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6 **Global methane and nitrous oxide emissions from inland waters and estuaries**7 Yajing Zheng^{‡1}, Shuang Wu^{‡1}, Shuqi Xiao[‡], Kai Yu[‡], Xiantao Fang[‡], Longlong Xia[&], Jinyang Wang^{‡¶},8 Shuwei Liu^{‡¶£*}, Chris Freeman[§] and Jianwen Zou^{‡¶£*}

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28 **Abstract**

29 Inland waters (rivers, reservoirs, lakes, ponds, streams) and estuaries are significant emitters of
30 methane (CH₄) and nitrous oxide (N₂O) to the atmosphere, while global estimates of these emissions
31 have been hampered due to the lack of a worldwide comprehensive dataset of CH₄ and N₂O flux
32 components. Here, we synthesize 2997 in-situ flux or concentration measurements of CH₄ and N₂O
33 from 277 peer-reviewed publications to estimate global CH₄ and N₂O emissions from inland waters and
34 estuaries. Inland waters including rivers, reservoirs, lakes and streams together release 95.18 Tg CH₄
35 yr⁻¹ (ebullition plus diffusion) and 1.48 Tg N₂O yr⁻¹ (diffusion) to the atmosphere, yielding an overall
36 CO₂-equivalent emission total of 3.06 Pg CO₂ yr⁻¹. The estimate of CH₄ and N₂O emissions represents
37 roughly 60% of CO₂ emissions (5.13 Pg CO₂ yr⁻¹) from these four inland aquatic systems, among
38 which lakes act as the largest emitter for both CH₄ and N₂O. Ebullition showed as a dominant flux
39 component of CH₄, contributing up to 62–84% of total CH₄ fluxes across all inland waters. Chamber-
40 derived CH₄ emission rates are significantly greater than those determined by diffusion model-based
41 methods for commonly capturing of both diffusive and ebullitive fluxes. Water dissolved oxygen (DO)
42 showed as a dominant factor among all variables to influence both CH₄ (diffusive and ebullitive) and
43 N₂O fluxes from inland waters. Our study reveals a major oversight in regional and global CH₄ budgets
44 from inland waters, caused by neglecting the dominant role of ebullition pathways in those emissions.
45 The estimated indirect N₂O EF₅ values suggest that a downward refinement is required in current IPCC
46 default EF₅ values for inland waters and estuaries. Our findings further indicate that a comprehensive
47 understanding of the magnitude and patterns of CH₄ and N₂O emissions from inland waters and
48 estuaries is essential in defining the way of how these aquatic systems will shape our climate.

1. Introduction

Inland waters (rivers, reservoirs, lakes, ponds and streams) and estuaries are important components for regional and global carbon (C) and nitrogen (N) cycles (Borges et al., 2015; Murray et al., 2015; Rosentreter et al., 2021; Sauniois et al., 2020; Soued et al., 2016). Large and increasing organic C and N loading from agricultural or non-agricultural pathways into inland waters and estuaries makes these aquatic systems active and critical in global methane (CH₄) and nitrous oxide (N₂O) budgets. However, estimates in the global emissions of CH₄ and N₂O from inland waters and estuaries 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 (Beaulieu et al., 2014a; Wu et al., 2019). Therefore, the knowledge gap still exists on our current understanding of global aquatic CH₄ fluxes to the atmosphere, and extremely poor accounting for the ebullitive component of CH₄ emissions (Wu et al., 2019). Moreover, the patterns and controls of N₂O emissions from inland waters and estuaries remain to be explored, such as the magnitudes and indirect N₂O emission factors (EF₅) involved in these aquatic systems. A robust estimate of CH₄ and N₂O emissions from inland waters and estuaries associated with various C and N sources can help in upcoming research work to refine the regional and global terrestrial greenhouse gas inventories with reduced uncertainties (Bastviken et al., 2004; Hu et al., 2016; Hama-Aziz et al., 2017).

Multiple approaches have been used to determine CH₄ fluxes (DelSontro et al., 2011; Rajkumar et al., 2008), mainly including 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 atmosphere (Wu et al., 2019). Ebullition represents an important

pathway for CH₄ release from aquatic systems, yet it has long been difficult to be quantified due to limited measurements and spatiotemporal heterogeneity, which ultimately hampers accurate estimates of the global CH₄ budget (Stanley et al., 2016). Thus, the contribution of ebullition to total CH₄ emissions from different inland waters and estuaries remains to be resolved.

Recently, the bottom-up method has been used to estimate global CH₄ and N₂O emissions from individual aquatic systems (e.g., rivers, streams or reservoirs), basically showing high spatio-temporal heterogeneity (Bastviken 2004, 2011; Saunois et al., 2020; Yao et al., 2020). Using a regression model, Hu et al. (2016) estimated global riverine N₂O emissions to be 30–35 Gg N₂O-N yr⁻¹, accounting for 0.16–0.19% of dissolved inorganic nitrogen (DIN) entering rivers and streams. Based on a review of available data, Stanley et al. (2016) estimated that global diffusive CH₄ emissions from streams and rivers can reach up to 26.8 Tg CH₄ yr⁻¹, equivalent to roughly 15–40% of CH₄ emissions from wetlands and lakes. However, these estimates did not distinguish the CH₄ and N₂O emissions through different emission pathways (diffusion vs. ebullition) and measurement methods (chamber-based vs. diffusion model-based). While natural wetlands are the largest natural source of CH₄ to the atmosphere, inland waters, such as lakes, rivers and reservoirs also contribute substantially to the global total of CH₄, yet not included in most global greenhouse gas (GHG) inventories due to lack of robust estimates with sufficient simultaneous measurement data on complete CH₄ flux components (Bastviken et al., 2011; Stanley et al., 2016). Besides, some small water bodies (i.e., streams or ponds) have been also documented as strong sources of CH₄ and N₂O to the atmosphere, although the attribution of these aquatic systems to total CH₄ and N₂O sources varies greatly in different data-derived approaches and the ways to estimate (Attermeyer et al., 2016; Saunois et al., 2020). In addition to inland waters, estuarine open waters have been also identified as small sources of CH₄ and N₂O to the atmosphere, but these

studies were limited in data size and did not partition sources from different flux components (Murray et al. 2015; Rosentreter et al., 2021). There is thus a need for a comprehensive understanding of the rates and drivers of CH₄ and N₂O fluxes across inland waters and estuaries.

In this study, we established a worldwide dataset by compiling 2997 direct measurements of CH₄ and N₂O fluxes or concentrations from six aquatic systems (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 fluxes using different flux-derived methods (chamber-based vs. diffusion model-based methods) across aquatic systems. Collectively, we aimed to estimate global CH₄ and N₂O emissions from inland waters and estuaries. We particularly focused on the relative contribution of the diffusive and ebullitive emission pathways to global total CH₄ emissions and environmental controls on CH₄ and N₂O emissions from inland waters and estuaries.

2. Methods

2.1. 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 aquatic systems 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

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gathering and reevaluating the older literature cited in the earlier reviews. We only included in-situ measurements of CH₄ and N₂O fluxes or concentrations from inland waters and estuaries. With the focus on natural or semi-natural aquatic systems, the gas flux data from small ponds constructed for sewage treatment or agricultural aquaculture production were excluded from our dataset due to extremely high C and N inputs. We 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 order (Yao et al., 2020). Specifically, riverine systems lower than fourth stream order were considered as streams, whereas those higher than fourth stream order were classified as rivers. 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 therefore alternatively 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. Surface water dissolved concentration measurements for CH₄ and/or N₂O were included in our dataset only provided that the flux data were simultaneously reported in the original studies.

The experimental locations were mostly clustered in Asia, Europe, and North America, with relatively few 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, with a fraction of 1333 flux measurements and 623 concentration measurements for CH₄ and a group of 673 flux measurements

and 368 concentration measurements for N₂O. Of these, 52 studies with 196 simultaneous flux measurements of CH₄ and N₂O were included (Supplementary Fig. S1).

Diffusive and ebullitive CH₄ fluxes spanned over four orders of magnitude, ranging from 0 to 56.00 mg m⁻² h⁻¹ and 0 to 60.42 mg m⁻² h⁻¹ in inland waters, and from -0.15 to 17.78 mg m⁻² h⁻¹ and 0.01 to 0.18 mg m⁻² h⁻¹ in estuaries, respectively. The CH₄ concentrations in inland waters and estuaries differed from 0 to 1070.40 and 0.01 to 2.27 μmol L⁻¹, respectively (Supplementary Table S1). Diffusive N₂O fluxes and concentrations had a range of -79.00 to 1151.77 μg m⁻² h⁻¹ and 0.50 to 1500.00 nmol L⁻¹ in inland waters, and a variation of -11.90 to 322.67 μg m⁻² h⁻¹ and 4.35 to 210.30 nmol L⁻¹ in estuarine open waters, respectively (Supplementary Table S2).

2.2. Upscaling and uncertainties

A Monte Carlo approach that allows for low uncertainty in determination of both surface areas and areal fluxes was performed to upscale CH₄ and N₂O fluxes from inland waters and estuaries to the global scale and estimate uncertainties (Rosentreter et al., 2021; Zhang et al., 2020). We ln-transformed all fluxes to guarantee a normal distribution before simulations. For each simulation, we generated a total of 1,000 random values from a normal distribution centered around means and with deviations confined for a given aquatic group areal and flux data (MATLAB R2021b). We multiplied randomly resampled fluxes by randomly selected surface areas to generate total emissions. Eventually, mean values and 95% confidence intervals of global CH₄ and N₂O emissions were obtained from these simulated results. In terms of CH₄ emissions, only studies with simultaneous measurement data on both diffusive and ebullitive fluxes were included in our estimates to reduce bias. For N₂O emissions, given that the ebullition was not the representative pathway of N₂O release from water bodies, we chose to only estimate diffusive N₂O emissions from inland waters and estuaries, 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 ebullitive CH₄ flux data. To generate annual mean gas fluxes, we assumed that 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 using a mixed-effects model by fitting a Boltzmann-Arrhenius function to the emission data (Yvon-Durocher et al., 2014):

$$\ln F(T) = \overline{E_M} \left(\frac{1}{kT_C} - \frac{1}{kT} \right) + \ln F(T_C)$$

Where $\ln F(T)$ and $\ln F(T_C)$ are the natural logarithm of CH₄ or N₂O emission rate at water temperature T and T_C , respectively. Of which, T is summer or winter water temperature in Kelvin, and T_C refers to annual water temperature. The parameter E_M (in eV), representing the apparent activation energy calculated from our dataset, is averaged to be 0.79 and 0.99 eV for CH₄ and N₂O, respectively. k is the Boltzmann constant (8.62×10^{-5} eV K⁻¹). However, we have failed to extrapolate CH₄ and N₂O emissions from ponds in this study due to small data size and large uncertainties in current available areal extents determination. All the data on global surface areas of aquatic systems were cited from recently published literature with solid updated estimates (Allen and Pavelsky, 2018; Murray et al., 2015; Raymond et al., 2013). The global distribution of observations used for CH₄ and N₂O upscaling in rivers, reservoirs, lakes, streams and estuaries has been provided in Fig. S2.

