



## Research article

## Human perturbation increases the fluxes of dissolved molybdenum from land to ocean — The case of the Jiulong River in China

Deli Wang<sup>a,\*</sup>, Shuimiao Lu<sup>a</sup>, Nengwang Chen<sup>a,b</sup>, Minhan Dai<sup>a</sup>, Céline Guéguen<sup>c</sup><sup>a</sup> State Key Laboratory of Marine Environmental Science, Xiamen University, Xiamen 361102, China<sup>b</sup> Fujian Provincial Key Laboratory for Coastal Ecology and Environmental Studies, College of the Environment and Ecology, Xiamen University, Xiamen 361102, China<sup>c</sup> Department of Chemistry, Trent University, ON, K9J 7B8 Canada

## ARTICLE INFO

## Article history:

Received 8 June 2017

Received in revised form

20 December 2017

Accepted 28 December 2017

## Keywords:

Trace elements

Dissolved molybdenum

Riverine fluxes

Weathering

Human perturbation

## ABSTRACT

Rivers contribute a substantial amount of trace metals including molybdenum (Mo) into the oceans. The driving forces controlling the riverine fluxes of dissolved metals still remain not fully understood. Our study then investigated the spatial variations of dissolved metals including molybdenum in a typically human perturbed river, the Jiulong River (JR), China. The aim of the study is to elucidate the relevance of anthropogenic perturbation on the fluxes of dissolved metals such as molybdenum from land to ocean. Our study shows a large spatial variability of dissolved Mo across tributary to main stream of the JR. Particularly, dissolved Mo was generally low (average:  $5 \pm 1$  nM) in the “pristine” JR headwaters, and elevated ( $19 \pm 6$  nM) along the lower river continuum. Sporadically high levels of dissolved Mo occurred in the upper North River ( $77 \pm 19$  nM), as a result of mining activities locally. Significant correlations of dissolved Mo with total dissolved solids (TDS) and dissolved strontium (Sr) were observed in the whole JR ( $\text{Mo} = 1.4 * \text{TDS} - 1.7$ ,  $R^2 = 0.86$ ,  $p < .01$ ;  $\text{Mo} = 1.2 * \text{Sr} - 2.2$ ,  $R^2 = 0.70$ ,  $p < .01$ , logarithmic scales). This indicates that dissolved Mo is mobilized mainly along with other major ions such as Sr during similar mineral dissolution processes. From the “pristine” headwaters to the mouth of the JR, riverine Mo fluxes at the mouth of the JR has elevated by at least 3 times due to human perturbation. Compiled historic data regarding metal fluxes from world rivers further confirmed that small and medium rivers are relatively more sensitive to human perturbation.

© 2017 Elsevier Ltd. All rights reserved.

## 1. Introduction

Rivers in land discharge a substantial amount of dissolved metals such as molybdenum (Mo) into the ocean, determine the global budgets of these elements and even influence biological activities in the ocean (Dagg et al., 2004; Harris, 2001; Howarth et al., 2011; Turner et al., 2003). Dissolved elements in rivers originate from bedrocks, and experience physical and chemical weathering, and erosion (e.g., Roy et al., 1999; Martin and Whitfield, 1983; Turekian and Scott, 1967). Once arriving into rivers, these elements are further subject to a series of geochemical processes including precipitation/dissolution, and adsorption/desorption (e.g., Reddy et al., 1997; Dalai et al., 2005; Ghoveisi et al., 2013,

2014). In addition, human activities such as consumption of fossil fuels, land mining, smelting of ore, and agricultural practices potentially impact the loadings of these elements from land into rivers (Kabata-Pendias, 2010), and influence the elemental composition in natural waters (Woodward and Foster, 1997; Oldfield and Dearing, 2003). Besides impacting river water quality directly, through exports of dissolved elements (mostly nutrients) in runoff, human disturbances such as agricultural practices are reported to interfere with geochemical processes that produce an impact on catchment water quality (Pacheco and Szocs, 2006; Pacheco et al., 2013). Consequently, dissolved constituents could be largely variable in rivers. For example, dissolved Mo in world rivers averaged with the concentration of  $\sim 8$  nM, and ranged from a few tenth nmol to as high as 100 nmol/l (e.g., Miller et al., 2011).

