

## Greenhouse gases concentrations and emissions in different inland water bodies in Chengdu Plain

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### ABSTRACT

Freshwater systems are important sources of greenhouse gases (CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>O) in the atmosphere, but their contributions to the regional GHGs budgets remain uncertain due to numerous types, complex carbon and nitrogen cycle processes, and human disturbance. This study monitored the concentrations and fluxes of CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub>O in different inland waters including rivers, irrigation canals, reservoirs and ponds in Chengdu Plain (Xinjin District), so as to explore the characteristics and influencing factors of greenhouse gas emission in different inland waters in Chengdu Plain. The total evasions of CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub>O from different types of waters were estimated. The results showed that the concentrations of carbon, nitrogen and phosphorus vary significantly in different inland waters with the highest level found in pond systems and polluted river sections, followed by the irrigation canals and the generally lower values detected in reservoirs and rivers. It was suggested that pollution load is higher in artificial waters. The dissolved CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>O concentrations in all inland waters ranged from 15.7–153.1 μmol L<sup>-1</sup>, 0.099–0.986 μmol L<sup>-1</sup> and 0.016–0.354 μmol L<sup>-1</sup>, respectively. And, CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub>O concentrations in artificial irrigation canals, ponds and polluted rivers were significantly higher than those in the unpolluted rivers and reservoirs. The estimation of greenhouse gas fluxes based on the boundary layer method showed that the CO<sub>2</sub> fluxes from irrigation canals were the highest (197 ± 52 mmol m<sup>-2</sup> d<sup>-1</sup>), followed by ponds (114.04 ± 42.20 mmol m<sup>-2</sup> d<sup>-2</sup>), rivers (65.49 ± 50.70 mmol m<sup>-2</sup> d<sup>-2</sup>), reservoirs (22 ± 30 mmol m<sup>-2</sup> d<sup>-1</sup>); the CH<sub>4</sub> and N<sub>2</sub>O fluxes from irrigation canals and ponds were the highest, approximately 2–3 times those from rivers and reservoirs; the greenhouse gases fluxes from seriously polluted rivers were also higher than these from other unpolluted rivers. Based on the extrapolation method, the total greenhouse gas evasions from inland waters in Xinjin District were estimated as 2.5 × 10<sup>4</sup> t CO<sub>2</sub> y<sup>-1</sup>, 107 t CH<sub>4</sub> y<sup>-1</sup> and 69 t N<sub>2</sub>O y<sup>-1</sup>, whose CO<sub>2</sub> equivalent converted was about 5.0 × 10<sup>4</sup> t y<sup>-1</sup> according to the global warming potential. The greenhouse gas fluxes from irrigation canals, ponds, reservoirs and rivers accounted for 19%, 24%, 1% and 56% of the total evasion from all inland water in Xinjin District, respectively. The irrigation canals and ponds had small water areas but showed high greenhouse gas emissions. The regression analysis showed that the concentrations and fluxes of CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>O were positively correlated with the conductivity and carbon, nitrogen and phosphorus concentrations, while negatively

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correlated with dissolved oxygen. The abundance of biogenic elements in freshwater and water pollution are crucial to the greenhouse gas fluxes, particularly, human activities have an obvious influence on greenhouse gas emissions from different inland waters.

*Keywords:* Chengdu Plain; Different freshwater; Greenhouse gas; Spatial characteristics; Influencing factors

## 1. Introduction

Freshwater ecosystem, including rivers, lakes, reservoirs, irrigation canals, ponds and so on, is an important confluence of carbon and nitrogen in terrestrial environment on the earth, as well as the most active place for biogeochemical cycling in the world [1–3]. Transferring through surface runoff, soil water and groundwater, land-sourced carbon and nitrogen integrate into surface freshwater system. Then, part of the carbon and nitrogen is transferred to water through rivers, part of those is buried into the sedimentary layer of the inland water system and the rest of those forms into  $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{N}_2\text{O}$  emitted into the atmosphere through microbial metabolism and physiochemical transformation, becoming an important emission source of greenhouse gases [1,3–6]. Studies showed that greenhouse gases in most rivers [1,7,8], lakes [1,3,9], reservoirs [1,9–12], and ponds [13,14] on the earth is over-saturated. It has been estimated that the global inland waters emitted 1.2–2.1 Pg  $\text{CO}_2$  [1,3] and 103 Tg  $\text{y}^{-1}$   $\text{CH}_4$  every year, which almost offsets 79% of annual net primary C production [15]; it also emitted 0.68–0.95 Tg  $\text{N}_2\text{O}$   $\text{y}^{-1}$  [16], which is equivalent to 10% of the global anthropogenic  $\text{N}_2\text{O}$  emission per year [17]. In spite of the fact that the total area of inland waters only accounts for 3% of the land area of the earth [1], the contribution of freshwater to the global GHGs budgets and global carbon and nitrogen cycle cannot be ignored. However, people are lack of understanding of greenhouse gas emissions of different freshwater due to diverse types, complex carbon and nitrogen cycle processes, and human disturbance. Which limits the estimation and cognition of global and regional greenhouse gas emission.

Greenhouse gases in freshwater mainly include two sources, one is the microbial metabolism of endogenous carbon and nitrogen; the other is external input which includes hydrological input of  $\text{CO}_2$  and  $\text{CH}_4$  produced by the decomposition of watershed soil organic carbon [18–20], sewage loading [21,22] and groundwater discharge [23,24]. Therefore, the emission of greenhouse gases from freshwater is controlled by multiple factors including water environment, watershed environment, hydrological and meteorological conditions and human activities [21,25,26], resulting in strong variability. The hydrological characteristics, environmental condition and human disturbance are varied in different freshwater systems, so greenhouse gas emission dynamics and key driving factors may also have great heterogeneity [21,27], leading to a great uncertainty in the cognition of their characteristics and the contribution to the regional carbon–nitrogen balance. In recent decades, researchers have studied the greenhouse gas emission in rivers [6,21], streams [17,19], lakes [28–30], reservoirs [31–34], ponds [13,14], irrigation canals [35,36], affirming

different spatial and temporal characteristics, influencing factors and formation mechanisms of greenhouse gases emission in different freshwater systems [1,21,27]. However, most of the current researches only focus on the emission from a single type of freshwater. There are relatively few studies on the comprehensive contribution of different types of freshwater in the same area. It is difficult to use the studies based on single type of freshwater to represent the overall characteristics of greenhouse gas emissions of regional freshwater ecosystem. Ortega et al. [25] and Martinez-Cruz et al. [37] made investigations on the  $\text{CH}_4$  emission from different inland water bodies in Berlin in Germany and Mexico City. Based on the results, they proposed that the emission intensity and emission load are significantly varied in different types of water bodies. Besides, small waters (<1 ha<sup>2</sup>) were proved to be the hot spots of greenhouse gases emission and human activity had enhanced the difference of  $\text{CH}_4$  emission in different types of water bodies. The studies on the  $\text{CO}_2$  and  $\text{CH}_4$  in rivers, lakes, reservoirs, ponds, springs, irrigation canals in three regions of southern India showed that the  $\text{CO}_2$  and  $\text{CH}_4$  concentrations in ponds and irrigation canals are 6 times that in lakes and 15 times that in rivers respectively. Therefore, the estimation of greenhouse gases emissions from inland waters on regional scale based on one preponderant water body types have deviations obviously [5]. Taking into consideration the diverse types of inland waters, emission characteristics of different inland waters and the difference of the driving factors, the study should further explore the intensity of greenhouse gases emission and influencing factors in different inland waters from a perspective of regional division. In addition, the assessment of relative contribution of greenhouse gases emission from different types inland waters should be done to better evaluate the contribution of freshwater to carbon–nitrogen balance and GHGs budgets in this region.

Chengdu Plain, a special inland alluvial fan area with large numbers of rivers, is formed by the alluvion of Minjiang River and its tributaries. Due to Dujiangyan irrigation system project, the river network has been reformed as an efficient irrigation system covering city and country area. There are many lakes, reservoirs and ponds widely distributed in the basin of crisscross rivers and channels, forming a unique river system pattern. Feng et al. [35] studied the  $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{N}_2\text{O}$  emission of irrigation canals with different functions in Chengdu Plain, and found that they vary greatly and the fluxes of greenhouse gas has been at a high level. At present, greenhouse gas emission of different freshwater is rarely reported. Because of a large population, advanced agriculturalization and urbanization as well as great human disturbance, it is hard to analyze the greenhouse gas emission of freshwater in Chengdu Plain. This study monitored the concentrations and emissions of greenhouse gases dissolved in rivers, irrigation canals, reservoirs and ponds in

Chengdu Plain (Xinjin District), in order to explore the difference of greenhouse gas emission among different freshwater in Chengdu Plain and the key influencing factors and evaluate their relative contribution, which provides a reference for a precise contribution of greenhouse gas emission of freshwater to regional carbon-nitrogen balance.

## 2. Materials and methods

### 2.1. Overview of the study area

Xinjin District of Chengdu is located in the west of Sichuan Basin and south of Chengdu Plain, with an area of 330 km<sup>2</sup>, (103°42′13″~103°55′59″E, 30°19′49″~30°31′32″N) north latitude (Fig. 1). Located in the water network area of Minjiang River, it is at the frontier of Minjiang River alluvial fan and foothill alluvial plain as well as the major ecological basin of Minjiang River basin. It has a subtropical monsoon humid climate and four seasons, with an annual average temperature of 16.4°C and an annual average precipitation of 978 mm. Xinjin District has a densely covered water network famous for Minjiang River and its main tributaries (Jinma River, Xihe River, Nanhe River, Yangliu River and Yangma River), with a total length of 82 km. Dujiangyan irrigation canal goes through the whole area, including more than 20 branch canals and 84 lateral canals, with a total length of 112.07 and 239.9 km, respectively. Among them, there are various reservoirs and ponds (most have been converted into aquacultural ponds). From the perspective of spatial morphological distribution, the rivers, irrigation canals, reservoirs and ponds in the area constitute a complete area with plenty of structures and functions. However, due to the different

characteristics of area, including flow speed, nutritional state, human disturbance intensity, the biogeochemical cycle of different inland waters is also distinctively varied.

