4 concentration
433 in a floating chamber as evidence of bubbling, and stated that approximately 50% of total
434 flux was due to ebullition. Other research using bubble traps has shown that ebullition in
435 wetland and agricultural streams can equal the diffusive flux (Wilcock & Sorrell, 2008,
436 Crawford *et al*., 2014). More measurements of ebullition in ditches are clearly needed.
437 Unlike CH_4, annual CO_2 fluxes did increase with land-use intensity, in the order semi-
438 natural<grassland<cropland. Estimates of annual ditch CO_2 fluxes are lacking from the

439 literature, but scaling up the measurements of Vermaat *et al*. (2011) would produce annual
440 fluxes of 1050 g CO_2 m^{-2} yr^{-1} for ditches in reed beds, and 1310 g CO_2 m^{-2} yr^{-1} for ditches in
441 rough pasture. Our semi-natural site is therefore similar, with a flux of 1100 g CO_2 m^{-2} yr^{-1},
442 although our grassland annual flux was 1170 g CO_2 m^{-2} yr^{-1}. Our median CO_2 fluxes ranged
443 from 488 mg m^{-2} d^{-1} to 8000 mg m^{-2} d^{-1}, and are therefore similar to those reported by
444 Schrier-Uijl *et al*. (2011), Teh *et al*. (2011) and Hyvönen *et al*. (2013). CO_2 fluxes at the semi-
445 natural site displayed less seasonality which may be a function of the deeper ditches
446 minimising temperature increases in the basal peat, and therefore suppressing productivity
447 (McEnroe *et al*., 2009).
448
449 *4.3. Dissolved GHGs*
450 For dissolved CH_4, CO_2 and N_2O, we found significant differences between the
451 cropland compared to the grassland and semi-natural sites. This suggests that intensive
452 agriculture has affected the biogeochemistry of the cropland ditches. Some sampling
453 locations showed similar concentrations of dissolved gases, and this could be due spatial
454 autocorrelation in dissolved GHGs (e.g. Chapra & Di Toro, 1991). This was most obvious for
455 CH_4 at the semi-natural site, and N_2O at the semi-natural site and grassland.
456 Once pH had been removed as a predictive variable, we were able to account for
457 29% of temporal and spatial (within and between site) variability in CH_4, and 50% of
458 variability in CO_2. For dissolved CO_2 there were positive relationships with depth to water
459 table, DIC concentration, SUVA, and ditch depth. A deeper water table within the peat
460 should result in increased decomposition, with CO_2 then exported laterally into ditches. A
461 negative relationship between CO_2 and water depth has been found for pools in natural
462 peatlands (McEnroe *et al*., 2009), and so our contrary finding could be due to the high
463 degree of management at these fens; e.g. irrigation at the cropland reversed the natural
464 seasonality in ditch depth and doubled the water level of the ditches in August, which
465 coincided with the growing season increase in dissolved CO_2.
466 Dissolved CH_4 concentrations fell within the same range as those in agricultural
467 streams (0.001-0.4 mg L^{-1}, Wilcock & Sorrell, 2008), and ditches in agricultural peatlands
468 (maximum of 0.04 mg L^{-1}, Schrier-Uijl *et al*., 2011). They were of the same magnitude as
469 0.022 mg L^{-1} which was the calculated mean fluvial CH_4 concentration from 111 published
470 studies (Stanley *et al*., 2016). Dissolved CH_4 correlated positively with air temperature, NO_3^-,

