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Spatial variations in CO₂ fluxes in a subtropical coastal reservoir of Southeast China were related to urbanization and land-use types

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Abstract
Carbon dioxide (CO$_2$) emissions from aquatic ecosystems are important components of the global carbon cycle, yet the CO$_2$ emissions from coastal reservoirs, especially in developing countries where urbanization and rapid land use change occur, are still poorly understood. In this study, the spatiotemporal variations in CO$_2$ concentrations and fluxes were investigated in Wenwusha Reservoir located in the southeast coast of China. Overall, the mean CO$_2$ concentration and flux across the whole reservoir were 41.85 ± 2.03 µmol/L and 2.87 ± 0.29 mmol/m$^2$/h, respectively, and the reservoir was a consistent net CO$_2$ source over the entire year. The land use types and urbanization levels in the reservoir catchment significantly affected the input of exogenous carbon to water. The mean CO$_2$ flux was much higher from waters adjacent to the urban land (5.05 ± 0.87 mmol/m$^2$/hr) than other land use types. Sites with larger input of exogenous substance via sewage discharge and upstream runoff were often the hotspots of CO$_2$ emission in the reservoir. Our results suggested that urbanization process, agricultural activities, and large input of exogenous carbon could result in large spatial heterogeneity of CO$_2$ emissions and alter the CO$_2$ biogeochemical cycling in coastal reservoirs. Further studies should characterize the diurnal variations, microbial mechanisms, and impact of meteorological conditions on reservoir CO$_2$ emissions to expand our understanding of the carbon cycle in aquatic ecosystems.

Keywords
Carbon dioxide fluxes; Spatiotemporal dynamics; Land use; Urbanization; Anthropogenic activities; Coastal reservoir
Introduction

Dams have been built for thousands of years to control water flow and utilize water resources (Nilsson et al., 2005). As an artificial aquatic ecosystem, reservoirs play an important role in irrigation, water supply, power generation, aquaculture and other aspects, while the impacts of such water projects on the local hydrological situation and ecosystem sustainability have not been fully explored (Hao et al., 2019; Rosenberg et al., 2000). With the inundation of land and vegetation in the reservoir area, nutrient transport and cycling in the flooded system will change substantially, with the consequence of changing the emission of greenhouse gases (GHGs), including CO₂, CH₄, and N₂O, into the atmosphere (Li et al., 2016; St Louis et al., 2000). Therefore, with the exacerbating climate change caused by increasing GHG concentrations (World Meteorological Organization, 2019), quantifying the carbon flux of reservoirs becomes increasingly important to improve the accuracy of carbon budget estimations from local to global scales.

Artificial reservoir, which includes various carbon sources from the catchment and inside the reservoir, is a major component of global carbon cycle (Bevelhimer et al., 2016; Kunz et al., 2011). Recent estimate indicates that global GHG emissions from reservoir water surfaces account to approximately 0.8 Pg CO₂-eq (100-year) per year, of which ~17% is contributed by CO₂ (Deemer et al., 2016). Reservoirs appear to be a net source of atmospheric CO₂ (Barros et al., 2011; Raymond et al., 2014), especially in the subtropical and tropical areas (e.g., Alshboul and Lorke, 2015; Almeida et al., 2019). CO₂ emissions from reservoirs on a per unit area basis tend to exceed those from natural lakes or wetlands. However, limited by the number of field observations available, these CO₂ estimates are largely uncertain (Li and Lu, 2012; Varis et al., 2012). More importantly, the spatial heterogeneity (across and within systems) caused by geographical location, reservoir age, microtopography, water temperature, organic matter, and other factors further pose challenges for the accurate estimate of CO₂ emissions from reservoirs.

Different from other natural water bodies, reservoirs have special ecosystem characteristics under the intervention of human activities (Fearinside, 2005; Soumis et al., 2007). Generally, the inundated sediment, suspended particles and other associated carbon trapped in reservoirs provide stable carbon sources for CO₂ production, but with large spatial heterogeneity (Hertwich, 2013; Kemenes et al., 2011; Zhou et al., 2017). On the other hand, some eutrophic waters with higher primary productivity can fix a large amount of CO₂, and even serve as a carbon sink for a certain period (Pacheco et al., 2015). Previous studies suggested several possible conditions for the dominance of autotrophic processes: (1) relatively enclosed and stagnant water environment (van Bergen et al., 2019); (2) warm and humid climate (Barros et al., 2011; Xiao et al., 2017); and (3) excessive import and accumulation of nutrients and organic matter in the reservoirs (Dodds and Cole, 2007; Outram and Hiscock, 2012). Furthermore, compared with inland areas, coastal reservoirs trend to have a higher salinity (Domingues et al., 2016; Hodson et al., 2019). CO₂ production and emission may also exhibit some spatial differences owing to variations in salinity.

With rapid urbanization and land use change in the coastal areas, various biogeochemical processes in the coastal aquatic ecosystems have been increasingly disturbed by municipal and agricultural activities in the catchment (Pérez et al., 2015; Williams et al., 2016), leading to the creation of critical “hotspots” of GHG emission (Yang and Flower 2012). High CO₂ production and emission in some river and lake systems have been shown to closely relate to the exogenous supply of sewage-derived organic matter from the watershed (e.g., Kaushal et al., 2018; Pugh et al., 2015). Coastal reservoirs, which can be affected by both terrestrial and marine ecosystems, are likely to exhibit unique CO₂ dynamics. Given that most
of the existing studies on CO$_2$ fluxes in reservoirs are mainly devoted to inland hydroelectric reservoirs only (e.g., Abril et al., 2005; Shi et al., 2017) but rapid urbanization occurs widely in the catchment of coastal reservoirs, particularly in the developing countries (Yang et al., 2017). Therefore, a deeper understanding about the influence of land use change and urbanization on CO$_2$ fluxes in the coastal reservoirs is needed.

