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# Human impact on the historical change of CO<sub>2</sub> degassing flux in River Changjiang

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### **Abstract**

The impact of water quality changes in River Changjiang (formally known as the Yangtze River) on dissolved CO2 and silicate concentrations and seasonal carbon flux in the past several decades (1960s-2000) was evaluated, based on monitoring data from hydrographic gauge. It was found that dissolved CO2 and silicate in Changjiang decreased dramatically during this decades, as opposed to a marked increase in nutrient (e.g. NO<sub>3</sub>-) concentrations. Our analyses revealed that dissolved CO<sub>2</sub> in Changjiang was over-saturated with the atmosphere CO2, and its concentration had showed a declining trend since the 1960s, despite that fluvial DIC flux had maintained stable. Analysis results also suggested that the decrease in dissolved CO2 concentration was attributed to changes on the riverine trophic level and river damming activities in the Changjiang drainage basin. Due to the economic innovation (e.g. agriculture and industry development) across the Changjiang watershed, fertilizers application and river regulations have significantly altered the original state of the river. Its ecosystem and hydrological condition have been evolving toward the "lacustrine/reservoir" autotrophic type prevailing with plankton. Accordingly, average CO2 diffusing flux to the atmosphere from the river had been reduced by three-fourth from the 1960s to 1990s, with the flux value being down to 14.2 mol.m<sup>-2</sup>.yr<sup>-1</sup> in the 1990s. For a rough estimate, approximately 15.3 Mt of carbon was degassed annually into the atmosphere from the entire Changjiang drainage basin in the 1990s.

### I. Background

 ${\rm CO_2}$  or carbon flux is the major cause in today's global climate change. Rivers, connecting the terrestrial and oceanic ecosystems, plays a unique role in the transportation of weathering products and pollutants from land to ocean. Global fluvial export of carbon is now a well-documented component in the global carbon cycle and is estimated ca.  $\sim 10^{15}$  g C.yr<sup>-1</sup> [1-4]. Although it is relatively

small compared with the fluxes at other interfaces (atmosphere-biosphere, atmosphere-ocean), the fluvial carbon flux contributes an important percentage to the regional carbon budget. In addition, carbon exports via rivers are not limited to fluvial discharge. Recently, it has also been found that river systems actively degasses  $CO_2$  into the atmosphere [2,5,6]. As observed in many studies, concentration of  $CO_2$  dissolved in rivers, lakes and coastal areas,

is higher than its equilibrium concentration relative to  $\mathrm{CO}_2$  in the atmosphere (*i.e.* 350 ppm at present), as a result of biogeochemical process imposed by the thermodynamic equilibrium between the riverine and atmospheric  $\mathrm{CO}_2$  [2,6-15]. Consequently, the excess of  $\mathrm{CO}_2$  can escape to the atmosphere due to physical water- air equilibration.

On the other hand, the increasing anthropogenic activities in river drainage basin, are significantly changing the continuum of land-sea interaction inter-linked by rivers [16,17]. For instance, river damming and eutrophication are widely regarded as the most remarkable and extensive changing events [18,19]. Environment changes (e.g. catchment landscape, water quality) can be recorded in riverine carbon inventory, which is closely related to the terrestrial ecosystem [3]. As a result, over-saturation of dissolved  $CO_2$  in rivers may be misestimated if the estimation is made based on a specific temporal and spatial scale. Hence, we need to look into some historical data from Changjiang for a new understanding in the river geochemistry.

