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# Management Effects on Greenhouse Gas Dynamics in Fen Ditches

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#### **Abstract**

12 to increase agricultural production. By lowering the water table it is often assumed that drainage reduces landscape-scale emissions of methane (CH<sub>4</sub>) into the atmosphere to 13 negligible levels. However, drainage ditches themselves are known to be sources of CH<sub>4</sub> and 14 other greenhouse gases (GHGs), but emissions data are scarce, particularly for carbon 15 16

Globally, large areas of peatland have been drained through the digging of ditches, generally

dioxide (CO<sub>2</sub>) and nitrous oxide (N<sub>2</sub>O), and show high spatial and temporal variability. Here, 17

we report dissolved GHGs and diffusive fluxes of CH<sub>4</sub> and CO<sub>2</sub> 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<sub>4</sub> fluxes were particularly large, with medians peaking at all

three sites in August at 120-230 mg m<sup>-2</sup> d<sup>-1</sup>. Significant between site differences were

detected between the cropland and the other two sites for CO<sub>2</sub> flux and all three dissolved

24 GHGs, suggested that intensive agriculture has major effects on ditch biogeochemistry.

Multiple regression models using environmental and water chemistry data were able to 25

26 explain 29-59% of observed variation in dissolved GHGs. Annual CH<sub>4</sub> fluxes from the ditches

were 37.8, 18.3 and 27.2 g CH<sub>4</sub> m<sup>-2</sup> yr<sup>-1</sup> for the semi-natural, grassland and cropland, and

annual CO<sub>2</sub> fluxes were similar (1100 to 1440 g CO<sub>2</sub> m<sup>-2</sup> yr<sup>-1</sup>) among sites. We suggest that

fen ditches are important contributors to landscape-scale GHG emissions, particularly for

CH<sub>4</sub>. Ditch emissions should be included in GHG budgets of human modified fens,

particularly where drainage has removed the original terrestrial CH<sub>4</sub> source, e.g. agricultural 31

peatlands. 32

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

#### 1. Introduction

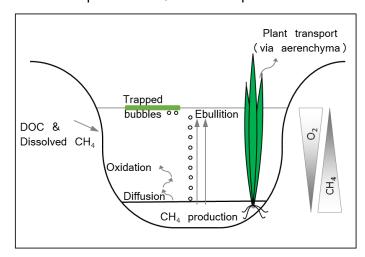
Northern peatlands store approximately 547 Pg of carbon (Yu *et al.*, 2010) and contribute to the global atmospheric balance of GHGs through the release and uptake of carbon dioxide (CO<sub>2</sub>), methane (CH<sub>4</sub>) and nitrous oxide (N<sub>2</sub>O). Intact peatlands are typically net sinks for CO<sub>2</sub>, and sources of CH<sub>4</sub> and N<sub>2</sub>O (Freeman *et al.*, 1993, Nykänen *et al.*, 1995, Smith *et al.*, 2004, Kirschke *et al.*, 2013). On a 100-year timescale CH<sub>4</sub> and N<sub>2</sub>O have global warming potentials (GWP) of 28 and 298, respectively, relative to CO<sub>2</sub> (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<sub>4</sub> emissions (to near-zero values), but increases in CO<sub>2</sub> and N<sub>2</sub>O 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<sub>4</sub> 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<sub>4</sub> 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<sub>4</sub> 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<sub>4</sub> m<sup>-2</sup> hr<sup>-1</sup> (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<sub>4</sub> fluxes compared to undrained sites (Roulet & Moore, 1995).



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

Large ditch CH<sub>4</sub> 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<sub>4</sub> flux of 59.7 kg CH<sub>4</sub> ha<sup>-2</sup> y<sup>-1</sup> from an open ditch in a blanket bog, and Sirin et al. (2012) measured a growing season flux of 9.9 mg CH<sub>4</sub> m<sup>2</sup> d<sup>-1</sup> from ditches in a forested bog. A recent review found mean fluxes for different peat/land-use types varied from approximately 30 g CH<sub>4</sub> m<sup>-2</sup> yr<sup>-1</sup> in forest/seminatural peatlands, to 200 g CH<sub>4</sub> m<sup>-2</sup> yr<sup>-1</sup> 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<sub>4</sub> concentration differential between the ditch and the atmosphere. Wetland plant aerenchyma may provide a chimney through which oxygen is transported into sediment and CH<sub>4</sub> escapes to the atmosphere. Finally, steady emissions may be punctuated by temporally and spatially heterogeneous ebullition, which can contribute significantly to net CH<sub>4</sub> 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<sub>4</sub>, drainage ditches emit N<sub>2</sub>O (Reay *et al.*, 2003, Teh *et al.*, 2011, Hyvönen *et al.*, 2013). Some ditches have been found to emit CO<sub>2</sub> (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<sub>2</sub> (e.g. Vermaat *et al.*, 2011). However, whilst ditches appear to be consistent hotspots for CH<sub>4</sub> emissions, CO<sub>2</sub> and N<sub>2</sub>O 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<sub>2</sub>O and CO<sub>2</sub>.

