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Q3 Export of dissolved carbonaceous and nitrogenous substances 2 in rivers of the “Water Tower of Asia”

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A B S T R A C T

Rivers are critical links in the carbon and nitrogen cycle in aquatic, terrestrial, and 21 atmospheric environments. Here riverine carbon and nitrogen exports in nine large rivers 22 on the Tibetan Plateau — the “Water Tower of Asia” — were investigated in the monsoon 23 season from 2013 to 2015. Compared with the world average, concentrations of dissolved 24 inorganic carbon (DIC, 30.7 mg/L) were high in river basins of the plateau due to extensive 25 topographic relief and intensive water erosion. Low concentrations of dissolved organic 26 carbon (DOC, 1.16 mg/L) were likely due to the low temperature and unproductive 27 land vegetation environments. Average concentrations of riverine DIN (0.32 mg/L) and 28 DON (0.35 mg/L) on the Tibetan Plateau were close to the world average. However, despite 29 its predominantly pristine environment, discharge from agricultural activities and urban 30 areas of the plateau has raised riverine N export. In addition, DOC/DON ratio (C/N, ~6.5) in 31 rivers of the Tibetan Plateau was much lower than the global average, indicating that 32 dissolved organic carbon in the rivers of this region might be more bioavailable. Therefore, 33 along with global warming and anthropogenic activities, increasing export of bioavailable 34 riverine carbon and nitrogen from rivers of the Tibetan Plateau can be expected in the 35 future, which will possibly influence the regional carbon and nitrogen cycle. 36

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46 Introduction

47 As the “Water Tower of Asia,” the Tibetan Plateau feeds quite 48 a few large rivers (e.g., the Yangtze River, the Yellow River, the 49 Brahmaputra, the Mekong) in Asia (Immerzeel et al., 2010). 50 There are more than 100 catchments with a drainage 51 area > 2000 km² on the plateau, among which twenty have

52 drainage areas larger than 10,000 km² (MWR, 2015). The 53 outflow area of the rivers on the Tibetan Plateau is 54 1.2 × 10⁶ km², accounting for more than half of the entire 55 land surface of the plateau (Cao et al., 2006). The Tibetan 56 Plateau is also referred to as the “Third Pole” of the earth due 57 to its extensive glacial and snow area (~100,000 km²) covering 58 the vast high-altitude region (Wang et al., 2000; Yao et al., 59 60 61 62

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2012). Snow and glacial melt water are important sources of rivers on the plateau, making up a contribution of 8%–27% to the regional river water flow (Lutz et al., 2014). Precipitation is another essential source for the Tibetan rivers. It was estimated that over 50% of total water flowing on the plateau was from local precipitation (Lutz et al., 2014). With global warming, the climate-sensitive glaciers on the Tibetan Plateau have shrunk ~10% during the years of 1970 to 2000 (Kang et al., 2010; Zhang et al., 2012a). In addition, the melting of glaciers can promote evapotranspiration and positively affect local precipitation (Du and Ma, 2004). Therefore, with the increasing glacier melt and precipitation, more runoff from rivers on the Tibetan Plateau can be expected in the future (Zhang et al., 2012b).

Considering the hydrologic and geochemical processes related to the outflows of the rivers, there could be some amount of carbon (C) and nitrogen (N) loss from the land surface of the Tibetan Plateau. Currently, most of the studies on the rivers of the Tibetan Plateau are related to water circulation and water quality, in consideration of its major role as a water resource for millions of people in both local and surrounding areas (Huang et al., 2009; Immerzeel et al., 2010; Li et al., 2011; Qu et al., 2015). However, data on the dissolved carbon and nitrogen substances in rivers of the Tibetan Plateau are still limited, despite their potential interactions with the regional carbon and nitrogen cycle in this area (Tong et al., 2016; Yang et al., 2014). Dissolved carbon (dissolved inorganic/organic carbon, DIC/DOC) and nitrogen (dissolved inorganic/organic nitrogen, DIN/DON) in rivers are critical components to the carbon and nitrogen cycle at both regional and global scales (IPCC, 2013). It has been proposed that concentrations of dissolved carbon and nitrogen in the global river systems have experienced a significant change due to human activity and global warming during the past hundred years (Evans et al., 2005; Howarth et al., 1996; Sillanpää, 2014; Valinia et al., 2015). Since the last century, the hydrologic processes on the Tibetan Plateau have been affected greatly by climate change (Immerzeel et al., 2010; Wang et al., 2013). Also, with increasing agricultural and industrial activities on the plateau, the local nitrogen cycles have been substantially altered in the preceding decades (Tong et al., 2016). Here we present the dissolved carbon and nitrogen concentrations from ten watersheds on the Tibetan Plateau, and the potential impact factors for the riverine carbon and nitrogen cycles in this ecologically fragile region are also discussed.