Compared to previous global estimates based on limited and localized CH₄ and N₂O flux data, we have dedicated to exploring the fractions of global total CH₄ emissions from inland waters through two major emission pathways (diffusion and ebullition) by gathering simultaneous flux measurement data. Meanwhile, we provided a full understanding of the magnitude and drivers of diffusive N₂O emissions from diverse inland waters and estuaries, relative to previously mostly limited in a single aquatic system

(Murray et al., 2015). However, uncertainties remained existed for our estimates. First, while a wide range in diffusive fluxes has been reported for estuarine open waters (Supplementary Table S2), measurements of ebullition remain notably scarce, especially for the simultaneous measurement data with diffusion (Rosentreter et al., 2021). 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 a mixed-effects model by fitting a Boltzmann-Arrhenius function (Yvon-Durocher et al., 2014). Third, we did not estimate the indirect EF_5 of N_2O based on the IPCC methodology to create a comparison in this study due to the 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 N_2O emissions from inland waters and estuaries, more extensive direct measurements of N_2O 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.

2.3. Calculation of indirect N_2O emission factors (EF_5)

Indirect N_2O 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% (Hergoualc'h et al., 2019). The indirect EF_5 of N_2O represents N_2O emissions from a given water body to the atmosphere as a fraction of N loading into the system (Hama-Aziz et al., 2017). IPCC defined the indirect EF_5 of N_2O as a ratio of N_2O -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 runoff (de Klein et al., 2006). Due to incomplete acquisition of the specific information (e.g., data on N leaching and runoff) required to determine the indirect EF_5 based on the IPCC methodology for all aquatic systems, we therefore

alternatively used the concentration method, i.e., the N_2O-N/NO_3^-N mass ratio derived from the concentration data of N_2O and nitrate (NO_3^-) reviewed from water bodies to estimate the indirect EF_5 of N_2O (Hama-Aziz et al., 2017) using the following equation:

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

Where EF_5 is the indirect emission factor determined by the N_2O-N/NO_3^-N mass ratio method, C_{N_2O-N} ($mg\ L^{-1}$) and $NO_3^- - N$ ($mg\ L^{-1}$) are concentrations measured at the water-air interface and dissolved in surface water of aquatic systems, respectively (Qin et al., 2019; Turner et al., 2015).

2.4. Estimation of CO_2 -equivalent emissions

Total CO_2 -equivalent emissions or emission intensity of CH_4 and N_2O from aquatic systems were estimated using the global warming potential of 28 for CH_4 and 265 for N_2O over the time horizon of 100 years (Ciais et al., 2014).

$$CO_2\text{-equivalent emissions} = 28 \times CH_4 + 265 \times N_2O$$

2.5. Statistical analyses

One-way analysis of variance (ANOVA) was performed to test the difference in CH_4 and N_2O fluxes between two CH_4 emission pathways (diffusion and ebullition), two flux-derived methods (chamber-based and model-based), and among different aquatic systems. Linear or nonlinear regressions were used to examine the dependence of CH_4 and N_2O 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 CH_4 and N_2O fluxes from inland waters and estuaries. All statistical analyses were carried out using JMP version 7.0 and R, and statistical significance was determined at the 0.05 probability level.

3. Results

3.1. Fluxes of CH₄ and N₂O among inland waters and estuaries

Ebullitive and diffusive CH₄ fluxes ranged from 0 to 60.42 mg m⁻² h⁻¹ and -0.15 to 56.00 mg m⁻² h⁻¹, with a global average of 3.20 mg m⁻² h⁻¹ and 1.29 mg m⁻² h⁻¹ across inland waters and estuaries, respectively (Fig. 1a). Ebullitive and diffusive CH₄ fluxes varied but showed no statistically significant difference among inland waters (Fig. 1a, $P > 0.05$), with the highest emission rate observed through ebullition from reservoirs (7.91 ± 1.57 mg m⁻² h⁻¹) and through diffusion from streams (3.20 ± 0.75 mg m⁻² h⁻¹). Diffusive N₂O fluxes varied from -0.08 to 1.15 mg m⁻² h⁻¹ across six water bodies. 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 seasonal fluxes of CH₄ from rivers showed a significant variation ($P < 0.01$), with the highest rates in summer and lowest rates in autumn and winter (Supplementary Fig. S3a). However, there was no such significant seasonal variation pattern for CH₄ or N₂O fluxes in the other water systems (Supplementary Fig. S3b-f, $P > 0.05$).

3.2. 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 aquatic systems. The mean CH₄ fluxes determined by chamber-based and diffusion model-based methods were largest in rivers (5.32 ± 1.30 mg m⁻² h⁻¹) and streams (2.50 ± 0.65 mg m⁻² h⁻¹), while the mean CH₄ fluxes were lowest in estuaries (1.56 ± 1.31 mg m⁻² h⁻¹) and reservoirs (0.41 ± 0.08 mg m⁻² h⁻¹), respectively (Fig. 2a). Generally, CH₄ fluxes measured by chamber-based methods were consistently greater than those determined by model-based methods, and significantly different results between the two methods were observed in rivers, reservoirs, lakes and ponds (Fig. 2a). 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 N₂O fluxes by the two methods occurred in ponds (Fig. 2b).

3.3. Ebullitive and diffusive CH₄ fluxes

We grouped available data of CH₄ fluxes into two categories as diffusive and ebullitive fluxes, where data were collected from studies that simultaneously measured both CH₄ flux components. Mean total CH₄ fluxes (ebullition plus diffusion) across five inland waters (rivers, reservoirs, lakes, ponds and streams) ranged from 0.01 to 54.90 mg m⁻² h⁻¹ (Fig. 3a), with the highest CH₄ fluxes in reservoirs (5.72±1.21 mg m⁻² h⁻¹) and the lowest in lakes (2.13±0.36 mg m⁻² h⁻¹). We calculated the relative contribution of diffusive and ebullitive components to total CH₄ fluxes in five inland waters. Ebullition occurred at each inland water system and contributed up to 62–84% of total CH₄ fluxes (Fig. 3a). The highest mean ebullitive CH₄ fluxes were captured in reservoirs (4.83±1.20 mg m⁻² h⁻¹), followed by those in rivers (4.18±1.84 mg m⁻² h⁻¹) and ponds (3.89±1.47 mg m⁻² h⁻¹). The mean diffusive CH₄ fluxes were highest in streams (1.36±0.36 mg m⁻² h⁻¹) and the lowest in lakes (0.46±0.08 mg m⁻² h⁻¹).

3.4. CO₂-equivalent fluxes of CH₄ and N₂O

Based on simultaneous flux measurement data, we calculated the CO₂-equivalent (CO₂-eq) fluxes of CH₄ and N₂O that reflect the emission intensity of a given terrestrial ecosystem from different gas components, independent of the extent of surface area it may cover (Fig. 3b). We found that, on average, CH₄ fluxes dominated the composition (78%) of the total emission intensity from CH₄ and N₂O across six aquatic systems. The highest emission intensity caused by CH₄ was found in ponds (137.90±42.31 mg CO₂-eq m⁻² h⁻¹), with the largest contribution up to 98%, while the lowest was found in estuaries

(6.59 ± 1.41 mg CO₂-eq m⁻² h⁻¹), with the smallest contribution of 62%. Streams showed the highest emission intensity (52.60 ± 16.61 mg CO₂-eq m⁻² h⁻¹) arising from N₂O fluxes, with a contribution of 35%, relative to the lowest contribution of 2% in ponds. Ponds and streams had the largest combined emission intensity of CH₄ and N₂O across six aquatic systems, while estuaries acted as the smallest potential aquatic emitter to the atmosphere.

3.5. Global CH₄ and N₂O emissions from inland waters and estuaries

In this study, the bottom-up approach was used to estimate global CH₄ and N₂O emissions from inland waters and estuaries. 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, while ponds were not considered in this global estimate due to small sample size of available flux measurements and limited information about area and global distribution of ponds. Annual total CH₄ emissions were estimated to be 75.00 Tg CH₄ yr⁻¹ through ebullition and 20.18 Tg CH₄ yr⁻¹ through diffusion, together yielding a global emission total of 95.18 Tg CH₄ yr⁻¹ (ebullition plus diffusion) from above four inland aquatic systems (Supplementary Table S4; Fig. 5). Of these, lakes (54.23 Tg CH₄ yr⁻¹) dominated this global emission total of CH₄, followed by emissions from rivers (18.51 Tg CH₄ yr⁻¹), reservoirs (12.53 Tg CH₄ yr⁻¹) and streams (9.92 Tg CH₄ yr⁻¹). In terms of the contribution of ebullition to total CH₄ emissions, reservoirs had the largest fraction of emissions (Fig. 5). Due to insufficient simultaneous ebullitive flux measurement data, we therefore chose to only estimate diffusive CH₄ emissions from estuaries, yielding a global total of 5.96 Tg CH₄ yr⁻¹ (Fig. 5).