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<sub>4</sub> emissions had been reported, for a total of 69 individual peatland sites where CH<sub>4</sub> was measured (Evans et al., 2016a). The same analysis suggested that studies of CO<sub>2</sub> and N<sub>2</sub>O are still too few to allow the data to be collated in a meaningful way. Just two studies to date have reported CH<sub>4</sub> 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<sup>-1</sup>; enough to exert effects on regional budgets, despite these features occupying small areas. Similarly, Bastviken *et al.* (2011) suggested that CH<sub>4</sub> 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<sub>2</sub>-equivalent emissions from CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub>O. Considering N<sub>2</sub>O, 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<sub>2</sub> and CH<sub>4</sub> 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 17<sup>th</sup> 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<sup>-3</sup>, 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<sup>-3</sup>, 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

arable use and re-seeded with an unknown "grass mixture" in 1995 and 1996, and is undergoing "open-ended" restoration (Hughes *et al.*, 2011); river water is pumped onto the site in autumn and winter to inundate it, and highland cattle and wild horses graze it. Much of the fen consists of species-poor, flood-plain pasture. Plant species vary across the site according to variations in hydrology and nutrient status, but include *Carex otrubae*, *Arrhenatherum elatius*, *Agrostis stolonifera*, *Cirsium arvense*, *Poa trivialis* and several *Juncus* species (Eades, 2016). *C. mariscus* and *P. australis* occur in some of the ditches.

3. Rosedene (cropland). 52.52 N, 0.49 E. Field area = 8.7 ha. The cropland site consists of ditches that surround a field near Methwold Hythe. The field is part of a much larger area (~90 km²) of drained fen that is now under intensive arable cultivation, and is bounded by rivers and canals. Peat depth is 1 m, bulk density is 0.32 g cm³, and C/N is 15 (Evans *et al.*, 2016b). The hydrology of the site is highly managed; the fields contain subsurface pipes at 1 m depth to aid irrigation and drainage, and water is actively pumped round field perimeter ditches in order to maintain water levels within the field, removing water during wet periods and providing irrigation water during dry periods. During 2015, the study site was used to cultivate celery (*Apjum graveolens*). This site is 28 km from the other two sites.

All three sites formed part of a larger study of GHG emissions from a total of fifteen lowland peatland sites at located across six regions of England and Wales, which included a broad suite of eddy covariance and static chamber gas flux, hydrological and water quality measurements. The results of this large-scale study are reported elsewhere (Evans et al., 2016b).

# 2.2. Sampling

The sites were visited on four occasions in 2015 in March, May, August and October. Because of proximity, the intact and restored site could be visited on the same day, whilst the agricultural site was visited within three days. The sampling dates were as follows: 11<sup>th</sup> March – semi-natural/grassland, 12<sup>th</sup> March – cropland; 5<sup>th</sup> May – semi-natural/grassland, 6<sup>th</sup> May – cropland; 17<sup>th</sup> August – cropland, 20<sup>th</sup> August – semi-natural/grassland; 12<sup>th</sup> October – cropland, 15<sup>th</sup> October – semi-natural/grassland. At each site, ditch sampling 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.

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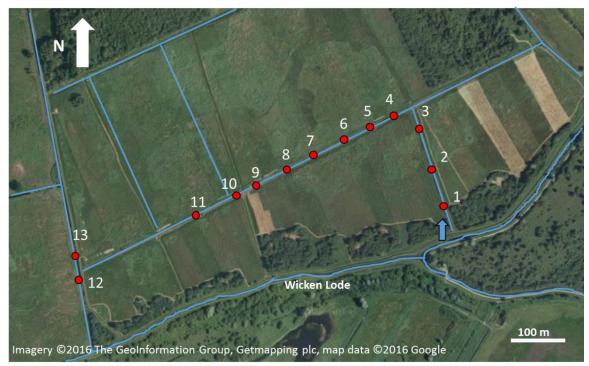
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A range of measurements were taken at each sampling location. Environmental and physical measurements were: air temperature, water temperature, atmospheric pressure, and water depth. A 50 ml water sample for water chemistry analysis was collected in 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<sub>4</sub> and CO<sub>2</sub> 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).





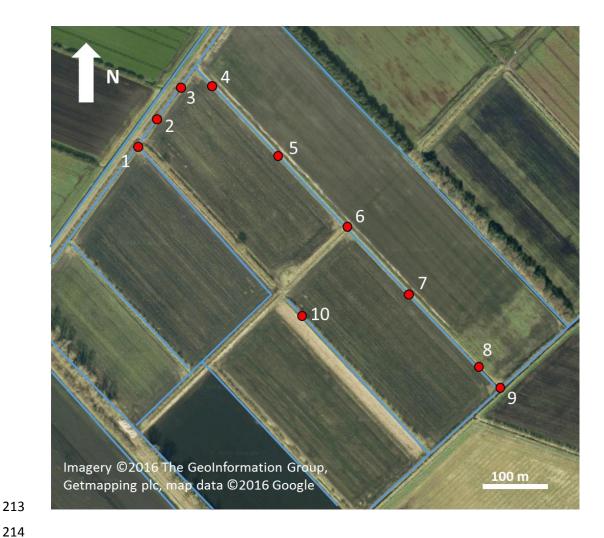


Figure 2. Maps of the semi-natural site (top panel), extensive grassland site (middle panel) and cropland site (bottom panel). Red dots mark numbered sampling locations, blue lines mark ditches/watercourses. For the semi-natural and extensive grassland sites, blue arrows mark where water is pumped onto 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  $\mu$ m 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 (NO3 $^-$ ) concentrations can interfere at wavelengths < 250 nm (Wang & Hsieh, 2001). Considering

