Dissolved nitrous oxide ($N_2O$) dynamics in agricultural field drains and headwater streams in an intensive arable catchment

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ABSTRACT

Indirect nitrous oxide ($N_2O$) emissions produced by nitrogen (N) leaching into surface water and groundwater bodies are poorly understood in comparison to direct $N_2O$ emissions from soils. In this study, dissolved $N_2O$ concentrations were measured weekly in both lowland headwater streams and subsurface agricultural field drain discharges over a two-year period (2013–2015) in an intensive arable catchment, Norfolk, UK. All field drain and stream water samples were found to have dissolved $N_2O$ concentrations higher than the water–air equilibrium concentration, illustrating that all sites were acting as a net source of $N_2O$ emissions to the atmosphere. Soil texture was found to significantly influence field drain $N_2O$ dynamics, with mean concentrations from drains in clay loam soils (5.3 µg N L$^{-1}$) being greater than drains in sandy loam soils (4.0 µg N L$^{-1}$). Soil texture also impacted upon the relationships between field drain $N_2O$ concentrations and other water quality parameters (pH, flow rate, and nitrate ($NO_3$) and nitrite ($NO_2$) concentrations), highlighting possible differences in $N_2O$ production mechanisms in different soil types. Catchment antecedent moisture conditions influenced the storm event mobilisation of $N_2O$ in both field drains and streams, with the greatest concentration increases recorded during precipitation events preceded by prolonged wet conditions. $N_2O$ concentrations also varied seasonally, with the lowest mean concentrations typically occurring during the summer months (JJA). Nitrogen fertiliser application rates and different soil inversion regimes were found to have no effect
on dissolved N$_2$O concentrations, whereas higher N$_2$O concentrations recorded in field drains under a winter cover crop compared to fallow fields revealed cover crops are an ineffective greenhouse gas emission mitigation strategy. Overall, this study highlights the complex interactions governing the dynamics of dissolved N$_2$O concentrations in field drains and headwater streams in a lowland intensive agricultural catchment.

**Keywords:** nitrous oxide; nitrate; nitrification; denitrification; river; tile drain.

1. **Introduction**

Nitrous oxide (N$_2$O) is a potent and persistent greenhouse gas with a present atmospheric concentration of 326.7 ppb (European Environment Agency, 2016). N$_2$O has 300 times greater global warming potential than CO$_2$ and accounts for ~5% of the total greenhouse effect (Omonode et al., 2011). N$_2$O participates in photochemical reactions in the stratosphere which lead to the destruction of the ozone (O$_3$) layer (Jacinthe and Dick, 1997) and is also linked to the release of nitric oxide and ammonia in the atmosphere which contribute to acid rain and the acidification of soils and drainage systems (Mosier and Kroeze, 1998).

Atmospheric N$_2$O concentrations are increasing at an annual rate of ~0.26% (Forster et al., 2007) and agriculture is the largest source of anthropogenic N$_2$O emissions, accounting for ~60% of the total human-produced N$_2$O. Globally, agricultural N$_2$O emissions increased by nearly 17% from 1990 to 2005 (Smith et al., 2007).

Global agricultural N$_2$O emissions originate from three sources: direct emissions from nitrogen (N) fertilised soil (1.8 Tg N a$^{-1}$); direct emissions from animal production (2.3 Tg N a$^{-1}$); and indirect emissions from N used in agricultural systems (1.3 Tg N a$^{-1}$) (Syakila and Kroeze, 2011). Indirect emissions are in turn derived from three sources: atmospheric deposition (0.4 Tg N a$^{-1}$); human sewage (0.3 Tg N a$^{-1}$); and nitrogen leaching and runoff into water bodies (0.6 Tg N a$^{-1}$). Thus, indirect emissions from N leaching and runoff are
significant, equating to 46% of the indirect emissions from agriculture and 11% of total agricultural N\textsubscript{2}O emissions. These indirect emissions from N leaching and runoff are equivalent to \sim33\% of the direct N\textsubscript{2}O emissions from soils. Other studies (e.g. Mühlherr and Hiscock, 1997; Seitzinger and Kroeze, 1998; Naqvi et al., 2000) have previously highlighted the significance of N\textsubscript{2}O emissions from agricultural N leaching and runoff to the overall N\textsubscript{2}O budget. However, compared to direct N\textsubscript{2}O emissions, these indirect emissions have been poorly studied to date (Outram and Hiscock, 2012).

Indirect emissions of N\textsubscript{2}O occur when N fertiliser is lost from agricultural soils through leaching and runoff. This mobilised N enters groundwater, rivers, riparian areas, wetlands and eventually the ocean (Mosier et al., 1998). Nitrogen in groundwater and surface waters increases the biological production of N\textsubscript{2}O as the N undergoes both nitrification and denitrification. Nitrification is an aerobic chemolithoautotrophic process in which bacteria oxidise ammonium (NH\textsubscript{4}\textsuperscript{+}) to nitrate (NO\textsubscript{3}\textsuperscript{-}) and N\textsubscript{2}O. Denitrification is an anaerobic process in which bacteria sequentially reduce NO\textsubscript{3}\textsuperscript{-} to N\textsubscript{2}O and dinitrogen (N\textsubscript{2}) with a small amount of N\textsubscript{2}O escaping in the process (Beaulieu et al., 2008). Therefore, the factors controlling nitrification and denitrification in the soil, such as moisture content, temperature, organic matter, availability of N and NH\textsubscript{4}\textsuperscript{+}, pH, redox conditions, texture and agricultural management practices may subsequently control both direct and indirect N\textsubscript{2}O emissions (Bouwman et al., 1993; Panek et al., 2000). However, the majority of existing studies (e.g. Włodarczyk et al., 2005; Jarecki et al., 2009; Hénault et al., 2012) have only investigated the effect of these parameters on direct N\textsubscript{2}O emissions, leaving the control of these parameters on indirect N\textsubscript{2}O emissions poorly investigated in the literature. The aim of this study was to address these deficiencies through the following objectives:

i. to investigate the spatial and temporal dynamics of dissolved N\textsubscript{2}O concentrations in subsurface agricultural field drains and lowland headwater streams;
ii. to assess the impact of water quality parameters, soil texture and crop cultivation regimes on dissolved N₂O concentrations.

