

Global methane and nitrous oxide emissions from non-marine waters

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Abstract

Non-marine waters (i.e., rivers, reservoirs, lakes, ponds, streams and estuaries) are globally significant emitters of methane (CH_4) and nitrous oxide (N_2O) to the atmosphere, while global estimates of these emissions have been hampered due to the lack of a worldwide comprehensive database with the collection of complete CH_4 and N_2O flux components. Here we synthesize 2997 in-situ flux or concentration measurements of CH_4 and N_2O from 277 peer-reviewed publications to examine the role of non-marine waters in shaping climate change. Here we estimate that inland waters including rivers, reservoirs, lakes and streams together release $94.49 \text{ Tg CH}_4 \text{ yr}^{-1}$ (ebullition plus diffusion) and $1.52 \text{ Tg N}_2\text{O yr}^{-1}$ (diffusion) to the atmosphere, yielding an overall CO_2 -equivalent emission total of $3.05 \text{ Pg CO}_2 \text{ yr}^{-1}$, representing roughly 59% of CO_2 emissions ($5.13 \text{ Pg CO}_2 \text{ yr}^{-1}$) from these four aquatic ecosystems, with lakes acting as the largest emitter for both trace gases. Ebullition is noticed as a dominant flux component, contributing up to 62–84% of total CH_4 fluxes across all inland waters. Chamber-derived CH_4 flux rates are significantly greater than those determined by diffusion model-based methods for commonly capturing of both diffusive and ebullitive fluxes. The synthesis of global N_2O measurements projected that rivers exhibit the highest indirect N_2O emission factor (EF_5 , 0.028%), while streams have the lowest EF_5 value (0.015%). Our study reveals a major oversight in regional and global CH_4 budgets from inland waters, caused by neglect of the dominant role of ebullition pathways in those emissions. The indirect EF_5 values established in this study generally suggest an order of magnitude downward revision is required in current IPCC default EF_5 values for inland waters and estuaries. Our findings further indicate that a comprehensive understanding of the magnitude and patterns of CH_4 and N_2O emissions from non-marine waters is essential in defining the way that these natural ecosystems shape our climate.

Introduction

Non-marine waters (rivers, reservoirs, lakes, ponds, streams and estuaries) constitute important regional and global carbon (C) and nitrogen (N) cycles^{1,2}. Large and increasing agricultural organic C and N loading into non-marine waters makes these aquatic systems active and critical in global methane (CH_4) and nitrous oxide (N_2O) budgets. However, estimates of the global exchange of CH_4 and N_2O between non-marine waters and the atmosphere remain poorly constrained, primarily due to a lack of data and limited geographic distribution of measurements, especially those rarely characterized by distinguishing different flux components and measurement methods^{3,4}. Therefore, there is substantial uncertainty in our current understanding of global fluvial CH_4 fluxes to the atmosphere, and extremely poor accounting for the ebullitive component of CH_4 emissions⁴. Particularly, the patterns and controls of N_2O emissions from non-marine waters remain to be explored, such as the magnitudes and indirect N_2O emission factors (EF_5) involved in these aquatic systems. A robust estimate of N_2O emissions from non-marine waters caused by various N loading sources can help in upcoming research work to refine the regional and global terrestrial greenhouse gas inventories with reduced uncertainties^{5,6}.

Multiple approaches have been used to determine CH₄ fluxes^{7,8}, mainly chamber-based or diffusion model-based methods. Chamber-based methods can generally capture both ebullitive and diffusive flux components of CH₄, relative to the model-associated methods with only diffusive fluxes determined based on surface water dissolved CH₄ concentrations in equilibrium with the atmosphere⁴. Ebullition constitutes an important pathway for CH₄ release from aquatic ecosystems, yet it has long been difficult to quantify due to limited measurements and spatiotemporal heterogeneity, which ultimately hampers accurate estimates of the global CH₄ budget⁹. Thus, the contribution of ebullition from different inland waters to total global freshwater CH₄ emissions remains to be resolved.

Recently, two approaches (top-down vs. bottom-up) have been used to estimate global CH₄ and N₂O emissions from individual aquatic ecosystems (e.g., rivers, streams or reservoirs), basically showing high spatio-temporal heterogeneity¹⁰⁻¹³. In general, bottom-up estimates are higher than results obtained from top-down inversion methods. Using a process-based modeling approach, Hu et al.⁵ estimated global riverine N₂O emissions as 30–35 Gg N₂O-N yr⁻¹, representing 16–19% dissolved inorganic nitrogen (DIN) entering rivers and streams. Based on a review of available data, Stanley et al.⁹ estimated that global CH₄ emissions from streams and rivers can reach up to 26.8 Tg CH₄ yr⁻¹, equivalent to roughly 15–40% of CH₄ fluxes originating from wetlands and lakes. However, these estimates on CH₄ and N₂O emissions from inland waters did not distinguish the source from different emission pathways (diffusion vs. ebullition) and flux-derived methods (chamber-based vs. diffusion model-based). Particularly, except natural wetlands are the largest source of CH₄ to the atmosphere, inland waters, such as lakes, rivers and reservoirs also contribute substantially to the global emission total of CH₄, yet not included in most global greenhouse gas (GHG) inventories due to lack of robust estimates with sufficient simultaneous flux measurement data by collecting complete CH₄ flux components^{9,12}. Besides, some small water bodies (i.e., streams or ponds) have been also identified as strong sources of CH₄ and N₂O to the atmosphere, depending on data-derived approaches and the ways to estimate^{10,14}. There is thus a need for a comprehensive understanding of the rates and drivers of CH₄ and N₂O fluxes across non-marine waters.

In this study, we established a worldwide dataset by compiling 2997 direct measurements of CH₄ and N₂O fluxes or concentrations from six non-marine aquatic ecosystems (rivers, reservoirs, lakes, ponds, streams and estuaries) based on 277 peer-reviewed publications (Supplementary Fig. S1). We divided available CH₄ fluxes into diffusive and ebullitive components based on simultaneous flux measurement data and distinguished CH₄ and N₂O flux rates using different flux-derived methods across aquatic ecosystems. Collectively, our ambition was to draw attention to the role of non-marine waters in shaping climate change, particularly by assessing the relative contribution of the diffusive and ebullitive emission pathways to global total freshwater CH₄ emissions, relating CH₄ and N₂O fluxes to environmental controls, and estimating global CH₄ and N₂O emissions from non-marine waters including these from inland and estuarine open waters.