the potential for high NO<sub>3</sub><sup>-</sup> concentrations in surface waters in areas of intensive agriculture a SUVA wavelength of 280 nm was selected. NO<sub>3</sub><sup>-</sup> was measured using a NICO 2000 ion-selective electrode and appropriate standards. Dissolved CH<sub>4</sub> and CO<sub>2</sub> were analysed using a Los Gatos Ultraportable Greenhouse Gas Analyzer equipped with a sampling loop (Baird *et al.*, 2010). Dissolved N<sub>2</sub>O was analysed on an Ai Cambridge GC94 equipped with an Electron Capture Detector (ECD).

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

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

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

$$F = k x (C_{aa} - C_{ea})$$

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

### 2.4 Statistics

Statistical analysis was carried out in SPSS to determine if differences in GHGs and piston velocity ( $CH_4$  and  $CO_2$  flux, and dissolved concentrations of  $CH_4$ ,  $CO_2$  and  $N_2O$ ) were 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  $p \le 0.05$ .

# 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  $I^{-1}$ ), presumably due to the use of fertilisers. At the grassland site  $NO_3^-$  was low ( $\leq 5$  mg  $I^{-1}$ ) except in March when the mean was 19 mg  $I^{-1}$ . 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  $\sim 30$  mg  $I^{-1}$ ), 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<sub>4</sub> fluxes were relatively low in March ( $\leq$  10.5 mg m<sup>-2</sup> d<sup>-1</sup>). Fluxes stayed low in May at the grassland and cropland fens, but were higher (80 mg m<sup>-2</sup> d<sup>-1</sup>) at the semi-natural fen. Median CH<sub>4</sub> fluxes peaked in August at all three sites, at 120-230 mg m<sup>-2</sup> d<sup>-1</sup>. Highest individual fluxes at each site were: 3650, 25400 and 7430 mg m<sup>-2</sup> d<sup>-1</sup> for the semi-natural (May), grassland (August) and cropland (August) site respectively. CO<sub>2</sub> flux was relatively stable at the semi-natural site at 2050-3250 mg m<sup>-2</sup> d<sup>-1</sup>, but fluctuated at the other two sites, peaking at 6600 mg m<sup>-2</sup> d<sup>-1</sup> in August at the grassland site, and at 4760 mg m<sup>-2</sup> d<sup>-1</sup> in October at the cropland site. Highest individual fluxes at each site were: 9580, 16800 and 13800 mg m<sup>-2</sup> d<sup>-1</sup> 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<sub>4</sub>, these produced estimates of 37.8, 18.3 and 27.2 g CH<sub>4</sub> m<sup>-2</sup>yr<sup>-1</sup> for the semi-natural, grassland and cropland sites respectively, with respective standard errors of 74.6, 244, and 97.3 g CH<sub>4</sub> m<sup>-2</sup>yr<sup>-1</sup>. For CO<sub>2</sub> the annual fluxes were 1100, 1170 and 1440 g CO<sub>2</sub> m<sup>-2</sup>yr<sup>-1</sup> for the semi-natural, grassland and cropland sites respectively, with respective SEs of 225, 340 and 312 g CO<sub>2</sub> m<sup>-2</sup>yr<sup>-1</sup>.

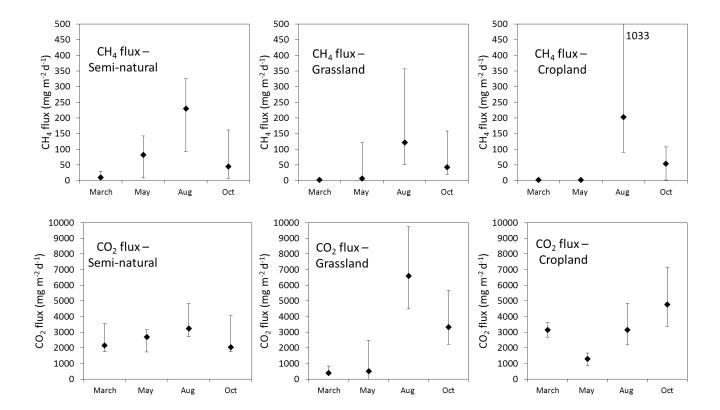


Figure 3. Median ditch fluxes of  $CH_4$  and  $CO_2$  measured using floating chambers at the three sites. Error bars represent first and third quartiles. Note that the error bar for  $CH_4$  in August at the cropland site exceeds the scale. There was a significant difference ( $p \le 0.001$ ) for 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

