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Key Points:

- Water column contribution in N removal and N_2O emissions increased with stream order and it played a dominant role in large rivers
- The increase in the contact area of suspended sediment-water accounted for the increasing water column contribution with river size
- Riverine N removal and N_2O emissions would be underestimated approximately by 50% if neglecting water column processes

Supporting Information:

Supporting Information may be found in the online version of this article.

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The Dominant Role of the Water Column in Nitrogen Removal and N_2O Emissions in Large Rivers

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Abstract Rivers are important sites for nitrogen (N) cycling processes. N removal is thought to occur predominantly in the benthic zone and the role of the water column is frequently neglected. Here, we find that the water-air and sediment-water fluxes of N_2 and N_2O decreased, while the water column production increased with stream order through 4-year observations across six river networks in China. The water column contribution increased with stream order and accounted for more than 50% in rivers above fifth order. The increase in the contact area of suspended sediment (SPS)-water caused by higher SPS concentrations and river depths resulted in the shift as river size increased. N removal and N_2O emissions would be underestimated approximately by 50% if neglecting water column processes for the six river networks. This study highlights the necessity and provides a pathway to incorporate water column processes into models to balance the global N budget.

Plain Language Summary The entire global N budget remains out of balance, with total N inputs exceeding N losses. Streams and rivers serve as substantial recipients and processors of reactive N transported from terrestrial landscapes. The benthic zone is traditionally identified as a hotspot for N processing in fluvial systems. However, the role of the water column is poorly understood. Here, we found that the water column area-basis production rates of N_2 and N_2O increased with stream order although volumetric-basis production rates did not change significantly with stream order through 4-year observations across six river networks in China. The water column contribution increased with stream order and became dominant in large rivers. The increase in the contact area of SPS-water caused by higher SPS concentrations and water volume accounted for the shift as river size increased. The current estimates would underestimate riverine N removal and N_2O emissions by approximately 50% if neglecting water column processes based on the upscaling results for the six large river networks ranging from first to eighth order. Thus, our findings provide insight into the understanding of riverine N dynamics and highlight the important role of water column processes in N upscaling for closing regional and global N budgets.

1. Introduction

Nitrogen (N) is a major nutrient element for all organisms on Earth (Canfield et al., 2010). However, excess N in the environment, caused by its widespread applications in domestic, agricultural, and industrial activities, can not only result in eutrophication and hypoxia in water bodies and the destruction of habitats for resident organisms (Finlay et al., 2013; Galloway et al., 2003; Rockstrom et al., 2009; Vitousek et al., 1997) but is also responsible for stratospheric ozone depletion and climate change due to the production of nitrous oxide (N_2O) during the microbial transformation of N via nitrification and denitrification (Seitzinger & Phillips, 2017; Tian et al., 2020). N removal processes, including denitrification and anaerobic ammonium oxidation (anammox), which convert dissolved inorganic nitrogen (DIN) to di-nitrogen (N_2), are considered to be globally significant pathways for reactive N removal in aquatic ecosystems (Birgand et al., 2007; Xia et al., 2018). Processes controlling N removal

in aquatic environments, however, remain unclear, and in particular, critical hotspots for N transformation in streams and rivers are poorly constrained (Pinay et al., 2015). Current studies based on various models and emission factors present a wide range of estimates of riverine N removal proportions (30%–70%) (Galloway et al., 2004) and riverine N_2O emissions (0.03–2.1 Tg N_2O-N yr^{-1}) (Beaulieu et al., 2011; Hu et al., 2016; Kroeze et al., 2005, 2010; Maavara et al., 2019; Marzadri et al., 2021; Yao et al., 2020). This wide range means high uncertainties in the aquatic N budget, which might be responsible for the imbalance of global N budgets (Galloway, 1998; Gruber & Galloway, 2008; Schlesinger, 2009); additionally, this condition limits the forecasting of riverine N export and N_2O emissions under a changing environment.

Benthic and hyporheic zones are viewed as hotspots for N removal processes in the current paradigm of N cycling in streams and rivers (Beaulieu et al., 2011; Gomez-Velez et al., 2015; Marzadri et al., 2014; Quick et al., 2016). However, recently, laboratory incubation experiments have shown that denitrification, coupled nitrification-denitrification, and anammox could occur on suspended sediments (SPS) in oxic water columns because SPS can provide aerobic-sub-oxic micro-interfaces for simultaneous oxidation and reduction processes of aquatic N (Liu et al., 2013; Xia et al., 2016; S. B. Zhang et al., 2017). Elevated SPS concentrations have been linked with increasing water column denitrification rates in laboratory experiments (Liu et al., 2013). Ongoing laboratory incubation experiments, such as those in the Muskegon, Tippecanoe (Reisinger et al., 2016), and Ohio Rivers (Beaulieu et al., 2010), have demonstrated that the rates of potential N removal and N_2O production in the water column were higher than those in sediment. Accordingly, the water column containing SPS might serve as another potential hotspot for N removal and N_2O production in rivers. However, the role of the water column in N cycling processes is poorly understood and quantifying the contribution of the water column to N removal and N_2O emissions is a blind spot due to the lack of in situ observation data, and factors that regulate the contribution of the water column to N removal across river sizes are not well understood.

