

Research on Spatial-Temporal Differentiation of CO₂ Flux across Water-Air Interface in Xiquanyan Reservoir in Harbin, China

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Abstract

Using the static chamber method, CO₂ flux across the water-air interface of Xiquanyan reservoir was measured for 24 hours over a one-year cycle in Harbin, China. Gas ebullition and gas emission in winter was not considered in this study. CO₂ fluxes showed significant spatial-temporal differentiation. The order of CO₂ flux in each test point was: A > C > D > B. The changes of water level and hydro-fluctuation zone and the distribution of aquatic plants were the main factors affecting the spatial variation of CO₂ flux. In terms of time, carbon flux of daytime in Xiquanyan was significantly lower than the night. Overall, seasonal variations of CO₂ flux was: spring > autumn > summer.

Keywords: CO₂ flux; spatial-temporal differentiation; water-air interface; Xiquanyan reservoir

1. Introduction

The major greenhouse gases (GHGs) are carbon dioxide (CO₂), methane (CH₄) and nitrous oxide (N₂O) [1], of which the greenhouse effect of CO₂ accounts for 50% of the total effect globally. Therefore, the questions on source and sink of atmospheric CO₂ were actually well discussed worldwide [2-4]. In recent years, researchers around the world have conducted many studies in the role of CO₂ emissions in freshwater reservoirs and their contribution to the atmospheric GHG concentrations [5, 6]. According to Tremblay and other studies [7, 8], GHG emissions of reservoirs (older >10 years) in boreal zone were similar to natural lakes. China's total area of reservoirs has reached more than 2×10^6 hm² (NBSC, 2015), its impact on atmospheric CO₂ concentration can not be ignored. Because the carbon flux between water and atmosphere was greater impacted by human activities, the studies on reservoirs have indicated functions for climate change. Evaluating the role of the boreal reservoirs in the global exchange of GHG and exploring the dynamic trends for gas emissions are academically necessary and valuable.

This study tried to use the static chamber method to measure CO₂ flux across water-air interface to evaluate source/sink Xiquanyan reservoir, explored the spatial-temporal differentiation of CO₂ flux and discussed the dominant factors that influence the variation of CO₂ flux in the reservoir ecosystem. It was expected that the study would provide necessary data to evaluate the impact of reservoir construction to climate changes in north China.

2. Materials and Methods

2.1. Site Description

Xiquanyan reservoir (45°125' N, 127°6' E) is located at the junction of Acheng District, Shangzhi and Wuchang City, Heilongjiang Province, which is the first large-scale reservoir for control engineering on Ash River. Xiquanyan reservoir has a catchment area of 1151 km², the total capacity of 4.78× 10⁶ m³ and the average depth of 12 m. The reservoir began to freeze in early November, with ice thickness of 0.7 ~ 1 m and unfreeze in mid-April. with frost-free period of 120 ~ 140 d. The annual average temperature is 3.4 °C and average annual rainfall of 563 mm, of which precipitation from June to September accounted for 70% of the year. Summer rainfall is relatively abundant but dry in winter. Xiquanyan reservoir is important water source for Harbin and its ecological status is significant.

2.2. Samples Collected

Sampling observation was conducted according daily and seasonal variations at eight sample spots (Figure 1).

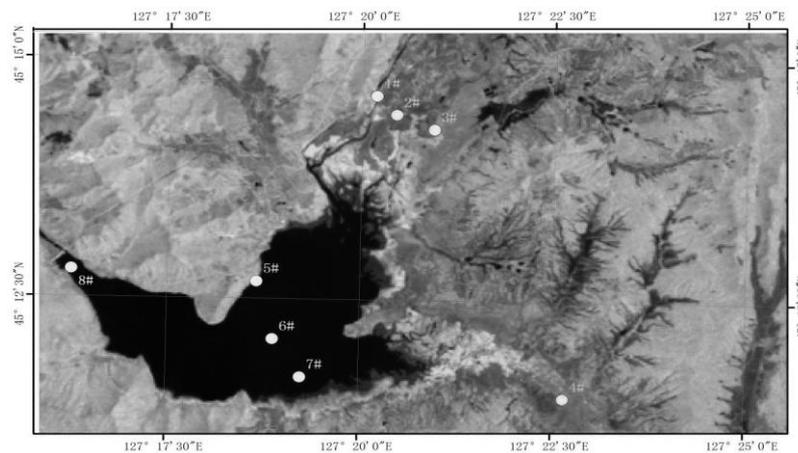


Figure 1. Sampling Spots in Xiquanyan Reservoir

1) Diurnal variation observation. Sampling started from 5:00 am at sample points, taken once every interval of 4 h, which came to six times continuous sampling within 24 h. At the same time, other environment factors were also observed including temperature, wind speed and physical and chemical indicators.

