

Dissolved nitrous oxide (N₂O) dynamics in agricultural field drains and headwater streams in an intensive arable catchment

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ABSTRACT

Indirect nitrous oxide (N₂O) emissions produced by nitrogen (N) leaching into surface water and groundwater bodies are poorly understood in comparison to direct N₂O emissions from soils. In this study, dissolved N₂O 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 N₂O concentrations higher than the water–air equilibrium concentration, illustrating that all sites were acting as a net source of N₂O emissions to the atmosphere. Soil texture was found to significantly influence field drain N₂O 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 N₂O concentrations and other water quality parameters (pH, flow rate, and nitrate (NO₃) and nitrite (NO₂) concentrations), highlighting possible differences in N₂O production mechanisms in different soil types. Catchment antecedent moisture conditions influenced the storm event mobilisation of N₂O in both field drains and streams, with the greatest concentration increases recorded during precipitation events preceded by prolonged wet conditions. N₂O 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

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3 28 on dissolved N₂O concentrations, whereas higher N₂O concentrations recorded in field drains
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5 29 under a winter cover crop compared to fallow fields revealed cover crops are an ineffective
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7 30 greenhouse gas emission mitigation strategy. Overall, this study highlights the complex
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9 31 interactions governing the dynamics of dissolved N₂O concentrations in field drains and
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11 32 headwater streams in a lowland intensive agricultural catchment.
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15 33 **Keywords:** nitrous oxide; nitrate; nitrification; denitrification; river; tile drain.
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17 18 34 **1. Introduction** 19

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21 35 Nitrous oxide (N₂O) is a potent and persistent greenhouse gas with a present atmospheric
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23 36 concentration of 326.7 ppb (European Environment Agency, 2016). N₂O has 300 times
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25 37 greater global warming potential than CO₂ and accounts for ~5% of the total greenhouse
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27 38 effect (Omonode et al., 2011). N₂O participates in photochemical reactions in the stratosphere
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29 39 which lead to the destruction of the ozone (O₃) layer (Jacinthe and Dick, 1997) and is also
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31 40 linked to the release of nitric oxide and ammonia in the atmosphere which contribute to acid
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33 41 rain and the acidification of soils and drainage systems (Mosier and Kroeze, 1998).
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35 42 Atmospheric N₂O concentrations are increasing at an annual rate of ~0.26% (Forster et al.,
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37 43 2007) and agriculture is the largest source of anthropogenic N₂O emissions, accounting for
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39 44 ~60% of the total human-produced N₂O. Globally, agricultural N₂O emissions increased by
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41 45 nearly 17% from 1990 to 2005 (Smith et al., 2007).
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46 46 Global agricultural N₂O emissions originate from three sources: direct emissions from
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48 47 nitrogen (N) fertilised soil (1.8 Tg N a⁻¹); direct emissions from animal production (2.3 Tg N a⁻¹)
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50 48 ¹); and indirect emissions from N used in agricultural systems (1.3 Tg N a⁻¹) (Syakila and
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52 49 Kroeze, 2011). Indirect emissions are in turn derived from three sources: atmospheric
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54 50 deposition (0.4 Tg N a⁻¹); human sewage (0.3 Tg N a⁻¹); and nitrogen leaching and runoff into
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56 51 water bodies (0.6 Tg N a⁻¹). Thus, indirect emissions from N leaching and runoff are
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3 52 significant, equating to 46% of the indirect emissions from agriculture and 11% of total
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5 53 agricultural N₂O emissions. These indirect emissions from N leaching and runoff are
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7 54 equivalent to ~33% of the direct N₂O emissions from soils. Other studies (e.g. Mühlherr and
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9 55 Hiscock, 1997; Seitzinger and Kroeze, 1998; Naqvi et al., 2000) have previously highlighted
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11 56 the significance of N₂O emissions from agricultural N leaching and runoff to the overall N₂O
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13 57 budget. However, compared to direct N₂O emissions, these indirect emissions have been
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15 58 poorly studied to date (Outram and Hiscock, 2012).

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19 59 Indirect emissions of N₂O occur when N fertiliser is lost from agricultural soils through
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21 60 leaching and runoff. This mobilised N enters groundwater, rivers, riparian areas, wetlands
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23 61 and eventually the ocean (Mosier et al., 1998). Nitrogen in groundwater and surface waters
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25 62 increases the biological production of N₂O as the N undergoes both nitrification and
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27 63 denitrification. Nitrification is an aerobic chemolithoautotrophic process in which bacteria
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29 64 oxidise ammonium (NH₄⁺) to nitrate (NO₃⁻) and N₂O. Denitrification is an anaerobic process
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31 65 in which bacteria sequentially reduce NO₃⁻ to N₂O and dinitrogen (N₂) with a small amount of
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33 66 N₂O escaping in the process (Beaulieu et al., 2008). Therefore, the factors controlling
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35 67 nitrification and denitrification in the soil, such as moisture content, temperature, organic
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37 68 matter, availability of N and NH₄⁺, pH, redox conditions, texture and agricultural
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39 69 management practices may subsequently control both direct and indirect N₂O emissions
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41 70 (Bouwman et al., 1993; Panek et al., 2000). However, the majority of existing studies (e.g.
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43 71 Włodarczyk et al., 2005; Jarecki et al., 2009; Hénault et al., 2012) have only investigated the
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45 72 effect of these parameters on direct N₂O emissions, leaving the control of these parameters on
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47 73 indirect N₂O emissions poorly investigated in the literature. The aim of this study was to
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49 74 address these deficiencies through the following objectives:

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56 75 i. to investigate the spatial and temporal dynamics of dissolved N₂O concentrations in
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58 76 subsurface agricultural field drains and lowland headwater streams;

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3 77 ii. to assess the impact of water quality parameters, soil texture and crop cultivation
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5 78 regimes on dissolved N₂O concentrations.
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8 79 **2. Methods**

10 80 **2.1 Study location**

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14 81 The study area is located to the northwest of Norwich in the Blackwater sub-catchment of the
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16 82 River Wensum, Norfolk, UK (Figure 1). The Blackwater sub-catchment is intensively
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18 83 monitored as part of the Wensum Demonstration Test Catchment (DTC) project which aims
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20 84 to evaluate the extent to which on-farm mitigation measures can cost-effectively reduce the
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22 85 level of diffuse agricultural pollution (McGonigle et al., 2014). The field sites are in an area
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24 86 of intensive arable farming which includes cereals, oilseed rape, spring beans and sugar beet
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26 87 grown in a seven-year rotation. The average annual rainfall total is 674 mm and the mean
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28 88 annual temperature is 10.1°C. The soil parent material comprises glacial deposits over
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30 89 Cretaceous Chalk, with soil textures varying from sandy loam to sandy clay loam and clay
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32 90 loam. Part of the sub-catchment is extensively under-drained by a dense network of
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34 91 subsurface agricultural field (“tile”) drains installed at a depth of 100–160 cm. Discharge
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36 92 from certain drains can be as high as 10 L s⁻¹, but varies greatly depending upon season,
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38 93 depth, catchment area and antecedent moisture conditions.
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43 94 In 2013, nine fields covering 143 ha of arable land were identified for the trialling of a winter
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45 95 cover crop and reduced tillage practices aimed at reducing diffuse nutrient losses into the
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47 96 River Blackwater (Figure 1 and Table I). These nine fields were divided into three blocks of
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49 97 mitigation measures, with each block sown with the same crop and same fertiliser application
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51 98 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
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53 99 (winter wheat; 220 kg N ha⁻¹, 22 kg P ha⁻¹, 85 kg K ha⁻¹) farm years (September to August).
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57 100 Two fields were kept as a control (block J) and were cultivated by mouldboard ploughing to
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3 101 25 cm depth prior to sowing. An oilseed radish (*Raphanus sativus*) cover crop (seed density =
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5 102 18 kg ha⁻¹) was sown in treatment blocks L and P in late-August 2013. Block P then
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7 103 underwent reduced tillage to a depth of 10 cm prior to sowing spring beans and block L
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9 104 underwent direct drilling with no inversion. A winter crop (winter wheat) was grown in the
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11 105 second year (2014/15) and so a cover crop was not sown, but direct drilling and reduced
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13 106 tillage practices continued in block L and block P, respectively.