Given the knowledge gap above, we measured CO$_2$ concentrations and fluxes in a subtropical coastal reservoir in Min River Estuary, Southeast China, from November 2018 to June 2019. The goals of this study were: (1) to assess the spatial variability of CO$_2$ concentration and flux in the subtropical coastal reservoir system, and (2) to determine the response of reservoir CO$_2$ release to the adjacent land use types. We hypothesized a large spatial heterogeneity in reservoir CO$_2$ fluxes because of the different land use types and urbanization levels in the catchment.

1. Materials and methods

1.1. Site description

This study was conducted in Wenwusha Reservoir (25°49′36″–25°54′00″N, 119°35′12″–119°38′11″E), which was located at the southern tip of the Min River Estuary, Southeast China (Fig. 1). The reservoir catchment is influenced by a subtropical monsoon climate with high temperature (annual average: 19.3 °C) and abundant precipitation (annual average: 1390 mm). Nearly 75% of the annual precipitation occurs from May to September (Yang et al., 2020). The reservoir water meets China’s Class III water quality standard (suitable for centralized drinking water source protection zone, fish protection zone and swimming zone), and the reservoir is mainly used for irrigation, aquaculture and flood control (Fuzhou Municipal Water Authorities, 2019). Different species of fish, including _Lateolabrax japonicus_, _Oreochromis mossambicus_, _Carassius auratus auratus_ and _Cyprinus carpio_, grow in the reservoir. The main land uses adjacent to the reservoir are urban area (5.99%), aquaculture pond (9.80%), forest (15.04%), farmland (3.34%), sand (2.14%) and wetland (14.41%) (Fig. 1 and Table 1).
Fig. 1. Location of the Wenwusha Reservoir and land use distribution in the catchment.

There are 11 sample transects (47 sampling sites) in the south reservoir area (SRA) and 10 sampling transects (56 sampling sites) in the north reservoir area (NRA).
Table 1

Summary of main characteristics and land use types in the Wenwusha Reservoir

<table>
<thead>
<tr>
<th></th>
<th>Surface area (ha)</th>
<th>Total volume (×10^8 m³)</th>
<th>Water depth (m)</th>
<th>Bank type</th>
<th>Sampling Site</th>
<th>Land use type (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>N/C</td>
<td>56</td>
<td>Urban</td>
</tr>
<tr>
<td>NRA</td>
<td>190</td>
<td>1.4</td>
<td>2.6</td>
<td>N/C</td>
<td>23.93</td>
<td>6.30</td>
</tr>
<tr>
<td>SRA</td>
<td>330</td>
<td>1.69</td>
<td>1.2</td>
<td>N</td>
<td>0.00</td>
<td>10.96</td>
</tr>
</tbody>
</table>

aN” and “C” represent natural and concreted banks. NRA and SRA are north reservoir area and sour reservoir area.
The total reservoir water area and mean water depth are 520 ha and 1.5 m, respectively. Two
dams were built in 1957 and 2004, respectively, which divided the reservoir into two main
reservoir areas: north reservoir area (NRA) and south reservoir area (SRA) (Fig. 1). The
NRA, with a surface area of 190 ha, is connected to the Nanyang River network. Influenced
by urbanization and human activities, the NRA and its upstream receive effluent discharge
from domestic, industrial and aquacultural activities (Table 1). The construction of the
southern seawall resulted in the SRA, with a surface area of 330 ha. Trees were planted in the
east of SRA, while extensive wetlands were formed along the west bank of SRA with some
agricultural landscapes (e.g., aquaculture ponds and farmlands) (Table 1). Water in the whole
reservoir is supplied by precipitation and upstream river discharge, with almost no exchange
with sea.

1.2. Water sampling and CO₂ measurement

Considering the possible spatiotemporal variations in dissolved CO₂ concentration and flux,
three sampling campaigns (November 2018, March and June 2019) were carried out across
21 sampling transects (103 sites) at the Wenzhuo reservoir, including 10 sampling transects
in NRA (56 sites) and 11 transects in SRA (47 sites). Moreover, according to different levels
of urbanization along the reservoir bank in the catchment, the reservoir was further divided
into four water areas (I, II, III, and IV) (Appendix A Table S1). The sampling points
basically covered all the water areas with the dominating land use types in the catchment
(Fig. 1). The coordinates of each sampling site were recorded so that the same sites were re-
visited in all three sampling campaigns. Water samples were collected using 55-mL
borosilicate serum bottles (~0.2 m below the water surface), which were then sealed with
butyl stoppers and aluminum caps without including any bubbles. In addition, 150-mL of
water sample was collected at each site using a polyvinylchloride sampling bottle for the
measurement of other auxiliary parameters (see below).

CO₂ concentration was determined using the headspace extraction technique (Bellido et al.,
2009). Specifically, 25 mL of water sample and equal volume of N₂ were added into a bottle
and the bottle was then violently shaken for 10 min to reach an equilibrium in
CO₂ concentration. 5 mL of headspace air sample was collected and subsequently injected
into a gas chromatograph (GC-2010, Shimadzu, Kyoto, Japan) with flame ionization
detection (FID) for determining the CO₂ concentration. Four CO₂ standard gases, i.e. 100,
500, 1000 and 10,000 ppm, were used to calibrate the FID. The injection port, column and
detector temperature were set at 100, 45 and 240 °C, respectively. Dissolved
CO₂ concentration in water was calculated following the method of Wanninkhof (1992),
based on the CO₂ concentration in the headspace air in the serum bottle and the Bunsen
solubility coefficient.

