



# Variations of total dissolved iron and its impacts during an extreme spring flooding event in the Songhua River



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## ABSTRACT

Total dissolved iron (TDFe) is a controlling factor in primary productivity in marine ecosystems, hence the variation of riverine TDFe output is attracting an increasing attention. Spring flooding is a key hydrological process in cold regions and the extreme spring flooding event (ESE) is thought to influence the output of TDFe considerably. In 2013, an ESE arose in the Songhua River, to reveal its impact on TDFe output and its species, water samples were collected in the river during this ESE as well as normal spring flooding period (NSP) in 2014 and 2015 to analyze the concentration and species of TDFe as well as other basic parameters. The speciation analysis was conducted by filtration and ultrafiltration methods. The results indicated the concentration of TDFe did not represent a significant difference during ESE, with an average concentration of 0.28 mg/L in ESE and 0.30 mg/L in NSP. The steady trend of TDFe concentration can be contributed to the limited intensity and duration of erosion by the snowmelt runoff and the construction of hydraulic works. Whereas, ESE intensified TDFe output increasing from 27.93 ton/day during NSP to 48.56 ton/day during ESE due to its high discharge. The species of TDFe was dominated by Fe(III) with the molecular weight lower than 10 kDa. The correlation analysis indicated that content and property of DOM were the main controlling factors of TDFe species. Furthermore, the dynamics and migration of TDFe were accompanied by the nutrient and heavy metal transport which may potentially influence the water quality in the river basin.

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## 1. Introduction

As one of the most abundant element in the Earth's crust, iron widely exists in different aquatic ecosystems, participating in various physiological and ecological processes (Boyd and Ellwood, 2010). Recently, dissolved iron was revealed to act as a controlling role in primary production in the ocean areas known as high-nitrate and low-chlorophyll (HNLC), where abundant dissolved macronutrients (e.g. N, P, Si) cannot be sufficiently utilized due to the lack of it (Martin and Fitzwater, 1988). Consequently, as a main source in the ocean, the variations of riverine dissolved iron output is attracting increasing attention (Labatut et al., 2014).

The Sea of Okhotsk is characterized by a highly productive ocean region, contributed to the sufficient dissolved iron transported from the Amur River (Suzuki et al., 2014). As the largest tributary, the Songhua River was indicated to be a crucial source of iron (Wang et al., 2012). It has been intensively studied on the features of total dissolved Fe (TDFe) concentration and species during summer flooding season (July–August) and normal flow period (September–October) in the

Songhua River (Pan et al., 2011; Levshina, 2012), however, characters of its output during spring flooding season were rarely reported.

Spring flooding is a key hydrological process in cold regions, the snowmelt is not only of considerable importance in water supply of soil and river systems, but also influences physicochemical properties of the river (Gao et al., 2015). Moreover, due to global climate change, the recession rate has been enhanced and snowfall has increased coupled with frequently occurred snowstorms, which may alter many aspects of hydrology during this period, such as flooding, erosion, hydrochemical and output (Stepanuskas et al., 2000; Ollivier et al., 2006; Vilímek et al., 2015), likewise the Songhua River Basin (Wang and He, 2013). During the winter season from 2012 to 2013, Northeastern China suffered from intensive and frequent snowfall, the precipitation reached 78 mm in the upper stream of Songhua River Basin (the Second Songhua River), and over 70 mm in the basin of mainstream, which was approximately 110% more than the annual average snowfall. The monthly average discharge at Harbin achieved 1290 m<sup>3</sup>/s in April and 1910 m<sup>3</sup>/s in May in 2013, which was 20% and 80% beyond the mean value (1067 m<sup>3</sup>/s) during the normal spring flooding period (NSF), respectively. It ranked the second maximum water level and discharge ever recorded since 1960s, thus, the 2013 spring flooding event can be defined as an extreme spring flooding event (ESE) (Eisenbies et al., 2007). Various studies have reported an increase trend of

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dissolved iron flux during spring flooding in different boreal rivers (Pokrovsky and Schott, 2002; Andersson et al., 2006; Sarkkola et al., 2013). It was also revealed that TDFe output in the Songhua River increased significantly during the flooding events induced by the extreme rainfall events (Guan et al., 2015, 2016). Therefore, it is hypothesized that extreme spring flooding event may also alter the trend of TDFe output in the Songhua River. So the current study is aimed (1) to observe the characteristics of TDFe output and its species during ESE, (2) to investigate the critical controlling factors, and (3) to discuss its potential impacts on the water quality of the Songhua River.

## 2. Materials and methods

### 2.1. Study site

The Songhua River Basin ( $41^{\circ}42'–51^{\circ}38' N$ ,  $119^{\circ}52'–132^{\circ}31' E$ ) is located in northeastern China (Fig. 1). The basin of Songhua River takes account for approximately 30% of the Amur River basin, with a total area of  $5.61 \times 10^5 \text{ km}^2$ ; the annual average temperature and precipitation are  $3–5^{\circ} C$  and  $400–750 \text{ mm}$ , respectively; the frost-free period is about 130 days per year; icebound season is from November until April in the next year and the spring flooding season last from April to May (Meng and Mo, 2012). Harbin City and Jiamusi City are located along the middle and lower reaches of the Songhua River, respectively, and Tongjiang City is situated at the confluence of the Songhua and the Amur Rivers (Fig. 1).