DIC, and depth to water table (in the fen/field), and negatively with EC. Higher temperatures could stimulate methanogenesis, leading to increased concentrations of CH_4. The positive correlation between dissolved CH_4 and depth to water table may, in part, be due to the confounding effect of seasonality; i.e. water tables were lower in the growing season when ditches become depleted in oxygen, leading to higher rate of methanogenesis. The positive correlation between NO_3^- and CH_4 is unexpected, as NO_3^- inhibits methanogenesis (Watson & Nedwell, 1998) and, as an electron acceptor, allows denitrifying bacteria to favourably out-compete methanogens (Le Mer & Roger, 2001). One possible explanation is that increased NO_3^- levels are associated with increased ammonium concentrations at the semi-natural fen (Conrad & Rothfuss, 1991), and the inhibitory effect of ammonium on methanotrophy is larger than the inhibitory effect of NO_3^- on methanogenesis. It may be that high nutrient levels associated with NO_3^- could coincide with inputs of labile organic matter, particularly at agricultural sites, thus stimulating methanogenesis when other electron acceptors have been depleted in the sediment. Alternatively, as discussed in section 4.2, it could be that CH_4 is produced in the saturated peat and then transported laterally into the ditch; i.e. methanogenesis occurs in zones distant from potential NO_3^- inhibition. Schade *et al*. (2016) did find a weak negative correlation between NO_3^- and CH_4 in a low NO_3^-/high DOC stream but found no correlation in a high NO_3^-/low DOC stream or in a high NO_3^-/high DOC stream. Similarly, Crawford *et al*. (2016) found no evidence that NO_3^- inhibited CH_4 production or emission in streams, and, in line with our hypothesis above, suggested that methanogenesis could be spatially removed from high NO_3^- concentrations. The absence of ditch depth from the CH_4 model is interesting as negative relationships between CH_4 flux and depth have been noted previously, although these are sometimes low; e.g. McEnroe *et al*. (2009) reported an R^2 value of 0.23 for pools, and Vermaat *et al*. (2011) found an R^2 of 0.15 for ditches. Pelletier *et al*. (2007) found both negative and positive relationships between CH_4 flux and depth in pools at different peatlands, and postulated that ebullition could be a confounding variable. The active water management at some sites could also be a confounding factor; as previously mentioned this management removes the natural seasonality in ditch depth. Finally, it is worth considering that wind speed may play a role in GHG dynamics. However, the ditches at our sites are predominantly sheltered by reedbeds or banks and, as previously

502 noted, the floating chamber did not drift, suggesting that wind speed was low on sampling
503 days.
504 Dissolved N_2O was present in the ditches at all three fens, but was low at the semi-
505 natural site. Concentrations were only high at the grassland site in March, but were high for
506 most of the year at the cropland site, presumably due to the application of fertilisers to
507 adjacent fields. Positive relationships between dissolved N_2O and N_2O flux have been
508 demonstrated in rivers (Yang *et al*., 2011). Diffusive fluxes of N_2O have been shown to occur
509 in oxygenated waters and it therefore seems highly probable that ditches at all three fens
510 were sources of N_2O to the atmosphere. Wilcock & Sorrell (2008) measured N2O
511 concentrations in agricultural streams between 0.26-28.5 µg l^{-1}, considerably higher than
512 our maximum individual measurements of 6.15 µg l^{-1}, whilst concentrations in a eutrophic
513 river have been reported as 0.66-1.14 µg l^{-1} (Silvennoinen *et al*., 2008). Sturm *et al*. (2014)
514 recorded average concentrations of N_2O in lake surface water as 0.61 µg l^{-1} and 0.74 µg l^{-1},
515 similar to median concentrations at our grassland and semi-natural site, although
516 concentrations at our cropland were higher. The authors also measured N_2O fluxes, with
517 averages of 3.7 and 5.3 µg m^{-2} hr^{-1}. Reay *et al*. (2003) reported a relationship between N_2O
518 fluxes and dissolved N_2O in UK agricultural ditches; applying that relationship to our data
519 allows estimates of median flux for each fen to be calculated as 300, 210, and 1150 µg m^{-2}
520 hr^{-1} for the semi-natural, grassland and cropland sites respectively. These fluxes at the
521 semi-natural and grassland sites are similar to those reported by Teh *et al*. (2011) for ditches
522 in a peatland pasture in the USA.
523 We found a statistically significant relationship between dissolved N_2O and NO_3^-, in
524 agreement with others (e.g. Reay *et al*., 2003, Hinshaw & Dahlgren, 2013, Schade *et al*.,
525 2016). However, a better fit was found between dissolved N_2O and the DOC:NO_3^- ratio.
526 Aquatic systems generally show an inverse relationship between DOC and NO_3^-
527 concentrations, which reflects a gradient from nitrogen limitation of microbial processes in
528 carbon-rich systems to labile organic matter limitation in carbon-poor systems (Goodale et
529 al., 2005; Taylor and Townsend, 2010). Our observation that dissolved N_2O only increases
530 above ambient atmospheric concentrations when DOC/NO_3^- ratios are low suggests both
531 that NO_3^- concentrations need to be high enough to allow denitrification to occur, and that
532 labile organic matter concentrations need to be low enough to favour this process over
533 other microbial processes such as NO_3^- reduction or assimilation. There were three samples