17 107 **2.2 Sample collection**

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20 108 Water samples for N₂O and nutrient analysis were collected in 13 field drains and 4 stream
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22 109 locations (A, B, E and M) on a weekly basis between April 2013 and April 2015 (Figure 1).
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24 110 Over the duration of the study, 621 water samples were collected from field drains and 308
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26 111 samples from stream sites, such that 929 samples were obtained in total. Samples for
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28 112 dissolved N₂O analysis were collected from the stream and drain outlet pipes in 20 mL glass
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30 113 syringes (SAMCO) with a three-way stopcock attached to each syringe by a Luer-Lock
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32 114 fitting. Syringes were flushed three times with water from the sampling point and any air
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34 115 bubbles contained in the syringes were expelled before the final sample was taken. No
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36 116 preservative was added to the sample. Samples were returned to cold storage at 4°C within 3
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38 117 h and analysed for N₂O within 72 h of collection. Samples for nutrient analysis were
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40 118 collected in 1 L polypropylene bottles and also analysed within 72 h of collection. Rainfall
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42 119 was measured via a tipping bucket rain gauge installed in mini-catchment A. Soil samples for
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44 120 texture analysis were collected in May and September 2013 from 12 locations per field in a
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46 121 ‘W’ layout at 0-30 cm depth using a Dutch auger and Hydrocare powered auger (Figure 1).
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48 122 Catchment areas of the field drains were divided into two dominant soil types (clay loam and
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50 123 sandy loam) based on the soil texture data collected in this study. Drains D3, D7, D8, D9,
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52 124 D10 and D13 were predominantly within clay loam soils, whereas drains D1, D2, D4, D5,
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3 125 D6, D11 and D16 were predominantly within sandy loam soils, albeit no drain area was
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5 126 entirely composed of just one soil texture.
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8 127 **2.3 Sample analysis**

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10 128 N₂O was analysed by gas chromatography with an electron capture detector (GC-ECD).
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12 129 Samples were injected directly into a purge column of a helium flushed gas extraction line,
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14 130 which included traps for water vapour and CO₂ removal. A reverse-flow Nafion dryer was
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16 131 used in the extraction line with N₂O. N₂O was trapped at -190 °C above liquid nitrogen in a
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18 132 3.2 mm stainless steel loop. The N₂O was remobilised by submerging the loop in a hot water
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20 133 bath at ~95 °C. The collected N₂O was analysed with a Shimadzu GC-8A at 300 °C using a
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22 134 3.6 m by 3.2 mm diameter stainless steel Poropak Q column at 50 °C. The accuracy of N₂O
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24 135 measurements was within ±3% with a detection limit of ~0.0008 µg N L⁻¹. Further details of
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26 136 this method can be found in Mühlherr and Hiscock (1998). Nitrate was determined by ion
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28 137 chromatography using a Dionex ISC 2000 instrument with an accuracy of 0.19 mg N L⁻¹.
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30 138 Ammonium and nitrite were determined by a Continuous Flow Analyser - Skalar San++ with
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32 139 accuracies of 4.57 µg N L⁻¹ and 1.52 µg N L⁻¹, respectively. Soil texture was determined by
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34 140 laser diffraction.
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40 141 For data analysis, the independent-sample *t*-test was used to examine the degree of
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42 142 significance (*p*-value < 0.05) between two groups, whilst multiple linear regression models
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44 143 for the prediction of N₂O concentration in stream and field drain waters were formulated in
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46 144 the *R* environment (R Core Team, 2016).
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49 145 **3. Results and Discussion**

50 146 **3.1 Spatial variability of nitrous oxide concentrations**

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53 147 N₂O concentrations in field drain (*n* = 621) and stream (*n* = 308) water samples collected
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55 148 throughout this study are presented in Figure 2. All of the drain and stream water samples
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3 149 were found to have dissolved N₂O concentrations higher than would be expected when
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5 150 atmospheric N₂O concentrations are at equilibrium with water (~0.36 µg N L⁻¹; Weiss and
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7 151 Price, 1980), illustrating that all sites were acting as a net source of N₂O emissions to the
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9 152 atmosphere. Field drain N₂O concentrations ranged from 0.4 µg N L⁻¹, just above the
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11 153 atmospheric-water equilibrium, to 34.4 µg N L⁻¹, 100 times greater than atmospheric-water
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13 154 equilibrium. Mean N₂O concentrations in drains within clay loam and sandy loam soils were
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15 155 5.3 and 4.0 µg N L⁻¹, respectively. Among the drains, D11 had the highest mean value (8.0
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17 156 µg N L⁻¹) and D2 the lowest (2.7 µg N L⁻¹), with both draining sandy loam soils in block L.

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22 157 There have been very few previously published studies of dissolved N₂O concentrations in
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24 158 field drains. Dowdell et al. (1979), who studied dissolved N₂O in agricultural drains for the
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26 159 first time, found a range of 1–132 µg N L⁻¹ in three different locations across southern
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28 160 England. In a study of N₂O discharged from 28 drained agricultural areas in the upper Neckar
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30 161 region, Germany, Hack and Kaupenjohann (2002) observed a N₂O range of 0.4–60 µg N L⁻¹,
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32 162 whilst Reay et al. (2004) recorded a narrow range in N₂O concentration (2–4 µg N L⁻¹) in one
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34 163 particular field drain under arable land planted with spring barley in Scotland over a 45 day
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36 164 period. Similar to the differences in soil texture reported here, differences in groundwater
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38 165 N₂O in the unsaturated zone between sites with contrasting geology was reported by Darling
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40 166 et al. (1998), who recorded mean N₂O concentrations of 2.8 and 1.5 µg N L⁻¹ in UK Chalk
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42 167 and Sandstone aquifers, respectively. Thus, the N₂O concentrations (0.4–34.4 µg N L⁻¹)
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44 168 measured in this study are within the range previously reported in the literature.

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49 169 Across all stream samples, a mean N₂O concentration of 1.4 µg N L⁻¹ was measured with a
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51 170 range of 0.36–7.3 µg N L⁻¹ (1–20 times greater than the atmospheric–water equilibrium).

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54 171 Among the stream sampling sites, site M had the lowest mean concentration (1.0 µg N L⁻¹)
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56 172 and site B the highest (1.8 µg N L⁻¹). Compared to the field drains, stream samples contained
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58 173 significantly ($p < 0.05$) lower N₂O concentrations, a consequence of N₂O being rapidly
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3 174 degassed from field drain water once it has come into contact with the atmosphere upon
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5 175 discharge into the stream. This degassing of supersaturated N₂O from subsurface drainage
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7 176 and groundwater after discharge to surface water has also been reported in previous studies
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10 177 (e.g. Bowden and Bormann, 1986; Reay et al., 2003; Minamikawa et al., 2011; Li et al.,
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12 178 2013). For comparison, in a 13-month study at nine sites on the eutrophic San Joaquin River,
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14 179 California, Hinshaw and Dahlgren (2013) reported a mean dissolved N₂O concentration in
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16 180 surface waters of 0.91 µg N L⁻¹, whilst Outram and Hiscock (2012) recorded a mean N₂O
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18 181 concentration of 1.7 µg N L⁻¹ in the lowland River Thurne, eastern England.