### 2.2. Sampling point design

Based on the characteristics of water network distribution, urban development and agricultural activities of Xinjin District, 5 rivers, 3 irrigation canals, 2 reservoirs and 5 ponds in Xinjin District, which covers all types of inland waters in the area, were selected as research objectives. According to the characteristics of inland waters, 37 sampling sections (Fig. 1) were set. The characteristics and sections of different inland waters are shown in Table 1. Every section had three sampling points for sample collection and monitoring the on-site environmental factors.

### 2.3. Sample collection

Field samples of different inland waters in Xinjin District were collected in December 2017 (winter). First, the surface water sample (<20 cm) was collected by a closed water sampler, and the bubble-free water sample was quickly injected into a head-space bottle by using a 50 mL syringe. This sample was used in the analysis of dissolved CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>O concentration by head-space equilibrium method. Then, the atmospheric sample at 1 m over the 180 mL water surface was collected by a vacuum gas extraction bag to determine the background concentration of CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>O at the sampling points. Finally, the 500 mL deep water sample was collected at 20 cm over the water surface by an organic glass sampler and put into a plastic bottle for physical and chemical parameters analysis of the inland waters.

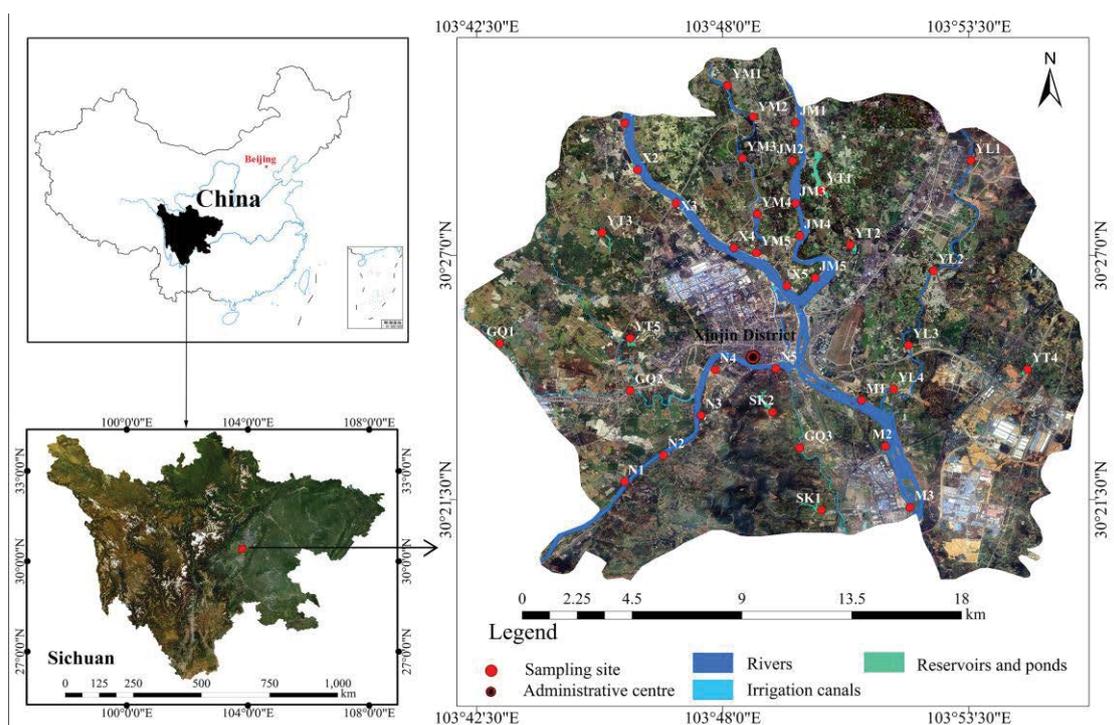


Fig. 1. Monitoring sections of different inland waters in Xinjin District.

Table 1  
Characteristics of different inland waters in Xinjin District

Inland waters	Length (km)	Area (ha)	Flow speed (m/s)	Width (m)	Sampling section	Notes
Xihe River	10.58	355.20	0–3.0	256.32–335.44	5 sections X1–X5	Fast flow speed, great disturbance to dam blocking by sand mining
Yangma River	9.71	81.59	0.2–5.0	25.14–226.62	5 sections YM1–YM5	Artificial restoration, wetland park
Jinma River	14.80	271.12	0.2–2.5	47.93–409.71	5 sections JM1–JM5	Close-to-nature river
Nanhe River	14.16	198.32	0–0.5	109.27–236.60	5 sections N1–N5	Fast flow speed, little human disturbance
Yangliu River	15.50	100.66	0.2–1.5	37.59–73.85	4 sections YL1–YL4	Serious pollution, poor water quality
Minjiang River	8.60	372.20	0.4–1.0	454.41–729.39	3 sections M1–M3	Good water quality
Irrigation canals	112.07	179.28	0–2.0	3–8	Kaimu River Branch Canal (GQ1), Tiexi River Branch Canal (GQ2), and Liberation Canal (GQ3)	Poor water quality, serious congestion, obvious household garbage pollution
Reservoirs	–	47.80	–	–	Wugou Reservoir (SK1) and Yucao Reservoir (SK2)	Irrigation-type reservoir
Ponds	–	269.75	–	–	Gonglinpan Contiguous Pond (YT1), Mumashan Contiguous Pond (YT2), Shilincun Contiguous Pond (YT3), Shima Temple Pond Group (YT4), Puhui Temple Fishpond Group (YT5)	Most of them are aquacultural ponds, Linpan ponds or landscape ponds

Note: All the data came from the Comprehensive Wetland Resources Survey and Master Planning of Xinjin County (2017).

As three duplicate samples were collected at each sampling point, all samples were stored at low temperature condition and brought back to the laboratory. When field sampling, the in-situ surface water temperature (WT), pH, dissolved oxygen (DO), conductivity, and Chlorophyll-a (Chl-a) were measured using the Manta™2 (Eureka Company, USA), a corrected multi-parameter controller.

#### 2.4. Sample analysis

The water quality parameters of total organic carbon (TOC), dissolved organic carbon (DOC), dissolved inorganic carbon (DIC), total nitrogen (TN),  $\text{NO}_3^-$ -N,  $\text{NH}_4^+$ -N, total phosphorus (TP),  $\text{PO}_4^{3-}$ -P. TOC, DOC, DIC were determined with an HACH QbD1200 TOC analyzer in this study, and TN,  $\text{NO}_3^-$ -N,  $\text{NH}_4^+$ -N, TP,  $\text{PO}_4^{3-}$ -P were determined with a FS3100 Flow injection analyzer (US OI Analytical).

The dissolved  $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{N}_2\text{O}$  concentration in inland waters was determined by head-space equilibrium method. First, 20 mL surface water was injected into a 35 mL vacuum bottle, and this was followed by an injection of 0.1 mL of saturated  $\text{HgCl}_2$  to inhibit microbial metabolism. After being brought back to the laboratory, 15 mL high purity  $\text{N}_2$  was blown into the vacuum bottle to form the head-space. Then, the head-space bottle was violently shaken for 3–5 min to make the dissolved  $\text{CO}_2$ ,  $\text{CH}_4$  and  $\text{N}_2\text{O}$  fully spread. After standing for 5 min of static culture to realize water-gas

balance in the head-space bottle, 5 mL head-space air was extracted by a syringe for concentration analysis by PE Clarus 500 gas chromatograph (Inc., USA). 10 mL atmospheric sample was extracted to detect the in-situ atmospheric  $\text{CO}_2$ ,  $\text{CH}_4$  and  $\text{N}_2\text{O}$  background concentration. Among them, the  $\text{CO}_2$  and  $\text{CH}_4$  detectors were Flame Ionization Detectors (FID), with an operating temperature of 200°C. The  $\text{CO}_2$  and  $\text{CH}_4$  were separated by the Porapak60/80 (2 mm) chromatographic column, with an operating temperature of 40°C and the carrier gas of high purity  $\text{N}_2$  and the flow of 20 mL  $\text{min}^{-1}$ . The  $\text{N}_2\text{O}$  detector was an ECD, with an operating temperature of 350°C. The  $\text{N}_2\text{O}$  was separated using the Porapak80/100 (2 mm) chromatographic column, with an operating temperature of 35°C and the carrier gas of high purity  $\text{N}_2$  as the carrier gas and the flow of 30 mL  $\text{min}^{-1}$ .

#### 2.5. Data calculation and analysis

##### 2.5.1. Data calculation

In this study, the dissolved greenhouse gas concentration of inland waters was determined based on head-space equilibrium method. The dissolved saturation of greenhouse gas (S) is the measured greenhouse gas concentration (C) divided by the greenhouse gas concentrations in the surface water that is in equilibrium with the atmospheric concentration ( $C_s$ ) [38]. The measured water concentration (C)

is equal to the sum of head-space gas-phase concentration and liquid-phase concentration under equilibrium condition the head-space gas component concentration is calculated by the Dalton partial pressure law. Under equilibrium condition, the CO<sub>2</sub> and N<sub>2</sub>O concentration of inland waters are calculated by Weiss and Price [39], and the CH<sub>4</sub> concentration is calculated by Wiesenburg and Guinasso Jr. [40]. See the calculation method in [41]. The calculation formula is:

$$S = C \div C_s \times 100\% \quad (1)$$

$$C = (C_a \times V_a + C_w \times V_w - C_{a1} \times V_a) \div V_w \quad (2)$$

The  $S$  is the greenhouse gas saturation of inland waters (%);  $C$  is the greenhouse gas concentration of inland waters ( $\mu\text{mol L}^{-1}$ );  $C_s$  is the saturated concentration of greenhouse gas of inland waters ( $\mu\text{mol L}^{-1}$ );  $C_a$  is the gas concentration in the gas component under equilibrium condition ( $\mu\text{mol L}^{-1}$ );  $V_a$  is the air volume in the head-space bottle (2 mL);  $C_w$  is the greenhouse gas concentration of inland waters under equilibrium condition ( $\mu\text{mol L}^{-1}$ );  $V_w$  is the water volume in the head-space bottle (10 mL);  $C_{a1}$  is the background concentration of atmospheric gas collected during the sampling ( $\mu\text{mol L}^{-1}$ ).