Results And Discussion

Patterns of CH₄ and N₂O fluxes among non-marine waters

Ebullitive and diffusive CH₄ fluxes ranged from 0.00 to 48.76 mg m⁻² h⁻¹ and 0.01 to 13.55 mg m⁻² h⁻¹, with a global average of 3.26 mg m⁻² h⁻¹ and 0.82 mg m⁻² h⁻¹ across non-marine waters, respectively (Fig. 1a). With the exception of estuaries, ebullitive and diffusive CH₄ fluxes varied but showed no significant differences among inland waters (Fig. 1a), with the highest flux rates observed through ebullition from reservoirs (4.83 ± 1.20 mg m⁻² h⁻¹) and through diffusion from streams (1.36 ± 0.36 mg m⁻² h⁻¹). The CH₄ fluxes released through ebullition were consistently higher than those through diffusion (Fig. 1a). The largest ebullitive CH₄ fluxes from reservoirs can be attributed to the degassing that will occur when water is routed through the dam^{3,15,16}. Diffusive N₂O fluxes varied from -0.08 to 1.15 mg m⁻² h⁻¹ across six non-marine waters. Streams had the highest rate of diffusive N₂O fluxes (0.14 ± 0.02 mg m⁻² h⁻¹), followed by rivers (0.12 ± 0.02 mg m⁻² h⁻¹) and reservoirs (0.05 ± 0.01 mg m⁻² h⁻¹) (Fig. 1b). The fluxes of CH₄ from rivers showed a significant seasonal variation, with the highest rates observed in summer and lowest rates occurring in autumn and winter (Supplementary Fig. S2a). However, there was no such significant seasonal variation for CH₄ or N₂O fluxes in the other waters (Supplementary Fig. S2b-f). Higher temperature and frequent events of rainfall and drainage during the summer increased C and N loading into rivers as a consequence of leaching and runoff, thereby stimulating the release of CH₄ and N₂O^{6,17}.

Chamber-derived vs. diffusion model-derived CH₄ and N₂O fluxes

We differentiated CH₄ and N₂O fluxes determined using chamber-based and diffusion model-based methods from six non-marine waters. The largest mean CH₄ fluxes determined by chamber-based and diffusion model-based methods were observed in rivers (5.32 ± 1.30 mg m⁻² h⁻¹) and streams (2.50 ± 0.65 mg m⁻² h⁻¹), while the lowest CH₄ fluxes were observed in estuaries (1.56 ± 1.31 mg m⁻² h⁻¹) and reservoirs (0.41 ± 0.08 mg m⁻² h⁻¹), respectively (Fig. 3a). Generally, CH₄ fluxes measured by chamber-based methods were consistently greater than those obtained from the use of model-based methods, and significantly different results were observed in rivers, reservoirs, lakes and ponds (Fig. 3a). Chamber-based methods can capture both diffusive and ebullitive flux components, while model-based methods can only obtain diffusive fluxes that were determined by the water-air gas exchange model⁴, suggesting that ebullitive fluxes from waters may have been overlooked when using the model-based methods^{4,8}. Unlike CH₄, there were no consistent differences in N₂O fluxes between the use of chamber-based and model-based methods. Similarly, the highest mean N₂O fluxes derived from chamber-based and model-based methods were also observed in rivers (0.13 ± 0.03 mg m⁻² h⁻¹) and streams (0.14 ± 0.02 mg m⁻²

h^{-1}), respectively, while the lowest mean N_2O fluxes by the two methods occurred in ponds (Fig. 3b). For chamber-based methods, uncertainties mainly come from the changes in natural turbulence at the water-air interface when deploying floating chambers¹⁸. However, the uncertainties for using model-based methods are associated with how the wind or water turbulence flow affects gas exchange across the water-air interface¹. Compared with other aquatic ecosystems, the lower wind and wave conditions in the rivers and streams that were included in our database led to lower uncertainties and higher rates of gas fluxes from these water bodies¹⁹.

Ebullitive and diffusive CH_4 fluxes

Ebullition and diffusion are two major pathways of CH_4 release from water bodies^{7,10,14}. Here we quantified the ebullitive and diffusive CH_4 fluxes by grouping data from studies that simultaneously measured both CH_4 flux components. Mean total CH_4 fluxes (ebullition plus diffusion) across five inland waters (rivers, reservoirs, lakes, ponds and streams) ranged from 0.01 to 54.90 $\text{mg m}^{-2} \text{h}^{-1}$ (Fig. 4a), with the highest CH_4 fluxes observed in reservoirs ($5.72 \pm 1.21 \text{ mg m}^{-2} \text{h}^{-1}$) and the lowest observed in lakes ($2.13 \pm 0.36 \text{ mg m}^{-2} \text{h}^{-1}$). Ebullition has been recognized as an important pathway of CH_4 release from inland waters^{4,7,20}. However, the ebullitive CH_4 fluxes are challenging to measure¹⁰ and the episodic and stochastic nature of CH_4 ebullition complicates the capturing and analysis of fluxes, thus few studies have quantified CH_4 ebullition in a recently updated global database⁹. We calculated the relative contribution of diffusive and ebullitive components to total CH_4 fluxes in five inland waters. Ebullition occurred at each inland freshwater system and contributed up to 62–84% of total CH_4 fluxes (Fig. 4a). Our results confirmed the findings in some shallow lakes and ponds with a substantial contribution of ebullition to total CH_4 fluxes, potentially accounting for 50–90% of the flux from these water bodies^{10,14}, while a range of 10–80% was reported on the contribution of ebullition to total CH_4 fluxes from streams and rivers^{2,21}. The highest mean ebullitive CH_4 fluxes were captured in reservoirs ($4.83 \pm 1.20 \text{ mg m}^{-2} \text{h}^{-1}$), followed by in rivers ($4.18 \pm 1.84 \text{ mg m}^{-2} \text{h}^{-1}$) and ponds ($3.89 \pm 1.47 \text{ mg m}^{-2} \text{h}^{-1}$). The highest mean diffusive CH_4 fluxes were observed in streams ($1.36 \pm 0.36 \text{ mg m}^{-2} \text{h}^{-1}$) and the lowest in lakes ($0.46 \pm 0.08 \text{ mg m}^{-2} \text{h}^{-1}$). The ebullition pathway of CH_4 in reservoirs has recently gained much attention, towards the conclusion that reservoirs acted as a hotspot of ebullitive CH_4 fluxes^{3,7}. Meanwhile, recent studies have emphasized the importance of ebullition in shallow flowing waters or high-elevation rivers^{21–23}. Ebullition rates tend to be higher from shallow water areas with more abundant exogenous inputs of CH_4 and organic materials than are found in deep water areas, and this may be also associated with short water residence times that limit the dissolution of CH_4 rich bubbles released from the sediment^{3,23}.

