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Environmental investments decreased partial pressure of CO_2 in a small eutrophic urban lake: Evidence from long-term measurements[☆]

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ABSTRACT

Inland waters emit large amounts of carbon dioxide (CO_2) to the atmosphere, but emissions from urban lakes are poorly understood. This study investigated seasonal and interannual variations in the partial pressure of CO_2 (pCO_2) and CO_2 flux from Lake Wuli, a small eutrophic urban lake in the heart of the Yangtze River Delta, China, based on a long-term (2000–2015) dataset. The results showed that the annual mean pCO_2 was 1030 ± 281 µatm (mean ± standard deviation) with a mean CO_2 flux of 1.1 ± 0.6 g m^{-2} d^{-1} during 2000–2015, suggesting that compared with other lakes globally, Lake Wuli was a significant source of atmospheric CO_2. Substantial interannual variability was observed, and the annual pCO_2 exhibited a decreasing trend due to improvements in water quality driven by environmental investment. Changes in ammonia nitrogen and total phosphorus concentrations together explained 90% of the observed interannual variability in pCO_2 ($R^2 = 0.90$, $p < 0.01$). The lake was dominated by cyanobacterial blooms and showed nonseasonal variation in pCO_2. This finding was different from those of other eutrophic lakes with seasonal variation in pCO_2, mostly because the uptake of CO_2 by algal-derived primary production was counterbalanced by the production of CO_2 by algal-derived organic carbon decomposition. Our results suggested that anthropogenic activities strongly affect lake CO_2 dynamics and that environmental investments, such as ecological restoration and reducing nutrient discharge, can significantly reduce CO_2 emissions from inland lakes. This study provides valuable information on the reduction in carbon emissions from artificially controlled eutrophic lakes and an assessment of the impact of inland water on the global carbon cycle.

1. Introduction

There are approximately 117 million lakes with a total surface area of 5 × 10^6 km^2 in the world, and small lakes are numerous (Verpoorter et al., 2014). The majority of these lakes are supersaturated with CO_2, and their role in the global CO_2 cycle has received increasing attention (Cole et al., 2007; Tranvik et al., 2009). It is estimated that global natural lakes emit 0.11–0.57 Pg (10^{15} g) C yr^{-1} to the atmosphere as CO_2 (Cole et al., 2007; Tranvik et al., 2009; Raymond et al., 2013) and therefore play a large role in the global CO_2 budget. China's lakes, with a total surface area of 82,232 km^2, emit 15.98 Tg (10^{12} g) C yr^{-1} to the atmosphere as CO_2 (Li et al., 2018). For comparison, the emissions of CO_2 from the world's volcanoes is 14.5 Tg (10^{12} g) C yr^{-1} (Fischer et al., 2019). Despite their global importance in the carbon cycle, studies of lake CO_2 dynamics have paid very little attention to urban lakes, resulting in limited data availability (Yang et al., 2008; Bellido et al., 2011; Peacock et al., 2019; van Bergen et al., 2019).

Urban lakes are common features of landscapes and important components of the urban living environment. Urban lakes are mostly shallow, small in size and characterized by high perimeter to surface area ratios (Birch and McCaskie, 1999). The specific

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physical properties indicate that urban lakes receive a relatively high input of terrestrial carbon and contribute to heterotrophic respiration (Hanson et al., 2007; Holgerson and Raymond, 2016). Urban lakes are stagnant and receive industrial and domestic wastewater discharge (Grimm et al., 2008; Waajen et al., 2016). Large anthropogenic disturbances can directly enhance urban lake CO_2 emissions via the external input of dissolved inorganic carbon (McDonald et al., 2013; Weyhenmeyer et al., 2015) or indirectly support emissions through high discharges of dissolved organic carbon and nutrients as a result of increased respiration and organic matter degradation (Sobek et al., 2005; Kortelainen et al., 2006; Li et al., 2020). Thus, urban lakes may be important hotspots of CO_2 emissions.

Lake eutrophication is a global water quality issue due to nutrient enrichment. Urban lakes commonly experience algal blooms due to increasing primary production as a result of eutrophication (Waajen et al., 2014; Duan et al., 2017). The effect of algal blooms on lake water quality has been well investigated (Waajen et al., 2014; Duan et al., 2017), but their effect on CO_2 flux has not yet been studied. Algal blooms are known to be able to uptake CO_2 and then decrease emissions due to high primary productivity (Schindler et al., 1997; Gu et al., 2011; Pacheco et al., 2014), and CO_2 has been shown to vary markedly seasonally because of algal blooms (Gu et al., 2011). However, a large amount of CO_2 can also be produced via the mineralization of algae-derived organic matter during the decay of algal blooms (Gudasz et al., 2010; Yan et al., 2017; Andrade et al., 2019). Considering the increasing frequency of algal blooms (Duan et al., 2017; Sinha et al., 2017), field measurements are needed to understand the effects of algal blooms on lake CO_2 emissions.

Lake Wuli, a typical subtropical natural urban lake, is located in the Yangtze River Delta, China. This lake has experienced drastic changes in its ecological state (Chen et al., 2013). The lake featured clear water and abundant submerged macrophytes before the 1970s, but the submerged macrophytes gradually disappeared, and algal blooms started to occur at the beginning of the 1990s due to the introduction of a large amount of external nutrients. Then, a series of environmental measures was implemented to improve the water quality through environmental investments by the local government. Considering the dramatic changes in the physical, chemical, and biological environments of the lake that have occurred over the past two decades due to environmental investment (Chen et al., 2009; Chen et al., 2013), it is interesting and important to examine how the lake CO_2 dynamics have responded to the changes in these aquatic environments. This study provides a unique opportunity to examine the CO_2 dynamics in an urban lake undergoing significant changes in its ecological state.