The CO₂ flux (F_{CO₂}) across the water-air interface was estimated using the thin-boundary
layer model based on gas diffusion between two media (e.g., Crawford et al., 2013) as
follows: (1) F_{CO₂}=k*(C_{water}-C_{atm}) where F_{CO₂} (mmol/m²/h) refers to the CO₂ flux from
water to air; k is the gas transfer velocity of CO₂ (m/hr); C_{water} is the CO₂ concentration in the
water column (mmol/L), and C_{atm} is the CO₂ concentration in the atmosphere (mmol/L). In the
lentic system, according to the empirical function driven by wind speed and temperature
(Crusius and Wanninkhof, 2003), the k value can be calculated
as: (2) k = (1.68 + 0.228 * U_{10.2}) * (600SC)n(3)SC = 1991.1−118.11t + 3.4527t²−0.04132t³
where \( U_{10} \) (m/sec) is the wind speed at 10 m above the water surface, which is approximated by \( U_{10} = 1.14 \, U \), where \( U \) is the wind speed at 2 m height; \( S_C \) is the CO₂ Schmidt number for water
temperature (\( t, \quad °C \)) (Wanninkhof, 1992); and \( n \) is the proportionality coefficient (value is 0.5).
1.3. Field and laboratory measurement of water physico-chemical properties

During the sampling period, various physio-chemical properties of surface water were also measured \textit{in situ}. Water temperature ($T_w$) and pH were measured by a portable pH/mV/temperature meter system (IQ150 Scientific Instruments, USA). Dissolved oxygen (DO) and salinity were determined by a portable water quality analyzer (HORIBA, Japan) and a salinity meter (Eutech Instruments-Salt6, USA), respectively. The relative standard deviations of pH, DO, and salinity analyses were $\leq 1.0\%$, $\leq 2.0\%$ and $\leq 1.0\%$, respectively. All equipment probes were calibrated following the manufacturer's specifications prior to deployment. Meteorological conditions (including wind speed, air pressure and temperature) were measured by a meteorological meter (NK3500, Kestrel, USA), and long-term precipitation data were obtained from the weather stations in Min River Estuary.

Laboratory analyses were conducted to determine the nutrient concentrations in reservoir water. Before the analysis of dissolved nutrients, water samples were filtered through 0.45–$\mu$m GF/F glass millipore filters. Dissolved organic carbon (DOC) concentration was analyzed by a total organic carbon analyzer (TOC-VCPI/CPN, Shimadzu, Japan) with a detection limit of 0.4 $\mu$g/L and a relative standard deviation (RSD) of $\leq 1.0\%$ in 24 h. Nitrogen (total dissolved nitrogen (TDN), NO$_3^-$, and NH$_4^+$) and phosphorus (total phosphorus (TP) and PO$_4^{3-}$) nutrients were detected using flow injection analyzer (Skalar Analytical SAN++, Netherlands). The detection limits for nitrogen and phosphorus were 6 $\mu$g/L and 3 $\mu$g/L, respectively, and the measurement reproducibilities were within 3.0% and 2.0%, respectively. Chlorophyll $a$ (Chl-$a$) was extracted using ethanol solution (90%) for 24 h and analyzed by a UV–VIS spectrophotometer (Shimadzu UV-2450, Japan).

1.4. Statistical analysis

All measured variables were checked for normality using the Kolmogorov-Smirnov's test. When necessary, the original data were transformed by the natural logarithm to meet the assumptions of normality and homoscedasticity. To fully consider the correlation between spatial variables, as well as the randomness and structural characteristics of the spatial distribution of samples, the Kriging method in ArcGIS 10.2 (Esri, Redland, CA, USA) was employed for the spatial interpolation. Significant differences in CO$_2$ concentration, flux and environmental variables among different water areas were tested by analysis of variance (ANOVA). Spearman correlation and simple regression analysis were conducted to explore the relationships between CO$_2$ concentration (or flux) and the physio-chemical properties of water. Statistical significance was examined at the level of 0.05. The key factors influencing the CO$_2$ concentration and flux in the two reservoir areas were further investigated using redundancy analysis (RDA) in CANOCO 5.0 (Ithaca, NY, USA). Statistical results and graphics were generated by using SPSS 17.0 (IBM, Chicago, IL, USA) and Origin 2017 (OriginLab Corporation, USA), separately.

2. Results

2.1. Meteorological conditions and physico-chemical properties of reservoir water

The general spatiotemporal variations of surface water physico-chemical properties have been reported in Yang et al. (2020) (Table 2 and Appendix A Fig. S2), while in this study, we focused on the effects of urbanization. Daily temperature, atmospheric pressure, wind speed, water salinity and Chl-$a$ concentration showed small spatial variations, and the mean difference was less than 4 °C, 10 hPa, 3 m/s, 2% and 9 $\mu$g/L, respectively, during the research period. Spatially, water DO, TOC, TDN, NH$_4^+$, and PO$_4^{3-}$ concentration varied...
considerably among the four areas. TOC, NH₄⁺ and TDN in Areas I and Area-II showed
much higher concentrations than those in Area-III and Area-IV ($p < 0.05$ or
0.01; Table 2 and Appendix A Fig. S2), with the highest values usually observed in Area-I.
In most of the time, DO concentrations increased in the order: Area-I < Area-III < Area-II <
Area-IV. However, in March, DO concentrations in Area-II were higher than those in other
three areas (Table 2 and Appendix A Fig. S2).
Table 2

Summary of the two-way ANOVA results determining the effect of sampling water areas, seasons, and their interactions on water environmental variables in Wenwusha Reservoir.