182 **3.2 Temporal variability of nitrous oxide concentrations**

183 **3.2.1 Annual trends**

184 The temporal variability in field drain and stream water N₂O concentration is presented in
185 Figure 3. Gaps in the measurement of drain N₂O concentration are due to a lack of drain flow
186 during the summer/autumn. As summer 2013 was approaching, N₂O concentrations gradually
187 decreased in all drains, likely due to both drier antecedent conditions and a decline in
188 potentially leachable nitrate due to crop uptake in this period. Drain samples contained lower
189 N₂O concentrations in summer 2013 than summer 2014, possibly reflecting the lower rainfall
190 totals in 2013 (106 mm) compared with 2014 (194 mm) reducing the amount of soil N
191 flushing. Although high rainfall totals were recorded in autumn 2013 (244 mm), including the
192 largest storm event in mid-October 2013 in which 68 mm fell in one week, N₂O
193 concentrations in field drains remained low with no obvious peak corresponding to this storm
194 event. In most drains, the low N₂O concentrations continued throughout winter 2013/14 and
195 spring and summer 2014 with a slight gradual increase. This trend may relate to most of the
196 drains being under fields planted with a spring bean crop which received either no N fertiliser
197 or only 30 kg N ha⁻¹, thus limiting the availability of N for leaching into the subsurface

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3 198 drainage network. A pronounced increase in N₂O concentration did, however, occur in
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5 199 autumn 2014 and winter 2014/15 when the highest values of the study period were recorded
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7 200 in drains D7 (32.9 µg N L⁻¹) and D8 (34.4 µg N L⁻¹) in clay loam soils. These higher N₂O
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9 201 concentrations under winter wheat continued throughout winter 2014/15, such that levels
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11 202 were considerably higher than they had been in the previous year (2013/14).

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14 203 Temporal variability in the N₂O concentration of stream water was not as apparent as in the
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16 204 drain samples, most likely due to stream water being a composite of water originating from
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18 205 several different sources (e.g. groundwater, field drains and fresh rainwater) with differing
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20 206 N₂O concentrations. However, elevated stream N₂O concentrations (4.7–7.3 µg N L⁻¹) were
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22 207 recorded in autumn 2014, corresponding with the higher concentrations observed in the field
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24 208 drains during this period.

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28 209 No significant increase in N₂O concentration of either field drains or stream waters were
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30 210 observed during periods of N fertiliser application, indicating the absence of any direct linear
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32 211 relationship between N application and N loss as N₂O (Figure 3). Reay et al. (2004) noted
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34 212 some effect of N application, with a positive response recorded for several days after each
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36 213 application event, followed by an eventual decline in concentration around two weeks after
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38 214 application. However, Reay et al. (2004) concluded that both the spatial and temporal
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40 215 complexity of the processes responsible for N₂O production in agricultural drainage waters
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42 216 make a straightforward relationship between N₂O concentration and N application rate
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45 217 unlikely, as was found to be the case in this study.

46 47 48 49 218 **3.2.2 Storm events**

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52 219 N₂O concentrations in the field drains and streams responded differently to the three main
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54 220 storm events that occurred during the study period (Figure 3). The largest rainfall event
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56 221 (event 1), which yielded a weekly rainfall total of 68 mm, occurred in mid-October 2013
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3 222 when the catchment had experienced dry antecedent conditions, with low stream flows
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5 223 ($\sim 0.005 \text{ m}^3 \text{ s}^{-1}$ at site A) and limited rainfall (3 mm) during the 14 days prior to the event.
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7 224 This event initiated no significant change in the N_2O concentration of either the flowing
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9 225 drains or stream water, although most of the dry drains did start flowing after event 1. The
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11 226 second event (event 2) during late May 2014, in which 62 mm of rainfall was recorded in one
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13 227 week, also produced no significant increase in the N_2O concentrations of most field drain and
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15 228 stream sites, with the exception of site M (0.5 to $1.6 \mu\text{g N L}^{-1}$), D1 (1.3 to $5.9 \mu\text{g N L}^{-1}$) and
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17 229 D8 (2.5 to $7.9 \mu\text{g N L}^{-1}$). Dry antecedent conditions had again preceded this event, with low
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19 230 stream flows ($\sim 0.014 \text{ m}^3 \text{ s}^{-1}$) and 0 mm of rainfall recorded in the 7 days prior to the event.
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21 231 In contrast, the storm event in mid-October 2014 (event 3), in which 54 mm of rainfall fell in
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23 232 one week, resulted in a pronounced rise in N_2O concentrations in all flowing field drains and
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25 233 stream sites. This event occurred during a period of wetter antecedent conditions in which 30
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27 234 mm of rainfall had fallen in the 14 days prior to event 3 and the average stream flow was
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29 235 $0.021 \text{ m}^3 \text{ s}^{-1}$. The highest N_2O concentrations recorded throughout the monitoring period at
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31 236 all four stream locations occurred during storm event 3, which may also be associated with
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33 237 nitrification of residual soil nitrate post-harvest. N_2O concentrations at site M, for example,
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35 238 did not exceed $2.5 \mu\text{g N L}^{-1}$ in the previous 18 months of data collection, but during event 3,
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37 239 a concentration of $7.1 \mu\text{g N L}^{-1}$ was measured. N_2O concentrations in the field drain samples
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39 240 also peaked in mid-October, but this was less pronounced as most of the drains were not
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41 241 flowing prior to this rainfall event.
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48 242 Overall, these results indicate that catchment antecedent moisture conditions influence the
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50 243 storm event mobilisation of N_2O into stream and field drain waters, with wetter conditions
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52 244 prior to an event typically resulting in elevated N_2O concentrations. There is some
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54 245 consistency here with the study by Reay et al. (2004) who found no clear relationship
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56 246 between field drain N_2O concentration and rainfall which they argued might be due to time
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3 247 lags between rainfall and the resulting impact on dissolved N₂O concentrations. Such time
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5 248 lags are themselves likely to be extremely variable depending upon antecedent moisture
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7 249 conditions and due to the spatial heterogeneity of soil N processing.
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11 250 **3.2.3 Seasonal trends**

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13 251 To evaluate seasonal changes in field drain and stream water N₂O concentrations, all samples
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15 252 collected in a particular season were combined for spring (MAM), summer (JJA), autumn
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17 253 (SON) and winter (DJF) months (Figure 4). In all seasons, N₂O concentrations were
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19 254 significantly lower in stream samples than in field drains due to the rapid degassing of N₂O
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21 255 from the drain water once in contact with the atmosphere. In stream waters and field drains in
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23 256 sandy loam soils, N₂O concentrations were significantly ($p < 0.05$) lower during summer than
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25 257 any other season, with mean concentrations of 1.0 and 2.3 $\mu\text{g N L}^{-1}$, respectively.
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27 258 Additionally, in field drains under sandy loam soils, N₂O concentrations were significantly
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29 259 lower in autumn (3.2 $\mu\text{g N L}^{-1}$) than during winter (4.7 $\mu\text{g N L}^{-1}$) or spring (4.8 $\mu\text{g N L}^{-1}$).
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31 260 These low summer and autumn concentrations likely reflect a combination of drier
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33 261 antecedent conditions and increased nutrient uptake by crops during the growing season
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35 262 reducing the flushing of leachable soil NO₃⁻ and thus reducing the pool of available N for
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37 263 conversion into N₂O. Lower summer N₂O concentrations in field drains and headwater
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39 264 streams has previously been reported for other arable catchments in southern Germany and
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41 265 Michigan, respectively, sites which have differing soil types and rainfall regimes to the study
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45 266 presented here (Hack and Kaupenjohann, 2002; Beaulieu et al., 2008).