The specific objectives of this study were (1) to investigate the long-term changes in CO_2 in an urban lake (Lake Wuli); (2) to elucidate the role of environmental investments in long-term lake CO_2 changes; (3) to determine the role of eutrophication on CO_2 flux variability; and (4) to compare the CO_2 flux of this natural urban lake with the CO_2 flux reported for other lakes. This study not only fills the gap in our knowledge of CO_2 dynamics in natural urban lakes but also provides powerful data sources for predicting how eutrophic lake CO_2 levels change in a changing environment. We hypothesized that the urban lake acted as a significant CO_2 source given the significant nutrient discharge and further hypothesized that the lake would show a decreasing trend in annual CO_2 dynamics considering the improvement of water quality due to environmental investment.

2. Materials and methods

2.1. Study area

Lake Wuli is located in Wuxi city, Jiangsu Province (Fig. 1). Wuxi, a large city located in the heart of the Yangtze Delta in East China (Fig. 1), is a highly industrialized area, has a high population density and economic development, and is experiencing a high rate of urbanization. Based on a report from the Statistics Bureau of Wuxi City in 2017, it has a population of more than four million (493.05×10^4 habitants) and a gross domestic product (GDP) of more than 105 billion RMB (approximately 15.3 billion US dollars). Importantly, the environmental investments per capita from Wuxi increased annually with increasing GDP per capita, and the ratio of environmental investments to GDP in Wuxi had a mean value of 0.024, which was significantly higher than the national mean value of 0.011 (Fig. 2a). Additionally, the region features an annual mean precipitation of 1100 mm, and heavy precipitation occurs in summer (Chen et al., 2013; Xiao et al., 2019b).

Lake Wuli is located in an area with an elevation of less than 10 m above mean sea level and has a surface area of 8.6 km^2, a mean depth of 2.1 m, and a maximum depth of 3.4 m. The lake receives millions of tons of untreated domestic sewage and industrial wastewater every day from Wuxi, but the external pollutant loadings have decreased significantly in recent years due to environmental investments (Fig. 2b). Lake Wuli is located close to Lake Taihu, a large (area 2400 km^2) and shallow (mean depth 2.0 m) eutrophic lake, but the lake is completely isolated from Lake Taihu by a dam (Fig. 1).

2.2. Data acquisition and water sampling

Long-term data (2000–2015) on Lake Wuli were obtained from the Taihu Laboratory for Lake Ecosystem Research (TLLER). TLLER is a long-term observation station in the Chinese Ecosystem Research Network (CERN). TLLER researchers performed field sampling in the lake at two sampling sites (Site A and Site B; Fig. 1). Field surveys were conducted at Site A from 2000 to 2015 and at Site B from 2005 to 2015. Notably, the long-term measurements at Site A were

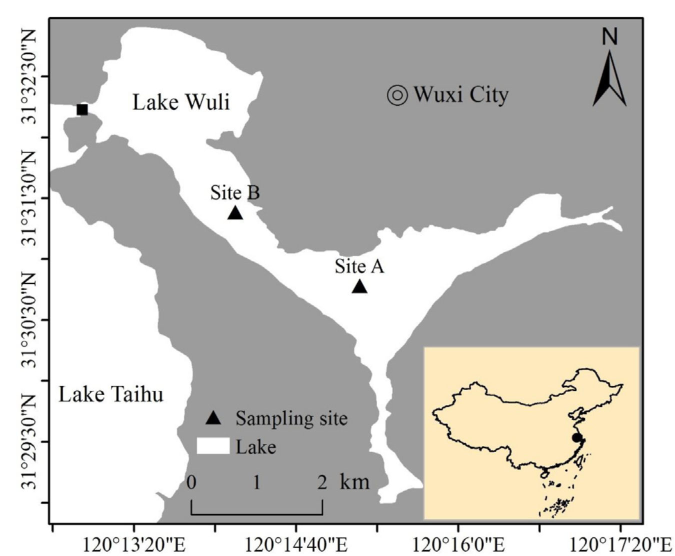

Fig. 1. Location of study sites. Site A and Site B were the sampling sites in Lake Wuli. The black square indicates the dam preventing water exchange between Lake Wuli and Lake Taihu. The gray area indicates the urban region. The black square circle in the inset map shows the geographic location of Lake Wuli in China.