<table>
<thead>
<tr>
<th></th>
<th>df</th>
<th>pH</th>
<th>DO</th>
<th>TOC</th>
<th>NH₄⁺</th>
<th>TDN</th>
<th>PO₄⁻³</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sampling area</td>
<td>3</td>
<td>17.00**</td>
<td>201.52**</td>
<td>1078.99**</td>
<td>22.02**</td>
<td>85.31**</td>
<td>7.368**</td>
</tr>
<tr>
<td>Season</td>
<td>2</td>
<td>1046.31**</td>
<td>1046.16**</td>
<td>2.37</td>
<td>32.65**</td>
<td>19.91**</td>
<td>14.953**</td>
</tr>
<tr>
<td>Sampling area × Season</td>
<td>6</td>
<td>11.64**</td>
<td>115.55**</td>
<td>4.78**</td>
<td>1.14</td>
<td>29.72**</td>
<td>9.012**</td>
</tr>
</tbody>
</table>

Symbols * and ** indicate significant differences at 0.05 and 0.01, respectively.
In general, sampling sites around human-dominated landscapes (residential area, aquaculture pond, and farmland) in NRA in the Wenwusha reservoir had higher nutrient levels (i.e. TOC, TDN, and NH$_4^+$ concentration), pH value and Chl-$a$ concentrations but lower DO concentrations than those near the natural landscapes, such as wetland and forest in SRA.

2.2. Spatial variation in CO$_2$ dynamics across four water areas

During the sampling period, large spatial variations in CO$_2$ concentrations were observed across different areas. Dissolved CO$_2$ concentrations in Area-I, Area-II, Area-III, and Area IV varied over the ranges of 1.80–178.26 µmol/L, 0.07–239.74 µmol/L, 3.21–59.17 µmol/L, and 1.02–64.91 µmol/L, respectively. Dissolved CO$_2$ concentrations decreased significantly in the order: Area-I (52.89 ± 3.64 µmol/L) > Area-II (49.22 ± 2.95 µmol/L) > Area-III (29.51 ± 2.88 µmol/L) > Area-IV (22.03 ± 1.53 µmol/L) ($p < 0.001$, Fig. 2 and Fig. 4a).

fig. 2. Spatial distribution of dissolved CO$_2$ concentrations in surface water (~0.2 m depth) of Wenwusha Reservoir from November 2018 to June 2019.

Across the three sampling campaigns, CO$_2$ fluxes across the water-air interface decreased in the order: Area-I (5.05 ± 0.87 mmol/m$^2$/hr) > Area-II (2.22 ± 0.27 mmol/m$^2$/hr) > Area-IV (1.62 ± 0.33 mmol/m$^2$/hr) > Area-III (1.46 ± 0.34 mmol/m$^2$/hr) (Fig. 3 and Fig. 4b). With the exception of March 2019, mean CO$_2$ fluxes across the water-air interface show large differences among the four water areas ($p < 0.05$, Fig. 4b).
Fig. 3. Spatial distribution of CO$_2$ fluxes across the water-air interface in Wenwusha Reservoir from November 2018 to June 2019.

Fig. 4. Variations in mean CO$_2$ concentrations (a) and fluxes (b) among the four water areas in Wenwusha Reservoir from November 2018 to June 2019. Different letters denote significant differences across water areas ($p<0.05$) based on the results of one-way ANOVA. Area I, mainly surrounded by urban land ($n=28$); Area II, mainly surrounded by agricultural land ($n=40$); Area III, mainly surrounded by wetland and sporadic agricultural land ($n=12$); Area IV, mainly surrounded by forest and sand ($n=22$). Data were shown with mean ± SE.

2.3. Spatial variation in CO$_2$ dynamics between two reservoir areas

Significant spatial differences of CO$_2$ dynamics were also observed between NRA and SRA. Mean CO$_2$ concentration and flux in NRA (51.32 ± 3.19 µmol/L and 3.72 ± 0.47 mmol/m$^2$/hr) were significantly higher than those in SRA (29.71 ± 1.87 µmol/L and 1.64 ± 0.22 mmol/m$^2$/hr) ($p < 0.01$, Appendix A Fig. S3). Larger CO$_2$ concentration and emission were often obtained in the water areas with higher urbanization level around, mainly in NRA (Fig. 2 and Fig. 3).
2.4. Spatial variation in CO$_2$ dynamics between different microtopographic zones

CO$_2$ concentration and flux were compared between different microtopographic zones (Appendix A Fig. S4). The mean dissolved CO$_2$ concentration in narrow waters (52.25 ± 4.62 µmol/L) was significantly higher than that in the open waters (37.58 ± 2.09 µmol/L) ($p < 0.05$, Appendix A Fig. S4a). No significant difference in mean dissolved CO$_2$ concentration was found between the shallow water zone and deep water zone (41.51 ± 3.09 and 42.09 ± 2.68 µmol/L, respectively, $p > 0.05$, Appendix A Fig. S4b).