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49 267 Lower summer N₂O levels were not apparent in field drains under clay loam soils where a
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51 268 high mean concentration (10.1 $\mu\text{g N L}^{-1}$) was recorded. However, the number of samples for
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53 269 summer clay loam drains was small ($n = 7$) and the mean N₂O concentration was biased by
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55 270 very high concentrations discharging from just one drain (D10) at this time. Nevertheless,
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3 271 further contrasts between field drains in clay loam and sandy loam soils were apparent during
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5 272 the autumn, when substantially higher mean concentrations under clay loam soils ($5.9 \mu\text{g N}$
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7 273 L^{-1}), particularly after the October 2014 storm event, indicate greater N_2O production and
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9 274 release from clay soils early in the hydrological year.

275 **3.3 Potential factors controlling N_2O concentrations**

276 **3.3.1 Soil texture**

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18 277 Soil texture strongly influenced field drain N_2O concentrations, with a mean N_2O
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20 278 concentration under clay loam soils ($5.3 \mu\text{g N L}^{-1}$) significantly ($p < 0.05$) higher than drains
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22 279 under sandy loam soils ($4.0 \mu\text{g N L}^{-1}$) (Figure 5). This difference was largely driven by drains
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24 280 D7, D8, D9 and D10 in clay loam soils having high mean N_2O concentrations, whilst drains
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26 281 D2 and D16 in sandy loam soils had much lower concentrations. This was particularly the
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28 282 case during autumn 2014 and winter 2014/15 when field drain N_2O concentrations were
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30 283 substantially higher in clay loam soils (Figure 3). However, drains within sandy loam soils
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32 284 did not always have low N_2O concentrations, as was the case for D4 and D11 which both had
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34 285 high N_2O concentrations. Nevertheless, the data presented here suggests that drains within
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36 286 clay loam soils have the potential to yield higher N_2O concentrations than drains within sandy
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38 287 loam soils.

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43 288 Very few of the published studies that investigated field drain N_2O concentrations considered
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45 289 soil texture as a potential controlling factor, thus direct comparison with the results presented
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47 290 here is difficult. One example is Jahangir et al. (2013), who observed that mean N_2O
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49 291 concentrations in groundwater at agricultural sites with high permeability soils (sandy clay
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51 292 loam and sandy loam) were significantly higher than low permeability soils (silty clay loam
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53 293 and clay loam), in contrast to the findings presented here. In terms of direct N_2O emissions,
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55 294 numerous studies have assessed the effects of soil texture. Rochette et al. (2008) stated that in
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3 295 fine textured soils, higher N₂O emissions are often observed as a result of reduced oxygen
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5 296 levels within the soil matrix due to poor drainage. Włodarczyk et al. (2005) emphasised that
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7 297 soil texture and particle size distribution significantly affected the production of N₂O and
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9 298 concluded that heavier soils provided more favourable conditions for N₂O production than
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11 299 sandy soils. It has also been reported that the increased frequency of anaerobic conditions
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13 300 associated with higher water contents in heavier soils favours the production of N₂O by
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15 301 denitrification (Hénault et al., 2012). Therefore, assuming that dissolved N₂O concentrations
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17 302 are consistent with direct N₂O emissions from soils, the higher N₂O concentrations recorded
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19 303 here under heavier clay loam soils may be explained by increased anoxia caused by poorer
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21 304 soil drainage than in areas of sandy loam soils.
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25 305 **3.3.2 Drain flow rate**

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28 306 N₂O is highly soluble in water and so field drains with higher flow rates are expected to
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30 307 export higher loads of dissolved N₂O. However, the relationship between N₂O concentration
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32 308 and flow varied greatly among the drains (Figure 6). D2 ($r = 0.77$) and D1 ($r = 0.75$) had very
33
34 309 strong positive correlations, whereas D10 ($r = -0.35$) and D8 ($r = -0.05$) had weak negative
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36 310 correlations. Figure 6 demonstrates that this variability is partially due to differences in soil
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38 311 texture across the study site, with drains in sandy loam soils having a stronger positive
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40 312 correlation ($r = 0.24$; $p < 0.05$) between the two parameters than drains in clay loam soils ($r =$
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42 313 0.06 ; $p > 0.05$). This is supported by the fact that the two drains with the strongest positive
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44 314 correlation (i.e. D1 and D2) were in sandy loam soils and the two drains with the strongest
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48 315 negative correlation (i.e. D8 and D10) were in clay loam soils. However, there were
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50 316 exceptions to this, with drain D13 in a clay loam soil having a strong positive correlation ($r =$
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52 317 0.60) and D4 in a sandy loam soil having a weak negative correlation ($r = -0.04$). Whilst
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54 318 overall there is no clear and dominant relationship between N₂O concentration and field drain
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3 319 flow rate, the data presented here nevertheless demonstrates that soil texture does exerts some
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5 320 controlling influence upon this relationship.
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8 321 **3.3.3 pH**

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10 322 As with flow rate, Figure 6 reveals that soil type affected the relationship between field drain
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12 323 N₂O concentration and pH. The pH values of the field drains ranged from 3.7 to 8.6, with a
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14 324 mean value of 7.7 and a 95% confidence interval for the mean of 7.67–7.76. A statistically
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16 325 significant, negative correlation ($r = -0.25$, $p < 0.05$) was established between pH and
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18 326 dissolved N₂O in clay loam soils, whereas a weaker negative correlation ($r = -0.13$; $p < 0.05$)
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20 327 was observed in sandy loam soils. Hénault et al. (2012) previously identified pH as one of the
21
22 328 key soil parameters which significantly influences direct N₂O emissions, suggesting that N₂O
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24 329 emissions from acidic soils generally exceed those from alkaline soils due to higher N₂O
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26 330 emissions from nitrification and/or higher N₂O:N₂ ratios at lower pH levels. Weslien et al.
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28 331 (2009) also observed that soil N₂O emissions were significantly and negatively ($r = -0.93$)
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30 332 correlated with soil pH and suggested that this strong negative correlation is due to N₂O
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32 333 production being inhibited by alkaline pH. Whilst such strong correlations between N₂O
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34 334 concentration and pH were not observed in this study, the results presented here do support
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36 335 the hypothesis that N₂O production increases with decreasing pH, with the strength of this
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38 336 association partially linked to soil texture.
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44 337 **3.3.4 Other nitrogen species**

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47 338 The relationships between dissolved N₂O concentration and three other N species measured
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49 339 in field drains and stream water samples are presented in Figure 7. N₂O concentrations were
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51 340 generally three orders of magnitude smaller than dissolved NO₃ (Figure 7A and Figure S1),
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53 341 similar to the findings of previous studies (e.g. Ueda et al., 1993; Hack and Kaupenjohann,
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55 342 2002; Vilain et al., 2011; Outram and Hiscock, 2012). The concentrations of N₂O and NO₃
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3 343 were significantly and positively correlated in both field drains in sandy loam soils ($r = 0.30$;
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5 344 $p < 0.05$) and in stream water samples ($r = 0.55$; $p < 0.05$). However, a non-significant weak
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7 345 correlation was observed for field drains in clay loam soils ($r = 0.06$; $p > 0.05$). The
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9 346 individual drains with the strongest positive correlations between N_2O and NO_3 were D2 ($r =$
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11 347 0.80), D6 ($r = 0.67$) and D1 ($r = 0.46$), all of which were located within sandy loam soils.
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13 348 Conversely, drains D8 ($r = -0.36$), D13 ($r = -0.29$) and D7 ($r = -0.15$) located within clay
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15 349 loam soils had the strongest negative correlations.

