

Nitrous oxide emission from agricultural drainage waters

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Abstract

Uncertainty about the amounts of the greenhouse gas nitrous oxide (N_2O), which arise from N leaching from agricultural soils, predominantly as nitrate (NO_3^-), is large. To date, the bulk of studies of N_2O in aquatic systems have relied upon measurement of dissolved N_2O concentrations at wide spatial intervals (of the order of km) down a stream, river or estuary. When we combined a fine-scale (m) assessment of N_2O concentrations in agricultural drainage water with novel measurement of net N_2O emission from the same drainage system, we found that dissolved N_2O in agricultural drainage water was very rapidly lost to the atmosphere, while dissolved NO_3^- in the same water was conserved. Consequently, the N_2O emission factor (as a proportion of the nitrate-N present, the IPCC's 'EF₅') fell by a factor of more than 5 within only 100 m. Direct measurement of N_2O emission from the drainage water confirmed the disappearance of N_2O as being due to emission from water to the atmosphere, rather than *in situ* consumption by denitrification. Our findings indicate that making widely spaced measurements of dissolved N_2O concentration and/or emissions from the water surface will not take account of this much more dynamic behaviour over short distances. Realistic assessment of the 'indirect' agricultural emissions of N_2O from leached N will necessitate much more intensive sampling of the whole drainage system, from ditch to stream to river to estuary, accompanied by measurements of in-stream production. The quantities of N_2O actually released in the ditches gave values for EF_{5-g} (the IPCC's emission factor for N_2O from surface drainage and groundwaters) of between 0.02 and 0.03%, compared with the IPCC value of 1.5%. For the latter to be realistic, the quantity of N_2O required to be formed after the initial entry of water into the drainage system would need to exceed the initial load by the order of 50-fold.

Keywords: denitrification, emission factor, nitrate, nitrification

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Introduction

A large proportion (~30%) of the nitrogen (N) applied to agricultural soils can be lost through leaching (IPCC, 1997). Through the processes of nitrification and denitrification, leached nitrogen enhances biogenic production of nitrous oxide in groundwaters, streams, rivers, and eventually in estuarine systems (Seitzinger & Koeze, 1998; Hasegawa *et al.*, 2000; Groffman *et al.*, 2002). Nitrous oxide (N_2O) is also leached directly from agricultural

soils, producing supersaturations of N_2O in the soil leachate (Dowdell *et al.*, 1979; Ueda *et al.*, 1991).

Nitrous oxide production arising from N leaching constitutes by far the largest component of indirect agricultural N_2O emissions, but is also one of the most poorly defined N_2O sources (Nevison, 1999). The current Intergovernmental Panel on Climate Change (IPCC) default value for the proportion of leached N emitted as N_2O (the Emission Factor, EF₅) is 2.5% (IPCC, 1996). Emission Factor (EF₅) represents the sum of N_2O emissions resulting from N leaching in groundwater and drainage ditches (EF_{5-g}), rivers (EF_{5-r}) and estuaries (EF_{5-e}) (Mosier *et al.*, 1998). The current IPCC default value for EF_{5-g} of 1.5% is based on measurements of the ratio of dissolved N_2O to NO_3^- . However, this default value is at the upper end of measured ratios, which,

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range from <0.02% to >1% (Dowdell *et al.*, 1979; Ueda *et al.*, 1993), and Nevison (2000) has suggested that the default value may need to be reduced to as low as 0.1%.

Traditionally, studies of $\text{N}_2\text{O}/\text{NO}_3^-$ ratios in groundwater and agricultural drainage systems have been based on a limited number of widely spaced sampling points, with an assumption that measured ratios were representative of the larger area. However, coarse-scale measurements may miss large variations in dissolved N_2O concentrations, due to rapid outgassing of N_2O to the atmosphere, and possibly new production by nitrification and denitrification, between sampling points. We have therefore combined a fine-scale (m) assessment of N_2O and NO_3^- concentrations in agricultural drainage water with novel measurement of direct N_2O emission, using tunnel-shaped gas-flux chambers placed over the surface of the water in a drainage ditch.

Methods

Study site

The main experimental site was located at the Bush Estate, Midlothian, UK (Lat. $65^\circ 50' \text{N}$, Long. $3^\circ 24' \text{W}$). The top of the drainage system catchment was dominated by upland livestock pasture. Downstream from the first sampling station the drainage catchment consisted of two large arable fields with total N fertilization rates of 112 and 74 kg N ha^{-1} , respectively, during 2001. In both fields the bulk of the N was applied as granular fertilizer (during April), with an additional application of liquid N fertilizer (56 kg ha^{-1}) at the end of May. The soil was predominantly a mixture of imperfectly drained Macmerry Series and unclassified alluvium. Sampling stations were situated at intervals along a 300-m stretch of drainage ditch running between the two arable fields. Over the full sampling transect (300 m) several high turbulence (riffle) features were identified and sampling stations were situated so as to include these features. The overall stream gradient was approximately 1:30. Flow rates in the upper half of the ditch were very low, but increased markedly at station 9 and beyond (Fig. 1). Winter floods several months after the initial six-month sampling period revealed the presence of a field drainage pipe entering the ditch just above site 9.

