A review of indirect N2O emission factors from agricultural nitrogen leaching and runoff to update of the default IPCC values

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Abstract

Indirect N_2O emissions from agricultural nitrogen (N) leaching and runoff in water bodies contribute significantly to the global atmospheric N_2O budget. However, considerable uncertainty regarding this source remains in the bottom-up N_2O inventory. Indirect N_2O emissions factor associated with N leaching and runoff (EF_5; kg N_2O-N per kg of $NO_3^{-}-N$) incorporate three components for groundwater and surface drainage (EF_{5g}), rivers (EF_{5r}), and estuaries (EF_{5e}). The 2006 IPCC default EF_5 value was based on a small number of studies available at the time. Here we present the synthesis of 254 measurements of EF_5, dissolved N_2O, and nitrate from 106 studies. Our results do not support the further downward revision of EF_{5g} by the IPCC and suggest an upward revision of EF_{5g} of 0.0060. The emission factors for groundwater and springs (0.0079) was higher than that for surface drainage (0.0040). The emission factor for lakes, ponds, and reservoirs was 0.0012, whereas that for rivers was 0.0030, and a combined EF_{5r} was 0.0026. Estimated EF_{5r} and EF_{5e} (0.0026) values from the study were close to the current IPCC default values (0.0025 each). We estimated an updated default EF_5 value of 0.01 for the refinement of IPCC guidelines.

Capsule

We summarized 254 field datasets and estimated indirect N_2O emission factor from leaching and runoff of agricultural N (EF_5) of 0.01, higher than IPCC 2006 default EF (0.0075).

Keywords: Emission factor; Global warming; IPCC methodology; Nitrate leaching; Nitrous oxide

Introduction

Nitrous oxide (N_2O) is a long-lived (approximately 121 years) and powerful greenhouse gas with approximately 265 times the global warming potential of carbon dioxide (CO_2) on a 100-year time horizon (IPCC, 2014). Additionally, N_2O is a major source of stratospheric nitrogen oxides (NO_x), which are involved in destroying the stratospheric ozone layer. Nitrous oxide has thus been considered a primary ozone-depleting substance (Ravishankara et al., 2009). The current atmospheric concentration of N_2O has increased by 20% compared with that during the preindustrial era (270 parts per billion (ppb)) with a steady increase of 0.73 ppb year^{-1} over the last three decades (IPCC, 2014).

The major cause of the increase in atmospheric N_2O concentrations is human activities, most of which are closely associated with food production for a growing human population (Syakila and Kroeze, 2011; Reay et al., 2012). Agriculture has therefore been acknowledged as the largest anthropogenic source of N_2O and accounts for about 60% of the total anthropogenic emissions (Ivens et al., 2011; Syakila and Kroeze, 2011). N_2O emissions from agriculture have increased mainly as a result of the widespread use of nitrogenous fertilizers in agricultural lands and the increase in animal production (Reay et al., 2012; Bouwman et al., 2013a). Agricultural N_2O emissions are likely to continue to rise with the need to increase food production to feed the increasing human population in the coming decades (Mosier and Kroeze, 2000; Galloway et al., 2008; Davidson, 2009; Reay et al., 2012).

Agricultural activities have strongly altered nitrogen (N) cycles. Nitrogen in excess of plant and animal needs may have a greater chance of transferring to the atmosphere and aquatic ecosystems thus the addition of agricultural N can result in increasingly N-saturated terrestrial ecosystems (Peterson et al., 2001; Galloway et al., 2008; Mulholland et al., 2008; Keuskamp et al., 2012). Emissions of N_2O from agriculture comprise direct N_2O emissions from agricultural land, direct N_2O emissions from animal production, and indirect (off-site)

N_2O emissions derived from N originating from agricultural systems (Mosier et al., 1998; Syakila and Kroeze, 2011).

Indirect N_2O emissions comprise emissions from agricultural N leaching and runoff, atmospheric deposition of reactive N, and disposal of human sewage. N leaching and runoff is the largest component of the indirect N_2O budget, which is also the largest source of uncertainty in the bottom-up inventory (Mosier et al., 1998; Syakila and Kroeze, 2011; Turner et al., 2015). An influential factor determining indirect N_2O emissions from N leaching and runoff is the fraction of N leached into aquatic ecosystems ($Frac_{LEACH}$). Approximately 30% of N inputs in agriculture are lost by leaching and runoff; therefore, indirect emissions resulting from this pathway are a globally significant N_2O source (Mosier et al., 1998; Well et al., 2005; IPCC, 2006). The specific N_2O emission factor for N leaching and runoff (EF_5, the proportion of N loading converted to N_2O in aquatic ecosystems) is another important determinant for estimating indirect N_2O emission with the bottom-up IPCC methodology (Mosier et al., 1998; Davidson, 2009; Reay et al., 2012).

