

1 Indirect nitrous oxide emission factors for agricultural field drains and 2 headwater streams

3

4 Zanist Q. Hama-Aziz¹, Kevin M. Hiscock¹, Richard J. Cooper^{1*}

5 ¹School of Environmental Sciences, University of East Anglia, Norwich Research Park, Norwich NR4
6 7TJ, UK

7

8 ABSTRACT

9 Agriculture is a major source of nitrous oxide (N₂O) emissions, a potent greenhouse gas. Whilst direct
10 N₂O emissions from soils have been widely investigated, indirect N₂O emissions from nitrogen (N)
11 enriched surface water and groundwater bodies are poorly understood. In this contribution, indirect
12 N₂O emissions from subsurface agricultural field drains and headwater streams were monitored over a
13 two-year period (2013–2015) in an intensive arable catchment in eastern England. Indirect N₂O
14 emission factors for groundwater (EF_{5g}) and surface runoff (EF_{5r}) were calculated for both field drain
15 and stream water samples, respectively, using two approaches: the N₂O-N/NO₃⁻-N ratio and the IPCC
16 (2006) methodology. Mean EF_{5g} values derived from the N₂O-N/NO₃⁻-N ratio were 0.0012 for field
17 drains and 0.0003 for stream water. Using the IPCC (2006) methodology, the mean EF_{5g} values were
18 0.0011 for field drains and 0.0001 for stream water. Thus, EF values derived from both methods were
19 below the current IPCC (2006) default value of 0.0025 and a downward revision to 0.0012 for EF_{5g}
20 and 0.0002 for EF_{5r} is recommended. Such revision would halve current estimates of N₂O emissions
21 associated with nitrogen leaching and runoff from agriculture for both the UK and globally.

22

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

24

25 1. Introduction

26 Nitrous oxide (N₂O) is a potent greenhouse gas with a present atmospheric concentration of 326.7 ppb
27 ¹. Not only does N₂O have a global warming potential 300 times that of CO₂ ², it also participates in
28 photochemical reactions in the stratosphere which lead to the destruction of ozone (O₃) ³. The
29 concentration of N₂O in the atmosphere is currently increasing at an annual rate of ~0.26% ⁴ and
30 agriculture is considered to be the largest source (~60%) of anthropogenic N₂O emissions ⁵. The
31 Intergovernmental Panel on Climate Change (IPCC) ⁶ has developed protocols for quantifying and
32 generating national inventories of N₂O emissions from industry, agriculture and natural ecosystems,
33 with total N₂O emissions from agriculture being categorised into direct and indirect sources. Whilst
34 direct N₂O emissions as a result of nitrogen (N) application to soils have been widely investigated,
35 indirect emissions produced in surface waters and groundwaters from agricultural N leaching and
36 runoff have, to date, been less well studied ⁷.

37 Indirect N₂O emission factors (EF₅) are a way of representing N₂O emissions from a water body as a
38 fraction of the original N flux into the system ⁸. The IPCC ⁶ defined N₂O emission factors for N
39 leaching and runoff from managed soils as follows (Equation 1):

40 (1)

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

41 where, EF_5 is the N₂O emission factor (kg N₂O–N/kg N) with a default value of 0.0075 (range =
42 0.0005–0.025); $N_2O_{(L)-N}$ is the emission of N₂O produced by the leaching and runoff of N additions
43 to managed soils (kg N₂O–N a⁻¹); $Total\ N\ input$ is the total annual amount of N added to the system,
44 including synthetic fertilisers and animal manure, that is lost through leaching and runoff (kg N a⁻¹);
45 and $Frac_{LEACH}$ is the fraction of all N added to, or mineralised within, managed soils that is lost
46 through leaching and runoff (kg N/kg of N additions a⁻¹), with a default value of 30% (range = 10–
47 80%).

48 Indirect N₂O emissions can either be calculated by using the default values of EF_5 and $Frac_{LEACH}$ in
49 Equation 1, or by measuring indirect N₂O emissions from dissolved N₂O concentrations and then

50 using this equation to calculate EF_5 . The IPCC ⁶ revised the default emission factor for indirect N_2O
51 emissions (EF_5) from 0.025 kg N_2O -N/kg N in 1997 to 0.0075 kg N_2O -N/kg N in 2006. The EF_5 was
52 further divided into three components according to the site of N_2O production: EF_{5g} for groundwater
53 and surface drainage (0.0025); EF_{5r} for rivers (0.0025); and EF_{5e} for estuaries (0.0025), thus giving an
54 overall EF_5 of 0.0075. EF_5 has a wide range of uncertainty (0.0005–0.025) as a result of natural
55 variability and a lack of data to support designation. However, as many studies are often lacking the
56 detailed mass balance information needed to determine EF_5 and evaluate national N_2O inventories by
57 the IPCC (2006) methodology, EF_5 values are commonly calculated by using a N_2O -N/ NO_3^- -N mass
58 ratio derived using the concentration data of N_2O and nitrate (NO_3) collected from the water body.
59 Therefore, most studies on emission factors from leaching and runoff calculate EF_5 by the following
60 method^{7, 9, 10-17} (Equation 2):

61 (2)

$$EF_5 = \frac{N_2O-N}{NO_3-N}$$

62 where N_2O -N and NO_3 -N are concentrations measured in groundwater, rivers or estuaries.

63 The objectives of this study are as follows:

- 64 i. To calculate indirect N_2O emission factors for subsurface agricultural field drains (EF_{5g}) and
65 headwater streams (EF_{5r}) in an intensive arable catchment;
- 66 ii. To assess the extent of temporal variability in indirect N_2O emission factors;
- 67 iii. To compare emission factors derived from the two different methods with the IPCC (2006)
68 default EF_{5g} and EF_{5r} values of 0.0025 and assess whether these general emission factors are
69 appropriate for predicting N_2O emissions in a temperate, lowland arable environment.

70 The findings of this study should provide useful information for updating indirect N_2O emission
71 factors used in future IPCC assessment reports.