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19 350 Previous studies have suggested that a positive correlation between N_2O and NO_3 indicates
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21 351 that nitrification is the principle production mechanism for N_2O , whilst a negative correlation
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23 352 indicates denitrification is occurring (Ueda et al., 1993; Mühlherr and Hiscock, 1998;
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25 353 Hiscock et al., 2003). On this basis, the results presented here indicate that nitrification is
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27 354 likely to be the main production mechanism for N_2O in stream waters and field drains in
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29 355 sandy loam soils, whereas in clay loam soils the production mechanism is likely to be a
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31 356 combination of both nitrification and denitrification. This combination of nitrification and
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33 357 denitrification processes is supported by evidence from previous research in the River
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35 358 Wensum and neighbouring River Bure catchments, in which groundwater NO_3-N isotope
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37 359 ($\delta^{15}N$) values in the range of -2.1 to $+13.7\%$ were measured at 36 locations (Feast et al.,
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39 360 1998). Isotopically light $\delta^{15}N$ values ($+4$ to $+8\%$) in these catchments are believed to be
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41 361 indicative of nitrification in areas covered by sand-rich glacial deposits in valley locations,
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43 362 whilst more enriched $\delta^{15}N$ values ($+8$ to $+11\%$) indicative of fractionation by denitrification

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46 363 are associated with the presence of clay-rich till deposits at the valley margins.

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51 364 Regarding other N species, N_2O was only weakly negatively correlated with NH_4 in stream
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53 365 water ($r = -0.13$; $p < 0.05$) and in field drains in clay loam ($r = -0.09$; $p > 0.05$) and sandy
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55 366 loam ($r = 0.01$; $p > 0.05$) soils, indicating the absence of any interconnected production
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57 367 mechanisms. Similarly, N_2O concentrations were not significantly correlated with NO_2 in
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3 368 either the stream water samples ($r = 0.04$, $p > 0.05$) or the clay loam field drains ($r = -0.01$; p
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5 369 > 0.05), although a significant positive correlation (albeit weak) with sandy loam drains ($r =$
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7 370 0.19 ; $p < 0.05$) was established, again highlighting potential differences in N₂O production
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9 371 mechanisms between different soil types.

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12 372 To better assess the complexity and overall importance of these different factors in
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14 373 determining the observed variability in N₂O concentrations, Table II presents the results of
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16 374 three multiple linear regression models for the prediction of N₂O concentrations in stream
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18 375 water and field drains in sandy loam and clay loam soils. The stream model proved to be the
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20 376 best performing, being able to explain 33.1% of the variability in N₂O concentrations from
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22 377 three significant predictors (NO₃, NH₄ and NO₂), although NO₃ was by far the most dominant
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24 378 predictor ($R^2 = 0.31$). By contrast the field drain sandy loam and field drain clay loam models
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26 379 were only able to explain 16.6% and 6.2% of the variability in N₂O concentrations,
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28 380 respectively, with pH being the only significant predictor of N₂O in clay loam field drains.
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30 381 These model results highlight the complexity of N₂O production mechanisms in field drains
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32 382 and indicate that other drivers of N₂O variability exist which are not captured by the
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34 383 regression models.
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39 384 **3.3.5 Impact of a cover crop**

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42 385 During autumn and winter 2013/14, dissolved N₂O concentrations in field drains below the
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44 386 winter oilseed radish cover crop ranged from 0.6–8.8 µg N L⁻¹, whereas concentrations in
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46 387 drains underlying fields without a cover crop ranged from 0.6–4.3 µg N L⁻¹ (Figure 8).
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49 388 Although the difference in the means was not statistically significant ($p > 0.05$), drains under
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51 389 the cover crop did have a slightly higher mean N₂O concentration (2.6 µg N L⁻¹) than drains
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53 390 under fields without a cover crop (2.2 µg N L⁻¹). This may be due to the accumulation of both
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55 391 carbon and N residues under the combined reduced tillage and cover crop management
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3 392 system and consequently higher substrate availability for nitrification and denitrification
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5 393 compared to conventional management (Abdalla et al., 2012). The primary goal of using a
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7 394 cover crop as a mitigation measure in agriculture is to improve soil fertility and decrease NO₃
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9 395 leaching rather than to reduce greenhouse gas emissions; however the latter should not be
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11 396 neglected when assessing the overall effectiveness of such measures. The mean field drain
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13 397 NO₃ concentration under the cover crop (2.5 mg N L⁻¹) was significantly ($p < 0.05$) lower
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15 398 than drains beneath fallow fields (13.9 mg N L⁻¹), representing a ~82% reduction in NO₃
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17 399 concentrations. Contradictory effects of cover crops on direct N₂O emissions from soil have
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19 400 been previously documented (e.g. Jarecki et al., 2009; Kallenbach et al., 2010; Dietzel et al.,
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21 401 2011; Abdalla et al., 2012; Sanz-Cobena et al., 2014), but to our knowledge the effects of a
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23 402 cover crop on indirect N₂O emissions from groundwater and surface waters has not been
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25 403 studied until now. Newell Price et al. (2011) did, however, summarise a list of mitigation
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27 404 measures to tackle environmental issues and stated that cover crops could reduce indirect
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29 405 N₂O emissions by a small amount. The results presented here contradict this and suggest that
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31 406 the use of cover crops (particularly oilseed radish) may actually increase indirect N₂O
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33 407 emissions. Thus, cover crops should not be recommended as a climate change mitigation
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35 408 strategy without further research.
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409 **3.3.6 Impact of reduced tillage**

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43 410 During the 2014/15 farm year, the different tillage options without a cover crop were
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47 411 continued as mitigation measures and the impact upon field drain N₂O concentrations is
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49 412 presented in Table III. Whilst the mean N₂O concentration in field drains under conventional
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51 413 tillage (6.9 µg N L⁻¹) was not significantly ($p > 0.05$) different from that under direct drill
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53 414 (6.2 µg N L⁻¹), the mean concentration under reduced tillage (4.8 µg N L⁻¹) was significantly
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55 415 ($p < 0.05$) lower. Despite this finding, the lower N₂O concentrations in field drains under
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57 416 reduced tillage are more likely to reflect that all these drains were within sandy loam soils
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3 417 rather than truly representing differences in tillage practice. This is because of the four field
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5 418 drains under reduced tillage, only D16 had significantly lower N₂O concentrations, whereas
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7 419 D1, D3 and D5 showed no substantial decline in N₂O compared to the other drains.
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9 420 Moreover, if N₂O concentrations were truly lower under reduced tillage relative to
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11 421 conventional ploughing, then N₂O concentrations should have been even lower under direct
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13 422 drill systems where soil disturbance, and thus N mobilisation, is even lower.
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17 423 To our knowledge, there have been no previous publications on the effects of different tillage
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19 424 methods on dissolved N₂O concentration until now, thus comparison with other studies is not
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21 425 possible. However, several studies have investigated the effects of soil management on direct
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23 426 N₂O emissions from soil and these have shown inconsistent results due to variability in
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25 427 environmental factors, such as soil water content, rates and types of fertiliser application, and
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27 428 depths of fertiliser placement (Baggs et al., 2003; Grant et al., 2004; Venterea et al., 2005;
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29 429 Omonode et al., 2011). Overall, the results presented here indicate that different soil
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31 430 inversion methods tended to have little impact on dissolved N₂O concentrations.
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34 35 431 **4. Conclusions**

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37 432 The research conducted here was undertaken to address the deficiency in the number of
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39 433 existing studies investigating indirect N₂O emissions from agriculture. The key findings from
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41 434 this work can be summarised as follows:
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46 435 (i) All field drain and stream water samples collected, regardless of time or location of
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48 436 sampling, contained a higher dissolved N₂O concentration than the water-air
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50 437 equilibrium, demonstrating that all sites were acting as a source of N₂O emissions to
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52 438 the atmosphere;
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54 439 (ii) Soil texture significantly influenced N₂O dynamics in field drains, with higher
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56 440 concentrations recorded in heavier clay loam soils than in lighter sandy loam. Soil
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3 441 texture also impacted upon the relationships between field drain N₂O concentration
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5 442 and other water quality parameters, highlighting possible differences in N₂O
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7 443 production mechanisms between different soil types;
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10 444 (iii) Antecedent moisture conditions influenced the storm event mobilisation of N₂O in
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12 445 field drains and streams, with the greatest concentration increases occurring during
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14 446 events preceded by wet conditions. N₂O concentrations also varied seasonally, with
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16 447 the lowest concentrations typically occurring during the summer months;
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19 448 (iv) Nitrogen fertiliser application and different soil inversion regimes were found to have
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21 449 no effect on dissolved N₂O concentrations either in field drains or stream waters;
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23 450 (v) Higher N₂O concentrations recorded in field drains under a winter cover crop relative
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25 451 to fallow fields indicate growing an oilseed radish cover crop is not an effective
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27 452 greenhouse gas emission mitigation strategy.