The mean CO$_2$ fluxes across the water-air interface in the narrow and open waters were 2.63 ± 0.50 mmol/m$^2$/hr and 2.83 ± 0.34 mmol/m$^2$/hr, respectively. The mean CO$_2$ fluxes in the shallow water zone and deep water zone were 2.33 ± 0.37 and 3.07 ± 0.40 mmol/m$^2$/hr, respectively (Appendix A Fig. S4c and Fig. S4d). All sampling sites showed no significant spatial differences of mean CO$_2$ flux between different reservoir microtopographic zones ($p > 0.05$, Appendix A Fig. S4).

2.5. Temporal variation in CO$_2$ concentration and flux

There were clear seasonal variations in dissolved CO$_2$ concentration throughout the reservoir (Fig. 2), with the highest concentration in Nov-2018 (66.11 ± 3.97 µmol/L), followed by Jun-2019 (40.77 ± 2.11 µmol/L) and Mar-2019 (18.67 ± 2.44 µmol/L). CO$_2$ undersaturation of water samples (i.e. saturation < 100%) were found in Mar-2019 and Jun-2019 (Fig. 2).

There were also seasonal variations in CO$_2$ fluxes across the water-air interface. CO$_2$ fluxes during the whole period ranged from −4.09 to 33.63 mmol/m$^2$/hr. More than half of the measurements made in the spring (Mar-2019) exhibited net CO$_2$ uptake (Fig. 3). Seasonal mean CO$_2$ fluxes were 5.19 ± 0.70 mmol/m$^2$/hr in Nov-2018, 0.13 ± 0.15 mmol/m$^2$/hr in Mar-2019, and 2.99 ± 0.29 mmol/m$^2$/hr in Jun-2019, respectively. The four water areas showed similar seasonal patterns of CO$_2$ concentrations and fluxes: Mar-2019 < Jun-2019 < Nov-2018 ($p < 0.001$, Figs. 2–4).

2.6. Relationship between CO$_2$ concentration / flux and water physio-chemical properties

Spearman correlations were conducted to examine the relationships between CO$_2$ concentration (or flux) with the physio-chemical properties of water (Fig. 5, 6 and Table 3). Dissolved CO$_2$ concentrations were positively correlated with pH, NH$_4^+$, TDN and TOC, but negatively correlated with water temperature and DO ($p < 0.01$, Table 3). CO$_2$ fluxes were positively correlated with TOC and NH$_4^+$, but negatively correlated with DO ($p < 0.05$, Table 3). Notably, the significance and strength of correlations were different among four water areas. CO$_2$ concentrations and fluxes were significantly and negatively correlated with DO concentrations in three water areas except Area-III (Fig. 5a and 6a). CO$_2$ concentrations were positively correlated with NH$_4^+$ and TOC concentrations, with stronger relationships found in Area-I and Area-II (Fig. 5b and 5c).
Fig. 5. Relationships of CO$_2$ concentration against DO (a), NH$_4^+$ (b), and TOC (c) in the four water areas. Letter A in the legend denotes all water areas combined.

Fig. 6. Relationships of CO$_2$ flux against DO (a), NH$_4^+$ (b), and TOC (c) in the four water areas. Letter A in the legend denotes all water areas combined.
Table 3

Spearman correlation coefficients of CO$_2$ concentration (flux) with environmental variables in the whole Wenwusha Reservoir during the research period.

<table>
<thead>
<tr>
<th>Environmental variables</th>
<th>CO$_2$ concentration</th>
<th>CO$_2$ flux</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water temperature (Tw)</td>
<td>-0.226**</td>
<td>NS</td>
</tr>
<tr>
<td>pH</td>
<td>0.195**</td>
<td>NS</td>
</tr>
<tr>
<td>Dissolved oxygen (DO)</td>
<td>-0.732**</td>
<td>-0.573**</td>
</tr>
<tr>
<td>Total organic carbon (TOC)</td>
<td>0.381**</td>
<td>0.137*</td>
</tr>
<tr>
<td>Ammonia (NH$_4^+$)</td>
<td>0.471**</td>
<td>0.323**</td>
</tr>
<tr>
<td>Total dissolved nitrogen (TDN)</td>
<td>0.151**</td>
<td>NS</td>
</tr>
<tr>
<td>Phosphate (PO$_4^{3-}$)</td>
<td>NS</td>
<td>NS</td>
</tr>
</tbody>
</table>

NS means “nonsignificant correlation”. Symbols * and ** indicate significant correlations at 0.05 and 0.01 levels, respectively.
Redundancy analysis (RDA) was performed for the two reservoir areas, NRA and SRA, with CO₂ concentration and flux as the response variables and water physio-chemical properties as the explanatory variables. In NRA, axis I explained 55.1% of the variations in CO₂ concentration and flux, with DO and TOC being the most powerful predictors (Fig. 7). In SRA, axis I explained 44.9% of the variations in CO₂ concentration and flux, with NH₄⁺, DO, and TOC being the major controlling factors (Fig. 7).

Fig. 7. Results of redundancy analysis (RDA) showing the relations between CO₂ concentration (or CO₂ flux) and water physico-chemical properties including T_w (water temperature), pH, EC (conductivity), DO (dissolved oxygen), NO₃⁻ (nitrate nitrogen), NH₄⁺ (ammonia nitrogen), PO₄³⁻ (phosphate), and TP (total phosphorus), in the north reservoir area (NRA) (a) and the south reservoir area (SRA) (b) in Wenwusha Reservoir.