The EF_5 is derived separately for groundwater and surface drainage (EF_{5g}), rivers (EF_{5r}), and estuaries (EF_{5e}) according to the IPCC guidelines (Mosier et al., 1998; IPCC, 2006). The derivation of each component of EF_5 involves a multi-step set of assumptions about the nitrification and denitrification in water bodies (Nevison, 2000). Mineral N in water bodies affected by agricultural N is primarily in the form of NO_3^-–N. EF_{5g} is an empirical parameter and can be estimated from the ratio of dissolved N_2O–N to NO_3^-–N (Mosier et al., 1998). The default IPCC EF_{5g} value was reduced from 0.015 (kg N_2O–N kg^{-1} NO_3^-–N) in the 1997 guidelines (IPCC, 1997) to 0.0025 in the 2006 guidelines (IPCC, 2006) based on reviews and field studies (Hiscock et al., 2002, 2003; Reay et al., 2004, 2005; Sawamoto et al., 2005). In the 1997 IPCC guidelines, default values of EF_{5r} and EF_{5e} were both estimated based on assumptions regarding the fraction of N nitrified, proportion of N denitrified, and N_2O yields during these two processes (IPCC, 1997; Mosier et al., 1998). IPCC (2006) proposed a reduction in the default EF_{5r} value from 0.0075 to 0.0025 based on two field studies (Dong et al., 2004; Clough et al., 2006), whereas the default EF_{5e} value remained at 0.0025 owing to a lack of data. Nonetheless, the default EF_5 values issued in 2006 were based on a small number of studies available at the time and are therefore associated with large uncertainty.

Indirect emissions of N_2O from lakes, ponds, and reservoirs affected by agricultural N leaching and runoff are also a source of N_2O (Outram and Hiscock, 2012), but they have not been included in IPCC guidelines. The exclusion of these water bodies from the landscape is a major limitation of the IPCC method (Baulch et al., 2012) and neglecting these N_2O emissions may result in serious uncertainties in the calculation of regional N_2O budgets, at least within lake-rich landscapes (Huttunen et al., 2003; Liu et al., 2011; Xia et al., 2013). The uncertainty is also partly linked to ambiguities in the classification of different water bodies (Beaulieu et al., 2008; Baulch et al., 2012). Some water bodies predominantly influenced by non-agricultural N (atmospheric N deposition, human sewage, and wastewater treatment plants) may have been included in the estimate of EF_5 in the current IPCC guidelines (Nevison, 2000; Hiscock et al., 2003; Sawamoto et al., 2005). Previous studies have reported that current default EF_5 may either overestimate (Reay et al., 2005; Hama-Aziz et al., 2017) or underestimate (Beaulieu et al., 2011; Outram and Hiscock, 2012) indirect N_2O emissions from water bodies. Consequently, there is a need for a further evaluation of EF_5 and reduction of uncertainty in its calculation.

Since 2006, a number of field studies have been conducted in different water bodies at multiple spatial and temporal scales, and additional data are therefore available to validate the default IPCC EF_5 values. The objective of this study was to update EF_{5g}, EF_{5r}, and EF_{5e} values based on available data to date in order to refine IPCC guidelines. The effect of water body type (e.g. groundwater and drainage) and climate on emission factors were also investigated. Moreover, we compared emission factors of water bodies affected by only agricultural N and by both agricultural N and non-agricultural N.