72

73 2. Materials and Methods

74 2.1 Study location

75 The study area is in the Blackwater sub-catchment of the River Wensum, Norfolk, UK (Figures S1–
76 S5). The Blackwater sub-catchment is intensively monitored as part of the Wensum Demonstration
77 Test Catchment (DTC) project which aims to evaluate the extent to which on-farm mitigation
78 measures can cost-effectively reduce the impact of diffuse agricultural pollution on aquatic ecology
79 whilst still maintaining food production capacity¹⁸. The area is under intensive arable cultivation with
80 spring and winter barley, winter wheat, winter oilseed rape, spring beans and sugar beet grown in a
81 seven-year rotation. The average annual rainfall total is 674 mm and the mean annual temperature is
82 10.1°C¹⁹. The western section of the Blackwater sub-catchment, hereafter termed “mini-catchment A”
83 (5.4 km²), is extensively under-drained by a dense network of agricultural tile drainage installed at a
84 depth of 100–160 cm below the ground surface. Discharge from drains can be as high as 10 L s⁻¹, but
85 varies greatly depending upon season, depth, catchment area and antecedent moisture conditions, with
86 most drains drying up completely during the summer months. The geology of the catchment is
87 comprised of Middle Pleistocene glacial deposits (0.5–20 m depth) overlying Cretaceous White Chalk
88 (>20 m depth), with surface soils varying from sandy loam to sandy clay loam and clay loam.

89 2.2 Sample collection

90 Over a two-year period (April 2013 to April 2015), a total of 929 water samples were collected from
91 13 field drains ($n = 621$) and four stream locations (sites A, B, E and M; $n = 308$) for N₂O and nutrient
92 analysis (Figure S1). Samples were collected at weekly intervals, with the exception of April–
93 September 2014 when field drains were sampled fortnightly and stream waters monthly. For dissolved
94 N₂O concentrations, samples were collected at field drain outlet pipes and from stream waters using
95 20 mL glass syringes (SAMCO) with a three-way stopcock attached to each syringe by a Luer-Lock
96 fitting. Syringes were flushed three times with water from the sampling point and any air bubbles
97 contained in the syringes were expelled before the final sample was taken. A single sample was taken
98 at each location and no preservative was added. Samples in syringes were returned to cold storage at

99 4°C within 3 h and analysed for N₂O within 72 h of collection. For the nutrient analysis, water
100 samples were collected in 1L plastic bottles and were also analysed within 72 h of collection. Field
101 drain flow was estimated in triplicate on each sampling occasion. Stream stage was measured at each
102 of the four stream sampling sites using a pressure transducer and converted into flow using a stage-
103 discharge rating curve. Maps of the field drain network were provided by the local farmer and the
104 drainage area of each drain was estimated by polygon digitising using GIS (Figure S1). Wind speed
105 data required for calculating N₂O emissions from streams were obtained from a weather station
106 installed in mini-catchment A.

107 **2.3 Sample analysis**

108 Dissolved N₂O was analysed by gas chromatography with an electron capture detector (GC-ECD).
109 Accuracy of N₂O measurements was within ±3% with a detection limit of ~0.0008 µg N L⁻¹. Nitrate
110 was determined by ion chromatography using a Dionex ISC 2000 with an accuracy of 0.19 mg N L⁻¹.
111 Ammonium (NH₄) and nitrite (NO₂) were determined by a Continuous Flow Analyser - Skalar San++
112 with accuracies of 4.57 µg N L⁻¹ and 1.52 µg N L⁻¹, respectively. Total organic nitrogen was measured
113 with a Skalar Formacs TOC/TN analyser with an accuracy of 0.08 mg N L⁻¹. Further details are
114 provided in the supporting information.

115 **2.4 Emission factors and flux calculations**

116 Fluxes of N₂O from field drains into the atmosphere were calculated based on the assumption that all
117 of the dissolved N₂O at concentrations above that of air saturation is subsequently lost to the
118 atmosphere^{10, 20-22}. Thus, the air saturation concentration of N₂O (0.36 µg N L⁻¹), calculated using
119 equilibrium equations²³, was subtracted from the measured dissolved N₂O concentration, then
120 multiplied by flow rate and divided by drain area to obtain the N₂O emission rates. Note, however,
121 that because field drain samples were taken at the drain outlets, there may be losses of N₂O from the
122 drains prior to reaching the sampling point and thus estimates of N₂O emissions could be
123 underestimated in this study. N₂O emission rates from stream water were calculated using the water-
124 air gas exchange Equation (3)⁷, as follows:

125 (3)

$$126 \quad F = kC_w - \frac{C_a}{k_h}$$

127 where F is the flux (or emission) of gas ($\text{mol cm}^{-2} \text{h}^{-1}$); k is the transfer velocity of N_2O across the
128 water-air interface (cm h^{-1}); C_w is the concentration of N_2O in water (mol cm^{-3}); C_a is the
129 concentration of N_2O in air (mol cm^{-3}); and k_h is the Henry's law constant for N_2O which is
130 dimensionless and obtained from literature as 1.02²⁴. k was calculated using a combined gas transfer
131 velocity approach that incorporates both wind and water turbulence²⁵. The water turbulence
132 component was calculated as follows (Equation 4):

133 (4)

$$134 \quad k_{\text{water}} = \mathbf{J} \frac{DV}{h}$$

135 where D is the N_2O diffusion coefficient ($\text{m}^2 \text{s}^{-1}$), V is the stream water velocity (m s^{-1}) and h is the
136 stream water depth (m). The wind component was calculated as follows (Equation 5):

137 (5)

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

138 where u is the wind speed (cm h^{-1}) and Sc is the Schmidt number for N_2O . The wind and water
139 components were then added together to form the combined gas transfer velocity, k .

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

144

145 **3. Results and Discussion**

146 **3.1 Concentration data**

147 Field drain and stream water NO_3 and N_2O concentrations for the period April 2013 to April 2015 are
148 presented in Figure 1 and summarised in Table 1. The mean N_2O concentration recorded across all
149 field drains ($4.49 \mu\text{g L}^{-1}$) was significantly ($p < 0.05$) greater than that recorded for the streams (1.43
150 $\mu\text{g L}^{-1}$), which reflects the rapid degassing of N_2O from field drain water upon contact with the
151 atmosphere prior to reaching the stream. Conversely, the mean NO_3 concentration recorded in field
152 drains (6.08 mg L^{-1}) was significantly lower ($p < 0.05$) than that recorded in stream water (6.70 mg L^{-1}).
153 In both field drains and streams, the mean NO_3 (4.17 and 4.49 mg L^{-1} , respectively) and N_2O (3.20
154 and $1.02 \mu\text{g L}^{-1}$, respectively) concentrations were significantly ($p < 0.05$) lower during the summer
155 (JJA) than any other season. The highest mean NO_3 concentrations in field drains (6.47 mg L^{-1}) and
156 streams (8.30 mg L^{-1}) occurred during the winter, whereas the highest mean N_2O concentrations in
157 field drains occurred during the spring ($4.95 \mu\text{g L}^{-1}$) and in streams during the autumn ($1.82 \mu\text{g L}^{-1}$).