3. Discussion

3.1. Effects of watershed urbanization and land use types on CO₂ dynamics

Land use change in the catchment can disturb the biogeochemical cycling on land and in adjacent waters (Lai et al., 2016; Zhang et al., 2015), resulting in large spatial variations in CO₂ fluxes (Kamjunke et al., 2013; Pacheco et al., 2015). In our study, the concentrations of carbon and nitrogen substrates (TOC, NH₄⁺ and TDN) in Area-III and Area-IV were substantially lower than those in Area-I and Area-II where waters were close to municipal and agricultural lands (Table 2 and Appendix A Fig. S3). The CO₂ concentrations and fluxes increased with TOC and NH₄⁺ concentrations across the whole reservoir (p < 0.05, Table 3). Our results revealed that the spatial variation in CO₂ flux in the subtropical Wenwusha reservoir was affected by anthropogenic activities (e.g., urbanization and land use change) in the catchment, which were similar to previous findings (Marescaux et al., 2018; Wang et al., 2017) that CO₂ production and emission in the waters increased with the levels of urbanization and sewage discharge. Two underlying processes may account for this: (1) the large TOC load from municipal and aquaculture effluents provides more substrates for in situ heterotrophic respiration (Almeida et al., 2016; Crawford et al., 2013); (2) additional nitrogen loading in water areas with high organic carbon concentrations (e.g. Area I) can...
ameliorate nitrogen limitation on microbial decomposition and promote net CO$_2$ production (Bodmer et al., 2016; Marescaux et al., 2018).

The highest mean CO$_2$ flux observed in Area-I provided additional evidence for the impact of urbanization on CO$_2$ emission from our reservoir. In general, urban and agricultural sewage carries abundant dissolved CO$_2$ (Webb et al., 2016; Yang et al., 2018; Yu et al., 2017). The spatial variation in reservoir CO$_2$ flux adjacent to urban areas is thus often affected by sewage discharge. In this study, we observed that the dissolved CO$_2$ concentrations in the sewage drainage channels, aquaculture ponds, and rivers adjacent to the reservoir were about three times higher than those in the reservoir surface water. This resulted in the direct input of dissolved CO$_2$ into the Wenwusha Reservoir, and subsequently a larger CO$_2$ diffusive flux because of the steeper CO$_2$ concentration gradient between the surface water and the atmosphere. Therefore, the discharge of CO$_2$-rich wastewater can directly contribute to CO$_2$ oversaturation in some polluted waters and lead to high CO$_2$ emissions from reservoir water to the atmosphere (Li et al., 2020a; 2020b).

Topography can also influence the transport and distribution of pollutants. Pollutants tend to accumulate in the narrow coastal waters due to their low water exchange and dilution effect (e.g. Arneth et al., 2017; Li et al., 2013; Ni et al., 2019). For instance, Natchimuthu et al. (2017) reported that small and narrow lakes had higher pCO$_2$ and CO$_2$ fluxes in a Swedish catchment. Similar observations have been found in other aquatic ecosystems with varying microtopography (Raymond and Cole, 2003; Schilder et al., 2013; Wang et al., 2017). Across the entire Wenwusha Reservoir, the mean CO$_2$ concentrations and fluxes from the shallow water zone to deep water zone showed no significant difference ($p > 0.05$, Appendix A Fig S4c and S4d). The reservoir was shallow, with mean and maximum depths of 1.5 and 4.0 m, respectively. The reservoir bottom was quite flat with little variations in sediment-to-water volume ratio among reservoir areas (Gruber et al., 2019; Roland et al., 2010; Wilson et al., 2015), which resulted in limited effects of depth on DOC concentration and sediment respiration. Moreover, CO$_2$ concentrations increased significantly from the open water areas to the narrow areas ($p < 0.05$, Appendix A Fig S4a), which might be related to the coupling of high pollution load and topography (Kortelainen et al., 2006; Roland et al., 2010; Zhang et al., 2019). On one hand, narrow waters have relatively lower velocity and a more enclosed environment than other parts of the reservoir (Holgerson, 2015; Xiao et al., 2017), providing favorable conditions for the accumulation of fresh sediments and thus respiratory CO$_2$ production. On the other hand, the narrow waters adjacent to aquaculture ponds and ditches can receive abundant non-point source sewage. Similar to the spatial patterns of CO$_2$ concentration, TOC, NH$_4^+$, and TDN concentrations at the narrow waters were approximately 28%, 100%, and 27% larger than those at the open areas, which supported the above hypothesis.

### 3.2. Temporal variation in CO$_2$ emission

During the study period, mean CO$_2$ concentrations in Wenwusha Reservoir exhibited prominent seasonal fluctuations with higher value in autumn (Nov-2018) and lower value in spring (Mar-2019) (Fig. 4a). Correspondingly, CO$_2$ flux followed the same temporal pattern (Fig. 4b). In general, net CO$_2$ flux (release / uptake) in aquatic ecosystems reflects the balance between CO$_2$ production and consumption (Jonsson et al., 2003; Bellido et al., 2009; Pacheco et al., 2015). Some researches attributed the variability of CO$_2$ flux to organic matter decomposition (Wang et al., 2017), primary productivity (Sobek et al., 2005), and meteorological conditions (Butman and Raymond, 2011; Natchimuthu et al., 2014).