Materials and methods

Literature search and study selection

We collected peer-reviewed literatures published before 25 June 2018 (the literature cut-off date of IPCC 2019 guidelines) on the indirect N_2O emission factors from agricultural N leaching and runoff into water bodies. Articles were retrieved from the ISI Web of Knowledge and Google Scholar databases by combining keywords related to N_2O emission (‘EF_5’, ‘N_2O flux’, or ‘dissolved N_2O concentration’) and specific types of water bodies (‘brook’, ‘creek’, ‘drainage’, ‘estuary’, ‘groundwater’, ‘lake’, ‘pond’, ‘reservoir’, ‘river’, ‘spring’, or ‘stream’). EF_5 values (calculated by dividing dissolved N_2O−N concentration by NO_3^-−N concentration in the water body) were collected from publications. To be included in the calculations of EF_5, the published data had to be reported from watersheds dominated by agricultural land use or main N source was agricultural N inputs. The following data criteria were applied to screen studies: (i) only in situ field studies were included and (ii) for studies with measurements through several sites or periods, in which the dominance of land use, bedrock and N loading (with NO_3^-–N as the predominant form of inorganic N) did not vary significantly, the values of emission factors and relevant variables were averaged for a water body type. Average values were adopted directly if there were no separated data available. Following these selection criteria, 106 publications in total were collected reporting 254 measurements.

Categorization of emission factors

A rationale to treat EF_{5g} and EF_{5r} differently is based on the assumption that the dominant source of N_2O for the EF_{5g} category derived from groundwater while in situ nitrification and denitrification dominated the N_2O source for EF_{5r} category (Beaulieu et al., 2008). Although the categorization of EF_{5g} and EF_{5r} for streams is not consistent among previous studies, we categorized data from upstream (supersaturated with N_2O) into EF_{5g} and data from downstream (supersaturated N_2O already degassed) into EF_{5r}. N_2O emission factors for groundwater (soil solution and lysimeter leaching water were not included), springs, upstream, or surface drainages (tile drainage and drainage ditch) were categorized as EF_{5g}. N_2O emission factors for downstream, rivers, lakes, ponds, or reservoirs were categorized as EF_{5r}. For estuaries, only inner estuaries were included and outer estuaries and coastal seawaters were excluded. Although most of studies on estuaries were impacted by urban waste water and fish farming in addition to agriculture, all available data were included owing to the limited number of observations and also the fact that most estuaries are affected not only by agriculture.

Studies for EF_{5g} were further grouped into two categories (groundwater and spring versus drainage water for water body type; temperate region versus subtropical region for climate zone type; other climate zone type could not be assessed in this study due to the lack of data). Studies for EF_{5r} were also grouped into two categories for water body type (rivers versus lakes, ponds and reservoirs) and three categories for climate zone type (temperate, subtropical, and tropical regions).

Data analysis

We tested two methods for estimating EF_5: (i) a linear regression model between observed N_2O–N concentrations and NO_3^-–N concentrations in each study and (ii) averaging all available EF_5 values obtained from the literature. For the regression model, scatterplots of residual N_2O concentrations against the explanatory variable (NO_3^-–N concentration) were performed to check the assumption of homoscedasticity for variables using SPSS version 17 (SPSS, Inc.).

Comparisons of mean values among more than three factors were made with SPSS using a one-way analysis of variance followed by a Hochberg's GT2 multiple comparison test ($P < 0.05$). An independent-sample *t*-test was used to compare two influencing factors with different sample sizes ($P < 0.05$). The mean, standard deviation, median, and the 95% confidence intervals (CI) of EF_5 were also calculated.

Results and discussion

Evaluation of emission factors

First, regression analysis between mean N_2O−N concentrations and NO_3^-−N concentrations was used to estimate EF_5, as in previous studies (Reay et al, 2005; Sawamoto et al., 2005). The pattern of the residual plots can show the heteroscedasticity of data, and the results of the regression analysis of N_2O−N concentrations and NO_3^-−N concentrations for EF_{5g}, EF_{5g}, and EF_{5e} for water bodies affected by agricultural N leaching or runoff revealed violations of homoscedasticity in all categories (Fig. S1). Scatterplots of N_2O concentrations and NO_3^-−N concentrations for the three categories demonstrated that the data were scattered and relationships were unclear in all the categories (Fig. 1). Thus, the population means of all available EF_5 values from the literature were used to estimate EF_{5g}, EF_{5r}, and EF_{5e}. The mean values for EF_{5g}, EF_{5r}, and EF_{5e} were 0.0060 (95% CI, 0.0041–0.0080), 0.0026 (0.0015–0.0036), and 0.0026 (0.0005–0.0047), respectively (Table 1).