In order to confirm that the trends identified for our sampling site on Bush Estate, Midlothian were representative of other agricultural drainage systems, a comparison site in Aberdeenshire was also investigated. An open drainage ditch, similar to that studied in Midlothian and situated at the top of the River Ythan catchment, was sampled over a relatively short stretch (20 m) at 2 m intervals down-stream from a field drain outfall. The site was chosen on the basis that no other field drainage inputs were observable over the 20 m sampling transect.

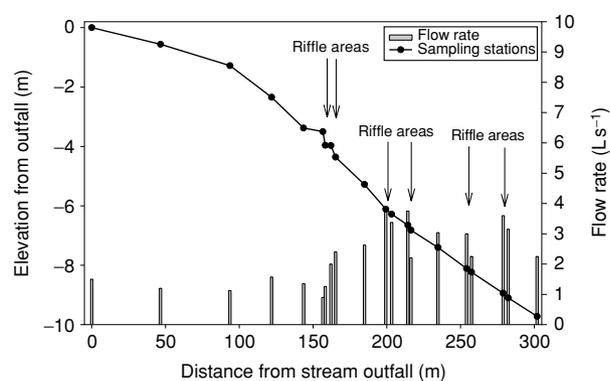


Fig. 1 Sampling sites intervals, elevation and water flow rates along Boghall drainage ditch transect in June 2001.

Dissolved nutrient and gas analysis

Triplicate water samples were collected at each sample station in 250 mL HDPE containers. Containers were completely filled and closed with a gas-tight inner cap held in place by a screw-top lid. Control samples from each sampling station were also preserved with a solution ($20 \mu\text{g L}^{-1}$ final concentration) of HgCl_2 (Kirkwood, 1992) to prevent any postsampling microbial activity; no differences between dissolved N_2O or NO_3^- concentrations in control and HgCl_2 free samples were observed. All water samples were stored in an insulated box containing ice-packs immediately after collection and during transfer to the laboratory, whereupon samples were stored at 4°C until analysed. Concentrations of both dissolved N_2O and inorganic N (NO_3^- and NH_4^+) in the drainage water were measured for each of the sampling stations, every month over a six-month period starting in June 2001 (nitrate concentrations represent combined nitrate-N and nitrite-N, as nitrite-N concentrations were found to be $<0.01 \text{ mg L}^{-1}$). Samples were collected at the same time of day and month, and analysed within 48 h of collection. Nitrous oxide concentrations were assessed in the laboratory by analysis of duplicate 5 mL subsamples from each initial water sample. Each subsample was injected with a syringe into a 22-mL vial sealed with a serum cap and vigorously shaken for 2 min followed by a 30-min standing period. Preliminary experiments showed this technique to give full equilibration between N_2O in the gas and aqueous phases. Nitrous oxide concentrations in the vial headspaces were determined by gas chromatography, using Agilent 6890 GC fitted with an electron capture detector. *In situ* dissolved N_2O concentrations were then calculated based on N_2O solubility at laboratory temperature and pressure vs. *in situ* temperature and pressure (Weiss & Price, 1980). Inorganic N concentrations were measured by

colourimetry using a segmented flow auto-analyser (Brian and Luebbe, Norderstedt, Germany).

Water samples collected at the Cairnbrogie site in Aberdeenshire were collected and analysed in an identical way to that described above, except that all samples were preserved with 20 µg L⁻¹ of HgCl₂ and stored at 4 °C for 3 weeks until analysis (Kirkwood, 1992). Preliminary experiments showed that no change in N₂O concentration occurred in samples preserved in this way over a 4-week period.

Predicted nitrous oxide emissions

For drainage waters in June 2001, N₂O emissions downstream from station 9 were predicted on the basis of the air-water gas exchange model of Liss & Slater (1974) and the dissolved N₂O concentration at station 9. Changes in dissolved N₂O concentration were also predicted using this method and compared with actual concentrations. Predicted values of N₂O flux rate were calculated assuming a wind speed of 3 m s⁻¹ at 2 m height, and no stratification of N₂O within the stream. Predicted N₂O concentrations in the drainage water were calculated assuming a stream flow velocity of 0.1 m s⁻¹ and a stream width of 40 cm. Wind and water speeds were obtained from measurements on the day of sampling using a digital flow meter fitted with 25 and 60 mm impellers, respectively (Flowatch, JDC Electronic, Switzerland). The air-water N₂O gas transfer equation used was:

$$F = v_w \left(C_w - \frac{C_a}{K'_h} \right)$$

where F is the flux of N₂O from the water surface to the air (mol cm⁻² s⁻¹), v_w is the water piston velocity (speed at which gas diffuses across the water-air interface) for N₂O, K'_h is the Henry's law constant (Weiss & Price, 1980) for N₂O [equilibrium concentration in gas phase (mol cm⁻³ air) divided by equilibrium concentration in liquid phase (mol cm⁻³ water)], C_w is the N₂O concentration in the water (mol cm⁻³) and C_a is the N₂O concentration in the air (mol cm⁻³). Air piston velocity was not included as its contribution was deemed to be insignificant. Water piston velocity for N₂O was calculated by multiplying that calculated for O₂ (Schwarzenbach *et al.*, 1993) by 0.913, based on differences in molecular weight (Holmen & Liss, 1984). Emissions were calculated on a 'per metre of stream' basis, with predicted losses from the preceding 1 metre stretch being subtracted from C_w for each 1 m section.

Direct measurement of nitrous oxide emission

Water sampling in the sixth and final month of sampling was combined with simultaneous measurement of N₂O

emission from sections of the same drainage system, using a novel 'tunnel chamber' technique. A tunnel, 3 m long, constructed from heavy-duty polyethylene sheet with gas-tight sampling ports, was placed over sections of the drainage stream. The bottom edge of the tunnel was pushed approximately 10 mm below the surface of the water, so as to minimize interference with water flow, but still provide an uninterrupted seal between the atmosphere in the tunnel and the outside air. Preliminary experiments showed that there was no significant variation in N₂O concentration along the length of the tunnel during gas collection (10 min). Gas samples were therefore collected from a single gas sampling port at the centre of the tunnel, using 60 mL syringes, each fitted with a 3-way luer type gas tap. Samples were taken both at the start and end (after 10 min) of each tunnel chamber closure period, and the net N₂O emission calculated from the resultant change in N₂O concentration in the chamber headspace. Gas samples were analysed by gas chromatography as previously described, following transfer from collection syringes to evacuated glass vials within 2 h of initial collection.

Air and water temperatures were measured before, during and after all experiments, over the six-month sampling period. The temperature inside and outside the tunnel chambers was also measured to check whether the chambers induced any warming effect, but no difference in temperature was identified. Ambient air samples were also collected during each experiment for subsequent analysis of background N₂O concentrations.

Nitrous oxide emission rates were predicted for drainage waters in November 2001, based on *in situ* dissolved N₂O concentrations, using the model of Liss & Slater (1974). These were then compared with actual emission rates for defined areas of drainage water, where the modelled water temperature was 10 °C, the flow rate was 0.3 m s⁻¹ the wind speed was 9.5 m s⁻¹ and water depth was 15 cm. All other variables used in predictions were as previously described.

Results

Dynamics of dissolved N₂O concentrations

Dissolved N₂O concentrations showed large variations over the 300 m stretch of drainage ditch examined in June 2001 (Fig. 2). Concentrations remained at or near to 100% of air saturation until station 5, where some slight elevation in N₂O concentrations was observed. At stations 6, 7 and 8 a gradual decrease in N₂O concentration was then seen. However, at station 9 N₂O concentrations increased to more than 6 times that of air saturation, equivalent to nearly 2 µg N₂O-N L⁻¹. Downstream from station 9, N₂O concentrations in the water fell rapidly,

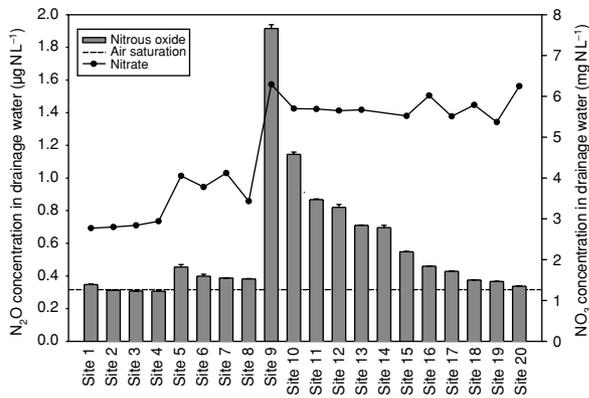


Fig. 2 Variation in dissolved nitrous oxide and nitrate concentrations along Boghall drainage ditch transect. Error bars represent standard error about the mean ($n = 3$).

dropping back to near the air saturation level by station 20.

Initial increases in N_2O concentrations observed at stations 5 and 9 coincided with increases in dissolved nitrate concentration in the water. However, while N_2O concentrations rapidly fell downstream of station 9, no such decrease in nitrate concentrations was observed. Consequently the emission factor, EF_{5-g} (IPCC, 1996) expressed as a percentage of the nitrate concentration, fell from 0.03% to less than 0.006% within a distance of only 100 m. Water exported from the study transect therefore contained a relatively high nitrate load, but no supersaturation of N_2O . The large increase in N_2O and nitrate concentration at station 9 also coincided with increased flow rate in this area of the drainage stream, which as mentioned previously, was the result of a hidden field drain outlet pipe.

