Indirect nitrous oxide emission factors for agricultural field drains and headwater streams

Zanist Q. Hama-Aziz, Kevin M. Hiscock, Richard J. Cooper

School of Environmental Sciences, University of East Anglia, Norwich Research Park, Norwich NR4 7TJ, UK

ABSTRACT

Agriculture is a major source of nitrous oxide (N\textsubscript{2}O) emissions, a potent greenhouse gas. Whilst direct N\textsubscript{2}O emissions from soils have been widely investigated, indirect N\textsubscript{2}O emissions from nitrogen (N) enriched surface water and groundwater bodies are poorly understood. In this contribution, indirect N\textsubscript{2}O emissions from subsurface agricultural field drains and headwater streams were monitored over a two-year period (2013–2015) in an intensive arable catchment in eastern England. Indirect N\textsubscript{2}O emission factors for groundwater (EF\textsubscript{5g}) and surface runoff (EF\textsubscript{5r}) were calculated for both field drain and stream water samples, respectively, using two approaches: the N\textsubscript{2}O-N/\textsubscript{NO}_{3}⁻-N ratio and the IPCC (2006) methodology. Mean EF\textsubscript{5g} values derived from the N\textsubscript{2}O-N/\textsubscript{NO}_{3}⁻-N ratio were 0.0012 for field drains and 0.0003 for stream water. Using the IPCC (2006) methodology, the mean EF\textsubscript{5g} values were 0.0011 for field drains and 0.0001 for stream water. Thus, EF values derived from both methods were below the current IPCC (2006) default value of 0.0025 and a downward revision to 0.0012 for EF\textsubscript{5g} and 0.0002 for EF\textsubscript{5r} is recommended. Such revision would halve current estimates of N\textsubscript{2}O emissions associated with nitrogen leaching and runoff from agriculture for both the UK and globally.

Keywords: nitrous oxide; emission factor; IPCC; nitrate; greenhouse gas; river; field drain

1. Introduction
Nitrous oxide ($N_2O$) is a potent greenhouse gas with a present atmospheric concentration of 326.7 ppb. Not only does $N_2O$ have a global warming potential 300 times that of $CO_2$, it also participates in photochemical reactions in the stratosphere which lead to the destruction of ozone ($O_3$). The concentration of $N_2O$ in the atmosphere is currently increasing at an annual rate of $\approx 0.26\%$ and agriculture is considered to be the largest source ($\approx 60\%$) of anthropogenic $N_2O$ emissions. The Intergovernmental Panel on Climate Change (IPCC) has developed protocols for quantifying and generating national inventories of $N_2O$ emissions from industry, agriculture and natural ecosystems, with total $N_2O$ emissions from agriculture being categorised into direct and indirect sources. Whilst direct $N_2O$ emissions as a result of nitrogen ($N$) application to soils have been widely investigated, indirect emissions produced in surface waters and groundwaters from agricultural $N$ leaching and runoff have, to date, been less well studied.

Indirect $N_2O$ emission factors ($EF_5$) are a way of representing $N_2O$ emissions from a water body as a fraction of the original $N$ flux into the system. The IPCC defined $N_2O$ emission factors for $N$ leaching and runoff from managed soils as follows (Equation 1):

$$EF_5 = \frac{N_2O_{(L)}-N}{(Total \ N \ input \times Frac_{LEACH})}$$

where, $EF_5$ is the $N_2O$ emission factor (kg $N_2O$–$N$/kg $N$) with a default value of 0.0075 (range = 0.0005–0.025); $N_2O_{(L)}-N$ is the emission of $N_2O$ produced by the leaching and runoff of $N$ additions to managed soils (kg $N_2O$–$N$ a$^{-1}$); $Total \ N \ input$ is the total annual amount of $N$ added to the system, including synthetic fertilisers and animal manure, that is lost through leaching and runoff (kg $N$ a$^{-1}$); and $Frac_{LEACH}$ is the fraction of all $N$ added to, or mineralised within, managed soils that is lost through leaching and runoff (kg $N$/kg of $N$ additions a$^{-1}$), with a default value of 30% (range = 10–80%).

