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Spatial patterns of diffusive greenhouse gas emissions from cascade hydropower reservoirs

Wenqing Shi[1,4,5], Taylor Maavara[3], Qiuwen Chen[1,2,4*], Jianyun Zhang[1,2], Jinren Ni[6], Daniele Tonina[7]

[1]State Key Laboratory of Hydrology-Water Resources & Hydraulic Engineering, Nanjing Hydraulic Research Institute, Nanjing 210098, China

[2]Yangtze Institute for Conservation and Green Development, Nanjing 210029, China

[3]School of the Environment, Yale University, New Haven CT 06511, USA

[4]Center for Eco-Environmental Research, Nanjing Hydraulic Research Institute, Nanjing 210098, China

[5]School of Environmental Science & Engineering, Nanjing University of Information Science & Technology, Nanjing 210044, China.

[6]The Key Laboratory of Water and Sediment Sciences, Ministry of Education, Peking University, Beijing 100871, China.

[7]Center for Ecohydraulics Research, University of Idaho, Boise, ID 83702, USA.

[*]Corresponding author: Qiuwen Chen (qwchen@nhri.cn)

Abstract

Greenhouse gas (GHG) emissions from reservoirs have received increasing attention in recent years. Despite extensive studies in single reservoirs, GHG emission patterns in cascades of multiple reservoirs, which are becoming increasingly common worldwide, remain unknown. This study investigates the spatial patterns of diffusive carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O) emissions, as well as their total CO_2-equivalent (CO_2-eq), for a cascade hydropower system in the heavily dammed upper Mekong River, China. Results demonstrated that GHG emissions in cascade reservoirs were higher than that in the upstream channel since the accumulated sediments fueled microbes for GHG production. In cascade reservoirs, CO_2 made the largest contribution (58.6%–84.8%) to total CO_2-eq, while the contribution of N_2O was marginal. Deep reservoirs emitted less CO_2, which was attributed to higher CO_2 consumption by phytoplankton. Reservoirs formerly occupying the most upstream position for the longest period of time in the cascade emitted the most CH_4, perhaps due to accumulations of river borne sediments. The total CO_2-eq generally increased with distance downstream except within deep reservoirs. These findings indicate that, with respect to mitigating GHG emissions, the deepest, most upstream reservoir should be constructed first in the configuration of cascade hydropower reservoirs, and less sediment will enter downstream reservoirs, which have higher CO_2-eq emissions.

Keywords: Upper Mekong River; dam; methane; carbon dioxide; nitrous oxide

1. Introduction

As climate warms, greenhouse gas (GHG) emissions from inland waters, particularly from reservoirs, have received widespread attentions (Deemer et al., 2016; Maavara et al., 2019). Global rivers are extensively dammed for the purposes of hydropower production, and over 8,600 dams primarily designed for hydropower generation are in operation (Zarfl et al., 2015). A cascade configuration, i.e. a sequence of multiple dams on the same river, is becoming increasingly common, particularly on large rivers (Grumbine and Xu, 2011). For instance, on the 1200-km mainstream of the upper Mekong River, China, 10 hydropower dams have been built and 11 dams are under construction or are being planned (Fan et al., 2015; Kondolf et al., 2014). The role of hydropower reservoirs as contributors to the emissions of GHGs such as carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O), however, remains a topic of controversy (Barros et al., 2011; Deemer et al., 2016; Prairie et al., 2017; Rosa and Schaeffer, 1995). GHG emissions from reservoirs have the potential to counteract the environmental benefits of hydropower (Giles, 2006; Qiu, 2009; Santos et al., 2006). It was estimated that global reservoirs emit 120.5 g CO_2-C m^{-2} $year^{-1}$, 43.8 g CH_4-C m^{-2} $year^{-1}$, and 0.1 g N_2O-N m^{-2} $year^{-1}$, which contribute greatly to global budgets of anthropogenic GHG emissions (Bastviken et al., 2011; Deemer et al., 2016).