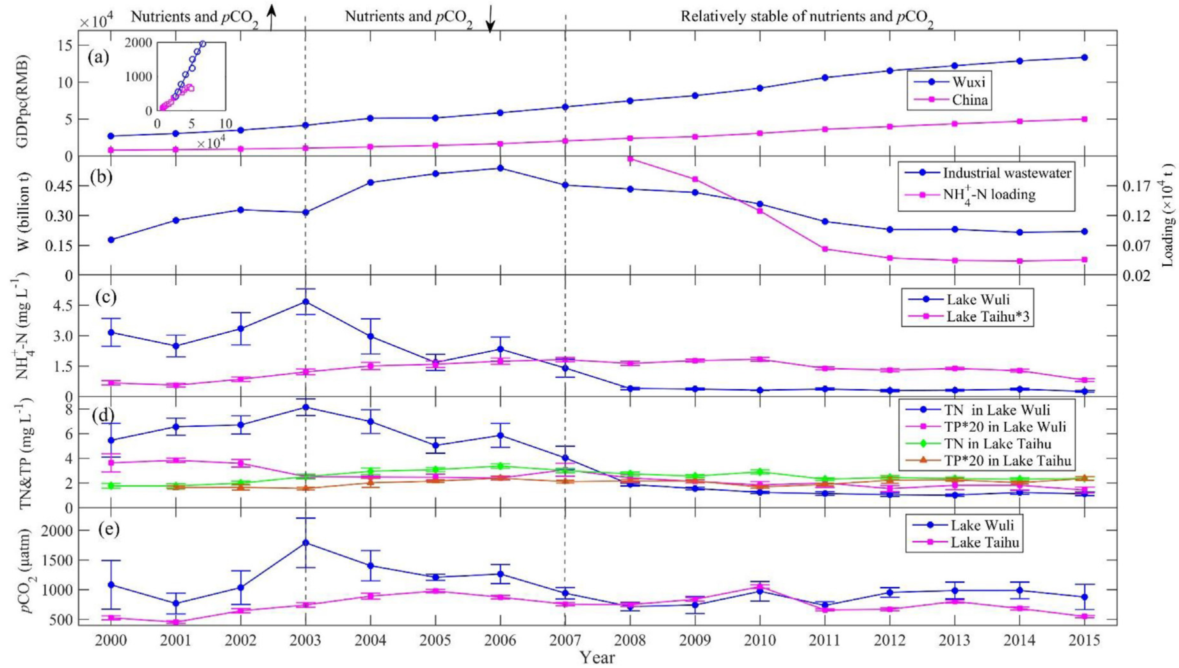

Fig. 2. Annual trend in (a) GDP per capita (GDPpc) of Wuxi and China; (b) the industrial wastewater discharge loading (W, billion t) and corresponding NH_4^+-N discharge loading in Wuxi, (c) the NH_4^+-N concentrations, (d) the TN and TP concentrations, and (e) the pCO_2 of Lake Wuli and Lake Taihu from 2000 to 2015. The error bars represent one standard error. The illustration in panel (a) shows the correlations between environmental investment per capita (RMB) and GDP per capita (RMB) in China (red: $R^2 = 0.96$, $p < 0.01$) and Wuxi (blue: $R^2 = 0.99$, $p < 0.01$). The dashed lines show the turning points for the nutrients and pCO_2 in Lake Wuli, and the upward (downward) arrow indicates an increasing (decreasing) trend. The GDP and environmental investment data were obtained from the statistics bureau. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

aimed at understanding the long-term patterns of the environmental variables in Lake Wuli. The measurements at Site B (2005–2015) were aimed at understanding the environmental changes in the western part of the lake and were conducted starting in 2005. At Site A, one water sample was collected monthly from 2001 to 2004 and seasonally for the remainder of the time. At Site B, one water sample was collected seasonally from 2005 to 2015. At each site, depth-integrated water samples were collected using a 10-cm-diameter, 2-m-long clear plastic tube. Seasonal sampling at both Site A and Site B was conducted in February, May, August, and November, and the sampling rate of four times per year was generally sufficient to reflect the seasonal variation in the lake environmental variables. Each field survey was completed between 10:00 and 15:00 local time on one day.

The environmental variables considered in this study were water temperature (T_w), alkalinity (Alk), pH, specific conductance (Spc), dissolved oxygen (DO), water clarity, ammonium nitrogen (NH_4^+-N) nitrate nitrogen (NO_3^--N), total nitrogen (TN), total phosphorus (TP), dissolved organic carbon (DOC), and chlorophyll *a* (Chl-a). Several previous studies have reported the procedure of sampling and measurement (Fan et al., 2003; Xu et al., 2010; Xiao et al., 2020). The parameters T_w, pH, Spc, and DO were measured with a calibrated multiparameter probe (YSI 6600, Yellow Springs Instruments) in the field. The pH probe was carefully calibrated with two standard buffer solutions prior to measurement, and the probe had a precision of ±0.01 pH units. Alk was measured via Gran titration with a precision of ±0.5%, and the Alk measurement was conducted on the sampling day in an open vessel (Fan et al., 2003). The uncertainties in the measurements of pH and Alk were 0.01 pH units and 4 μeq L^{-1} (Fan et al., 2003), respectively. The concentration of NH_4^+-N was determined by the indophenol blue method, and the concentration of NO_3^--N was determined with the cadmium reduction method. The concentrations of TN and TP were analyzed with combined persulfate digestion (Ebina et al., 1983), followed by spectrophotometric measurement for NO_3^--N and soluble reactive phosphorus. The DOC concentration was measured with a Shimadzu TOC-5000A analyzer, and Chl-a was measured spectrophotometrically after extraction with 90% hot ethanol. The water samples for the analysis of nutrients (TN, NH_4^+-N, NO_3^--N, and TP), DOC, and Chl-a were stored in 5-L acid-washed plastic containers and were kept cool while in the field. Then, these samples were transported to the laboratory for immediate filtration and analysis. Water clarity was obtained in situ based on the Secchi disk depth (SDD).

2.3. Calculations

We calculated the partial pressure of CO_2 (pCO_2), CO_2 exchange flux at the lake-air interface (F_c), degree of dissolved oxygen saturation (S_{do}), and trophic state index (TSI) based on the TLLER dataset. The lake pCO_2 was calculated based on the pH, Alk, and in situ T_w, and the details of the calculation equations are given in the Supporting Information (Text S1). Lake pCO_2 is generally calculated from pH, alkalinity, and water temperature (Abril et al., 2015; Raymond et al., 2013; Wen et al., 2017; Weyhenmeyer et al., 2015), but the calculated pCO_2 may be overestimated due to the contribution of organic acids to alkalinity and the lower carbonate system buffering capacity at low pH (Abril et al., 2015). In this study, because none of the samples had a pH below 7 (pH range: 7.45–9.06) and there was a relatively low DOC concentration (Table S1), overestimation was unlikely (Abril et al., 2015). The uncertainty of pCO_2 calculation was ±2.3%, arising from the uncertainty in the measurements of pH and Alk.

F_c (g m^{-2} d^{-2}; a positive value indicates CO_2 emission from the lake to the atmosphere) was calculated based on the bulk diffusion model (Cole and Caraco, 1998):

$$F_c = 0.044 \times k \times K_H \times (pCO_2 - p_a) \quad (1)$$

where 0.044 is a conversion factor, p_a is the partial pressure of CO_2 in the atmosphere (μatm) and k is the gas transfer coefficient (m d^{-1}). The local p_a was measured by a CO_2 gas analyzer (Xiao et al., 2014). In this study, k was estimated based on the study of Cole and Caraco (1998). More details on the k estimation are presented in the Supporting Information (Text S2).

DO dynamics are a useful parameter to indicate lake metabolic balances. The S_{do} was computed by dividing the measured oxygen concentration in the lake by the solubility concentration of oxygen at the in situ temperature. S_{do} indicates the balance between autotrophic and heterotrophic activity (Brigham et al., 2019). $S_{do} > 1$ indicates that the dissolved oxygen concentration is oversaturated due to high photosynthesis rates (CO_2 consumption), and $S_{do} < 1$ indicates undersaturation due to high respiration rates (CO_2 production).