The greenhouse gas diffusion rate of water-gas interface is calculated by thin boundary layer method, which is widely applied to the water-gas interface gas exchange rate of inland waters. The calculation formula is:

$$F = k_0 \times (C - C_{w1}) \quad (3)$$

The  $F$  is the greenhouse gas diffusion rate ( $\text{mmol m}^{-2} \text{d}^{-1}$ );  $k_0$  is the gas transfer velocity ( $\text{m d}^{-1}$ ), which is calculated by the general temperature-wind speed model [29].

### 2.5.2. Data analysis

All the raw data is standardized and obtained in Excel 2010. The SPSS 19 (SPSS Inc., Chicago, IL, USA) software is used for statistical analysis, including normal distribution testing, Pearson correlation analysis, PCA (principal

component analysis), progressive multiplex regression analysis, etc., and all statistical significance levels represent  $p < 0.05$ . The Excel 2010 and GraphPad Prism 8 are adopted to make figures in this paper.

## 3. Results and analysis

### 3.1. Physical and chemical parameters of inland waters

The physical parameters of different inland waters in Xinjin District are shown in Table 2. There is no significant difference among inland waters in temperature and pH in Xinjin District, but the DO of irrigation canals and heavily polluted Yangliu River is much lower than that of other inland waters. The Chl-a content fluctuates greatly ( $1.0\text{--}27.0 \mu\text{g L}^{-1}$ ), and the Chl-a mean of irrigation canals, reservoirs and ponds is high with strong data variability, and some of the sampling points show eutrophication. Conductivity is a characteristic index of water pollution. The conductivity mean value of different inland waters is  $473 \pm 154 \mu\text{S cm}^{-1}$ . Yangliu River is the highest ( $722 \pm 7 \mu\text{S cm}^{-1}$ ), followed by irrigation canals ( $663 \pm 82 \mu\text{S cm}^{-1}$ ), with no significant differences among rivers, reservoirs, and ponds.

The variation range of TIC, TOC, DOC in different inland waters was  $21.38\text{--}43.18 \text{ mg L}^{-1}$ ,  $4.23\text{--}31.73 \text{ mg L}^{-1}$ ,  $1.66\text{--}28.17 \text{ mg L}^{-1}$ , respectively. The order from high to low was irrigation canals, ponds, rivers, reservoirs (Fig. 2). Among the rivers, Yangliu River, the most affected by human activities, had the highest carbon content, while Yangma River, affected by artificial ecological restoration, had the lowest carbon content, and the mainstream and tributaries of Minjiang River had the same carbon content. The variation range of TN, NO<sub>3</sub><sup>-</sup>-N, NH<sub>4</sub><sup>+</sup>-N in different inland waters was  $1.14\text{--}17.67 \text{ mg L}^{-1}$ ,  $0.83\text{--}14.66 \text{ mg L}^{-1}$ ,  $0.046\text{--}1.787 \text{ mg L}^{-1}$  that featured greater variability, and the lowest value in each monitoring section was found in reservoirs, Minjiang River, Jinma River and Xihe River. The N abundance of Yangliu River and ponds was significantly higher than that of other inland waters. The nitrogen content of different inland waters varied greatly, and the order from high to low was ponds, irrigation canals, rivers, reservoirs. Similar to the carbon and

Table 2  
Mean value of the physical parameters of different inland waters in Xinjin District

Inland waters	Water temperature WT (°C)	pH	DO (mg L <sup>-1</sup> )	Chl-a (μg L <sup>-1</sup> )	Conductivity (μS cm <sup>-1</sup> )
Minjiang River	10.78 ± 0.48 <sup>a</sup>	7.96 ± 0.31 <sup>b</sup>	10.9 ± 1.53 <sup>a</sup>	4.74 ± 1.54 <sup>b</sup>	476 ± 10 <sup>c</sup>
Jinma River	12.35 ± 0.45 <sup>b</sup>	7.31 ± 0.41 <sup>ab</sup>	9.72 ± 0.94 <sup>a</sup>	1.00 ± 0.53 <sup>a</sup>	314 ± 49 <sup>a</sup>
Xihe River	10.83 ± 0.54 <sup>a</sup>	6.87 ± 0.36 <sup>a</sup>	9.10 ± 1.16 <sup>a</sup>	3.22 ± 1.09 <sup>ab</sup>	395 ± 45 <sup>b</sup>
River					
Nanhe River	11.77 ± 0.47 <sup>b</sup>	7.95 ± 0.75 <sup>b</sup>	11.56 ± 4.90 <sup>a</sup>	2.38 ± 2.49 <sup>ab</sup>	528 ± 59 <sup>c</sup>
Yangma River	10.43 ± 0.64 <sup>a</sup>	6.78 ± 0.34 <sup>a</sup>	9.57 ± 0.47 <sup>a</sup>	1.05 ± 0.79 <sup>a</sup>	296 ± 9 <sup>a</sup>
Yangliu River	11.67 ± 0.14 <sup>b</sup>	7.68 ± 0.06 <sup>b</sup>	7.44 ± 0.63 <sup>a</sup>	1.21 ± 1.27 <sup>a</sup>	722 ± 6 <sup>d</sup>
Mean value of rivers	11.33 ± 0.84 <sup>A</sup>	7.38 ± 0.65 <sup>A</sup>	9.71 ± 2.62 <sup>A</sup>	2.12 ± 1.90 <sup>A</sup>	444 ± 149 <sup>A</sup>
Irrigation canals	11.25 ± 0.74 <sup>A</sup>	7.37 ± 0.21 <sup>A</sup>	7.25 ± 0.56 <sup>A</sup>	21.56 ± 25.83 <sup>AB</sup>	663 ± 67 <sup>A</sup>
Reservoirs	11.56 ± 1.51 <sup>A</sup>	7.59 ± 0.19 <sup>A</sup>	8.74 ± 1.37 <sup>A</sup>	13.69 ± 16.84 <sup>AB</sup>	520 ± 149 <sup>A</sup>
Ponds	11.13 ± 0.66 <sup>A</sup>	7.57 ± 0.57 <sup>A</sup>	10.62 ± 2.52 <sup>A</sup>	34.47 ± 26.70 <sup>B</sup>	496 ± 108 <sup>A</sup>
Total mean value	11.32 ± 0.90	7.41 ± 0.59	9.53 ± 2.55	8.13 ± 16.59	473 ± 153

Note: Lower case 'a, b' were the significant difference between rivers, and upper case 'A, B' were the difference between different inland waters.

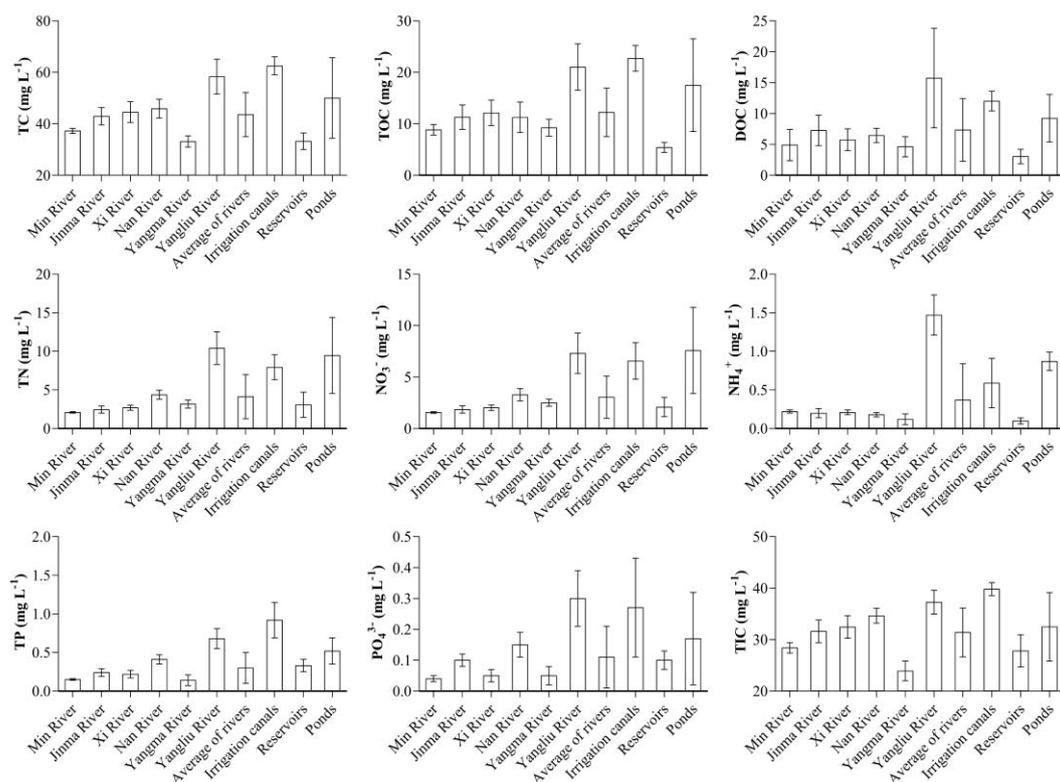


Fig. 2. The concentrations of different forms of carbon, nitrogen and phosphorus in different inland waters in Xinjin District.

nitrogen contents, the TP and  $\text{PO}_4^{3-}\text{-P}$  of irrigation canals and ponds were higher than those of rivers and reservoirs. But Yangliu River also had high P content, which was equivalent to irrigation canals. The mean value of TP and  $\text{PO}_4^{3-}\text{-P}$  in each monitoring section of different inland waters was  $0.38 \pm 0.26 \text{ mg L}^{-1}$  and  $0.13 \pm 0.12 \text{ mg L}^{-1}$  respectively, which of 1.19 and  $0.46 \text{ mg L}^{-1}$  for irrigation canals. In short, the carbon, nitrogen and phosphorus variability of different inland waters in Xinjin District was large, and the pollution load of irrigation canals and ponds was significantly higher than that of most rivers and reservoirs; Yangliu River was the most heavily polluted, and the water quality of Yangma River and mainstream of Minjiang River maintained a good momentum, representing an outstanding spatial characteristics of water environment.