The trend of decreasing N_2O concentration downstream from station 9 followed, very closely, that predicted for N_2O emission derived from the air-water exchange equation described previously, based on the concentration at station 9 (Fig. 3). Indeed, a plot of predicted N_2O concentrations against actual concentrations fitted the 1:1 relationship extremely well (Fig. 4). The largest deviations from this relationship were seen towards the end of the transect, where actual N_2O concentrations tended to be slightly lower than those predicted.

Further samplings of the drainage ditch subsequent to that in June 2001, over a 6-month period, confirmed a clear and consistent trend of significant N_2O input in the vicinity of station 9 and subsequent rapid loss from the water column down-stream (Fig. 5). Trends in N_2O concentration along the stream transect for October and November 2001 were notable for the relatively high N_2O concentrations observed at station 1 and for the

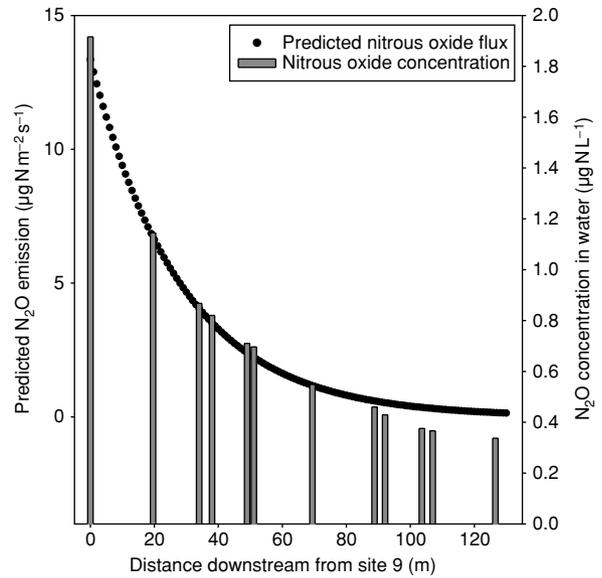


Fig. 3 Predicted nitrous oxide flux rate derived from a simple air-water gas transfer model and actual change in dissolved nitrous oxide concentration down the drainage ditch transect from site 9.

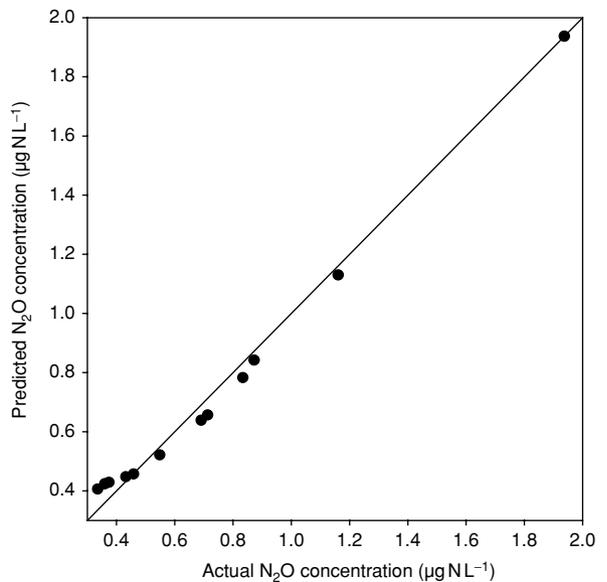


Fig. 4 Relationship between actual and predicted dissolved nitrous oxide concentrations, based on a simple air-water gas transfer model. Line represents 1:1 ratio.

slower rate of N_2O disappearance downstream from station 9. The NO_3^-/N_2O emission factor, EF_{5-g} , consistently followed the trend of rapid decrease within the 100 m of drainage ditch examined below station 9. Water temperatures ranged between 10 and 14 °C during the experimental period.

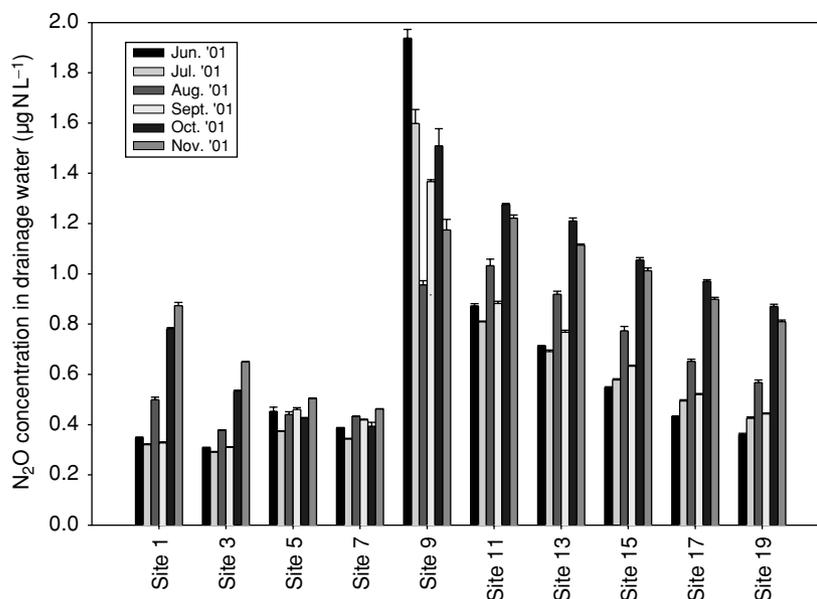


Fig. 5 Change in dissolved nitrous oxide concentration at 10 sites along the Boghall drainage ditch transect observed for six consecutive months in 2001.