In this study, the role of the water column in N removal and N_2O emissions was investigated across six large river networks, including third- to eighth-order streams and rivers in China, with a consecutive 4-year sampling campaign from 2017 to 2020 (Figures S1 and S2 in Supporting Information S1). The flux of N_2, the final product of N removal processes, is used to quantify the capacity of N removal from aquatic systems (Zhao et al., 2015). We measured both sediment-water and water-air fluxes of N_2 and N_2O and calculated their water column production based on a mass balance method, further quantifying the water column contribution to N removal and N_2O emission across river sizes. We also studied the effects of riverine physiochemical and hydrologic variables and catchment characteristics on N_2 and N_2O production to explore the mechanisms controlling the relative role of the benthic zone and water column across river sizes. In addition, the simulation models were established to estimate water column production rates of N_2 and N_2O, providing a pathway to incorporate water column processes for better upscaling global riverine N_2 and N_2O emissions.

2. Materials and Methods

2.1. Study Area and Sampling Schedule

The six studied river networks (Liao River, Hai River, Yellow River, Huai River, Yangtze River, and Pearl River) are located within six individual large basins with watershed areas ranging from 3.15×10^5 to 1.78×10^6 km^2 (Figure S1 and Table S1 in Supporting Information S1). Due to the wide range of spatial extents (21°31′ to 45°10′ N, 90°13′ to 125°28′ E), the region covers distinct climate, land cover, geomorphology, and hydrology conditions (Table S1 in Supporting Information S1). The region is located within subtropical and temperate climate zones. Watershed-scale sampling campaigns were conducted at 55 sites with Strahler stream order ranging from third to eighth during a consecutive 4-year period from 2017 to 2020 (Figure S2 in Supporting Information S1). The sites were far away from reservoirs to eliminate their effects on riverine N_2 and N_2O emissions (details in Materials and Methods 1 in Supporting Information S1). Three seasonal sampling events, including spring (March or April), summer (August), and autumn-winter (October, November, or December), were performed during the daytime for each year. In addition, weekly/biweekly and diurnal observations were performed at two sites in 2019 (details in Supporting Information S1).

2.2. Sample Collection and Measurement

At each sampling, samples were collected at the mid-point between river bank and mid-channel for the determination of dissolved concentrations, water-air and sediment-water fluxes of N_2 and N_2O, and riverine physicochemical characteristics. Surface water samples were collected at wrist depth with a stainless water sampler (Purity WB-SS, China), and transferred to 12-ml Exetainer vials (Labco, UK) and 120-ml glass serum vials for the determination of dissolved N_2 and N_2O, respectively, which were preserved with 50% (w/v) $ZnCl_2$ solution. During transfer, water samples were drained into the bottom of the vials with a silicone tube slowly, allowing to overflow to avoid contamination by atmospheric N_2 and N_2O. Triplicate water samples were collected for the determination of dissolved N_2 and N_2O. The headspace equilibrium technique was adopted in situ by replacing 10 ml water with ultrahigh-purity helium in 120-ml glass serum vials to determine the dissolved N_2O concentration (Beaulieu et al., 2008). Gas equilibrium was achieved by vigorously shaking the glass vials for 10 min. The equilibrated headspace gas was extracted from each glass vial with an airtight syringe and injected into a pre-evacuated 30-ml aluminum foil airbag for later laboratory determination. The gas samples were stored at ambient temperature in the dark and measured by a gas chromatograph with an electron capture detector (Agilent 7890B GC-ECD). The dissolved N_2 concentration was measured using the N_2:Ar method by membrane-inlet mass spectrometry (MIMS) with a precision of 0.03% for the N_2:Ar ratio (Kana et al., 1994). The details on collecting samples and laboratory physicochemical analyses of samples were described in Supporting Information S1.

To determine the water-air N_2O flux, three floating chambers were deployed at the water surface at each sampling site. The shape, size, and material of the floating chambers have been described in our previous study (L. W. Zhang et al., 2020). After mixing the chamber gas, a 100-ml homogeneous gas sample was extracted from the chamber through a plastic tube and immediately transferred to airtight bags. The airbag was made from aluminum foil and evacuated before use. The headspace gas in the chambers was sampled every 10 min for a total duration of 60 min, and three duplicate samples were collected from each chamber at each sampling time point. An ambient sample of atmospheric air was sampled simultaneously at each site.

The sediment-water N_2 and N_2O fluxes were determined in situ by the open-bottom benthic chamber method (Eyre et al., 2013; Qin et al., 2017). At each site, three benthic chambers were gently deployed on the sediment at the same position as the floating chambers (right below the position of the floating chambers). The chambers were made of clear acrylic plastic, had a cylindrical shape (inner diameter 30 cm × inner height 20 cm) and had a total volume of ~14 L. Each chamber was equipped with a micropump (WKY1000, China) connected to two ports of the chamber with supple silicone tubes for circulating and mixing the water in the chamber. We fitted the chamber with another sampling port for water sample collection. In addition, the chamber had a 5-cm lip that allowed the chamber to insert into the sediment to ensure its tightness. Before installation, the chamber was filled with water to expel air. Water samples in the chamber were collected with a micropump at a 1-hr interval for a 6-hr incubation period, and the subsequent procedure was the same as that used to collect surface water samples for the determination of N_2 and N_2O. Equivalent surface water was added into the chamber through the sampling port after sampling at each time point. The water samples collected from the chamber at time 0 were measured as the N_2 and N_2O concentrations in the bottom water. The concentrations of N_2 and N_2O in the water samples were determined as described above. The N_2 and N_2O fluxes were calculated according to the concentration variation of samples in chambers, which was detailed in Supporting Information S1. The geographical and hydrological analyses, the method of upscaling N removal and N_2O emissions, and statistical analyses were also described in Supporting Information S1.