Indirect $N_2O$ emissions can either be calculated by using the default values of $EF_5$ and $Frac_{LEACH}$ in Equation 1, or by measuring indirect $N_2O$ emissions from dissolved $N_2O$ concentrations and then
using this equation to calculate EF5. The IPCC \(^6\) revised the default emission factor for indirect N\(_2\)O emissions (EF5) from 0.025 kg N\(_2\)O-N/kg N in 1997 to 0.0075 kg N\(_2\)O-N/kg N in 2006. The EF5 was further divided into three components according to the site of N\(_2\)O production: EF5\(_g\) for groundwater and surface drainage (0.0025); EF5\(_r\) for rivers (0.0025); and EF5\(_e\) for estuaries (0.0025), thus giving an overall EF5 of 0.0075. EF5 has a wide range of uncertainty (0.0005–0.025) as a result of natural variability and a lack of data to support designation. However, as many studies are often lacking the detailed mass balance information needed to determine EF5 and evaluate national N\(_2\)O inventories by the IPCC (2006) methodology, EF5 values are commonly calculated by using a N\(_2\)O-N/NO\(_3\)-N mass ratio derived using the concentration data of N\(_2\)O and nitrate (NO\(_3\)) collected from the water body. Therefore, most studies on emission factors from leaching and runoff calculate EF5 by the following method\(^7,9,10,17\) (Equation 2):

\[
\text{EF5} = \frac{\text{N}_2\text{O-N}}{\text{NO}_3\text{-N}}
\]

where N\(_2\)O-N and NO\(_3\)-N are concentrations measured in groundwater, rivers or estuaries.

The objectives of this study are as follows:

i. To calculate indirect N\(_2\)O emission factors for subsurface agricultural field drains (EF5\(_g\)) and headwater streams (EF5\(_r\)) in an intensive arable catchment;

ii. To assess the extent of temporal variability in indirect N\(_2\)O emission factors;

iii. To compare emission factors derived from the two different methods with the IPCC (2006) default EF5\(_g\) and EF5\(_r\) values of 0.0025 and assess whether these general emission factors are appropriate for predicting N\(_2\)O emissions in a temperate, lowland arable environment.

The findings of this study should provide useful information for updating indirect N\(_2\)O emission factors used in future IPCC assessment reports.
2. Materials and Methods

2.1 Study location

The study area is in the Blackwater sub-catchment of the River Wensum, Norfolk, UK (Figures S1–S5). The Blackwater sub-catchment is intensively monitored as part of the Wensum Demonstration Test Catchment (DTC) project which aims to evaluate the extent to which on-farm mitigation measures can cost-effectively reduce the impact of diffuse agricultural pollution on aquatic ecology whilst still maintaining food production capacity. The area is under intensive arable cultivation with spring and winter barley, winter wheat, winter oilseed rape, spring beans and sugar beet grown in a seven-year rotation. The average annual rainfall total is 674 mm and the mean annual temperature is 10.1°C. The western section of the Blackwater sub-catchment, hereafter termed “mini-catchment A” (5.4 km²), is extensively under-drained by a dense network of agricultural tile drainage installed at a depth of 100–160 cm below the ground surface. Discharge from drains can be as high as 10 L s⁻¹, but varies greatly depending upon season, depth, catchment area and antecedent moisture conditions, with most drains drying up completely during the summer months. The geology of the catchment is comprised of Middle Pleistocene glacial deposits (0.5–20 m depth) overlying Cretaceous White Chalk (>20 m depth), with surface soils varying from sandy loam to sandy clay loam and clay loam.

2.2 Sample collection

Over a two-year period (April 2013 to April 2015), a total of 929 water samples were collected from 13 field drains (n = 621) and four stream locations (sites A, B, E and M; n = 308) for N₂O and nutrient analysis (Figure S1). Samples were collected at weekly intervals, with the exception of April–September 2014 when field drains were sampled fortnightly and stream waters monthly. For dissolved N₂O concentrations, samples were collected at field drain outlet pipes and from stream waters using 20 mL glass syringes (SAMCO) with a three-way stopcock attached to each syringe by a Luer-Lock fitting. Syringes were flushed three times with water from the sampling point and any air bubbles contained in the syringes were expelled before the final sample was taken. A single sample was taken at each location and no preservative was added. Samples in syringes were returned to cold storage at
4°C within 3 h and analysed for N$_2$O within 72 h of collection. For the nutrient analysis, water samples were collected in 1L plastic bottles and were also analysed within 72 h of collection. Field drain flow was estimated in triplicate on each sampling occasion. Stream stage was measured at each of the four stream sampling sites using a pressure transducer and converted into flow using a stage-discharge rating curve. Maps of the field drain network were provided by the local farmer and the drainage area of each drain was estimated by polygon digitising using GIS (Figure S1). Wind speed data required for calculating N$_2$O emissions from streams were obtained from a weather station installed in mini-catchment A.

2.3 Sample analysis

Dissolved N$_2$O was analysed by gas chromatography with an electron capture detector (GC-ECD). Accuracy of N$_2$O measurements was within ±3% with a detection limit of ~0.0008 µg N L$^{-1}$. Nitrate was determined by ion chromatography using a Dionex ISC 2000 with an accuracy of 0.19 mg N L$^{-1}$. Ammonium (NH$_4$) and nitrite (NO$_2$) were determined by a Continuous Flow Analyser - Skalar San++ with accuracies of 4.57 µg N L$^{-1}$ and 1.52 µg N L$^{-1}$, respectively. Total organic nitrogen was measured with a Skalar Formacs TOC/TN analyser with an accuracy of 0.08 mg N L$^{-1}$. Further details are provided in the supporting information.