After river damming, sediment accumulation supplies rich substrates (nitrogen, organic carbon) to fuel microbes for GHG production, creating hotspots of GHG emissions (Barros et al., 2011; Berberich et al., 2020; Maavara et al., 2017; Tranvik et al., 2009), which have been extensively studied in single hydropower reservoirs (Abril et al., 2005; Chen et al., 2009; DelSontro et al., 2016; Harrison et al., 2017; Lu et al., 2011; Maeck et al., 2013; Zheng et al., 2011). Maeck et al.

(2013) found that sediment accumulation in deposition zones, such as dam forebays, fuels high CH_4 emissions in the reservoir. Before being emitted to the atmosphere, GHG concentrations may also change due to biogeochemical cycles along their pathway (Liang et al., 2019). For example, CO_2 can be consumed through photosynthetic uptake by phytoplankton (Van Dam et al., 2018), which is potentially controlled by hydraulic residence time, since phytoplankton prefer to proliferate in reservoirs with long hydraulic residence time (Chen et al., 2020). In a reservoir cascade, the order of dam construction, location, and the physical properties (hydraulic residence time etc.) of the constructed reservoirs may drive trends in GHG emission patterns by affecting sediment transport, phytoplankton growth and biogeochemical cycling. Recently, ebullitive emissions of GHG from cascade reservoirs have been documented (Liu et al., 2020); however the spatial patterns of diffusive GHG emissions from cascade reservoirs and the driving factors remain unclear.

In this study, we aim to explore spatial patterns of diffusive GHG emissions. In particular, we investigate the role of known drivers (water and sediment properties, hydraulic residence time, reservoir age and water depth) on diffusive GHG emissions from individual reservoirs, and quantify the interacting impacts of parameters specifically associated with reservoir cascades, including the spatial order and timing of construction of dams within a cascade. The microbes responsible for GHG production were also analyzed using quantitative polymerase chain reaction (qPCR) method. The findings can add our understanding of diffusive GHG emissions from cascade hydropower reservoirs.

2. Materials and methods

2.1 Study area

The Mekong River (Fig. 1) originates in the Tibetan Plateau and empties into the South China Sea after flowing along 4,909 km through six nations (China, Myanmar, Lao PDR, Thailand, Cambodia and Viet Nam), making it among the largest river systems in the world. The mean annual discharge at the outlet of this river is 457 km^3 yr^{-1} and it has a watershed area of 760,000 km^2 (Shi et al., 2017). It is customary to divide the Mekong Basin into an upper basin that resides within China, where it is known as the Lancang River, and a lower basin extending from Yunnan, China through Southeast Asia. The most precipitous drop in the Mekong River occurs in the upper basin, where it falls 4,500 m over 2139 km and has a flow over 76.5 km^3 yr^{-1}, creating large potential for hydropower production. From 1993 through 2018, nine hydropower dams were built on the mainstream of the upper Mekong River. They are, from upstream, Dahua (R1), Huangdeng (R2), Miaowei (R3), Gongguoqiao (R4), Xiaowan (R5), Manwan (R6), Dachaoshan (R7), Nuozhadu (R8), and Jinghong (R9), creating a system of connected reservoirs along the river channel. The basic information of the nine reservoirs is shown in Fig. 1. The heavily dammed upper Mekong River provides a distinct case to investigate spatial patterns of diffusive GHG emissions.