### 3.2. $\text{CO}_2$ concentration and diffusion flux of different inland waters

The variation range of dissolved  $\text{CO}_2$  concentration of different inland waters was  $15.7\text{--}153.1 \mu\text{mol L}^{-1}$  (saturation: 77%–822%), and the mean value was  $62.8 \pm 33.2 \mu\text{mol L}^{-1}$  (saturation:  $328\% \pm 177\%$ ). The dissolved  $\text{CO}_2$  concentration of different inland waters was different, and the order from high to low was irrigation canals, ponds, rivers, reservoirs (Fig. 3), with the mean value of  $129.9 \pm 28.2 \mu\text{mol L}^{-1}$ ,  $83.5 \pm 23.7 \mu\text{mol L}^{-1}$ ,  $55.7 \pm 28.2 \mu\text{mol L}^{-1}$  and  $31.4 \pm 16.5 \mu\text{mol L}^{-1}$ , respectively. Besides, the  $\text{CO}_2$  concentration of different rivers varied greatly. Among them, Yangliu River ( $102.0 \pm 23.9 \mu\text{mol L}^{-1}$ ) was of the highest  $\text{CO}_2$  concentration, which was about 4 times that of Minjiang River

( $22.1 \pm 3.1 \mu\text{mol L}^{-1}$ ) and Xihe River ( $30.0 \pm 6.1 \mu\text{mol L}^{-1}$ ). Thus, man-made pollution determined the variation pattern of  $\text{CO}_2$  concentration in different rivers.

Based on the wind speed model and thin boundary layer model, it was estimated that the  $\text{CO}_2$  diffusion flux range of different inland waters in winter is  $-5.9\text{--}244.7 \text{ mmol m}^{-2} \text{ d}^{-2}$ , with the mean value of  $77.9 \pm 59.4 \text{ mmol m}^{-2} \text{ d}^{-2}$ , which is the net emission source of greenhouse gases. Similar to the  $\text{CO}_2$  concentration pattern, the  $\text{CO}_2$  diffusion flux of irrigation canals ( $197.1 \pm 51.7 \text{ mmol m}^{-2} \text{ d}^{-2}$ ) was significantly higher than that of ponds ( $114.0 \pm 42.2 \text{ mmol m}^{-2} \text{ d}^{-2}$ ) and rivers ( $65.5 \pm 50.7 \text{ mmol m}^{-2} \text{ d}^{-2}$ ), and reservoirs was the lowest ( $22.5 \pm 30.0 \text{ mmol m}^{-2} \text{ d}^{-2}$ ). In addition, the  $\text{CO}_2$  diffusion flux of small-scale Yangliu River that is heavily polluted by land-sourced pollution ( $147.2 \pm 43.2 \text{ mmol m}^{-2} \text{ d}^{-2}$ ) was significantly higher than that of other rivers and it was 29 times that of the mainstream of Minjiang River ( $5.1 \pm 5.5 \text{ mmol m}^{-2} \text{ d}^{-2}$ ).

### 3.3. $\text{CH}_4$ concentration and diffusion flux of different inland waters

The mean value of dissolved  $\text{CH}_4$  concentration in each monitoring section of different inland waters was  $304 \pm 206 \text{ nmol L}^{-1}$  (99–986  $\text{nmol L}^{-1}$ ). The saturation was  $386\% \pm 268\%$  compared with the atmosphere under equilibrium condition, and the  $\text{CH}_4$  concentration was oversaturated. Judging from the arithmetic mean value, the ponds had the highest  $\text{CH}_4$  concentration ( $583 \pm 342 \text{ nmol L}^{-1}$ ), next was the irrigation canals ( $526 \pm 157 \text{ nmol L}^{-1}$ ), and both of which were significantly higher than rivers ( $256 \pm 160 \text{ nmol L}^{-1}$ )

while the reservoirs were the lowest ( $146 \pm 43 \text{ nmol L}^{-1}$ ). Six rivers in the study area showed significant differences in  $\text{CH}_4$  concentration. Among them, Minjiang River and Yangma River were the lowest, while Jinma River, Nanhe River and Xihe River were high, all of which were prominently lower than the serious polluted Yangliu River ( $543 \pm 168 \text{ nmol L}^{-1}$ ).

Through calculation, the  $\text{CH}_4$  diffusion flux range of various air-water interfaces was  $0.08\text{--}3.64 \text{ mmol m}^{-2} \text{ d}^{-1}$ , with the mean value of  $0.89 \pm 0.82 \text{ mmol m}^{-2} \text{ d}^{-1}$  (Fig. 4), which is the net emission source of atmospheric greenhouse gases. The  $\text{CH}_4$  diffusion flux of different inland waters showed that the ponds ( $1.98 \pm 1.37 \text{ mmol m}^{-2} \text{ d}^{-1}$ ) and irrigation canals ( $1.75 \pm 0.64 \text{ mmol m}^{-2} \text{ d}^{-1}$ ) were significantly higher than the rivers ( $0.70 \pm 0.64 \text{ mmol m}^{-2} \text{ d}^{-1}$ ) and reservoirs ( $0.27 \pm 0.17 \text{ mmol m}^{-2} \text{ d}^{-1}$ ). Similar to the  $\text{CO}_2$  flux, the  $\text{CH}_4$  diffusion flux of Yangliu River ( $1.83 \pm 0.66 \text{ mmol m}^{-2} \text{ d}^{-1}$ ) was

significantly higher than that of other rivers, representing about 20 times the mainstream of Minjiang River.

### 3.4. $\text{N}_2\text{O}$ concentration and diffusion flux of different inland waters

The variation range of dissolved  $\text{N}_2\text{O}$  concentration was  $16\text{--}354 \text{ nmol L}^{-1}$  (saturation:  $130\%\text{--}2,941\%$ ) in each monitoring section of different inland waters, and the mean value was  $106 \pm 85 \text{ nmol L}^{-1}$  (saturation:  $724\% \pm 593\%$ ) (Fig. 5). Similar to the  $\text{CH}_4$  concentration, the order of the  $\text{N}_2\text{O}$  concentrations from high to low was ponds, irrigation canals, rivers, reservoirs ( $217 \pm 123 \text{ nmol L}^{-1}$ ,  $184 \pm 80 \text{ nmol L}^{-1}$ ,  $89 \pm 66 \text{ nmol L}^{-1}$ ,  $35 \pm 17 \text{ nmol L}^{-1}$ , respectively), which in the ponds were 6 times higher than these in reservoirs. Of the rivers, the dissolved  $\text{N}_2\text{O}$  concentration increased as the river scale decreased from the mainstream of Minjiang

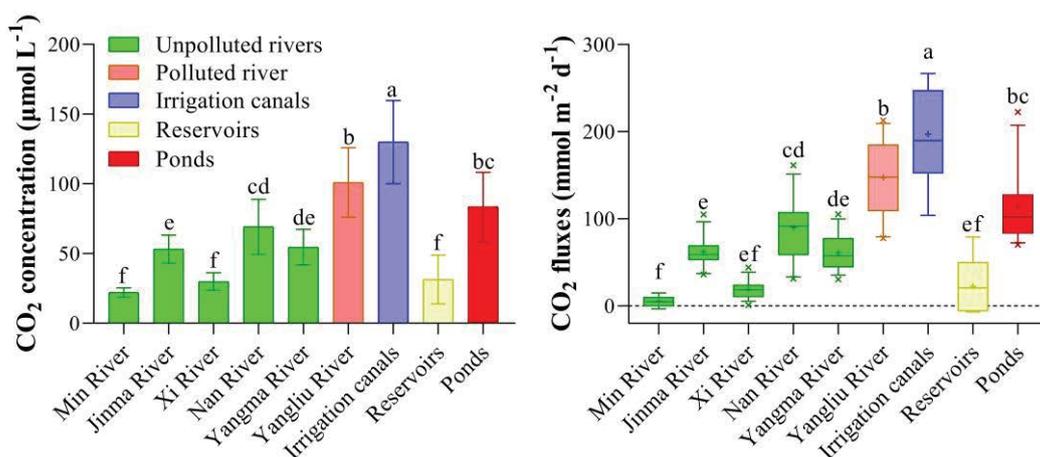


Fig. 3. Dissolved  $\text{CO}_2$  concentration and flux from different water bodies in Xinjin District. The case letters above the boxes and bars indicate the significance of the difference in  $\text{CO}_2$  concentration and flux among different water bodies at  $p < 0.05$ . The solid line and "+" in boxes in the right plot denote the median and mean of the datasets, respectively.

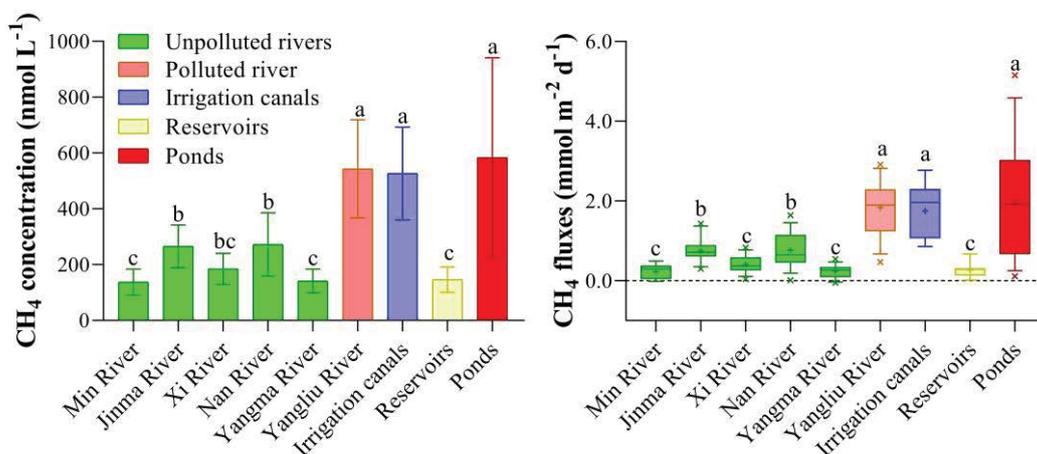


Fig. 4. Dissolved  $\text{CH}_4$  concentration and flux from different water bodies in Xinjin District. The case letters above the boxes and bars indicate the significance of the difference in  $\text{CH}_4$  concentration and flux among different water bodies at  $p < 0.05$ . The solid line and "+" in boxes in the right plot denote the median and mean of the datasets, respectively.