The element Mo is one of bio-essential elements, and mainly exists as in dissolved oxyanions including  $\text{MoO}_4^{2-}$  and  $\text{HMoO}_4^-$  in oxygenated rivers (Wang, 2012; Wang et al., 2016). Dissolved Mo originates from weathering of Mo containing minerals including

\* Corresponding author. State Key Laboratory of Marine Environmental Science, Xian'an South Rd., Xiamen, 361102, China.

E-mail address: [deliwang@xmu.edu.cn](mailto:deliwang@xmu.edu.cn) (D. Wang).

molybdenite ( $\text{MoS}_2$ ), powellite ( $\text{CaMoO}_4$ ), ferrimolybdenite [ $\text{Fe}_2(\text{MoO}_4)_3$ ], wulfenite ( $\text{PbMoO}_4$ ), and ilsemanite ( $\text{Mo}_3\text{O}_8$ ) (Lyalikova and Lebedeva, 1984). Once in rivers, dissolved Mo also experiences a series of geochemical reactions such as dissolution/precipitation, desorption from/adsorption onto particles including organic materials, manganese (Mn) oxides and pyrites (Goldberg and Forster, 1988; Barling and Anbar, 2004; Wang et al., 2016). Previous researchers further suggested the possibility of using dissolved Mo as an indicator reflecting the dissolution of minerals including pyrite and gypsum (Neubert et al., 2011).

With the currently increasing human perturbation around the world, the dissolved constituents are further subject to vary in those freshwater systems. For example, previous researchers showed that dissolved elements could be variable due to human perturbation such as mining and agricultural activities (e.g., Carvalho et al., 2002; Meybeck, 2003; Pacheco and Szocs, 2006; Pacheco et al., 2013). Compared with those large rivers, small or medium-sized rivers are located within a single system, and therefore might be more sensitive to human perturbations in terms of the cycling of dissolved constituents. Over the past decades, China experiences a rapid economic development, and a substantial amount of contaminants including metals are discharged into rivers and even coastal waters (Pan and Wang, 2012; Wang et al., 2013). For example, mining activities of coal and minerals widely exist in mainland China, and consequently soils/minerals are increasingly loaded into nearby waters (e.g., Li et al., 2014). However, there is still lack of field data regarding the influence of such human perturbation on the mobility of dissolved elements in freshwater systems. The objective of the study is therefore to examine the dynamics of dissolved metals such as molybdenum in a typical river under severe human perturbation.

## 2. Material and methods

### 2.1. Description of study sites

The Jiulong River (JR) is the 13th largest river in China and is located in a subtropical zone in southeastern China, with a catchment area of 14,747  $\text{km}^2$  (Fig. 1). The watershed has an average annual temperature of 19.9–21.1  $^\circ\text{C}$ , and the river discharges of 12.4 billion  $\text{m}^3/\text{yr}$  of water (Cao et al., 2005). JR includes two major branches: the North River and the West River. The two rivers converge at the mouth of the JR. The JR flows through nine cities (Longyan, Zhangping, Hua'an, Changtai, Zhangzhou, Nanjing, Pinghe, Longhai, and Xiamen) and the Xiamen Bay until it reaches the Taiwan Strait.

The Jiulong River watershed covers a wide agricultural area including crop fields and pig farms, and receives industrial and sewage effluents (Yu et al., 2015). A total population of over 3.5 million lives alongside the river, and land use in the watershed includes 70% forest and upland orchard, and 18% arable land (Chen et al., 2013). The main soil types include lateritic red soil (rich in Mn/iron/aluminum oxides), and paddy soil (Chen et al., 2013). The lithology of the watershed includes intrusive rocks (granite, gabbro, and diorite) and a small amount of sedimentary rocks (clastic rocks and limestone). Granite minerals dominate the West River and lower North River, while shale, limestone, sandstone and rhyolite commonly exist in the upper North River (Chen et al., 2014). Mo contents are generally high in soils in the watershed (1.73 ppm, Lin, 2005). In particular, the upper North River is also well known for its mining activities, since there are located several major mines including the mines of Makeng and Panluo. The Makeng mine covers an area of 4  $\text{km}^2$  with an iron reserve of 0.4 billion tons, and a Mo reserve of 80,000 tons (Zhang, 2010).