CO_2 -equivalent fluxes of CH_4 and N_2O

Based on simultaneous flux measurement data, we calculated the CO₂-equivalent fluxes of CH₄ and N₂O that reflect the emission intensity of a given terrestrial ecosystem, independent of the extent of surface area it may cover (Fig. 4b). We found that CH₄ fluxes dominated the flux composition (78%) of CH₄ and N₂O across six non-marine waters. The highest emission intensity caused by CH₄ was found in ponds ($137.90 \pm 42.31 \text{ mg m}^{-2} \text{ h}^{-1}$), with the largest contribution of 98%, while the lowest was found in estuaries ($6.59 \pm 1.41 \text{ mg m}^{-2} \text{ h}^{-1}$), with the smallest contribution of 62%. Streams showed the highest emission intensity ($52.60 \pm 16.61 \text{ mg m}^{-2} \text{ h}^{-1}$) arising from N₂O fluxes, with a contribution of 35%, relative the lowest observed in ponds, with a minor contribution of 2%. Ponds and streams had the largest combined emission intensity of CH₄ and N₂O across non-marine waters, while estuaries acted as the smallest potential aquatic emitter to the atmosphere. These results indicated that small water bodies (i.e., ponds or streams) with a high surface-area-to-volume ratio and shallow depth likely play a greater role in controlling land-atmosphere fluxes than are currently represented in global C budget^{13,24}.

Global CH₄ and N₂O emissions from non-marine waters

Bottom-up approaches are typically used to estimate global and regional CH₄ and N₂O emissions from inland waters, such as the data-driven approaches and extrapolations⁹. Based on area-scaled emission rates, we estimated global CH₄ and N₂O emissions from four major inland waters (rivers, reservoirs, lakes and streams) and estuaries. Annual total CH₄ emissions were estimated to be 74.07 Tg CH₄ yr⁻¹ through ebullition and 20.42 Tg CH₄ yr⁻¹ through diffusion, together yielding a global emission total of 94.49 Tg CH₄ yr⁻¹ (ebullition plus diffusion) from above four inland aquatic ecosystems (Table S1; Fig. 5). Of which, lakes (51.01 Tg CH₄ yr⁻¹) dominated this global emission total of CH₄, followed by rivers (20.80 Tg CH₄ yr⁻¹), reservoirs (13.08 Tg CH₄ yr⁻¹) and streams (9.60 Tg CH₄ yr⁻¹). In terms of the contribution of ebullition to total CH₄ emissions, reservoirs had the largest fraction of emissions as ebullition relative to diffusion (Fig. 5). Our estimate of global CH₄ emissions (94.49 Tg CH₄ yr⁻¹) from freshwaters is close to the results of 103 Tg CH₄ yr⁻¹ reported by Bastviken et al.¹² when summing emission sources from the same four freshwater systems as included in this study. A recent estimate by DelSontro et al.²⁵ led to a global total of 159 Tg CH₄ yr⁻¹ (with a range of 117–212 Tg CH₄ yr⁻¹) from inland freshwater systems, substantially higher than our estimate. This high estimate may be partially ascribed to their inclusion of areal emissions from intensively managed ponds, which was beyond our focus on relatively natural inland waters. Moreover, they did not distinguish the emission sources from different pathways (i.e., ebullition or diffusion) based on simultaneous flux measurement data. Bastviken et al.¹² initially estimated CH₄ emissions to be 1.5 Tg CH₄ yr⁻¹ from rivers and streams, but was limited by only including measurements from 21 sites globally. Our calculation yielded a diffusive emission total of 7.27 Tg CH₄ yr⁻¹ from rivers and streams globally (Fig. 5), lower than the rate of 27 Tg CH₄ yr⁻¹ estimated by Stanley et al.⁹ using a diffusive dataset dominated with modeling data. Our estimation of total CH₄ emissions from lakes (51.01 Tg CH₄ yr⁻¹) was less than a previous estimate of 71.6 Tg CH₄ yr⁻¹ by integrating

separate ebullitive and diffusive emissions¹², which may lead to an overestimation of CH₄ emissions from lakes due to a failure to incorporate simultaneous flux measurement data. Our estimated CH₄ emissions from reservoirs reached 13.08 Tg CH₄ yr⁻¹ (Table S1), which was comparable or close to some recent estimates using total CH₄ flux measurement data^{26,27}. Due to insufficient simultaneous ebullitive flux measurement data, we therefore chose to only estimate diffusive CH₄ emissions from estuaries, yielding a global total of 5.69 Tg CH₄ yr⁻¹ (Fig. 1). However, our estimated rate of CH₄ emissions from estuarine open waters will need in future to be further constrained by integrating the ebullitive flux component.

Total N₂O diffusive emissions were estimated to be 1.52 Tg N₂O yr⁻¹ from the four aquatic ecosystems (rivers, reservoirs, lakes and streams), with a range from - 0.21 to 4.15 Tg N₂O yr⁻¹ (Table S2). Of these, riverine N₂O emissions totaled 0.51 Tg N₂O yr⁻¹, close to the results reported by Yao et al.¹³ using a modeling approach, which estimated that the global riverine N₂O emissions have increased from 0.11 Tg N₂O yr⁻¹ in 1990 to 0.46 Tg N₂O yr⁻¹ in 2016. Given projections for future increases in N loading into freshwaters^{28,29}, modeling and predicting N₂O emissions from freshwaters are critical for developing and refining global N₂O emission inventories and seeking potential mitigation strategies. However, the existing studies estimating N₂O emissions from freshwaters have been dominated by efforts in rivers^{5,30,31}, with extremely limited information available from other inland waters, such as lakes, reservoirs and streams. Therefore, the global N₂O emissions from freshwaters remain to be quantified, particularly in respect of inland waters, which represent integral parts of the terrestrial landscape yet remain to be included in the terrestrial greenhouse gas (GHG) budgets. Expressed as CO₂-equivalents (eq), total CH₄ and N₂O emissions from inland waters estimated in this study led to an emission total of 3.05 Pg CO₂-eq yr⁻¹ (or 0.83 Pg C yr⁻¹) over a 100-year time scale (Fig. 5), representing at least 32% of the estimated terrestrial GHG sink^{12,32}. Compared with inland waters, total diffusive N₂O emissions from estuaries were estimated to be 0.39 Tg N₂O yr⁻¹, which is close to a recent bottom-up estimate by Murray et al.¹⁸ of 0.36 Tg N₂O yr⁻¹, and also falls well within the scope of 0.20–0.71 Tg N₂O yr⁻¹ reported by Robinson et al.³³.

We simulated indirect emission factors (EF_{5r}/EF_{5e}) of N₂O for rivers, reservoirs (including lakes and ponds), streams and estuaries (Fig. 2), with a range of 0.002–5.60% across all water bodies. Consistently, N₂O and NO₃⁻ concentrations exhibited strong linear positive correlations with relatively narrow uncertainty ranges in all water bodies, indicating that NO₃⁻ is a primary driver of aquatic N₂O production. Of which, rivers (0.028%) showed to have the highest EF_{5r} value, as compared to streams (0.015%) with the lowest EF_{5r} value. As shown in Fig. 2, the EF₅ values estimated using the concentration method differed among aquatic ecosystems, which were generally an order in magnitude lower than the IPCC default value of 0.26% (ref.³⁴). These results suggest that a downward revision of IPCC default value is

required in the future to more accurately estimate indirect N₂O emissions from aquatic ecosystems as previously stressed^{6,35,36}.