2.4 Emission factors and flux calculations

Fluxes of N$_2$O from field drains into the atmosphere were calculated based on the assumption that all of the dissolved N$_2$O at concentrations above that of air saturation is subsequently lost to the atmosphere $^{10, 20-22}$. Thus, the air saturation concentration of N$_2$O (0.36 µg N L$^{-1}$), calculated using equilibrium equations$^{23}$, was subtracted from the measured dissolved N$_2$O concentration, then multiplied by flow rate and divided by drain area to obtain the N$_2$O emission rates. Note, however, that because field drain samples were taken at the drain outlets, there may be losses of N$_2$O from the drains prior to reaching the sampling point and thus estimates of N$_2$O emissions could be underestimated in this study. N$_2$O emission rates from stream water were calculated using the water-air gas exchange Equation (3)$^{7}$, as follows:
\( F = kC_w - \frac{C_a}{k' h} \)

where \( F \) is the flux (or emission) of gas (mol cm\(^{-2}\) h\(^{-1}\)); \( k \) is the transfer velocity of N\(_2\)O across the water-air interface (cm h\(^{-1}\)); \( C_w \) is the concentration of N\(_2\)O in water (mol cm\(^{-3}\)); \( C_a \) is the concentration of N\(_2\)O in air (mol cm\(^{-3}\)); and \( k' h \) is the Henry’s law constant for N\(_2\)O which is dimensionless and obtained from literature as 1.02 \(^{24}\). \( k \) was calculated using a combined gas transfer velocity approach that incorporates both wind and water turbulence \(^{25}\). The water turbulence component was calculated as follows (Equation 4):

\[ k_{\text{water}} = \frac{D V}{h} \]

where \( D \) is the N\(_2\)O diffusion coefficient (m\(^2\) s\(^{-1}\)), \( V \) is the stream water velocity (m s\(^{-1}\)) and \( h \) is the stream water depth (m). The wind component was calculated as follows (Equation 5):

\[ k_{\text{wind}} = 0.31u^2 \left( \frac{Sc}{660} \right)^{0.5} \]

where \( u \) is the wind speed (cm h\(^{-1}\)) and \( Sc \) is the Schmidt number for N\(_2\)O. The wind and water components were then added together to form the combined gas transfer velocity, \( k \).

For emission factors calculated by the IPCC (2006) methodology, FracLEACH was determined from the total load of dissolved organic and inorganic N in field drain and stream water, divided by the total N fertiliser input. For stream water, this was only calculated at site A (the outlet of mini-catchment A) as this site had the most complete N fertiliser application data (2012–2014).
3. Results and Discussion

3.1 Concentration data

Field drain and stream water NO$_3$ and N$_2$O concentrations for the period April 2013 to April 2015 are presented in Figure 1 and summarised in Table 1. The mean N$_2$O concentration recorded across all field drains (4.49 µg L$^{-1}$) was significantly ($p < 0.05$) greater than that recorded for the streams (1.43 µg L$^{-1}$), which reflects the rapid degassing of N$_2$O from field drain water upon contact with the atmosphere prior to reaching the stream. Conversely, the mean NO$_3$ concentration recorded in field drains (6.08 mg L$^{-1}$) was significantly lower ($p < 0.05$) than that recorded in stream water (6.70 mg L$^{-1}$). In both field drains and streams, the mean NO$_3$ (4.17 and 4.49 mg L$^{-1}$, respectively) and N$_2$O (3.20 and 1.02 µg L$^{-1}$, respectively) concentrations were significantly ($p < 0.05$) lower during the summer (JJA) than any other season. The highest mean NO$_3$ concentrations in field drains (6.47 mg L$^{-1}$) and streams (8.30 mg L$^{-1}$) occurred during the winter, whereas the highest mean N$_2$O concentrations in field drains occurred during the spring (4.95 µg L$^{-1}$) and in streams during the autumn (1.82 µg L$^{-1}$).

In stream water, N$_2$O and NO$_3$ concentrations exhibited a relatively strong positive correlation ($r = 0.55$) indicating that NO$_3$ is an important driver of riverine N$_2$O production in this catchment (Figure 1). However, in field drains the correlation between N$_2$O and NO$_3$ was much weaker ($r = 0.19$), implying a greater role from other biotic and abiotic factors in the production of N$_2$O in soils. In contrast to previous studies, there was no strong correlation between stream water N$_2$O and either dissolved oxygen concentration ($r = 0.19$) or water temperature ($r = 0.05$).