534 that appeared to deviate from the observed relationship, and it may be that higher
535 concentrations of ammonium cause elevated N_2O concentrations, particularly if dissolved
536 oxygen is not limiting (Liikanen & Martikainen, 2003).
537
538 *4.4. Implications for GHG accounting and conclusions*
539 Our data support previous studies in showing that ditches in both semi-natural and
540 agricultural peatlands act as sources of CH_4, CO_2 and N_2O emissions. It is widely recognised
541 that intact fens are important emitters of CH_4 (Turetsky *et al*., 2014). Although not intact,
542 our semi-natural fen is under conservation management, and therefore the vegetation is
543 similar to intact fens. As such, the annual terrestrial flux from our semi-natural site is 11.7 g
544 CH_4 m^{-2} yr^{-1} (Evans *et al*., 2016b) , compared to 37.8 g CH_4 m^{-2} yr^{-1} from the ditches. When
545 weighted by area for the entire fen, ditches would therefore be responsible for 0.53 g CH_4
546 m^{-2} yr^{-1}, approximately 5% of total emissions. Although ditches occupy only a fraction of the
547 landscape, the magnitude of the fluxes observed here suggest that ditches in modified fen
548 landscapes must be considered when calculating carbon balances, particularly for studies
549 relying on static chamber, rather than eddy-covariance, methods, since this component of
550 CO_2 and CH_4 emissions will otherwise be missed. In drained peatland systems, the
551 contribution of ditches to the overall CH_4 budget is even more marked, because CH_4 fluxes
552 from drained peat surfaces tend to be near zero (Willison, 1998, IPCC, 2014). At our
553 cropland site, the field surface acted consistently as a small net sink for CH_4 (Evans et al.,
554 2016b) and ditches were thus responsible for the entirety of CH_4 emissions from the system
555 as a whole, which would give an areally-weighted flux of 0.44 g CH_4 m^{-2} yr^{-1} compared to the
556 field sink of -0.17 g CH_4 m^{-2} yr^{-1}. This is probably true for agriculturally drained peatlands in
557 general (IPCC, 2014, Evans et al., 2016a). Terrestrial fluxes at our grassland restoration site
558 show that both uptake and emission of CH_4 occur, but the annual flux is approximately zero
559 (Evans et al., 2016a). Thus, the ditches here are responsible for the majority of CH_4
560 emissions to the atmosphere, calculated on an areal basis as 0.31 g CH_4 m^{-2} yr^{-1}.
561 Our CO_2 fluxes were similar to others reported in the literature from ditches, which
562 have often been of the same magnitude as fluxes from terrestrial fen (e.g. Schrier-Uijl *et al*.,
563 2011, Hyvönen *et al*., 2013). Our median estimated N_2O fluxes for the semi-natural and
564 grassland sites are slightly higher than terrestrial fluxes from a Finnish drained
565 minerotrophic fen (Martikainen *et al*., 1995) whilst our calculated N_2O fluxes were in the

same range as mean terrestrial fluxes from a German agricultural fen (Flessa *et al*., 1998). These observations support previous suggestions that ditches do not act as hotspots for CO_2 and N_2O in the same way that they do for CH_4 (Evans *et al*., 2016a, Teh *et al*., 2011).

Future work should continue to examine the role that ditches play in releasing GHGs to the atmosphere, but a particular focus should be on CH_4. It is likely that high-frequency measurements combined with sampling replication on both small (i.e. field) and large (i.e. regional) scales would elucidate in greater detail the drivers between both dissolved GHGs concentrations and their efflux to the atmosphere. It is apparent that neglecting to consider ditches in drained peatlands will lead to significant errors when calculating landscape-scale GHG budgets.

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Table 1. Mean environmental, physical and water chemistry measurements for ditches at the three sites on the four sampling occasions. Numbers in brackets are standard error of the mean. Depth is ditch water depth.