2.2 Sample collection and analyses

A field survey was carried out at 65 sites (Fig. 1) along the upper Mekong River in September 2018. To minimize the variations incurred by the timing of sampling, the field survey at different sites was conducted synchronously by several workgroups. At each site, triplicate measurements of CO_2, CH_4 and N_2O fluxes across air-water interfaces were made (method described in Section 2.3), while surface water (500 mL volume grab samples) and bed sediment (50 g wet mass) were

sampled in triplicate. Bed sediment samples were collected with an Ekman grab sampler (ZG0204, Shanghai Zigui Instrument Co. Ltd., China), completely homogenized after removing large debris (stone, tree branches etc.), and then kept frozen in liquid nitrogen. Due to the lack of bed sediment deposited immediately downstream of dams (up to ~5 km downstream) of R1, R2, R3, R4, R6 and R7, 59 sediment samples were collected in the field survey in total. In the upstream channel, sampling (sediment, water and GHGs) was conducted on a bridge. In each reservoir, sampling (water and GHGs) at the site right after the front dam was conducted at the shore; sampling (sediment, water and GHGs) at the sites in the lacustrine zone was conducted on a boat in the middle of the channel. The water depth and the distance from the dam of each sampling site were presented in Supplementary Table S1. In the laboratory, portions of the homogenized sample were randomly selected for the analyses of sediment characteristics and microbes in triplicate (*See* the details below). 300 mL of water samples (or 200 mL when phytoplankton was very dense) was filtered on GF/F filters (0.45 μm) to collect phytoplankton for *Chl-a* analysis using the hot ethanol extraction method (Chen et al., 2016). A Vario MACRO cube elemental analyser (Elementar Inc., Germany) was used to measure sediment organic carbon and total nitrogen concentrations following the freeze-drying and hand-grinding of these sediment samples. Grain size was analysed by using an ultrasonic oscillator (PS-60A, Shenzhen Shenghuatai ultrasonic equipment Co. Ltd., China) to disperse raw sediment samples, after which measurements were made with a Mastersizer 2000 Laser Grain-size Meter. Grain size was presented as median diameter value ($d_{50,}$ μm). Water temperature and turbidity were measured *in situ* via a YSI multiparameter meter (Yellow Springs, OH, USA).

2.3 Diffusive CO_2, CH_4 and N_2O flux measurements

Diffusive GHG fluxes were estimated using the thin boundary layer model (Encinas Fernández et al., 2014; Musenze et al., 2014b; Whitfield et al., 2011):

$$F = K \cdot \left(C_{\mathrm{w}} - C_{\mathrm{eq}}\right) \cdot M \quad (1)$$

where F corresponds to gas flux between water and atmosphere, g m^{-2} h^{-1}, which can be converted to the value in mg m^{-2} d^{-1} by multiplying 24,000; C_w is the concentration of dissolved gas in surface water, mol m^{-3}; C_{eq} is the concentration of dissolved gas in surface water that is in equilibrium with atmospheric concentrations, mol m^{-3}; K is gas transfer velocity, m h^{-1}; M is gas molar mass (g mol^{-1}). C_{eq} is calculated based on the GHG concentrations in the air above the sampling site, measured at the time of sampling using the headspace method (described below).

Gas transfer velocity was computed as described in prior studies using Equation 2 (Shi et al., 2020; Xue et al., 2016):

$$K = k_{600} \cdot \left(\frac{S_c}{600}\right)^n \quad (2)$$

where the k_{600} (m s^{-1}) was estimated using Equation 3 in the lentic reservoirs (62 sampling sites) (Wanninkhof, 2014), and Equation 4 in the turbulent upper channel (3 sampling sites) (Raymond et al., 2012; Ulseth et al., 2019), respectively. S_c corresponds to the Schmidt number at water surface temperature as per prior studies (Wanninkhof, 2014); n was -2/3 for $U_{10} \leq 3.7$ m s^{-1} and -1/2 for $U_{10} > 3.7$ m s^{-1}.

$$k_{600} = 2.07 + 0.215 \cdot U_{10}^{1.7} \quad (3)$$

where U_{10} corresponds to the wind speed at 10 m above the surface of the water, m s^{-1}. U_{10} was obtained from the wind speed at 5 m above water surface by multiplying a factor of 1.06 (Jiang et

al., 2008), and the wind speed at 5 m above water surface was measured using a portable wind meter (16026, Aice Biotechnology Co., Ltd, Hangzhou, China) at the time of sampling.