River to its tributary (Yangliu River) and the Yangliu River was significantly higher than the other rivers.

Through calculation by thin boundary layer model method, the variation range of  $N_2O$  diffusion flux of various monitoring sections was 7.5–780.9  $\mu\text{mol m}^{-2} \text{d}^{-1}$ , with the mean value was  $209.2 \pm 191.4 \mu\text{mol m}^{-2} \text{d}^{-1}$ , which is the net emission source of atmospheric greenhouse gases. The  $N_2O$  diffusion flux of ponds, irrigation canals, rivers and reservoirs were  $456.0 \pm 280.2 \mu\text{mol m}^{-2} \text{d}^{-1}$ ,  $390.1 \pm 186.8 \mu\text{mol m}^{-2} \text{d}^{-1}$ ,  $170.1 \pm 147.9 \mu\text{mol m}^{-2} \text{d}^{-1}$ ,  $50.7 \pm 38.7 \mu\text{mol m}^{-2} \text{d}^{-1}$ , respectively. The  $N_2O$  diffusion flux of the heavily polluted Yangliu River was higher than that of irrigation canals, Jinma River ( $24.6 \pm 20.9 \mu\text{mol m}^{-2} \text{d}^{-1}$ ) and Minjiang River ( $24.7 \pm 10.8 \mu\text{mol m}^{-2} \text{d}^{-1}$ ) were the lowest.

### 3.5. Relations with environmental factors

According to the findings of the analysis on the correlation between dissolved concentration and emission of greenhouse gases under the water environment parameters (Table 3), the dissolved concentration and diffusion flux of  $CO_2$ ,  $CH_4$ ,  $N_2O$  were positively correlated ( $P < 0.01$ ) with

carbon (TIC, TOC, DOC), nitrogen (TN,  $NO_3^-$ -N,  $NH_4^+$ -N) and phosphorus (TP,  $PO_4^{3-}$ -P), showing that the difference in water environmental quality among inland waters had an important impact on the produce and emission of greenhouse gases. The dissolved concentration and diffusion flux of greenhouse gases were significantly positively correlated with conductivity. In addition, the  $CH_4/N_2O$  concentration were significantly positively correlated ( $P < 0.01$ ) with Chl-a. Regarding all inland waters types in the study area, the biogenic elements and conductivity had a strong positive driving effect on the dissolved concentration and diffusion flux of greenhouse gases, indicating that the greenhouse gas emission was sensitive to the input of external pollution. The water environment factor was an important predictor for the intensity of greenhouse gas emitted from different types of inland waters systems in the region.

The PCA was employed in this study to clarify the relationships among all these environmental variables and resulted in three components that together explain 76.73% of the total variance (Table 4). The principal component 1 interpreted 53.01% of the variables, which were closely related to the carbon, nitrogen, phosphorus and electrical

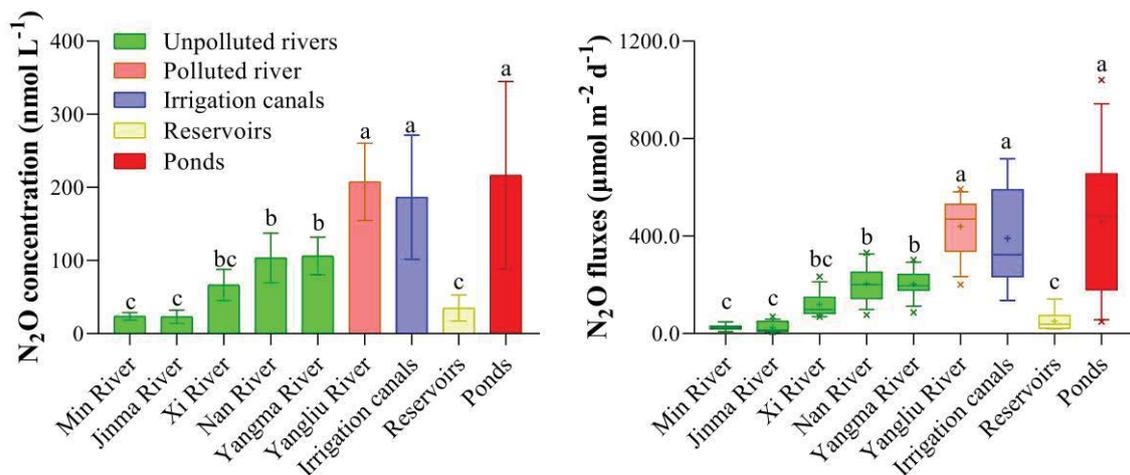


Fig. 5. Dissolved  $N_2O$  concentration and flux from different water bodies in Xinjin District. The case letters above the boxes and bars indicate the significance of the difference in  $N_2O$  concentration and flux among different water bodies at  $p < 0.05$ . The solid line and “+” in boxes in the right plot denote the median and mean of the datasets, respectively.

Table 3

Correlation between concentration and diffusion flux of greenhouse gases ( $CO_2$ ,  $CH_4$ ,  $N_2O$ ) and environmental variables (obtained by calculating Pearson's coefficient by using correlation analysis)

	TIC	TOC	DOC	TN	$NO_3^-$ -N	$NH_4^+$ -N	TP	$PO_4^{3-}$ -P	pH	DO	Conductivity	Chl-a
$CO_2$ concentration	0.558**	0.695**	0.573**	0.666**	0.670**	0.587**	0.786**	0.522**	0.185	-0.228	0.538**	0.281
$CO_2$ diffusion flux	0.570**	0.690**	0.576**	0.671**	0.676**	0.594**	0.795**	0.534**	0.194	-0.219	0.542**	0.271
$CH_4$ concentration	0.722**	0.887**	0.773**	0.894**	0.920**	0.734**	0.784**	0.732**	0.252	0.01	0.419*	0.558**
$CH_4$ diffusion flux	0.725**	0.887**	0.771**	0.894**	0.921**	0.732**	0.785**	0.737**	0.254	0.019	0.416*	0.550**
$N_2O$ concentration	0.570**	0.777**	0.606**	0.886**	0.907**	0.719**	0.749**	0.632**	0.111	0.018	0.415*	0.463**
$N_2O$ diffusion flux	0.581**	0.782**	0.608**	0.891**	0.912**	0.721**	0.756**	0.642**	0.120	0.026	0.420*	0.459**
n	37	37	37	37	37	37	37	37	37	37	37	37

“\*\*” was significant correlation;

“\*\*\*” was extremely significant correlation.

Table 4  
PCA results of the environmental variables of different inland waters

Environmental variable	TIC	TOC	DOC	TN	NO <sub>3</sub> -N	NH <sub>4</sub> <sup>+</sup> -N	TP	PO <sub>4</sub> <sup>3-</sup> -P	WT	pH	DO	Conductivity	Chl-a	Interpretation percentage%
Principal component 1	0.119	0.132	0.119	0.134	0.134	0.121	0.131	0.125	0.041	0.046	-0.008	0.094	0.056	53.010
Principal component 2	0.085	0.039	-0.009	-0.003	0.034	-0.162	-0.071	0.018	0.116	0.397	0.526	-0.232	0.205	13.145
Principal component 3	0.067	-0.147	-0.018	-0.130	-0.165	0.052	0.075	0.144	0.534	0.198	0.047	0.183	-0.517	10.575

conductivity of inland waters, characterizing the biogenic element and pollution of inland waters; the principal component 2 interpreted 13.15% of the variables, which were strongly correlated with pH and DO, characterizing the alkalinity and biological metabolic conditions of inland waters; the principal component 3 interpreted 10.58% of the variables, which were dominated by water temperature and Chl-a, characterizing the eutrophic state of inland waters. Through stepwise multiple linear regression analysis, the relationship between principal component score and greenhouse gas emission was shown in Table 5. Thus, the principal component 1 had a significant effect on the variability of concentration and emission of three greenhouse gases ( $P < 0.001$ ), the principal component 2 only affected the emission of CH<sub>4</sub> ( $p < 0.05$ ), the principal component 3 had a significant effect on the emission of CH<sub>4</sub> and N<sub>2</sub>O ( $P < 0.01$ ).

#### 4. Discussion

##### 4.1. Greenhouse gas emission characteristics of different inland waters in Chengdu Plain

The generation, consumption, input, emission of greenhouse gas of inland waters is a complex process involving sediment-overlying water, air-water, water-land, ground-water-surface water [1,21,27], which is influenced by a variety of ecological factors and shows a strong variability. This causes an uncertainty of estimation of GHGs emissions in the global and regional scale [1,5,12,42,43]. Due to different hydrological processes and environmental conditions of inland waters and sediments, there is a huge difference in emission intensity of greenhouse gas and potential contribution to GHGs budgets. The result of CH<sub>4</sub> emission of different inland waters in Berlin showed that the CH<sub>4</sub> fluxes of ponds was more than 4 times that of rivers and streams, and freshwater types were the most important factor affecting the variability of CH<sub>4</sub> emission of inland waters in Berlin as compared to season and location [25]. In the four different types of inland waters in Xinjin District, the concentration and diffusion flux of CO<sub>2</sub> was different, and the order from high to low was irrigation canals, ponds, rivers, reservoirs; in terms of CH<sub>4</sub>, N<sub>2</sub>O, the order from high to low was ponds, irrigation canals, rivers, reservoirs. Panneer [5]'s studies on different inland waters in southern India showed that the ponds had the highest CO<sub>2</sub>, CH<sub>4</sub> concentration and flux, followed by the irrigation canals. Rivers, streams, reservoirs and lakes were the lowest, which is similar to those of this study. Irrigation canal, a special kind of inland waters in Chengdu Plain, had transformed into a system with shallow water, serious siltation, slow flow speed and deteriorating water quality due to the urbanization and the development of modern agricultural technology, forming a hotpots of biochemical circulation and greenhouse gas emission [44]. Wu [45]'s research on greenhouse gas emission of different inland waters in Chengdu Plain showed that the greenhouse gas emission of irrigation canals was much higher than other types of inland waters. The ecological environment survey and water environment analysis in this study also showed that the irrigation canals contained high content of carbon and nitrogen, fluxes with shallow water, causing that the