The overall mean EF_{5g} based on 101 observations (Table 1) was 2.4 times that of the current IPCC default EF_{5g} (IPCC, 2006) and 2–6 times larger than those reported in other studies based on limited observations or regional investigations (Nevison, 2000; Reay et al., 2005; Sawamoto et al., 2005). However, the overall mean EF_{5g} was 1.5 times lower than the

1997 default value (IPCC, 1997). Our results do not support the further downward revision of EF_{5g} and indicate that an upward revision of the current default EF_{5g} is needed. Meanwhile, overall means EF_{5r} and EF_{5e} (Table 1) were similar to the current IPCC default values (IPCC, 2006), implying that the adjustments for the new default EF_{5r} and EF_{5e} would be relatively small. When the EF values of those three categories were combined, EF_5 was estimated at 0.01, which was higher than the current IPCC default value of 0.0075 (IPCC, 2006).

The definition of EF_5 merely represents the N_2O emission factor for N leaching and runoff from all agricultural sources (e.g., synthetic and organic fertilizers and urine and dung deposition) in water bodies (Mosier et al., 1998; IPCC, 2006). However, owing to a lack of data, previous studies have calculated EF_5 (specifically EF_{5g}) based on data from water bodies predominantly affected by both agricultural N and non-agricultural N (Mosier et al., 1998; Nevison, 2000; Sawamoto et al., 2005; IPCC, 2006). In the present study, mean and median results suggest that including data from both agricultural and non-agricultural sources will generate higher EF_{5g} and EF_{5r} values compared with excluding data from non-agricultural sources (Table 1). This is mainly due to the fact that the main N form in water bodies affected by non-agricultural N is not NO_3^-–N. In addition, extremely high EF_5 may occur even when the dissolved N_2O concentration is relatively low due to very low concentrations of NO_3^-–N (Hendzel et al., 2005; Wang et al., 2015). Thus, data from non-agricultural sources should be excluded when estimating N_2O emissions related to N leaching and runoff from agricultural sources.

Although EF_5 was estimated for agricultural N leaching and runoff, the combined EF of EF_{5r} and EF_{5e} was also used to estimate N_2O emission from waste water in the IPCC 2006 guidelines (IPCC, 2006). We found that the EF_{5r} including agricultural and non-agricultural N sources was significantly higher than the EF_{5r} including only agricultural N sources. However, it may not be suitable to use higher EF_{5r} for the waste water sector because NO_3^- is not the main N form in sewage-affected water bodies. In such water bodies, high N_2O–N and low NO_3^-–N result in a high emission factor which could lead to an overestimation of EF_{5r}. EF_{5r} (0.0026) and EF_{5e} (0.0026) values in our study can be used in the waste water sector as tier 1. In a higher tier, other N forms can be also considered in the waste water sector and using the N_2O–N / TDN (total dissolved nitrogen) ratio may result in a more accurate estimate for the waste water sector.

Although only a single emission factor for groundwater and surface drainage has been proposed by IPCC (1997, 2006), we found that the mean emission factor for groundwater and springs (0.0079, 95% CI: 0.0047–0.0111) was significantly higher than that for drainage water (0.0040, 95% CI: 0.0019–0.0062) (Fig. 2a). Our finding is in agreement with a previous investigation by Mosier et al. (1998), which found that the ratios of N_2O–N to NO_3^-–N in agricultural drainage ditches were generally lower than those in agricultural groundwater. Rapid N_2O degassing to the atmosphere once groundwater rises to the surface and flows downstream as well as more a complete reduction of NO_3^-–N to N_2 in drainage ditches may account for the lower emission factor for drainage water (Mosier et al., 1998; McAleer et al., 2017).

More accurate estimates of N_2O emission from all river networks in agricultural watersheds would reduce the difference between top-down and bottom-up N_2O emission inventories. However, the current IPCC default EF_{5r} considered only rivers (IPCC, 1997; 2006) and did not reflect the N_2O emission potential of lakes, ponds, and reservoirs connected to rivers. Here we estimated the EF_{5r} value for lakes, ponds, and reservoirs (0.0012, 95% CI: 0.0001–0.0023), which was significantly lower than that for rivers (0.0030, 95% CI: 0.0017–0.0044) (Fig. 3a). Although lakes are considered as hotspots of N_2O production because of long water-retention times as well as high inorganic N and dissolved organic carbon concentrations, a high potential for the complete reduction of NO_3^-–N to N_2 may also occur under these circumstances (Beaulieu et al., 2015; Chen et al., 2015). The lower percentage of denitrified N released as N_2O from lakes is therefore possibly related to the lower emission factor for lakes compared with rivers. In addition, no significant differences were found among different climate zones for EF_{5g} and EF_{5r} (Fig. 2b and Fig. 3b); therefore, our results indicate that EF_5 can be adopted in all climate zones.