2) Seasonal variation observation. Samplings were selected in ice-free period. They were in spring of 2010 (May 8th – 9th, June 3rd to 4th), summer (July 7th – 8th, August 7th to 8th) and autumn (September 5th – 6th, October 13th- 14th), respectively, for about once a month. Every spot was taken sampling two times, one time in morning and another in afternoon, and then average value of twice was taken.

2.3. Analysis of Samples

Gas samples were delivered to the laboratory for analysis: CO₂ concentrations were analyzed with GCI (Gas Chromatograph Instrument, Hp-4890D, USA); TN, TP with U-VLS (UV – visible Light Spectrophotometer, type 2401, Japan); TOC with TOC analyzer (1020A type, USA); MWQA (Multi-function Water Quality Analyzer) was used for measuring dissolved oxygen (DO), Ph, chlorophyll (chl_a) , water temperature, conductance, turbidity, NH₄-N and Cl⁻ *etc.*

2.4. CO₂ Flux Calculation Method [9]

According to the results of the analysis by gas chromatography (values of gas concentration), the change rate of gas concentration can be calculated over time ($\Delta C / \Delta t$). The formula of CO₂ flux across water - air interface can be written as:

$$F = \rho \frac{V}{A} \frac{P}{P_0} \frac{T_0}{T} \frac{dC_t}{dt}$$

Where: F = CO₂ flux; V = air volume inside box; ρ = CO₂ density of the standard state; A = coping area of box; P = air pressure of sampling spot; T_0 and P_0 = air absolute temperature and pressure in the standard state; T = absolute temperature at sample time; ΔC = the difference of CO₂ mass concentration at time interval; Δt = sampling time interval. Positive value indicated the net emission of CO₂ from water, while negative value indicated net consumptions of CO₂ from atmosphere.

All data analysis was performed using statistic software (SPSS ver.15.0). Correlation Analysis and regression analysis was adopted in our test.

3. Result

3.1. Temporal Variations

Throughout the experiment, CO₂ flux diurnal fluctuation across water - air interface in Xiquanyan reservoir range from $-57.78 \text{ mg m}^{-2} \text{ h}^{-1}$ to $118.86 \text{ mg m}^{-2} \text{ h}^{-1}$ with the average values of $13.37 \pm 24.83 \text{ (mg m}^{-2} \text{ h}^{-1})$. The diurnal variation of CO₂ flux was obvious. Carbon flux minimum were often seen between 13:00 and 17:00 (Figure 2).

