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Flux characteristics of total dissolved iron and its species during extreme rainfall event in the midstream of the Heilongjiang River

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ABSTRACT

The occurrence of extreme rainfall events and associated flooding has been enhanced due to climate changes, and is thought to influence the flux of total dissolved iron (TDI) in rivers considerably. Since TDI is a controlling factor in primary productivity in marine ecosystems, alteration of riverine TDI input to the ocean may lead to climate change via its effect on biological productivity. During an extreme rainfall event that arose in northeastern China in 2013, water samples were collected in the midstream of the Heilongjiang River to analyze the concentration and species of TDI as well as other basic parameters. The speciation of TDI was surveyed by filtration and ultrafiltration methods. Compared with data monitored from 2007 to 2012, the concentration of TDI increased significantly during this event, with an average concentration of 1.11 mg/L, and the estimated TDI flux reached 1.2×10^5 tons, equaling the average annual TDI flux level. Species analysis revealed that low-molecular-weight complexed iron was the dominant species, and the impulse of TDI flux could probably be attributed to the hydrological connection to riparian wetlands and iron-rich terrestrial runoff. Moreover, dissolved organic matter played a key role in the flux, species and bioavailability of TDI. In addition, there is a possibility that the rising TDI flux could further influence the transport and cycling of nutrients and related ecological processes in the river, estuary coupled with the coastal ecosystems, which merits closer attention in the future.

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Introduction

Iron, a critical nutrient element in aquatic ecosystems, participates in most physiological processes of organisms (Zou et al., 2011). Reportedly, in comparison with balanced cell growth on the basis of fixed nitrogen, a 60- to 100-fold higher iron concentration was required in diazotrophy development in cells of planktonic diazotrophic cyanobacteria, such as *Trichodesmium*, the predominant autotrophic diazotroph in the pelagic marine environment (Berman-Frank et al., 2001; Brand, 1991). The biogeochemical effects of total dissolved iron (TDI) rely on both its concentration and speciation, including ferrous (Fe(II)) and ferric (Fe(III)) iron, organically and inorganically complexed iron and colloidal iron (Stumm and Sulzberger, 1992). In rivers, the ionic iron largely involves Fe(II) since Fe(III) is extremely insoluble, but it can be dissolved by means of binding to dissolved organic matter (DOM) to enhance the overall solubility, and most (>99%) of the dissolved Fe(III) emerges in organic complexed form (Perdue et al., 1976;

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Meunier et al., 2005). Recently, the riverine input to the ocean, which is one of the primary sources of TDI in the ocean, has attracted increasing attention because of the likelihood that riverine input will generate climate changes, by virtue of its effect on primary biological production and the carbon sequestration rate in ocean regions (Blain et al., 2007; Chen et al., 2014).

Rainfall and subsequent territorial runoff are the chief driving forces of TDI transport (Vuori, 1995). On account of climate change, the occurrence of extreme rainfall events and associated flooding has been heightened worldwide in recent decades, especially in temperate areas at high latitudes (IPCC, 2012). This results in momentous changes of regional hydrology together with ecosystem processes and services, such as the biogeochemical cycles of nutrient elements (Knapp et al., 2008). Variations of DOM and nutrients have been studied intensively during an extreme rainfall event (Siemann et al., 2007); nevertheless, the transport and flux of TDI, the mobility of which can be impacted strongly by rainfall events, has rarely been documented.

The Heilongjiang River (also called the Amur River), located in northeastern China, flows into the Okhotsk Sea, which has a relatively high abundance of phytoplankton biomass because of the sufficient TDI transported from the Heilongjiang River (Yoshimura et al., 2010). A surge of TDI flux related to the flood in 1998 was documented during the late 1990s in the midstream of the Heilongjiang River (MHR) (Kulakov et al., 2010). A similar trend was also observed during intensive rainfall events in different studies, which might owe to the iron-rich runoff and large amounts of DOM inputs (Abesser et al., 2006; Jiann et al., 2013). An extreme rainfall event occurred in August, 2013 in northeastern China, causing severe flooding in the Heilongjiang River. Driven by the desire to understand the alteration of TDI flux resulting from this extreme event, this article presents the water quality data of MHR within the period of the extreme rainfall event as well as historical data from 2007 to 2012, (1) to study the characteristics of TDI flux and species during the extreme rainfall event, (2) to investigate the sources and critical decisive factors of this process, and (3) further to discuss the potential effects of an impulse flux of TDI to the aquatic ecosystem.

1. Materials and methods

1.1. Study area

The Heilongjiang River, stretching from western Manchuria to the Strait of Tartary, whose length is 2825 km (mainstream) with a catchment area about 1.85 million km², of which 48% is located in northeastern China, is the tenth largest watercourse in the world (Yan et al., 2013).