Drivers of CH₄ and N₂O emissions from non-marine waters

We found that CH₄ and N₂O fluxes increased linearly with surface water dissolved CH₄ and N₂O concentrations (Supplementary Figs. S3 and S4), suggesting a dependence of CH₄ and N₂O emission rates on their dissolved concentrations in aquatic ecosystems. Mean CH₄ fluxes were positively related to dissolved organic C (DOC) concentrations in lakes and streams, while they were negatively dependent on dissolved oxygen (DO) concentrations in ponds (Supplementary Fig. S5a and b), indicating that DOC-rich waters favor CH₄ fluxes from aquatic ecosystems, especially under low-oxygen conditions^{4,11}. Similarly, N₂O fluxes also had a negative relationship with DO (Supplementary Fig. S5d), confirming the dominant role of denitrification in aquatic N₂O production^{19,37}. Mean CH₄ and N₂O fluxes and the indirect EF₅ of N₂O in rivers and reservoirs were negatively dependent on water pH, to a larger extent in rivers for CH₄ (Supplementary Fig. S6b-d). Presumably, the high pH may suppress microbial activities involved in the decomposition of organic matter, nitrification and denitrification processes, in addition to the insufficient supply of substrates needed by bacteria in high pH aquatic environments^{17,38}. Mean N₂O fluxes showed positive dependence on water inorganic N components (NH₄⁺-N and NO₃⁻-N), different from the indirect EF₅ of N₂O having a positive correlation with NH₄⁺-N concentrations while a negative correlation with NO₃⁻-N concentrations (Supplementary Fig. S7). Our results confirmed previous findings that denitrification-derived N₂O emissions in N-loaded waters may not always increase with the rise of water NO₃⁻-N concentrations, especially in N-saturated water environments³⁹⁻⁴¹.

To predict CH₄ and N₂O fluxes from non-marine waters, linear stepwise regression models with the personality of Ordinary Least Squares (OSL) were used to fit CH₄ and N₂O fluxes by environmental parameters. We found that DO showed as a dominant factor among all variables to influence CH₄ release from individual freshwaters, such as in reservoirs, lakes and ponds (Table S3). However, when pooling data from all inland waters, dissolved oxygen (DO) together with temperature poorly accounted for the variance in CH₄ fluxes (Table S3). Our results were consistent with previous findings in riverine systems^{4,42}. Specifically, CH₄ fluxes were best predicted in ponds by DO and the interaction of temperature with mean annual precipitation (MAP) that jointly could explain 40% the variance in CH₄ fluxes (Table S3), suggesting that MAP showed a trend to refine the prediction of CH₄ fluxes based on independent parameters in small waters⁴³. For N₂O release, NO₃⁻-N predominated among all variables to affect N₂O fluxes across aquatic ecosystems, and it together with DO could explain 41% of the variance in N₂O fluxes (Table S3). Different from in freshwaters, N₂O fluxes in estuaries were well predicted by interactions of NO₃⁻-N with latitude and MAP with latitude ($r^2 = 0.65$, $p < 0.001$), indicating an important role of spatial variability for influencing N₂O prediction in open waters. Similar to N₂O fluxes, the indirect

EF₅ of N₂O across inland waters were also partially predicted by NO₃⁻-N and DO, and a better simulation was obtained in reservoirs by incorporating NO₃⁻-N and its interaction with pH ($r^2 = 0.45$, $p < 0.001$). It suggested that pH, as an important parameter regulating aquatic N₂O fluxes, tended to benefit for improving the prediction of indirect EF₅ in reservoirs¹⁹.

Methods

Data acquisition. We launched a detailed review of the literature published in peer-reviewed journals through the year 1978-2020 (cut-off date on October 20, 2020). We extracted original experimental data from publications on aquatic CH₄ and N₂O fluxes as well as related parameters from six non-marine waters including rivers, reservoirs, lakes, ponds streams and estuaries. A combination of search terms ["CH₄" OR "methane" AND "N₂O" OR "nitrous oxide" AND "flux" OR "emission" OR "release" OR "evasion" AND "river" OR "reservoir" OR "lake" OR "pond" OR "stream" OR "estuary"]. All selected data were extracted from the Web of Science and Google Scholar, and also the publication sources by gathering and reevaluating the older literature cited in the earlier reviews. The experimental locations were mostly clustered in Asia, Europe, and North America, with only several studies scattered in South and Northern Hemispheres with high latitudes (Supplementary Fig. S1). Overall, we established a solid dataset consisting of 2997 in-situ flux or concentration measurements of CH₄ and N₂O sourced from 277 peer-reviewed publications, of which 52 studies with 196 simultaneous flux measurements of CH₄ and N₂O were included (Supplementary Fig. S1).

We only included in-situ measurements of CH₄ and N₂O fluxes or concentrations from non-marine waters. With the focus on natural aquatic systems, the gas flux data from artificial constructed ponds used for sewage treatment or agricultural aquaculture ponds were excluded from our dataset due to intensive human impacts. We only incorporated studies in which aquatic systems were clearly defined. For studies in which the type of riverine systems was not clearly defined, we grouped them into rivers or streams according to the specific Strahler stream order⁴⁴. We ensured that the data on gas fluxes and geographical information were reported or can be made available from authors. In case of absence of data on climate (e.g., temperature, precipitation) information, we obtained relevant data from the World Meteorological Organization (<http://www.worldweather.cn/zh/home.html>). When the same site was reported in multiple studies, we used the study that included the largest number of sampling dates, either across seasons or years. If the data were collected across multiple years, we calculated the average fluxes or concentrations over the whole measurement period. Generally, diffusive and ebullitive CH₄ fluxes spanned over four orders of magnitude, ranging from 0.00 to 56.00 mg m⁻² h⁻¹ and 0.00 to 60.42 mg m⁻² h⁻¹ in inland waters, and varied from -0.15 to 17.78 mg m⁻² h⁻¹ and 0.01 to 0.18 mg m⁻² h⁻¹ in estuaries (Supplementary Table S4). Diffusive N₂O fluxes and concentrations had a range from -79.00 to 1151.77 μg m⁻² h⁻¹ and 0.50 to 1500.00 nmol L⁻¹ in inland waters, and from -11.90 to 322.67 μg m⁻² h⁻¹ and 4.35 to 210.30 nmol L⁻¹ in estuarine open waters (Supplementary Table S5).