158 In stream water, N_2O and NO_3 concentrations exhibited a relatively strong positive correlation ($r =$
159 0.55) indicating that NO_3 is an important driver of riverine N_2O production in this catchment (Figure
160 1). However, in field drains the correlation between N_2O and NO_3 was much weaker ($r = 0.19$),
161 implying a greater role from other biotic and abiotic factors in the production of N_2O in soils. In
162 contrast to previous studies²⁶, there was no strong correlation between stream water N_2O and either
163 dissolved oxygen concentration ($r = 0.19$) or water temperature ($r = 0.05$),

164

165 **3.2 $\text{N}_2\text{O-N}/\text{NO}_3\text{-N}$ ratio method**

166 The $\text{EF}_{5\text{g}}$ emission factor (ratio of $\text{N}_2\text{O-N}$ to $\text{NO}_3\text{-N}$) in field drain samples varied between 0.00003
167 and 0.01063 , with a mean value of 0.00120 . The $\text{EF}_{5\text{r}}$ emission factor for stream water samples ranged
168 from 0.00006 to 0.00282 , with a mean value of 0.00029 (Table 1). Thus, the $\text{EF}_{5\text{g}}$ emission factors for
169 90% of field drain samples collected in this study were lower than the IPCC default value of 0.0025 ⁶,
170 whilst ~15% of collected samples were one order of magnitude lower. Similarly, 100% of the stream

171 samples (EF_{5r}) had emission factors lower than the IPCC default. These results indicate that the
172 previously downward revised IPCC (2006) default value of 0.0025 may still be overestimating
173 indirect N_2O emissions in agricultural systems similar to that studied here.

174 As illustrated in Figure 1, the N_2O-N/NO_3^-N ratios varied substantially across field drain and stream
175 water samples. In this study, temporal variability in these ratios was monitored over the two-year
176 sampling period (Figure 2). The mean N_2O-N/NO_3^-N ratio of the stream water samples was
177 significantly lower ($p < 0.05$) than that for the field drains throughout the entire study period,
178 amounting to approximately one order of magnitude difference (Table 1). For both field drains and
179 stream samples, EF ratios were observed to increase during the summer months (JJA) before returning
180 to relatively stable levels in mid-autumn (October). The mean summer EF_{5r} for the stream sites
181 (0.00039) was significantly ($p < 0.05$) higher than that recorded in winter or spring, although it was
182 the same as that recorded during the autumn (Table 1). In the field drains, the mean summer EF_{5g}
183 (0.00135) was higher than any other season, although wide variability meant this difference was not
184 significant ($p > 0.05$). This trend was repeated in both sampling years and appears to be due to the
185 substantial decrease in NO_3^- concentrations during the summer as a result of a decline in water flow
186 and a decline in potentially leachable NO_3^- due to nutrient uptake by crops during this period. This
187 summer period of high EF ratios represents ~10% of collected samples shown in Figure 2. It is clear
188 from the data presented here that EF values varied over time and it may be more appropriate to have
189 different EF values for different seasons rather than one EF value throughout the year, as is suggested
190 by the IPCC⁶.

191 **3.3 IPCC 2006 method**

192 In this study, it was possible to estimate EF_5 emission factors using the IPCC⁶ methodology. Unlike
193 the N_2O-N/NO_3^-N ratio method, this approach requires more detailed flow, nutrient input and spatial
194 information which were available here for all field drains and for stream site A (the outlet of mini-
195 catchment A) (Table 2 and Figure 3). The total field drainage area in mini-catchment A was estimated
196 to be 21.14 ha, whilst the stream surface water area was estimated to be 0.33 ha. Measured field drain
197 flow rates during the study period ranged from 0.001 to 2.35 $L s^{-1}$ with an average for all drains of

198 0.14 L s⁻¹. Field drain flow rate was positively correlated ($r = 0.53$) with field drainage area. Measured
199 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
200 flow data, the calculated mean N₂O emission rate across all field drains during the study period was
201 0.05 kg N ha⁻¹ a⁻¹. In contrast, the mean N₂O emission rate for stream water in mini-catchment A was
202 significantly ($p < 0.05$) higher, with a calculated rate of 5.75 kg N ha⁻¹ a⁻¹.

203 Total N input for mini-catchment A was calculated for the 2012–2013 and 2013–2014 farming years
204 using available farm business data (Figure 3). The total N fertiliser applied across the whole of mini-
205 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
206 annual mean fertiliser application of 64,545 kg N. For the field drain area, the total applied N fertiliser
207 was 2,659 kg N a⁻¹ for 2012–2013 and 3,080 kg N a⁻¹ for 2013–2014, giving a mean fertiliser
208 application rate of 2,870 kg N a⁻¹ (Table 2).

209 For stream site A, a mean of 15,885 kg N a⁻¹ were lost during the two years through leaching from the
210 total applied N of 64,545 kg N a⁻¹, giving a mean $\text{Frac}_{\text{LEACH}}$ of 25%. For the field drains, $\text{Frac}_{\text{LEACH}}$
211 was calculated separately for each drain from the N leached divided by the total N applied over a
212 given field drain area, giving a mean estimated $\text{Frac}_{\text{LEACH}}$ value for all drains of 34%. This mean
213 $\text{Frac}_{\text{LEACH}}$ value for the field drains is just above the default value given by the IPCC (2006) (30%).
214 However, a wide uncertainty range (10–80%) is given by the IPCC⁶ and a similarly wide range of
215 values (4–83%) was measured for the field drains sampled in this study. The mean $\text{Frac}_{\text{LEACH}}$ value for
216 the stream (25%) was lower than for the field drains, albeit not significantly ($p > 0.05$), which is
217 potentially explained by dilution from groundwater with a lower NO₃ concentration (note -
218 groundwater NO₃ was not analysed in the study).