The TSI is used to assess the trophic level of lakes. The TSI is calculated based on four water quality indices (Zhang et al., 2018): TN, TP, Chl-a, and SDD, which are shown in the Supporting Information (Text S3). According to the standard trophic categories (Zhang et al., 2018), TSI values of >70, 50–70, 30–50, and <30 indicate hypereutrophic, eutrophic, mesotrophic, and oligotrophic, respectively.

2.4. Statistical analysis

Simple linear and multilinear regression tests were performed to find the relationships between the environmental variables and CO_2. In the multiple linear regression, a variance inflation factor (VIF) was used to determine if multicollinearity was a significant factor. When VIF was greater than the threshold of 5, any of the variables in the regression equation were removed to reduce multicollinearity (Xiao et al., 2017). The best regression equation had the lowest Akaike information criterion (AIC) value.

The environmental variables, including pCO_2 and CO_2 flux, were summarized as the mean value for the spring (from March to May), summer (from June to August), autumn (from September to November), and winter (from December to February in the next year) to determine the seasonal variation and as annual mean values from 2000 to 2015 for analysis of the interannual variation. Since 2005, the measurements at Sites A and B were averaged to determine the seasonal and annual mean values. A least significant difference post hoc test was carried out using SPSS (version 18.0) to determine the differences among the measured variables, and differences at the $p < 0.05$ level were deemed statistically significant.

3. Results

3.1. Physical, chemical and biological conditions

There was good consistency in the environmental variables between the two sampling sites (Site A and Site B) during the sampling period (Fig. S1). Moreover, there were no significant differences ($p > 0.05$) in these measured variables, including the water temperature, nutrients (TN, NH_4^+-N, NO_3^--N, and TP), Chl-a, DOC, and DO between the two sites. The variables examined herein at the two sites were first averaged for an analysis of the temporal variation. The nutrient concentrations in the lake exhibited remarkable interannual variations (Fig. 2c–d and Fig. S1), which can be divided into three stages: (1) from 2000 to 2003, the concentrations increased significantly; (2) from 2003 to 2007, the concentrations decreased significantly; and (3) after 2007, the concentrations were relatively stable with low values.

The annual mean water temperature was 18.2 ± 8.6 °C and had a strong seasonality (Table S1): summer (29.5 ± 2.0 °C) > spring (20.7 ± 3.7 °C) > autumn (16.2 ± 4.8 °C) > winter (7.5 ± 2.1 °C). Water temperature showed a nonsignificant difference between the two sites (Fig. S1a). The nutrient concentrations (TN, NH_4^+-N, NO_3^--N, and TP) in the lake also showed strong seasonal variation (Fig. S1 and Table S1). Specifically, the lowest concentrations of TN (2.71 ± 1.63 mg L^{-1}), NH_4^+-N (0.75 ± 0.81 mg L^{-1}), and NO_3^--N (0.49 ± 0.53 mg L^{-1}) occurred in the summer, mostly due to the high denitrification rate, rainfall dilution and phytoplankton uptake (Xu et al., 2010), while the highest concentrations appeared in the winter (Table S1). In contrast, the peak TP concentration occurred in the summer, with a mean value of 0.16 ± 0.05 mg L^{-1}, which was significantly ($p < 0.01$) higher than that in the spring, autumn, and winter. The Chl-a concentration also varied seasonally and was consistent with water temperature (Fig. S1), with the peak occurring in the summer and spring (Table S1). The temporal correlations between Chl-a and the nutrients were significant (Table S2), indicating that nutrient concentrations, especially TP concentrations, dominated the lake algal blooms. Moreover, Chl-a was positively correlated with S_{do} (Table S2). The annual TSI ranged from 54.79 to 69.84, with a mean value of 62.48, suggesting that the urban lake was eutrophic.

3.2. Interannual variability in pCO_2

The lake exhibited remarkable interannual variations in pCO_2 (Fig. 2e). The highest pCO_2 of the lake occurred in 2003, with a mean value of 1790 ± 1324 μatm, and the lowest pCO_2 occurred in 2008 (mean value: 717 ± 207 μatm; Table S3). The substantial pCO_2 interannual variability can also be divided into three stages, similar to the trends of the nutrients: (1) from 2000 to 2003, the pCO_2 increased significantly, with the peak occurring in 2003; (2) from 2003 to 2007, the pCO_2 decreased significantly; and (3) after 2007, the pCO_2 was relatively low, with minor variation. The mean pCO_2 values in the three stages were 1170 ± 436 μatm, 1221 ± 372 μatm, and 872 ± 122 μatm. The annual mean pCO_2 based on long-term measurements from 2000 to 2015 was 1030 ± 281 μatm.

3.3. CO_2 flux

The lake was a source of atmospheric CO_2, with an annual mean CO_2 flux of 1.1 ± 0.6 g m^{-2} d^{-1} over the span of the long-term field measurements based on the calculated pCO_2 (Table S3). There were no statistically significant differences ($p > 0.05$) in CO_2 flux among seasons. Consistent with the annual trend of pCO_2, the CO_2 flux also varied annually (Table S3). The peak CO_2 emissions appeared in 2003, with an annual mean value of 2.6 ± 2.5 g m^{-2} d^{-1}, mostly due to high nutrient loadings, and this value was approximately six times higher than the lowest emission value in 2008, with an annual mean value of 0.4 ± 0.3 g m^{-2} d^{-1}.