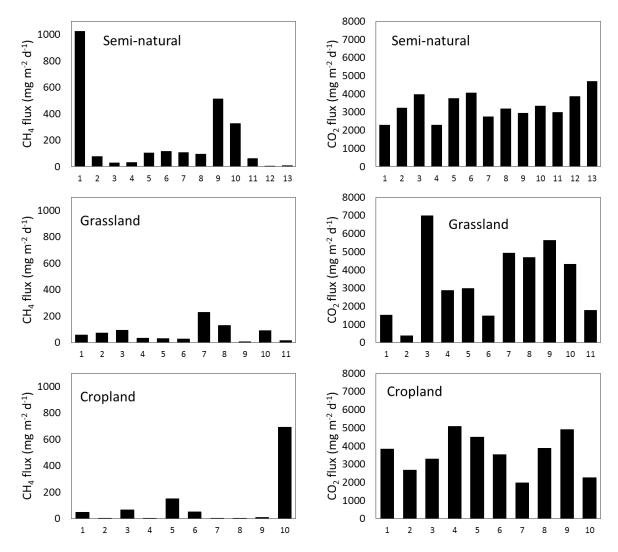


Figure 4. Median CH<sub>4</sub> (left) and CO<sub>2</sub> (right) fluxes for each individual numbered sampling point, grouped by site. Fig.2 displays numbered sampling points on site maps.

# 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  $I^{-1}$ , except for a spike of 0.43 mg  $I^{-1}$  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  $I^{-1}$ ), whilst there was an increase through the year at the grassland site (1.7-7.5 mg  $I^{-1}$ ). Dissolved  $CO_2$  at the cropland site also peaked later in the year (15 mg  $I^{-1}$  in August and October). Median  $N_2O$  concentrations were under

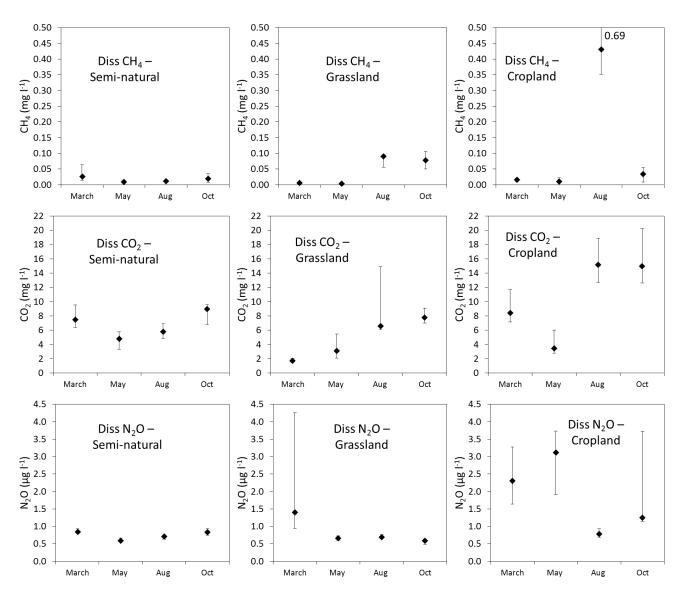


Figure 5. Median ditch dissolved concentrations of  $CH_4$ ,  $CO_2$  and  $N_2O$  at the three sites. Error bars represent first and third quartiles.. Note that the error bar for  $CH_4$  in August at the cropland site exceeds the scale. There were significant differences between the cropland and other 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).

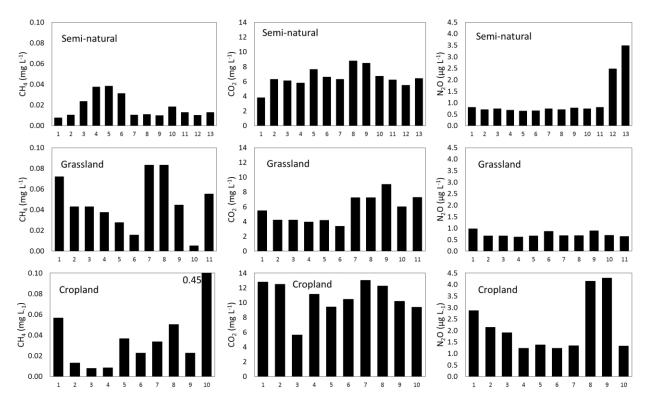


Figure 6. Median CH<sub>4</sub> (left) CO<sub>2</sub> (middle) and N<sub>2</sub>O (right) concentrations for each individual numbered sampling point, grouped by site. Fig.2 displays numbered sampling points on site maps.

# 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  $\mu$ g  $I^{-1}$  until DOC: $NO_3^-$  fell below 5. This relationship was consistent across all three sites.