Inorganic N load and dissolved nitrous oxide

Nitrate concentrations in the drainage water were very similar for all months, with the exception of October where concentrations in the top two thirds of the transect were relatively high (Fig. 6a). Nitrous oxide concentrations showed no dependence on ammonium concentration in the drainage water, which tended to be highest at station 1 and decreased thereafter. Ammonium concentrations were markedly higher in June and July 2001 than in the last 4 months of the study (Fig. 6b).

The close relationship identified between increased nitrate and N₂O concentration at station 9 in June 2001 was evident in all subsequent sampling transects, again with a fall in N₂O, but not nitrate concentrations, downstream from station 9. In all of the 6 monthly transects, N₂O concentration showed a significant positive relationship ($P < 0.01$, $r^2 = 0.4$) with nitrate concentration across the entire sampling transect, despite the apparent divergence at stations downstream from stations 9 (Fig. 7).

Net nitrous oxide emission

The novel 'tunnel chamber' method, developed for assessment of net N₂O emission from the drainage waters to the atmosphere, proved both practical and effective. Installation of the tunnel chambers so as to give a complete seal between water and chamber while minimizing interference with water flow was straightforward. During this study tunnel chamber were only employed during overcast Autumn days. However, a potentially important limitation may be super-ambient heating inside the tunnel chambers when exposed to direct sunlight, which would be expected to increase emissions.

Precautions to avoid this where necessary, such as shading by a suspended tarpaulin, are recommended. Also, the removal of wind disturbance may result in such chamber methods underestimating actual emissions. However, during November 2001, N₂O emissions measured during 'tunnel chamber' experiments followed an almost identical trend to that seen for N₂O concentrations in the water (Fig. 8), suggesting that the exclusion of wind from the surface was unimportant in the circumstances of this experiment.

A notable increase in atmospheric emissions relative to water concentration was observed downstream from station 9 and coincided with a steep riffle area at approximately 215 m from the stream outfall pipe (station 1). Despite such variations a significant positive relationship ($P < 0.01$, $r^2 = 0.78$) between N₂O concentration in the water and N₂O emission was evident for the transect as a whole (Fig. 9). Variation in N₂O concentrations in replicate water samples was negligible in all but samples from station 9, where concentrations varied by no more than 0.3 µg N₂O-NL⁻¹. The proximity of station 9 to the hidden field drain outfall is a likely explanation for this higher than normal interreplicate variation.

Predicted emission rates of N₂O-N, based on the simple air-water gas exchange model, substantially underestimated actual emission rates in the November 'tunnel chamber' experiments (Figure 10). Actual rates of emission in areas of high turbulence were up to 5 times higher than those predicted and it appears that the combination of the greater flow velocity and water turbulence encountered in November, compared with earlier in the year made use of the simple gas exchange model inappropriate on this occasion.