2. Methods

2.1 Study location

The study area is located to the northwest of Norwich in the Blackwater sub-catchment of the River Wensum, Norfolk, UK (Figure 1). The Blackwater sub-catchment is intensively monitored as part of the Wensum Demonstration Test Catchment (DTC) project which aims to evaluate the extent to which on-farm mitigation measures can cost-effectively reduce the level of diffuse agricultural pollution (McGonigle et al., 2014). The field sites are in an area of intensive arable farming which includes cereals, oilseed rape, spring beans and sugar beet grown in a seven-year rotation. The average annual rainfall total is 674 mm and the mean annual temperature is 10.1°C. The soil parent material comprises glacial deposits over Cretaceous Chalk, with soil textures varying from sandy loam to sandy clay loam and clay loam. Part of the sub-catchment is extensively under-drained by a dense network of subsurface agricultural field (“tile”) drains installed at a depth of 100–160 cm. Discharge from certain drains can be as high as 10 L s⁻¹, but varies greatly depending upon season, depth, catchment area and antecedent moisture conditions.

In 2013, nine fields covering 143 ha of arable land were identified for the trialling of a winter cover crop and reduced tillage practices aimed at reducing diffuse nutrient losses into the River Blackwater (Figure 1 and Table I). These nine fields were divided into three blocks of mitigation measures, with each block sown with the same crop and same fertiliser application rate during the 2013/14 (spring beans; 0 kg N ha⁻¹, 30 kg P ha⁻¹, 55 kg K ha⁻¹) and 2014/15 (winter wheat; 220 kg N ha⁻¹, 22 kg P ha⁻¹, 85 kg K ha⁻¹) farm years (September to August). Two fields were kept as a control (block J) and were cultivated by mouldboard ploughing to...
25 cm depth prior to sowing. An oilseed radish (*Raphanus sativus*) cover crop (seed density = 18 kg ha\(^{-1}\)) was sown in treatment blocks L and P in late-August 2013. Block P then underwent reduced tillage to a depth of 10 cm prior to sowing spring beans and block L underwent direct drilling with no inversion. A winter crop (winter wheat) was grown in the second year (2014/15) and so a cover crop was not sown, but direct drilling and reduced tillage practices continued in block L and block P, respectively.

### 2.2 Sample collection

Water samples for N\(_2\)O and nutrient analysis were collected in 13 field drains and 4 stream locations (A, B, E and M) on a weekly basis between April 2013 and April 2015 (Figure 1). Over the duration of the study, 621 water samples were collected from field drains and 308 samples from stream sites, such that 929 samples were obtained in total. Samples for dissolved N\(_2\)O analysis were collected from the stream and drain outlet pipes in 20 mL glass syringes (SAMCO) with a three-way stopcock attached to each syringe by a Luer-Lock fitting. Syringes were flushed three times with water from the sampling point and any air bubbles contained in the syringes were expelled before the final sample was taken. No preservative was added to the sample. Samples were returned to cold storage at 4°C within 3 h and analysed for N\(_2\)O within 72 h of collection. Samples for nutrient analysis were collected in 1 L polypropylene bottles and also analysed within 72 h of collection. Rainfall was measured via a tipping bucket rain gauge installed in mini-catchment A. Soil samples for texture analysis were collected in May and September 2013 from 12 locations per field in a ‘W’ layout at 0-30 cm depth using a Dutch auger and Hydrocare powered auger (Figure 1). Catchment areas of the field drains were divided into two dominant soil types (clay loam and sandy loam) based on the soil texture data collected in this study. Drains D3, D7, D8, D9, D10 and D13 were predominantly within clay loam soils, whereas drains D1, D2, D4, D5, D6, D11 and D12 were predominantly within clay loam soils.
D6, D11 and D16 were predominantly within sandy loam soils, albeit no drain area was entirely composed of just one soil texture.

2.3 Sample analysis

N$_2$O was analysed by gas chromatography with an electron capture detector (GC-ECD). Samples were injected directly into a purge column of a helium flushed gas extraction line, which included traps for water vapour and CO$_2$ removal. A reverse-flow Nafion dryer was used in the extraction line with N$_2$O. N$_2$O was trapped at -190 °C above liquid nitrogen in a 3.2 mm stainless steel loop. The N$_2$O was remobilised by submerging the loop in a hot water bath at ~95 °C. The collected N$_2$O was analysed with a Shimadzu GC-8A at 300 °C using a 3.6 m by 3.2 mm diameter stainless steel Poropak Q column at 50 °C. The accuracy of N$_2$O measurements was within ±3% with a detection limit of ~0.0008 µg N L$^{-1}$. Further details of this method can be found in Mühlherr and Hiscock (1998). Nitrate was determined by ion chromatography using a Dionex ISC 2000 instrument with an accuracy of 0.19 mg N L$^{-1}$. Ammonium and nitrite were determined by a Continuous Flow Analyser - Skalar San++ with accuracies of 4.57 µg N L$^{-1}$ and 1.52 µg N L$^{-1}$, respectively. Soil texture was determined by laser diffraction.