3.2 N$_2$O-N/NO$_3$-N ratio method

The EF$_{5g}$ emission factor (ratio of N$_2$O-N to NO$_3$-N) in field drain samples varied between 0.00003 and 0.01063, with a mean value of 0.00120. The EF$_{5g}$ emission factor for stream water samples ranged from 0.00006 to 0.00282, with a mean value of 0.00029 (Table 1). Thus, the EF$_{5g}$ emission factors for 90% of field drain samples collected in this study were lower than the IPCC default value of 0.0025, whilst ~15% of collected samples were one order of magnitude lower. Similarly, 100% of the stream
samples (EF5) had emission factors lower than the IPCC default. These results indicate that the previously downward revised IPCC (2006) default value of 0.0025 may still be overestimating indirect N₂O emissions in agricultural systems similar to that studied here.

As illustrated in Figure 1, the N₂O-N/NO₃⁻-N ratios varied substantially across field drain and stream water samples. In this study, temporal variability in these ratios was monitored over the two-year sampling period (Figure 2). The mean N₂O-N/NO₃⁻-N ratio of the stream water samples was significantly lower (p < 0.05) than that for the field drains throughout the entire study period, amounting to approximately one order of magnitude difference (Table 1). For both field drains and stream samples, EF ratios were observed to increase during the summer months (JJA) before returning to relatively stable levels in mid-autumn (October). The mean summer EF5 for the stream sites (0.00039) was significantly (p < 0.05) higher than that recorded in winter or spring, although it was the same as that recorded during the autumn (Table 1). In the field drains, the mean summer EF5 (0.00135) was higher than any other season, although wide variability meant this difference was not significant (p > 0.05). This trend was repeated in both sampling years and appears to be due to the substantial decrease in NO₃⁻ concentrations during the summer as a result of a decline in water flow and a decline in potentially leachable NO₃ due to nutrient uptake by crops during this period. This summer period of high EF ratios represents ~10% of collected samples shown in Figure 2. It is clear from the data presented here that EF values varied over time and it may be more appropriate to have different EF values for different seasons rather than one EF value throughout the year, as is suggested by the IPCC⁶.

3.3 IPCC 2006 method

In this study, it was possible to estimate EF5 emission factors using the IPCC⁶ methodology. Unlike the N₂O-N/NO₃⁻-N ratio method, this approach requires more detailed flow, nutrient input and spatial information which were available here for all field drains and for stream site A (the outlet of mini-catchment A) (Table 2 and Figure 3). The total field drainage area in mini-catchment A was estimated to be 21.14 ha, whilst the stream surface water area was estimated to be 0.33 ha. Measured field drain flow rates during the study period ranged from 0.001 to 2.35 L s⁻¹ with an average for all drains of
0.14 L s⁻¹. Field drain flow rate was positively correlated ($r = 0.53$) with field drainage area. Measured stream flows at site A ranged from 2 to 271 L s⁻¹, with a mean flow rate of 25.4 L s⁻¹. Using these flow data, the calculated mean N₂O emission rate across all field drains during the study period was 0.05 kg N ha⁻¹ a⁻¹. In contrast, the mean N₂O emission rate for stream water in mini-catchment A was significantly ($p < 0.05$) higher, with a calculated rate of 5.75 kg N ha⁻¹ a⁻¹.

Total N input for mini-catchment A was calculated for the 2012–2013 and 2013–2014 farming years using available farm business data (Figure 3). The total N fertiliser applied across the whole of mini-catchment A was 67,985 kg N a⁻¹ in 2012–2013 and 61,106 kg N a⁻¹ in 2013–2014, thus giving an annual mean fertiliser application of 64,545 kg N. For the field drain area, the total applied N fertiliser was 2,659 kg N a⁻¹ for 2012–2013 and 3,080 kg N a⁻¹ for 2013–2014, giving a mean fertiliser application rate of 2,870 kg N a⁻¹ (Table 2).

For stream site A, a mean of 15,885 kg N a⁻¹ were lost during the two years through leaching from the total applied N of 64,545 kg N a⁻¹, giving a mean Frac_LEACH of 25%. For the field drains, Frac_LEACH was calculated separately for each drain from the N leached divided by the total N applied over a given field drain area, giving a mean estimated Frac_LEACH value for all drains of 34%. This mean Frac_LEACH value for the field drains is just above the default value given by the IPCC (2006) (30%). However, a wide uncertainty range (10–80%) is given by the IPCC and a similarly wide range of values (4–83%) was measured for the field drains sampled in this study. The mean Frac_LEACH value for the stream (25%) was lower than for the field drains, albeit not significantly ($p > 0.05$), which is potentially explained by dilution from groundwater with a lower NO₃ concentration (note - groundwater NO₃ was not analysed in the study).