$$k_{600} = 5937 \cdot [1 - 2.54 \cdot V^2/(gD)] \cdot (VS)^{0.89} \cdot D^{0.58} \quad (4)$$

where V is the flow velocity, m s^{-1}; D is the water depth, m; g is the gravitational acceleration, 9.8 m s^{-2}; S is the bed slope (unitless). The bed slop was calculated by using the bed elevation data, which was obtained from Huaneng Lancang River Hydropower Co., Ltd. The cross-sectional averaged flow velocity and water depth were measured in-situ by using a propeller-typed current meter (LS20B, Nanjing Water Conservancy and Hydrology Automation Institute, China) and a sounding rod (GeeLii 5552, Shanghai GeeLii Co., Ltd. China), respectively.

Surface water GHG concentrations were quantified via the headspace equilibration approach (Wang et al., 2009; Whitfield et al., 2011). Briefly, water samples (20 mL) were collected in pre-evacuated 60 mL polypropylene syringes with three-way stopcocks at 5 cm below the water surface, after which a headspace was generated via adding 20 ml of ambient air into the syringe. Samples were then shaken for 2 minutes, after which the headspace gas was injected into a 12-ml pre-evacuated Exetainer® vial (839 W, Labco, UK) and was analyzed via a Agilent 7890 B (Agilent Technologies, Inc., USA) gas chromatograph equipped with autosampler and a thermal conductivity detector (TCD) for CO_2, a flame ionization detector (FID) for CH_4 and a micro-electron capture detector (ECD) for N_2O analyses. N_2 and He were used as carrier gases at a flow rate of 20 ml min^{-1}. Gas analyses were conducted within 7 days after collection. The concentrations of dissolved GHG in surface water were calculated using Equation 5 (Hu et al., 2018):

$$Cw = \frac{(C_h - C_0) \times V_h + \alpha \times C_h \times V_w}{V_w} \quad (5)$$

where C_0 and C_h are headspace gas concentrations before and after shaking, respectively, mol L^{-1}; V_h is headspace volume, ml; V_w is water volume (20 mL); α is the Bunsen coefficient (0.622).

2.4 CO_2-eq emission calculation

Total CO_2-eq emissions at each sampling site were calculated by summing CO_2-eq of each GHG gas for the given time horizon (Davidson et al., 2015; IPCC, 2021). Here we used the 100-year horizon values, reported most recently by the Sixth Assessment Report of the Intergovernmental Panel on Climate Change (IPCC), which are 27.2 and 273 for CH_4 and N_2O, respectively (IPCC, 2021). Since CH_4 can produce higher radiative forcing than CO_2, a higher CO_2-eq will be generated when more organic carbon is mineralized to CH_4 rather than CO_2. Thus, CH_4/CO_2 was also calculated in this study according to Holgerson and Raymond (2016).

2.5 Microbial abundance analyses

Microbes associated with GHG production in sediments were quantified via qPCR. Most of microbes are responsible for CO_2 production during the degradation of organic matter, and total bacterial 16S rDNA was used as biomarker for analyzing microbial CO_2 production (Shi et al., 2017). According to Fernández-Baca et al. (2019), *mcrA* was used as biomarker for microbes associated with CH_4 production. N_2O is a nitrification and denitrification byproduct (Kuypers et al., 2018). Nitrifier *amoA* and denitrifiers *nirS* were used as biomarkers to quantify microbes associated with N_2O production (Hou et al., 2013; Morales et al., 2010). A FastDNA Power-Max Soil DNA Isolation Kit (MP Biomedical, USA) was used based on the provided instructions to isolate sediment DNA, which was then utilized for qPCR analyses conducted in an iQ5 cycler