3.4. Factors influencing pCO_2

The temporal variations in pCO_2 were correlated with several environmental variables (Table 1). Overall, the pCO_2 was positively correlated with NH_4^+-N and DOC but negatively correlated with DO, S_{do}, TP, and Chl-a based on the measurements from 2000 to 2015. However, the correlations between pCO_2 and some of these variables, not including DO and S_{do}, varied seasonally (Table 1). No significant correlations between pCO_2 and N concentrations were found except in the winter. A significant negative correlation

Table 1
Relationships between normalized pCO_2 and key aquatic environmental variables in different seasons from 2000 to 2015.[a]

	DO	S_{do}	NO_3^--N	NH_4^+-N	TN	TP	DOC	Chl-a	TSI
Spring	−0.66[b]	−0.64[b]	−0.22	0.09	−0.02	−0.45[b]	0.43[b]	−0.61[b]	−0.34
Summer	−0.48[b]	−0.48[b]	0.15	0.34	0.09	−0.17	0.40[b]	0.08	0.18
Autumn	−0.67[b]	−0.72[b]	−0.12	0.13	0.09	−0.31	−0.06	−0.28	−0.06
Winter	−0.66[b]	−0.70[b]	0.08	0.48[b]	0.38[c]	0.18	0.15	−0.41[c]	−0.03
Overall	−0.51[b]	−0.61[b]	−0.08	0.21[c]	0.10	−0.25[b]	0.24[b]	−0.40[b]	−0.15

[a] DO, dissolved oxygen; S_{do}, dissolved oxygen saturation; TN, total nitrogen concentration; TP, total phosphorus concentration; DOC, dissolved organic carbon; Chl-a, chlorophyll *a* concentration; TSI, trophic state index.
[b] Correlation is significant at the 0.01 level.
[c] Correlation is significant at the 0.05 level.

between pCO_2 and TP was found only in the spring. The pCO_2 was positively correlated with DOC in the warm seasons (spring: $r = 0.43$, $p < 0.01$, $n = 24$; summer: $r = 0.40$, $p < 0.01$, $n = 25$) but not in the cool seasons (autumn: $p = 0.79$; winter: $p = 0.47$). For Chl-a, the correlations were only significant in the spring and winter (Table 1).

The variability in annual pCO_2 was highly correlated with NH_4^+-N, TN, and DOC (Fig. 3), moderately correlated with S_{do} (Table S4), and not correlated with the lake trophic state (as represented by TSI and Chl-a, Table S4). Multilinear stepwise regression analysis revealed that the NH_4^+-N concentration (mg L^{-1}) and TP concentration (mg L^{-1}) can best explain the interannual variability in pCO_2 (μatm) from 2000 to 2015 in the lake. The regression equation is

$$pCO_2 = 255.42NH_4^+ - N - 6183.41\ TP + 1389.49 \quad (2)$$

This regression equation explained 90% of the observed interannual variability in the pCO_2 ($R^2 = 0.90$, $p < 0.01$). This equation was the best, as it had the lowest AIC value, and the AIC increased if one of the two explanatory variables was removed. NH_4^+-N and TP were correlated (Table S2), but the VIF between them had a value of 1.904, which was lower than the threshold of 5, indicating that multicollinearity was negligible.

3.5. Seasonal and monthly variability in pCO_2

The mean pCO_2 at Site A was 1039 ± 1034 μatm in the spring, 1129 ± 823 μatm in the summer, 1155 ± 597 μatm in the autumn, and 1124 ± 670 μatm in the winter, showing no statistically significant differences ($p > 0.05$) among the seasons. At Site B, the pCO_2 also showed no statistically significant differences ($p > 0.05$) among the seasons. Importantly, the pCO_2 measurements at Sites A and B showed good consistency and were highly correlated ($r = 0.70$, $p < 0.01$, n = 40) during the synchronous observation

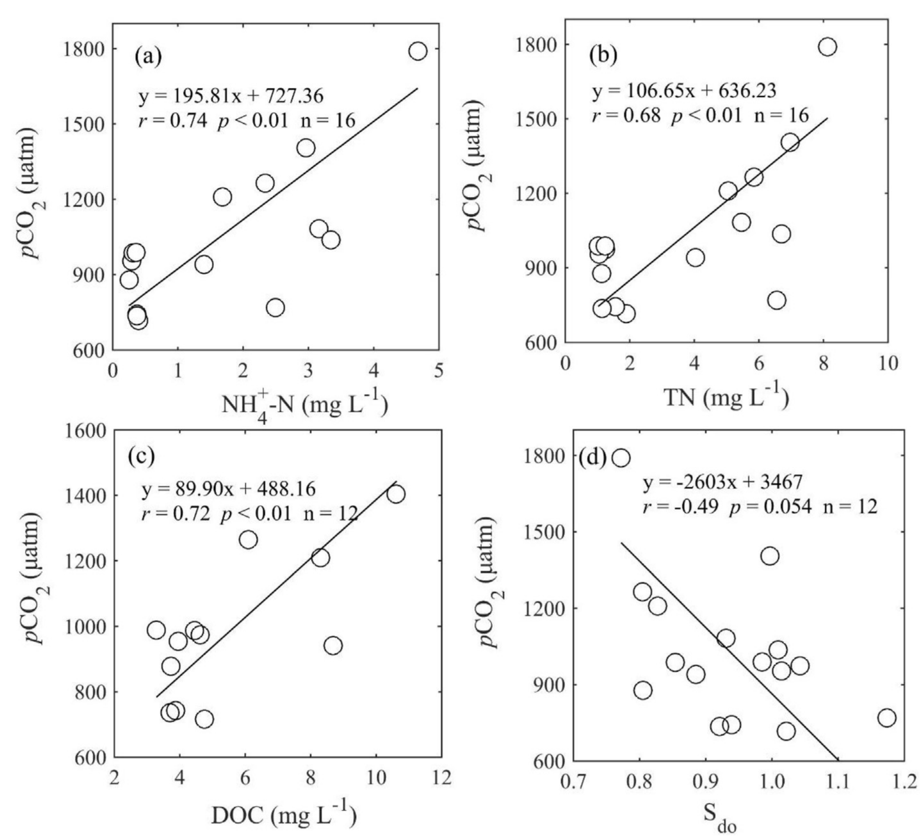

Fig. 3. Correlations between the annual mean lake pCO_2 and (a) NH_4^+-N concentration, (b) TN concentration, (c) DOC concentration, and (d) S_{do}. Note that the measurement of DOC was conducted from 2004 to 2015.

period (2005−2015, Fig. S2), and there were no statistically significant differences in pCO_2 between the two sites ($p = 0.46$). Hence, the two pCO_2 measurements were averaged below. The site-averaged pCO_2 in the spring (964 ± 563 μatm), summer (1006 ± 581 μatm), autumn (1097 ± 409 μatm), and winter (1022 ± 356 μatm; Table S3) also showed no statistically significant ($p > 0.05$) differences.