Table 5

Regression equation of the three principal components and the concentration and diffusion flux of CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>O

	Regression equation	R	F
CO <sub>2</sub> concentration	$Y = 62.8 + 24.5X_1 - 4.88X_2 - 1.22X_3$	0.744	13.625
CO <sub>2</sub> diffusion flux	$Y = 77.9 + 44.4X_1 - 8.28X_2 - 0.82X_3$	0.750	14.147
CH <sub>4</sub> concentration	$Y = 304.2 + 191.2X_1 + 23.1X_2 - 36.4X_3$	0.938	80.607
CH <sub>4</sub> diffusion flux	$Y = 0.886 + 0.759X_1 + 0.097X_2 - 0.133X_3$	0.937	79.609
N <sub>2</sub> O concentration	$Y = 106.2 + 70.4X_1 + 0.121X_2 - 23.8X_3$	0.865	32.707
N <sub>2</sub> O diffusion flux	$Y = 209.2 + 160.5X_1 + 1.95X_2 - 50.6X_3$	0.868	33.457

The principal components of regression included: X<sub>1</sub> was the principal component 1, X<sub>2</sub> was the principal component 2, and X<sub>3</sub> was the principal component 3.

greenhouse gas fluxes was much higher than that of other types of inland waters and act as a emission hotpots.

In addition, the greenhouse gas fluxes of ponds was much higher than that of most rivers, lakes and reservoirs (Table 6), which was more than 10 times that of reservoirs, representing an emission hotpots of greenhouse gas and another important heat source, which was consistent with most research results [5,25,37]. In this study, the CO<sub>2</sub> and CH<sub>4</sub> diffusion flux of ponds were higher than the average values of ponds worldwide [13], but the CH<sub>4</sub> diffusion flux of ponds was still lower than that of aquacultural ponds at the subtropical Minjiang River estuary [46] and the urban artificial ponds in other climate zones [25,33]. Both studies by Panneer [5] and Ortega [25] showed that the CH<sub>4</sub> emission of ponds was 4.7 times that of rivers and 4 times that of lakes and reservoirs, which further proved the conclusions of this study. More and more studies on the emission of inland waters with small area have been conducted in recent years, and most of them indicated that the ponds was the most emission potential in GHGs emission of regional inland waters for its small area, shallow water, large water-collecting area and water area and sensitivity to nutrients loading [47]. However, the greenhouse gas emission of ponds was of large variability (Fig. 1). This is because that some of the ponds in the study were transformed into aquacultural ponds (Table 2). By contrast, the greenhouse gas emission of ponds with less human disturbance were low. After the ponds in Chengdu Plain were transformed into aquacultural ponds, the artificial supply of organic carbon and nitrogen boosted, resulting in a strong emission potential. This research believed that the number of small ponds was large in world, and their role and emission contribution was quite remarkable in the global land carbon and nitrogen cycle [48]. There were many ponds in Chengdu Plain, and most of them had been converted into ponds or contiguous fisheries. The extensive management caused a fast accumulation of carbon and nitrogen in inland waters, which might be transformed into important emission sources of atmospheric greenhouse gases. However, more researches needed be conducted on inland waters for the lack of the data such as the contribution data and freshwater area.

The river in Xinjin District is the main body of the regional inland waters, their greenhouse gas fluxes was lower than the ponds and irrigation canals (Figs. 3–5), with slightly higher than the reservoirs. The CO<sub>2</sub> and CH<sub>4</sub> diffusion flux of rivers in the study area were below the average

values of global rivers [24,49,50]. They were far below the US subtropical source streams [51], tropical rivers in Southern Africa [43] and Shanghai, Berlin [25,52] and heavily polluted Liangtan River [26], but higher than Heishuitan River of Chongqing that was less affected by urbanization [50]. The N<sub>2</sub>O diffusion flux of rivers was higher than that of some tropical African rivers [43], Adyar River [53], the suburban Heishuitan River [50], and Tuojiang River [54] which is an agricultural river, but lower than the Grand River [55] in frigid zone and the heavily polluted Liangtan River [26]. However, the greenhouse gas concentrations and fluxes of rivers showed a strong variation, with significant differences between rivers or river reaches (Figs. 3–5). The mainstream of Minjiang River, Jinma River and Xihe River was low in greenhouse gas fluxes, while the heavily polluted Yangliu River was significantly higher than other rivers or reaches and even equivalent to most urban rivers (Table 6). Therefore, polluted rivers were also a potential emission source of atmospheric greenhouse gases in regional inland waters.

There were few reservoirs in this area, most of which were water-source reservoirs with small man-made pollution load, so the greenhouse gas fluxes were low. The concentration and diffusion flux of greenhouse gases of reservoirs in the study area was significantly lower than those of Indian tropical reservoir [5], Chongqing small reservoir [32] and Maotiaohe cascade reservoir [56]. To sum up, the greenhouse gas emission rate of irrigation canals, ponds and polluted rivers or river reaches was large. In the process of agriculturalization and urbanization, a large number of natural inland waters was polluted and their functions were changed, making them a potential emission hotpots of atmospheric greenhouse gas [57,58].

#### 4.2. Greenhouse gas emission of artificial inland waters was higher than that of natural inland waters

Chengdu Plain is a representative agricultural irrigation plain in southwest China, which is densely covered with rivers, irrigation canals and ponds. Affected by human activities, the water environment and biological localization process of different inland waters in this area are greatly varied [35,45]. In this study, different inland waters in Xinjin District were affected by the changes of land use type, hydrological process, pollution load caused by agriculturalization and urbanization, which increased the input of external pollution [50,59]. In particular, artificial inland waters such as

Table 6

Comparison of greenhouse gas diffusion flux of some inland waters at home and abroad ( $\text{mmol m}^{-2} \text{d}^{-1}$ )

Inland waters	Type	Region	Climate	CO <sub>2</sub>	CH <sub>4</sub>	N <sub>2</sub> O	References
Different inland waters in Xinjin District	River			54.30 ± 20.66	0.60 ± 0.29	0.14 ± 0.05	This study
	Canal			172.10 ± 47.60	1.50 ± 0.57	0.33 ± 0.17	
	Reservoir			3.27 ± 12.94	0.17 ± 0.10	0.02 ± 0.01	
Shanghai River network	Pond			90.10 ± 39.90	1.42 ± 1.22	0.32 ± 0.25	
	River			66 – 294	0.19 – 18.5	–	
Taihu Lake	Lake			–	0.09 ± 0.05	–	[30]
Small reservoirs in Chongqing	Forest area reservoir			30.40 ± 32.20	0.25 ± 0.07	0.04 ± 0.04	
	Agricultural area reservoir			48.20 ± 17.00	0.52 ± 0.25	0.15 ± 0.15	[32]
	Urban area reservoir			137.50 ± 81.00	2.74 ± 1.94	0.51 ± 0.58	
Heishuitan River	River	China		29.90 ± 46.50	0.50 ± 0.27	0.06 ± 0.05	[50]
Liangtan River	River			–6.10 – 786.90	0.31 – 27.62	0.06 – 1.08	[26]
Minjiang River estuary	Aquacultural pond		Subtropical zone	–	2.16 – 55.70	–	[46]
Tuojiang River	River			–	–	0.004 – 0.03	[54]
	Hongfeng Reservoir			15	–	–	
	Baihua Reservoir			24	–	–	
	Xiuwen Reservoir			47	–	–	
	Hongyan Reservoir			22.40	–	–	
	Urban inland waters	River, lake, reservoir, etc.	Mexico		–	2.50 – 141.00	–
Headwater Stream in Baltimore	Stream	America		58 – 262	0.42 – 6.41	0.12 – 3.40	[51]
Headwater streams	Stream			–	–	–0.0006 – 0.0123	[17]
Rivers in Sub-Saharan Africa	River	Africa		894	9.61	0.01	[43]
Freshwater in South India	Open-air water wells			146.30 ± 76.20	2.30 ± 3	–	
	Lake		Tropical zone	2.10 ± 23.80	4 ± 6.40	–	
	Pond	India		67.10 ± 64	17.90 ± 18.50	–	[5]
	River			20.10 ± 38.50	6.20 ± 12.40	–	
Adyar River	Canal			18.10 ± 1.60	10.90 ± 17	–	
	Reservoir			8.40	0.20	–	
Urban inland waters in Berlin	River			–	0.002 – 59.09	0.0002 – 0.122	[53]
	Lake			–	2.40 ± 3.40	–	
	Pond	Germany	Temperate zone	–	7.50 ± 10.40	–	[25]
Grand River	River			–	1.30 ± 2.20	–	
	River	Canada		–	2.40 ± 4.60	–	
Rivers of Québec	River			–	–	–0.035 – 4.20	[55]
Boreal Lakes	River			–	0.36 – 3.53	–	[58]
Vesijärvi Lake	Lake	Northern Europe	Frigid zone	20.48	2.32	0.0048	[42]
Rotsee Lake	Lake	Finland		12.40 ± 2.38	0.24 ± 0.06	–	[28]
Artificial ponds	Lake	Switzerland		–	0.01 – 0.44	–	[29]
Globe freshwater	Pond (<0.1 km <sup>2</sup> )	Sweden		17.10	1.89	–	[33]
	Lake (>0.1 km <sup>2</sup> )			–	0.44	–	[15]
	River			–	8.22 ± 25.50	–	[49]
				93	–	–	[24]
	Pond (<0.1 km <sup>2</sup> )			25.99	1.07	–	
	Lake (>0.1 km <sup>2</sup> )			19.67	0.11	–	[13]

irrigation canals and fishponds were more affected by human activities than natural inland waters such as rivers and reservoirs. The input of a large number of exogenous organic matters and nutrients into artificial inland waters resulted in higher contents of carbon, nitrogen, phosphorus and conductivity than natural inland waters, which was consistent with most research results of inland inland waters [5,25,45]. It was found that the concentration of carbon, nitrogen and phosphorus in the mainstream and tributaries of Minjiang River, except the Yangma River, was negatively correlated with those of the watershed scale (Fig. 2). With the excessive input of regional agricultural and urban external pollution, the water environment of different inland waters was deteriorated, which dramatically changed the biochemical process of different inland waters, thus affecting the generation and emission process of greenhouse gases in inland waters.