For data analysis, the independent-sample $t$-test was used to examine the degree of significance ($p$-value < 0.05) between two groups, whilst multiple linear regression models for the prediction of N$_2$O concentration in stream and field drain waters were formulated in the $R$ environment (R Core Team, 2016).

3. Results and Discussion

3.1 Spatial variability of nitrous oxide concentrations

N$_2$O concentrations in field drain ($n = 621$) and stream ($n = 308$) water samples collected throughout this study are presented in Figure 2. All of the drain and stream water samples
Among the stream sampling sites, site M had the lowest mean concentration (1.0 µg N L\(^{-1}\)) and site B the highest (1.8 µg N L\(^{-1}\)). Compared to the field drains, stream samples contained significantly (\(p < 0.05\)) lower N\(_2\)O concentrations, a consequence of N\(_2\)O being rapidly

were found to have dissolved N\(_2\)O concentrations higher than would be expected when atmospheric N\(_2\)O concentrations are at equilibrium with water (~0.36 µg N L\(^{-1}\); Weiss and Price, 1980), illustrating that all sites were acting as a net source of N\(_2\)O emissions to the atmosphere. Field drain N\(_2\)O concentrations ranged from 0.4 µg N L\(^{-1}\), just above the atmospheric-water equilibrium, to 34.4 µg N L\(^{-1}\), 100 times greater than atmospheric-water equilibrium. Mean N\(_2\)O concentrations in drains within clay loam and sandy loam soils were 5.3 and 4.0 µg N L\(^{-1}\), respectively. Among the drains, D11 had the highest mean value (8.0 µg N L\(^{-1}\)) and D2 the lowest (2.7 µg N L\(^{-1}\)), with both draining sandy loam soils in block L.

There have been very few previously published studies of dissolved N\(_2\)O concentrations in field drains. Dowdell et al. (1979), who studied dissolved N\(_2\)O in agricultural drains for the first time, found a range of 1–132 µg N L\(^{-1}\) in three different locations across southern England. In a study of N\(_2\)O discharged from 28 drained agricultural areas in the upper Neckar region, Germany, Hack and Kaupenjohann (2002) observed a N\(_2\)O range of 0.4–60 µg N L\(^{-1}\), whilst Reay et al. (2004) recorded a narrow range in N\(_2\)O concentration (2–4 µg N L\(^{-1}\)) in one particular field drain under arable land planted with spring barely in Scotland over a 45 day period. Similar to the differences in soil texture reported here, differences in groundwater N\(_2\)O in the unsaturated zone between sites with contrasting geology was reported by Darling et al. (1998), who recorded mean N\(_2\)O concentrations of 2.8 and 1.5 µg N L\(^{-1}\) in UK Chalk and Sandstone aquifers, respectively. Thus, the N\(_2\)O concentrations (0.4–34.4 µg N L\(^{-1}\)) measured in this study are within the range previously reported in the literature.

Across all stream samples, a mean N\(_2\)O concentration of 1.4 µg N L\(^{-1}\) was measured with a range of 0.36–7.3 µg N L\(^{-1}\) (1–20 times greater than the atmospheric–water equilibrium). Among the stream sampling sites, site M had the lowest mean concentration (1.0 µg N L\(^{-1}\)) and site B the highest (1.8 µg N L\(^{-1}\)). Compared to the field drains, stream samples contained significantly (\(p < 0.05\)) lower N\(_2\)O concentrations, a consequence of N\(_2\)O being rapidly
concentrations in field drains remained low with no obvious peak corresponding to this storm event. In most drains, the low N$_2$O concentrations continued throughout winter 2013/14 and spring and summer 2014 with a slight gradual increase. This trend may relate to most of the drains being under fields planted with a spring bean crop which received either no N fertiliser or only 30 kg N ha$^{-1}$, thus limiting the availability of N for leaching into the subsurface

3.2 Temporal variability of nitrous oxide concentrations

3.2.1 Annual trends

The temporal variability in field drain and stream water N$_2$O concentration is presented in Figure 3. Gaps in the measurement of drain N$_2$O concentration are due to a lack of drain flow during the summer/autumn. As summer 2013 was approaching, N$_2$O concentrations gradually decreased in all drains, likely due to both drier antecedent conditions and a decline in potentially leachable nitrate due to crop uptake in this period. Drain samples contained lower N$_2$O concentrations in summer 2013 than summer 2014, possibly reflecting the lower rainfall totals in 2013 (106 mm) compared with 2014 (194 mm) reducing the amount of soil N flushing. Although high rainfall totals were recorded in autumn 2013 (244 mm), including the largest storm event in mid-October 2013 in which 68 mm fell in one week, N$_2$O concentrations in field drains remained low with no obvious peak corresponding to this storm event. In most drains, the low N$_2$O concentrations continued throughout winter 2013/14 and spring and summer 2014 with a slight gradual increase. This trend may relate to most of the drains being under fields planted with a spring bean crop which received either no N fertiliser or only 30 kg N ha$^{-1}$, thus limiting the availability of N for leaching into the subsurface...
drainage network. A pronounced increase in N$_2$O concentration did, however, occur in autumn 2014 and winter 2014/15 when the highest values of the study period were recorded in drains D7 (32.9 µg N L$^{-1}$) and D8 (34.4 µg N L$^{-1}$) in clay loam soils. These higher N$_2$O concentrations under winter wheat continued throughout winter 2014/15, such that levels were considerably higher than they had been in the previous year (2013/14).