Upscaling and uncertainties. We used a bottom-up approach to upscale CH₄ and N₂O emissions from non-marine waters by multiplying averaged emission rates by the estimated global areal extents of water bodies^{12,18}. In terms of CH₄ emissions, only studies with simultaneous measurement data for both diffusive and ebullitive fluxes were included in our estimates to reduce bias. For N₂O emissions, considering the ebullition was not the representative pathway of N₂O release from water bodies, we chose to only estimate diffusive N₂O emissions from non-marine waters, finally leading to exclusion of several sporadic ebullitive N₂O fluxes from our dataset. Moreover, in order to reduce uncertainties, we only estimated diffusive CH₄ emissions from estuaries due to insufficient data on ebullitive CH₄ fluxes. To generate annual mean gas fluxes, we assumed the average seasonal fluxes were representative of the entire year in tropical and frigid regions. In other regions with typical seasonal differences, the seasonal flux data (collected in summer or winter) were rectified by the annual mean temperature using a temperature-dependent empirical model reviewed by Yan et al.⁴⁵. However, we did not extrapolate CH₄ and N₂O emissions from ponds in this study due to large uncertainties in current available areal extents determination. All the data on global surface areas of aquatic ecosystems were cited from recently published literature with solid updated estimates^{18,46,47}.

Compared to previous global estimates based on limited and localized CH₄ and N₂O flux rates, we have dedicated to exploring the fractions of global total freshwater CH₄ emissions resulting from two different emission pathways (diffusion and ebullition) by incorporating simultaneous flux measurement data. Meanwhile, we provided a full understanding of the magnitude and drivers of diffusive N₂O emissions from diverse non-marine waters, relative to previously mostly limited in a single aquatic system^{5,18}. However, uncertainties remained existed for our estimates. First, while a wide range in diffusive fluxes has been reported for estuarine open waters, measurements of ebullition remain notably scarce, especially for the simultaneous measurement data with diffusion (Supplementary Table S4). Second, except in tropical and frigid regions, flux data showed considerable variations with seasons, with general higher flux rates occurring in summer than in other seasons, although we have attempted to account for this in our analysis by rectifying the flux data using an earlier established temperature-dependent empirical model⁴⁵. Third, we did not estimate the indirect EF₅ of N₂O based on the IPCC methodology to create a comparison in this study due to lack of detailed information on N inputs in most studies. Thus, given that future changes in climate and anthropogenic N loading are expected to increase N₂O emissions from non-marine waters, more extensive direct measurements of N₂O fluxes coupled with aquatic N loading rates are highly needed to make the IPCC methodology applicable to bridge the gap between global bottom-up and top-down inventories.

Calculation of indirect N₂O emission factors (EF₅). Indirect N₂O emission factors for riverine systems (EF_{5r}) and estuaries (EF_{5e}) were estimated in this study to create a comparison with the recently updated IPCC default value of 0.26% (ref.³⁴). The indirect EF₅ of N₂O represents N₂O emissions from a given water body to the atmosphere as a fraction of N loading into the system⁶. IPCC defined the indirect EF₅ of N₂O

as a ratio of N₂O-N emitted from leached N and N in runoff divided by the fraction of all N added to, or mineralized within managed soils that is lost through leaching and runoff⁴⁸. Due to incomplete acquisition of the specific information (e.g., data on N leaching and runoff) required to determine the indirect EF₅ based on the IPCC methodology for all aquatic systems, we therefore alternatively used the concentration method, i.e., the N₂O-N/NO₃⁻-N mass ratio derived from the concentration data of N₂O and nitrate (NO₃⁻) reviewed from water bodies to estimate the indirect EF₅ of N₂O (ref.⁶) using the following equation:

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

Where EF₅ is the indirect emission factor determined by the N₂O-N/NO₃⁻-N mass ratio method, C_{N₂O-N} and NO₃⁻-N are concentrations measured at the water-air interface and dissolved in surface water of aquatic ecosystems, respectively^{35,44}.

Estimation of CO₂-equivalent emissions. Total CO₂-equivalent emissions or emission intensity of CH₄ and N₂O from aquatic ecosystems were estimated using the conversion factors (mass basis) of 28 for CH₄ and 265 for N₂O over the time horizon of 100 years⁴⁹.

Statistical analyses. One-way analysis of variance (ANOVA) was performed to test the difference in CH₄ and N₂O fluxes between two CH₄ emission pathways (diffusion and ebullition), two flux-derived methods (chamber-based and model-based), and among different aquatic ecosystems. Linear or nonlinear regressions were used to examine the dependence of CH₄ and N₂O fluxes on potential driving factors. Linear stepwise regression models with the personality of Ordinary Least Squares (OSL) were conducted to identify the appropriate subset of environmental parameters that can best predict CH₄ and N₂O fluxes from inland waters or individual aquatic systems. All statistical analyses were carried out using JMP version 7.0 and R, and statistical significance was determined at the 0.05 probability level.

Declarations

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Author contributions

S.W.L. and J.W.Z. designed the investigation. Y.J.Z., K.Y. and S.W. extracted the data from literature and constructed the database. S.W.L., Y.J.Z., X.T.F. and S.W. performed the statistical analyses. C.F. was the key international collaborator during this research. The manuscript was drafted by S.W.L., S.W. and C.F., with all authors contributing to the final version.

Competing interests

The authors declare no competing interests.