### 2.2. Field sampling and laboratory analyses

The entire Jiulong River was investigated in January 2013. Generally, surface water samples from 41 stations along the Jiulong River were taken using a peristaltic pump with an extended pole and Teflon tube at a depth of 0.5 m below surface and at least 3 m from the riverside at a nearby bridge.

Water quality parameters (temperature, electric conductivity, pH and DO) were measured *in-situ* using a Multi-Parameter Water Quality Meter (WTW 340i). The precisions of water quality parameters were  $\pm 0.1$   $^\circ\text{C}$  of temperature,  $\pm 0.01$  of pH value,  $\pm 1\%$  of EC value, and  $\pm 0.1$   $\text{mg/L}$  of DO, respectively. Total dissolved solids (TDS, ppm) were calculated from electric conductivity ( $\mu\text{S}/\text{cm}$ ) multiplying by a factor of 0.67 (Alfonso et al., 2017).

All samples for dissolved metals and hydrochemical parameters were filtered on site using acid-cleaned inline polypropylene capsule filters (0.22  $\mu\text{m}$ ). Chlorophyll *a* (Chl-*a*) was measured by fluorescence analysis following the method of Parsons et al. (1984). Filtered samples for metals were then collected in acid-washed high-density polyethylene bottles and acidified to pH < 2.0 with 6.0 N  $\text{HNO}_3$ , and later held in the laboratory for at least one month until further processing (Wang et al., 2012).

All acidified samples for dissolved metals were processed under clean hoods (Class-100) within a clean room (Class-1000) in Xiamen University and analyzed via Chelex-100 resin preconcentration and extraction (Wang et al., 2012). The detection limits of the method was 0.1, 0.06 and 0.3  $\text{nmol/L}$  ( $n = 3$ ) for Mo, Mn, and Sr, based on three times the procedural blank. The accuracy of the method was further assured by processing standard reference water samples (river water SLRS-4 and coastal water CASS-4) with less than 10% deviation for all measured metals ( $n = 3$ ).

## 3. Results and discussion

### 3.1. Elevated concentrations of dissolved Mo in the Jiulong River due to human activities

The entire JR is divided into four parts based on hydrochemical data and geochemical settings: the pristine JR headwaters, the mining affected waters, the West River and North River. Accordingly, our measurements of dissolved Mo and hydrochemical parameters in each part are summarized in Table 1. We observed a large variability of dissolved Mo within the entire Jiulong River (Fig. 1). Generally, the pristine JR headwaters were characterized with relatively low levels of dissolved Mo ( $5 \pm 1$   $\text{nM}$ ; range: 3–6  $\text{nM}$ ). These dissolved levels are similar to other “pristine” rivers around the world (the Kolyma, 1.5  $\text{nM}$ ; Lena, 3.0  $\text{nM}$ ; and Maghna, 2.4  $\text{nM}$ ; Miller et al., 2011). The low levels of dissolved Mo could be attributed to the low contents of the source minerals. For example, Neubert et al. (2011) suggested that low Mo in the small river catchments (Entlebuch and Aare, Switzerland, 0.5–9.0  $\text{nM}$ ) could be related to the dissolution of two types of minerals: pyrite and gypsum. The low concentrations of dissolved Mo in the JR headwaters observed in our study could be attributed to the low weathering intensity and/or low Mo content in weathered minerals.

In contrast, the rest parts of the Jiulong River shows a large elevation of dissolved Mo concentrations. Sporadically high levels of dissolved Mo were observed in mining affected waters near the iron mines of Makeng and Panluo (average:  $77 \pm 19$   $\text{nM}$ , range: 50–96  $\text{nM}$ ). The downstream JR waters were characterized with elevated concentrations of dissolved Mo (North River:  $18 \pm 5$   $\text{nM}$ ; West River:  $20 \pm 6$   $\text{nM}$ ). In general, dissolved Mo levels in most parts of JR are higher than in those “pristine” waters, e.g., in the JR headwaters. In addition, we observed that the concentrations of

Download English Version:

<https://daneshyari.com/en/article/7478105>

Download Persian Version:

<https://daneshyari.com/article/7478105>

[Daneshyari.com](https://daneshyari.com)