Temporal variability in the N$_2$O concentration of stream water was not as apparent as in the drain samples, most likely due to stream water being a composite of water originating from several different sources (e.g. groundwater, field drains and fresh rainwater) with differing N$_2$O concentrations. However, elevated stream N$_2$O concentrations (4.7–7.3 µg N L$^{-1}$) were recorded in autumn 2014, corresponding with the higher concentrations observed in the field drains during this period.

No significant increase in N$_2$O concentration of either field drains or stream waters were observed during periods of N fertiliser application, indicating the absence of any direct linear relationship between N application and N loss as N$_2$O (Figure 3). Reay et al. (2004) noted some effect of N application, with a positive response recorded for several days after each application event, followed by an eventual decline in concentration around two weeks after application. However, Reay et al. (2004) concluded that both the spatial and temporal complexity of the processes responsible for N$_2$O production in agricultural drainage waters make a straightforward relationship between N$_2$O concentration and N application rate unlikely, as was found to be the case in this study.

### 3.2.2 Storm events

N$_2$O concentrations in the field drains and streams responded differently to the three main storm events that occurred during the study period (Figure 3). The largest rainfall event (event 1), which yielded a weekly rainfall total of 68 mm, occurred in mid-October 2013
when the catchment had experienced dry antecedent conditions, with low stream flows
(~0.005 m$^3$ s$^{-1}$ at site A) and limited rainfall (3 mm) during the 14 days prior to the event.

This event initiated no significant change in the N$_2$O concentration of either the flowing
drains or stream water, although most of the dry drains did start flowing after event 1. The
second event (event 2) during late May 2014, in which 62 mm of rainfall was recorded in one
week, also produced no significant increase in the N$_2$O concentrations of most field drain and
stream sites, with the exception of site M (0.5 to 1.6 µg N L$^{-1}$), D1 (1.3 to 5.9 µg N L$^{-1}$) and
D8 (2.5 to 7.9 µg N L$^{-1}$). Dry antecedent conditions had again preceded this event, with low
stream flows (~0.014 m$^3$ s$^{-1}$) and 0 mm of rainfall recorded in the 7 days prior to the event.

In contrast, the storm event in mid-October 2014 (event 3), in which 54 mm of rainfall fell in
one week, resulted in a pronounced rise in N$_2$O concentrations in all flowing field drains and
stream sites. This event occurred during a period of wetter antecedent conditions in which 30
mm of rainfall had fallen in the 14 days prior to event 3 and the average stream flow was
0.021 m$^3$ s$^{-1}$. The highest N$_2$O concentrations recorded throughout the monitoring period at
all four stream locations occurred during storm event 3, which may also be associated with
nitrification of residual soil nitrate post-harvest. N$_2$O concentrations at site M, for example,
did not exceed 2.5 µg N L$^{-1}$ in the previous 18 months of data collection, but during event 3,
a concentration of 7.1 µg N L$^{-1}$ was measured. N$_2$O concentrations in the field drain samples
also peaked in mid-October, but this was less pronounced as most of the drains were not
flowing prior to this rainfall event.

Overall, these results indicate that catchment antecedent moisture conditions influence the
storm event mobilisation of N$_2$O into stream and field drain waters, with wetter conditions
prior to an event typically resulting in elevated N$_2$O concentrations. There is some
consistency here with the study by Reay et al. (2004) who found no clear relationship
between field drain N$_2$O concentration and rainfall which they argued might be due to time
lags between rainfall and the resulting impact on dissolved N$_2$O concentrations. Such time
lags are themselves likely to be extremely variable depending upon antecedent moisture
conditions and due to the spatial heterogeneity of soil N processing.

3.2.3 Seasonal trends

To evaluate seasonal changes in field drain and stream water N$_2$O concentrations, all samples
collected in a particular season were combined for spring (MAM), summer (JJA), autumn
(SON) and winter (DJF) months (Figure 4). In all seasons, N$_2$O concentrations were
significantly lower in stream samples than in field drains due to the rapid degassing of N$_2$O
from the drain water once in contact with the atmosphere. In stream waters and field drains in
sandy loam soils, N$_2$O concentrations were significantly ($p < 0.05$) lower during summer than
any other season, with mean concentrations of 1.0 and 2.3 µg N L$^{-1}$, respectively.
Additionally, in field drains under sandy loam soils, N$_2$O concentrations were significantly
lower in autumn (3.2 µg N L$^{-1}$) than during winter (4.7 µg N L$^{-1}$) or spring (4.8 µg N L$^{-1}$).
These low summer and autumn concentrations likely reflect a combination of drier
antecedent conditions and increased nutrient uptake by crops during the growing season
reducing the flushing of leachable soil NO$_3^-$ and thus reducing the pool of available N for
conversion into N$_2$O. Lower summer N$_2$O concentrations in field drains and headwater
streams has previously been reported for other arable catchments in southern Germany and
Michigan, respectively, sites which have differing soil types and rainfall regimes to the study
presented here (Hack and Kaupenjohann, 2002; Beaulieu et al., 2008).