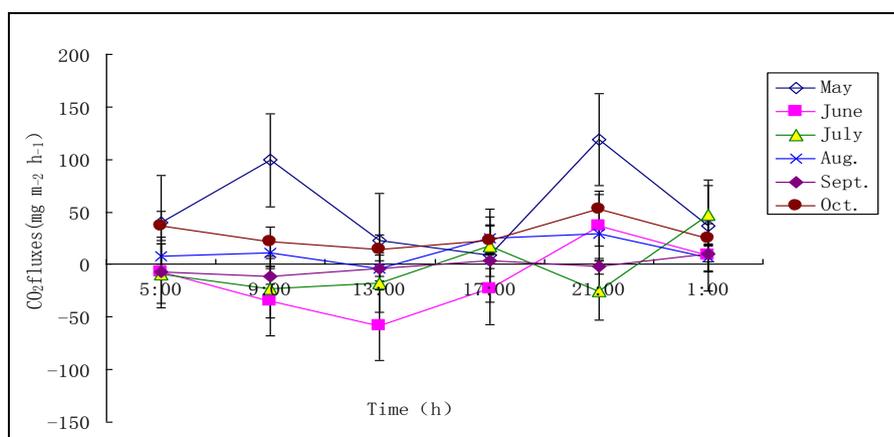


Figure 2. Diurnal Variation of CO₂ Fluxes in Different Months

CO₂ diurnal fluxes in May were higher and showed a strong carbon source. Carbon flux of June fluctuated distinctly. Minimum value of Day $-57.78 \text{ (mg m}^{-2} \text{ h}^{-1})$ appeared in the afternoon at 13:00, which was also the minimum of whole diurnal change observation. However, Maxima demonstrated bimodal characteristics in June. The diurnal variation of carbon flux in the following three months was relatively flat, expressing as carbon sinks during the day and carbon source at night. The average values of CO₂ fluxes were -9.05 ± 11.23 , 12.95 ± 12.40 , $-1.065 \pm 7.42 \text{ mg m}^{-2} \text{ h}^{-1}$. CO₂ fluxes sharply increased in October, each time point of the day let off CO₂ to the atmosphere with mean value of $29.06 \pm 13.86 \text{ (mg m}^{-2} \text{ h}^{-1})$.

From the measurement results, seasonal variation of CO₂ flux in the reservoir was obvious. Arranging in order of numerical size, they were spring ($787.42 \pm 43.03 \text{ mg m}^{-2} \text{ d}^{-1}$) > autumn

$(409.24 \pm 13.64 \text{ mg m}^{-2} \text{ d}^{-1}) > \text{summer } (255.21 \pm 28.2 \text{ mg m}^{-2} \text{ d}^{-1})$. Mean value of CO_2 flux was $483.96 \pm 28.30 \text{ mg m}^{-2} \text{ d}^{-1}$ (Figure3).

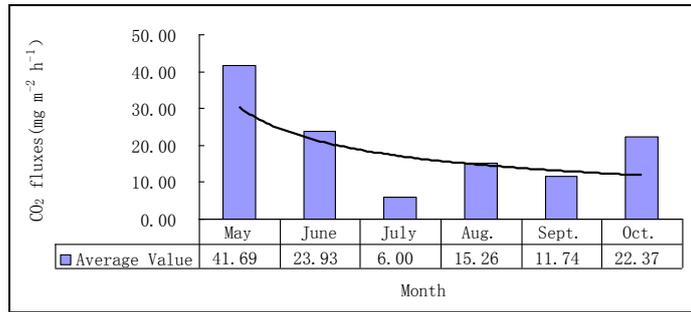


Figure 3. Seasonal Variation of CO_2 Fluxes

3.2. Spatial Variations

At the same time, four measurement regions were different. The average value of CO_2 flux in District A was $29.62 \text{ mg m}^{-2} \text{ h}^{-1}$, ranged from $-55.63 \sim 141.45 \text{ mg m}^{-2} \text{ h}^{-1}$, seasonal variation was obvious. CO_2 flux showed gradually decreasing trend. District B was located in the mouth of Huangni River, one of the water inlets for Xiquanyan reservoir. The water depth of B was shallow with the average depth of 2.5m, basically no water stratification, carbon flux and therefore a volatile region. Seasonal variation was obvious B CO_2 flux has and downs. The overall performance was high in spring and lower in summer ranging from $28.39 \sim 18.35 \text{ mg m}^{-2} \text{ h}^{-1}$. District C was the heart of the reservoir with an average depth of 13m and no large emergent plants and floating plants. The overall performance was a strong source of atmospheric CO_2 . Carbon flux of D varied widely ranging from $-40.78 \sim 95.18 \text{ mg m}^{-2} \text{ h}^{-1}$. The average of carbon fluxes was $11.1 \text{ mg m}^{-2} \text{ h}^{-1}$. The overall trends were the highest in spring and then in autumn, and the lowest in summer.