Biodegradation of organic carbon is regarded as an important source of CO$_2$ production (Barros et al., 2011; Crawford et al., 2013; Demarty et al., 2009). However, our
measurements showed no significant seasonal change in TOC (Table 2), which was different from the temporal patterns of CO$_2$ concentrations and fluxes in the reservoir. Therefore, substrate supply was likely not a key factor affecting the temporal dynamics of CO$_2$ in Wenwusha Reservoir. Algal photosynthesis consumes CO$_2$, which can play an important role in governing the temporal variation in CO$_2$ flux (Kutzbach et al., 2007; Scofield et al., 2016; Yao et al., 2007). Chl-$a$ is an important parameter characterizing algal primary production. Despite the lack of significant correlation observed between Chl-$a$ and CO$_2$ flux in the current research, the seasonal pattern of mean water Chl-$a$ concentration was opposite to that of CO$_2$ (Fig. 4 and Appendix A Fig. S5). Limited by the low temperature, relatively lower Chl-$a$ concentration and the highest CO$_2$ emissions were seen in November 2018. Higher Chl-$a$ concentration coincided with rising temperature in spring, accounting for the lower CO$_2$ concentration and flux in March 2019 (Appendix A Fig. S5). It should be noted that precipitation and its dilution effect on Chl-$a$ in water could also influence the seasonal variation in CO$_2$ flux (Holgerson, 2015; Zhang et al., 2019). In addition, on rainy days, photosynthesis could be constrained by lower solar radiation. Frequent rainfall events between April and June 2019 (total precipitation of 625.6 mm) (Appendix A Fig. S1) reduced Chl-$a$ concentration in the reservoir to some extent. Thus, the higher CO$_2$ flux detected in summer (June-2019) than in spring (Mar-2019) was probably in part due to the greater number of rainy days and the subsequent decline of sunlight-driven photosynthesis. In the subtropical coastal reservoir, therefore, our findings demonstrated that primary productivity could exert an impact on the seasonal variation in CO$_2$ fluxes between seasons, which in turn would be related to precipitation and temperature.

3.3. CO$_2$ fluxes in comparison with previous estimates

The average CO$_2$ flux from Wenwusha Reservoir was 2.77 ± 0.28 mmol/m$^2$/h, which was lower than those reported in some tropical waters (e.g. Abril et al., 2005; Dos Santos et al., 2006; Guérin et al., 2006) (Table 4). However, we noticed that the CO$_2$ fluxes from our reservoir were markedly higher than those in most temperate and subtropical reservoirs worldwide, such as Lake Lynch in Chile (Gerardo-Nieto et al., 2017), Eagle Creek reservoir in the USA (Jacinthe et al., 2012), cascade reservoirs on Maotiao river in China (Wang et al., 2011), and Danjiangkou reservoir in China (Li and Zhang, 2014) (Table 4). Our results of flux upscaling to the whole-reservoir scale based on our high spatial resolution data showed that Wenwusha reservoir emitted approximately 3.91 Gg CO$_2$ per year. The total CO$_2$ flux from Wenwusha reservoir would hence account for approximately 0.0241% of the annual total from all the reservoirs in China (Li et al., 2018). The results of this study showed that the subtropical coastal reservoir such as Wenwusha reservoir could be potential sources of atmospheric CO$_2$ and therefore would deserve more attention.
### Table 4

Ranges of CO$_2$ fluxes (mmol m$^{-2}$ h$^{-1}$) from different types of reservoirs in the world.

<table>
<thead>
<tr>
<th>Climate</th>
<th>Site</th>
<th>Main land use in the catchment</th>
<th>$F_{CO_2}$ (mmol m$^{-2}$ h$^{-1}$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperate</td>
<td>Lake Lynch, Chile</td>
<td>Forest</td>
<td>0.49 – 0.57 (0.52)</td>
<td>Gerardo-Nieto et al., 2017</td>
</tr>
<tr>
<td></td>
<td>L. Skinnemuddselet, Sweden</td>
<td>Forest, mire</td>
<td>------ (0.83)</td>
<td>Áberg et al., 2004</td>
</tr>
<tr>
<td></td>
<td>Porttipahta, Finland</td>
<td>Forest, pond</td>
<td>0.83 – 2.17 (1.46)</td>
<td>Huttunen et al., 2003</td>
</tr>
<tr>
<td></td>
<td>Lokka, Finland</td>
<td>Peatland</td>
<td>0.46 – 3.04 (1.44)</td>
<td>Huttunen et al., 2003</td>
</tr>
<tr>
<td></td>
<td>Eagle Creek, USA</td>
<td>Agriculture, grassland, forest</td>
<td>-1.28 – 15.10 (1.90)</td>
<td>Jacinthe et al., 2012</td>
</tr>
<tr>
<td>Subtropical</td>
<td>Danjiangkou, China</td>
<td>Forest, grassland, farmland</td>
<td>-0.34 – 1.31 (0.38)</td>
<td>Li &amp; Zhang, 2014</td>
</tr>
<tr>
<td></td>
<td>Xiuwen, China</td>
<td>------</td>
<td>-0.25 – 3.71 (1.96)</td>
<td>Wang et al., 2011</td>
</tr>
<tr>
<td></td>
<td>Chongqing, China</td>
<td>Urban</td>
<td>-0.42 – 21.25 (5.73)</td>
<td>Wang et al., 2017</td>
</tr>
<tr>
<td></td>
<td>Chongqing, China</td>
<td>Agriculture</td>
<td>-0.48 – 7.20 (2.01)</td>
<td>Wang et al., 2017</td>
</tr>
<tr>
<td></td>
<td>Al-Wihdeh, King Talal, Wadi, Al-Arab, Jordan</td>
<td>------</td>
<td>-1.10 – 16.52 (3.12)</td>
<td>Alshboul et al., 2015</td>
</tr>
<tr>
<td></td>
<td>Wenwusha, China</td>
<td>Urban, agriculture, forest, wetland</td>
<td>-4.09 – 33.63 (2.77)</td>
<td>This study</td>
</tr>
<tr>
<td>Tropical</td>
<td>Petit Saut, French Guiana</td>
<td>Tropical forest</td>
<td>-0.42 – 15.42 (5.54)</td>
<td>Abril et al., 2005</td>
</tr>
<tr>
<td></td>
<td>Tucurui, Brazil</td>
<td>Tropical forest</td>
<td>------ (7.92)</td>
<td>Dos Santos et al., 2006</td>
</tr>
<tr>
<td></td>
<td>Samuel, Balbina, Brazil</td>
<td>Tropical forest</td>
<td>10.58 – 16.33</td>
<td>Guerin et al., 2006</td>
</tr>
<tr>
<td></td>
<td>Cerrado, Brazil</td>
<td>------</td>
<td>-0.34 – 16.62</td>
<td>Roland et al., 2011</td>
</tr>
<tr>
<td></td>
<td>China's reservoirs</td>
<td>------</td>
<td>------ (1.85)</td>
<td>Li et al., 2018</td>
</tr>
<tr>
<td></td>
<td>Global reservoirs</td>
<td>------</td>
<td>------ (1.14)</td>
<td>Deemer et al., 2016</td>
</tr>
</tbody>
</table>