4. Discussion

4.1. Anthropogenic influences on CO_2 variations

Wuxi city deposits large amounts of nutrients, carbon, and pollutants into the lake (Chen et al., 2013). Our dataset showed that the substantial interannual variability in lake CO_2 was highly correlated with NH_4^+-N and DOC (Fig. 3), two indicators of urban anthropogenic inputs (Yang et al., 2008; Yu et al., 2013; Wang et al., 2017). Importantly, our results demonstrated that the nutrient concentrations (NH_4^+-N and TP) explained 90% of the observed interannual variability in the lake pCO_2 ($R^2 = 0.90$, $p < 0.01$). This was consistent with previous studies showing the importance of anthropogenic loading in understanding and predicting CO_2 variability in urban watersheds (Wang et al., 2017; Yu et al., 2017; Brigham et al., 2019; Peacock et al., 2019).

Urban sewage discharge may lead to high CO_2 emissions from the lake. The NH_4^+-N concentration was highly positively correlated with CO_2 in the lake (Table 1 and Fig. 3). NH_4^+-N is a good indicator of sewage loads (Garnier et al., 2009; Yu et al., 2013; Xiao et al., 2019a), and the lake NH_4^+-N concentration was associated with the NH_4^+-N discharge loading from city domestic wastewater (Fig. S3a), explicitly linking urban sewage inputs to the CO_2 level. The large amount of sewage-derived nutrients could promote lake CO_2 production by reinforcing in situ respiration (Kortelainen et al., 2006; Wang et al., 2017; Li et al., 2020). Moreover, urban lakes could also receive anthropogenic carbon from sewage input (Yang et al., 2008; Yu et al., 2013; Wang et al., 2017), which could fuel lake CO_2 emissions, as shown in previous studies (Sobek et al., 2005; McDonald et al., 2013; Weyhenmeyer et al., 2015). Although the relatively high DO supersaturation (Table S1) indicated that the lake was productive (Balmer and Downing, 2011; Gu et al., 2011), it was still a significant source of atmospheric CO_2 (Table S3), mostly driven by significant urban sewage discharge.

The substantial interannual variations in the CO_2 level indicate that anthropogenic disturbances play a large role in lake CO_2 dynamics. From 2000 to 2003, the increasing CO_2 level mostly resulted from urban sewage discharge (Fig. 2b and Fig. S3), which is also evidenced by the increasing nutrient concentration in the lake (Fig. 2c). Ecological restoration measures and watershed management, such as sediment dredging, reducing the external pollutant input, planting with aquatic vegetation, and the construction of wetlands around the lake, imposed by the local government were carried out to improve the lake water quality after 2003 (Chen et al., 2009; Chen et al., 2013). These measures likely led to the improvement in the water environment and subsequently lower CO_2 levels in the lake. For comparison, the pCO_2 and nutrient loading in Lake Taihu, which did not receive environmental protection measures, continued to increase after 2003 (Fig. 2e; Xiao et al., 2020).

Another inflection point appeared in 2007, after which the pCO_2 showed a relatively low value (Fig. 2e). This mostly resulted from the highly publicized drinking water crisis in Wuxi city, which occurred in May 2007 due to serious algal blooms (Qin et al., 2010); this event promoted a wide range of environmental protection actions (e.g., building wastewater treatment plants and closing some polluting factories; Chen et al., 2013; Qin et al., 2010; Xiao et al., 2019b). The significantly lower wastewater discharge from Wuxi city and lower nutrient concentrations in the lake after 2007 also support this finding (Fig. 2 and Fig. S3). These actions may have directly contributed to the decrease in the CO_2 levels considering the role of the external input in lake CO_2 production and emission. The long-term measurements in this study suggested that environmental protection actions should be taken to decrease watershed pollutant discharge into the lake to reduce lake CO_2 emissions.

4.2. Effect of eutrophication and algal blooms

The annual mean TSI, with a value of 62.48, and the mean Chl-a concentration of 30.34 μg L^{-1} suggested that the urban lake was eutrophic and featured algal blooms. Generally, eutrophic lakes with algal blooms tend to have low CO_2 emission fluxes due to high primary production (Schindler et al., 1997; Gu et al., 2011; Pacheco et al., 2014). The significant negative correlation between pCO_2 and Chl-a throughout the measurement period (Table 1) indicated that the algal blooms decreased the lake CO_2 emissions, as shown in previous studies (Schindler et al., 1997; Xing et al., 2005; Gu et al., 2011).

However, the influences of Chl-a, an indicator of algal abundance, on CO_2 varied seasonally (Table 1). Despite the highest Chl-a concentration occurring in the summer (Table S1), summertime Chl-a was not related to pCO_2 ($p = 0.66$; Table 1). The higher water temperature in the summer may enhance the mineralization of DOC, an important substrate for CO_2 production (Huttunen et al., 2003; Gudasz et al., 2010; Chen et al., 2016), and eventually lead to a high CO_2 level despite the high Chl-a concentration. The significant correlations between DOC and pCO_2 in the warm seasons also supported this finding (Table 1).

Interestingly, Chl-a was positively correlated with DOC (Table S2). This is mostly due to the decomposition of algae, which releases large amounts of DOC (Ye et al., 2011). Previous studies showed that algal-derived DOC is biodegradable and that the supply of fresh organic carbon from primary production can increase aerobic respiration and subsequent CO_2 production (Huttunen et al., 2003; Wen et al., 2017; Yan et al., 2017). Although the lake DOC concentration showed a nonsignificant ($p > 0.05$) difference among seasons, a high DOC concentration was found during algal blooms (Table S1). Both of these findings may explain why lower CO_2 emissions were not found in the warm seasons with high primary production, a significant difference from other eutrophic lakes (Schindler et al., 1997; Xing et al., 2005; Gu et al., 2011; Trolle et al., 2012).