Limitations of the IPCC methodology for indirect N_2O emission from agricultural N leaching and runoff

We have estimated emission factors for the indirect N_2O emissions from agricultural N leaching and runoff based on currently available data from the world. However, it should be noted that the estimation of present EF_5 values were predominantly determined by the measurements from the nutrient-rich (eutrophic, or at least mesotrophic) water bodies, while less measurements were conducted on places in nutrient-poor (oligotrophic) water bodies. The EF_5 may thus be overestimated in oligotrophic water bodies under the circumstances of extremely low N_2O with a certain amount of NO_3^-, and may be underestimated in oligotrophic water bodies with a certain amount of N_2O with very limited NO_3^-. The data bias can be reduced if more *in situ* observations of indirect N_2O emissions in oligotrophic water bodies became available. However, the effect of agricultural N is more likely to be less important in such oligotrophic water bodies, thus the EF_5 value in our study would be reasonable to estimate indirect N_2O emission from agricultural N leaching and runoff.

As a mean to represent N_2O release from a water body as a fraction of N loaded into the system, the EF_5 can also be calculated by several new methods (Well et al., 2005; Beaulieu et al., 2008; Weymann et al., 2008; Beaulieu et al., 2011; Hu et al., 2016). The mean and median results for EF_{5g}, EF_{5r} and EF_{5e} derived based on these methods were always lower than those calculated based on IPCC methodology (Table 1). However, many studies did not provide detailed data required for the alternative methods, it was thus not possible to calculate EF_5 using the concept of these new methods in most cases. Also, it is difficult to apply the alternative methods to a country scale due to limited availability of data required for these methods.

In addition, the IPCC default EF_5 does not consider that N_2O is simultaneously produced and consumed by geochemical processes (e.g., nitrification, nitrifier denitrification, and denitrification), which might vary markedly in water bodies with various environmental conditions (Sebilo et al., 2006; Nikolenko et al., 2018). Nevertheless, given denitrification and N_2O production rates increase with water NO_3^- concentration (Mulholland et al., 2008; Tian et al., 2018), the uncertainty intrigued by multiple N transformation processes might be less important in high NO_3^- loading water bodies, where denitrification is the dominant N_2O producing process.

Furthermore, considering the $Frac_{LEACH}$ varies from one site to another (Jahangir et al., 2012; Bouwman et al., 2013b), $Frac_{LEACH}$ in a country may differ largely from that proposed by the IPCC (30%; IPCC, 2006). Thus, the use of country-specific $Frac_{LEACH}$ value is required in order to estimate indirect N_2O emissions more accurately in a country scale.

Conclusions

Our study quantitatively analyzed *in situ* field studies from 1979 to 2018 to evaluate EF_5 to contribute to the refinement of the IPCC guidelines. The newly estimated EF_{5g} was greater than the IPCC default value, while newly estimated EF_{5r} and EF_{5e} did not apparently vary from the default values in IPCC 2006 guidelines (IPCC, 2006). However, there were significant difference between the emission factors for groundwater and surface drainage, as well as between lakes and rivers, indicating more detailed classifications for different water bodies might be required in future. In addition, there were no significant differences among different climate zones for EF_5 values based on the available data with majority of the measurements came from temperate regions, and more studies should be conducted in subtropical and tropical regions in future research. In conclusion, the present study provides a more accurate estimation of indirect N_2O emission from agricultural watersheds based on currently available data and can help resolve the discrepancy between top-down and bottom-up N_2O emission estimates around the world.

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Supplemental material

The supplemental material is available online. The supplementary dataset contains the complete dataset used in this synthesis and accompanying references.