Changjiang is the largest river in Euro-Asian Continent, draining an area of 1.80 × 106 km<sup>2</sup>. It is ranked third in length (6300 km), fourth for freshwater flow (900  $\times$  10<sup>9</sup>  $m^3.yr^{-1}$ ) and sediment discharge (0.5 × 10<sup>9</sup> tons.yr<sup>-1</sup>) in the world [20,21]. During the past several decades (i.e. 1960s-1990s), the Changjiang watershed had experienced a significant development of industry and agriculture. Population in the drainage basin had grown over 434,430,000 in 2000, being 1.7 folds that in 1960 [22]. Reported concentration in NO<sub>3</sub>-N, NH<sub>4</sub>+-N and NO<sub>2</sub>-N in Changjiang had reached a value that was 5-10 folds higher than the global background values of river water [23]. A recent study suggested that 95% of the nitrate flux of Changjiang could be linked to anthropogenic activities in the 1990s [24], and that DIN in the river was found being doubled in the past two decades [25]. As a result of increases in the nutrients load, the primary productivity (such as diatom) in river can be boosted, by absorbing inorganic nutrients elements (e.g. C, N, P, Si) according to Redfield ratio, and then changes the chemical composition of river water. CO<sub>2</sub> dissolved in the river water can be modified by a disequilibrium of the balance between respiration and photosynthesis in the aquatic ecosystem [26]. It is now well understood that dissolved CO<sub>2</sub> concentration is a variable rapidly responding to the water quality evolution and trophic status, followed by carbon feedbacks to the atmosphere.

In this study, our main objective was to analyze the influence of human activities on the carbon degassing flux in Changjiang. The historical trend of dissolved CO<sub>2</sub> concentration in Changjiang was analyzed for the past decades

(1960s–2000) based on the monitoring data from select hydrographic station. The change of the inorganic carbon fluvial flux of Changjiang to the East China Sea was also re-evaluated.

# 2. Methods

## 2.1 Area of study

The Changjiang drainage basin is situated within 24°30′–35°45′N and 90°33′–122°25′E, draining almost one fifth of the total area of China. The major tributaries in this region include Yalongjiang, Minjiang, Tuojiang, Jialingjiang, Wujiang, Hanshui, Xiangjiang, Yuanjiang, and Ganjiang (Fig. 1). Xiangjiang and Yuanjiang join into the main channel via Lake Dongting and Ganjiang via Lake Poyang. Lake Poyang and Dongting are the two largest freshwater lakes in China [27].

Datong Hydrographic Station (DHS;  $117^{\circ}37^{\circ}E$ ,  $30^{\circ}46^{\circ}N$  as shown in Fig. 1), located 625 km inland from the river mouth on the mainstream, is free from tide influence. There is no major sewage discharge from the industrial and domestic sources nearby. DHS gauges the drainage area of  $1.71 \times 10^{6} \, \mathrm{km^2}$ , i.e., 95% of the Changjiang watersheds. Therefore, data from DHS have extensively been used to evaluate the variation of water quality of Changjiang and to calculate the seaward flux by the world river in the literatures.

### 2.2. Data source and calculation

DHS was established in 1935. In 1956, the Ministry of Water Resources of China (MWRC) started to systematically monitor the hydrological parameters and water quality along Changjiang, as well as other rivers in China [28]. Data were reported in the internal (unpublished) Hydrological Yearbooks. Monitoring data of water chemistry at DHS over the period 1962 – 1984 presented or used in this study was extracted from the unpublished Hydrological Yearbooks [29]. Data over the period 1985–2000 was officially provided by DHS since data compilation in hydrological yearbooks has been discontinued after 1985. All monitoring data were processed by month, while the annual values were obtained by discharge weighted chemical parameters.

According to station, water was sampled twice per month at DHS. Chemical analyses of the water samples were performed in the laboratory under the authority of the Changjiang Water Resource Commission and following the methods described by Alekin et al. in 1973 [30] and by the American Public Health Association in 1985 [31]. The MWRC also issued its own water quality analytical methods (SL78~94-1994). Specifically, raw water samples were siphoned to determine dissolve CO<sub>2</sub> concentration using base titration. This method is suitable for surface water analysis, and its standard deviation was reported as

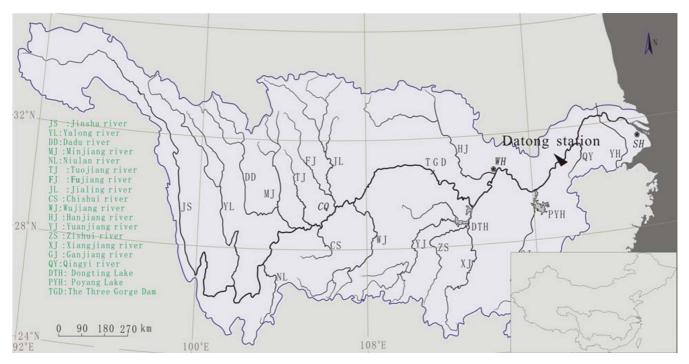


Figure I
The Changjiang drainage basin and its main tributaries.