The mass balance model (Beaulieu et al., 2011) was modified to determine the net production of gaseous N (N_2 and N_2O) in the water column within the river system. We assumed that the discharge and the water column concentration of gaseous N remained constant for a short river reach, in which case the water-air flux of gaseous N (F_T) was the sum of the sediment-water flux of gaseous N (F_B) and the production rate of gaseous N in the water column (F_W) as follows:

$$F_T = F_B + F_W \quad (1)$$

Then, the production rate of gaseous N in the water column can be calculated with the following equation:

$$F_W = F_T - F_B \quad (2)$$

3. Results and Discussion

3.1. Spatiotemporal Patterns of Sediment-Water and Water-Air Fluxes of N_2 and N_2O

Across all sites, the sediment-water N_2 fluxes ranged from −5.9 to 20.8 mmol m^{-2} d^{-1} with an average of 2.2 ± 2.6 mmol m^{-2} d^{-1}, and the sediment-water N_2O fluxes ranged from −3.1 to 278.8 μmol m^{-2} d^{-1} with an average of 8.6 ± 20.3 μmol m^{-2} d^{-1}. In total, 93% and 95% of the measured sediment-water fluxes (n = 223) were positive for N_2 and N_2O, respectively, suggesting that the sediment acts principally as a source of N_2 and N_2O to the overlying water and atmosphere. The mean sediment-water N_2 and N_2O fluxes in the Liao and Hai Rivers were higher than those of the Huai, Pearl, Yangtze, and Yellow Rivers (Figure S3 in Supporting Information S1). Such a spatial pattern of sediment-water fluxes was generally consistent with the spatial variations in DIN in the overlying waters of the rivers (Figure S4 in Supporting Information S1). Moreover, sediment-water N_2 and N_2O fluxes were positively correlated with the total nitrogen (TN) in sediment and the DIN in overlying water ($p < 0.05$, Figure S5c in Supporting Information S1) because TN and DIN serve as substrates for N_2 and N_2O production (Birgand et al., 2007). The sediment-water N_2 and N_2O fluxes were positively related ($p < 0.05$), suggesting that N_2 and N_2O production in sediment may be mainly attributed to the same processes (i.e., denitrification and coupled nitrification-denitrification).

The sediment-water N_2 and N_2O fluxes of each river network exhibited significant seasonal variations, with the highest mean fluxes in summer (3.25 ± 2.77 mmol m^{-2} d^{-1} for N_2 and 13.42 ± 32.41 μmol m^{-2} d^{-1} for N_2O), followed by spring (1.16 ± 1.46 mmol m^{-2} d^{-1} and 7.22 ± 8.20 μmol m^{-2} d^{-1}) and autumn-winter (1.60 ± 2.20 mmol m^{-2} d^{-1} and 3.65 ± 3.82 μmol m^{-2} d^{-1}, Figure S3 in Supporting Information S1), implying water temperature had an impact on sediment-water N_2 and N_2O production (the effect of other variables is shown in Results and Discussion 1 in Supporting Information S1). Consistently, weekly/biweekly and diurnal variations in sediment-water N_2 and N_2O fluxes (Results and Discussion 2 in Supporting Information S1) exhibited almost the same trend as that of water temperature (Figure S7 in Supporting Information S1). Across all observations, the sediment-water N_2 and N_2O fluxes were positively related to water temperature ($p < 0.01$, Figure S5 in Supporting Information S1) and negatively correlated with dissolved oxygen (DO) ($p < 0.01$, Figure S5 in Supporting Information S1), resulting from the fact that both high temperature and low levels of DO are conducive to N removal processes, including denitrification and anammox.

Dissolved N_2 and N_2O concentrations in the water column were supersaturated at almost all sites and times (Results and Discussion 3 in Supporting Information S1). The total N_2 fluxes at the water-air interface across all studied rivers ranged from −9.3 to 61.4 mmol m^{-2} d^{-1}, with an average of 7.7 ± 8.7 mmol m^{-2} d^{-1}. The total N_2O fluxes ranged from −4.9 to 712.2 μmol m^{-2} d^{-1}, with an average of 26.1 ± 64.7 μmol m^{-2} d^{-1}. The N_2 and N_2O fluxes observed in the studied river networks were within the reported range for global rivers (Table S2 in Supporting Information S1). The temporal variation in the total fluxes of N_2 and N_2O was the same as that of the sediment-water fluxes (Figure S8 in Supporting Information S1), showing higher rates in summer with higher temperatures. In addition, the total N_2 and N_2O fluxes generally decreased with latitude except for the Liao River due to the much higher level of DIN in the Liao River network than in the other river networks (Figures S4 and S8 in Supporting Information S1).