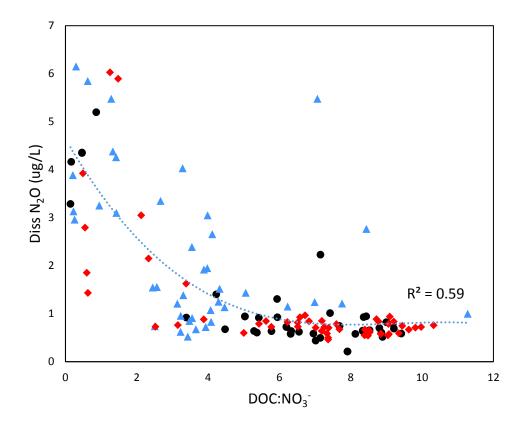


Figure 7. Relationship between dissolved  $N_2O$  and  $DOC:NO_3^-$  ratio for all individual samples. Red diamonds = semi-natural fen, black circles = grassland, blue triangles = cropland. Trend line is  $3^{rd}$  order polynomial.

#### 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<sub>2</sub> and CH<sub>4</sub> fluxes

We no significant differences between sites for CH<sub>4</sub> fluxes, but fluxes were CO<sub>2</sub> fluxes were significantly higher at the cropland compared to the grassland and semi-natural sites.. There were seasonal patterns in fluxes of CH<sub>4</sub>; 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

extensive within-site variation in gas fluxes, particularly for CH<sub>4</sub>. For instance, at the seminatural fen, sample point 1 had CH<sub>4</sub> fluxes an order of magnitude higher than the adjacent sample point 2. Sample point 1 was close to the wind pump that pumps river water onto the fen, and it could be that the mixing between low DOC/high NO<sub>3</sub>- river water and high DOC/low NO<sub>3</sub><sup>-</sup> fen water produces a 'hotspot' of organic carbon processing resulting in CH<sub>4</sub> production (sensu Palmer et al., 2016). The lowest CH<sub>4</sub> fluxes were recorded at a ditch that bounded the edge of the fen, which displayed lower DOC concentrations and higher NO<sub>3</sub>concentrations, suggesting that this ditch was connected to the river, and contained less organic substrates for methanogenesis. At the grassland site, CH<sub>4</sub> fluxes were highest at adjacent sample points 7 and 8 though this was not obviously related to any measured variables, e.g. EC, DIC and DOC were not elevated at these locations. At the cropland site, sample point 10 was extremely high compared to the other points. This ditch was shaded by a dense cover of trees and was near to a dead-end in the ditch system. This point had elevated levels of EC (25% higher compared to the mean of the other sample points) and DOC (114% higher), and it is likely that standing water here leads to an accumulation of organic matter and stagnation, and hence higher rates of methanogenesis (fig.1). This hypothesis is supported by the fact that dissolved CH<sub>4</sub> concentrations at this location were higher than any other sampling point at any site (fig. 6).

Although we only sampled four times within a year, our design featured large numbers of sampling points per site, and different sites were sampled at the same times of year. Calculated mean fluxes may not therefore be an accurate representation of the annual values, but should provide a reasonable representation of between-site differences. Mean CH<sub>4</sub> fluxes followed the order semi-natural>cropland>grassland. The mean flux for the semi-natural fen, 38 g CH<sub>4</sub> m<sup>-2</sup> yr<sup>-1</sup>, falls within the range of other reported fluxes from ditches in semi-natural peatlands; e.g. 12 g CH<sub>4</sub> m<sup>-2</sup> yr<sup>-1</sup> and 164 g CH<sub>4</sub> m<sup>-2</sup> yr<sup>-1</sup> from drained boreal fens (Glagolev *et al.*, 2008, Minkkinen & Laine, 2006). The only reported annual ditch CH<sub>4</sub> flux from a temperate semi-natural site are 5.5 g CH<sub>4</sub> m<sup>-2</sup> yr<sup>-1</sup> from a UK upland blanket bog (Cooper *et al.*, 2014). The considerably higher flux reported from our semi-natural site therefore shows the effect of nutrient status on ditch emissions. It has been suggested that ditch CH<sub>4</sub> emissions increase as land-use intensity increases (Evans *et al.*, 2016a) but our data do not show this. The flux from our grassland site, 18 g CH<sub>4</sub> m<sup>-2</sup> yr<sup>-1</sup> is low compared to values such as 43, 66, 77 and 70 g CH<sub>4</sub> m<sup>-2</sup> yr<sup>-1</sup> from other low-intensity grasslands (Schrier-