Lower summer N$_2$O levels were not apparent in field drains under clay loam soils where a
high mean concentration (10.1 µg N L$^{-1}$) was recorded. However, the number of samples for
summer clay loam drains was small ($n = 7$) and the mean N$_2$O concentration was biased by
very high concentrations discharging from just one drain (D10) at this time. Nevertheless,
further contrasts between field drains in clay loam and sandy loam soils were apparent during
the autumn, when substantially higher mean concentrations under clay loam soils (5.9 µg N
L⁻¹), particularly after the October 2014 storm event, indicate greater N₂O production and
release from clay soils early in the hydrological year.

3.3 Potential factors controlling N₂O concentrations

3.3.1 Soil texture

Soil texture strongly influenced field drain N₂O concentrations, with a mean N₂O
centration under clay loam soils (5.3 µg N L⁻¹) significantly (p < 0.05) higher than drains
under sandy loam soils (4.0 µg N L⁻¹) (Figure 5). This difference was largely driven by drains
D7, D8, D9 and D10 in clay loam soils having high mean N₂O concentrations, whilst drains
D2 and D16 in sandy loam soils had much lower concentrations. This was particularly the
case during autumn 2014 and winter 2014/15 when field drain N₂O concentrations were
substantially higher in clay loam soils (Figure 3). However, drains within sandy loam soils
did not always have low N₂O concentrations, as was the case for D4 and D11 which both had
high N₂O concentrations. Nevertheless, the data presented here suggests that drains within
clay loam soils have the potential to yield higher N₂O concentrations than drains within sandy
loam soils.

Very few of the published studies that investigated field drain N₂O concentrations considered
soil texture as a potential controlling factor, thus direct comparison with the results presented
here is difficult. One example is Jahangir et al. (2013), who observed that mean N₂O
concentrations in groundwater at agricultural sites with high permeability soils (sandy clay
loam and sandy loam) were significantly higher than low permeability soils (silty clay loam
and clay loam), in contrast to the findings presented here. In terms of direct N₂O emissions,
numerous studies have assessed the effects of soil texture. Rochette et al. (2008) stated that in
3.3.2 Drain flow rate

$\text{N}_2\text{O}$ is highly soluble in water and so field drains with higher flow rates are expected to export higher loads of dissolved $\text{N}_2\text{O}$. However, the relationship between $\text{N}_2\text{O}$ concentration and flow varied greatly among the drains (Figure 6). D2 ($r = 0.77$) and D1 ($r = 0.75$) had very strong positive correlations, whereas D10 ($r = -0.35$) and D8 ($r = -0.05$) had weak negative correlations. Figure 6 demonstrates that this variability is partially due to differences in soil texture across the study site, with drains in sandy loam soils having a stronger positive correlation ($r = 0.24; p < 0.05$) between the two parameters than drains in clay loam soils ($r = 0.06; p > 0.05$). This is supported by the fact that the two drains with the strongest positive correlation (i.e. D1 and D2) were in sandy loam soils and the two drains with the strongest negative correlation (i.e. D8 and D10) were in clay loam soils. However, there were exceptions to this, with drain D13 in a clay loam soil having a strong positive correlation ($r = 0.60$) and D4 in a sandy loam soil having a weak negative correlation ($r = -0.04$). Whilst overall there is no clear and dominant relationship between $\text{N}_2\text{O}$ concentration and field drain...
flow rate, the data presented here nevertheless demonstrates that soil texture does exerts some controlling influence upon this relationship.

3.3.3 pH

As with flow rate, Figure 6 reveals that soil type affected the relationship between field drain $N_2O$ concentration and pH. The pH values of the field drains ranged from 3.7 to 8.6, with a mean value of 7.7 and a 95% confidence interval for the mean of 7.67–7.76. A statistically significant, negative correlation ($r = -0.25$, $p < 0.05$) was established between pH and dissolved $N_2O$ in clay loam soils, whereas a weaker negative correlation ($r = -0.13$; $p < 0.05$) was observed in sandy loam soils. Hénault et al. (2012) previously identified pH as one of the key soil parameters which significantly influences direct $N_2O$ emissions, suggesting that $N_2O$ emissions from acidic soils generally exceed those from alkaline soils due to higher $N_2O$ emissions from nitrification and/or higher $N_2O$:N$_2$ ratios at lower pH levels. Weslien et al. (2009) also observed that soil $N_2O$ emissions were significantly and negatively ($r = -0.93$) correlated with soil pH and suggested that this strong negative correlation is due to $N_2O$ production being inhibited by alkaline pH. Whilst such strong correlations between $N_2O$ concentration and pH were not observed in this study, the results presented here do support the hypothesis that $N_2O$ production increases with decreasing pH, with the strength of this association partially linked to soil texture.

3.3.4 Other nitrogen species

The relationships between dissolved $N_2O$ concentration and three other N species measured in field drains and stream water samples are presented in Figure 7. $N_2O$ concentrations were generally three orders of magnitude smaller than dissolved NO$_3$ (Figure 7A and Figure S1), similar to the findings of previous studies (e.g. Ueda et al., 1993; Hack and Kaupenjohann, 2002; Vilain et al., 2011; Outram and Hiscock, 2012). The concentrations of $N_2O$ and NO$_3$
were significantly and positively correlated in both field drains in sandy loam soils ($r = 0.30; p < 0.05$) and in stream water samples ($r = 0.55; p < 0.05$). However, a non-significant weak correlation was observed for field drains in clay loam soils ($r = 0.06; p > 0.05$). The individual drains with the strongest positive correlations between $N_2O$ and $NO_3$ were D2 ($r = 0.80$), D6 ($r = 0.67$) and D1 ($r = 0.46$), all of which were located within sandy loam soils. Conversely, drains D8 ($r = -0.36$), D13 ($r = -0.29$) and D7 ($r = -0.15$) located within clay loam soils had the strongest negative correlations.