0.105-9.81% when analyzing 17 different kind water samples with dissolved CO<sub>2</sub> concentration ranging from 2.73–2028 mg/L (SL80-1994). Dissolved water samples were decanted or filtrated through a 0.45- $\mu$ m membrane from the raw water samples, and analyzed for HCO<sub>3</sub>- (by acid titration, with a standard deviation of 0.71%), and SiO<sub>2</sub> (by the Hetropoly blue method, with a standard deviation of 1.01%) concentration.

Water samples were filtered through filter papers before 1987 and 0.45-µm filter membranes after 1987 prior to nitrate determination. The filtrates were measured using spectrophotometry with a phenol disulfonic acid before 1987 and UV spectrophotometry after 1987. The phenol method is suitable for measuring concentration ranging from 0.02–2.0 mg/L with a standard deviation of 6.7%, while the UV method is suitable for the concentrations from 0.08–4.0 mg/L with a standard deviation of 1.1%. Both methods are the current Chinese standard for nitrate determination. Therefore, the change of methods had a negligible impact on the accuracy of the data, as has been discussed in detail by Yan et al [21].

Generally, no detailed quality assurance/quality control information is available on historical monitoring data

from the annual hydrological reports. Chemical elements in Changjiang are measured at the mg/L scale and the analytical methods are routinely practiced in the national laboratories. Data reported in the yearbooks are therefore considered to be reliable. In fact, Chen et al. (2002) compared the data from another hydrological station on the Changjiang mainstream (Wuhanguan) with data monitored by GEMS/Water Program at the same station. It was found that two sets of data were in good agreement, indicating the reliability of data in the hydrological yearbooks. For detailed reliability analysis of the data in the hydrological yearbooks, see Chen et al., 2000, and Yan, et al., 2003 [21,27].

### 3. Results and Discussion

### 3.1 Hydrographic regime

Fig. 2 illustrates the seasonal variations of water discharge at DHS in the lower reach of Changjiang, where the maximum monthly water discharge occurs in July and the minimum occurs in January. The magnitude of variation (five folds difference) of water discharge in July and January draws attention to the substantial water input from precipitation in the summer flood season. In addition, as shown in Fig. 2, the annual average of water discharge and minimum discharge were relatively stable, with a slight

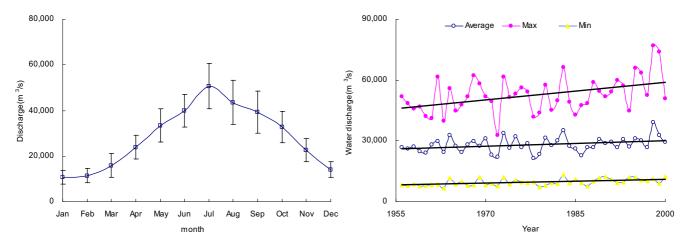


Figure 2 Hydrographic features of Changjiang at Datong. Left:Monthly variation in the water discharge of Changjiang at Datong (average for the period 1956–2000). Right: the annual variation, minimum and maximum water discharge of Changjiang at Datong (from 1956 to 2000). Fit equation for the trend analysis of annual water discharge:  $y = 87.773x - 145469 r^2 = 0.1029 p < 0.05$ .

increase of maximum discharge in the period 1956–2000. It indicates a steady hydrographic feature of Changjiang in the past decades.

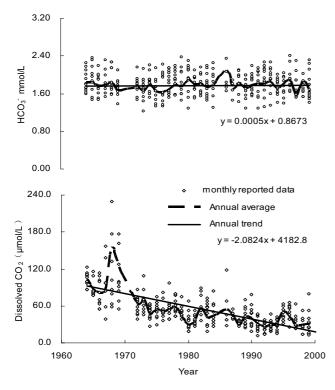


Figure 3
Temporal variations of HCO<sub>3</sub>- and dissolved CO<sub>2</sub> in Changiang at DHS (1960s – 2000).