Uijl et al., 2010, Vermaat et al., 2011, McNamara, 2013, Hendricks et al., 2007), although van den Pol-van Dasselaar et al. (1999) recorded an annual flux of just 11 g CH<sub>4</sub> m<sup>-2</sup> yr<sup>-1</sup>. To our knowledge, our annual ditch flux calculation of 27 g CH<sub>4</sub> m<sup>-2</sup> yr<sup>-1</sup> for the cropland is, along with the fluxes in our broader project report (Evans et al., 2016a), the first annual flux estimate for a temperate peatland under agriculture. There are several possible reasons for the highest annual flux being observed at the semi-natural site. Firstly, subsidence at our grassland site has resulted in the loss of the majority of peat soil, and it may be that the low organic content of the soil has led to a reduction in CH<sub>4</sub> production. This could be especially relevant if CH<sub>4</sub> is produced in the saturated peat, then transported laterally and degassed from ditches (e.g. fig.1); the grassland site dries out completely, presumably resulting in zero methanogenesis, whilst the water table remains in the peat at a deep level at the cropland, making this a plausible hypothesis. Secondly, the semi-natural site is likely to have a wellestablished methanogenic community compared to the other two sites where severe drainage and loss of peat (Stroh et al., 2013) may have disrupted the microbial communities (Jerman et al., 2009). Thirdly, the ditches at the semi-natural site were relatively deep, and depth fluctuations were minimal compared to the other two sites. This could lead to the formation of anoxic conditions, thus stimulating CH<sub>4</sub> emissions and reducing oxidation in the water column (O<sub>2</sub> measurements on future sampling campaigns would help to resolve this). Finally, Vermaat et al. (2011) recorded more ebullition in ditches sheltered by reed beds. It is therefore possible that steady ebullition contributed to the high fluxes at the semi-natural fen, as well as being responsible for the individual high fluxes (e.g. 25400 and 7430 mg m<sup>-2</sup> d<sup>-1</sup> 1) that were observed at the grassland and cropland. Ebullition from ditches in a Finnish mire measured using bubble traps was 3-37 mg m<sup>-2</sup> d<sup>-1</sup>, and was negligible (0.2-2.3% compared to diffusive emissions) in flowing ditches but substantial in ditches with standing water (10-22% of diffusive flux) (Minkkinen et al., 1997, 2006). Vermaat et al. (2011) calculated ditch ebullition by interpreting steep, short-term increases in CH<sub>4</sub> concentration in a floating chamber as evidence of bubbling, and stated that approximately 50% of total flux was due to ebullition. Other research using bubble traps has shown that ebullition in wetland and agricultural streams can equal the diffusive flux (Wilcock & Sorrell, 2008, Crawford et al., 2014). More measurements of ebullition in ditches are clearly needed.

Unlike CH<sub>4</sub>, annual CO<sub>2</sub> fluxes did increase with land-use intensity, in the order semi-

natural<grassland<cropland. Estimates of annual ditch CO2 fluxes are lacking from the

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literature, but scaling up the measurements of Vermaat *et al.* (2011) would produce annual fluxes of 1050 g CO<sub>2</sub> m<sup>-2</sup> yr<sup>-1</sup> for ditches in reed beds, and 1310 g CO<sub>2</sub> m<sup>-2</sup> yr<sup>-1</sup> for ditches in rough pasture. Our semi-natural site is therefore similar, with a flux of 1100 g CO<sub>2</sub> m<sup>-2</sup> yr<sup>-1</sup>, although our grassland annual flux was 1170 g CO<sub>2</sub> m<sup>-2</sup> yr<sup>-1</sup>. Our median CO<sub>2</sub> fluxes ranged from 488 mg m<sup>-2</sup> d<sup>-1</sup> to 8000 mg m<sup>-2</sup> d<sup>-1</sup>, and are therefore similar to those reported by Schrier-Uijl *et al.* (2011), Teh *et al.* (2011) and Hyvönen *et al.* (2013). CO<sub>2</sub> fluxes at the seminatural site displayed less seasonality which may be a function of the deeper ditches minimising temperature increases in the basal peat, and therefore suppressing productivity (McEnroe *et al.*, 2009).

### 4.3. Dissolved GHGs

For dissolved  $CH_4$ ,  $CO_2$  and  $N_2O$ , we found significant differences between the cropland compared to the grassland and semi-natural sites. This suggests that intensive agriculture has affected the biogeochemistry of the cropland ditches. Some sampling locations showed similar concentrations of dissolved gases, and this could be due spatial autocorrelation in dissolved GHGs (e.g. Chapra & Di Toro, 1991). This was most obvious for  $CH_4$  at the semi-natural site, and  $N_2O$  at the semi-natural site and grassland.

Once pH had been removed as a predictive variable, we were able to account for 29% of temporal and spatial (within and between site) variability in CH<sub>4</sub>, and 50% of variability in CO<sub>2</sub>. For dissolved CO<sub>2</sub> there were positive relationships with depth to water table, DIC concentration, SUVA, and ditch depth. A deeper water table within the peat should result in increased decomposition, with CO<sub>2</sub> then exported laterally into ditches. A negative relationship between CO<sub>2</sub> and water depth has been found for pools in natural peatlands (McEnroe *et al.*, 2009), and so our contrary finding could be due to the high degree of management at these fens; e.g. irrigation at the cropland reversed the natural seasonality in ditch depth and doubled the water level of the ditches in August, which coincided with the growing season increase in dissolved CO<sub>2</sub>.