Total diffusive N₂O emissions were estimated to be 1.48 Tg N₂O yr⁻¹ from the four inland waters, with a 95% CI range from 1.39 to 1.56 Tg N₂O yr⁻¹ (Supplementary Table S5). Of these, lakes (0.52 Tg N₂O yr⁻¹) and rivers (0.49 Tg N₂O yr⁻¹) are the two largest N₂O sources, followed by streams (0.36 Tg

N_2O yr^{-1}) and reservoirs (0.11 Tg N_2O yr^{-1}). Total CH_4 and N_2O emissions expressed as CO_2 -equivalents (eq) were estimated to be 3.06 Pg CO_2 -eq yr^{-1} (or 0.83 Pg C yr^{-1}) from inland waters over a 100-year time scale (Fig. 5). In addition, diffusive N_2O emissions from estuaries were estimated to be 0.40 Tg N_2O yr^{-1} , accounting for 27% of the total from inland waters (Fig. 5).

4. Discussion

4.1. Greater fluxes derived from chamber-based than model-based methods

Given the chamber-based and diffusion model-based methods have been commonly used to measure aquatic GHG fluxes (Deemer et al., 2016), mean CH_4 fluxes measured by chamber-based methods were greater than those determined by model-based methods, especially in rivers, reservoirs, lakes and ponds with significant differences (Fig. 2a). It is likely that 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 model (Wu et al., 2019), suggesting that ebullitive fluxes from waters may have been overlooked when using the model-based methods (Rajkumar et al., 2008; Wu et al., 2019). However, mean N_2O fluxes as reviewed in this study were comparable or similar in rates between the use of chamber-based and model-based methods. For chamber-based methods, uncertainties mainly come from the changes in natural turbulence at the water-air interface when deploying floating chambers (Murray et al., 2015). 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 interface (Wang et al., 2020). Compared with other aquatic systems, the lower wind and associated 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 bodies (Liu et al., 2016).

4.2. Ebullition dominating over diffusion in total CH_4 emissions from inland waters

Ebullition and diffusion have been recognized as two important pathways of CH_4 release from inland waters (DelSontro et al., 2011; McGinnis et al., 2006; Wu et al., 2019). However, the ebullitive CH_4 fluxes are challenging to measure (Saunois et al., 2020) and the episodic and stochastic nature of CH_4 ebullition complicates the capturing and analysis of fluxes, thereby few studies have quantified CH_4 ebullition in a recently updated global dataset (Stanley et al., 2016). In this study, we quantified the ebullitive and diffusive CH_4 fluxes by grouping data from studies that simultaneously measured both CH_4 flux components. Ebullition was found to be a dominant flux component of CH_4 , responsible for 62–84% of total emissions across all inland waters (Fig. 3a). 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 composition from these water bodies (Attermeyer et al., 2016; Saunois et al., 2020), while a relatively wider range of 10–80% was reported on the contribution of ebullition to total CH_4 fluxes from streams and rivers (Baulch et al., 2011; Sawakuchi et al., 2014). Reservoirs showed the highest mean ebullitive CH_4 fluxes, followed by in rivers and ponds (Fig. 3a). 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 (Beaulieu et al., 2014a; DelSontro et al., 2011). Meanwhile, recent studies have emphasized the importance of ebullition in shallow flowing waters or high-elevation rivers (Sawakuchi et al., 2014; Tranvik et al., 2009). Ebullition rates tend to be higher in shallow water areas with more abundant exogenous inputs of CH_4 and organic materials than in deep water areas (Beaulieu et al., 2014a; Zhang et al., 2020). Moreover, shallow aquatic habitats favoring bubble formation is also attributed to shorter water residence time and lower hydrostatic pressure that can limit the oxidation and dissolution of CH_4 rich bubbles released from the sediment (Wik et al., 2013;

Wu et al., 2019).

4.3. Drivers of CH₄ and N₂O emissions from inland waters and estuaries

We found that diffusive and ebullitive CH₄ fluxes increased linearly with surface water dissolved CH₄ concentrations across aquatic systems, but there was no significant difference in their dependence between the two flux components (Supplementary Fig. S4). Mean N₂O fluxes also increased with surface water dissolved N₂O concentrations in aquatic systems, whereas stronger relationships were observed in rivers and streams (Supplementary Fig. S5). Ebullitive CH₄ fluxes in lakes were only found to have a positive correlation with dissolved organic C (DOC) concentrations, with a more sensitive response than diffusive CH₄ fluxes (Supplementary Fig. S6a), which was supported by Deemer and Holgerson (2021), showing that the dependence of CH₄ fluxes on water DOC primarily occurred for diffusive fluxes, but was rarely observed for ebullitive fluxes in inland waters. Similarly, the indirect EF₅ of N₂O also showed a positive dependence on water DOC (Supplementary Fig. S6c), suggesting increasing N₂O emissions with water DOC enrichment (Liu et al., 2016). However, only diffusive CH₄ and N₂O fluxes in reservoirs had a negative correlation with water dissolved oxygen (DO) (Supplementary Fig. S6b). Similar negative dependence of N₂O on water DO was observed in rivers (Supplementary Fig. S6d), confirming the dominant role of denitrification in aquatic N₂O production (Freeman et al., 1997; Liu et al., 2016). Mean CH₄ fluxes were negatively dependent on water pH in rivers and ponds, to a larger extent in rivers for ebullitive fluxes (Supplementary Fig. S7a-b). Similarly, N₂O fluxes and the indirect EF₅ of N₂O in reservoirs had negative relationships with water pH (Supplementary Fig. S7c-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 (Tamimi et al., 1994). Both

diffusive and ebullitive CH₄ fluxes showed positive dependence on water temperature in rivers and lakes, with a stronger dependence for ebullitive fluxes observed in lakes (Supplementary Fig. S8). Mean N₂O fluxes showed positive dependence on water inorganic N components (NH₄⁺-N and NO₃⁻-N), different from the indirect EF₃ of N₂O having a positive correlation with NH₄⁺-N concentrations while a negative correlation with NO₃⁻-N concentrations (Supplementary Fig. S9). Our results confirmed previous experimental 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 environments (Burgos et al., 2015; Tian et al., 2018; Wu et al., 2021).

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 controlling factors. We found that water DO showed as a dominant factor among all variables to influence CH₄ (diffusive and ebullitive) and N₂O fluxes from inland waters (Supplementary Table S3), which was confirmed by previous findings that water DO appears to be strongly related to diffusive and ebullitive CH₄ fluxes in aquatic systems (Beaulieu et al., 2010; Chen et al., 2021). Water DO and DOC together could even explain 60% of the variance in diffusive CH₄ fluxes from inland waters. In terms of N₂O, NO₃⁻-N predominated among all parameters to affect N₂O fluxes across aquatic systems, and it together with water DO could explain 40% of the variance in N₂O fluxes from inland waters ($r^2 = 0.40$, $P < 0.001$), while a better simulation was obtained in estuaries by incorporating NO₃⁻-N with water temperature ($r^2 = 0.44$, $P < 0.001$). These findings suggested that specific statistical models should be developed to predict CH₄ and N₂O fluxes from divergent aquatic systems with contrasting water environments (Rasilo et al., 2015; Yao et al., 2020).

4.4. Global estimates of CH₄ and N₂O emissions in comparison with previous studies

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Generally, our estimate of global CH₄ emissions (95.18 Tg CH₄ yr⁻¹) from inland waters is close to the results of 103 Tg CH₄ yr⁻¹ reported by Bastviken et al. (2011) when summing emission sources from the same four freshwater systems as included in this study. A recent estimate by DelSontro et al. (2018) led to a global total of 159 Tg CH₄ yr⁻¹ (with a range of 117-212 Tg CH₄ yr⁻¹) from inland waters, 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 or semi-natural inland waters. However, they did not distinguish the emission sources from different pathways (i.e., ebullition or diffusion) based on simultaneous flux measurement data. Bastviken et al. (2011) initially estimated CH₄ emissions to be 1.5 Tg CH₄ yr⁻¹ from rivers and streams, which was limited by only including measurements from 21 sites globally. Our calculation yielded a diffusive emission total of 7.05 Tg CH₄ yr⁻¹ from rivers and streams globally (Fig. 5), lower than the rate of 26.8 Tg CH₄ yr⁻¹ estimated by Stanley et al. (2016) using a diffusive dataset dominated with modeling data. Our estimation of total CH₄ emissions from lakes (54.23 Tg CH₄ yr⁻¹) was less than a previous estimate of 71.6 Tg CH₄ yr⁻¹ by integrating separate ebullitive and diffusive emissions (Bastviken et al., 2011), 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 12.53 Tg CH₄ yr⁻¹ (Supplementary Table S4), which was comparable or close to some recent estimates using total CH₄ flux data (Deemer et al., 2016; Saunois et al., 2016).

Our estimation of riverine N₂O emissions totaled 0.49 Tg N₂O yr⁻¹ (Supplementary Table S5), close to the results reported by Yao et al. (2020) using a modeling approach, revealing 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 inland waters and estuaries (Boyer et al., 2006;

Dumont et al., 2005), modeling and predicting N₂O emissions from inland waters and estuaries are critical for developing and refining global N₂O emission inventories and seeking potential mitigation strategies. However, the existing studies estimating N₂O emissions from inland waters have been dominated by efforts in rivers (Cole and Caraco, 2001; Hu et al., 2016; Sawakuchi et al., 2014), with extremely limited information available in other inland waters, such as lakes, reservoirs and streams. Therefore, the global N₂O emissions from inland waters and estuaries remain to be quantified, particularly those from inland waters, which represent integral parts of the terrestrial landscape yet remain to be included in terrestrial greenhouse gas (GHG) budgets. Our global estimate of CH₄ and N₂O emissions from inland waters (0.83 Pg C yr⁻¹) could represent at least 32% of the estimated terrestrial GHG sink (Bastviken et al., 2011; Menson et al., 2007). Our estimation of diffusive N₂O emissions from estuaries (0.40 Tg N₂O yr⁻¹) is close to a recent bottom-up estimate of 0.36 Tg N₂O yr⁻¹ by Murray et al. (2015), and also falls well within the scope of 0.20–0.71 Tg N₂O yr⁻¹ reported by Robinson et al. (1998) based on a global extrapolation using regional data.