Previous studies have suggested that a positive correlation between $N_2O$ and $NO_3$ indicates that nitrification is the principle production mechanism for $N_2O$, whilst a negative correlation indicates denitrification is occurring (Ueda et al., 1993; Mühlherr and Hiscock, 1998; Hiscock et al., 2003). On this basis, the results presented here indicate that nitrification is likely to be the main production mechanism for $N_2O$ in stream waters and field drains in sandy loam soils, whereas in clay loam soils the production mechanism is likely to be a combination of both nitrification and denitrification. This combination of nitrification and denitrification processes is supported by evidence from previous research in the River Wensum and neighbouring River Bure catchments, in which groundwater $NO_3$-N isotope ($\delta^{15}N$) values in the range of -2.1 to +13.7‰ were measured at 36 locations (Feast et al., 1998). Isotopically light $\delta^{15}N$ values (+4 to +8‰) in these catchments are believed to be indicative of nitrification in areas covered by sand-rich glacial deposits in valley locations, whilst more enriched $\delta^{15}N$ values (+8 to +11‰) indicative of fractionation by denitrification are associated with the presence of clay-rich till deposits at the valley margins.

Regarding other N species, $N_2O$ was only weakly negatively correlated with $NH_4$ in stream water ($r = -0.13; p < 0.05$) and in field drains in clay loam ($r = -0.09; p > 0.05$) and sandy loam ($r = 0.01; p > 0.05$) soils, indicating the absence of any interconnected production mechanisms. Similarly, $N_2O$ concentrations were not significantly correlated with $NO_2$ in
either the stream water samples ($r = 0.04, p > 0.05$) or the clay loam field drains ($r = -0.01; p > 0.05$), although a significant positive correlation (albeit weak) with sandy loam drains ($r = 0.19; p < 0.05$) was established, again highlighting potential differences in $N_2O$ production mechanisms between different soil types.

To better assess the complexity and overall importance of these different factors in determining the observed variability in $N_2O$ concentrations, Table II presents the results of three multiple linear regression models for the prediction of $N_2O$ concentrations in stream water and field drains in sandy loam and clay loam soils. The stream model proved to be the best performing, being able to explain 33.1% of the variability in $N_2O$ concentrations from three significant predictors ($NO_3$, $NH_4$ and $NO_2$), although $NO_3$ was by far the most dominant predictor ($R^2 = 0.31$). By contrast the field drain sandy loam and field drain clay loam models were only able to explain 16.6% and 6.2% of the variability in $N_2O$ concentrations, respectively, with pH being the only significant predictor of $N_2O$ in clay loam field drains. These model results highlight the complexity of $N_2O$ production mechanisms in field drains and indicate that other drivers of $N_2O$ variability exist which are not captured by the regression models.

### 3.3.5 Impact of a cover crop

During autumn and winter 2013/14, dissolved $N_2O$ concentrations in field drains below the winter oilseed radish cover crop ranged from 0.6–8.8 $\mu g \text{ N L}^{-1}$, whereas concentrations in drains underlying fields without a cover crop ranged from 0.6–4.3 $\mu g \text{ N L}^{-1}$ (Figure 8).

Although the difference in the means was not statistically significant ($p > 0.05$), drains under the cover crop did have a slightly higher mean $N_2O$ concentration (2.6 $\mu g \text{ N L}^{-1}$) than drains under fields without a cover crop (2.2 $\mu g \text{ N L}^{-1}$). This may be due to the accumulation of both carbon and N residues under the combined reduced tillage and cover crop management.
system and consequently higher substrate availability for nitrification and denitrification compared to conventional management (Abdalla et al., 2012). The primary goal of using a cover crop as a mitigation measure in agriculture is to improve soil fertility and decrease NO$_3$ leaching rather than to reduce greenhouse gas emissions; however the latter should not be neglected when assessing the overall effectiveness of such measures. The mean field drain NO$_3$ concentration under the cover crop (2.5 mg N L$^{-1}$) was significantly ($p < 0.05$) lower than drains beneath fallow fields (13.9 mg N L$^{-1}$), representing a ~82% reduction in NO$_3$ concentrations. Contradictory effects of cover crops on direct N$_2$O emissions from soil have been previously documented (e.g. Jarecki et al., 2009; Kallenbach et al., 2010; Dietzel et al., 2011; Abdalla et al., 2012; Sanz-Cobena et al., 2014), but to our knowledge the effects of a cover crop on indirect N$_2$O emissions from groundwater and surface waters has not been studied until now. Newell Price et al. (2011) did, however, summarise a list of mitigation measures to tackle environmental issues and stated that cover crops could reduce indirect N$_2$O emissions by a small amount. The results presented here contradict this and suggest that the use of cover crops (particularly oilseed radish) may actually increase indirect N$_2$O emissions. Thus, cover crops should not be recommended as a climate change mitigation strategy without further research.