3.2. Key Controls on Water Column Production of N_2 and N_2O

The average ratios of surface to bottom water concentrations of N_2 and N_2O were higher than 1 (Figure 1a), suggesting the production of N_2 and N_2O in the water column. The water column N_2 production rates ranged from −10.3 to 48.5 mmol m^{-2} d^{-1} with an average of 5.5 ± 7.5 mmol m^{-2} d^{-1}, and the water column N_2O production rates ranged from −5.9 to 711.9 μmol m^{-2} d^{-1} with an average of 17.5 ± 60.0 μmol m^{-2} d^{-1}. There were significantly positive relationships between water column N_2 and N_2O production rates and river depth (Figure S9d in Supporting Information S1). The water column volumetric-basis N_2 production rates (areal-basis rates divided by depth) ranged from −5.5 to 39.1 mmol m^{-3} d^{-1} with an average of 2.1 ± 3.6 mmol m^{-3} d^{-1}, and the water column N_2O production rates on volumetric basis ranged from −3.1 to 50.3 μmol m^{-3} d^{-1} with an average of 4.1 ± 5.4 μmol m^{-3} d^{-1}. The error propagation leads to an uncertainty of approximately 17% and 16% for the water column production rates of N_2 and N_2O, respectively (See details of the error propagation calculations in Supporting Information S1). The Liao and Yellow Rivers had higher water column production rates of N_2 and N_2O than the other four rivers (Figure S10 in Supporting Information S1). The temporal variation in the water

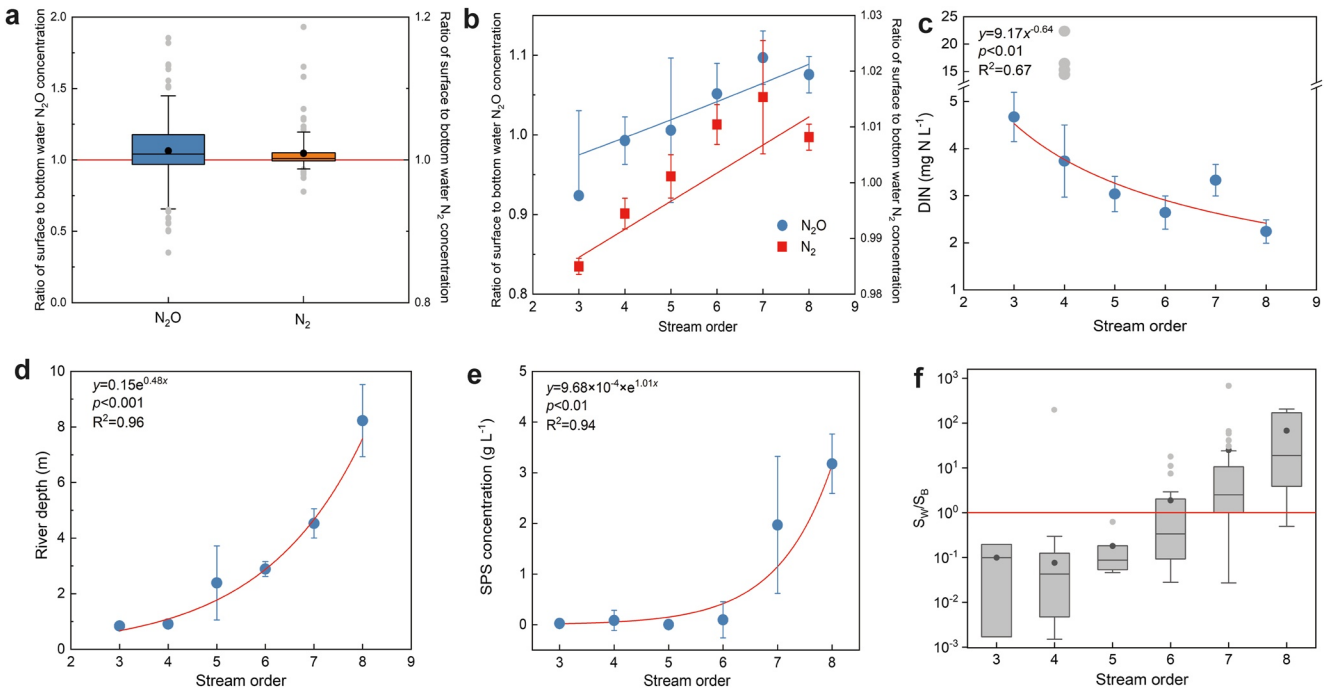

Figure 1. Ratios of surface to bottom water concentration of N_2 and N_2O (a), and variation in the ratios (b), DIN concentrations (c), river depth (d), SPS concentration (e), and S_W/S_B (f) with stream order. The gray dots in c represent urban sites that were excluded from the analysis. The solid red lines in c-e represent the fit of power or exponential regressions through observed data. S_W/S_B in f represent the ratio of SPS-water contact area (S_W) to sediment-water contact area (S_B, details in Supporting information S1), and the solid red line represents $S_W/S_B = 1$. Boxes in a and f are bounded by the 25th (Q1) and 75th percentiles (Q3), and whiskers represent 1.5× the interquartile range (IQR), and the solid line is the median value. The values greater than Q3 + 1.5 × IQR or Q1 − 1.5 × IQR are identified as outliers. The ratios of surface to bottom water concentration, DIN concentration, depth, and SPS concentration in b to e are the mean values of the sampling sites for each stream order. All error bars show mean ± 1 s.e.m.

column production rates of N_2 and N_2O was the same as that of the sediment-water N_2 and N_2O fluxes, showing higher rates in summer with higher temperatures (Figures S7 and S10 in Supporting Information S1).