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Figures

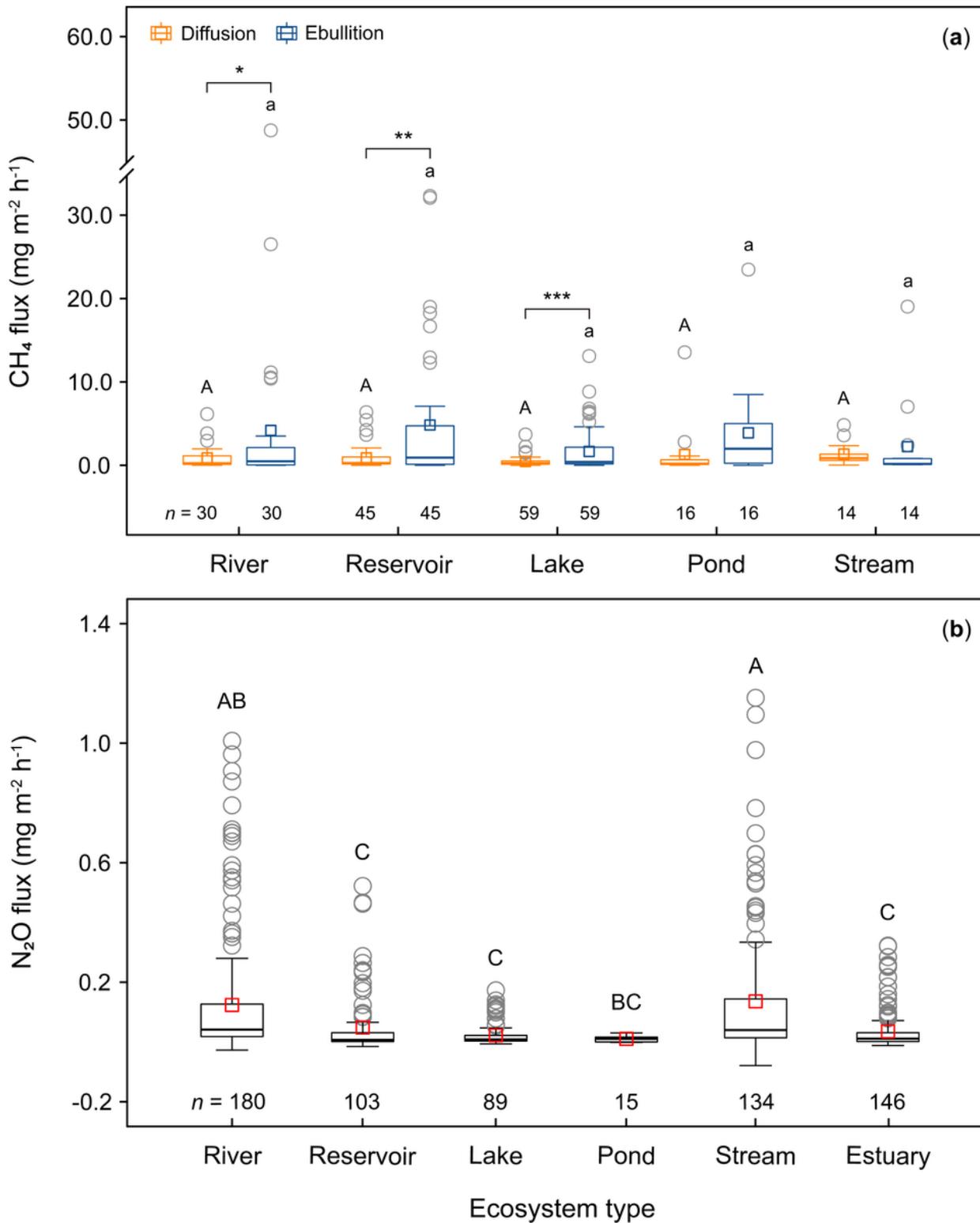


Figure 1

Comparisons of diffusive and ebullitive CH₄ fluxes (a) and N₂O fluxes (b) among aquatic ecosystems. Estuaries are absent from Fig. 1a due to limited observations available to reduce uncertainties. The number of observations (n) for each water body is shown next to the x-axis. The empty squares, lines within each box, lower and upper edges, bars and grey circles represent the means, median values, 25th and 75th, 10th and 90th percentiles and outliers of data, respectively. Different uppercase and lowercase

letters indicate significant differences in diffusive CH₄ and N₂O fluxes and ebullitive CH₄ fluxes, respectively. Asterisks in Fig. 1a indicate statistical differences in CH₄ fluxes between through diffusion and ebullition pathways (*p < 0.05; **p < 0.01; ***p < 0.001).

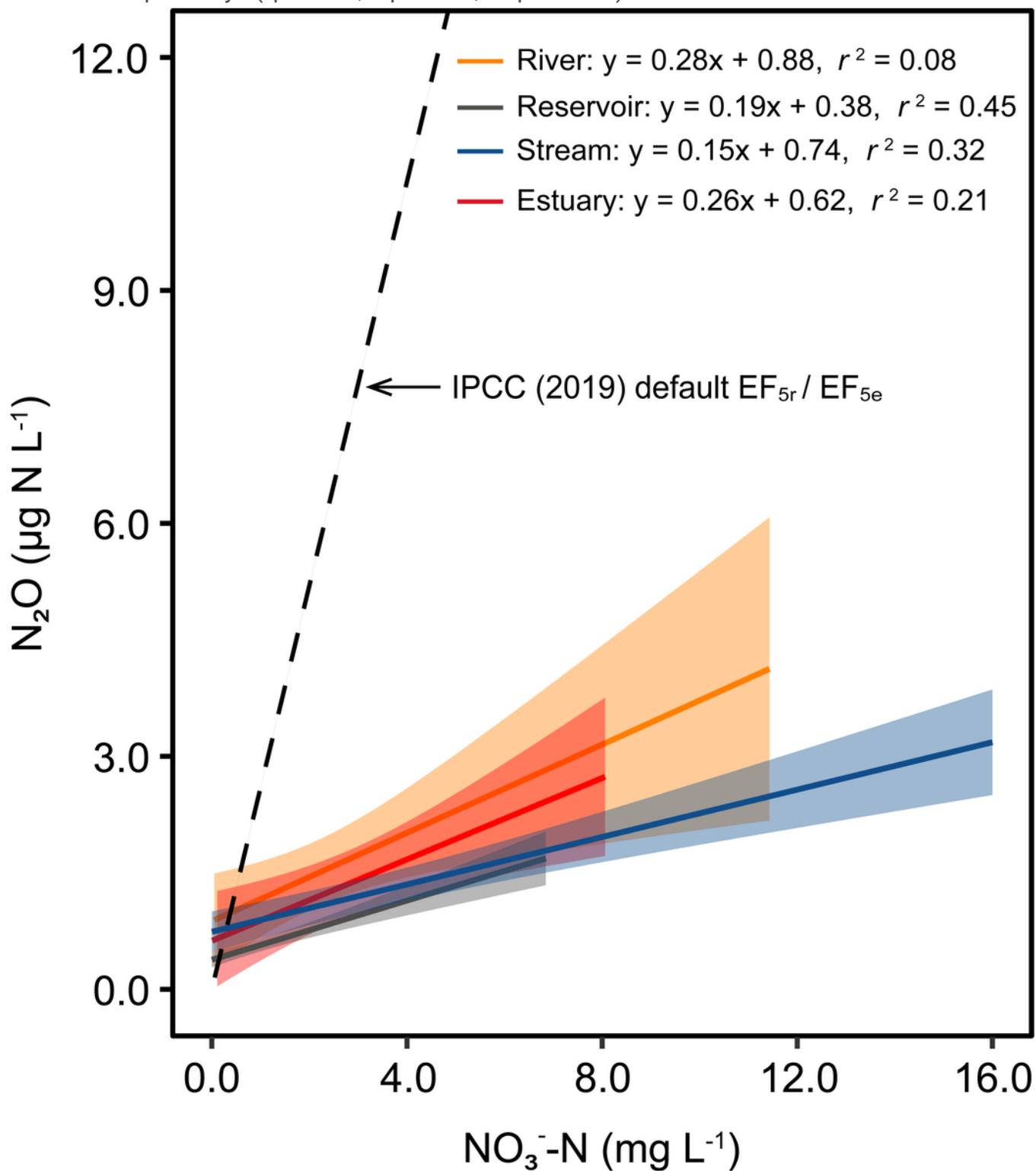


Figure 2

Linear simulated indirect emission factors of N₂O ($\text{EF}_{5r}/\text{EF}_{5e}$) based on the concentration method ($\text{N}_2\text{O-N}/\text{NO}_3^- \text{-N}$ mass ratio) for specific aquatic ecosystems. The black dashed line represents the IPCC (2019)

default emission factor for riverine systems and estuaries. The indirect EF5r/EF5e of N₂O for rivers, reservoirs (including lakes and ponds), streams and estuaries derived from this study are 0.028%, 0.019%, 0.015% and 0.026%, respectively, which are generally one order magnitude lower than the IPCC default value of 0.26%.