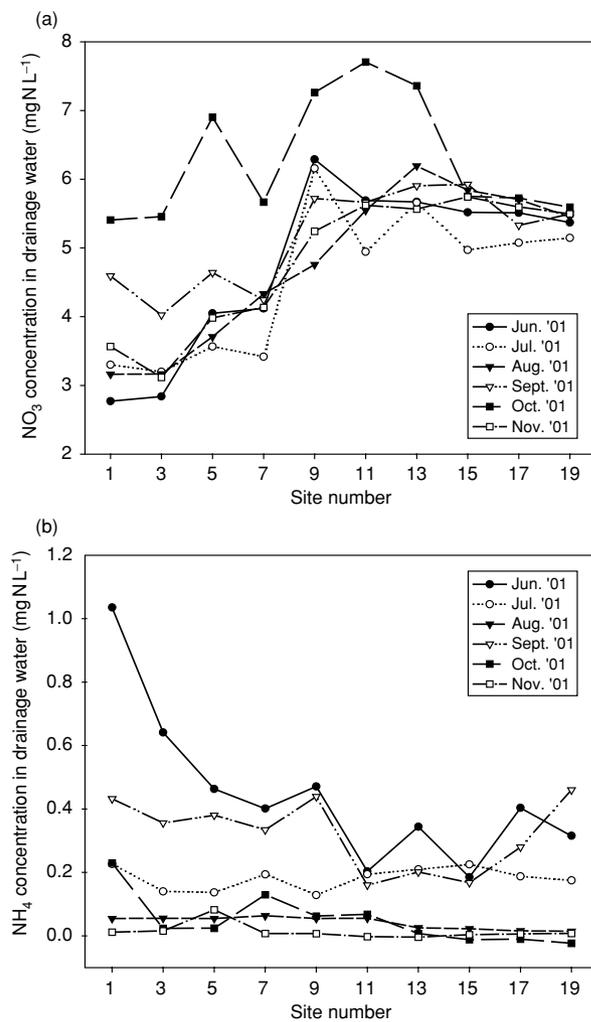


Fig. 6 (a) Change in dissolved nitrate concentrations at 10 sites along the Boghall drainage ditch transect observed for six consecutive months in 2001, (b) Change in dissolved ammonium concentrations at 10 sites along the Boghall drainage ditch transect observed for six consecutive months in 2001.

Our comparison experiment in Aberdeenshire produced the same trend of N_2O loss from water in open agricultural drainage ditches as that observed in Midlothian (Fig. 11). The distance over which this comparison study was conducted was limited by the frequent occurrence of additional field drain outfalls along the open ditch. Nevertheless, the rapid loss of N_2O from water on entry to an open drainage system was evident even over the 20 m transect examined.

Discussion

The few published measurements of N_2O concentrations in agricultural drainage waters have given rise to an extremely uncertain emission factor. We find that relating

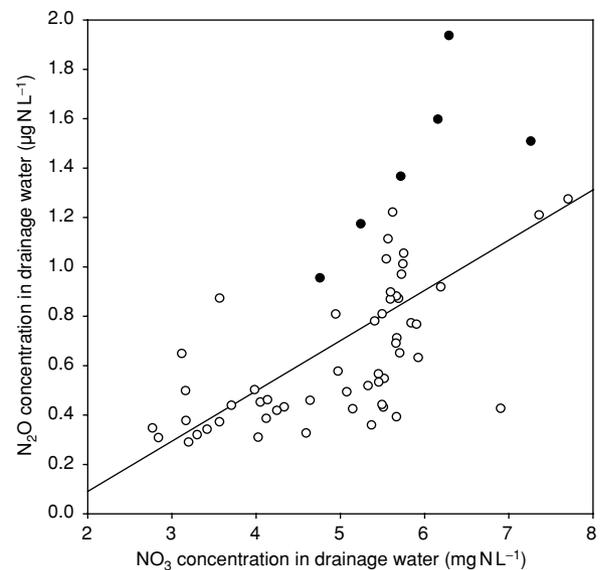


Fig. 7 Relationship between dissolved nitrate and dissolved nitrous oxide concentration in drainage water at 10 sites along the Boghall drainage ditch transect observed for six consecutive months in 2001. Solid circles denote samples from site 9.

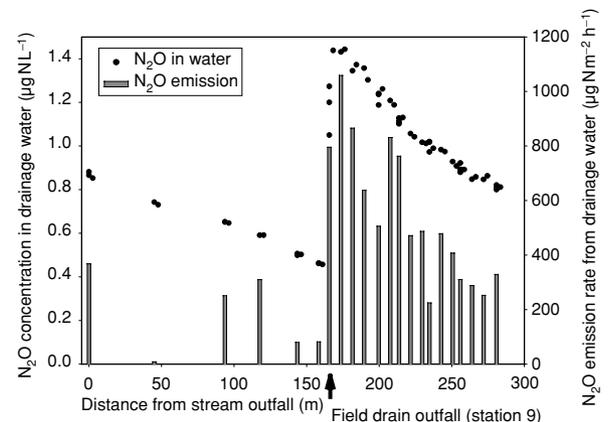


Fig. 8 Change in nitrous oxide emission and dissolved nitrous oxide concentration in drainage water along the Boghall drainage ditch transect. Arrow indicates entry point of the field drain outfall just above station 9.

N_2O concentrations in drainage waters to N application, or to dissolved inorganic N concentrations within the drainage water, is subject to error due to the rapid degassing of the N_2O on exposure to the atmosphere, without a simultaneous decrease in N load. To obtain a reliable emission factor for N_2O from leached N a more complete view of the degassing of dissolved N_2O and in-stream processing of leached inorganic N (leading to the production of additional N_2O) is required.