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30 453 Given the paucity of existing studies into the mechanisms involved in the production of
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32 454 indirect N₂O emissions from N leaching into surface water and groundwater bodies, further
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34 455 research conducted in a wider variety of agricultural catchments with a range of different soil
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36 456 types and rainfall regimes is highly recommended.

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3 465 **Supporting Information**
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6 466 Figure S1: Time series of the mean N₂O/NO₃ ratio in stream water and field drains.
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612 **Tables**

613 Table I Description of the study area experimental treatments

Block	Field name	Area (ha)	Field drain	2013/14				2014/15			
				Cover crop	Tillage	Crop	Applied fertiliser (kg N ha ⁻¹)	Cover crop	Tillage	Crop	Applied fertiliser (kg N ha ⁻¹)
J	Far Hemskey	13.8	-	No	Plough	SB	0	No	Plough	WW	226
	Potash	26.8	D8, D10	No	Plough	SB	7	No	Plough	WW	228
P	Gatehouse Hyrne	17.3	D5	Yes	Reduced	SB	38	No	Reduced	WW	221
	Dunkirk	12.9	D1, D3	Yes	Reduced	SB	30	No	Reduced	WW	219
	Moor Hall Field	20.4	D16	Yes	Reduced	SB	0	No	Reduced	WW	229
L	Swanhills	10.4	D4, D6	Yes	DD	SB	26	No	DD	WW	219
	Sheds Field	14.9	-	Yes	DD	SB	28	No	DD	WW	227
	First Hemskey	14.1	D2	Yes	DD	SB	34	No	DD	WW	229
	Middle Hemskey	11.8	-	Yes	DD	SB	7	No	DD	WW	222

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

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

Field drains: sandy loam	Predictor	Estimate	Std. Error	<i>t</i> -value	<i>p</i> -value	VIF	Proportion of VE (<i>R</i> ²)
	NO ₃	0.197	0.043	4.55	<0.001	1.05	0.064
	Flow	3.180	0.795	3.99	<0.001	1.04	0.045
	NO ₂	0.105	0.030	3.52	<0.001	1.02	0.034
	pH	-0.807	0.366	-2.20	0.03	1.07	0.023
						Total VE	0.166
Field drains: clay loam	Predictor	Estimate	Std Error	<i>t</i> -value	<i>p</i> -value	VIF	Proportion of VE (<i>R</i> ²)
	pH	-2.174	0.562	-3.87	<0.001	1.00	0.062
						Total VE	0.062
Streams	Predictor	Estimate	Std Error	<i>t</i> -value	<i>p</i> -value	VIF	Proportion of VE (<i>R</i> ²)
	NO ₃	0.146	0.013	11.16	<0.001	1.04	0.310
	NH ₄	-0.001	0.001	-1.45	0.015	1.30	0.012
	NO ₂	0.005	0.002	2.21	0.028	1.26	0.009
						Total VE	0.331

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

Tillage type	<i>n</i>	Mean N ₂ O (μg N L ⁻¹)	Standard Deviation
Conventional tillage	33	6.9 ^a	7.0
Reduced tillage	75	4.8 ^b	3.3
Direct drill	73	6.3 ^a	4.0

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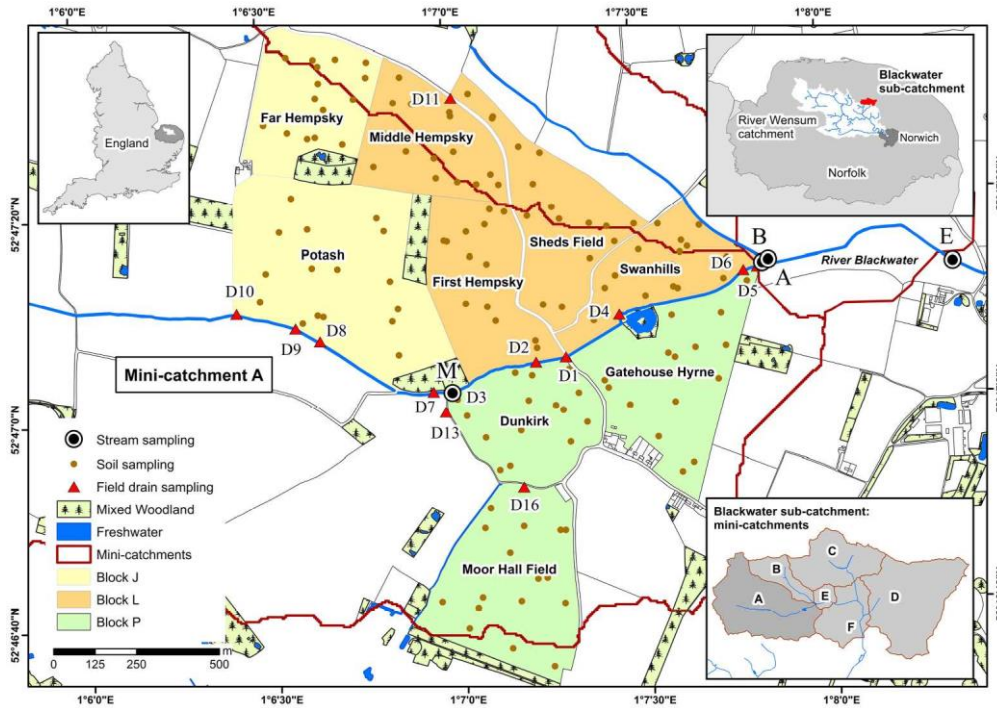


Figure 1: Location of the study area in the Blackwater sub-catchment of the River Wensum, Norfolk, UK. Map shows the locations of field drain, stream water and soil sampling sites.

99x70mm (600 x 600 DPI)

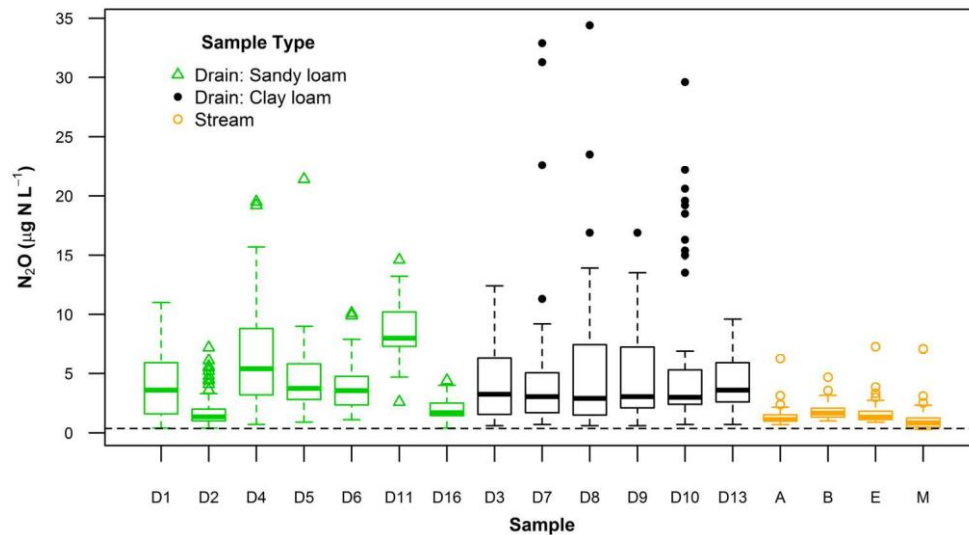


Figure 2: Boxplot of dissolved N_2O concentrations in field drains in sandy loam and clay loam soils and in stream waters for samples collected during April 2013–April 2015. The central line is the median, the box is the interquartile range and the whiskers are 1.5 times the interquartile range. The horizontal dashed line represents the atmospheric N_2O concentration when in equilibrium with water ($0.36 \mu\text{g N L}^{-1}$).