Overall, an EF₅₉ of 0.0011 was calculated for the field drains using the IPCC (2006) methodology, whilst an EF₅₉ of 0.0001 was calculated for stream water at site A (Table 2). Both these estimates are substantially below the current IPCC default EF value of 0.0025.
### 3.4 Comparisons with previous studies

In addition to this study, a number of other studies have also observed lower $\text{N}_2\text{O}-\text{N}/\text{NO}_3\text{-N}$ ratios (EF$_{g}$) in both groundwater and river water than the IPCC (2006) default value (Table S3). An EF$_{g}$ value of 0.0019 was calculated for chalk groundwater in eastern England \(^{13}\), whilst a value of 0.0008 was calculated for field drain water on arable land in the upper Neckar region, Southern Germany \(^{10}\). Conversely, only a few studies have calculated EF$_{g}$ values higher than the current IPCC (2006) default value. A value of 0.0030 (range 0.00008–0.036) was derived for water samples collected from field drain outfalls in an intensively managed grazed pasture in the Ythan catchment, Aberdeenshire \(^{11}\), whilst a value of 0.0028 (0.0012–0.0069) was calculated for EF$_{r}$ in a study of the eutrophic San Joaquin River, California \(^{16}\).

According to current IPCC \(^{6}\) protocol, stream water (EF$_{r}$) and groundwater (EF$_{g}$) are assigned the same emission factor of 0.0025. However, it is clear from the data presented here that stream water had significantly ($p < 0.05$) lower EF values (mean = 0.0002) than field drains (mean = 0.0012). These low stream water EF$_{r}$ values reflect the low dissolved $\text{N}_2\text{O}$ concentrations recorded in streams and are likely a consequence of the rapid degassing of $\text{N}_2\text{O}$ from field drains upon contact with the atmosphere prior to reaching the stream. Different EF$_{r}$ emission factors for different water compartments within a single catchment have been reported previously \(^{7}\), and this highlights the need to distinguish EF$_{r}$ among different hydrological environments.

Critically examining the default Frac$_{\text{LEACH}}$ value, a review of six case studies in the Midwestern United States found that Frac$_{\text{LEACH}}$ values were typically ~20% (range = 3–70%) depending on inter-annual variability in rainfall \(^{27}\). One of the reasons that this comparatively low Frac$_{\text{LEACH}}$ value was obtained in all six of these case studies was that organic N was not considered as a component, even though it may constitute a significant fraction of the total leached N \(^{28}\). Consequently, this could lead to a substantial underestimate of the true amount of N leaching. The calculated Frac$_{\text{LEACH}}$ values in this study (which included both organic and inorganic N) of 34% and 25% for field drains and stream water, respectively, are similar to the modelling results for the UK as a whole in which Frac$_{\text{LEACH}}$ values of 16–24% were estimated for the Norfolk area \(^{29}\).
3.5 Comparison of emission factor methods

The results from this study show that both the EF$_5g$ and EF$_5r$ values were lower using the IPCC (2006) methodology than the N$_2$O-N/NO$_3$-N ratio approach (Table 2). The lower EF$_5g$ value calculated using the IPCC methodology was expected based on previous research which has shown that denitrification in near-surface groundwater can result in some of the leached NO$_3$ and N$_2$O being denitrified before groundwater is discharged into the stream.

Calculation of EF$_5g$ and EF$_5r$ values using the two different approaches clearly does not necessarily ensure the same result. Most studies calculate EF$_5g$ using the N$_2$O-N/NO$_3$-N ratio since detailed mass balance information is often lacking and few studies calculate EF$_5g$ using the IPCC (2006) approach even if they have detailed mass balance information available for a catchment. However, Outram and Hiscock (2012) calculated the EF$_5g$ for different water bodies using both approaches and found that values of EF$_5g$ calculated using the IPCC approach were very different from those calculated using the N$_2$O-N/NO$_3$-N ratio\textsuperscript{,7}. The EF$_5g$ calculated for drainage channels using the IPCC (2006) approach was found to be an order of magnitude higher than that obtained when using the N$_2$O-N/NO$_3$-N ratio, with values of 0.0530 and 0.0061, respectively\textsuperscript{,7}. Similarly, the EF$_5r$ calculated for the River Thurne using the IPCC (2006) approach was nine times higher than that calculated using the N$_2$O-N/NO$_3$-N ratio, with values of 0.0090 and 0.0011, respectively\textsuperscript{,7}. Therefore, to achieve an accurate result and avoid miscalculation from using different approaches, the IPCC (2006) may need to propose one comprehensive and consistent approach.