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Figure captions

Fig. 1. Scatterplots of N_2O−N and NO_3^-−N concentrations for EF_{5g} (a), EF_{5g} (b), and EF_{5e} (c) categories for water bodies affected by agricultural nitrogen (N) leaching or runoff. EF_{5g}: N_2O emission factors for groundwater (soil solution and lysimeter leaching water were not included), springs, upstream, or surface drainages (tile drainage and drainage ditch). EF_{5r}: N_2O emission factors for downstream, rivers, lakes, ponds, or reservoirs. EF_{5e}: N_2O emission factors for estuaries. Only inner estuaries were included and outer estuaries and coastal seawaters were excluded.

Fig. 2. EF_{5g} for different water bodies (groundwater and spring versus drainage water) and different climate zones (temperate region versus subtropical region). Symbols and bars represent the mean EF_{5g} values and 95% confidence intervals, respectively. Numbers shown in parentheses correspond to the number of observations in each class, on which the statistical analysis was based. Different lowercase letters following the same symbols indicate significant differences between study groups at $P < 0.05$.

Fig. 3. EF_{5r} for different water bodies (rivers versus lakes, ponds, and reservoirs) and different climate zones (temperate, subtropical, and tropical regions). Symbols and bars represent mean EF_{5r} values and 95% confidence intervals, respectively. Numbers shown in parentheses correspond to the number of observations in each class, on which the statistical analysis was based. Different lowercase letters following the same symbols indicate significant differences among study groups at $P < 0.05$.

Fig. 1.