instrument (Bio-Rad, USA). All qPCR reactions were conducted in a 20 μL total volume, composed of 10 μL SYBR® Premix Ex TaqTM (Toyobo, Japan), 0.5 mM each of forward and reverse primers, 0.8 μL of 3mg/mL bovine serum albumin (Sigma, USA), template DNA, and ddH_2O. The primers and qPCR programs are presented in Table S2. In order to construct a standard curve, plasmid DNA containing the target fragment was serially diluted (10^{-2}–10^{-8}). These qPCR reactions were conducted in sealed 96-well plates (Bio-Rad), and triplicate DNA-free negative control samples were run on each plate. The abundance value of the microbe corresponding to each GHG gas ($m_{i,j}$) were transformed to a ratio ($a_{i,j}$) relative to the largest abundance value among all the sampling sites using Equation 6. Then, a microbe indicator (B_i) for total GHG production at each sampling site was calculated by summing the ratios at this site using Equation 7.

$$a_{i,j} = \frac{m_{i,j}}{m_j^{max}} \quad (6)$$

$$B_i = \sum_j a_{i,j} \quad (7)$$

where $m_{i,j}$ is the abundance of microbe j (j = 16s rDNA, *mcrA*, *amoA*, *nirS*) at sampling site I; m_j^{max} is the maximum abundance of microbe j among all sampling sites; B_i is the microbe indicator for total GHG production at sampling site i.

2.6 Statistical analysis

SPSS v22.0 (SPSS Inc., IL, USA) was used in all statistical testing. Logarithmic transformation on the original data was conducted to improve data normality. Difference in CH_4 fluxes between the upstream channel and the most downstream R9 reservoir was compared via t-tests, after data normality had been assessed by the Kolmogorov-Smirnov and variance homogeneity tests. $P < 0.05$ was the significance threshold. The correlation between GHG emissions and hydro-

environmental parameters was analyzed based on the simple linear regression after data normalization. Outliers in datasets are defined as values that fall more than 3.0 standard deviations from the normal (Hansen et al., 2012).

3. Results

3.1 Hydro-environmental and microbial conditions

The reservoirs within the cascade on the mainstem of the upper Mekong River range in hydraulic residence time from 0.01 to 2.36 years and in age from 1 to 25 years at the time of our field survey in 2018 (Fig. 1c). These reservoirs were neither built in order from upstream to downstream or vice versa (Fig. 1b).

Along the flow direction, water temperature showed a general increasing trend from < 12.5℃ in the upstream channel to 23.2 ± 1.0℃ (mean ± SD) in the downstream reservoirs (Fig. 2a). Sediment organic carbon and total nitrogen rose from 11.2 ± 2.9 mg g^{-1} (mean ± SD) and 0.20 ± 0.01 mg g^{-1} (mean ± SD) in the upstream channel to 20.3 ± 2.5 mg g^{-1} (mean ± SD) and 1.25 ± 0.12 mg g^{-1} (mean ± SD) in the most downstream R9, respectively (Fig. 2b). *Chl-a* was generally below 5.0 μg L^{-1} in the upper Mekong River, with peak values observed in the largest reservoirs of R5 and R8. *Chl-a* reached maximum values of 35.2 and 82.0 μg L^{-1} in R5 and R8, respectively (Fig. 2c). The abundance of microbes associated with GHG production showed generally an increasing trend along the upper Mekong River. The GHG microbe indicator increased from 0.43 ± 0.05 (mean ± SD) in the upstream channel to 1.26 ± 0.39 (mean ± SD) in the most downstream R9 (Fig. 2d).