Using the concentration method, we calculated indirect emission factors (EF₅) of N₂O for inland waters and estuaries (Fig. 1c), with a range of 0.002% to 5.60% across all water bodies. Of these, ponds (1.43%) showed to have the highest EF₅ value, with a significant difference from other aquatic systems ($P < 0.001$), as compared to the lowest EF₅ value (0.07%) in estuaries. Generally, N₂O and NO₃⁻ concentrations exhibited linear positive correlations with relatively narrow uncertainty ranges in all water bodies, indicating that NO₃⁻ is a primary driver of aquatic N₂O production (Fig. 4). Although the ratios of N₂O-N/NO₃⁻-N varied substantially among aquatic ecosystems, over 90% of them were lower than the IPCC default value of 0.26% (Fig. 4). These results suggest that a downward refinement of the current IPCC default value is required in the future to more accurately estimate indirect N₂O emissions

from aquatic ecosystems as previously stressed (Qin et al., 2019; Xiao et al., 2019).

5. Conclusions

In this study, worldwide in-situ flux or concentration measurements of CH₄ and N₂O are compiled to estimate global CH₄ and N₂O emissions from four major inland waters (river, reservoir, lake and stream) and estuaries, particularly focusing on the contribution of different emission pathways to CH₄ emissions. Chamber-derived CH₄ flux rates are clearly greater than those determined by diffusion model-based methods, while not for N₂O with comparable rates between the two methods. Indirect N₂O emission factors (EF₅) from inland waters and estuaries in this study are fully estimated using the concentration method, to facilitate further development of IPCC default EF₅ values. Our results shed light on the role of ebullition in global CH₄ budgets from inland waters, which will strengthen our ability to define the way of how these natural/semi-natural ecosystems shape our climate.

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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.

Declaration of Competing Interest

The authors declare no competing interests.

Data Accessibility Statement

Our Supplementary Dataset supporting results of this study has been deposited in Dryad at: doi:10.5061/dryad.7m0cfxpwz for permanent citation or use.

References

- Allen, G. H., & Pavelsky, T. M. (2018). Global extent of rivers and streams. *Science*, 361(6402), 585–588. <https://doi.org/10.1126/science.aat0636>
- Attermeyer, K., Flury, S., Jayakumar, R., Fiener, P., Steger, K., Arya, V., Wilken, F., van Geldern, R., & Premke, K. (2016). Invasive floating macrophytes reduce greenhouse gas emissions from a small tropical lake. *Scientific Reports*, 6, 20424. <https://doi.org/10.1038/srep20424>
- Bastviken, D., Cole, J., Pace, M., & Tranvik, L. (2004). Methane emissions from lakes: Dependence of lake characteristics, two regional assessments, and a global estimate. *Global Biogeochemical Cycles*, 18(4), GB4009. <https://doi.org/10.1029/2004GB002238>

Bastviken, D., Tranvik, L. J., Downing, J. A., Crill, P. M., & Enrich-Prast, A. (2011). Freshwater methane emissions offset the continental carbon sink. *Science*, 331(6014), 50.

<https://doi.org/10.1126/science.1196808>

Baulch, H. M., Dillon, P. J., Maranger, R., & Schiff, S. L. (2011). Diffusive and ebullitive transport of methane and nitrous oxide from streams: Are bubble-mediated fluxes important?. *Journal of Geophysical Research: Biogeosciences*, 116, G04028. <https://doi.org/10.1029/2011JG001656>

Beaulieu, J. J., Shuster, W. D., & Rebholz, J. A. (2010). Nitrous oxide emissions from a large, impounded river: The Ohio River. *Environmental Science & Technology*, 44(19), 7527–7533.

<https://doi.org/10.1021/es1016735>

Beaulieu, J. J., Smolenski, R. L., Nietch, C. T., Townsend-Small, A., & Elovitz, M. S. (2014a). High methane emissions from a midlatitude reservoir draining an agricultural watershed. *Environmental Science & Technology*, 48(19), 11100–11108. <https://doi.org/10.1021/es501871g>

Beaulieu, J. J., Smolenski, R. L., Nietch, C. T., Townsend-Small, A., Elovitz, M. S., & Schubauer-Brigan, J. P. (2014b). Denitrification alternates between a source and sink of nitrous oxide in the hypolimnion of a thermally stratified reservoir. *Limnology and Oceanography*, 59(2), 495–506.

<https://doi.org/10.4319/lo.2014.59.2.0495>

Borges, A. V., Darchambeau, F., Teodoru, C. R., Marwick, T. R., Tamooh, F., Geeraert, N., Omengo, F. O., Guérin, F., Lambert, T., Morana, C., Okuku, E., & Bouillon, S. (2015). Globally significant greenhouse-gas emissions from African inland waters. *Nature Geoscience*, 8(6), 637–642.

<https://doi.org/10.1038/nego2486>

Boyer, E. W., Howarth, R. W., Galloway, J. N., Dentener, F. J., Green, P. A., & Vörösmarty, C. J. (2006). Riverine nitrogen export from the continents to the coasts. *Global Biogeochemical Cycles*, 20(1),

GB1S91. <https://doi.org/10.1029/2005GB002537>

Burgos, M., Sierra, A., Ortega, T., & Forja, J. M. (2015). Anthropogenic effects on greenhouse gas (CH₄ and N₂O) emissions in the Guadalete River Estuary (SW Spain). *Science of the Total Environment*, 503-504, 179–189. <https://doi.org/10.1016/j.scitotenv.2014.06.038>

Chen, S., Wang, D., Ding, Y., Yu, Z., Liu, L., Li, Y., Yang, D., Gao, Y., Tian, H., Cai, R., & Chen, Z. (2021). Ebullition controls on CH₄ emissions in an urban, eutrophic river: a potential time-scale bias in determining the aquatic CH₄ flux. *Environmental Science & Technology*, 55(11), 7287-7298. <https://doi.org/10.1021/acs.est.1c00114>

Ciais, P., Sabine, C., Bala, G., Bopp, L., Brovkin, V., Canadell, J., Chhabra, A., DeFries, R., Galloway, J., Heimann, M., Jones, C., Le Quéré, C., Myneni, R. B., Piao, S., & Thornton, P. (2014). Carbon and other biogeochemical cycles. In: *Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change* (pp. 465-570). Cambridge University Press.

Cole, J. J., & Caraco, N. (2001). Emissions of nitrous oxide (N₂O) from a tidal, freshwater river, the Hudson River, New York. *Environmental Science & Technology*, 35(6), 991–996. <https://doi.org/10.1021/es0015848>

Deemer, B. R., Harrison, J. A., Li, S., Beaulieu, J. J., DelSontro, T., Bezerra-Neto, J. F., Powers, S. M., dos Santos, M. A., & Vonk, J. A. (2016). Greenhouse gas emissions from reservoir water surfaces: A new global synthesis. *BioScience*, 66(11), 949–964. <https://doi.org/10.1093/biosci/biw117>

Deemer, B. R., & Holgerson, M. A. (2021). Drivers of methane flux differ between lakes and reservoirs, complicating global upscaling efforts. *Journal of Geophysical Research: Biogeosciences*, 126(4), e2019JG005600. <https://doi.org/10.1029/2019JG005600>

- DelSontro, T., Kunz, M. J., Kempter, T., Wüest, A., Wehrli, B., & Senn, D. B. (2011). Spatial heterogeneity of methane ebullition in a large tropical reservoir. *Environmental Science & Technology*, 45(23), 9866–9873. <https://doi.org/10.1021/es2005545>
- DelSontro, T., Beaulieu, J. J., & Downing, J. A. (2018). Greenhouse gas emissions from lakes and impoundments: Upscaling in the face of global change. *Limnology and Oceanography Letters*, 3(3), 64–75. <https://doi.org/10.1002/lol2.10073>
- De Klein, C., Novoa, R. S., Ogle, S., Smith, K. A., Rochette, P., Wirth, T. C., McConkey, B. G., Mosier, A., Rypdal, K., Walsh, M., & Williams, S. A. (2006). N₂O emissions from managed soils, and CO₂ emissions from lime and urea application. In: *2006 IPCC Guidelines for National Greenhouse Gas Inventories, Prepared by the National Greenhouse Gas Inventories Programme* (pp. 1-54). IGES.
- Dumont, E., Harrison, J. A., Bakker, E. J., & Seitzinger, S. P. (2005). Global distribution and sources of dissolved inorganic nitrogen export to the coastal zone: Results from a spatially explicit, global model. *Global Biogeochemical Cycles*, 19(4), GB4S02. <https://doi.org/10.1029/2005GB002488>
- Freeman, C., Lock, M. A., Hughes, S., Reynolds, B., & Hudson, J. A. (1997). Nitrous oxide emissions and the use of wetlands for water quality amelioration. *Environmental Science & Technology*, 31(8), 2438–2440. <https://doi.org/10.1021/es9604673>
- Hama-Aziz, Z. Q., Hiscock, K. M., & Cooper, R. J. (2017). Indirect nitrous oxide emission factors for agricultural field drains and headwater streams. *Environmental Science & Technology*, 51(1), 301–307. <https://doi.org/10.1021/acs.est.6b05094>
- Hergoualc’h, K., Akiyama, H., Bernoux, M., Chirinda, N., del Prado, A., Kasimir, Å., MacDonald, J. D., Ogle, S. M., Regina, K., van der Weerden, T. J., Liang, C., & Noble, A. (2019). N₂O emissions from managed soils, and CO₂ emissions from lime and urea application. In: *2019 Refinement to the*