### 3.3.6 Impact of reduced tillage

During the 2014/15 farm year, the different tillage options without a cover crop were continued as mitigation measures and the impact upon field drain N$_2$O concentrations is presented in Table III. Whilst the mean N$_2$O concentration in field drains under conventional tillage (6.9 µg N L$^{-1}$) was not significantly ($p > 0.05$) different from that under direct drill (6.2 µg N L$^{-1}$), the mean concentration under reduced tillage (4.8 µg N L$^{-1}$) was significantly ($p < 0.05$) lower. Despite this finding, the lower N$_2$O concentrations in field drains under reduced tillage are more likely to reflect that all these drains were within sandy loam soils.
rather than truly representing differences in tillage practice. This is because of the four field
drains under reduced tillage, only D16 had significantly lower N\textsubscript{2}O concentrations, whereas
D1, D3 and D5 showed no substantial decline in N\textsubscript{2}O compared to the other drains.
Moreover, if N\textsubscript{2}O concentrations were truly lower under reduced tillage relative to
conventional ploughing, then N\textsubscript{2}O concentrations should have been even lower under direct
drill systems where soil disturbance, and thus N mobilisation, is even lower.

To our knowledge, there have been no previous publications on the effects of different tillage
methods on dissolved N\textsubscript{2}O concentration until now, thus comparison with other studies is not
possible. However, several studies have investigated the effects of soil management on direct
N\textsubscript{2}O emissions from soil and these have shown inconsistent results due to variability in
environmental factors, such as soil water content, rates and types of fertiliser application, and
depths of fertiliser placement (Baggs et al., 2003; Grant et al., 2004; Venterea et al., 2005;
Omonode et al., 2011). Overall, the results presented here indicate that different soil
inversion methods tended to have little impact on dissolved N\textsubscript{2}O concentrations.

4. Conclusions

The research conducted here was undertaken to address the deficiency in the number of
existing studies investigating indirect N\textsubscript{2}O emissions from agriculture. The key findings from
this work can be summarised as follows:

(i) All field drain and stream water samples collected, regardless of time or location of
sampling, contained a higher dissolved N\textsubscript{2}O concentration than the water-air
equilibrium, demonstrating that all sites were acting as a source of N\textsubscript{2}O emissions to
the atmosphere;

(ii) Soil texture significantly influenced N\textsubscript{2}O dynamics in field drains, with higher
concentrations recorded in heavier clay loam soils than in lighter sandy loam. Soil
texture also impacted upon the relationships between field drain N\textsubscript{2}O concentration and other water quality parameters, highlighting possible differences in N\textsubscript{2}O production mechanisms between different soil types;

(iii) Antecedent moisture conditions influenced the storm event mobilisation of N\textsubscript{2}O in field drains and streams, with the greatest concentration increases occurring during events preceded by wet conditions. N\textsubscript{2}O concentrations also varied seasonally, with the lowest concentrations typically occurring during the summer months;

(iv) Nitrogen fertiliser application and different soil inversion regimes were found to have no effect on dissolved N\textsubscript{2}O concentrations either in field drains or stream waters;

(v) Higher N\textsubscript{2}O concentrations recorded in field drains under a winter cover crop relative to fallow fields indicate growing an oilseed radish cover crop is not an effective greenhouse gas emission mitigation strategy.

Given the paucity of existing studies into the mechanisms involved in the production of indirect N\textsubscript{2}O emissions from N leaching into surface water and groundwater bodies, further research conducted in a wider variety of agricultural catchments with a range of different soil types and rainfall regimes is highly recommended.

**Acknowledgements**

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Supporting Information

Figure S1: Time series of the mean N₂O/NO₃ ratio in stream water and field drains.

References


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Tables

Table I Description of the study area experimental treatments

<table>
<thead>
<tr>
<th>Block</th>
<th>Field name</th>
<th>Area (ha)</th>
<th>Field drain</th>
<th>Cover crop</th>
<th>Tillage</th>
<th>Crop</th>
<th>Applied fertiliser (kg N ha⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>J</td>
<td>Far Hempsky</td>
<td>13.8</td>
<td>-</td>
<td>No Plough</td>
<td>SB</td>
<td>0</td>
<td>No Plough WW</td>
</tr>
<tr>
<td>P</td>
<td>Gatehouse Hyrne</td>
<td>26.8</td>
<td>D8, D10</td>
<td>No Plough</td>
<td>SB</td>
<td>7</td>
<td>No Plough WW</td>
</tr>
<tr>
<td>D1</td>
<td>Dunkirk</td>
<td>12.9</td>
<td>D1, D3</td>
<td>Yes Reduced</td>
<td>SB</td>
<td>38</td>
<td>No Reduced WW</td>
</tr>
<tr>
<td>D16</td>
<td>Moor Hall Field</td>
<td>20.4</td>
<td>Yes Reduced</td>
<td>SB</td>
<td>No Plough WW</td>
<td>30</td>
<td>No Reduced WW</td>
</tr>
<tr>
<td>L</td>
<td>Swanhills</td>
<td>10.4</td>
<td>D4, D6</td>
<td>Yes DD</td>
<td>SB</td>
<td>26</td>
<td>No DD WW</td>
</tr>
<tr>
<td>J</td>
<td>Sheds Field</td>
<td>14.9</td>
<td>-</td>
<td>Yes DD</td>
<td>SB</td>
<td>28</td>
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</tr>
<tr>
<td>L</td>
<td>First Hempsky</td>
<td>14.1</td>
<td>D2</td>
<td>Yes DD</td>
<td>SB</td>
<td>24</td>
<td>No DD WW</td>
</tr>
<tr>
<td>L</td>
<td>Middle Hempsky</td>
<td>11.8</td>
<td>-</td>
<td>Yes DD</td>
<td>SB</td>
<td>7</td>
<td>No DD WW</td>
</tr>
</tbody>
</table>

Note: DD: Direct drill, SB: spring beans, WW: winter wheat

Table II: Linear and multiple linear regression model results for the prediction of stream water and field drain N₂O concentrations. VIF is the variance inflation factor; VE is the variance explained. Only significant (p < 0.05) predictors were retained in the models.