219 Overall, an EF_{5g} of 0.0011 was calculated for the field drains using the IPCC (2006) methodology,
220 whilst an EF_{5r} of 0.0001 was calculated for stream water at site A (Table 2). Both these estimates are
221 substantially below the current IPCC default EF value of 0.0025.

222 3.4 Comparisons with previous studies

223 In addition to this study, a number of other studies have also observed lower $\text{N}_2\text{O-N}/\text{NO}_3^-\text{-N}$ ratios
224 ($\text{EF}_{5\text{g}}$) in both groundwater and river water than the IPCC (2006) default value (Table S3). An $\text{EF}_{5\text{g}}$
225 value of 0.0019 was calculated for chalk groundwater in eastern England ¹³, whilst a value of 0.0008
226 was calculated for field drain water on arable land in the upper Neckar region, Southern Germany ¹⁰.
227 Conversely, only a few studies have calculated $\text{EF}_{5\text{g}}$ values higher than the current IPCC (2006)
228 default value. A value of 0.0030 (range 0.00008-0.036) was derived for water samples collected from
229 field drain outfalls in an intensively managed grazed pasture in the Ythan catchment, Aberdeenshire
230 ¹¹, whilst a value of 0.0028 (0.0012–0.0069) was calculated for $\text{EF}_{5\text{r}}$ in a study of the eutrophic San
231 Joaquin River, California ¹⁶.

232 According to current IPCC ⁶ protocol, stream water ($\text{EF}_{5\text{r}}$) and groundwater ($\text{EF}_{5\text{g}}$) are assigned the
233 same emission factor of 0.0025. However, it is clear from the data presented here that stream water
234 had significantly ($p < 0.05$) lower EF values (mean = 0.0002) than field drains (mean = 0.0012).
235 These low stream water $\text{EF}_{5\text{r}}$ values reflect the low dissolved N_2O concentrations recorded in streams
236 and are likely a consequence of the rapid degassing of N_2O from field drains upon contact with the
237 atmosphere prior to reaching the stream. Different EF_5 emission factors for different water
238 compartments within a single catchment have been reported previously ⁷, and this highlights the need
239 to distinguish EF_5 among different hydrological environments.

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

249 3.5 Comparison of emission factor methods

250 The results from this study show that both the EF_{5g} and EF_{5r} values were lower using the IPCC (2006)
251 ⁶ methodology than the N_2O-N/NO_3^-N ratio approach (Table 2). The lower EF_{5g} value calculated
252 using the IPCC methodology was expected based on previous research ³⁰ which has shown that
253 denitrification in near-surface groundwater can result in some of the leached NO_3 and N_2O being
254 denitrified before groundwater is discharged into the stream.

255 Calculation of EF_{5g} and EF_{5r} values using the two different approaches clearly does not necessarily
256 ensure the same result. Most studies calculate EF_{5g} using the N_2O-N/NO_3^-N ratio since detailed mass
257 balance information is often lacking and few studies calculate EF_{5g} using the IPCC (2006) approach
258 even if they have detailed mass balance information available for a catchment. However, Outram and
259 Hiscock (2012) calculated the EF_{5g} for different water bodies using both approaches and found that
260 values of EF_{5g} calculated using the IPCC approach were very different from those calculated using the
261 N_2O-N/NO_3^-N ratio ⁷. The EF_{5g} calculated for drainage channels using the IPCC (2006) approach was
262 found to be an order of magnitude higher than that obtained when using the N_2O-N/NO_3^-N ratio, with
263 values of 0.0530 and 0.0061, respectively ⁷. Similarly, the EF_{5r} calculated for the River Thurne using
264 the IPCC (2006) approach was nine times higher than that calculated using the N_2O-N/NO_3^-N ratio,
265 with values of 0.0090 and 0.0011, respectively ⁷. Therefore, to achieve an accurate result and avoid
266 miscalculation from using different approaches, the IPCC (2006) may need to propose one
267 comprehensive and consistent approach.

268 According to this study, regardless of the method used for calculation of EF_{5g} and EF_{5r} , the default
269 value set by IPCC ⁶ of 0.0025 appears to overestimate indirect N_2O emissions (Table 2). The default
270 value is one order of magnitude higher than the EF_{5r} for stream water calculated by either method,
271 with a value of 0.0001 using the IPCC (2006) approach and 0.0003 using the N_2O-N/NO_3^-N ratio. For
272 the field drains, the default EF_{5g} value is more than double that calculated using the IPCC (2006)
273 approach (0.0011) and the N_2O-N/NO_3^-N ratio (0.0012). Furthermore, the EF_5 values calculated using
274 both the IPCC (2006) methodology and the N_2O-N/NO_3^-N ratio revealed that emissions factors are
275 not uniform for different water bodies. Hence, within a single catchment different water bodies can

276 yield different amounts of N₂O with unique emission factor values. Ideally, different water bodies
277 need to be separated when emission factors are calculated, unlike the current IPCC (2006) approach
278 which uses one EF value for all water bodies. If the EF₅ emission factor was to be revised by the
279 IPCC, regardless of soil type, crop type and land use practices, then a value of 0.0012 (about half of
280 the current value) for EF_{5g} and a value of 0.0002 (one order of magnitude lower than the current
281 value) for EF_{5r} may be more reasonable estimates for the type of system studied here.

282 3.6 Implications of the measured EF values

283 The results of this study suggest that the indirect emissions component of the UK agricultural N₂O
284 budget may be overestimated using the current default emission factor (EF₅). Revision of this
285 emission factor in line with the findings presented here would result in a large reduction in the
286 estimated N₂O emissions in both the UK and globally (Table 3). For the UK, the indirect N₂O
287 emissions arising from N leaching and runoff from agroecosystems total ~14.3 Gg N a⁻¹, based on the
288 1997 guideline default EF₅ value of 0.025³¹. Using the revised IPCC⁶ EF₅ value of 0.0075, these
289 indirect emissions were reduced significantly to 6.71 Gg N₂O-N a⁻¹³². If the calculated value for EF₅
290 of 0.0039 (the sum of all EF_{5g}, EF_{5r} and EF_{5e}) in this study is applied, these emissions would be
291 further reduced to 3.49 Gg N₂O-N a⁻¹ (Table 3).