Dissolved CH<sub>4</sub> concentrations fell within the same range as those in agricultural streams (0.001-0.4 mg L<sup>-1</sup>, Wilcock & Sorrell, 2008), and ditches in agricultural peatlands (maximum of 0.04 mg L<sup>-1</sup>, Schrier-Uijl *et al.*, 2011). They were of the same magnitude as 0.022 mg L<sup>-1</sup> which was the calculated mean fluvial CH<sub>4</sub> concentration from 111 published studies (Stanley *et al.*, 2016). Dissolved CH<sub>4</sub> correlated positively with air temperature,  $NO_3^-$ ,

DIC, and depth to water table (in the fen/field), and negatively with EC. Higher 471 temperatures could stimulate methanogenesis, leading to increased concentrations of CH<sub>4</sub>. 472 The positive correlation between dissolved CH<sub>4</sub> and depth to water table may, in part, be 473 474 due to the confounding effect of seasonality; i.e. water tables were lower in the growing 475 season when ditches become depleted in oxygen, leading to higher rate of methanogenesis. 476 The positive correlation between NO<sub>3</sub> and CH<sub>4</sub> is unexpected, as NO<sub>3</sub> inhibits 477 methanogenesis (Watson & Nedwell, 1998) and, as an electron acceptor, allows denitrifying bacteria to favourably out-compete methanogens (Le Mer & Roger, 2001). One possible 478 479 explanation is that increased NO<sub>3</sub>- levels are associated with increased ammonium 480 concentrations at the semi-natural fen (Conrad & Rothfuss, 1991), and the inhibitory effect 481 of ammonium on methanotrophy is larger than the inhibitory effect of NO<sub>3</sub> on methanogenesis. It may be that high nutrient levels associated with NO<sub>3</sub>- could coincide 482 483 with inputs of labile organic matter, particularly at agricultural sites, thus stimulating 484 methanogenesis when other electron acceptors have been depleted in the sediment. 485 Alternatively, as discussed in section 4.2, it could be that CH<sub>4</sub> is produced in the saturated peat and then transported laterally into the ditch; i.e. methanogenesis occurs in zones 486 487 distant from potential NO<sub>3</sub> inhibition. Schade et al. (2016) did find a weak negative 488 correlation between NO<sub>3</sub> and CH<sub>4</sub> in a low NO<sub>3</sub>/high DOC stream but found no correlation in a high NO<sub>3</sub>-/low DOC stream or in a high NO<sub>3</sub>-/high DOC stream. Similarly, Crawford et al. 489 (2016) found no evidence that NO<sub>3</sub><sup>-</sup> inhibited CH<sub>4</sub> production or emission in streams, and, in 490 491 line with our hypothesis above, suggested that methanogenesis could be spatially removed from high NO<sub>3</sub> concentrations. The absence of ditch depth from the CH<sub>4</sub> model is 492 interesting as negative relationships between CH<sub>4</sub> flux and depth have been noted 493 494 previously, although these are sometimes low; e.g. McEnroe et al. (2009) reported an R<sup>2</sup> value of 0.23 for pools, and Vermaat et al. (2011) found an R<sup>2</sup> of 0.15 for ditches. Pelletier 495 et al. (2007) found both negative and positive relationships between CH<sub>4</sub> flux and depth in 496 497 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 498 previously mentioned this management removes the natural seasonality in ditch depth. 499 Finally, it is worth considering that wind speed may play a role in GHG dynamics. However, 500 501 the ditches at our sites are predominantly sheltered by reedbeds or banks and, as previously noted, the floating chamber did not drift, suggesting that wind speed was low on sampling days.

Dissolved N<sub>2</sub>O was present in the ditches at all three fens, but was low at the seminatural site. Concentrations were only high at the grassland site in March, but were high for most of the year at the cropland site, presumably due to the application of fertilisers to adjacent fields. Positive relationships between dissolved N<sub>2</sub>O and N<sub>2</sub>O flux have been demonstrated in rivers (Yang et al., 2011). Diffusive fluxes of N<sub>2</sub>O have been shown to occur in oxygenated waters and it therefore seems highly probable that ditches at all three fens were sources of N<sub>2</sub>O to the atmosphere. Wilcock & Sorrell (2008) measured N2O concentrations in agricultural streams between 0.26-28.5 μg l<sup>-1</sup>, considerably higher than our maximum individual measurements of 6.15 μg l<sup>-1</sup>, whilst concentrations in a eutrophic river have been reported as 0.66-1.14 μg l<sup>-1</sup> (Silvennoinen *et al.*, 2008). Sturm *et al.* (2014) recorded average concentrations of N<sub>2</sub>O in lake surface water as 0.61 μg l<sup>-1</sup> and 0.74 μg l<sup>-1</sup>, similar to median concentrations at our grassland and semi-natural site, although concentrations at our cropland were higher. The authors also measured N<sub>2</sub>O fluxes, with averages of 3.7 and 5.3 μg m<sup>-2</sup> hr<sup>-1</sup>. Reay et al. (2003) reported a relationship between N<sub>2</sub>O fluxes and dissolved N<sub>2</sub>O in UK agricultural ditches; applying that relationship to our data allows estimates of median flux for each fen to be calculated as 300, 210, and 1150 μg m<sup>-2</sup> hr<sup>-1</sup> for the semi-natural, grassland and cropland sites respectively. These fluxes at the semi-natural and grassland sites are similar to those reported by Teh et al. (2011) for ditches in a peatland pasture in the USA.