MHR is defined as the river section between the embouchures of the Zeya River (Blagoveshchensk City) and Ussuri River (Khabarovsk City), with a length of approximately 950 km. Not only snowmelt in spring but also monsoonal rain in the course of summer to autumn, which accounts for 15%–20% and 65%–80% of total runoff supply, respectively, comprises the main sources of the flow (Yan et al., 2013). Extensive lowland wetlands exist widely in the basin of MHR, which serves as vital parts in buffering floods and biogeochemical processes in the river ecosystem. In the junction of the Heilongjiang River, the Songhua River and the Ussuri River lie along Tongjiang City and Fuyuan City (Fig. 1), where the annual average temperature is 2–3°C, precipitation around 600 mm per year, of which nearly 80% occurs from June to September, and frost period about 180 days per year, lasting from late October to April of the next year. The average annual discharge of MHR is 8260 m³/sec, which has fluctuated from 4290 (in 1979) to 14,000 (in 1897) m³/sec, with maximum flow of 39,200 m³/sec recorded in 1897 at Khabarovsk. The MHR has a water catchment area of 1.63 million km², accounting for 87.9% of the total basin area of the Heilongjiang River, with the main control station situated in Khabarovsk City after the convergence of the Rivers of Zeya, Bureya, Songhua and Ussuri (Yan et al., 2013).

1.2. The extreme rainfall event

An extreme rainfall event in this study is defined as rainfall with precipitation over 20 mm with a high frequency (average frequency 3.78 times per year) within a gap of 1–5 days (Yang et al., 2008). In 2013, four intensive rainfall events with precipitation over 20 mm were monitored from August 14th to 22nd in the research area (Fig. 2), which could be defined as "extreme rainfall event". The water level in MHR peaked around September 1st during the event and ebbed away to the normal level on September 22nd. No extreme rainfall event was observed during 2007–2012 in this area. The runoff depth during the extreme rainfall event was calculated according to the Soil Conservation Service Curve Number (SCS-CN) method (Mishra and Singh, 2003).

1.3. Sample collection and analysis

Water samples were taken from the depth of 50 cm below the water surface at Tongjiang City and Fuyuan City (Fig. 1) in the flood period (July and August) after the rainfall and normal flow period (May, June, September and October) from 2007 to 2012, as well as in the period of the extreme rainfall event from August to September in 2013. After collection, all samples were then stored in a portable refrigerator (4°C)

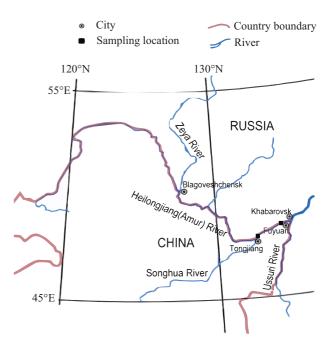


Fig. 1 – Location of sampling sites in the midstream of the Heilongjiang River (MHR).

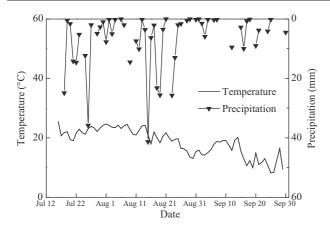


Fig. 2 – Air temperature and precipitation during the extreme rainfall event in midstream of the Heilongjiang River (MHR) (data source: The Sanjiang Experimental Station of Wetland Ecology, Chinese Academy of Sciences).

immediately for further treatment and analysis. Three replicate samples were collected during each sampling event.

Chemical speciation of TDI was analyzed by filtration and ultrafiltration methods that were established in previous research by our team (Pan et al., 2010). First and foremost, the samples were filtered by acid-cleaned Whatman GF/F membranes (Whatman International Ltd., Kent, England) to analyze TDI concentration. Then, by cross-flow ultrafiltration, TDI was severally split into low-molecular-weight iron (LMWI), mediummolecular weight iron (MMWI) and high-molecular-weight iron (HMWI) with the sizes of <0.01 μ m (10 kDa MWCO PES), 0.01– 0.05 μ m (50 kDa MWCO PES), and 0.05–0.7 μ m (Whatman GF/F), respectively. In the present study, the colloidal iron fraction is defined as the sum of HMWI and MMWI. LMWI contains ionic and complexed iron, which separately refers to Fe(II) and Fe(III). The difference between LMWI and ionic iron is calculated as complexed iron. The cross-flow ultrafiltration setup, cleaning procedure and quality control were implemented on the basis of the processes that were already established in previous research (Pan et al., 2010). In addition, the recovery rate was 95.4%-103.5% and the detection limit was 0.002 mg/L.