292 Similarly, global estimates of indirect N₂O emissions from leaching and runoff would be reduced by
293 using the emission factors calculated here. Initially, these emissions were estimated to be 1.90 Tg
294 N₂O-N a⁻¹ based on the default value for EF₅ of 0.025 reported by the IPCC in 1997. However, with a
295 revised default value of 0.0075, these estimates were substantially reduced to 0.60 Tg N₂O-N a⁻¹ in
296 2006³². Should the suggested emission factor from this study (0.0039) be applied to global indirect
297 N₂O emissions, the estimates would be further reduced to 0.31 Tg N₂O-N a⁻¹. This emphasises that
298 despite the revision of emission factors in 2006, the current IPCC inventory may still overestimate
299 actual N₂O emissions. If the emission factors calculated in this study were to be applied, further
300 significant reductions in indirect N₂O emissions similar to the level of reductions achieved in the 2006
301 revision, would again be observed. Several studies investigating emission factors and indirect N₂O
302 emissions from leaching and runoff have been carried out since 2006 which suggest lowering of the

303 EF₅ value. Updating the IPCC guidelines and indirect N₂O emission factor estimates to reflect these
304 new findings is recommended.

305 **Supporting Information**

306 The supporting information contains additional details on the analytical methods, a location map and
307 photographs of the study site, summary tables of field drain and stream water data, and a review table
308 of previously published N₂O emission factor values.

309 **Author Information**

310 *Corresponding Author: Richard J. Cooper; Richard.J.Cooper@uea.ac.uk; +44(0)1603592922;
311 School of Environmental Sciences, University of East Anglia, Norwich Research Park, Norwich NR4
312 7TJ, UK

313

314 **Acknowledgements**

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

322 **References**

- 323 (1) European Environment Agency; Atmospheric concentration of carbon dioxide, methane and
324 nitrous oxide. [http://www.eea.europa.eu/data-and-maps/daviz/atmospheric-concentration-of-carbon-](http://www.eea.europa.eu/data-and-maps/daviz/atmospheric-concentration-of-carbon-dioxide-2#tab-chart_4)
325 [dioxide-2#tab-chart_4](http://www.eea.europa.eu/data-and-maps/daviz/atmospheric-concentration-of-carbon-dioxide-2#tab-chart_4).
- 326 (2) Omonode, R. A.; Smith, D. R.; Gál, A.; Vyn, T. J. Soil nitrous oxide emissions in corn following
327 three decades of tillage and rotation treatments. *Soil Science Society of America Journal* **2011**, *75*, (1),
328 152-163.

- 329 (3) Jacinthe, P.-A.; Dick, W. A. Soil management and nitrous oxide emissions from cultivated fields
330 in southern Ohio. *Soil and Tillage Research* **1997**, *41*, (3–4), 221-235.
- 331 (4) Forster, P.; Ramaswamy, V.; Artaxo, P.; Berntsen, T.; Betts, R.; Fahey, D. W.; Haywood, J.; Lean,
332 J.; Lowe, D. C.; Myhre, G. Changes in atmospheric constituents and in radiative forcing. *Climate*
333 *Change* **2007**, *20*, (7), 129-234.
- 334 (5) Smith, P.; Martino, D.; Cai, Z.; Gwary, D.; Janzen, H.; Kumar, P.; McCarl, B.; Ogle, S.; O'Mara,
335 F.; Rice, C.; Scholes, B.; Sirotenko, O. *Agriculture. Climate Change 2007: mitigation*; Cambridge
336 University Press, Cambridge, UK, and New York, 2007.
- 337 (6) De Klein, C.; et al. N₂O emissions from managed soils, and CO₂ emissions from lime and urea
338 application. In *IPCC guidelines for national greenhouse gas inventories*; Eggleston, S., Buendia, L.,
339 Miwa, K., Ngara, T., Tanabe, K., Eds.; Intergovernmental Panel for Climate Change (IPCC), UN
340 and WMO 2006; p 54.
- 341 (7) Outram, F. N.; Hiscock, K. M. Indirect nitrous oxide emissions from surface water bodies in a
342 lowland arable catchment: a significant contribution to agricultural greenhouse gas budgets?
343 *Environmental Science & Technology* **2012**, *46*, (15), 8156-8163.
- 344 (8) Well, R.; Weymann, D.; Flessa, H. Recent research progress on the significance of aquatic
345 systems for indirect agricultural N₂O emissions. *Environmental Sciences* **2005**, *2*, (2-3), 143-151.
- 346 (9) Reay, D.; Edwards, A.; Smith, K. Determinants of nitrous oxide emission from agricultural
347 drainage waters. *Water, Air & Soil Pollution: Focus* **2004**, *4*, (6), 107-115.
- 348 (10) Hack, J.; Kaupenjohann, M. N₂O discharge with drain water from agricultural soils of the upper
349 Neckar region in Southern Germany. In *Non-CO₂ greenhouse gases: scientific understanding, control*
350 *options and policy aspects. Proceedings of the Third International Symposium*, , Van Ham, J.; Baede,
351 A. P. M. R.; Guicherit, J. G.; Williams-Jacobse, F. M., Eds. Millpress Science Publishers: Maastricht,
352 Netherlands, 2002; pp 185-190.
- 353 (11) Reay, D. S.; Edwards, A. C.; Smith, K. A. Importance of indirect nitrous oxide emissions at the
354 field, farm and catchment scale. *Agriculture, Ecosystems & Environment* **2009**, *133*, (3), 163-169.