3.2 Diffusive CH_4, CO_2, N_2O fluxes

Along the flow direction, CO_2 fluxes generally increased with distance downstream, with outlier values at some sampling sites in R5 and R8. The CO_2 flux increased from 548.5 ± 38.7 mg m^{-2} d^{-1} (mean ± SD) in the upstream channel to 1328.3 ± 369.7 mg m^{-2} d^{-1} (mean ± SD) in the most downstream R9, but was below 210.0 mg m^{-2} d^{-1} at some sampling sites in R5 and R8 (Fig. 3a). The CH_4 flux was below 1.5 mg m^{-2} d^{-1} in the upstream channel, which was lower than in the downstream reservoirs (t-test, $p < 0.05$). The CH_4 fluxes in downstream cascade reservoirs reached 1.0–12.2 mg m^{-2} d^{-1}, with extreme values observed in R4 and R6. The CH_4 fluxes reached maximum values of 8.7 and 12.2 mg m^{-2} d^{-1} in R4 and R6, respectively (Fig. 3a). CH_4/CO_2 mass ratio indicated that there were extreme values in R4, R6 and R8, which were 0.022, 0.027 and 0.014, respectively. The remaining CH_4/CO_2 values generally exhibited an increasing trend along the flow direction (Fig. 3b). Similarly, N_2O fluxes also exhibited a consistent rising trend along the flow direction. N_2O fluxes increased from 0.015 ± 0.001 mg m^{-2} d^{-1} (mean ± SD) in the upstream channel to 0.032 ± 0.001 (mean ± SD) mg m^{-2} d^{-1} in the most downstream R9 (Fig.3a). Total CO_2-eq emissions exhibited an increasing trend with outlier values in R5 and R8, which increased from 591.5 ± 40.4 mg m^{-2} d^{-1} (mean ± SD) in the upstream channel to 1404.9 ± 393.1 mg m^{-2} d^{-1} (mean ± SD) in the most downstream R9, while the outlier values were below 250.0 mg m^{-2} d^{-1} (Fig. 3c). Compared with CH_4 and N_2O, CO_2 has the largest contribution to the total CO_2-eq emissions, which reached 84.7 ± 9.3% (mean ± SD). CH_4 and N_2O contributed to 14.0 ± 8.9% (mean ± SD) and 1.4 ± 0.8% (mean ± SD) of total CO_2-eq emissions, respectively (Fig. 4).

3.3 Relations between diffusive GHG emissions and hydro-environmental conditions

The relations between diffusive GHG emissions and the hydro-environmental factors were shown

in the heatmap based on correlation analysis (Fig. 5). The CO_2 was negatively correlated with *Chl-a* (R^2 = -0.40, p = 0.29), hydraulic residence time (R^2 = -0.23, p = 0.55) and water depth (R^2 = -0.43, p = 0.25). The CH_4 was positively correlated with reservoir age (R^2 = 0.62, p = 0.08), but was negatively correlated with water depth (R^2 = -0.24, p = 0.54). The CH_4/CO_2 ratio was positively correlated to phytoplankton (R^2 = 0.38, p = 0.32) and water depth (R^2 = 0.08, p = 0.83). N_2O emissions showed a positive relationship with all these hydro-environmental factors, with the dominant influences of sediment TN (R^2 = 0.81, p = 0.01) and water temperature (R^2 = 0.79, p = 0.01).

4. Discussion

Rivers act as "leaky pipes" for terrestrial sediment transport to coastal waters (Cole et al., 2007). After river damming, the flow velocity decreases, allowing suspended particles to settle in reservoirs, providing substrates (nitrogen, organic carbon) for microbial consumption and associated GHG production in reservoirs (Maeck et al., 2013). As a result, higher CO_2, CH_4 and N_2O emissions were detected in cascade reservoirs relative to the upstream channel (Fig. 3a). Following the gradually intensified land use from upstream to downstream (Fig. S1), the contents of organic carbon and nitrogen in sediments generally increased along the flow direction (Fig. 2b). Concurrently, water temperature increases gradually (Fig. 2a) due to the large decrease in elevation, the flow direction from north towards south, and the thermal accumulation in reservoirs (Ren et al., 2020), which favors microbial proliferation in sediments with the presence of sufficient substrates. Microbes associated with GHG production (methanogens, nitrifiers and denitrifiers) generally exhibited an increase from the upstream channel to cascade reservoirs (Fig. 2d), leading