Fe(II) concentrations were measured using a Fe Concentration Tester (ET7406 Lovibond, Tintometer GmbH, Dortmund, Germany) with o-phenanthroline spectrophotometry; the concentrations of Fe and Mn, an atomic absorption spectrophotometer (GBC 932, GBC Scientific Equipment Pty, Ltd, Braeside, Australia); the pH values, a portable pH electrode (Rex, INESA Scientific Instrument, Shanghai, China); dissolved organic carbon (DOC), a TOC-V_{CPH} analyzer (TOC-V_{CPH}, SHIMADZU, Kyoto, Japan); and NH⁴₄-N, NO₃-N, and PO⁴₄-P concentrations in each sample, an automatic chemical analyzer (Mode Smartchem 200, AMS, Rome, Italy).

1.4. Estimation of TDI flux

Considering that the majority of the river sections of MHR are lines of demarcation between China and Russia, the recent hydrological information is classified. Thereby, the discharge of MHR was estimated based on historical discharge information recorded at the Khabarovsk Hydrological Station by the Heilongjiang River from 1897 to 2005 (Yan et al., 2013). The historic maximum discharge recorded is 39,200 m³/sec. The water level in 2013 reached 808 cm, exceeding the historical maximum water level (642 cm) for nearly one month – the monitored period in current studies is also within this time interval – from mid-August to mid-September at Khabarovsk. Since the historical data are comparable to that in the current study, TDI flux during the extreme rainfall event was estimated using the average TDI concentration and historic maximum discharge (39,200 m³/sec) within a period of 30 days.

1.5. Statistical analysis

All statistical analysis was conducted by SPSS 20.0 statistical software (SPSS Inc., Chicago, USA). Spearman correlation analysis was performed to analyze the relationship between iron concentrations and the other analyzed parameters, since the data did not fit a normal distribution pattern tested by Q–Q probability plot analysis. One-way analysis of variance (ANOVA) was executed to compare the differences between concentrations monitored in different periods; differences were considered significant if p < 0.05.

2. Results

2.1. Aquatic parameter set in MHR

The statistics of water quality in MHR in the normal flow period (2007-2012), flood period (2007-2012) and extreme rainfall event (2013) are displayed in Fig. 3. Most of these parameters showed a variation trend among different periods, except pH, which remained relatively stable (on average around 7.40) in all periods. Dissolved Mn in the flood period reached a maximum of $64 \mu g/L$, while the concentration averaged 34 μ g/L during both the normal flow period and extreme rainfall event. The mean contents of DOC, $\mathrm{NH}_4^{\scriptscriptstyle +}\mathrm{-N}$ and NO3-N peaked during the extreme rainfall event and displayed minimum levels during the normal flow period. Taking NH₄⁺-N as an example, the mean concentration was 0.05 mg/L during the normal flow period, but it rose to 0.12 mg/L during the flood period, and climbed up to more than 0.20 mg/L during the extreme rainfall period. Contents of PO₄³⁻-P showed a similar pattern; however, its concentration decreased from 0.04 mg/L in the normal flow period to 0.02 mg/L in the flood period.

2.2. TDI flux and its species during the extreme rainfall event in MHR

Similar to PO_4^3 --P, average TDI concentrations varied significantly (p < 0.01) in these three periods (Fig. 4). TDI was 0.43 mg/L in the normal flow period while 0.28 mg/L in the flood period, and these TDI levels were comparable with research findings in a similar area of the Heilongjiang River (Levshina, 2012). Yet, a sharp increase of TDI concentration was observed during the extreme rainfall event (p < 0.01), with mean value of 1.11 mg/L. Most TDI was in the form of LMWI, and the ionic and complexed iron was the main species during the regular period in MHR (Fig. 5). Even though LMWI

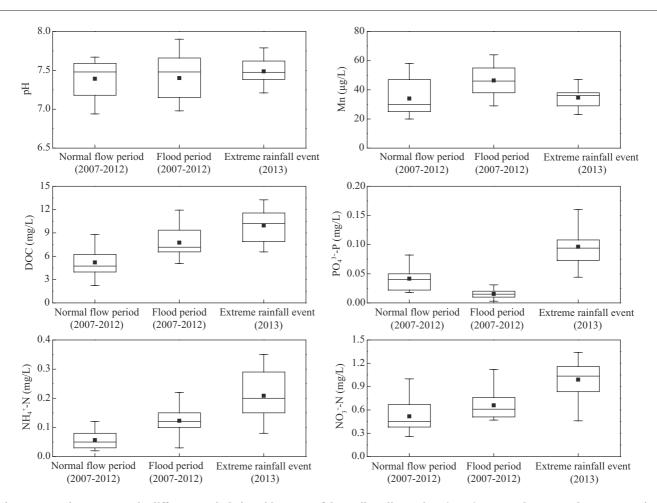


Fig. 3 – Aquatic parameter in different periods in midstream of the Heilongjiang River (MHR). Box-and-square plot representing the maximum, mean, median, 25th to 75th percentiles, and minimum.

was still the main form of TDI, complexed iron became the dominant species, with the relative proportions of iron species varying in the sequence of complexed iron > colloidal iron > ionic iron.