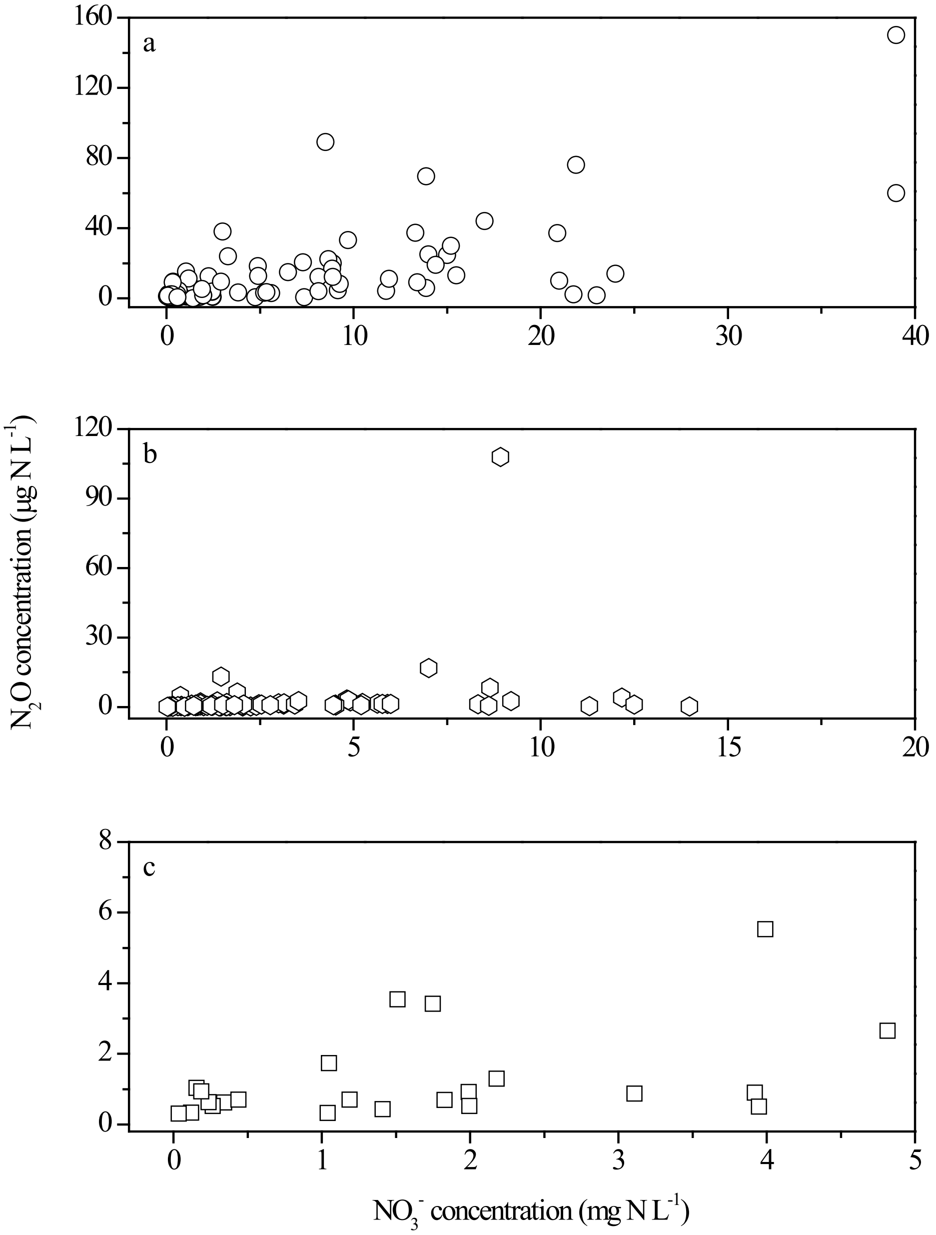
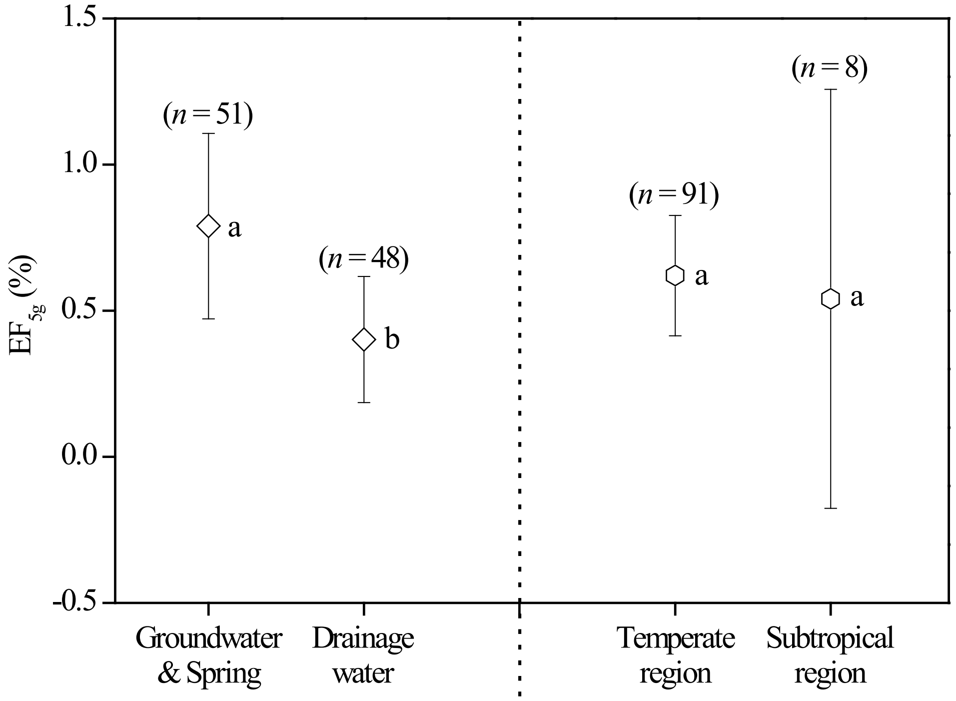
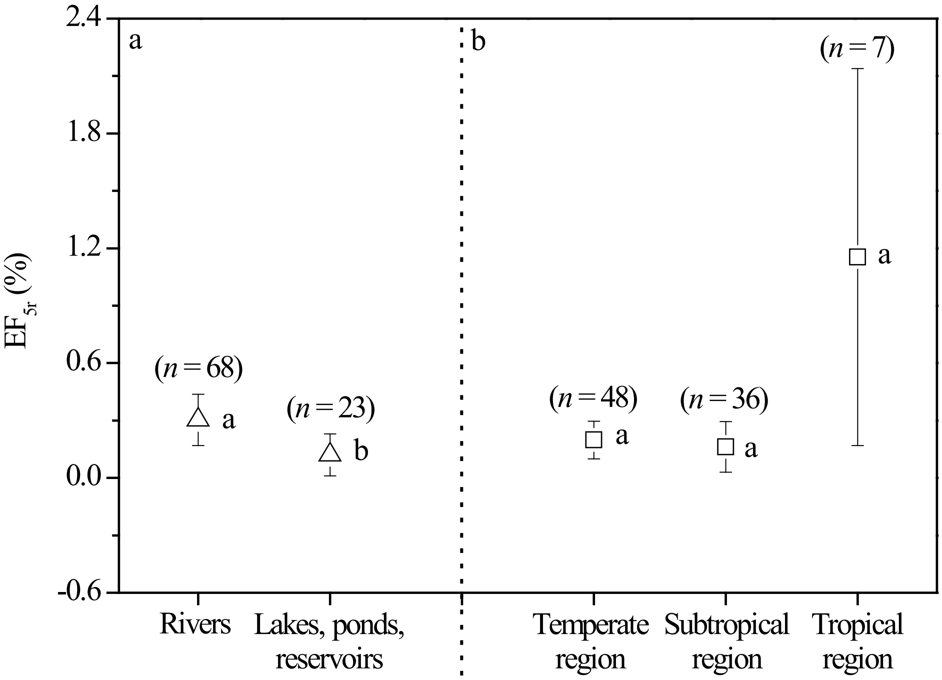