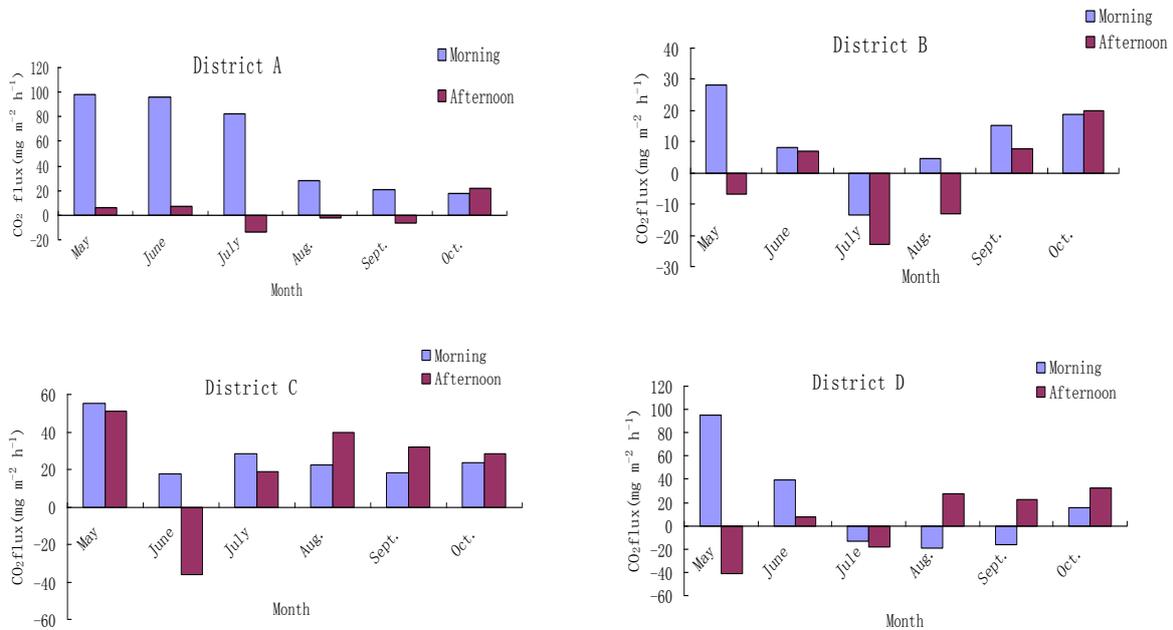


Figure 4. Spatial Variation of CO_2 Flux

4. Discuss

4.1. The Reasons for Spatial Variations

1) The locations of the experimental zone were different. District A is located at Inlet of Ashe River, belonging to seasonal flooded areas where on large amounts of plant humus deposited on the surface of soil layer. In spring with snow melt, the water of reservoir increased, so that the original surface of A was flooded. Under the water erosion, large amounts of organic carbon released from soil emitted into the atmosphere, resulting in CO₂ flux across water-air interface increased. District B is located at water Inlet of Huangni River where the depth is the shallowest, with an average depth of 2.5m. The CO₂ flux was the lowest level in year-round observation which was consistent with the observations of Teodoru about the different ecological types of reservoirs. That is CO₂ flux values are low at relatively shallow river.

2) The impact of Hydrophyte. District C and D are located in the heart of the reservoir and outlet area, respectively. The water is deep and obvious stratification, where hardly any floating leaves and heavy water-plants exist but mainly algae. Deepwater area of reservoir is the main area for fish aggregation. In the case of lower aquatic plant biomass, the respiration of aquatic organisms dominated in water that made CO₂ concentration increase [10]. So CO₂ fluxes of C and D were relatively high and this situation continued until July. With the air temperature rising and photosynthesis of aquatic plants enhancing, CO₂ fluxes of each experimental zone were significantly decreased.

3) Differences of content and distribution of nutrients in water was also a factor that can not be ignored. Measure data suggested that distribution law of total phosphorus (TP) concentration was significant. TP concentration both at inlet of the reservoir were higher, with annual mean values of 0.105 mgL⁻¹ and 0.103 mgL⁻¹, while the central region and outlet is relatively low with 0.098mg L⁻¹ and 0.096 mg L⁻¹, respectively. The highest TP value appeared in the July at spot B (0.116 mg L⁻¹). This was mainly decided by the TP input source a steel plant locating at upstream of Ash River, which waste water flows into the reservoir indirectly. Its main pollutants were nitrogen and phosphorus so that the concentration of TP in July was higher than the other months.

A positive correlation between TP and CO₂ fluxes was found with correlation coefficient of 0.834 (P <0.01), especially in the spring. The impact of phosphorus, nitrogen on CO₂ fluxes mainly achieved through indirectly influencing carbon sequestration of aquatic plants. TP is an important limiting factor for eutrophication in the water. High concentration of TP will inhibit the photosynthesis of phytoplankton and algae, thereby reducing the absorption of CO₂ into the water. Changes of concentration of DOC was contrary to TP, a higher at central area and outlet while relatively low at district A and B. Correlation analysis also showed that there were negative correlations between CO₂ flux and DOC coinciding with experimental results.

