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## Influences of anthropogenic activities on dissolved silica migration in a granite-hosted basin, Hainan Island, China

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### ABSTRACT

The continent–ocean transfer of dissolved silica (DSi, formed as SiO<sub>2</sub>) via rivers constitutes an important part of the global silica cycle. The uptake of terrestrial vegetation and riverine phytoplankton are the key process controlling DSi migration within the drainage basin. Anthropogenic activities (including land use change and damming) have been altering DSi export by changing biological uptakes in the basin. A significant artificial lake effect of damming was exhibited on the spatial variations of chlorophyll-a (Chl.a) and DSi, which caused 15.39% of riverine DSi to be detained in the reservoir region of Changhuajiang River basin, Hainan Island, China. The biological uptake of terrestrial vegetation was behindhand responsible for seasonal fluctuations of DSi. The DSi uptake yields ranged from 19.44 t/km<sup>2</sup>/yr to 86.76 t/km<sup>2</sup>/yr during the different terrestrial vegetation types in the basin, in turn, tropical rainforest > crops > artificial economic forests > grassland. The try calculating of the DSi yield released by the silicates weathering was carried out taking biological processes in the basin into account. Taking into the plants uptake within the basin consideration, the corrected DSi yield from the silicates weathering was 18.6 t/km<sup>2</sup>/yr. Accordingly, the silicates weathering rate was up to 41.55 t/km<sup>2</sup>/yr, which was 1.36 times higher than that (30.39 t/km<sup>2</sup>/yr) without consideration of the biological uptake, and close to the fastest weathering rate of the granite basin (Puerto Rico) in the earth surface. Of the DSi released by the silicates weathering, 28.56% was absorbed by terrestrial vegetation, and 31.43% was consumed by riverine phytoplankton, and the rest was drained into the South China Sea.

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### 1. Introduction

Silicon, the second-most-abundant (28.8%) element on the earth (Hans, 1995), exists mostly with the form of H<sub>2</sub>SiO<sub>4</sub> in natural water, which is also called as dissolved silica (DSi). DSi is one of the major nutrients of terrestrial vegetation and aquatic phytoplankton (Epstein, 1994, 1999; Datnoff et al., 2001) and essential to the growth of the oceanic diatoms. Oceanic phytoplankton photosynthesis is an important carbon sink mechanism consuming 24% of CO<sub>2</sub> released by burning fossil fuel and changing land use, which almost equals to the uptake amount of terrestrial vegetation

(<http://co2now.org/>). Meanwhile, about 240 × 10<sup>12</sup> mol DSi is transformed into biogenic silica (BSi) in the course of photosynthesis (Tréguer et al., 1995). The sustained and stable transport DSi into marine ecosystem is essential for the oceanic biological pump process regulating the atmospheric CO<sub>2</sub> concentrations and the global climate (Berner et al., 1983; Meybeck, 1987; Raymo and Ruddiman, 1992; Dupré et al., 2003; Huh, 2003; Liu et al., 2011; Recasens, 2012; Brovkin, 2012). The global rivers, linking the marine ecosystems with terrestrial ecosystems, have played an important role to transport the terrestrial matter into the marine environments (Meybeck, 1982; Richey et al., 1990). Comparing with other external sources of silica (aeolian, submarine groundwater and deep-sea hydrotherm) in the marine ecosystem, the global rivers contribute 62% of total silica, 85% of which is formed with DSi (Tréguer and De La Rocha, 2013).

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Increasing rapidly population in the world, forecasted up to two hundred million in 2100 (Lal, 2010), alter profoundly the earth surface environment. At present, changing land use and damming are the main human activities affecting the basin DSi export. It is reported that about  $60\text{--}200 \times 10^{12}$  mol DSi is annually absorbed by the global terrestrial plants (Conley, 2002), which is merely diverse from the oceanic BSi storage in the same order of magnitude. Hence, the conversion of terrestrial vegetation type could affect the basin DSi export flux owing to the altered plants absorption (Conley, 2002; Fulweiler and Nixon, 2005; Struyf and Conley, 2012; Chen et al., 2014). For example, the DSi export flux negatively correlated with the vegetation coverage in the basin, and the seasonal difference of the plants absorption could result in the 40% fluctuation of DSi fluxes (Carey and Fulweiler, 2012). At initial forest degenerate, the DSi fluxes significantly increase. Subsequently, the DSi fluxes are closely related to the subsequent land use pattern: e.g., the DSi fluxes could be increased with increasing hardened land from urbanization; the DSi fluxes could be decreased from natural recovery in the basin; the DSi fluxes tend to be lower from farming than those in the natural recovery area (Carey and Fulweiler, 2012). Since 3000 B.C., the emergence of agricultural activities has caused the content of amorphous silicon (ASi) to reduce by 10% in the global soils. However, the total silica flux exported from terrestrial ecosystem to aquatic ecosystem annually increased  $1.1 \pm 0.8 \times 10^{12}$  mol since 1700 B.C. (Clymans et al., 2011), which accounted for 20% of the DSi export flux of the global rivers. The reason may be that urbanization and water loss and soil erosion appeared on the earth's surface.