Measured ratios of $\text{N}_2\text{O-N}$ to $\text{NO}_3\text{-N}$ in agricultural drainage ditches are generally lower than those

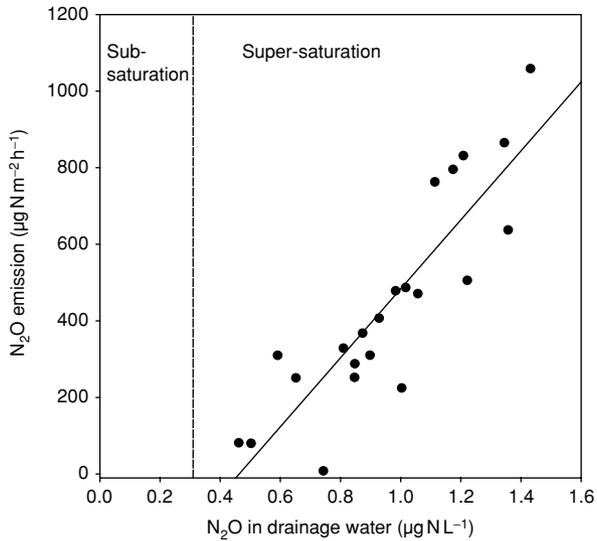


Fig. 9 Relationship between dissolved nitrous oxide concentration in agricultural drainage water and nitrous oxide emission from the water surface to the atmosphere. Dashed line represents dissolved nitrous oxide concentration at air saturation.

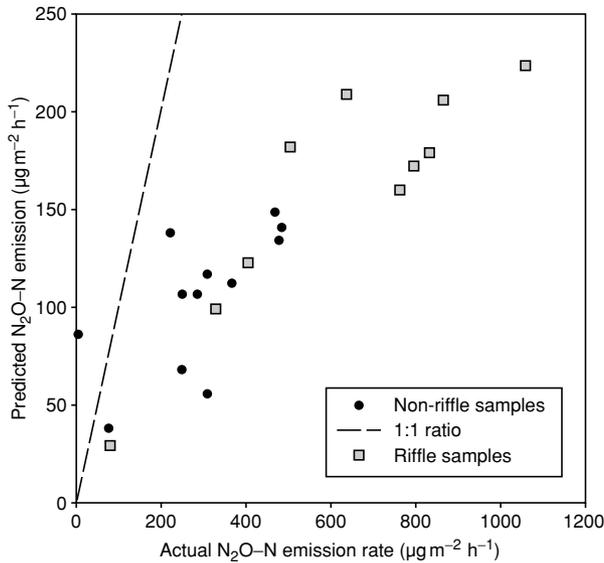


Fig. 10 Relationship between predicted nitrous oxide emission, based on a simple air-water gas transfer model, and actual emission.

measured for agricultural groundwater, and until now this disparity has been attributed to out-gassing, but without direct evidence (IPCC, 1996). We have now clearly demonstrated such out-gassing to be both significant and very rapid, and have therefore established the likely source for the apparent discrepancy in N₂O-N to

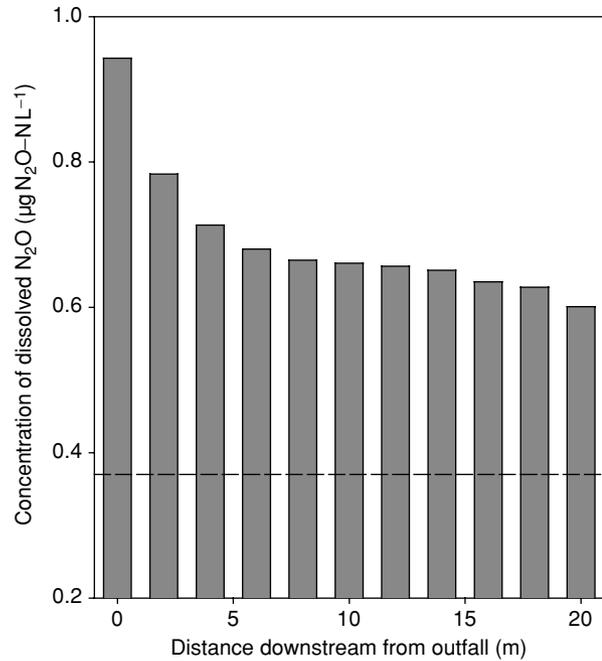


Fig. 11 Dissolved nitrous oxide concentrations in agricultural drainage water at a comparison site at Cairnbrogie, Ythan Catchment, Aberdeenshire. Data are for a 20-m stretch of open drainage ditch downstream of a field drain outfall. Nitrous oxide concentration in the field drain water was 1.4 µg L⁻¹. Dashed line represents air saturation concentration for nitrous oxide in ditch water.

NO₃-N ratios between agricultural drainage ditches and groundwaters.

The large increase in water flow and dissolved N₂O concentrations at site 9 suggested the presence of a field drain outfall at this point and, indeed, such an outfall was exposed by bank erosion during winter flooding. Such large variations in N₂O over distances of only a few metres highlight the need for caution when basing total N₂O flux estimates for drainage waters on measurements made at widely spaced sampling points. The super-saturations of N₂O observed during our six-month study period are well within the range of values previously published for such freshwater drainage systems (e.g. Dowdell *et al.*, 1979; MacMahon & Dennehy, 1999).