89x50mm (600 x 600 DPI)

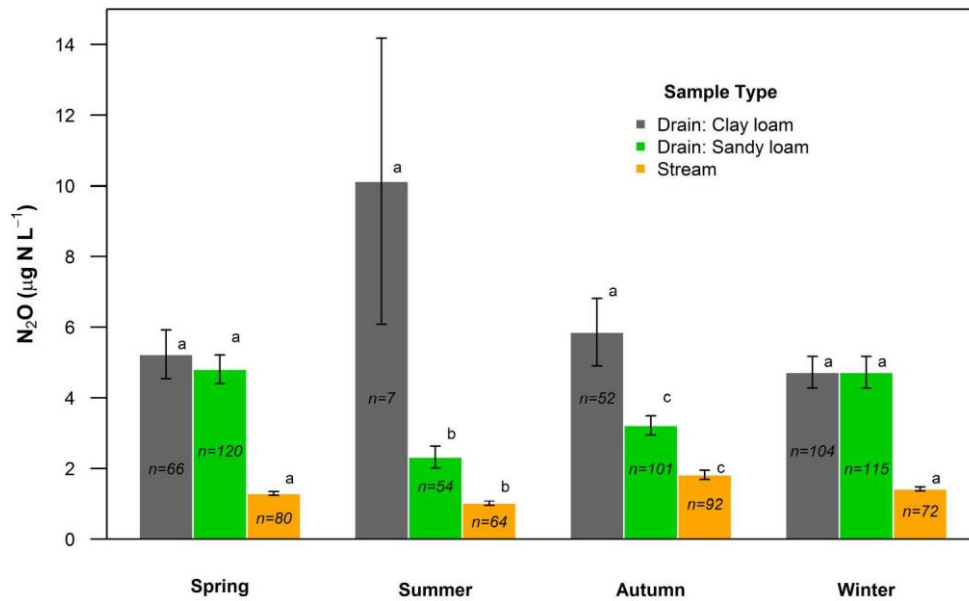


Figure 4: Average N₂O concentrations recorded in field drains and stream waters during different seasons in samples collected during April 2013–April 2015. Error bars represent one standard error. Significant differences ($p < 0.05$) are indicated by different letters for the same type of water sample.

99x62mm (600 x 600 DPI)

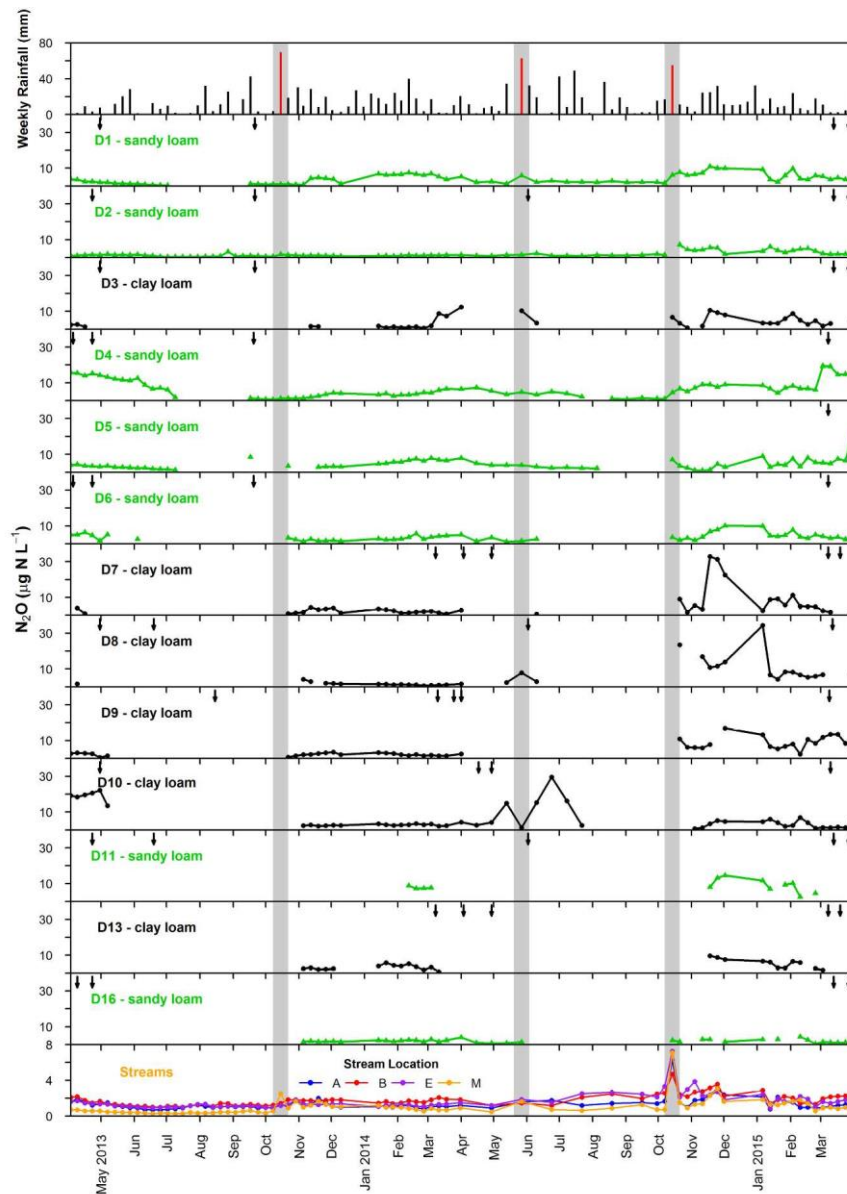


Figure 3: Time-series plot showing weekly rainfall totals and dissolved N₂O concentrations in field drains (clay loam and sandy loam) and stream water samples throughout the study period. The three largest rainfall events are highlighted in grey. Vertical arrows indicate the times of N fertiliser application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

219x302mm (300 x 300 DPI)