During the growth of aquatic phytoplankton, DSi is largely absorbed and transformed into BSi buried at the bottom of riverbed (Gao et al., 2013; Zhu et al., 2013; Jung et al., 2014). When aquatic phytoplankton flourish, the BSi content could get up to 50%–70% of the total of DSi and BSi, conversely, merely 10%–20% of the total of DSi and BSi in the depression period (Conley, 1997), and the difference of BSi content between phytoplankton flourish period and depression period reached up to 40% (Admiraal et al., 1990; Conley, 1997). With the intensification of water body eutrophication (Schelske et al., 1983; Conley et al., 1993; Sun et al., 2013) and construction of dams in the rivers (Gao et al., 2013; Varol et al., 2013; Zhu et al., 2013; Jung et al., 2014), the global aquatic diatoms explosively bloom, which leads to the decrease of riverine DSi concentrations and exported fluxes. Due to damming, the DSi concentrations of Vistula River and Daugava River in Europe reduced by 15%–50% (Humborg et al., 2006), and the 41% of DSi was resident in Masinga Reservoir (Hughes et al., 2012), and Three Gorges Dam detained the 44% of BSi (Ran et al., 2013a,b). Generally, the above phenomena were called as “artificial lake effect” (Humborg et al., 2000; Harrison et al., 2012). Over the past 100 years, the “artificial lake effect” caused the input flux of DSi into the Baltic Sea and Black Sea to reduce by 30%–40% (Humborg et al., 2008) and 66.7% (Humborg et al., 1997), respectively.

Clearly, anthropogenic activities significantly altered the DSi cycle in the basin. However, there is fewer report on coupled DSi source, migration and its major controlling factors. In this study, the Changhuajiang River (CHJR) basin, located at the mid-west of the Hainan Island, China, was selected to address the influence of terrestrial vegetation variation and damming on DSi dynamics in the basin. Furthermore, the try calculating of the DSi yield released by the silicates weathering was carried out taking biological processes in the basin into account.

## 2. Study area

The CHJR, originating from the Wuzhi Mountain located in the central of Hainan Island, China, and flows to southwest and turns to northwest in the Ledong County (Fig. 1), and drains into the South

China Sea at Changcheng County (Fig. 1). It has 232 km length with the average slope of 13.9‰ and drains 5150 km<sup>2</sup> of the total area. The climate is of the tropical monsoon climate and is obviously divided into the wet season (from May to October) and dry season (from November to April of the second year). The CHJR discharged  $22.3 \times 10^8$  m<sup>3</sup> water into the South China Sea in 2014 (at the Baoqiao hydrologic station, representing 90% of the total basin area), accounting for 53.48% of average discharge ( $41.7 \times 10^8$  m<sup>3</sup>) over years, of which,  $18.7 \times 10^8$  m<sup>3</sup> was exported in the wet season and  $3.6 \times 10^8$  m<sup>3</sup> in the dry season. The Indosinian and Variscan granites including biotite-monzonite granite, granodiorite, quartz-diorite and granite-porphry are widely exposed, which represent 66.84% of total area. The basin is mainly covered with Acrisols containing Ferric Acrisols, Gleyic Acrisols and Humic Acrisol, etc. Tropical monsoon forests are predominant in the basin. Artificial economic forests (eucalyptus, rubber and mango) are largely planted in the middle and lower reach. Banana and cane are main crops. Two large-scale reservoirs, Daguangba (DGB) Reservoir ( $17.1 \times 10^8$  m<sup>3</sup> of the total capacity) and Shilu (SL) Reservoir ( $1.41 \times 10^8$  m<sup>3</sup> of the total capacity), situated at the main stream and Shilu River tributary, control the drainage area of 3498 km<sup>2</sup> and 353.63 km<sup>2</sup>, respectively.

## 3. Sampling and methods

66 water samples were collected and positioned from the river mouth to the headwater in January and August of 2014, respectively (Fig. 1), of which, the samples of 7#, 8#, 9# and 12# were distributed in SL Reservoir, and the samples of 26#, 28#–34# and 36# were collected in DGB Reservoir. Water samples were filtered through 0.7 μm-porosity Whatman GF/F filters for measuring DSi and dissolved organic carbon (DOC). Samples were kept in the refrigerator at 4 °C before analysis, and all the analytical works were completed within 1 week. Concentrations of DSi were measured by inductively coupled plasma atomic emission spectrometry (ICP 6500 Duo) model IRIS Advantage (Thermo Jarrell Ash Corporation, USA). Analytical results were better than 0.5%. Concentrations of DOC were measured by TOC-VCPH analyzer, Shimadzu Co., Japan under the precision of 0.01 mg/L. The concentrations of chlorophyll-a (Chl-a) were determined by Hydrolab DS5, Hach Co., America (precision  $\pm 0.01$  μg/L) in situ.

The normalized differential vegetation index (NDVI) is a remote sensing index reflecting plants growth, which is defined as the ratio of the reflectivity difference and sum between the near infrared channel and the visible light channel (Equation (1)). The NDVI data used in this paper was obtained through moderate-resolution imaging spectroradiometer (MODIS) under the 250 M spatial resolution in China (<http://www.gscloud.cn/>).

$$NDVI = \frac{TM_4 - TM_3}{TM_4 + TM_3 + 0.0000001} \quad (1)$$

TM<sub>3</sub> and TM<sub>4</sub> are respectively the near infrared and the visible light channels.

All data were analysed by SPSS 18.0.

## 4. Results

The DSi concentrations range from 179.14 μmol/L to 675.00 μmol/L with an average of 376.39 μmol/L, which is 2 times higher than the average (158 μmol/L) of the global river (Dürr et al., 2011) and higher than the global granite areas (Fig. 2). The concentrations of cations (Ca<sup>2+</sup>, Mg<sup>2+</sup>, K<sup>+</sup> and Na<sup>+</sup>) in the CHJR water are higher comparing with the other rivers in the global granite areas (Fig. 2), implying that the basin is characterized by rapid chemical weathering rate (Appendix Table 1).

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