- 355 (12) Sawamoto, T.; Nakajima, Y.; Kasuya, M.; Tsuruta, H.; Yagi, K. Evaluation of emission factors
356 for indirect N₂O emission due to nitrogen leaching in agro-ecosystems. *Geophysical Research Letters*
357 **2005**, 32, (3), L03403.
- 358 (13) Hiscock, K.; Bateman, A.; Mühlherr, I.; Fukada, T.; Dennis, P. Indirect emissions of nitrous
359 oxide from regional aquifers in the United Kingdom. *Environmental Science & Technology* **2003**, 37,
360 (16), 3507-3512.
- 361 (14) Weymann, D.; Well, R.; Flessa, H.; Heide, C.; Deurer, M.; Meyer, K.; Konrad, C.; Walther, W.
362 Groundwater N₂O emission factors of nitrate-contaminated aquifers as derived from denitrification
363 progress and N₂O accumulation. *Biogeosciences* **2008**, 5, (5), 1215-1226.
- 364 (15) Höll, B. S.; Jungkunst, H. F.; Fiedler, S.; Stahr, K. Indirect nitrous oxide emission from a
365 nitrogen saturated spruce forest and general accuracy of the IPCC methodology. *Atmospheric*
366 *Environment* **2005**, 39, (32), 5959-5970.
- 367 (16) Hinshaw, S. E.; Dahlgren, R. A. Dissolved nitrous oxide concentrations and fluxes from the
368 eutrophic San Joaquin River, California. *Environmental Science & Technology* **2013**, 47, (3), 1313-
369 1322.
- 370 (17) Minamikawa, K.; Eguchi, S.; Nishimura, S.; Ihara, H.; Maeda, M.; Yagi, K.; Komada, M.
371 Groundwater-induced emissions of nitrous oxide through the soil surface and from subsurface
372 drainage in an Andosol upland field: A monolith lysimeter study. *Soil Science and Plant Nutrition*
373 **2013**, 59, (1), 87-95.
- 374 (18) McGonigle, D.; Burke, S.; Collins, A.; Gartner, R.; Haft, M.; Harris, R.; Haygarth, P.; Hedges,
375 M.; Hiscock, K.; Lovett, A. Developing Demonstration Test Catchments as a platform for
376 transdisciplinary land management research in England and Wales. *Environmental Science: Processes*
377 *& Impacts* **2014**, 16, (7), 1618-1628.
- 378 (19) Meteorological Office UK climate averages;
379 <http://www.metoffice.gov.uk/public/weather/climate/u12gmt1fz>.
- 380 (20) Lemon, E.; Lemon, D. Nitrous oxide in freshwaters of the Great Lakes Basin. *Limnology and*
381 *Oceanography* **1981**, 26, (5), 867-879.

- 382 (21) Bowden, W. B.; Bormann, F. Transport and loss of nitrous oxide in soil water after forest clear-
383 cutting. *Science* **1986**, *233*, (4766), 867-869.
- 384 (22) Reay, D.; Smith, K.; Edwards, A. Nitrous Oxide in Agricultural Drainage Waters Following
385 Field Fertilisation. *Water, Air and Soil Pollution: Focus* **2004**, *4*, (2-3), 437-451.
- 386 (23) Weiss, R.; Price, B. Nitrous oxide solubility in water and seawater. *Marine Chemistry* **1980**, *8*,
387 (4), 347-359.
- 388 (24) Sander, R. Compilation of Henry's law constants for inorganic and organic species of potential
389 importance in environmental chemistry. In Report of the Max Planck Institute of Chemistry, Mainz,
390 Germany: 1999.
- 391 (25) Clough, T.J.; Buckthought, L. E.; Kelliher, F. M.; Sherlock, R. R. Diurnal fluctuations of
392 dissolved nitrous oxide (N₂O) concentrations and estimates of N₂O emissions from a spring-fed river:
393 implications for IPCC methodology. *Global Change Biology* **2007**, *13*, 1016-1027.
- 394 (26) Ventikeswaran, J. J.; Rosamond, M. S.; Schiff, S. L. Nonlinear response of riverine N₂O fluxes to
395 oxygen and temperature. *Environmental Science & Technology* **2014**, *48*, 1566-1573.
- 396 (27) Nevison, C. Review of the IPCC methodology for estimating nitrous oxide emissions associated
397 with agricultural leaching and runoff. *Chemosphere - Global Change Science* **2000**, *2*, (3-4), 493-500.
- 398 (28) Seitzinger, S. P.; Kroeze, C. Global distribution of nitrous oxide production and N inputs in
399 freshwater and coastal marine ecosystems. *Global Biogeochemical Cycles* **1998**, *12*, (1), 93-113.
- 400 (29) Cardenas, L.; Gooday, R.; Brown, L.; Scholefield, D.; Cuttle, S.; Gilhespy, S.; Matthews, R.;
401 Misselbrook, T.; Wang, J.; Li, C. Towards an improved inventory of N₂O from agriculture: model
402 evaluation of N₂O emission factors and N fraction leached from different sources in UK agriculture.
403 *Atmospheric Environment* **2013**, *79*, 340-348.
- 404 (30) Well, R.; Butterbach-Bahl, K. Indirect emissions of nitrous oxide from nitrogen deposition and
405 leaching of agricultural nitrogen. In *Nitrous Oxide and Climate Change*, K, S., Ed. Earthscan
406 Publications Ltd: Sterling, UK, 2010; p 162.
- 407 (31) Reay, D. S.; Smith, K. A.; Edwards, A. C.; Hiscock, K. M.; Dong, L. F.; Nedwell, D. B. Indirect
408 nitrous oxide emissions: revised emission factors. *Environmental Sciences* **2005**, *2*, (2-3), 153-158.

409 (32) Syakila, A.; Kroeze, C. The global nitrous oxide budget revisited. *Greenhouse Gas Measurement*
410 *and Management* **2011**, *1*, (1), 17-26.

411 (33) National Atmospheric Emissions Inventory Website; <http://naei.defra.gov.uk/>.

412

413

414

415

416

417

418

419

420

421

422

423

424

425

426

427

428

429 **Tables**

430 Table 1: Summary of the field drain and stream water NO₃ and N₂O concentration data differentiated
 431 by season for the period April 2013 to April 2015. Different superscript letters reflect significant
 432 differences (*t*-test *p* < 0.05) between seasons of the same sample type. Different subscript letters
 433 reflect significant differences between different sample types.