4.2. Impact Factors for Temporal Variation

1) Phytoplankton: Negative correlation between chlorophyll and CO₂ fluxes was obvious according to linear correlation (Figure 5-A), Chlorophyll content was an important indicator to reflecting biomass of phytoplankton and algal which distribution affected the space variation of CO₂ fluxes. The average annual biomass of four districts was 10.54mg L⁻¹, 12.19 mg L⁻¹, 10.69 mg L⁻¹ and 9.67 mg L⁻¹ respectively. The corresponding lowest CO₂ flux was district B.

2) pH: The pH value was found little change in the reservoir ranging from 6.81-9.92, which generally belongs to weakly alkaline water. When the water was alkaline water with high pH, CO₂ is more soluble in water forming carbonates in the water, leading to lower CO₂ partial pressure of water. It made the CO₂ get into the water from the atmosphere, so the CO₂ flux

was low [11]. According to linear regression analysis, a significant negative correlation between CO₂ flux and pH can be seen (Figure5-B).

In addition, pH and chlorophyll has close relationship. The increasing of algal biomass led to pH increased in water. Since spring water temperature is low, the number of algae was small, so the pH was low; while algae bloomed in summer with high temperature, pH value was also increased. This point consistent with Li Xianghua's conclusions of negatively correlation between CO₂ flux and pH in Taihu[12].

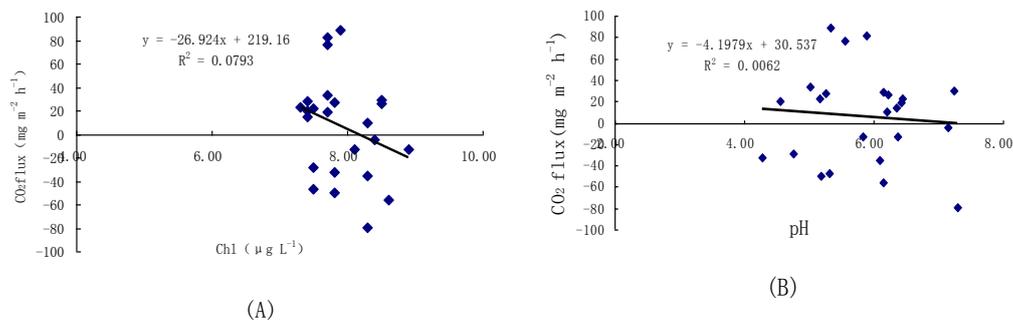


Figure 5 (A). The Relationship between CO₂ Flux and Chlorophyll; (B) the Relationship between CO₂ Flux and pH

3) Wind speed: CO₂ flux and wind speed in the spring and autumn had the same variation trend. The impact of winds on CO₂ fluxes was mainly through increasing fragmentation of the water surface, increasing the water surface area to facilitate the exchange of gases. The analysis found that the impact of wind on CO₂ flux was not obvious when the wind speed was small (<3.5m / s), while the impact was significant when the average wind speed reaches 3.5m / s or more.

Through data analysis, we also found differences of wind speed in the experimental area would affect the spatial distribution of CO₂ fluxes. During the observation, the average wind speeds of four experimental areas were 2.54 m s⁻¹, 2.04 m s⁻¹, 2.10 m s⁻¹, 2.34 m s⁻¹. Of which the lowest point of wind was district B. We could speculate that relative low CO₂ flux of B may be associated with a lower wind speed. From this point we can see, changes of CO₂ flux was the result of interaction of multiple environmental factors, just different factors played a leading role in a different time and space.

4) Water level: There is little research about the impact of water level changes on CO₂ fluxes in reservoir. According to linear analysis between CO₂ flux and mean value of water level in different months in reservoir, positive correlation was found between the two. It meant that the water level rose would increase CO₂ emissions. The water level of Xiquanyan reservoir rose to 209.53m in May from 205.11m in March just because the water was completely open and the CO₂ flux value was the highest in May. Besides a lot of organic carbon contained at freezing period increasing CO₂ emissions, variation of water level enlarged flooding area and created a favorable environment for the recovery of soil bacteria and microorganisms which accelerated soil humus decomposition and release, resulting in CO₂ fluxes increased.

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