a
160
120
80
40
0
0
10
20
30
40
b
120
90
60
30
0
0
5
10
15
20
c
8
6
4
2
0
0
1
2
3
4
5
N_2O concentration (μg N L^{-1})
NO_3^- concentration (mg N L^{-1})

Fig. 2.



1.5
1.0
0.5
0.0
-0.5
EF_{5g} (%)
(n = 51)
a
(n = 48)
b
(n = 91)
a
(n = 8)
a
Groundwater & Spring
Drainage water
Temperate region
Subtropical region

Fig. 3.


2.4
1.8
1.2
0.6
0.0
-0.6
EF_{5r} (%)
a
b
(n = 68)
a
(n = 23)
b
(n = 48)
a
(n = 36)
a
(n = 7)
a
Rivers
Lakes, ponds, reservoirs
Temperate region
Subtropical region
Tropical region

Tables

Table 1 Emission factors from water bodies affected by agricultural nitrogen (N) and all water bodies influenced by both agricultural N and non-agricultural N.

Category	Emission factor (%)				
	Sample size	Mean	Standard deviation	Median	Confidence interval
Water bodies affected by agricultural N					
EF_{5g}	101	0.60	0.97	0.21	0.19
$EF_{5g\,(1)}$#	2	0.07	0.01	0.07	0.09
$EF_{5g\,(2)}$#	60	0.37	0.49	0.19	0.13
$EF_{5g\,(3)}$#	33	0.15	0.20	0.08	0.07
EF_{5r}	91	0.26	0.50	0.06	0.10
$EF_{5r\,(1)}$	24	-0.03	0.32	0.03	0.13
$EF_{5r\,(2)}$	51	0.07	0.09	0.04	0.03
$EF_{5r\,(3)}$	1	0.02	/	/	/
EF_{5e}	23	0.26	0.49	0.14	0.21
$EF_{5e(1)}$	4	0.07	0.09	0.03	0.14
$EF_{5e(2)}$	20	0.09	0.12	0.05	0.05
$EF_{5e(3)}$	/	/	/	/	/
Water bodies affected by both agricultural and non-agricultural N					
EF_{5g}	110	0.74	1.94	0.22	0.37
EF_{5r}	119	1.61	7.80	0.09	1.42

EF_{5g}: N_2O emission factors for groundwater (soil solution and lysimeter leaching water were not included), springs, upstream, or surface drainages (tile drainage and drainage ditch).

EF_{5r}: N_2O emission factors for downstream, rivers, lakes, ponds, or reservoirs.

EF_{5e}: N_2O emission factors for estuaries. Only inner estuaries were included and outer estuaries and coastal seawaters were excluded. All available data were included to calculate EF_{5e} due to the limited number of observations.

$EF_{5\,(1)}$ was calculated based on the ratio of excess dissolved N_2O concentration (dissolved N_2O-N concentration in excess of equilibrium) and NO_3^-–N concentration (Beaulieu et al., 2008). $EF_{5\,(2)}$ was estimated as the ratio of dissolved N_2O–N concentration and DIN (NO_3^-–N + NO_2^-–N + NH_{4+}–N, assuming NO_2^-–N was zero if no data was available) concentration (Beaulieu et al., 2011; Hu et al., 2016). $EF_{5\,(3)}$ was estimated as the ratio of dissolved N_2O concentration and initial NO_3^-–N (excess N_2–N + NO_3^-–N + N_2O–N) concentration (Well et al., 2005; Weymann et al., 2008).