# 3.2 Temporal trends of HCO<sub>3</sub>- and dissolved CO<sub>2</sub> in Changjiang

HCO<sub>3</sub> is mainly derived from the weathering reaction of carbonate and silicate minerals with atmospheric CO<sub>2</sub>, for which atmospheric contribution represents one half of the alkalinity in the case of carbonate weathering and all in the case of silicate weathering. Given the fact that carbonate rocks are well spread in the Changilang drainage basin, the major element composition of Changjiang and its tributaries is dominated by the HCO<sub>3</sub>- anion. On average, HCO<sub>3</sub>- accounts for 64% (in mg/L units) of the TDS [27]. From Fig. 3, it is clear that there was no clear temporal increase in the HCO<sub>3</sub>-concentrations over the period of 1960s-2000, whereas its inter-annual variation fluctuates between 1.2 and 2.4 mM, with an annual average of 1.7 mM. At the opposite of Changiang, it was reported that for the Mississippi (the largest river in North America), the export of alkalinity has dramatically increased during the past half-century [32]. The authors ascribed this increase to the change in land cover and heavier rainfall, which resulted in an increase in the rate of chemical weathering. Generally speaking, the rate of long-term chemical weathering involving CO2 is mainly correlated with precipitation, stream flow, and temperature [33]. With regard to Changjiang, however, such increase was not observed (Fig. 2, 3), indicating that chemical weathering rate in the Changjiang basin had been maintained a constant for the past decades.

To illustrate the seasonal variation, monthly change of the HCO<sub>3</sub>-concentrations in period of 1964–2000 are plotted in Fig. 4. It reveals that HCO<sub>3</sub>-concentrations was measured high in the winter, and low in April through May (Fig. 4a). Although the water discharge of Changjiang

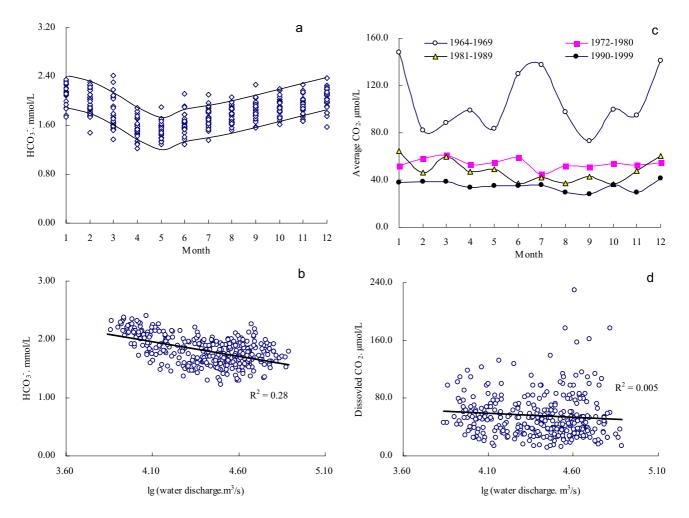


Figure 4
Seasonal variations of HCO<sub>3</sub>- and dissolved CO<sub>2</sub> in Changjiang at Datong and their relation with water discharge.

showed negative relationship with its  $HCO_3$ -concentration (Fig. 4d), it reached a maximum in July (Fig. 2). This means that dilution was compensated by the effect of increasing dissolution of carbonates as a result of an intensification of soil erosion and elevated  $pCO_2$  during flood season [27].

Data for the past decades (1964s–2000) shows that dissolved  $\rm CO_2$  concentration of Changjiang has declined dramatically with discharge weighted annual average being reduced from >100  $\mu$ M in the 1960s to nearly 30  $\mu$ M by the end of the 1990s (Fig. 3). A peak of dissolved  $\rm CO_2$  was observed around 1968. Compared with data after the 1970s, monthly concentrations average of dissolved  $\rm CO_2$  in the 1960s had a higher fluctuation (Fig. 4c). Collectively, water discharge had a less impact on changing the dissolved  $\rm CO_2$  concentration (Fig. 4d).