According to this study, regardless of the method used for calculation of EF$_5g$ and EF$_5r$, the default value set by IPCC\textsuperscript{,6} of 0.0025 appears to overestimate indirect N$_2$O emissions (Table 2). The default value is one order of magnitude higher than the EF$_5r$ for stream water calculated by either method, with a value of 0.0001 using the IPCC (2006) approach and 0.0003 using the N$_2$O-N/NO$_3$-N ratio. For the field drains, the default EF$_5g$ value is more than double that calculated using the IPCC (2006) approach (0.0011) and the N$_2$O-N/NO$_3$-N ratio (0.0012). Furthermore, the EF$_5$ values calculated using both the IPCC (2006) methodology and the N$_2$O-N/NO$_3$-N ratio revealed that emissions factors are not uniform for different water bodies. Hence, within a single catchment different water bodies can...
yield different amounts of N\textsubscript{2}O with unique emission factor values. Ideally, different water bodies
need to be separated when emission factors are calculated, unlike the current IPCC (2006) approach
which uses one EF value for all water bodies. If the EF\textsubscript{5} emission factor was to be revised by the
IPCC, regardless of soil type, crop type and land use practices, then a value of 0.0012 (about half of
the current value) for EF\textsubscript{2} and a value of 0.0002 (one order of magnitude lower than the current
value) for EF\textsubscript{r}, may be more reasonable estimates for the type of system studied here.

### 3.6 Implications of the measured EF values

The results of this study suggest that the indirect emissions component of the UK agricultural N\textsubscript{2}O
budget may be overestimated using the current default emission factor (EF\textsubscript{5}). Revision of this
emission factor in line with the findings presented here would result in a large reduction in the
estimated N\textsubscript{2}O emissions in both the UK and globally (Table 3). For the UK, the indirect N\textsubscript{2}O
emissions arising from N leaching and runoff from agroecosystems total \textasciitilde 14.3 Gg N a\textsuperscript{-1}, based on the
1997 guideline default EF\textsubscript{5} value of 0.025 \textsuperscript{31}. Using the revised IPCC \textsuperscript{6} EF\textsubscript{5} value of 0.0075, these
indirect emissions were reduced significantly to 6.71 Gg N\textsubscript{2}O-N a\textsuperscript{-1} \textsuperscript{32}. If the calculated value for EF\textsubscript{5}
of 0.0039 (the sum of all EF\textsubscript{2}, EF\textsubscript{r} and EF\textsubscript{5}) in this study is applied, these emissions would be
further reduced to 3.49 Gg N\textsubscript{2}O-N a\textsuperscript{-1} (Table 3).

Similarly, global estimates of indirect N\textsubscript{2}O emissions from leaching and runoff would be reduced by
using the emission factors calculated here. Initially, these emissions were estimated to be 1.90 Tg
N\textsubscript{2}O-N a\textsuperscript{-1} based on the default value for EF\textsubscript{5} of 0.025 reported by the IPCC in 1997. However, with a
revised default value of 0.0075, these estimates were substantially reduced to 0.60 Tg N\textsubscript{2}O-N a\textsuperscript{-1} in
2006 \textsuperscript{32}. Should the suggested emission factor from this study (0.0039) be applied to global indirect
N\textsubscript{2}O emissions, the estimates would be further reduced to 0.31 Tg N\textsubscript{2}O-N a\textsuperscript{-1}. This emphasises that
despite the revision of emission factors in 2006, the current IPCC inventory may still overestimate
actual N\textsubscript{2}O emissions. If the emission factors calculated in this study were to be applied, further
significant reductions in indirect N\textsubscript{2}O emissions similar to the level of reductions achieved in the 2006
revision, would again be observed. Several studies investigating emission factors and indirect N\textsubscript{2}O
emissions from leaching and runoff have been carried out since 2006 which suggest lowering of the
EF\textsubscript{3} value. Updating the IPCC guidelines and indirect N\textsubscript{2}O emission factor estimates to reflect these new findings is recommended.

**Supporting Information**

The supporting information contains additional details on the analytical methods, a location map and photographs of the study site, summary tables of field drain and stream water data, and a review table of previously published N\textsubscript{2}O emission factor values.

**Author Information**

*Corresponding Author: Richard J. Cooper; Richard.J.Cooper@uea.ac.uk; +44(0)1603592922;
School of Environmental Sciences, University of East Anglia, Norwich Research Park, Norwich NR4 7TJ, UK

**Acknowledgements**

This research was funded by the Defra Agricultural Greenhouse Gas Platform (project AC0116) and Iraqi Kurdistan Regional Government. The authors would like to thank: Gilla Sünnenberg for GIS mapping; Jenny Stevenson, Christopher Adams, Faye Outram, Simon Ellis, Nick Garrard, Steve Warnes and Steve Dugdale for fieldwork support; Ayan Fleischmann and Lucas Favero for mapping and calculating field drain areas; and Liz Rix, Alina Mihailova, Kim Goodey, Tony Hinchliffe and Andy Hind for laboratory analytical support. The authors would like to thank the Salle Park Estate for their cooperation in providing access to the field sites.