Studies showed that the  $\text{CO}_2$  concentration in inland waters depends on the microbial decomposition of organic matter in freshwater and the input of  $\text{CO}_2$  generated by terrestrial soil and plant root respiration [21], while the  $\text{CH}_4$  concentration depends on the anaerobic methan bacteria metabolism of underwater sediments [49] and the  $\text{N}_2\text{O}$  comes from nitrification, denitrification, and the coupled nitrification-denitrification process [17,60]. In this study, there was a strong spatial variability of  $\text{CO}_2$ ,  $\text{CH}_4$  and  $\text{N}_2\text{O}$  concentration in different freshwater and their spatial distribution roughly coincided with the water pollution load gradient. The greenhouse gas concentration of artificial freshwater that had high pollution load such as irrigation canals and fishponds was higher than that of natural inland waters with low pollution load such as rivers and reservoirs. The corresponding greenhouse gas diffusion flux also showed a similar pattern (Figs. 2 and 3), which was similar to the research results of different freshwater in Chongzhou [45] and Berlin [25]. The correlation analysis in this study further proved that the greater the water pollution load, the higher the greenhouse gas concentration (Table 3). Irrigation canal is a water body with low environmental capacity, which is affected by human activities and human nutrient input [35,61,62]. It is also an important place for biogeochemical interaction between biogenic elements, microorganisms and aquatic plants [63]. Under the dual stimulation of domestic sewage and agricultural fertilizer, the organic matter decomposition process and microbial activity of irrigation canals were enhanced [35], making irrigation canals a hot spot of greenhouse gas emission. Wu [45] found that the high  $\text{CO}_2$  and  $\text{CH}_4$  fluxes of irrigation canals were related to a large number of pollutants containing the domestic sewage. Feng [35] also made it clear that the  $\text{CO}_2$  fluxes of agricultural-household irrigation canals was significantly higher than that of agricultural irrigation canals and household irrigation canals. As a typical hydrostatic freshwater system, fish ponds is rich in organic matter and is more likely to form a sediment anaerobic environment [48]. Because of its strong biogeochemical process caused by great human disturbance, it is also a hotspots of greenhouse gas emission [31,34]. As river system covers large water area and is less affected by human activities than the irrigation canals and fishponds and is to the running water body, it was hard to the generation of anaerobic environment

and greenhouse of gas [50]. However, the high levels of organic pollutants contributed to greenhouse gas emissions in freshwater, affected by industrial and domestic sewage in some rivers (such as Yangliu River) [60]. To sum up, the freshwater affected by human activities is an important contributor to total greenhouse gas emission.

#### 4.3. Analysis of influencing factors

The internal physicochemical factors of different freshwater in Xinjin District influenced the microbial metabolic process and gas diffusion rate [32], thus affecting the spatial pattern of greenhouse gas emission in different freshwater. The  $\text{CO}_2$  concentration was significantly positively correlated with carbon, nitrogen, phosphorus and conductivity (Table 3, Fig. 6) except for water temperature, pH and Chl-a, which was inconsistent with most inland water studies [26,31,33,52]. It might be because that the survey was conducted in winter and the metabolic process of freshwater was weak. Meanwhile, human activity leads to large differences in carbon, nitrogen and phosphorus contents among different freshwater (Fig. 2), limiting the organic carbon and nutrient of the water [53]. The principal component analysis (PCA) showed that the human activity causes a large input of carbon, nitrogen and phosphorus, affecting the spatial distribution characteristics of  $\text{CO}_2$  concentration in different freshwater (Tables 4 and 5). Studies of subtropical reservoirs by Wang et al. [32] also found that DOC,  $\text{NO}_3^-$ , phosphorus contents (TP, DTP,  $\text{PO}_4^{3-}$ ) and conductivity significantly affected the  $p\text{CO}_2$  and its diffusion flux. Moreover, regression analysis demonstrated that the interpretation of TOC,  $\text{NO}_3^-$  and TP reached to 48%, 45%, 45% and 62% of the variation characteristics of  $\text{CO}_2$  concentration, which is the key factor affecting the  $\text{CO}_2$  emission of different freshwater (Fig. 6). Yang's [42] studies on 75 northern lakes in northern Europe showed that TOC and TP are major predictors of  $\text{CO}_2$  concentration, which affects  $\text{CO}_2$  concentration by promoting mineralization of TOC by heterotrophic bacteria in water and promoting autotrophic production. Wang [56] also pointed out that land-source organic carbon is an important carbon source for aquatic biological processes, and parts of  $\text{CO}_2$  in water is produced by in situ respiration of organic carbon [50]. In addition, studies of artificial ponds by Yang [31] and Peacock [33] found a significant correlation of  $\text{CO}_2$  emission with  $\text{NO}_3^-$  and  $\text{NH}_4^+$ . Therefore, under the influence of human activity, the concentration and diffusion flux of  $\text{CO}_2$  in freshwater with different pollution levels are extremely sensitive to the input of carbon, nitrogen and phosphorus, setting a limitation on biogenic elements except for biological metabolic process.

In most studies, the researchers identified DOC and DO as key factors of  $\text{CH}_4$  emission [30,35,64], which is consistent with the results of this study. Research showed that DOC in water provides carbon sources and methanogen substrates for methanogen growth and has an important impact on  $\text{CH}_4$  production under the metabolic action of microbes [15,65]. And DO oxidized  $\text{CH}_4$  from the fermentation of acetic acid anaerobic in the sediment [35] to reduce  $\text{CH}_4$  emission. Studies of subtropical shrimp ponds by Yang [31] also found a significant positive correlation

between organic carbon and  $\text{CH}_4$  fluxes. In this study,  $\text{CH}_4$  concentration was also significantly positively correlated with nutrient (N and P) and conductivity (Table 3). The regression analysis also showed that TN, TP and conductivity interprets the variation characteristics of  $\text{CH}_4$  concentration, so they are the key factors affecting  $\text{CH}_4$  emission. Studies of artificial ponds by Peacock [33] found that water nutritional status is an important driver to  $\text{CH}_4$  emission and TP is significantly positively correlated with  $\text{CH}_4$  concentration, in which the two presented a strong predictive relationship (Fig. 7). Research showed that the input of exogenous phosphorus directly promotes the metabolism of methanogen and the growth of plankton, while the plankton residues provide fresh carbon sources for  $\text{CH}_4$  production [42] to promote  $\text{CH}_4$  emission. The input of nitrogen-containing pollutants from exogenous agricultural and domestic sewage outside the county can reduce the restriction of nitrogen by microorganisms, thus

improving the activity of methanogen and enhancing  $\text{CH}_4$  emission [66–69]. In addition, conductivity, a characteristic index of water pollution, reflects the pollution degree of agricultural activities and urban sewage in this area, which can explain the change of  $\text{CH}_4$  concentration in 52% of freshwater (Table 3, Fig. 7). It shows that the large input of pollutants caused by urbanization and agriculturalization directly changes the spatial distribution of  $\text{CH}_4$  concentration.

$\text{N}_2\text{O}$  is derived from the nitrogen metabolic process [17] and is influenced by a variety of environmental factors. In this study, there was a significant negative correlation between  $\text{N}_2\text{O}$  concentration and DO (Table 3), which is consistent with Smith [51] and Feng [35]. It could be that the DO reduced the activity of denitrifying bacteria and limited the denitrification process. In the future study, DO should be taken into account in the  $\text{N}_2\text{O}$  prediction estimation model [55]. PCA analysis showed that  $\text{N}_2\text{O}$  concentration is significantly

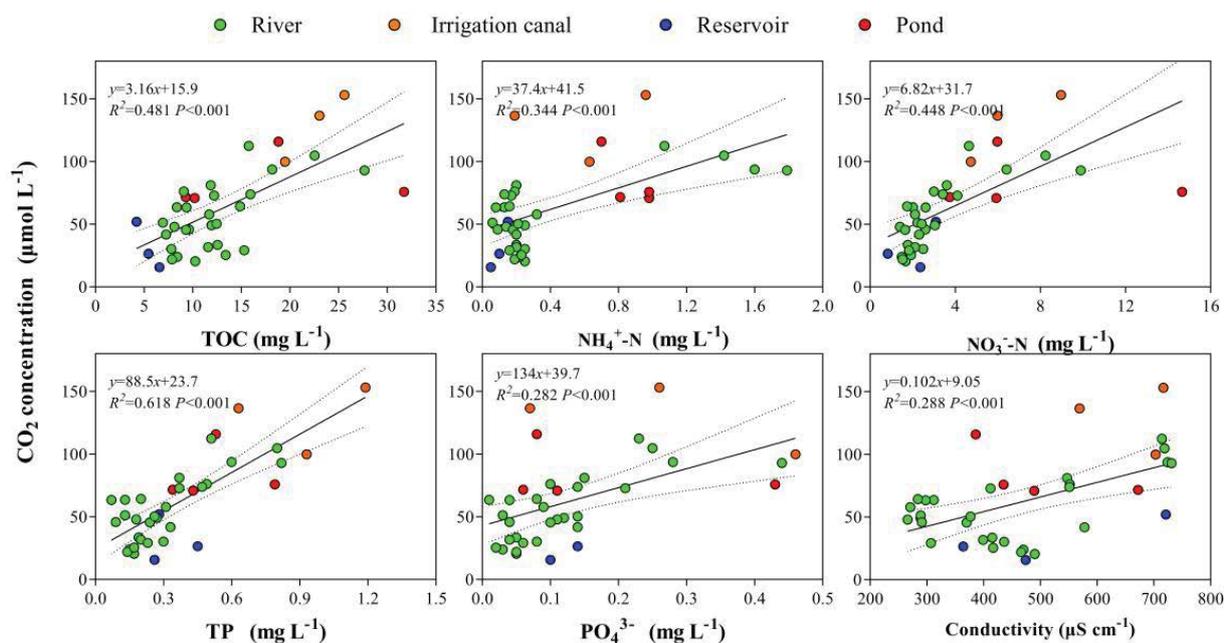


Fig. 6. Relation between  $\text{CO}_2$  concentration and TOC,  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ , TP,  $\text{PO}_4^{3-}$  and conductivity in each monitoring section (linear regression analysis) river canal reservoir fishpond  $\text{CO}_2$  concentration.