2006 IPCC Guidelines for National Greenhouse Gas Inventories (pp. 1-39). IGES.

- Hu, M., Chen, D., & Dahlgren, R. A. (2016). Modeling nitrous oxide emission from rivers: a global assessment. *Global Change Biology*, 22(11), 3566–3582. <https://doi.org/10.1111/gcb.13351>
- Liu, S., Hu, Z., Wu, S., Li, S., Li, Z., & Zou, J. (2016). Methane and nitrous oxide emissions reduced following conversion of rice paddies to inland crab-fish aquaculture in southeast China. *Environmental Science & Technology*, 50(2), 633–642. <https://doi.org/10.1021/acs.est.5b04343>
- McGinnis, D. F., Greinert, J., Artemov, Y., Beaubien, S. E., & Wüest, A. (2006). Fate of rising methane bubbles in stratified waters: How much methane reaches the atmosphere?. *Journal of Geophysical Research: Oceans*, 111, C09007. <https://doi.org/10.1029/2005JC003183>
- Menon, S., Denman, K. L., Brasseur, G., Chidthaisong, A., Ciais, P., Cox, P. M., Dickinson, R. E., Hauglustaine, D., Heinze, C., Holland, E., Jacob, D., Lohmann, U., Ramachandran, S., Wofsy, S. C., & Zhang, X. (2007). *Couplings between changes in the climate system and biogeochemistry* (No. LBNL-464E). Lawrence Berkeley National Lab. (LBNL), Berkeley, CA (United States).
- Murray, R. H., Erler, D. V., & Eyre, B. D. (2015). Nitrous oxide fluxes in estuarine environments: response to global change. *Global Change Biology*, 21(9), 3219–3245. <https://doi.org/10.1111/gcb.12923>
- Qin, X., Li, Y., Goldberg, S., Wan, Y., Fan, M., Liao, Y., Wang, B., Gao, Q., & Li, Y. (2019). Assessment of indirect N₂O emission factors from agricultural river networks based on long-term study at high temporal resolution. *Environmental Science & Technology*, 53(18), 10781–10791. <https://doi.org/10.1021/acs.est.9b03896>
- Rajkumar, A. N., Barnes, J., Ramesh, R., Purvaja, R., & Upstill-Goddard, R. C. (2008). Methane and nitrous oxide fluxes in the polluted Adyar River and estuary, SE India. *Marine Pollution Bulletin*,

56(12), 2043–2051. <https://doi.org/10.1016/j.marpolbul.2008.08.005>

Rasilo, T., Prairie, Y. T., & Del Giorgio, P. A. (2015). Large-scale patterns in summer diffusive CH₄ fluxes across boreal lakes, and contribution to diffusive C emissions. *Global Change Biology*, 21(3), 1124–1139. <https://doi.org/10.1111/gcb.12741>

Raymond, P. A., Hartmann, J., Lauerwald, R., Sobek, S., McDonald, C., Hoover, M., Butman, D., Striegl, R., Mayorga, E., Humborg, C., Kortelainen, P., Dürr, H., Meybeck, M., Ciais, P., & Guth, P. (2013). Global carbon dioxide emissions from inland waters. *Nature*, 503(7476), 355–359. <https://doi.org/10.1038/nature12760>

Robinson, A. D., Nedwell, D. B., Harrison, R. M., & Ogilvie, B. G. (1998). Hypernutrified estuaries as sources of N₂O emission to the atmosphere: the estuary of the River Colne, Essex, UK. *Marine Ecology Progress Series*, 164, 59–71. <https://doi.org/10.3354/meps164059>

Rosentreter, J. A., Borges, A. V., Deemer, B. R., Holgerson, M. A., Liu, S., Song, C., Melack, J., Raymond, P. A., Duarte, C. M., Allen, G. H., Olefeldt, D., Poulter, B., Battin, T. I., & Eyre, B. D. (2021). Half of global methane emissions come from highly variable aquatic ecosystem sources. *Nature Geoscience*, 14(4), 225–230. <https://doi.org/10.1038/s41561-021-00715-2>

Saunois, M., Bousquet, P., Poulter, B., Pregon, A., Ciais, P., Canadell, J. G., ... & Zhu, Q. (2016). The global methane budget 2000–2012. *Earth System Science Data*, 8(2), 697–751. <https://doi.org/10.5194/essd-8-697-2016>

Saunois, M., Stavert, A. R., Poulter, B., Bousquet, P., Canadell, J. G., Jackson, R. B., ... & Zhuang, Q. (2020). The global methane budget 2000–2017. *Earth System Science Data*, 12(3), 1561–1623. <https://doi.org/10.5194/essd-12-1561-2020>

Sawakuchi, H. O., Bastviken, D., Sawakuchi, A. O., Krusche, A. V., Ballester, M. V., & Richey, J. E.

- (2014). Methane emissions from Amazonian Rivers and their contribution to the global methane budget. *Global Change Biology*, 20(9), 2829–2840. <https://doi.org/10.1111/gcb.12646>
- Soued, C., Del Giorgio, P. A., & Maranger, R. (2016). Nitrous oxide sinks and emissions in boreal aquatic networks in Québec. *Nature Geoscience*, 9(2), 116–120. <https://doi.org/10.1038/nego2611>
- Stanley, E. H., Casson, N. J., Christel, S. T., Carwford, J. T., Loken, L. C., & Oliver, S. K. (2016). The ecology of methane in streams and rivers: patterns, controls, and global significance. *Ecological Monographs*, 86(2), 146–171. <https://doi.org/10.1890/15-1027>
- Tamimi, A., Rinker, E. B., & Sandall, O. C. (1994). Diffusion coefficients for hydrogen sulfide, carbon dioxide, and nitrous oxide in water over the temperature range 293–368 K. *Journal of Chemical and Engineering data*, 39(2), 330–332. <https://doi.org/10.1021/je00014a031>
- Tian, L., Akiyama, H., Zhu, B., & Shen, X. (2018). Indirect N₂O emissions with seasonal variations from an agricultural drainage ditch mainly receiving interflow water. *Environmental Pollution*, 242, 480–491. <https://doi.org/10.1016/j.envpol.2018.07.018>
- Tranvik, L. J., Downing, J. A., Cotner, J. B., Loiselle, S. A., Striegl, R. G., Ballatore, T. J., ... & Weyhenmeyer, G. A. (2009). Lakes and reservoirs as regulators of carbon cycling and climate. *Limnology and Oceanography*, 54, 2298–2314. https://doi.org/10.4319/lo.2009.54.6_part_2.2298
- Turner, P. A., Griffis, T. J., Lee, X., Baker, J. M., Venterea, R. T., & Wood, J. D. (2015). Indirect nitrous oxide emissions from streams within the US Corn Belt scale with stream order. *Proceedings of the National Academy of Sciences*, 112(32), 9839–9843. <https://doi.org/10.1073/pnas.1503598112>
- Wang, R., Zhang, H., Zhang, W., Zheng X., Butterbach-Bahl, K., Li, S., & Han, S. (2020). An urban polluted river as a significant hotspot for water-atmosphere exchange of CH₄ and N₂O. *Environmental Pollution*, 264, 114770. <https://doi.org/10.1016/j.envpol.2020.114770>

- Wik, M., Crill, P. M., Varner, R. K., & Bastviken, D. (2013). Multiyear measurements of ebullitive methane flux from three subarctic lakes. *Journal of Geophysical Research: Biogeosciences*, 118(3), 1307-1321. <https://doi.org/10.1002/jgrg.20103>
- Wu, S., Li, S., Zou, Z., Hu, T., Hu, Z., Liu, S., & Zou, J. (2019). High methane emissions largely attributed to ebullitive fluxes from a subtropical river draining a rice paddy watershed in China. *Environmental Science & Technology*, 53(7), 3499–3507. <https://doi.org/10.1021/acs.est.8b05286>
- Wu, S., Zhang, T., Fang, X., Hu, Z., Hu, J., Liu, S., & Zou, J. (2021). Spatial-temporal variability of indirect nitrous oxide emissions and emission factors from a subtropical river draining a rice paddy watershed in China. *Agricultural and Forest Meteorology*, 307, 108519. <https://doi.org/10.1016/j.agrformet.2021.108519>
- Xiao, Q., Hu, Z., Fu, C., Bian, H., Lee, X., Chen, S., & Shang, D. (2019). Surface nitrous oxide concentrations and fluxes from water bodies of the agricultural watershed in Eastern China. *Environmental Pollution*, 251, 185–192. <https://doi.org/10.1016/j.envpol.2019.04.076>
- Yao, Y., Tian, H., Shi, H., Pan, S., Xu, R., Pan, N., & Canadell, J. G. (2020). Increased global nitrous oxide emissions from streams and rivers in the Anthropocene. *Nature Climate Change*, 10(2), 138–142. <https://doi.org/10.1038/s41558-019-0665-8>
- Yvon-Durocher, G., Allen, A. P., Bastviken, D., Conrad, R., Gudas, C., St-Pierre, A., Thanh-Duc, N., & Del Giorgio, P. A. (2014). Methane fluxes show consistent temperature dependence across microbial to ecosystem scales. *Nature*, 507(7493), 488–491. <https://doi.org/10.1038/nature13164>
- Zhang, L., Xia, X., Liu, S., Zhang, S., Li, S., Wang, J., Wang, G., Yang, Z., Stanley, E. H., & Raymond, P. A. (2020). Significant methane ebullition from alpine permafrost rivers on the East Qinghai-Tibet Plateau. *Nature Geoscience*, 13(5), 349–354. <https://doi.org/10.1038/s41561-020-0571-8>

Figure Legend

Fig. 1 Comparisons of diffusive and ebullitive CH₄ fluxes (a), diffusive N₂O fluxes (b) and indirect emission factors (EF₅) among aquatic systems. 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 and indirect emission factors, respectively. Asterisks in Fig. 1a indicate statistical differences in CH₄ fluxes between through diffusive and ebullitive pathways (**p* < 0.05; ***p* < 0.01; ****p* < 0.001).