4.3. Comparison of the CO_2 flux with the findings of other published studies

Previous studies reported that the urban lake CO_2 flux ranged from 0.3 g m^{-2} d^{-1} to 3.5 g m^{-2} d^{-1}, with a mean value of 1.2 g m^{-2} d^{-1} (Table S5). The annual CO_2 flux in this study, ranging from 0.4 g m^{-2} d^{-1} to 2.6 g m^{-2} d^{-1} with a mean value of 1.1 g m^{-2} d^{-1} (Table S3), was similar to previously reported lake flux values. For comparison, the CO_2 emission flux from eutrophic Lake Taihu was 0.8 g m^{-2} d^{-1} (Xiao et al., 2020). Studies have shown that the CO_2 emission flux in lakes in peatland-dominated catchments is significantly higher than that in other habitat types (Huttunen et al., 2002; Sobek et al., 2003; Zhu et al., 2012; Abril et al., 2014), and importantly, the CO_2 emission flux in this study was comparable to those from peatland lakes (Table S5). Moreover, the CO_2 flux in Lake Wuli was higher than that in lakes in forest-dominated and agriculture-dominated catchments (Table S5). Previous studies showed that volcanic lakes are significant sources of atmospheric

CO_2 due to the input of large amounts of magmatic gases, and our results found that the CO_2 emissions of the studied urban lake were comparable to those of volcanic lakes without hydrothermal sources and lower than those with depth contribution (Andrade et al., 2016; Andrade et al., 2019).

The mean CO_2 flux in Lake Wuli was higher than that expected based on the area-dependent scaling relationship. A previous study indicated that small lakes have high CO_2 emission fluxes and that CO_2 fluxes increase with decreasing lake size (Holgerson and Raymond, 2016). This study showed that the CO_2 flux from Lake Wuli, with an area of 8.6 km^2, was much higher than that from lakes with similar or smaller sizes (Holgerson and Raymond, 2016). One reason for this high flux was that CO_2 emissions from the urban lake may be fueled by the high anthropogenic pollutant input (McDonald et al., 2013; Weyhenmeyer et al., 2015; Brigham et al., 2019; Peacock et al., 2019). Therefore, we propose that urban lakes with high anthropogenic pollutant inputs are hotspots of CO_2 emissions. Lake CO_2 fluxes have been intensively investigated in rural areas surrounded by forests (Huttunen et al., 2003; Huotari et al., 2011; Buffam et al., 2011; Fontes et al., 2015), peatlands (Casper et al., 2000; Huttunen et al., 2002; Sobek et al., 2003; Repo et al., 2007), and farmland (Kortelainen et al., 2006; Balmer and Downing, 2011; Gu et al., 2011). To better understand the carbon cycle in inland lakes, more measurements from other urban lakes are needed, especially lakes in landscapes with large proportions of urban land.

4.4. Implications and perspectives

In this study, we reported the long-term CO_2 dynamics in a eutrophic urban lake and found that the lake was a significant source of atmospheric CO_2 during 2000–2015. This study has two implications. First, this study provides useful data sources for urban lake CO_2 emission flux estimates. Urban lakes are widespread because they play an irreplaceable role in multiple ecological and societal functions (Waajen et al., 2014). However, the CO_2 dynamics and their controlling factors in urban lakes have rarely been studied. Lake Wuli is a typical representative of urban lakes, and this study improves our understanding of the CO_2 cycle in urban lakes.

Second, the effects of human activities on the CO_2 dynamics in the lake provide valuable information for management practices for urban lakes. The annual mean pCO_2 and CO_2 flux were highly sensitive to nutrient concentrations (Figs. 2 and 3), suggesting the key role of watershed management in lake CO_2 dynamics. The deterioration of water quality and ecological degradation in Lake Wuli led to a series of environmental protection measures (Chen et al., 2009; Qin et al., 2010; Chen et al., 2013), and these measures eventually reduced the urban pollutant loading and decreased the CO_2 level in the lake. Although there was substantial interannual variability with a decreasing trend in the annual gas exchange coefficient of the lake, the annual variability in the CO_2 flux was not related to the gas exchange coefficient ($p = 0.46$). Additionally, the gas transfer coefficient, with an annual mean value of 0.99 m d^{-1}, showed significant ($p < 0.01$) differences among seasons. In contrast, the pCO_2 and CO_2 flux showed nonsignificant ($p > 0.05$) differences among seasons. These results show that nutrient loading was the important factor controlling the lake CO_2 variability.

Our results demonstrated that urban lakes are significant sources of atmospheric CO_2 emissions. Lakes are often considered and constructed by city designers because they not only contribute to biodiversity and provide societal benefits, such as water diversion and entertainment in urban areas (Waajen et al., 2014), but also regulate microclimates and reduce urban heat (Robitu et al., 2006; Theeuwes et al., 2013). Our results are consistent with those of van Bergen et al., (2019), who showed that constructing lakes in urban areas was not a CO_2-neutral option. However, this study found that urban lake CO_2 emissions decreased with improving water quality induced by the reduction in anthropogenic pollutant discharge (Fig. 2). This emphasizes the importance of watershed management, which can not only improve the water quality but also counteract high CO_2 emissions.

The water quality of lakes in China has improved markedly due to environmental investment (Tong et al., 2017; Zhou et al., 2017). The GDP per capita in both China and the study region has increased rapidly over the past two decades, leading to a corresponding increase in environmental investment (Zhou et al., 2017; Fig. 2 and Fig. S3). Increasing investment, such as in the establishment of sewage treatment plants and urban sewer systems, has reduced pollutant discharge into the nation's urban lakes and the study lake (Chen et al., 2009; Tong et al., 2017; Zhou et al., 2017). This was exemplified by the decreasing domestic NH_4^+-N discharge loading with increasing domestic wastewater loading (Fig. S3b). In this study, significant negative correlations were found between the annual mean nutrient dynamics (Fig. 4a and b), lake CO_2 dynamics (Fig. 4c and d) and local GDP, indicating the positive effect of GDP-driven environmental investments in improving the water quality and reducing the associated CO_2 emissions.