Nitrous oxide concentrations much higher than those seen in this study, as high as 130 µg NL⁻¹, have been reported for agricultural drainage waters (Dowdell *et al.*, 1979). However, on the basis of our results, in the shallow well-mixed waters of open drainage streams even these very elevated levels of nitrous oxide will quickly (within a few hundred metres) be lost to the atmosphere. As noted previously, the exact stage at which drainage water is sampled is crucial. In the study of MacMahon

& Dennehy (1999), one of very few to measure N_2O emissions directly, sampling stations were approximately 20 km apart. Consequently, large variations in dissolved and emitted N_2O may have been overlooked, and integration of N_2O emission between sample stations may have produced substantial errors in the 'whole river' estimate.

The correlation between increased N_2O concentration and dissolved nitrate in the drainage water agrees with previous studies where both variables were measured (Muelherr & Hiscock, 1997; MacMahon & Dennehy, 1999; Hack & Kaupenjohann, 2002) and is indicative of the link, albeit a complex one, between N application, nitrification, denitrification and net N_2O production. The almost complete lack of variation in dissolved nitrate downstream from site 9 indicates very little biological processing of N in the drainage waters examined. Instead, the inorganic N load is presumably transported downstream until conditions favourable to N assimilation or denitrification are encountered (Garcia-Ruiz *et al.*, 1998; Pattinson *et al.*, 1998; Hasegawa *et al.*, 2000). Such divergence between dissolved nitrate and N_2O load will inevitably result in a poorer relationship between these two variables with increasing distance downstream. Consequently, the overall relationship between nitrate and N_2O concentration may be relatively poor for widely spaced sampling stations (e.g. MacMahon & Dennehy, 1999).

The dominance of physical, rather than biological, factors in controlling N_2O loss from the drainage waters was confirmed in our study by the very strong relationship between N_2O loss predicted by physical gas-liquid transfer laws and actual downstream decreases in dissolved N_2O concentrations. The slight divergence of actual N_2O concentrations from those predicted in the lower third of the sampled stretch is likely to be due to areas of much increased water turbulence in this region of the drainage stream.

Similar trends in N_2O concentration along the stream in all 6 months are again indicative of a single dominant input of drainage water super-saturated with N_2O , such as that identified subsequent to the study just above station 9. Slower rates of N_2O disappearance downstream from site 9 in October and November, compared to preceding months, are likely to have resulted from the lower water temperatures and hence greater N_2O solubility during these months.

Relatively high nitrate concentrations, as observed in October, coincided with a substantial increase in rainfall and so may represent increased leaching rates of N from the catchment soil. However, much more intensive sampling would be required to be sure of such a relationship. High ammonium concentrations at site 1 are likely to be

a result of the predominance of livestock grazing in the catchment immediately upstream of the outfall.

The very good correlation between N_2O concentration in the drainage waters in November 2001 and the measured N_2O emission using the 'tunnel chamber' technique, confirmed that the observed decrease in N_2O concentration downstream from site 9 was a result of physical out-gassing to the atmosphere, rather than *in situ* consumption. Further more, the tunnel-chamber method identified higher N_2O emissions associated with areas of high water turbulence in the stream, a change in emission, which was difficult to identify from dissolved N_2O concentrations alone. These 'riffle' areas are clearly of importance as areas of increased N_2O degassing and may be of particular importance in deeper, slow moving water. Indeed, where slow moving, stratified waters carry N_2O at super-saturated concentrations, areas of high turbulence such as weirs may prove to be very strong local sources of N_2O to the atmosphere.

In headstream systems, such as the one investigated here, predictions of N_2O emission to the atmosphere using the simple air-water gas transfer model developed for describing gas flux from the ocean surface (Liss & Slater, 1974) are liable to underestimate emission rates in some conditions. Though the model predicted downstream changes in N_2O concentration well during a period of low flow in June 2001, higher flow conditions during November 2001 resulted in a clear divergence from the model. Additionally, where conditions are favourable for denitrification, the basing of N_2O emission on N_2O concentration in the water may be flawed due to *in situ* N_2O consumption. Hence, use of surface chambers to measure the actual net flux of N_2O to the atmosphere should be made wherever possible.

We conclude, then, that much of the past variation in measured values of EF_5-g has been a consequence of rapid outgassing of N_2O , relative to a conserved dissolved NO_3^- load. Rapid outgassing of N_2O from aquatic systems poses similar problems for studies of N_2O emission in river (EF_5-r) and estuarine (EF_5-e) systems, where sampling points are often even more widely spaced (e.g. Law *et al.*, 1992; Bange *et al.*, 1996). Though point-source inputs of N_2O , comparable to that observed in this study, are unlikely to be encountered in estuarine systems, N_2O production rates from estuarine sediments can be highly variable over both space and time (Middelburg *et al.*, 1995). Such variability necessitates careful interpretation when attempting to formulate N_2O emission budgets for whole estuaries. If the certainty of N_2O emissions from this indirect agricultural source is to be increased, an integrated sampling strategy encompassing all three components of EF_5 at a higher resolution than that employed to date is desirable.

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