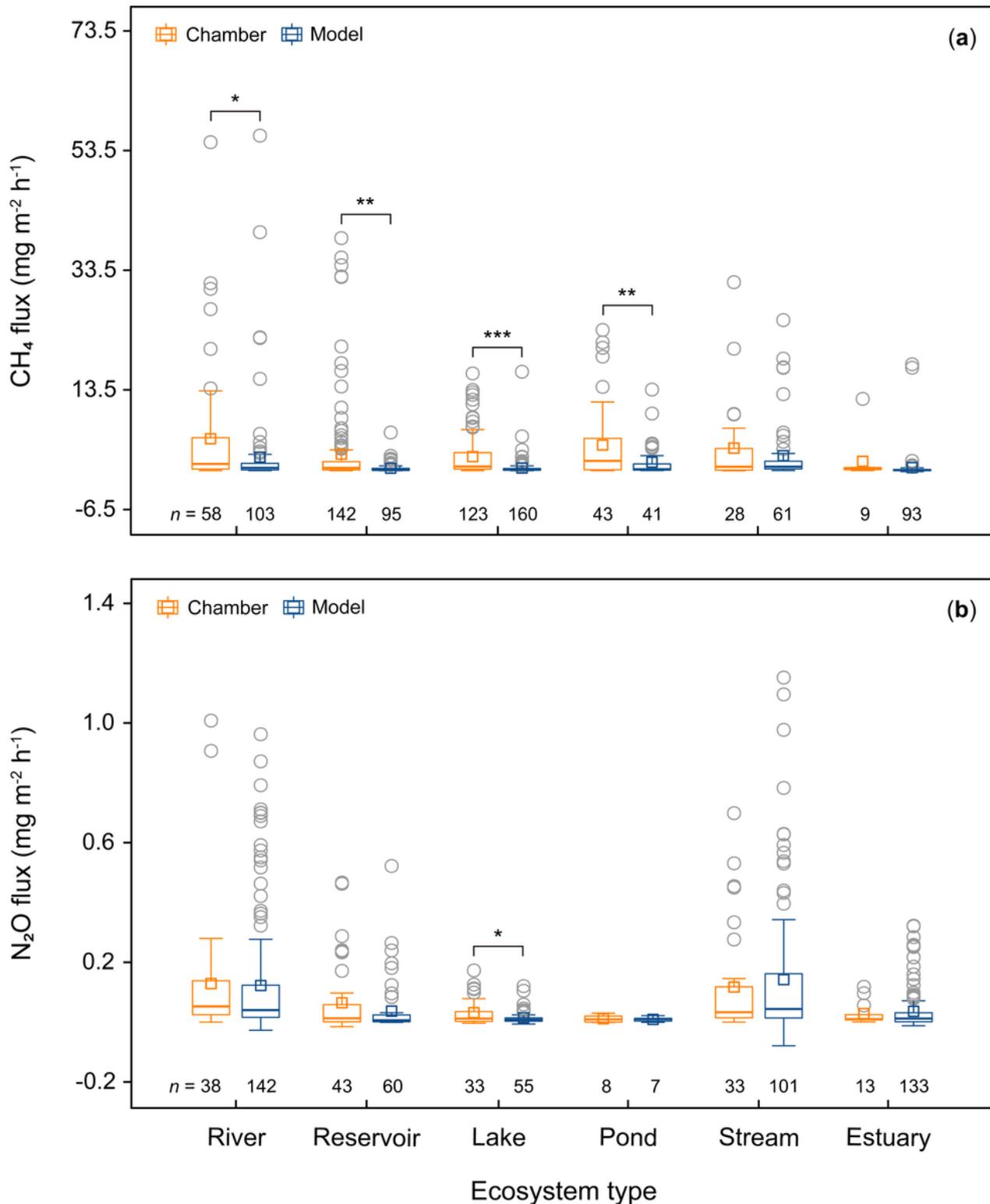


Figure 3

Comparisons of CH₄ (a) and N₂O fluxes (b) between chamber-based and diffusion model-based methods across aquatic ecosystems. Asterisks indicate statistical differences in gas fluxes between two measuring methods (*p < 0.05; **p < 0.01; ***p < 0.001). The number of observations (n) for each water body is shown next to the x-axis. The empty squares, lines within each box, lower and upper edges, bars and grey circles represent the means, median values, 25th and 75th, 10th and 90th percentiles and outliers of data, respectively.