Similar to sediment-water fluxes, the water column production rates of N_2 and N_2O on both areal and volumetric basis were significantly correlated with the DIN, water temperature, and DO ($p < 0.05$, Figures S9 and S11 in Supporting Information S1). Previous studies suggest that SPS can facilitate N transformation, as SPS provide microsites, substrates, and favorable oxygen conditions for microbial growth in water columns (Liu et al., 2013; Xia et al., 2016, 2017). Across all the data for the six river networks, the SPS concentration had a significantly positive relationship with volumetric-basis water column production rates while had no relationship with areal-basis production rates (Figure S12 in Supporting Information S1). Besides SPS concentration, the large difference in SPS physiochemical characteristics among different networks, such as the content of total organic carbon (TOC), may play a role in water column production rates of N_2 and N_2O. When considering the SPS concentration and TOC simultaneously, there was a significantly elevated correlation between the water column volumetric-basis production rates and SPS × TOC (Figure S12 in Supporting Information S1). This result is probably due to the effect of organic carbon as an electron donor and oxygen consumer on the N removal processes occurring on SPS (Xia et al., 2016). This is evidential by the higher water column production rates associated with the higher values of SPS × TOC of the Liao and Yellow Rivers than those of the other four rivers (Figures S4 and S10 in Supporting Information S1).

The above analysis showed that DIN, temperature, and SPS × TOC were the key factors that predicted temporal and spatial variability in the water column production of N_2 and N_2O. Further considering the mechanisms by which DIN, temperature, and SPS affect N transformation rates (details, Materials and Methods in Supporting Information S1), the following formula can be used to fit the water column volumetric-basis production rates of

N_2 (F_{w-N_2}, mmol m^{-3} d^{-1}) and N_2O (F_{w-N_2O}, μmol m^{-3} d^{-1}) through multivariate nonlinear regression with the measured values:

$$F_{w-N_2} = 2.89 \times 10^7 \times [\mathrm{DIN}]^{0.50} \times [\mathrm{SPS} \times \mathrm{TOC}]^{0.22} \times e^{-\frac{4948}{T}} \quad (3)$$

$$F_{w-N_2O} = 8.92 \times 10^7 \times [\mathrm{DIN}]^{0.69} \times [\mathrm{SPS} \times \mathrm{TOC}]^{0.10} \times e^{-\frac{5134}{T}} \quad (4)$$

where [DIN] (mg N L^{-1}) is the concentration of DIN in the water column; [SPS] (g L^{-1}) denotes the concentration of SPS; [TOC] (mg g^{-1}) represents the content of TOC in SPS; and T (K) is the absolute temperature. We found a reasonably good fit between the measured and fitted values of the water column production rates of N_2 ($n = 159$, $R^2 = 0.41$, Figure S13 in Supporting Information S1) and N_2O ($n = 160$, $R^2 = 0.40$, Figure S13 in Supporting Information S1). Furthermore, the calculated activation energy based on the estimated values was within the reported range for the activation energy of N_2 and N_2O production processes (Results and Discussion 4 in Supporting Information S1). Hence, the simulation models were robust and applicable for estimating the water column production rates of N_2 and N_2O in river networks.

3.3. Variations in Water Column Contributions With River Size

Across all data, we found that water-air N_2 and N_2O fluxes decreased with stream order as a power function (Figure 2a). Potential explanations of this decline with stream order include the decrease in wetted-perimeter to cross-sectional area ratio (Rode et al., 2015) and DIN. Overlying-water DIN decreased with stream order as a power function (Figure 1c). Together, we observed a positive relationship between the mean DIN and the fraction of arable land cover for the six river networks ($p < 0.01$, Figure S4a in Supporting Information S1), suggesting the importance of terrestrial reactive N inputs in sustaining N removal processes within river networks. High-order rivers are generally characterized by the longer transport of N derived from terrestrial landscapes, and a part of the N is removed during transport and released to the atmosphere, thus leading to lower DIN concentrations than those found in headstreams and low-order rivers (Turner et al., 2015).

In contrast to decreasing water-air fluxes along stream order, the ratios of surface to bottom water concentrations of N_2 and N_2O (Figure 1b) and the water column areal-basis production rates increased significantly with stream order (Figure 2a) although the volumetric-basis water column production rates exhibited insignificant relationships ($p > 0.05$) with stream order (Figure S14 in Supporting Information S1). We determined the water column contributions to N removal and N_2O emissions by calculating the percentages of areal-basis water column production rates to total fluxes. The average water column contributions were 61 ± 31% and 58 ± 26% for N_2 and N_2O across all observations, respectively, and they were greater than 50% in all seasons and in all river networks except for the Hai River (Figure 3). The water column contributions to N_2 and N_2O fluxes increased with stream order, and the water column accounted for more than 50% of the N_2 and N_2O fluxes in rivers greater than fifth order (Figure 2b). In addition, according to the high-resolution temporal observations at the Huainan and Aishan sites, which have stream orders greater than six, the water column contributions to the N_2 and N_2O fluxes were higher than 50% on average for the weekly or biweekly and diurnal observations (Figures S16 and S17 in Supporting Information S1). The above results infer that water column plays a dominant role in N removal and N_2O emissions in large rivers despite some uncertainties caused by groundwater inputs (see uncertainty analysis in Results and Discussion 5 in Supporting Information S1).