Sample type	Season	Mean NO ₃ (mg L ⁻¹) ± SD	Mean N ₂ O (µg L ⁻¹) ± SD	Mean N ₂ O-N/NO ₃ -N Ratio ± SD
Field drain	Overall (<i>n</i> = 621)	6.08 ± 4.78 _a	4.49 ± 4.46 _a	0.00120 ± 0.00134 _a
	Spring (<i>n</i> = 187)	5.98 ± 4.64 ^a	4.95 ± 4.86 ^a	0.00123 ± 0.00143 ^a
	Summer (<i>n</i> = 62)	4.17 ± 4.30 ^b	3.20 ± 4.69 ^b	0.00135 ± 0.00158 ^a
	Autumn (<i>n</i> = 153)	6.42 ± 5.16 ^a	4.12 ± 4.73 ^a	0.00113 ± 0.00137 ^a
	Winter (<i>n</i> = 219)	6.47 ± 4.65 ^a	4.71 ± 3.72 ^a	0.00117 ± 0.00116 ^a
Stream	Overall (<i>n</i> = 308)	6.70 ± 3.20 _b	1.43 ± 0.84 _b	0.00029 ± 0.00030 _b
	Spring (<i>n</i> = 80)	6.61 ± 1.92 ^a	1.30 ± 0.47 ^a	0.00021 ± 0.00008 ^a
	Summer (<i>n</i> = 64)	4.49 ± 2.79 ^b	1.02 ± 0.51 ^b	0.00039 ± 0.00038 ^b
	Autumn (<i>n</i> = 92)	7.05 ± 4.29 ^a	1.82 ± 1.24 ^c	0.00039 ± 0.00041 ^b
	Winter (<i>n</i> = 72)	8.30 ± 1.55 ^c	1.42 ± 0.47 ^a	0.00018 ± 0.00007 ^c

434

435

436 Table 2: Emission factors EF_{5g} and EF_{5r} calculated for field drains and stream water using two
 437 different methods, the default IPCC (2006) emission factors (EF₅), and the proposed EF_{5g}, EF_{5r} from
 438 this study. Values presented as the mean ± 1 standard deviation.

Parameter	Units/methodology	Field drains (All)	Stream water (Site A)
Total area	ha	21.09	0.33
Indirect N ₂ O emissions	kg N ₂ O-N ha ⁻¹ a ⁻¹	0.05 ± 0.10	5.75 ± 6.42
Mean total indirect N ₂ O emissions	kg N ₂ O-N a ⁻¹	1.04 ± 2.13	1.90 ± 2.12
Total N input	kg N a ⁻¹	2,870	64,545
Frac _{LEACH}	%	34 ± 29	25 ± 27
EF _{5g} , EF _{5r}	IPCC ⁶ method	0.0011 ± 0.0022	0.0001 ± 0.0001
EF _{5g} , EF _{5r}	N ₂ O-N/NO ₃ -N method	0.0012 ± 0.0013	0.0003 ± 0.0003
EF _{5g} , EF _{5r}	IPCC (2006) default	0.0025	0.0025
Proposed EF _{5g} , EF _{5r}	This study	0.0012	0.0002

439

440

441 Table 3: Summary of current and previous IPCC (2006) default emission factors for indirect N
 442 leaching from agriculture, calculated emission factors from this study and implications for indirect
 443 N₂O emission estimates from the UK and globally

	IPCC 1997	IPCC 2006	This study
EF _{5g}	0.015	0.0025	0.0012
EF _{5r}	0.0075	0.0025	0.0002
EF _{5e}	0.0025	0.0025	0.0025 ^b
EF ₅ ^a	0.025	0.0075	0.0039
Indirect UK N ₂ O emissions (Gg N a ⁻¹) from N leaching and runoff	14.30 ^c	6.71 ^d	3.49
Indirect global N ₂ O emissions (Tg N a ⁻¹) from N leaching and runoff	1.90 ^e	0.60 ^e	0.31

444 ^aEF₅ is the sum of EF_{5g}+EF_{5r}+EF_{5e}.

445 ^bNot studied here. Assumed unchanged.

446 ^cFrom Reay et al. ³¹.

447 ^dTotal UK N₂O emissions are 59 Gg N a⁻¹ for 2013 according to the National Atmospheric Emissions Inventory ³³, and from
 448 this amount, indirect emissions account for 24%, with 46% associated with N leaching and runoff ³².

449 ^eFrom Syakila and Kroeze ³².

450

451

452

453

454

455

456

457

458

459

460 Figure Captions

461 Figure 1: Relationship between $\text{N}_2\text{O-N}$ and $\text{NO}_3\text{-N}$ in field drain ($n = 621$) and stream water ($n = 308$)
462 samples collected during April 2013–April 2015. 90% of drain samples and 100% of stream water
463 samples had lower $\text{N}_2\text{O-N}/\text{NO}_3\text{-N}$ ratios than the IPCC (2006) default value of 0.0025.

464

465 Figure 2 Temporal variability in the mean $\text{N}_2\text{O-N}/\text{NO}_3\text{-N}$ ratio for field drain and stream water
466 samples collected during April 2013–April 2015. Error bars represent one standard error.

467

468 Figure 3: Input of nitrogen fertiliser (kg N ha^{-1}) across mini-catchment A for the (a) 2012–2013 and
469 (b) 2013–2014 farming years.