In general, dissolved  $CO_2$  in water will reach equilibrium with the atmosphere  $CO_2$ , as described by the Henry's Law [34]:

$$CO_2(g) + aq = H_2CO_3^*$$
 (1)

$$K_{H} = [H_{2}CO_{3}^{*}]/pCO_{2} (M \text{ atm}^{-1})$$
 (2)

Where, aq stands for the water phase;  $K_H$  is the Henrys Constant;  $pCO_2$  is the partial pressure of  $CO_2$ .

 ${\rm H_2CO_3}^*$  is mainly composed of [CO<sub>2</sub>] (*i.e.* dissolved CO<sub>2</sub>) in the natural water phase. In this study, we calculated  $p{\rm CO_2}$  in Changjiang based on dissolved CO<sub>2</sub> concentrations according to Equations (1, 2). Results showed that the  $p{\rm CO_2}$  in the Changjiang riverine system is significantly higher than that of the atmosphere (350 ppm), and it appeared a clear trend of reduction since the 1960s (Fig.

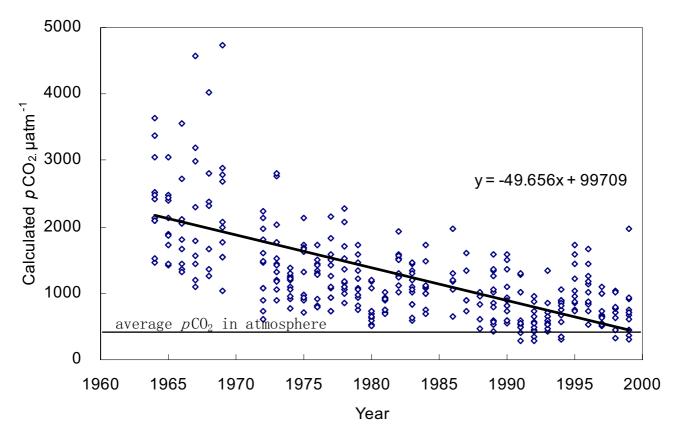


Figure 5 Distribution of  $pCO_2$  in Changjiang at Datong, calculated from dissolved  $CO_2$ .

5). In addition, few data in the 1990s have become comparable to the equilibrium concentration of atmospheric  $CO_2$  (Fig. 5). In fact, it is often the case that  $CO_2$  is oversaturated in rivers worldwide (Table 1). Compared with rivers listed in Table 1,  $pCO_2$  in Changjiang was 1297  $\pm$  901 ppm, lower than that of other large rivers like Amazon or the Mississippi.

 $\mathrm{CO}_2$  dissolved in river has sources mainly from the atmosphere  $\mathrm{CO}_2$ , respired  $\mathrm{CO}_2$  and dissolution of carbonate [15]. Because  $p\mathrm{CO}_2$  in Changjiang was clearly higher than that of the atmosphere, Changjiang should be a potential source for  $\mathrm{CO}_2$  emission to the atmosphere. The basin weathering (such as soil respiration, carbonate dissolution) generally provides a stable input of  $\mathrm{CO}_2$  to river water due to the constant chemical weathering rate. Consequently, in-channel respiration and photosynthesis, i.e. change in water quality, can be responsible for the decline of dissolved  $\mathrm{CO}_2$  in Changjiang.

# 3.3 Decline of dissolved $CO_2$ and change of water quality in Changiang

It is generally accepted that CO<sub>2</sub> exchange between rivers and atmosphere is an important but still uncertain factor

in the global carbon cycle [5,6]. Recent studies estimated that, nearly 0.5 Gt C.yr<sup>-1</sup> escapes into the atmosphere from the Amazon basin through air-water  $CO_2$  exchange, almost an order of magnitude higher than the organic carbon flux from Amazon to the ocean [13]. Since rivers in the world are generally  $CO_2$  over-saturated (Table 1), the gross emission of  $CO_2$  from rivers into the atmosphere can be substantial, and it can balance off some important terrestrial carbon sink [35]. On the contrary, the emission flux of  $CO_2$  from Changjiang had remarkably decreased due to the downtrend of dissolved  $CO_2$  concentration since the 1960s (Fig. 5). This can greatly affect the estimation of overall  $CO_2$  exchange flux between Changjiang and the atmosphere, even at the global scale.