5. Conclusions

Long-term (2000–2015) pCO_2 and CO_2 flux in Lake Wuli, a small urban lake in the heart of the Yangtze River Delta of China, were investigated. Results showed that the lake was eutrophic with algal blooms. Meanwhile, the lake had experienced a decreasing trend in annual nutrient loading due to environmental investment. The annual mean pCO_2 of the lake was 1030 ± 281 μatm from 2000 to 2015, with an annual mean CO_2 emission flux of 1.1 ± 0.6 g m^{-2} d^{-1}, suggesting that the urban lake was a significant source of atmospheric CO_2 compared with the role of other lakes in atmospheric CO_2 contribution worldwide. Variability in the annual pCO_2 was highly correlated with nutrients (NH_4^+-N and TN) and DOC, and NH_4^+-N and TP together explained 90% of the observed interannual variability in the pCO_2 ($R^2 = 0.90$, $p < 0.01$), suggesting that the CO_2 dynamics from the urban lake were driven by anthropogenic pollutant loading.

On average, the lake CO_2 dynamics showed statistically nonsignificant differences across seasons; however, the CO_2 dynamics varied annually. The peak pCO_2 and CO_2 flux in the lake occurred in 2003, which had the highest N loadings, and the lake has had a significantly lower CO_2 level since 2007 due to the decreases in external discharge. This emphasized the importance of yearlong measurements in obtaining unbiased urban lake CO_2 flux data during changes in the water environment and watershed characteristics.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Qitao Xiao: Conceptualization, Methodology, Formal analysis, Resources, Writing - original draft, Writing - review & editing. **Hongtao Duan:** Conceptualization, Methodology, Writing - review & editing, Supervision, Funding acquisition. **Tianci Qi:** Formal analysis, Resources, Writing - review & editing. **Zhenghua Hu:**

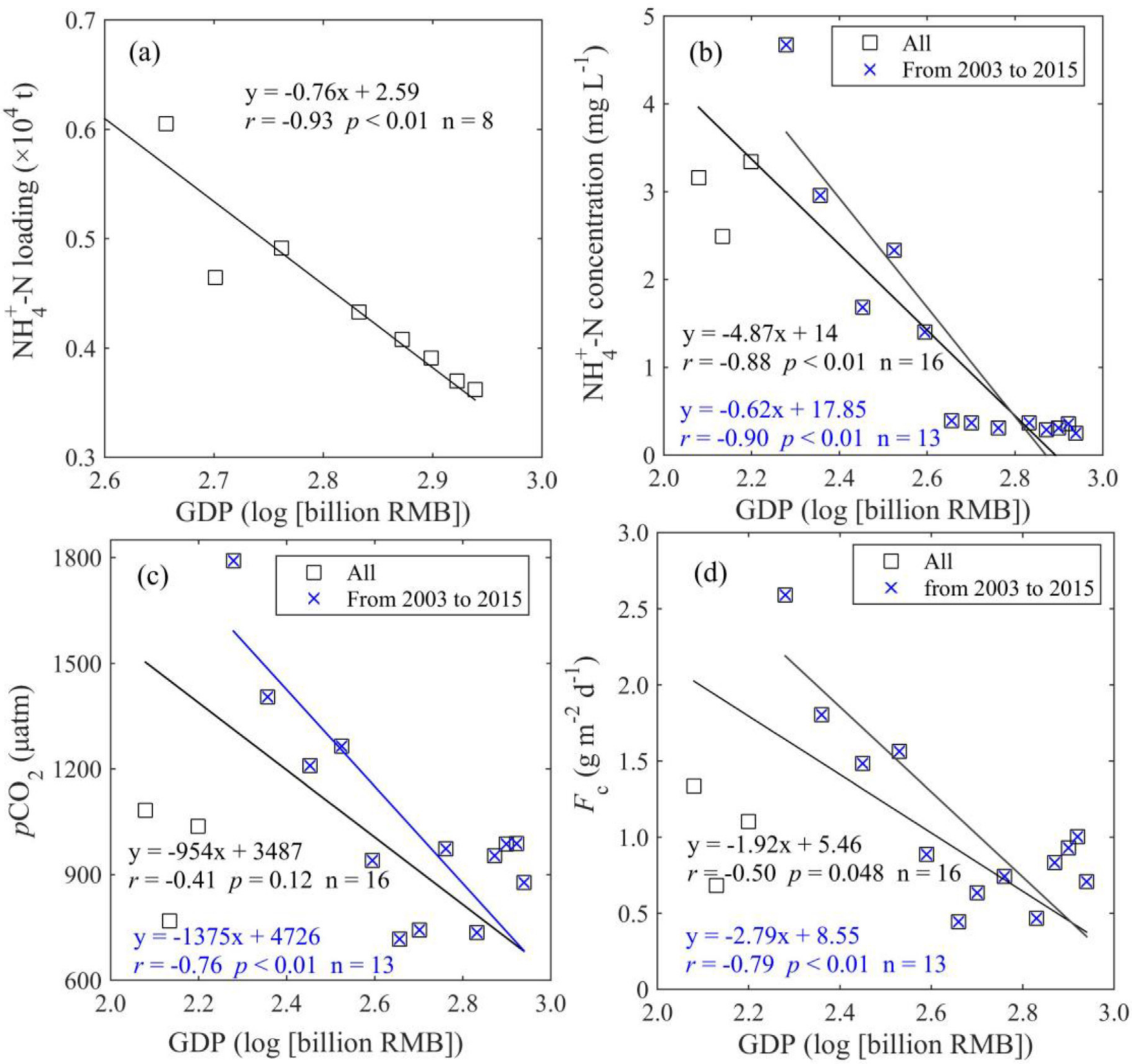

Fig. 4. Correlation between the GDP of Wuxi city and (a) the corresponding NH_4^+-N discharge loading from wastewater from 2008 to 2015, (b) the lake annual mean NH_4^+-N concentration, (c) pCO_2, and (d) CO_2 flux (F_c) during the measurement period.

Methodology, Writing - review & editing. **Shoudong Liu:** Resources. **Mi Zhang:** Resources. **Xuhui Lee:** Resources.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2020.114433.

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