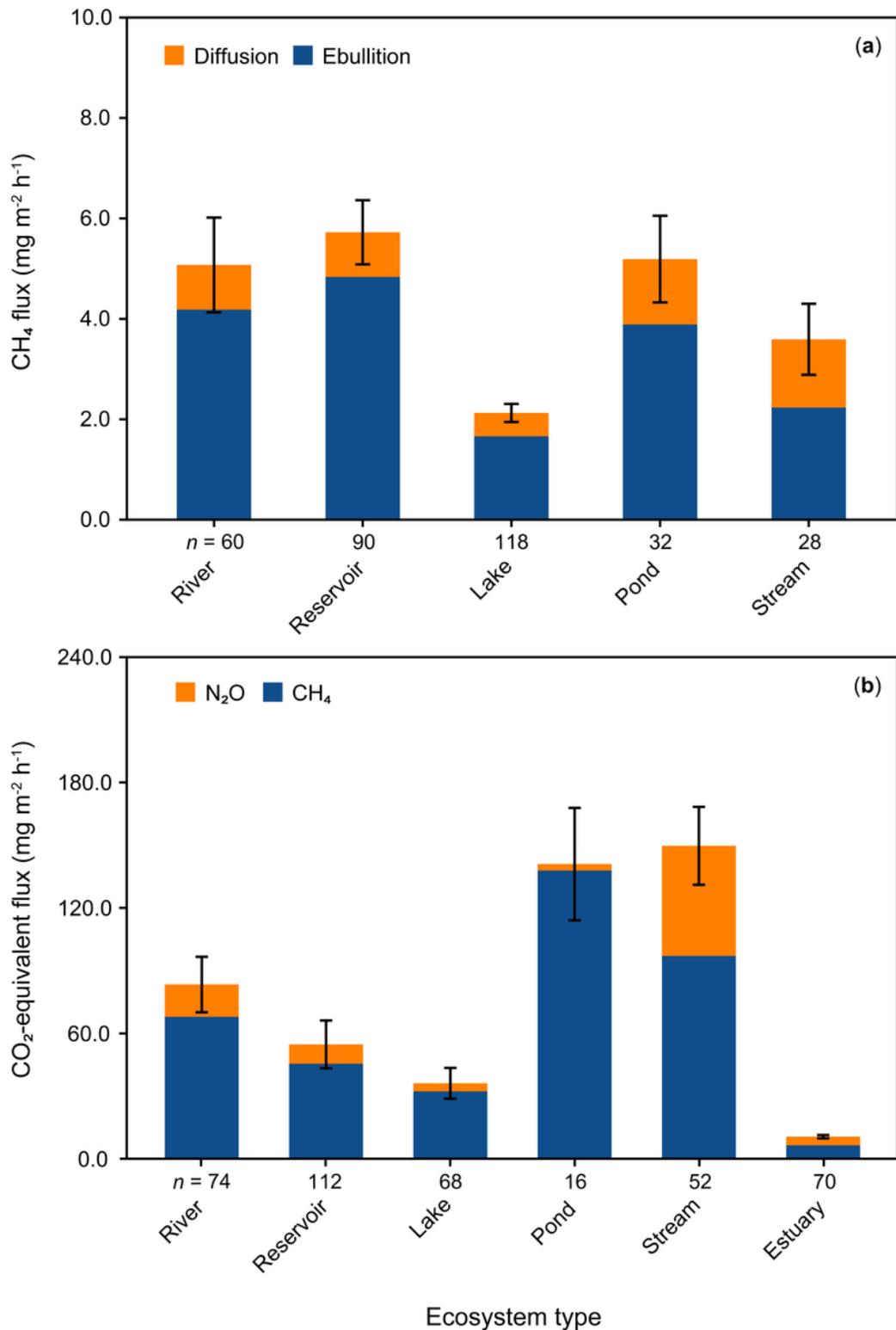


Figure 4

Relative contributions of diffusive and ebullitive CH₄ fluxes (a) and CO₂-equivalent fluxes of CH₄ and N₂O (b) based on simultaneous flux measurement data across various aquatic ecosystems. Estuaries are excluded from Fig. 4a due to insufficient observations available to reduce uncertainties. Bars represent the mean ± SE. The number of observations (n) for each water body is shown next to the x-axis. The CO₂-equivalent fluxes of CH₄ and N₂O are calculated using IPCC conversion factors (mass basis) of 28 and 265 over the time horizon of 100 years, respectively.

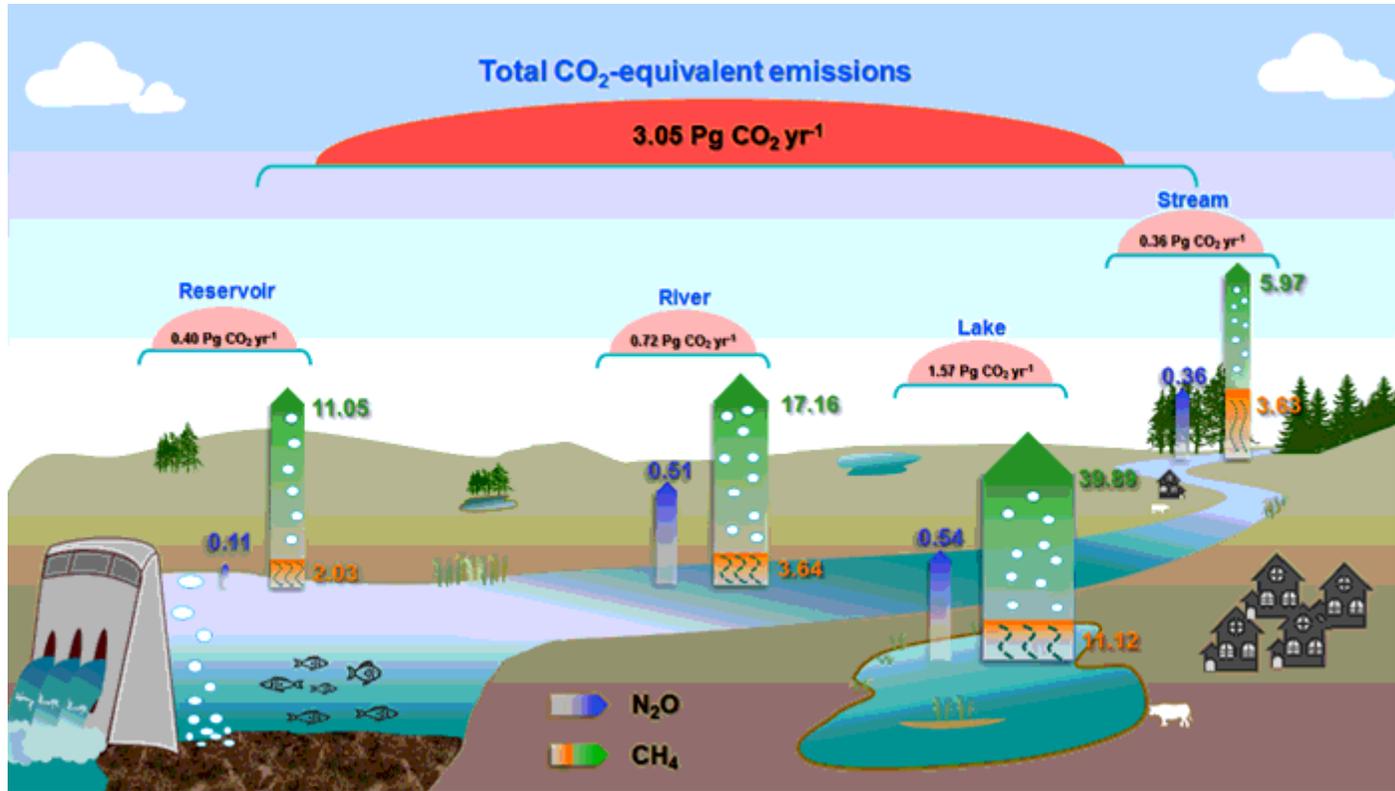


Figure 5

Global budgets of CH₄ and N₂O emissions from four major inland waters. The colored arrows represent estimated CH₄ and N₂O emissions (Tg CH₄/N₂O yr⁻¹) from specific freshwater systems, where orange and green parts of the arrows indicate diffusive and ebullitive CH₄ emissions, respectively; blue arrows indicate diffusive N₂O emissions; The source strength of CH₄ and N₂O is depicted here by the width of arrows in different inland waters.

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