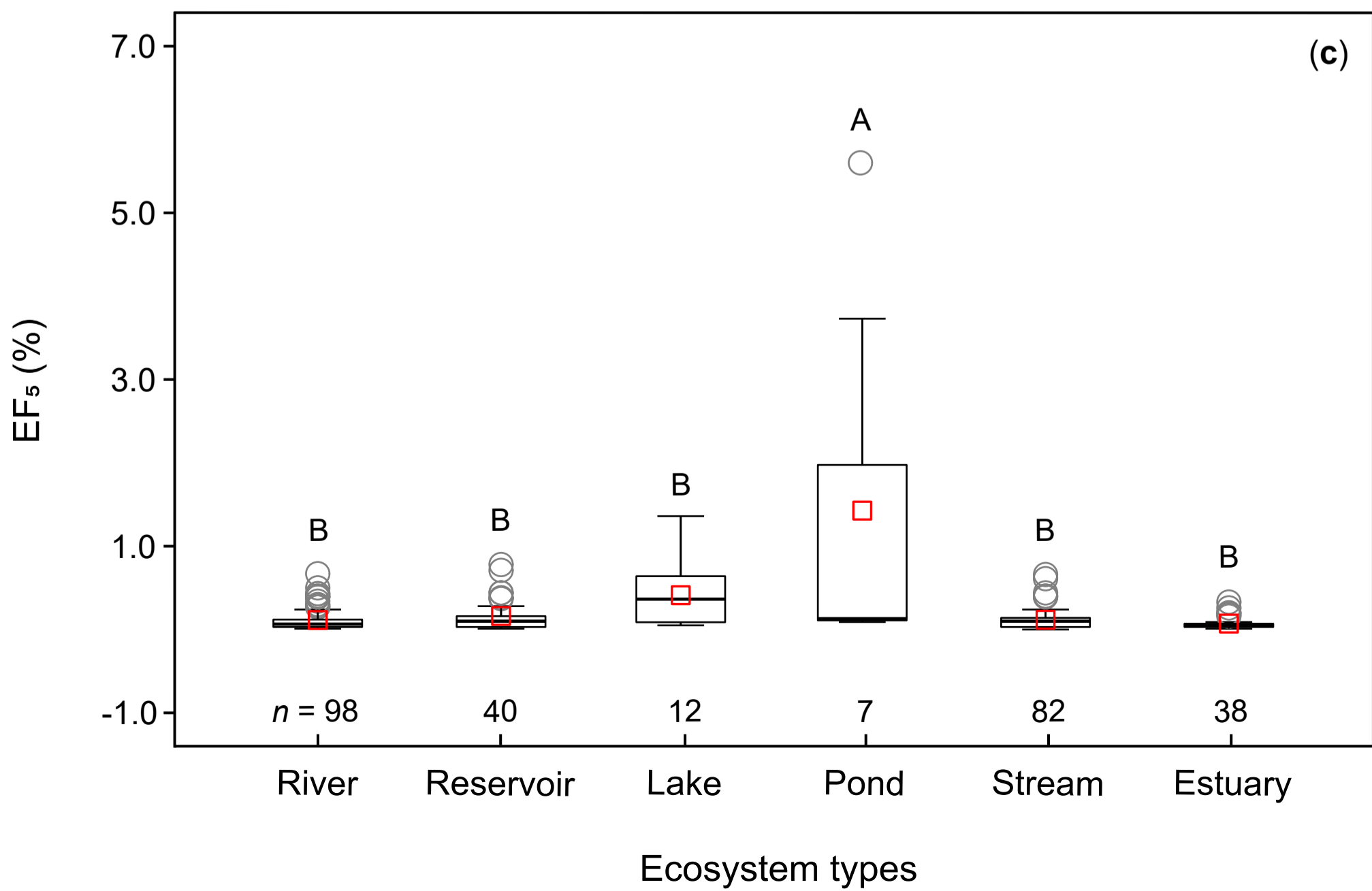
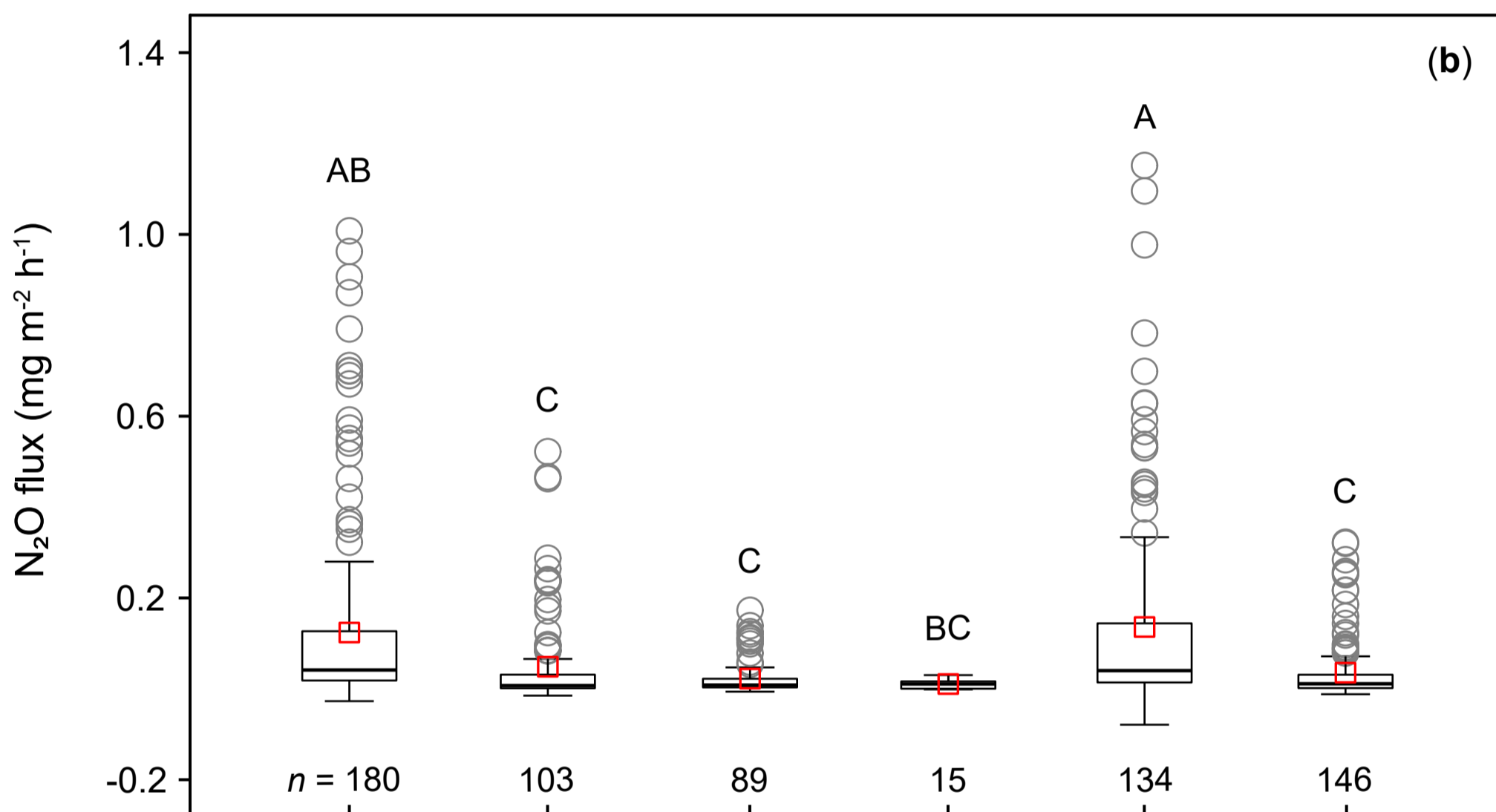
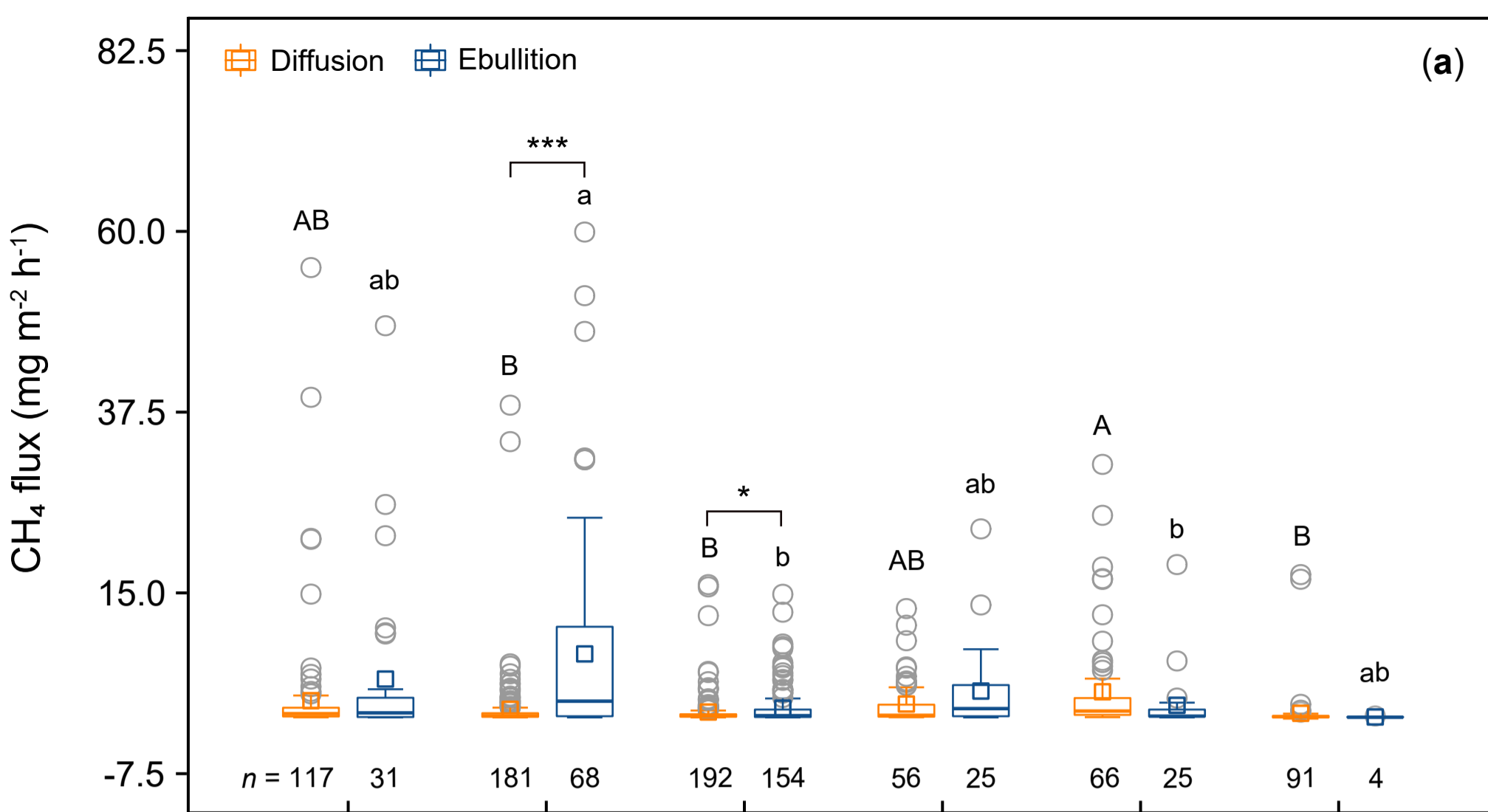
Fig. 2 Comparisons of CH₄ (a) and N₂O fluxes (b) between chamber-based and diffusion model-based methods across aquatic systems. Asterisks indicate statistical differences in gas fluxes between two measuring methods (**p* < 0.05; ***p* < 0.01; ****p* < 0.001). The number of observations (n) for each 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.