### 3.3.1 Historical change of water quality in Changjiang

In the aquatic ecosystems, two primary biological processes influence  $pCO_2$ . They are  $CO_2$  fixation by photosynthesis and  $CO_2$ emission by respiration [36]. Organic carbon (OC) from the terrestrial ecosystem generally has a steady composition and fixed sources and it is an important carbon source for the aquatic biological processes. This organic carbon, including POC and DOC, usually is of higher proportion in riverine total organic carbon

Table 1: CO<sub>2</sub> partial pressure in large rivers in the world

| River                                | –<br>Country        | pCO <sub>2</sub> μatm |      |            |
|--------------------------------------|---------------------|-----------------------|------|------------|
|                                      |                     | Mean                  | s.d. | Reference  |
| Central Amazon                       | Brazil              | 4350                  | 1900 | 13         |
| Colorado                             | USA                 | 4295                  | 195  | 9 #        |
| Columbia                             | Canada              | 1123                  | 1175 | 9 *        |
| Elbe                                 | Germany             | 4095                  | 1758 | 9 *        |
| Hudson River Estuary                 | USA                 | 1125                  | 403  | 6          |
| Humber                               | U.K                 | 1500-6000             | -    | 12         |
| Illinois                             | USA                 | 4419                  | 240  | 9 #        |
| Lagan River                          | N. Ireland          | 2722                  | 1457 | 55         |
| Main channel of Upper<br>St.Lawrence | Canada              | 381                   | 93   | 8          |
| Mississippi                          | USA                 | 4593                  | 183  | 9 #        |
| Parana                               | Brazil              | 3139                  | 3240 | 56         |
| Rhone                                | France              | 2015                  | 944  | 9*         |
| Scheldt estuary                      | Belgium/Netherlands | 5700-9500             | -    | 2          |
| Seine                                | France              | 1982                  | 780  | 9 *        |
| St.Lawrence                          | Canada              | 1300                  | -    | П          |
| Upper Jordan                         | Jordan              | 2461                  | 608  | 57         |
| Weser                                | Germany             | 4395                  | 2966 | 9 *        |
| Meech Lake                           | Canada              | 6929                  | 8405 | 26         |
| Changjiang                           | China               | 1297                  | 901  | This study |

<sup>#:</sup> Originally from Alt, 1993;

(TOC) [9,37]. However, the anthropogenic activities in the past decades have changed the Changjiang river system. Dam constructions and hydrological regulations were among the most typical activities [38-44]. In addition, the riverine nutrient loads in Changjiang have been greatly increased by the industrial and agricultural activities [45,21]. As a result, the river's pristine status in hydrological condition, nutrients structure and aquatic ecosystem has been shifted to "lacustrine/reservoir" autotrophic type prevailing with planktons [46].

Phytoplankton such as diatoms assimilates dissolved  $CO_2$  and nutrient elements (e.g. N, P, Si) to synthesize organic components, according to the Redfield Ratio(C:Si:N = 106:16:16) [47,48]. For instance, seriously polluted River Zenne has a lower super-saturation degree of dissolved

CO<sub>2</sub> than unpolluted rivers [2]. With regard to Changiang, sustaining increase in nutrients concentrations (particularly nitrate) was reported after the 1960s [23]. Increasing in nutrient load stimulates the aquatic photosynthesis. Signatures of C/N and their isotopes composition in the suspend matter also show complex features from both the terrestrial and aquatic ecosystems [49]. Fig. 5 illustrates that the partial pressure of CO<sub>2</sub> in Changjiang was significantly higher than the atmospheric pCO<sub>2</sub>, indicating that carbon source for aquatic photosynthesis was mainly originated from river DIC, not from the atmosphere. During photosynthesis, nutrients are assimilated by phytoplankton (e.g. diatoms). Because dissolve silica is derived exclusively from the weathering of silicate in the drainage basin, its concentration (expressed as SiO<sub>2</sub>, data after 1984 are not available) reveals a clear drop

Table 2: D/z ratio in world rivers

|                    | D/z (cm/h) | Reference |  |
|--------------------|------------|-----------|--|
| Rhône              | 15         | 53        |  |
| Saône              | 8–15       | 53        |  |
| Amazon mainstream  | 10         | 13        |  |
| Amazon tributaries | 5          | 13        |  |
| St Lawrence        | 15         | 58        |  |
| Ottawa             | 4          | 15        |  |
| Hudson             | 4.1        | 6         |  |
| Changjiang         | 8          |           |  |

<sup>\*:</sup> Originally from Kempe, 1982;

<sup>-:</sup> Not available.