1. Materials and methods

1.1. Field sampling

Water samples from 29 sites in nine large rivers on the Tibetan Plateau were collected during the monsoon season (July and August) from 2013 to 2015 (Fig. 1). The sampling work was conducted in three water systems: (1) In the Indian Ocean water system (IOWS), samples were collected in the Yarlung Tsangpo, Nu Jiang and Shiquan He, which are the upper reaches of the Brahmaputra River, the Salween River and the Indus, respectively. (2) In the Pacific Ocean water system

(POWS), the sampling sites are situated in the headwaters of the Yangtze River, the Yellow River and the Lantsang River (the upstream of the Mekong River). (3) In the Inland river watershed (IRW), we selected the rivers of Hei He, Shule He and the Buha River running on the north and central Tibetan Plateau. A total of 58 samples were collected from these rivers in this work. The hydrological and climatic conditions of the rivers are listed in Table 1. In general, the rivers of the IOWS and POWS are larger than those of the IRW due to the former two water systems being located in the eastern and southern part of the Tibetan Plateau, where they are prominently influenced by the India/South Asia monsoon and receive abundant precipitation in the summer, while rivers in the IRW running in the central and north part are mainly controlled by the westerlies and usually receive little precipitation year-round (Yang et al., 2014). All these rivers run across the plateau and cover a large area with variable meteorological characteristics, landscape and vegetation covers (Fig. 1) (MWR, 2015).

Sample handling and preservation were conducted according to standard guidelines (Raymond and Bauer, 2001). Two parallel samples were collected against the water flow direction at 10 cm depth below the surface at each sampling site, and the water was filtered with 0.7 μm glass fiber filters in the field. Samples for DIC measurement were stored at room temperature in 500-mL gas-tight brown glass bottles and preserved with 100 μL HgCl_2 to avoid degradation due to light and biological activity (Raymond et al., 2004; Seitzinger and Sanders, 1997). Samples for DOC and dissolved nitrogen were preserved in 500-mL acid-cleaned polypropylene bottles and stored in containers at -18°C until analysis (Raymond et al., 2004; Seitzinger and Sanders, 1997). Concentrations of DIN (NO_3^- , NH_4^+ and NO_2^-) in the water samples were detected by HPLC (Dionex ICS 2000 and Dionex ICS 2500) (Lee et al., 2014). The limits of detection (LOD) for NO_3^- , NH_4^+ and NO_2^- were 1.5, 0.5 and 0.2 mg/L, respectively. DIC (comprising HCO_3^- , CO_3^{2-} and CO_2), DOC, and total nitrogen (TN, comprising DIN and DON) were measured with a TOC analyzer (SHIMADZU-TOC-VCPH). The LOD for the dissolved carbon (DIC and DOC) and TN were 4 $\mu\text{g-C/L}$ and 5 $\mu\text{g-N/L}$, respectively.

1.2. Data preparation

Different climates usually lead to different vegetation coverage. For instance, due to lower precipitation (Table 1), the land vegetation cover rate in IRW is not as high as that of the IOWS and POWS (Fig. 1, Table 3), and the vegetation compositions in the three water systems also differ from each other due to the diverse climatic conditions. Although the land cover conditions differ in the river basins of the Tibetan Plateau, it can be observed that more than 80% of the entire drainage area was covered by meadows, steppes, alpine vegetation, and scrub (Fig. 1). Thus, we chose these four land vegetation cover types as the parameters for natural vegetation conditions to study their effects on the riverine C and N. In addition, the cultivated vegetation cover rate was also used as the index of anthropogenic activities since they were important factors affecting carbon and nitrogen characteristics in river areas (Meybeck, 1982).

Drainage area data was from the HydroSHEDS (Lehner et al., 2008) and land vegetation data were adopted from Vegetation Atlas of China (Hou, 2001). The index of land cover type in the

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