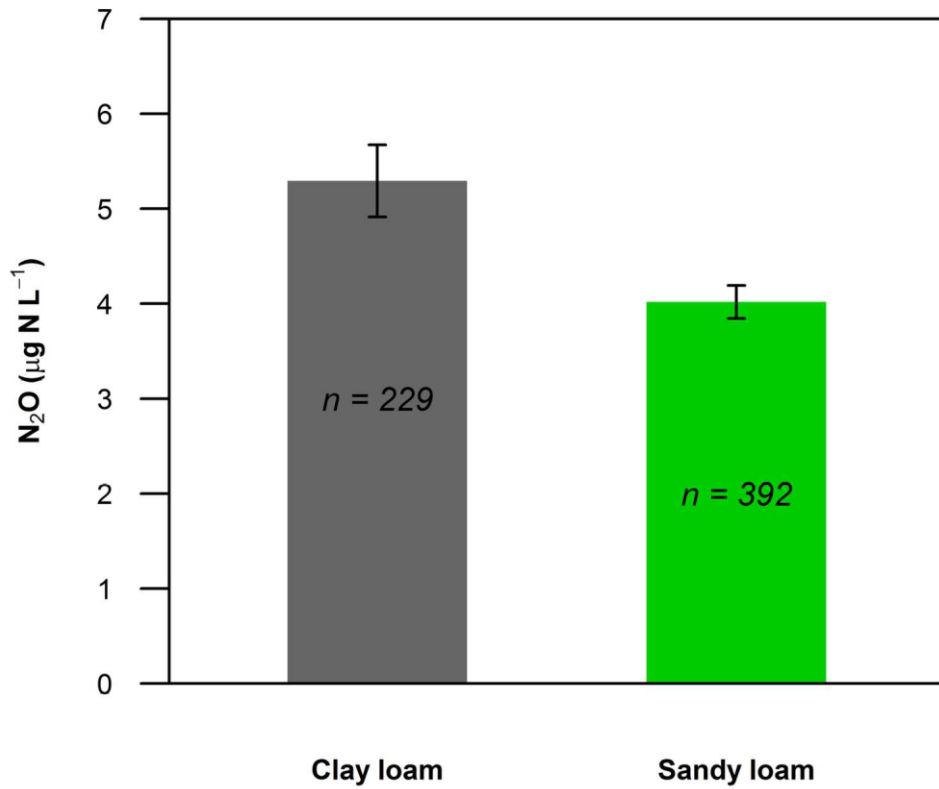


Figure 5: Mean field drain N₂O concentrations for drains underlying the two dominant soil texture types in the study area, clay loam and sandy loam, for samples collected during April 2013–April 2015. Error bars represent one standard error.

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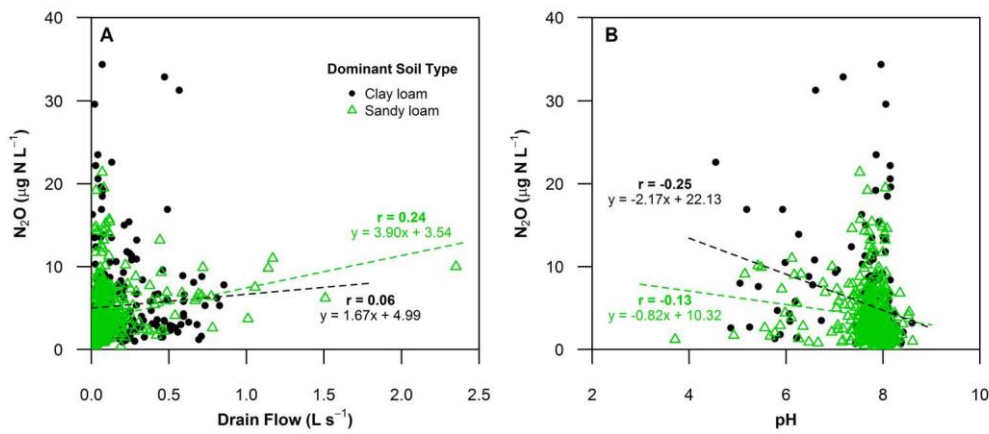


Figure 6: Relationships between field drain N₂O concentration and (A) flow rate and (B) pH, split by dominant soil type for samples collected during April 2013–April 2015. Dashed lines are linear regressions.

79x35mm (600 x 600 DPI)

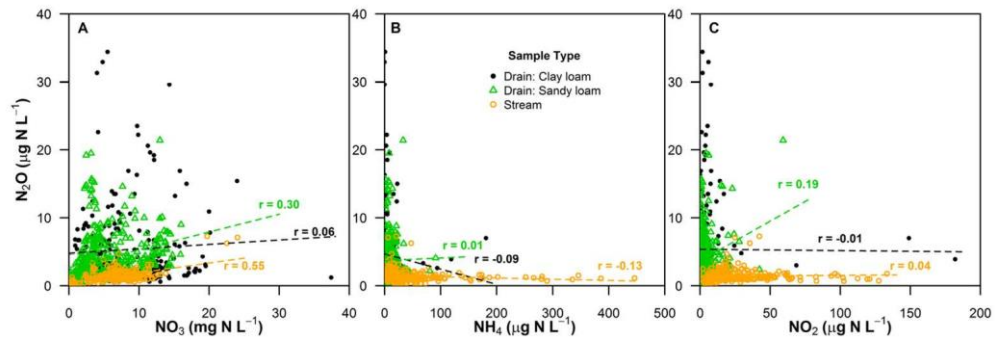


Figure 7: Relationships between N₂O concentration and (A) NO₃, (B) NH₄ and (C) NO₂ concentrations in stream water and field drain samples from different soil types collected during April 2013–April 2015. Dashed lines are linear regressions.

64x22mm (600 x 600 DPI)

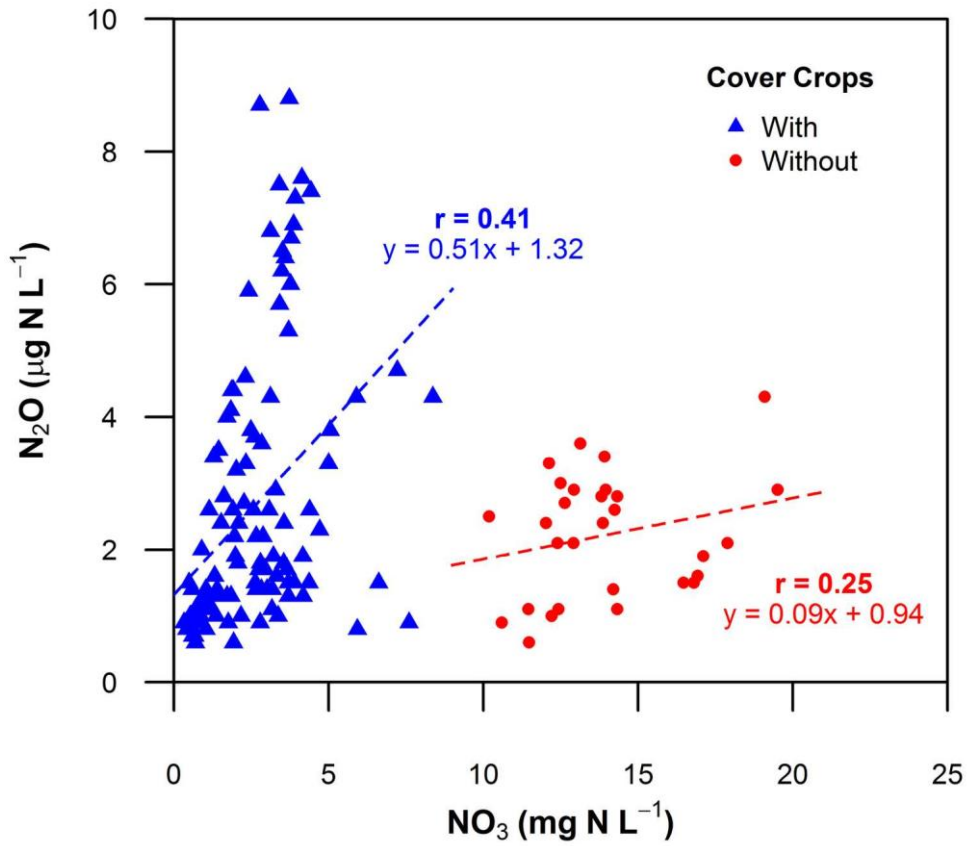


Figure 8: Relationship between dissolved N_2O and NO_3 concentrations in field drain samples collected during the growth of a winter oilseed radish cover crop (September 2013 to March 2014) from fields with ($n = 114$) and without ($n = 29$) the cover crop. Dashed lines are linear regressions.

79x71mm (600 x 600 DPI)