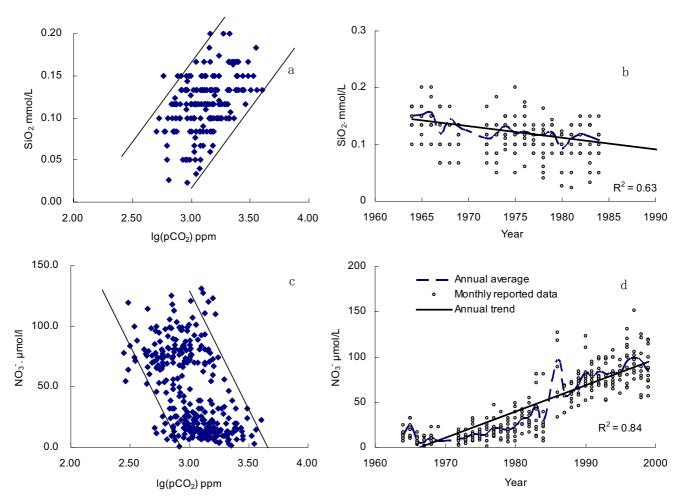


Figure 6 Temporal variation of dissolved  $SiO_2$  and  $NO_3$ -concentrations in Changjiang at Datong, and their relations with  $log(pCO_2)$ .

in the 1960s-1980s and shows a positive correlation to  $log(pCO_2)$  (Fig. 6a,b). However, a dramatic increase of nitrate concentration was observed in the same period, particularly after 1984, with a negative correlation to  $log(pCO_2)$  (Fig. 6c,d). This was because that nitrate in Changjiang had long being compensated by the anthropogenic inputs like fertilizers application, similar to rivers around the world [45,50]. In addition to the plentiful nutrient elements introduced by the agricultural activities [21], river damming in the drainage basin also boosted

river eutrophication by reducing hydrodynamic condition. More than 40,000 reservoirs had been constructed in the Changjiang basin by 2000, of which over 1100 reservoirs have storage capacities greater than  $0.1 \times 10^9$  m<sup>3</sup>. The ecosystems in many reservoirs were facing with the burden of eutrophication [51]. Thus, increasing aquatic photosynthesis will improve the primary productivity, and reduce the dissolved  $CO_2$  level. In general, the fate of newly formed organic matter in rivers can be (1) buried in lakes and reservoirs as sediments [52]; (2) decomposed in

Table 3: Historical variation of  ${\rm CO_2}$  emission flux and DIC fluvial flux in Changjiang

|  | 1960s | 1970s | 1980s | 1990s |
|--|-------|-------|-------|-------|
| Fex mol.m-2.yr-1   | -54.4 | -29.7 | -21.6 | -14.2 |
| CO <sub>2</sub> degassed from the<br>Changjiang basin. Mt C.yr <sup>-1</sup> | 58.8  | 32.1  | 23.3  | 15.3  |
| DIC flux. Mt C.yr-   | 20.6  | 17.6  | 20.4  | 20.3  |

<sup>-:</sup> means  $CO_2$  is transferred from river into the atmosphere. **Fex**:  $CO_2$  flux by evasion into the atmosphere from river

water column; (3) exported into ocean as POC and DOC. Part of the organic matter will be decomposed in estuary, causing the estuarine emission of  $CO_2[2,7]$ .