The pattern of increasing water column contribution with stream order was attributed to the different responses of sediment-water fluxes and areal-basis water column production rates of N_2 and N_2O to the increase in river size (Figure 2a). The load of SPS, the habitat for associated microorganisms driving water column biogeochemical processes, showed an exponential increase with river size in this study (Figure 1e), and the abundance of relevant N transformation bacteria increased with SPS concentration as a power function (Xia et al., 2017). Additionally, a high SPS concentration was associated with a lower O_2 concentration ($p < 0.01$), creating conditions favorable for anaerobic N transformation (i.e., denitrification and anammox). In addition, with the increase in SPS concentration, river depth, and water column volume (Figure 1 and Figure S14 in Supporting Information S1), the ratio of SPS-water to sediment-water contact area (Materials and Methods in Supporting Information S1) increased with stream order and was larger than one in rivers greater than fifth order in this study (Figure 1f), which was similar to the results for the main stems of 10 large US rivers (Gardner & Doyle, 2018). In other words, compared

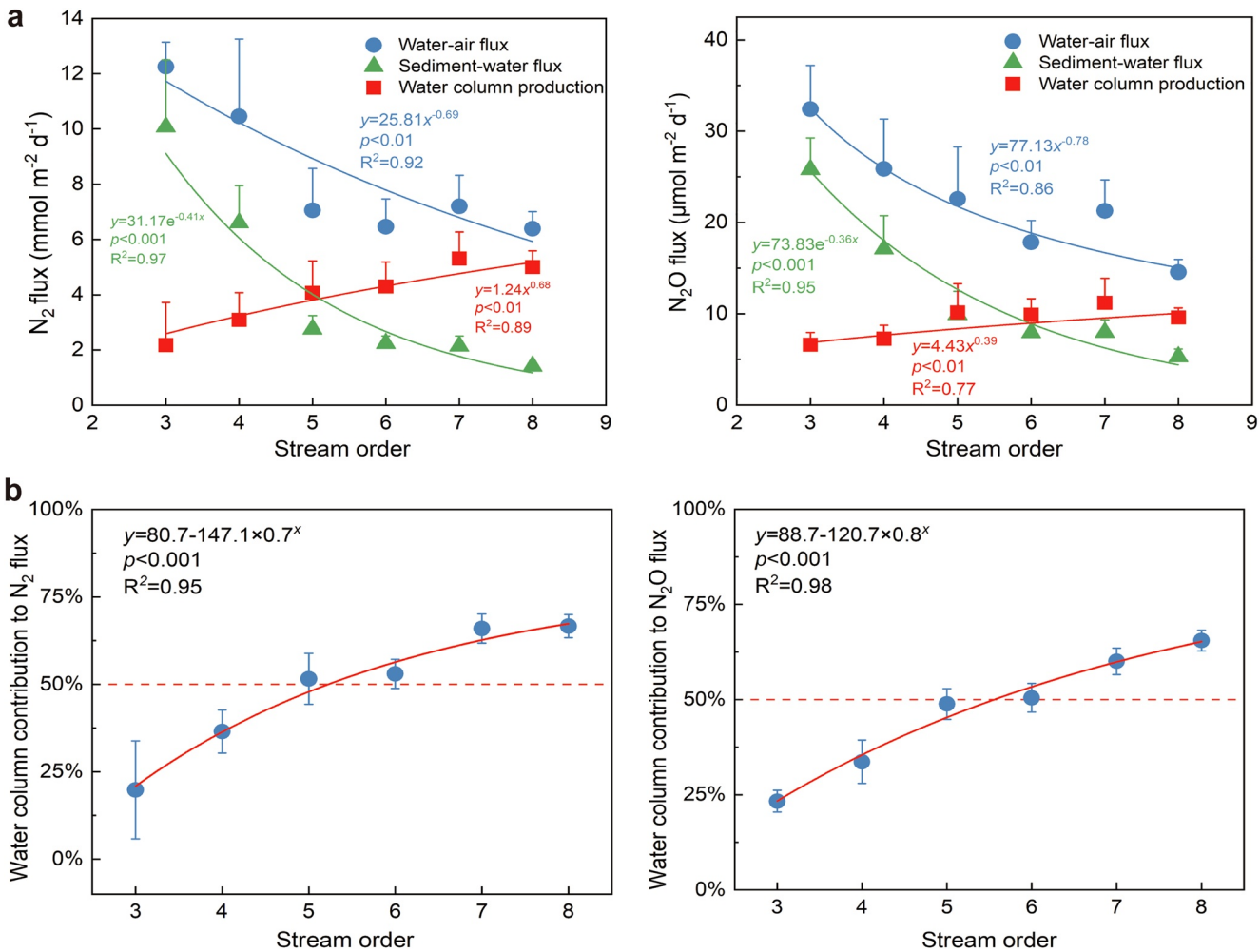

Figure 2. Relationship between stream order and water-air fluxes, sediment-water fluxes, and water column production rates of N_2 and N_2O, as well as water column contributions. The blue and red line in (a) represents the fit of a power function, and the green line represents the fit of an exponential function. The red solid line in (b) represents the fit of an exponential function, and the red dash line represents water column contributions equal to 50%, above which water column is dominant for production of N_2 and N_2O. Data points in (a) and (b) are the mean for each stream order, and error bars are +1 s.e.m in (a), and ±1 s.e.m in (b).

to the benthic zone, the water column can provide more habitat area for relevant microorganisms mediating N removal processes and N_2O production for rivers greater than fifth order. Furthermore, the increase in river depth with stream order (Figure 1d) reduces the contact between sediment and the water column, thus decreasing the streambed hydraulic connectivity and hyporheic exchange rate with overlying water (Anderson et al., 2005; Marzadri et al., 2017), which will lead to a low transfer of DIN from the water column to the benthic zone and low reaction rates within the benthic zone (Birgand et al., 2007). Collectively, the increase in areal-basis water column production rates and decrease in sediment-water fluxes account for the increasing water column contribution with river size.