		March	May	Aug	Oct		March	May	Aug	Oct
Air temp (°C)	Semi-natural	8	12.5	12.7	12.2	Water temp (°C)	7.3 (0.2)	15.5 (0.2)	18.6 (0.2)	10.2 (0.1)
	Grassland	8	12.5	12.7	12.2		10.7 (0.3)	15.2 (0.3)	17.6 (0.4)	10.1 (0.2)
	Cropland	6.9	13.7	15.9	9.1		9.9 (0.6)	12.6 (0.2)	15.5 (0.4)	9.8 (0.2)
Depth (cm)	Semi-natural	85.6 (4.8)	86.9 (3.5)	64.0 (6.7)	70.1 (5.5)	pH	7.7 (0.02)	7.9 (0.05)	7.6 (0.04)	7.6 (0.02)
	Grassland	23.3 (7.3)	36.4 (3.9)	16.2 (1.4)	21.1 (2.8)		8.0 (0.06)	7.8 (0.09)	7.3 (0.06)	7.6 (0.03)
	Cropland	18.4 (3.1)	32.7 (4.6)	60.6 (3.5)	20.5 (3.9)		7.5 (0.04)	7.8 (0.05)	7.2 (0.07)	7.2 (0.04)
EC (µS cm^{-1})	Semi-natural	921 (62)	907 (18)	810 (73)	965 (51)	NO_3^- (mg l^{-1})	11.6 (4.2)	6.7 (1.8)	5.2 (0.8)	6.5 (1.2)
	Grassland	994 (32)	1117 (102)	1306 (80)	1584 (99)		19.1 (5.8)	4.1 (0.1)	3.9 (0.1)	5.0 (0.2)
	Cropland	1263 (87)	968 (69)	888 (28)	1134 (65)		9.9 (1.4)	18.2 (4.6)	4.8 (0.7)	5.3 (0.4)
DOC (mg l^{-1})	Semi-natural	28.7 (0.9)	28.9 (2.1)	27.4 (0.8)	37.4 (2.2)	SUVA	2.8 (0.1)	2.8 (0.1)	3.3 (0.1)	2.8 (0.1)
	Grassland	19.7 (2.7)	28.8 (1.1)	30.3 (1.6)	37.6 (2.4)		2.3 (0.1)	2.2 (0.0)	2.4 (0.1)	2.2 (0.2)
	Cropland	27.4 (3.3)	15.2 (4.8)	18.0 (2.8)	25.5 (3.7)		2.1 (0.1)	2.1 (0.1)	2.8 (0.1)	2.3 (0.1)
DIC (mg l^{-1})	Semi-natural	92 (2)	80 (3)	70 (2)	97 (2)					
	Grassland	72 (2)	59 (6)	79 (4)	102 (3)					
	Cropland	69 (2)	52 (6)	68 (4)	77 (5)					

Table 2. Median piston velocities (m s^{-1}) for each site and each month, with first and third quartiles

		March	May	Aug	Oct
Semi-natural	Median	5.87E-06	1.16E-04	2.65E-04	8.58E-06
	1st	2.97E-06	1.33E-05	8.72E-05	3.96E-06
	3rd	1.33E-05	2.42E-04	4.17E-04	1.23E-04
Grassland	Median	4.89E-06	3.80E-05	9.18E-06	8.89E-06
	1st	2.23E-06	3.75E-06	7.99E-06	2.21E-06
	3rd	9.76E-06	7.87E-04	6.75E-05	2.33E-05
Cropland	Median	2.25E-06	2.26E-06	4.31E-06	8.01E-06
	1st	1.62E-06	1.67E-06	2.88E-06	4.39E-06
	3rd	3.40E-06	3.18E-06	7.20E-05	3.61E-05

Table 3. Results of the multiple linear regressions to determine the relationships between dissolved CO_2/CH_4 and other measured variables for the intact, restoration, and agricultural site. Note that depth to WT refers to the water table depth in the terrestrial part of the fen.

Diss CO_2	Slope coefficient	p
Intercept	-15.1	<0.001
Depth to WT	0.101	<0.001
DIC	0.133	<0.001
SUVA	2.594	0.001
Ditch depth	0.032	0.02

Diss CH_4	Slope coefficient	p
Intercept	-0.63	<0.001
Air temp	0.0148	<0.001
NO_3^-	0.0066	<0.001
DIC	0.0066	<0.001
Depth to WT	0.0019	<0.001
EC	-0.0002	0.02