Figures in brackets are averages. “------” means no data.
Notably, the average CO$_2$ flux in waters adjacent to the urban area (Area-I, 5.05 ± 0.87 mmol/m$^2$/hr) was 1.72 – 3.46 times of that in other water areas in Wenwusha Reservoir (Fig. 3 and Fig. 4b). Moreover, the mean CO$_2$ flux in Area-I was close to the level seen in some tropical reservoirs (Barros et al., 2011) and urban reservoirs in Chongqing, Southwest China (5.73 ± 3.38 mmol/m$^2$/hr) (Wang et al., 2017), where urban pollution was the major contributor to CO$_2$ production. In contrast with the findings from several reservoirs in Chongqing (Wang et al., 2017), our results showed that the influence of urbanization on CO$_2$ emission from adjacent waters could also exist in different areas within a single reservoir ecosystem. These results together indicated the crucial role of urbanization in carbon biogeochemical cycling in reservoir waters.

3.4. Uncertainties and further outlook

There are several limitations in our study that are worthy addressing. Firstly, our results have shown large spatiotemporal variations in CO$_2$ concentration and flux in the reservoir. In future studies, field sampling with a greater frequency over multiple years can provide more detailed information about the temporal variations in CO$_2$ dynamics at multiple scales. Secondly, the diel fluctuations of GHG flux have been reported in various aquatic ecosystems (Natchimuthu et al., 2014; Xiao et al., 2013; Xing et al., 2004). Photosynthesis is typically strong during the day, while respiration dominates CO$_2$ exchange with markedly higher CO$_2$ emission at night (Hirota et al., 2007). Therefore, aquatic ecosystems can be a net carbon sink during the daytime due to the strong phytoplankton photosynthesis, but change to a net carbon source when considering a complete 24-hour cycle owing to the strong carbon emission at night (Natchimuthu et al., 2014). Similar diel patterns can also occur in the reservoir on top of the seasonal variation. A greater number of in situ measurement of the diurnal CO$_2$ fluxes in different seasons will further improve our development of annual CO$_2$ budgets in the aquatic ecosystems. Furthermore, some studies have shown the important role of meteorological variables in affecting CO$_2$ emission (Li and Lu, 2012; Natchimuthu et al., 2014; Zhao et al., 2013). Although the effect of extreme weather events, such as heavy rain and typhoon, on CO$_2$ flux was not examined in this study, we found some clear impacts of continuous precipitation on reservoir CO$_2$ fluxes. The impacts of meteorological events deserve more attention in future studies. Due to the limitation of equipment, we did not measure sewage discharge and nutrient concentrations in this study. In future work, quantifying the rates of water and nutrient inputs from sewage can provide useful information to improve the understanding of the impact of urbanization and land use on carbon cycling in reservoirs. Lastly, we focused our investigation of the controls of CO$_2$ concentration and flux on various environmental parameters (e.g. water quality, weather condition, and reservoir morphology). Future research can quantify the biogeochemical processes of CO$_2$ using molecular biotechnology and isotope methods to yield a better mechanistic understanding of the spatiotemporal dynamics of CO$_2$ in aquatic ecosystems.

4. Conclusions

With the worsening climate change, GHG emission from reservoirs have received increasing attention. In this study, dissolved CO$_2$ concentration and flux were investigated at high spatial resolution from a subtropical coastal Wenwusha Reservoir, Southeast China. Overall, our results showed that CO$_2$ concentrations in the reservoir were supersaturated (average: 24.25 mol/m$^2$/y) in most periods, varying over a wide range from −35.82 to 294.60 mol/m$^2$/y. CO$_2$ concentrations and fluxes from waters adjacent to regions with intensive human activity were much higher than those in other areas, due to larger input of allochthonous carbon and nitrogen via municipal sewage, aquaculture wastewater and upstream runoff. Urbanization
and agricultural activities in the catchment appeared to create CO₂ emission hotspots in some parts of the reservoir. Apart from the spatial differences across the reservoir, reservoir CO₂ emissions also exhibited clear seasonal variations that were related to primary productivity, temperature, and rainfall events. Our results highlighted that subtropical coastal reservoir was a net source of atmospheric CO₂ with high spatiotemporal heterogeneity.

Considering the rapid urbanization in coastal areas around the world, proactive measures are needed to mitigate the large GHG emission from coastal reservoirs arising from human activities.

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