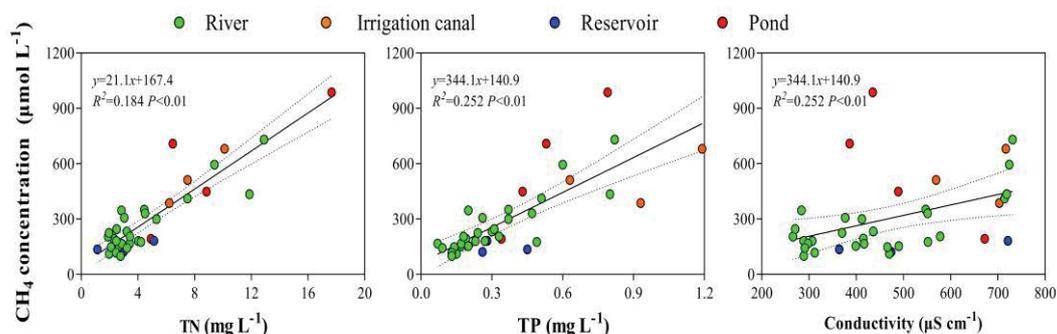


Fig. 7. Relation between  $\text{CH}_4$  concentration and TN, TP and conductivity in each monitoring section river canal reservoir fishpond  $\text{CH}_4$  concentration.

positively correlated with nutrient (N and P) and conductivity (Table 3, Fig. 8), which is consistent with most studies [32,36]. It further shows that the  $N_2O$  containing the sewage discharge in the study area is the direct source of  $N_2O$  in freshwater. The study of Grand River by Rosamond [55] showed that the  $NO_3^-$  is significantly positively correlated with  $N_2O$  emission, but the coefficient value is small ( $R = 0.19$ ), which is consistent with the results of this study. Studies by Deng also suggested that  $NH_4^+$  is a major factor affecting  $N_2O$  emission in the irrigation canals, which is stronger than  $NO_3^-$  [61]. It could be that the increase of  $NH_4^+$  in domestic sewage promotes the nitrification of water body to produce more  $N_2O$ . Yang [42] also indicated that TP has a strong predictive relationship with  $N_2O$  concentration. Therefore, the pollutants discharged by people change the spatial pattern of  $N_2O$  emission of freshwater. Therefore, more research on impact mechanism of man-made nitrogen and phosphorus load on  $N_2O$  emission is needed in future studies.

#### 4.4. Analysis of the estimation and relative contribution of total greenhouse gas emission of different freshwater

The estimation result of this study based on the extrapolation method for greenhouse gases from different

freshwater in Xinjin District is shown in Table 7. The total emissions of greenhouse gases from different freshwater in Xinjin District are  $2.5 \times 10^4$  t  $CO_2$   $y^{-1}$ , 107 t  $CH_4$   $y^{-1}$ , and 69 t  $N_2O$   $y^{-1}$ , respectively. Since the centenary warming effect potential of  $CH_4$  and  $N_2O$  are 34 times and 298 times that of  $CO_2$ , respectively, they are converted to  $CO_2$  equivalent. Therefore, the total greenhouse gas emission of freshwater in the study area is about  $5.0 \times 10^4$  t  $CO_2$ -eq  $y^{-1}$ . The total greenhouse gas emission of rivers and reservoirs account for 56% and 1% of that of all freshwater in Xinjin District [70,71]. The total water area of irrigation canals and ponds account for only 9% and 14% of that of all freshwater in Xinjin District, but their total greenhouse gas emission are 19% and 24%, with significantly higher than those of other freshwater. The  $CO_2$  equivalent of rivers in the study is greatly different. The Minjiang River and Yangma River are the lowest, while the Jinma River and Xihe River are at high level, but all of them are lower than the Nanhe River and the heavily polluted Yangliu River.

To sum up, the contribution of artificial freshwater such as irrigation canals and ponds in Xinjin District in the global greenhouse gas emission cannot be ignored. The greenhouse gas diffusion flux of different freshwater in the study area are lower than those of seriously polluted

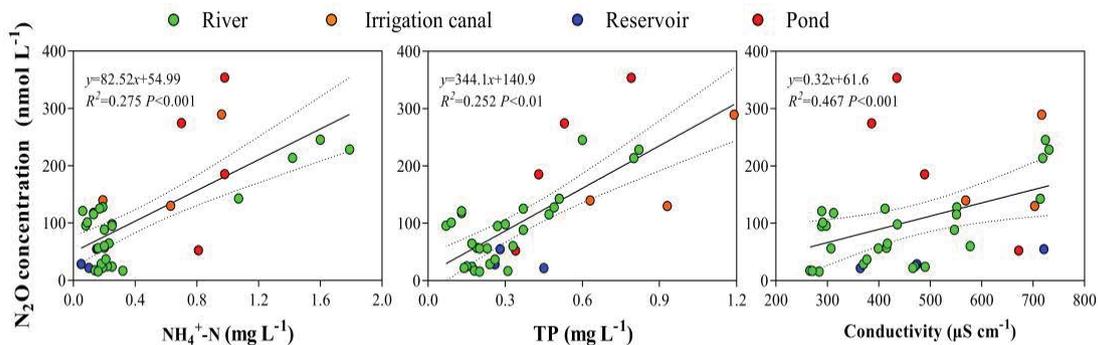


Fig. 8. Relation between  $N_2O$  concentration and  $NH_4^+$ , TP and conductivity in each monitoring section river canal reservoir fishpond  $N_2O$  concentration.

Table 7  
Estimated quantity of GHGs in different freshwater in Xinjin District

Freshwater	Area (ha)	$CO_2$ emission (t $y^{-1}$ )	$CH_4$ emission (t $y^{-1}$ )	$N_2O$ emission (t $y^{-1}$ )	$CO_2$ equivalent (t $y^{-1}$ )	Ratio	
Minjiang River	372.2	305.04	4.87	1.48	910.56	2%	
Jinma River	271.12	2,716.96	11.94	1.07	3,442.15	7%	
Xihe River	355.2	1,083.60	8.52	6.80	3,398.57	7%	
River	Nanhe River	198.32	2,869.18	8.87	6.55	5,122.26	10%
Yangma River	81.59	804.69	1.13	2.66	1,637.11	3%	
Yangliu River	100.66	2,380.26	10.79	7.10	4,864.01	10%	
Total of rivers	1,379.09	14,508.79	56.24	37.69	27,653.87	56%	
Irrigation canals	179.28	5,675.95	18.38	11.24	9,648.85	19%	
Reservoirs	47.8	172.42	0.74	0.39	313.66	1%	
Ponds	269.75	4,941.29	31.29	19.76	11,893.96	24%	
Total	–	25,298.44	106.65	69.08	49,510.34		

freshwater and some urban freshwater, while higher than those of most natural freshwater. Continuous agriculturalization and urbanization in Xinjin District will lead to the accumulation of biogenic elements of freshwater and to enhance the emission of greenhouse gases in freshwater. In recent years, many studies have been conducted in terms of the greenhouse emission of rivers [7,8,16,52], but there remains an uncertainty in estimating the contribution due to the variability of the data [1,15].

Finally, this study evaluated the greenhouse gas diffusion flux in different freshwater without consideration of the bubbling and plant transport. The studies of different freshwater by Panneer Selvam [5] and Herrero [25] suggested that the bubbling of ponds and irrigation canals is an important route of CH<sub>4</sub> emission (contribution rate >80%), especially in cities [37] and heavily polluted freshwater in agricultural areas [57]. Therefore, the CH<sub>4</sub> emission of irrigation canals and ponds in this study might be seriously underestimated, but it is still significantly higher than rivers and reservoirs (Fig. 3). So the study needs to focus on the CH<sub>4</sub> emission control of canal and ponds in Chengdu Plain and its surrounding areas. This study emphasized that both the degradation of irrigation canals and the man-made nutrition input of ponds might evolve into an indirect anthropogenic greenhouse gas emitter.

## 5. Conclusions

- The CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub>O concentrations in different inland waters in the study area were at high level and acted as important emission sources of greenhouse gases to atmosphere. There was a strong spatial variability in the greenhouse gas concentrations among different water bodies, whose spatial distribution were roughly consistent with the water pollution load gradient. And the greenhouse gas concentrations of artificial freshwater such as irrigation canals and ponds with high pollution load is significantly higher than that of natural freshwater such as rivers and reservoirs with low pollution load. Affected by the external pollution input discharged by human activities along the river, from Minjiang River to its tributary (Yangliu River), the N<sub>2</sub>O concentration increased showed strongly variation. The tributaries with higher pollution load contain higher N<sub>2</sub>O concentration than the mainstream. In general, the terrestrial human activities in Xinjin District affected the biogenic elements and other physical and chemical properties, resulting in changes in the spatial pattern of greenhouse gas emission in different freshwater. The irrigation canals and ponds had become important emission sources of greenhouse gases.
- The CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub>O concentrations are significantly positively correlated with carbon, nitrogen, phosphorus and conductivity except for water temperature, pH and Chl-a. The pollutant input brought by sustained urbanization and agriculturalization represents the major driving factor in affecting the spatial difference of greenhouse gas concentration in these inland waters. The CO<sub>2</sub> and CH<sub>4</sub> concentration in freshwater is also influenced by partial carbon, which can provide carbon sources for the production of CO<sub>2</sub> and CH<sub>4</sub>. The DO can also significantly affect the concentration of CO<sub>2</sub> and CH<sub>4</sub> by

influencing the anaerobic methanogen and nitrification/denitrification.

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