**References**


(6) De Klein, C.; et al. N₂O emissions from managed soils, and CO₂ emissions from lime and urea application. In *IPCC guidelines for national greenhouse gas inventories*; Eggelston, S., Buendia, L., Miwa, K., Ngara, T., Tanabe, K., Eds.; Intergovernmental Panel for Climate Change (IPCC), UN and WMO 2006; p 54.


(33) National Atmospheric Emissions Inventory Website: [http://naei.defra.gov.uk/](http://naei.defra.gov.uk/).
Tables

Table 1: Summary of the field drain and stream water NO$_3$ and N$_2$O concentration data differentiated by season for the period April 2013 to April 2015. Different superscript letters reflect significant differences (t-test $p < 0.05$) between seasons of the same sample type. Different subscript letters reflect significant differences between different sample types.

<table>
<thead>
<tr>
<th>Sample type</th>
<th>Season</th>
<th>Mean NO$_3$ (mg L$^{-1}$) ± SD</th>
<th>Mean N$_2$O (µg L$^{-1}$) ± SD</th>
<th>Mean N$_2$O-N/NO$_3$-N Ratio ± SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Field drain</td>
<td>Overall (n = 621)</td>
<td>6.08 ± 4.78$^a$</td>
<td>4.49 ± 4.46$^a$</td>
<td>0.00120 ± 0.00134$^a$</td>
</tr>
<tr>
<td></td>
<td>Spring (n = 187)</td>
<td>5.98 ± 4.64$^a$</td>
<td>4.95 ± 4.86$^a$</td>
<td>0.00123 ± 0.00143$^a$</td>
</tr>
<tr>
<td></td>
<td>Summer (n = 62)</td>
<td>4.17 ± 4.30$^b$</td>
<td>3.20 ± 4.69$^b$</td>
<td>0.00135 ± 0.00158$^a$</td>
</tr>
<tr>
<td></td>
<td>Autumn (n = 153)</td>
<td>6.42 ± 5.16$^a$</td>
<td>4.12 ± 4.73$^a$</td>
<td>0.00113 ± 0.00137$^a$</td>
</tr>
<tr>
<td></td>
<td>Winter (n = 219)</td>
<td>6.47 ± 4.65$^a$</td>
<td>4.71 ± 3.72$^a$</td>
<td>0.00117 ± 0.00116$^a$</td>
</tr>
<tr>
<td>Stream</td>
<td>Overall (n = 308)</td>
<td>6.70 ± 3.20$^b$</td>
<td>1.43 ± 0.84$^b$</td>
<td>0.00029 ± 0.00030$^b$</td>
</tr>
<tr>
<td></td>
<td>Spring (n = 80)</td>
<td>6.61 ± 1.92$^a$</td>
<td>1.30 ± 0.47$^a$</td>
<td>0.00021 ± 0.00008$^a$</td>
</tr>
<tr>
<td></td>
<td>Summer (n = 64)</td>
<td>4.49 ± 2.79$^b$</td>
<td>1.02 ± 0.51$^b$</td>
<td>0.00039 ± 0.00038$^b$</td>
</tr>
<tr>
<td></td>
<td>Autumn (n = 92)</td>
<td>7.05 ± 4.29$^a$</td>
<td>1.82 ± 1.24$^a$</td>
<td>0.00039 ± 0.00041$^b$</td>
</tr>
<tr>
<td></td>
<td>Winter (n = 72)</td>
<td>8.30 ± 1.55$^c$</td>
<td>1.42 ± 0.47$^a$</td>
<td>0.00018 ± 0.00007$^c$</td>
</tr>
</tbody>
</table>