### 2.2. Sample collection

Water samples were collected according to standard methods from Water Quality-Technical Regulation on the Design of Sampling Programs (HJ 495-2009, China EPA) conducted at Road Bridge ( $45^{\circ}45'46'' N$ ,  $126^{\circ}34'60'' E$ ), Songpu Bridge ( $45^{\circ}47'51'' N$ ,  $126^{\circ}39'03'' E$ ) in the Harbin City, Fusui Bridge ( $47^{\circ}14'14'' N$ ,  $131^{\circ}58'16'' E$ ) in Jiamusi City and

Sanjiangkou ( $47^{\circ}41'24'' N$ ,  $132^{\circ}30'20'' E$ ) in Tongjiang City (Fig. 1) from April to May during the 2013 ESE and NSP in both 2014 and 2015. The collected water sample of 1.0 L for each sampling event were immediately stored in a portable refrigerator ( $4^{\circ} C$ ) and transported to the laboratory for further treatment and analysis.

### 2.3. Sample analysis

In current study, fractions of TDFe were determined by the ultrafiltration method (i.e. cross-flow filtration, CFF) established in previous researches (Pan et al., 2011). The samples were firstly filtered through Whatman GF/F membrane (Whatman, England) which are acid-cleaned and pre-combusted at  $450^{\circ} C$  for 4 h to analyze TDFe concentration as well as other aquatic parameters. Then CFF was conducted to divide TDFe into  $TDFe_L$ ,  $TDFe_M$  and  $TDFe_H$  with the molecular weight lower than 10 kDa (10 kDa MWCO PES), between 10 and 50 kDa (50 kDa MWCO PES), and larger than 50 kDa in the filtrate (Whatman GF/F), respectively. The recovery rate was 94.7–104.0% and the detection limit was 0.002 mg/L. All the pretreated samples were acidified to pH 2.0 to reduce Fe oxidation, and then stored at  $4^{\circ} C$  prior to further analysis. In current study, colloidal Fe is defined as the sum of  $TDFe_H$  and  $TDFe_M$ ;  $TDFe_L$  consists of Fe(II) and Fe(III), Fe(II) concentration were measured using ET7406 Fe Tester (Lovibond, Germany) with o-Phenanthroline spectrophotometric method in situ and Fe(III) concentration were calculated as the difference between  $TDFe_L$  and Fe(II) (Borman et al., 2010).

The concentrations of TDFe as well as different molecular weight iron and Mn were determined by a flame atomic absorption spectrophotometer (GBC 932, GBC Scientific Equipment Pty, Ltd, Braeside, Australia), Fe and Mn concentrations of each samples were calculated from the corresponding linear regression equation ( $R^2 > 0.999$ ) using six different dilutions of Fe and Mn standard solution (Standard Material Center of China). pH was measured by a portable pH meter (Rex, INESA Scientific Instrument, Shanghai, China). Dissolved organic carbon

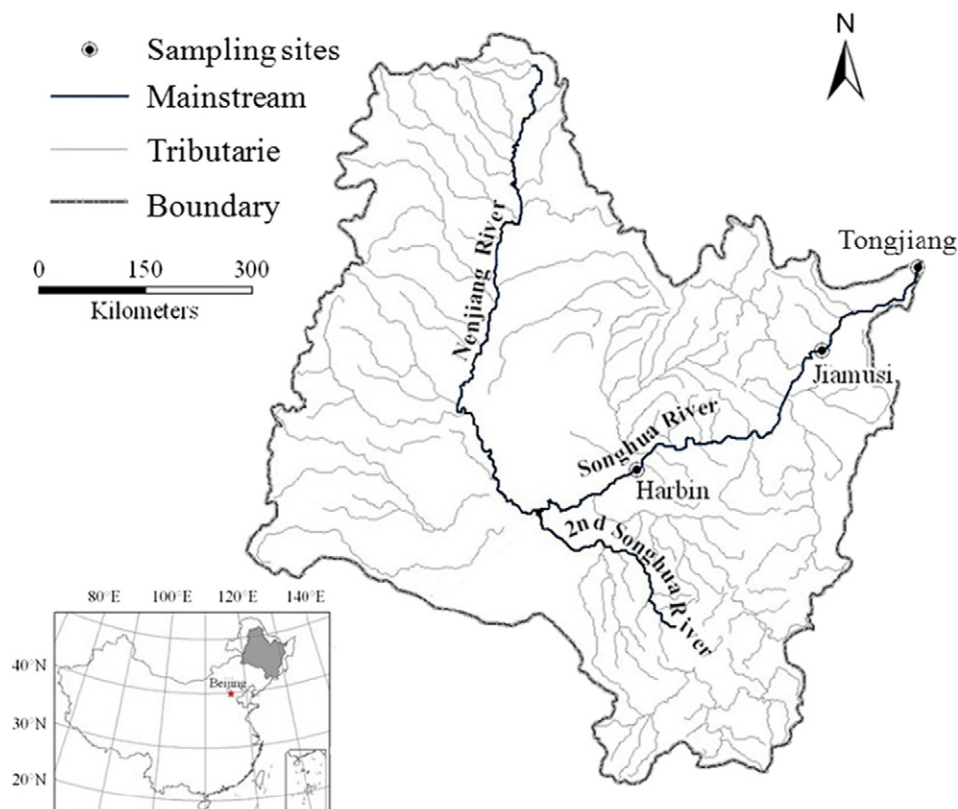


Fig. 1. Location of sampling sites.

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