3.4. Important Role of the Water Column in N Removal and N_2O Emissions

We used a Monte Carlo approach to upscale the total water column production and water-air emissions of N_2 and N_2O for each stream order of the six river networks with stream orders from first to eighth, further yielding water column contributions to N removal and N_2O emissions (Materials and Methods and Table S3 in Supporting Information S1). Across all six river networks from the first to eighth orders, the contributions of the water column to N removal and N_2O emissions were 39% (range: 32%–46%) and 34% (range: 29%–40%), respectively, and they increased to 73% (range: 57%–94%) and 62% (range: 48%–79%), respectively, for rivers with stream orders greater than five. Such upscaling results mean that riverine N removal and N_2O emissions would be

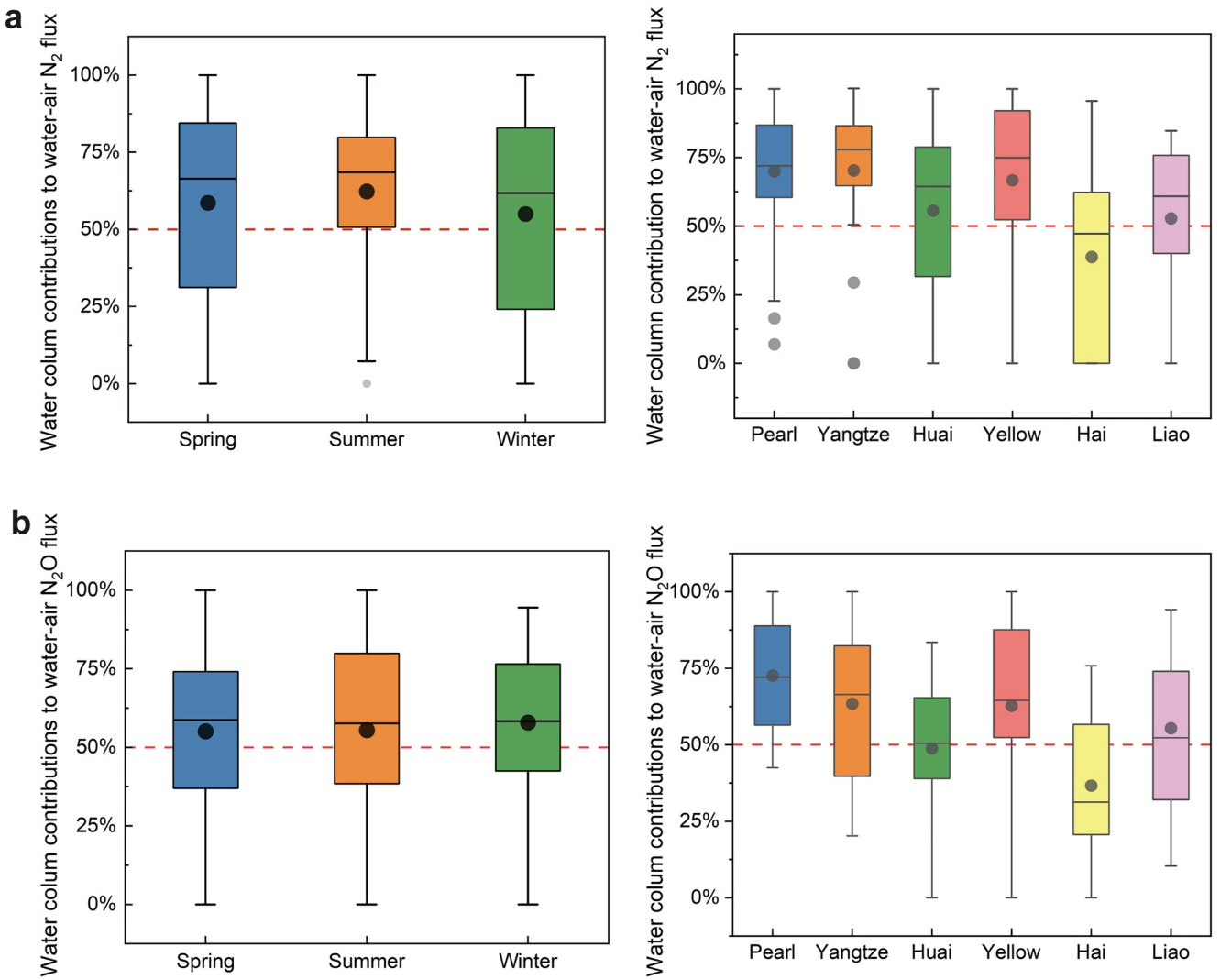

Figure 3. Seasonal and spatial variations of the water column contributions to N_2 (a) and N_2O (b) fluxes. Boxes are bounded by the 25th and 75th percentiles, and whiskers represent 1.5× the interquartile range, and the solid line is the median value. The black dots are arithmetic means, and the gray dots are outliers that are greater than Q3 + 1.5 × IQR or Q1 − 1.5 × IQR. The red dash lines represent water column contributions equal to 50%.

underestimated approximately by 50% if only benthic processes are considered in all six river networks from the first to eighth orders. Despite some limitations and uncertainties in our estimates (Results and Discussion 6 in Supporting Information S1), this study emphasizes the necessity of incorporating water column processes into N cycling in fluvial networks.