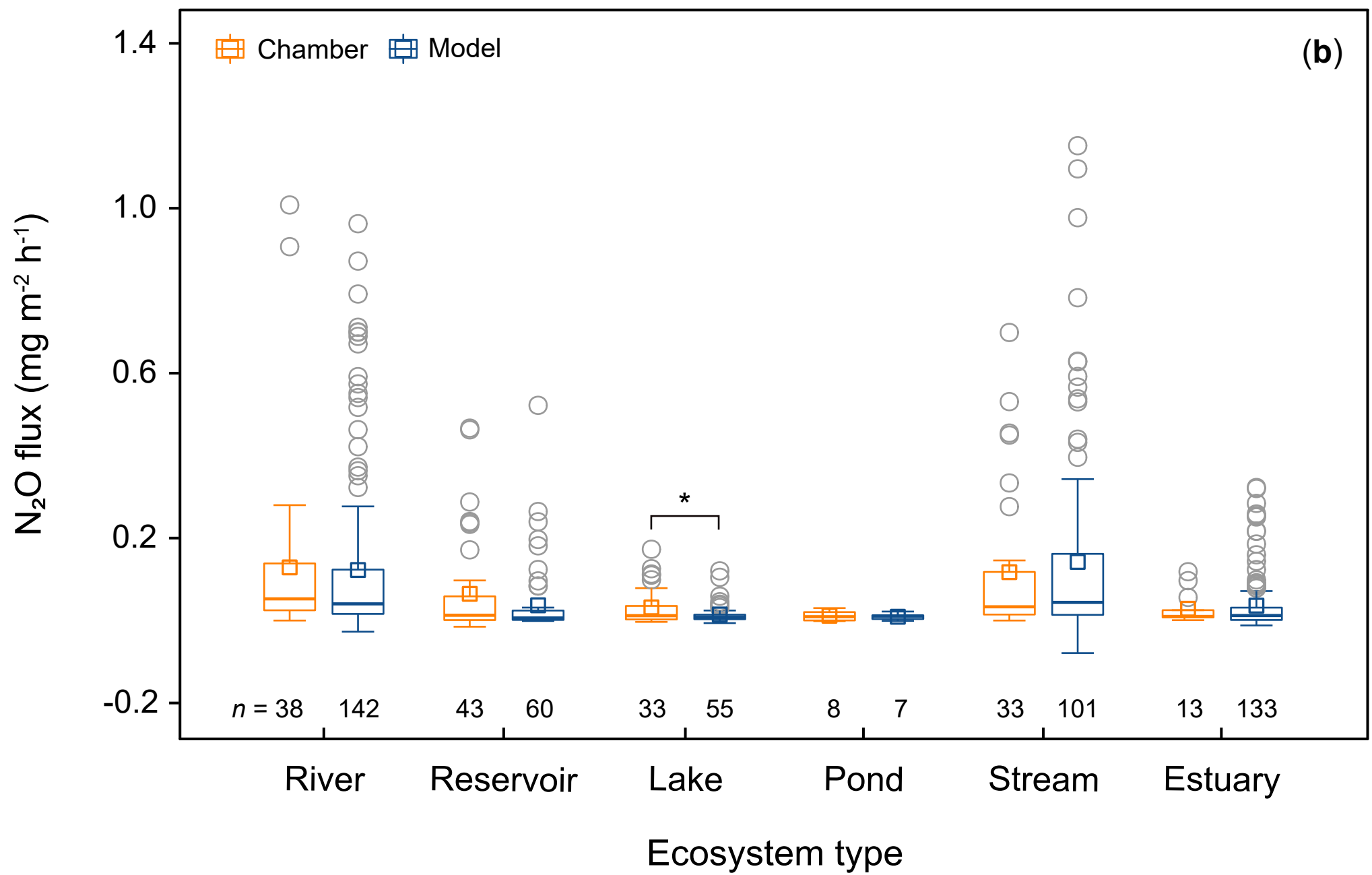
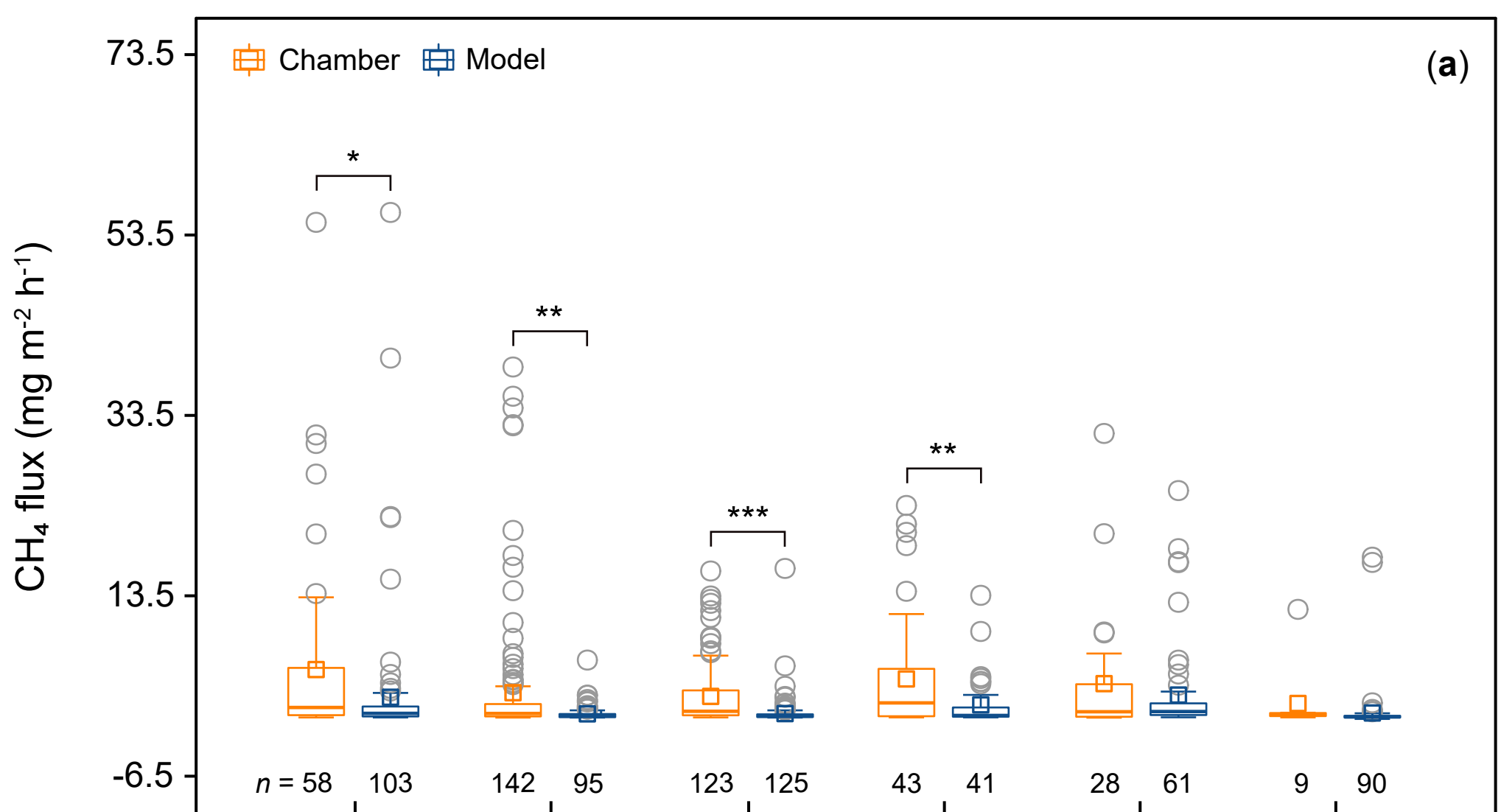
Fig. 3 Relative contributions of diffusive and ebullitive CH₄ fluxes (a) and CO₂-equivalent fluxes of CH₄ and N₂O (b) based on simultaneous flux measurement data across various aquatic systems. Estuaries are excluded from Fig. 4a due to insufficient observations available to reduce uncertainties. Bars 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.