265 to the increasing trends of diffusive GHG emissions along the flow direction, especially for N_2O
266 emissions (Fig. 3a).
267 CO_2 was the dominant contributor to the total CO_2-eq emissions, making the total CO_2-eq
268 emissions exhibit similar spatial patterns to CO_2 along the river, which generally increased along
269 the flow direction except sharp decreases in the large reservoirs of R5 and R8 (Fig. 3a). CO_2
270 emissions were most strongly controlled by water depth and phytoplankton biomass, which are
271 interrelated and show inverse relationships with CO_2 emissions (Fig. 5). Large water depth often
272 means high dam and hence big reservoirs with long hydraulic residence time. After river damming,
273 riverine or lotic environments are converted to lentic habitat, favoring phytoplankton proliferation,
274 especially evident in large reservoirs with long hydraulic residence times (Chen et al., 2020;
275 Soballe and Kimmel, 1987). In the upper Mekong River, R5 and R8 are the two largest reservoirs
276 with the hydraulic residence time over 1.8 years, enabling the development of dense phytoplankton
277 for consuming CO_2 (Fig. 2c), indicating the primary drivers of CO_2 emissions in the upper Mekong
278 River are controlled by the hydraulic properties of each individual reservoir.
279 CH_4 was found to be positively correlated to reservoir age (Fig. 5). However, Barros et al (2011)
280 reported that CH_4 emissions declined with reservoir age. The different findings in this study could
281 be because of strict biomass removal policies implemented in the flooded areas prior to reservoir
282 impoundment in China (Shi et al., 2017). Therefore, the emissions are not mainly dependent on
283 initial organic matter stored in flooded areas, but on reservoir primary production as well as the
284 magnitude of subsequently accumulated sediment and substrate from influxes. In particular, the
285 old reservoirs (with larger age) are mainly located in the downstream (after MW reservoir in Fig.

1), where there are larger drainage areas as well as higher contents of organic carbon and nitrogen in runoff due to intensified land use (Fig. S1). Meanwhile, CH_4 emissions as well as their contributions to total CO_2-eq emissions are closely related to the historic location within the dam cascade. High CH_4 concentrations were observed in R4 and R6, which are formerly occupied the most upstream position in the cascade. In reservoirs, high deposition of suspended particles builds up thick, potentially anoxic sediment layers, which is favorable for CH_4 production, and thus a large fraction of organic carbon can be recycled as CH_4 rather than CO_2 (Shi et al., 2018). In the upper Mekong River, water turbidity decreased sharply after passing through the cascade dams (Fig. S2). Furthermore, the sediment input of the most upstream reservoir is mainly from the headwater region due to the narrow drainage area along the upstream reach of this canyon river (Fig. S1). R4 and R6 were the most upstream reservoirs for the longest time, 26 and 7 years, respectively (Fig. 1c), and received and subsequently deposited large amounts of sediments from the upstream region (Fig. S2), potentially promoting anoxia in the deep bottom sediments and enabling high CH_4 emissions. Accordingly, CH_4 emission peaks were observed after the dam (Fig. 3a) due to turbine degassing, an important GHG emission pathway (Deemer et al., 2016). Since CH_4 has a higher CO_2-eq value than CO_2, organic carbon mineralizing to CH_4 rather than CO_2 result in greater warming effects. Therefore, the elevated contribution of CH_4 to total CO_2-eq emissions should receive attentions in future evaluation of global warming effects on dammed river systems, particularly if a high sediment load is anticipated, as in the most upstream reservoir in a cascade. In the upper Mekong, additional long-term monitoring should be continued in the current upstream-most reservoir (R1), which was built in the same year of the data collection and

307 already showed elevated CH_4 emissions (Fig. 3a).