We proposed a conceptual framework for assessing the relative role of different zones in riverine N processing along a theoretical stream-river continuum (Figure 4). Small rivers have a high ratio of sediment-water contact area to water column volume. Additionally, the high transport efficiency of substrates and hyporheic exchange with overlying water due to the low water depth leads to high production potential within the benthic zone in these streams. However, with increasing river size, the increasing river depth enlarges the water column volume, thus creating more reaction space in the water column. In addition, the larger contact area of SPS-water caused by the higher concentration of SPS in large rivers can provide more habitats for microorganisms, driving higher potential production rates of N_2 and N_2O in the water column. All these factors lead to the increase trend of areal-basis production rates with stream order although volumetric-basis production rate did not change significantly with stream order. Together with the reduction in benthic production rates, the dominant role in N transformations changes from the benthic zone to the water column with increasing river size.

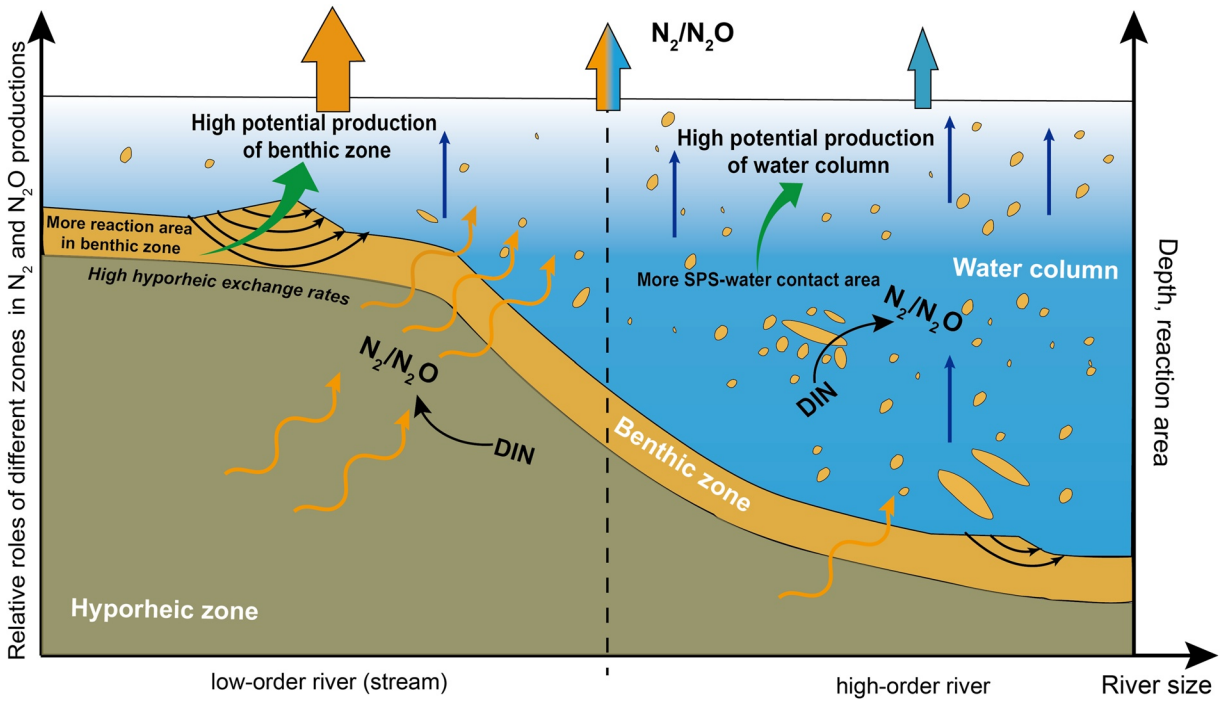

Figure 4. A conceptual framework for assessing the relative role of different zones in riverine N processing along a theoretical stream-river continuum. N_2 and N_2O emissions decrease with river size and shift from benthic dominance to water column-dominance.

4. Implications for Understanding Riverine N Dynamics

Overall, we revealed the relative role of the water column in N removal and N_2O emissions along the stream-river continuum and identified the potential coupled hydrologic and biogeochemical controls on gaseous N efflux and water column contributions. Some previous research conducted in other regions, such as North America, Europe, and Africa, suggests that the water column might play a dominant role in N removal and N_2O emissions in large rivers (Beaulieu et al., 2010; Marzadri et al., 2017; Reisinger et al., 2021). This study provides direct relevant evidence at a continental scale, suggesting that the conceptual framework in Figure 4 might be applied to assess the role of different zones in N removal and N_2O emissions across scales from streams to rivers draining different geographical and climatic regions in the world.

Based on the observations across different stream orders, our study proposes a simulation model considering geochemical (i.e., DIN and water temperature) and hydrodynamic conditions (i.e., SPS concentration) to estimate the water column production rates of N_2 and N_2O in rivers. This model might be applied in other regions and used to predict the change of water column production rates of N_2 and N_2O with geochemical and hydrodynamic conditions caused by climate and land use change. Incorporating water column processes into regional and global predictive models and elaborating production in subzones will improve our ability to attribute sources and better quantify rates of N removal and N_2O emissions from the world's river networks under the context of global change.

Data Availability Statement

The data archiving is in the repository Zenodo (https://zenodo.org/), and the N_2 and N_2O dataset for the six river networks and the Monte Carlo simulation code for upscaling and analyzing uncertainties is available at https://doi.org/10.5281/zenodo.5515451. The 90-m-resolution DEM data for hydrological analyses are accessible via https://www.resdc.cn/data.aspx?DATAID=284.

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