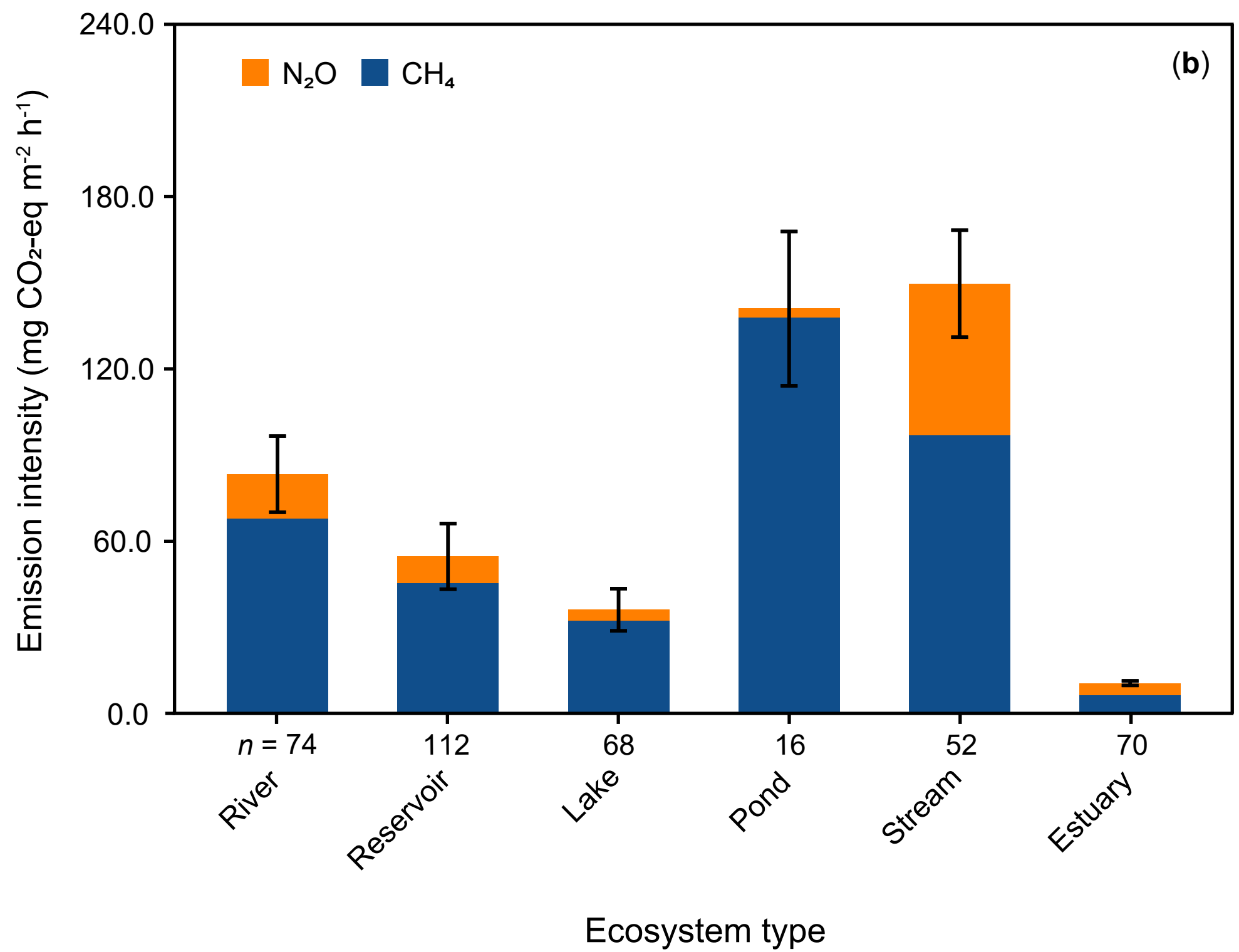
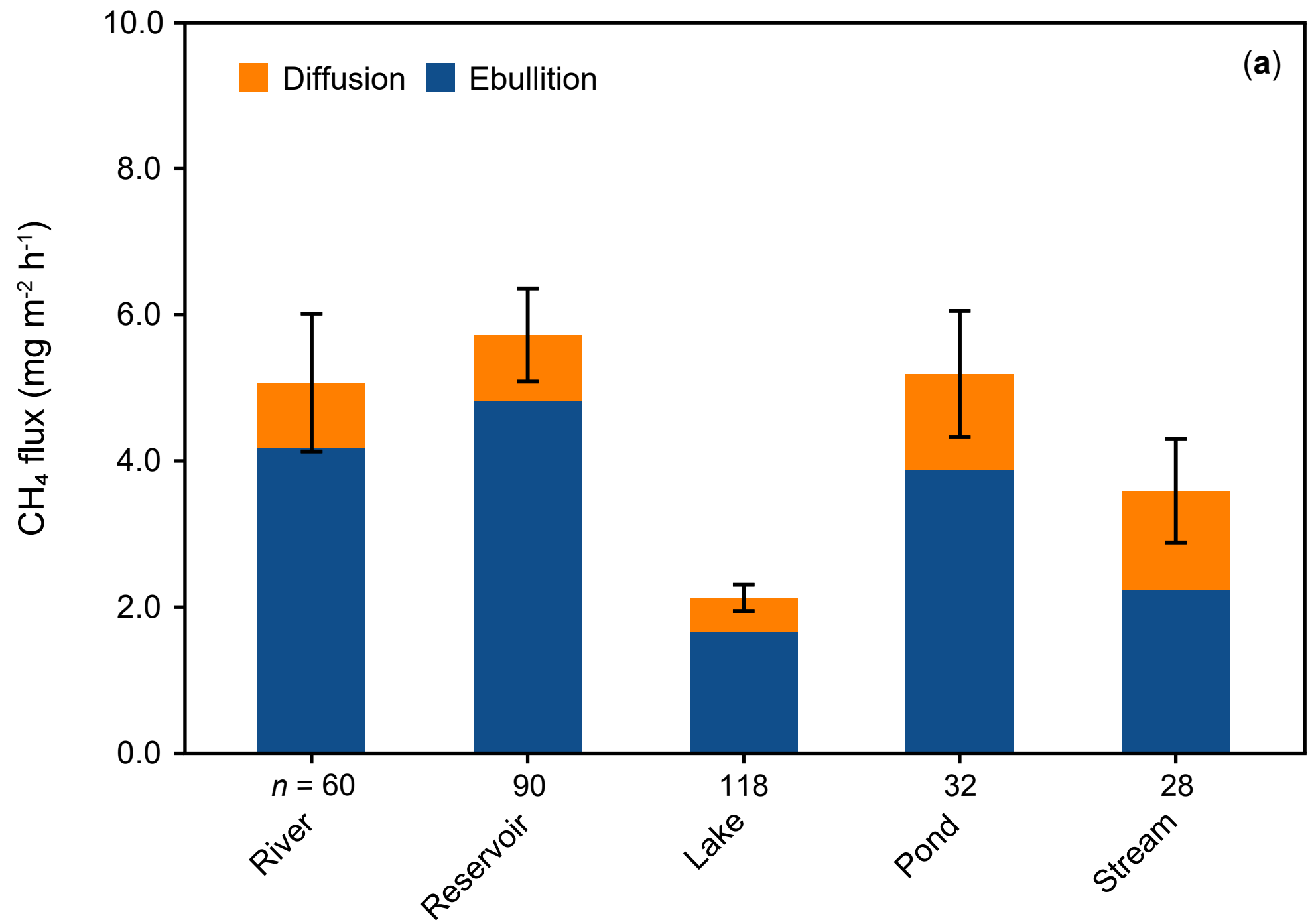
Fig. 4 Relationships between dissolved N₂O-N and NO₃⁻-N concentrations based on our dataset across

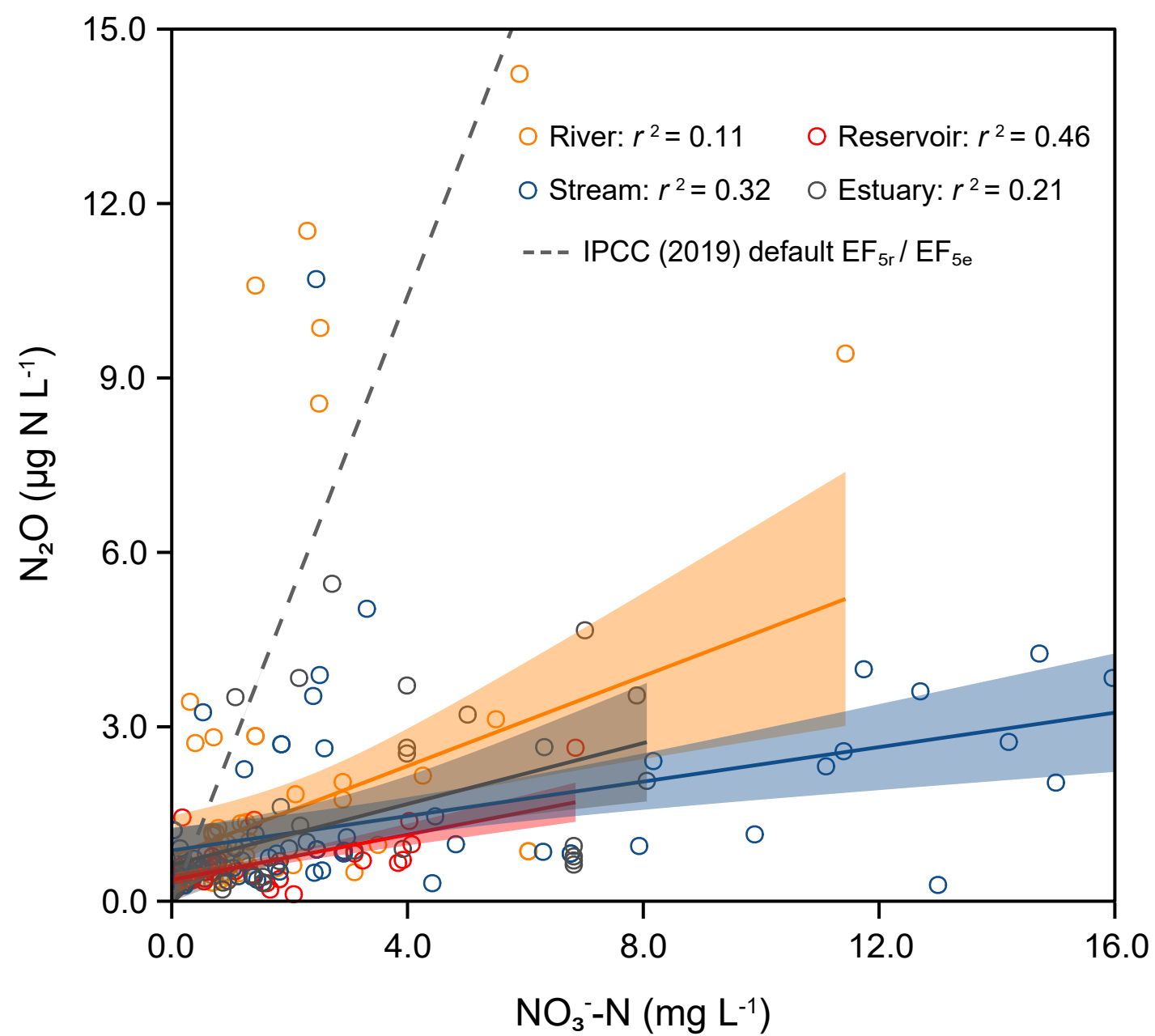
aquatic systems. Lines show the linear regressions for each aquatic system.

Fig. 5 Global budgets of CH₄ and N₂O emissions from four major inland waters and estuaries. The colored arrows represent estimated CH₄ and N₂O emissions (Tg CH₄/N₂O yr⁻¹) from specific inland waters and the estuarine system, 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 aquatic systems.









Total CO₂-equivalent emissions

3.33 Pg CO₂ yr⁻¹