<table>
<thead>
<tr>
<th>Field drains: sandy loam</th>
<th>Predictor</th>
<th>Estimate</th>
<th>Std. Error</th>
<th>t-value</th>
<th>p-value</th>
<th>VIF</th>
<th>Proportion of VE (R²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO₃</td>
<td>0.197</td>
<td>0.043</td>
<td>4.55</td>
<td>&lt;0.001</td>
<td>1.05</td>
<td>0.064</td>
<td></td>
</tr>
<tr>
<td>Flow</td>
<td>3.180</td>
<td>0.795</td>
<td>3.99</td>
<td>&lt;0.001</td>
<td>1.04</td>
<td>0.045</td>
<td></td>
</tr>
<tr>
<td>NO₂</td>
<td>0.105</td>
<td>0.030</td>
<td>3.52</td>
<td>&lt;0.001</td>
<td>1.02</td>
<td>0.034</td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td>-0.807</td>
<td>0.366</td>
<td>-2.20</td>
<td>0.03</td>
<td>1.07</td>
<td>0.023</td>
<td></td>
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</tbody>
</table>

Field drains: clay loam

<table>
<thead>
<tr>
<th>Predictor</th>
<th>Estimate</th>
<th>Std Error</th>
<th>t-value</th>
<th>p-value</th>
<th>VIF</th>
<th>Proportion of VE (R²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>-2.174</td>
<td>0.562</td>
<td>-3.87</td>
<td>&lt;0.001</td>
<td>1.00</td>
<td>0.062</td>
</tr>
</tbody>
</table>

Streams

<table>
<thead>
<tr>
<th>Predictor</th>
<th>Estimate</th>
<th>Std Error</th>
<th>t-value</th>
<th>p-value</th>
<th>VIF</th>
<th>Proportion of VE (R²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO₃</td>
<td>0.146</td>
<td>0.013</td>
<td>11.16</td>
<td>&lt;0.001</td>
<td>1.04</td>
<td>0.310</td>
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<tr>
<td>NH₄</td>
<td>-0.001</td>
<td>0.001</td>
<td>-1.45</td>
<td>0.015</td>
<td>1.30</td>
<td>0.012</td>
</tr>
<tr>
<td>NO₂</td>
<td>0.005</td>
<td>0.002</td>
<td>2.21</td>
<td>0.028</td>
<td>1.26</td>
<td>0.009</td>
</tr>
</tbody>
</table>

Total VE 0.331

Table III Field drain N₂O concentrations under different tillage practice during October 2014 to April 2015. Numbers followed by different superscripted letters are significantly different (p > 0.05).

<table>
<thead>
<tr>
<th>Tillage type</th>
<th>n</th>
<th>Mean N₂O (µg N L⁻¹)</th>
<th>Standard Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conventional tillage</td>
<td>33</td>
<td>6.9ᵃ</td>
<td>7.0</td>
</tr>
<tr>
<td>Reduced tillage</td>
<td>75</td>
<td>4.8ᵇ</td>
<td>3.3</td>
</tr>
<tr>
<td>Direct drill</td>
<td>73</td>
<td>6.3ᵃ</td>
<td>4.0</td>
</tr>
</tbody>
</table>
Figure 1: Location of the study area in the Blackwater sub-catchment of the River Wensum, Norfolk, UK. Map shows the locations of field drain, stream water and soil sampling sites.

99x70mm (600 x 600 DPI)
Figure 2: Boxplot of dissolved N2O concentrations in field drains in sandy loam and clay loam soils and in stream waters for samples collected during April 2013–April 2015. The central line is the median, the box is the interquartile range and the whiskers are 1.5 times the interquartile range. The horizontal dashed line represents the atmospheric N2O concentration when in equilibrium with water (0.36 µg N L⁻¹).
Figure 4: Average N2O concentrations recorded in field drains and stream waters during different seasons in samples collected during April 2013–April 2015. Error bars represent one standard error. Significant differences (p < 0.05) are indicated by different letters for the same type of water sample.

99x62mm (600 x 600 DPI)
Figure 3: Time-series plot showing weekly rainfall totals and dissolved N2O concentrations in field drains (clay loam and sandy loam) and stream water samples throughout the study period. The three largest rainfall events are highlighted in grey. Vertical arrows indicate the times of N fertiliser application (30-70 kg N ha⁻¹).

219x302mm (300 x 300 DPI)
Figure 5: Mean field drain N2O concentrations for drains underlying the two dominant soil texture types in the study area, clay loam and sandy loam, for samples collected during April 2013–April 2015. Error bars represent one standard error.

74x62mm (600 x 600 DPI)
Figure 6: Relationships between field drain N2O concentration and (A) flow rate and (B) pH, split by dominant soil type for samples collected during April 2013–April 2015. Dashed lines are linear regressions.

79x35mm (600 x 600 DPI)
Figure 7: Relationships between N2O concentration and (A) NO3, (B) NH4 and (C) NO2 concentrations in stream water and field drain samples from different soil types collected during April 2013–April 2015. Dashed lines are linear regressions.
Figure 8: Relationship between dissolved N2O and NO3 concentrations in field drain samples collected during the growth of a winter oilseed radish cover crop (September 2013 to March 2014) from fields with (n = 114) and without (n = 29) the cover crop. Dashed lines are linear regressions.

\[ r = 0.41, \quad y = 0.51x + 1.32 \]

\[ r = 0.25, \quad y = 0.09x + 0.94 \]