### 3.3.2 Temporal trend of CO<sub>2</sub> diffusion flux

The diffusion flux of CO<sub>2</sub> can be calculated with the following equation:

$$F_{ex} = \frac{D}{z}(c_{eq} - c) \tag{3}$$

Where,  $F_{ex}$  is the diffusion flux of CO<sub>2</sub> between river water and the atmosphere; D represents the diffusion coefficient of CO<sub>2</sub> in the river; z is the thickness of boundary layer;  $C_{eq}$  in  $\mu$ mol/L is the dissolved CO<sub>2</sub> concentration in equilibrium with the atmosphere; and C in  $\mu$ mol/L stands for the measured dissolved CO<sub>2</sub> concentration in the water.

Exchanging rate D/z of  $CO_2$  at the water-air interface, can be affected by different factors such as river runoff, turbidity, velocity of flow, wind speed and water depth [2]. It is required to make the estimation of D/z a priority, in order to calculate the diffusion flux of  $CO_2$  in a given system. D/z varies from 115 cm/h in a turbulent flow, to 8 cm/h in the rivers without agitation [53]. D/z estimates by other researchers are listed in Table 2. Based on the comparison of hydrographic features between Changjiang and world rivers, a D/z estimate of 8 cm/h was used for the calculation of  $CO_2$  diffusion flux from Changjiang.

Calculation results showed that Changjiang had been degassing CO<sub>2</sub> into the atmosphere in a declining behavior in the past decades (Table 3). In the 1990s, the diffusing flux of CO<sub>2</sub> was around 14.2 mol.m<sup>-2</sup>.yr<sup>-1</sup>, similar to that of River Ottawa [15], slightly higher than that of Hudson  $(5.8-13.5 \text{ mol.m}^{-2}.\text{yr}^{-1})[6]$ , and Amazon  $(10 \pm 2.5 \text{ mol.m}^{-2}.\text{yr}^{-1})[6]$ mol.m<sup>-2</sup>.yr<sup>-1</sup>) [13]. The CO<sub>2</sub> degassed from the Amazon basin was estimated almost 13 folds of its fluvial TOC flux (36 Tg C.yr<sup>-1</sup>) or DIC flux (36 Tg C.yr<sup>-1</sup>). Water surface area of the entire Changjiang basin is reported as 9.3 × 106 ha, or  $8.7 \times 10^4$  km<sup>2</sup>. Others reported that it is about 4% of the entire drainage area of the river [54]. In this study, water surface area of 90,000 km<sup>2</sup> of the Changjiang drainage basin was taken as an approximate for the flux calculation. Extrapolating across the entire basin, the degassing flux of CO<sub>2</sub> from Changjiang in the 1990s, was calculated as 15.3 Mt C.yr-1, about 5 Mt C.yr-1 less than the DIC flux of Changjiang, much less than that of Amazon (0.5 Gt C.yr 1). However, this flux of Changjiang in the 1960s was calculated up to 58.8 Mt C.yr-1 (Table 3).

### 4 Conclusion

Our calculation of  $CO_2$  emission from Changjiang revealed an important pathway for carbon transport from the river to atmosphere. The  $CO_2$  emission from

Changjiang was estimated around 15.3 Mt C.yr<sup>-1</sup> in the 1990s, despite that dissolved  $\rm CO_2$  was less than 5% in DIC. Although  $\rm CO_2$  degassed from Changjiang had sharply declined by 75% within the past several decades based on our temporal data analyses, it should still be considered as an important source of  $\rm CO_2$  emission at present.

On the other hand, the nutrient load in Changjiang increased significantly during the past several decades owing to the industrial and agricultural activities and the construction of thousands of reservoirs in the river basin. Consequently, dissolved CO<sub>2</sub> concentration in the water column had decreased gradually corresponding to changes in the trophic levels of Changjiang over the period of 1960s–2000. As many large rivers around the world are currently facing the increasing anthropogenic impacts similar to Changjiang, re-evaluation of CO<sub>2</sub> flux between rivers and the atmosphere has become an increasingly important issue in the study of global climate change.

### **Authors' contributions**

FSW drafted the manuscript, participated in the data calculation and conceived of this study. YCW participated in the data collection. JZ participated in its design and discussion. HX carried out part of the data calculation. XGW helped in the data collection and analysis. All authors have approved this final manuscript.

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