308 N_2O showed the clearest relationship between distance downstream and emissions magnitude (Fig.
309 3a). N_2O is a byproduct of nitrification and denitrification (Beaulieu et al., 2011; Ni et al., 2011;
310 Su et al., 2019). N_2O emissions in the upper Mekong dam cascade were positively correlated with
311 all the environmental parameters tested, but most strongly related to substrate availability and
312 water temperature. Given the continuous, nearly linear increase with distance through the cascade,
313 the N_2O emissions are most strongly controlled by the north-south upstream to downstream
314 temperature gradient from high elevation to low elevation. Increases in water temperature along
315 the flow direction enhances microbe-mediated N_2O production (Shi et al., 2020). Additionally,
316 nitrogen substrates and organic carbon often act as limiting factors of N_2O emissions in aquatic
317 systems (Gómez-Alday et al., 2014; Wang et al., 2014). The additionally strong correlation with
318 sediment TN, which increases with distances downstream due to intensifying land use (Fig. 2b),
319 suggests that N_2O emissions are highly dependent on the available N substrate.

320 Largely following the trends in CH_4 emissions, the CH_4/CO_2 ratio increased gradually along the
321 cascade reservoirs. This is because thick bottom anoxic sediments in the reservoirs can make
322 organic carbon mineralize more into CH_4 than CO_2, causing high CH_4/CO_2 ratio (Maeck et al.,
323 2013). According to the bathymetry survey in 2017, the depth of deposited sediment was on
324 average about 15-20 m in the reservoirs. The highest values of CH_4/CO_2 ratio were observed in
325 R4 and R6, which are formerly occupied the most upstream position in the cascade for the longest
326 time. The reason was similar to that of CH_4, which had already been elaborated above. The
327 CH_4/CO_2 ratio was found to be positively correlated to reservoir age (Fig. 5), which could be

attributed to the high positive correlation between CH_4 and reservoir age. The total CO_2-eq emissions has negative correlations to *Chl-a* and water depth, but positive correlations to TN and OC. The reason is straightforward, as CO_2 was the dominant contributor to total CO_2-eq emissions, making the total CO_2-eq behave similarly to CO_2.

These findings provide an important step forward in our understanding of GHG emissions during the development of cascade hydropower reservoirs. Our findings suggest that, with respect to mitigating GHG emissions in canyon rivers, the most upstream reservoir could be constructed first, if possible, and that it should ideally be deep. In such cases, the majority of organic matter will be trapped in the most upstream reservoir, and less organic matter enters downstream reservoirs, where it is favorable for CO_2-eq emissions (Fig. 3c). Although the spatial patterns of GHGs were found to be mainly controlled by the order of dam construction, location, and reservoir physical properties in the reservoir cascade, more field surveys are still needed in future to identify their seasonal variations. Recently, studies have reported that ebullition makes an important contribution to CH_4 emissions (Deemer et al., 2016; Liu et al., 2020), particularly in shallow and organic-rich reservoirs. In this study, we did not measure the ebullition flux, but focused on diffusive emissions. Some information about ebullition of CH_4 from cascading reservoirs in the upper Mekong River can be found in Liu et al. (2020).

5. Conclusions

Recently, GHG emissions from hydropower reservoirs have received considerable attention. In this study, we investigated the spatial patterns of diffusive GHG emissions in the heavily dammed upper Mekong River. Our main conclusions are:

(1) The total CO_2-eq emissions in each reservoir generally increased with distance downstream except within deep reservoirs. The deep reservoirs had the lower CO_2-eq emissions.

(2) CO_2 made the largest contribution to total CO_2-eq relative to CH_4 and N_2O, and their emissions were mainly controlled by the hydraulic residence time of each individual reservoir.

(3) High CH_4 emissions were observed in reservoirs that are formerly occupied the most upstream position in the cascade for the longest periods of time, and were thus strongly related to the properties of the reservoir cascade.

(4) N_2O emissions showed the clearest linear increase with distance downstream through the cascade, and were strongly controlled by the water temperature gradient.

(5) With respect to the mitigation of GHG emission from cascade hydropower reservoirs, the most upstream reservoir is suggested to be constructed first.

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