Table 2: Emission factors EF$_{5g}$ and EF$_{5r}$ calculated for field drains and stream water using two different methods, the default IPCC (2006) emission factors (EF$_{5}$), and the proposed EF$_{5g}$, EF$_{5r}$ from this study. Values presented as the mean ± 1 standard deviation.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Units/methodology</th>
<th>Field drains (All)</th>
<th>Stream water (Site A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total area</td>
<td>ha</td>
<td>21.09</td>
<td>0.33</td>
</tr>
<tr>
<td>Indirect N$_2$O emissions</td>
<td>kg N$_2$O-N ha$^{-1}$ a$^{-1}$</td>
<td>0.05 ± 0.10</td>
<td>5.75 ± 6.42</td>
</tr>
<tr>
<td>Mean total indirect N$_2$O emissions</td>
<td>kg N$_2$O-N a$^{-1}$</td>
<td>1.04 ± 2.13</td>
<td>1.90 ± 2.12</td>
</tr>
<tr>
<td>Total N input</td>
<td>kg N a$^{-1}$</td>
<td>2.870</td>
<td>64.545</td>
</tr>
<tr>
<td>FracLEACH</td>
<td>%</td>
<td>34 ± 29</td>
<td>25 ± 27</td>
</tr>
<tr>
<td>EF$<em>{5g}$, EF$</em>{5r}$</td>
<td>IPCC 6 method</td>
<td>0.0011 ± 0.0022</td>
<td>0.0001 ± 0.0001</td>
</tr>
<tr>
<td>EF$<em>{5g}$, EF$</em>{5r}$</td>
<td>N$_2$O-N/NO$_3$-N method</td>
<td>0.0012 ± 0.0013</td>
<td>0.0003 ± 0.0003</td>
</tr>
<tr>
<td>EF$<em>{5g}$, EF$</em>{5r}$</td>
<td>IPCC (2006) default</td>
<td>0.0025</td>
<td>0.0025</td>
</tr>
<tr>
<td>Proposed EF$<em>{5g}$, EF$</em>{5r}$</td>
<td>This study</td>
<td>0.0012</td>
<td>0.0002</td>
</tr>
</tbody>
</table>
Table 3: Summary of current and previous IPCC (2006) default emission factors for indirect N leaching from agriculture, calculated emission factors from this study and implications for indirect N₂O emission estimates from the UK and globally

<table>
<thead>
<tr>
<th></th>
<th>IPCC 1997</th>
<th>IPCC 2006</th>
<th>This study</th>
</tr>
</thead>
<tbody>
<tr>
<td>EF₅g</td>
<td>0.015</td>
<td>0.0025</td>
<td>0.0012</td>
</tr>
<tr>
<td>EF₅r</td>
<td>0.0075</td>
<td>0.0025</td>
<td>0.0002</td>
</tr>
<tr>
<td>EF₅e</td>
<td>0.0025</td>
<td>0.0025</td>
<td>0.0025ᵇ</td>
</tr>
<tr>
<td>EF₅ᵃ</td>
<td>0.025</td>
<td>0.0075</td>
<td>0.0039</td>
</tr>
<tr>
<td>Indirect UK N₂O emissions (Gg N a⁻¹) from N leaching and runoff</td>
<td>14.30ᶜ</td>
<td>6.71ᵈ</td>
<td>3.49</td>
</tr>
<tr>
<td>Indirect global N₂O emissions (Tg N a⁻¹) from N leaching and runoff</td>
<td>1.90ᵉ</td>
<td>0.60ᵉ</td>
<td>0.31</td>
</tr>
</tbody>
</table>

ᵃEF₅ is the sum of EF₅g+EF₅r+EF₅e.
ᵇNot studied here. Assumed unchanged.
ᶜFrom Reay et al. ³¹.
ᵈTotal UK N₂O emissions are 59 Gg N a⁻¹ for 2013 according to the National Atmospheric Emissions Inventory ³³, and from this amount, indirect emissions account for 24%, with 46% associated with N leaching and runoff ³².
ᵉFrom Syakila and Kroeze ³².
Figure Captions

Figure 1: Relationship between N₂O-N and NO₃-N in field drain \((n = 621)\) and stream water \((n = 308)\) samples collected during April 2013–April 2015. 90% of drain samples and 100% of stream water samples had lower N₂O-N/NO₃-N ratios than the IPCC (2006) default value of 0.0025.

Figure 2: Temporal variability in the mean N₂O-N/NO₃-N ratio for field drain and stream water samples collected during April 2013–April 2015. Error bars represent one standard error.

Figure 3: Input of nitrogen fertiliser (kg N ha⁻¹) across mini-catchment A for the (a) 2012–2013 and (b) 2013–2014 farming years.
Figure 1: Relationship between N2O-N and NO3-N in field drain (n = 621) and stream water (n = 308) samples collected during April 2013–April 2015. 90% of drain samples and 100% of stream water samples had lower N2O-N/NO3-N ratios than the IPCC (2006) default value of 0.0025.
Figure 2 Temporal variability in the mean N2O-N/NO3-N ratio for field drain and stream water samples collected during April 2013–April 2015. Error bars represent one standard error.
Figure 3: Input of nitrogen fertiliser (kg N ha$^{-1}$) across mini-catchment A for the (a) 2012–2013 and (b) 2013–2014 farming years.