470

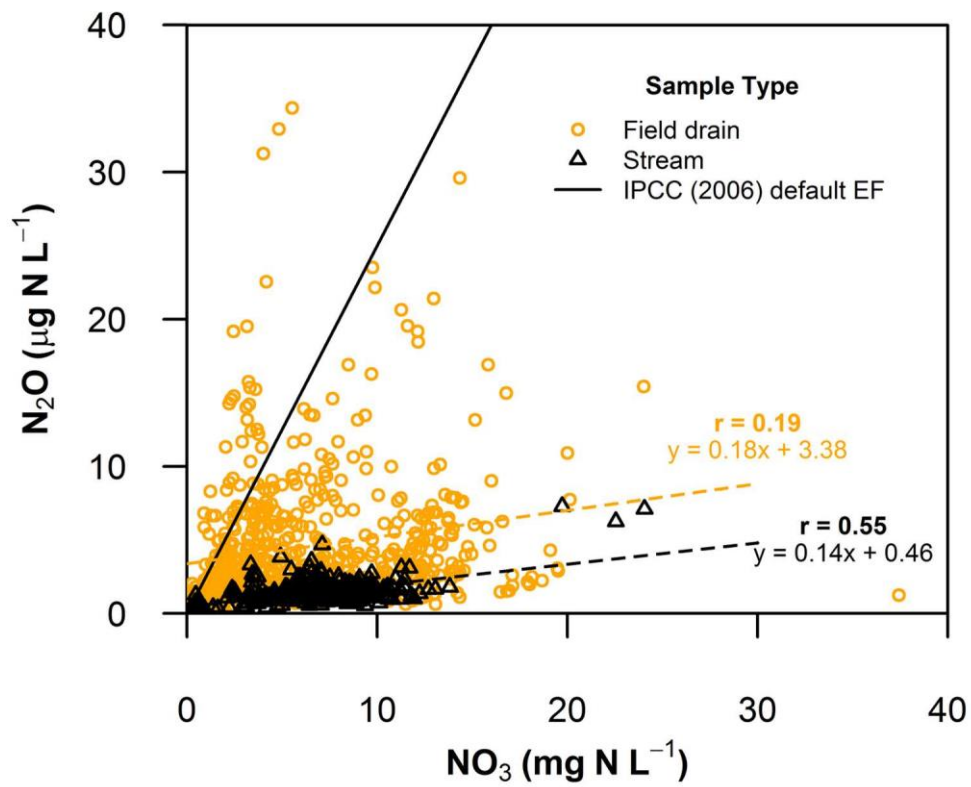


Figure 1: Relationship between N_2O-N and NO_3-N in field drain ($n = 621$) and stream water ($n = 308$) samples collected during April 2013–April 2015. 90% of drain samples and 100% of stream water samples had lower N_2O-N/NO_3-N ratios than the IPCC (2006) default value of 0.0025.

69x57mm (600 x 600 DPI)

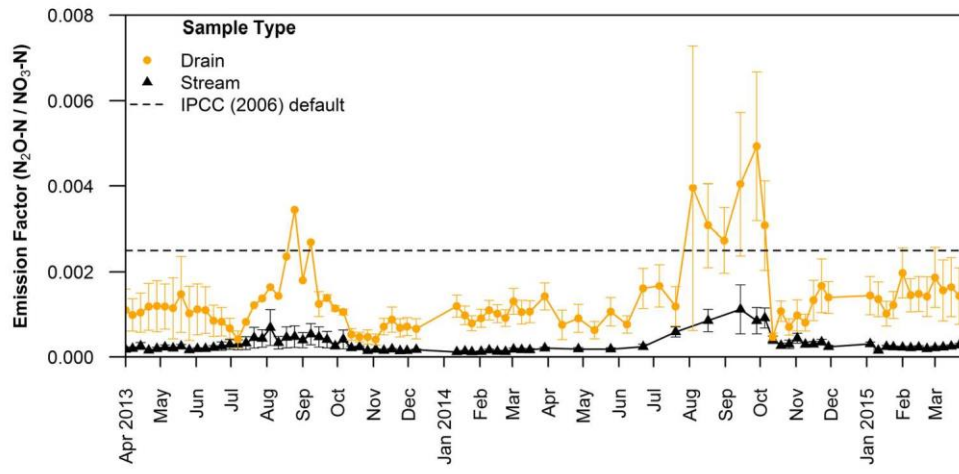


Figure 2 Temporal variability in the mean N₂O-N/NO₃-N ratio for field drain and stream water samples collected during April 2013–April 2015. Error bars represent one standard error.

79x39mm (600 x 600 DPI)

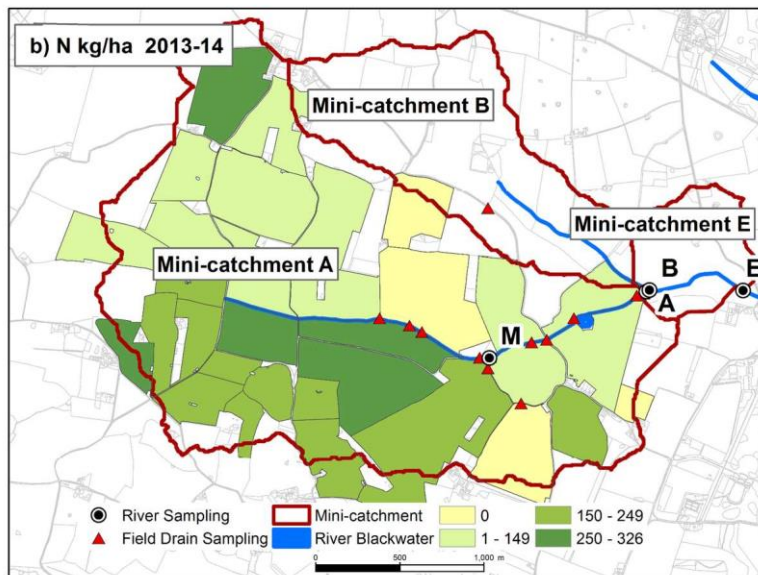
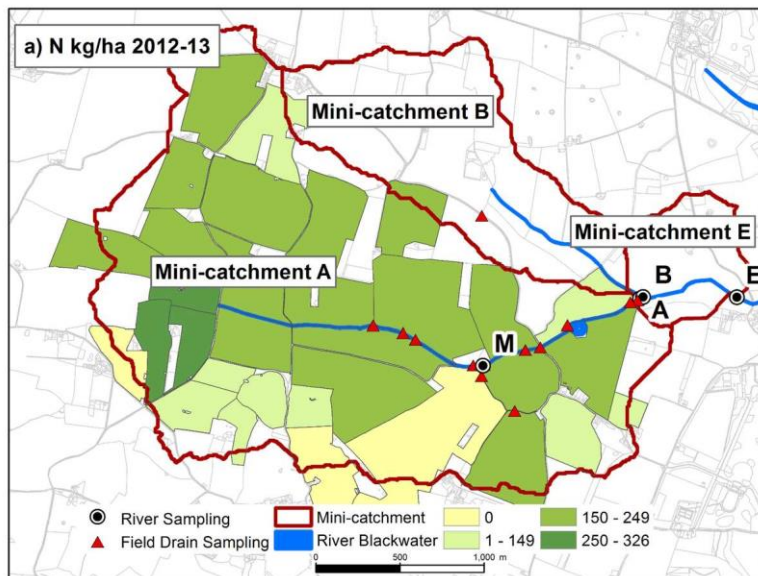


Figure 3: Input of nitrogen fertiliser (kg N ha⁻¹) across mini-catchment A for the (a) 2012–2013 and (b) 2013–2014 farming years.

130x200mm (300 x 300 DPI)