We found a statistically significant relationship between dissolved N<sub>2</sub>O and NO<sub>3</sub><sup>-</sup>, in agreement with others (e.g. Reay *et al.*, 2003, Hinshaw & Dahlgren, 2013, Schade *et al.*, 2016). However, a better fit was found between dissolved N<sub>2</sub>O and the DOC:NO<sub>3</sub><sup>-</sup> ratio. Aquatic systems generally show an inverse relationship between DOC and NO<sub>3</sub><sup>-</sup> concentrations, which reflects a gradient from nitrogen limitation of microbial processes in carbon-rich systems to labile organic matter limitation in carbon-poor systems (Goodale et al., 2005; Taylor and Townsend, 2010). Our observation that dissolved N<sub>2</sub>O only increases above ambient atmospheric concentrations when DOC/NO<sub>3</sub><sup>-</sup> ratios are low suggests both that NO<sub>3</sub><sup>-</sup> concentrations need to be high enough to allow denitrification to occur, and that labile organic matter concentrations need to be low enough to favour this process over other microbial processes such as NO<sub>3</sub><sup>-</sup> reduction or assimilation. There were three samples

that appeared to deviate from the observed relationship, and it may be that higher concentrations of ammonium cause elevated N₂O concentrations, particularly if dissolved oxygen is not limiting (Liikanen & Martikainen, 2003).

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#### 4.4. Implications for GHG accounting and conclusions

Our data support previous studies in showing that ditches in both semi-natural and agricultural peatlands act as sources of CH<sub>4</sub>, CO<sub>2</sub> and N<sub>2</sub>O emissions. It is widely recognised that intact fens are important emitters of CH<sub>4</sub> (Turetsky et al., 2014). Although not intact, our semi-natural fen is under conservation management, and therefore the vegetation is similar to intact fens. As such, the annual terrestrial flux from our semi-natural site is 11.7 g  $CH_4\ m^{-2}\ yr^{-1}$  (Evans  $et\ al.$ , 2016b) , compared to 37.8 g  $CH_4\ m^{-2}\ yr^{-1}$  from the ditches. When weighted by area for the entire fen, ditches would therefore be responsible for 0.53 g CH<sub>4</sub> m<sup>-2</sup> yr<sup>-1</sup>, approximately 5% of total emissions. Although ditches occupy only a fraction of the landscape, the magnitude of the fluxes observed here suggest that ditches in modified fen landscapes must be considered when calculating carbon balances, particularly for studies relying on static chamber, rather than eddy-covariance, methods, since this component of CO<sub>2</sub> and CH<sub>4</sub> emissions will otherwise be missed. In drained peatland systems, the contribution of ditches to the overall CH<sub>4</sub> budget is even more marked, because CH<sub>4</sub> fluxes from drained peat surfaces tend to be near zero (Willison, 1998, IPCC, 2014). At our cropland site, the field surface acted consistently as a small net sink for CH<sub>4</sub> (Evans et al., 2016b) and ditches were thus responsible for the entirety of CH<sub>4</sub> emissions from the system as a whole, which would give an areally-weighted flux of 0.44 g  $\rm CH_4~m^{-2}\,yr^{-1}$  compared to the field sink of -0.17 g CH<sub>4</sub> m<sup>-2</sup> yr<sup>-1</sup>. This is probably true for agriculturally drained peatlands in general (IPCC, 2014, Evans et al., 2016a). Terrestrial fluxes at our grassland restoration site show that both uptake and emission of CH<sub>4</sub> occur, but the annual flux is approximately zero (Evans et al., 2016a). Thus, the ditches here are responsible for the majority of CH<sub>4</sub> emissions to the atmosphere, calculated on an areal basis as 0.31 g CH<sub>4</sub> m<sup>-2</sup> yr<sup>-1</sup>.

Our CO<sub>2</sub> fluxes were similar to others reported in the literature from ditches, which have often been of the same magnitude as fluxes from terrestrial fen (e.g. Schrier-Uijl *et al.*, 2011, Hyvönen *et al.*, 2013). Our median estimated N<sub>2</sub>O fluxes for the semi-natural and grassland sites are slightly higher than terrestrial fluxes from a Finnish drained minerotrophic fen (Martikainen *et al.*, 1995) whilst our calculated N<sub>2</sub>O 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<sub>4</sub>. 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) | рН                                      | 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 <sup>-1</sup> ) | Semi-natural | 921 (62)   | 907 (18)   | 810 (73)   | 965 (51)   | NO <sub>3</sub> - (mg l <sup>-1</sup> ) | 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 <sup>-1</sup> ) | 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 <sup>-1</sup> ) | 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<sup>-1</sup>) 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<sub>2</sub>/CH<sub>4</sub> 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 <sub>2</sub> | Slope coefficient | р      |
|----------------------|-------------------|--------|
| 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 <sub>4</sub> | Slope coefficient | р      |
| Intercept            | -0.63             | <0.001 |
| Air temp             | 0.0148            | <0.001 |
| NO <sub>3</sub> -    | 0.0066            | <0.001 |
| DIC                  | 0.0066            | <0.001 |
| Depth to WT          | 0.0019            | <0.001 |
| EC                   | -0.0002           | 0.02   |