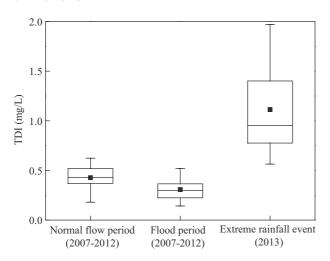


Fig. 4 – Concentrations of total dissolved iron (TDI) in different periods in midstream of the Heilongjiang River (MHR). Box-and-square plot representing the maximum, mean, median, 25th to 75th percentiles, and minimum.

2.3. Dynamic of TDI during the extreme rainfall event in MHR

The dynamics of all species during this extreme rainfall are illustrated in Fig. 6. The results indicated that ionic iron decreased with the augmentation of complexed iron as well as colloidal iron. TDI concentration kept increasing from 0.43 mg/L (before the event) and rose up to a peak of 1.97 mg/L on September 1st, when the water level reached the maximum in MHR, and declined gradually to 0.65 mg/L with the abated water level after that. The complexed and colloidal iron followed a similar pattern as TDI. Export of TDI during the extreme rainfall event in 2013 yielded 1.2×10^5 tons.

3. Discussion

3.1. Water quality variation and potential causes in MHR

The nitrogen and phosphorus concentrations rose significantly during the extreme rainfall event (p < 0.01) due to excessive fertilizer application, which is the principal source in this area. The consumption of chemical fertilizers was 1.58×10^6 tons (converting the gross weight into weight containing 100% efficacious components) in the basin of MHR in China in 2012, of which nitrogen fertilizer was 5.70×10^5 tons

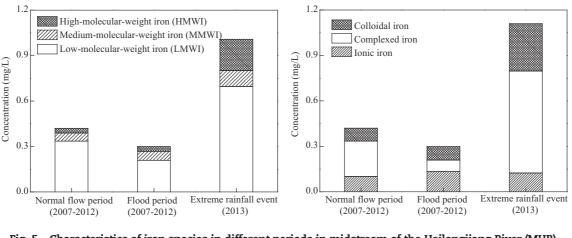


Fig. 5 - Characteristics of iron species in different periods in midstream of the Heilongjiang River (MHR).

while phosphorus fertilizer was 3.47×10^5 tons (Heilongjiang Bureau of Statistics and National Bureau of Statistics Survey Office in Heilongjiang, 2013). Phosphorus could be easily leached by runoff, and then flow into receiving water bodies, giving rise to freshwater eutrophication and/or biodiversity loss in the aquatic ecosystem (Yang et al., 2010). Compared with the regular flood period, DOC values increased considerably as well (p < 0.01) during the extreme rainfall event, which was in agreement with other studies, suggesting that the majority of annual DOC export occurred during intensive rainfall events

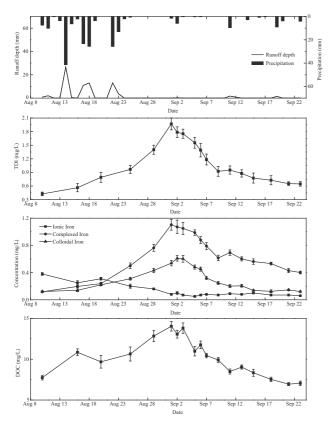


Fig. 6 – Dynamic of total dissolved iron (TDI) and dissolved organic carbon (DOC) during the extreme rainfall event in midstream of the Heilongjiang River (MHR).

(Clark et al., 2007). It was also observed that the concentration of TDI increased during the rainfall events, dominated by species in the organic complexed form, and indicated that the maximum contribution from iron sources occurred at peak discharge (Lorieri and Elsenbeer, 1997; Gaiero et al., 2003).

High TDI contents during the extreme rainfall event can be attributed to iron output from wetlands induced by high water level. During the event, the river buffered more widely, resulting in effective hydrological connection to the wetlands and, according to remote sensing monitoring within the research area, over 50% of the total inundated area was swamp wetlands previously. Moreover, the finding that the iron species in the surface water of wetlands were in the order of LMWI > HMWI > MMWI, dominated by the species of complexed iron (Pan et al., 2010), was the same as what was found in this study. Hence, the riparian wetlands were the main source of TDI in MHR, which was probably the territorial runoff during the extreme rainfall event (Chi et al., 2010).

3.2. Analysis of factors controlling TDI flux and species during the extreme rainfall event in MHR

In order to identify the critical controlling factor, Spearman correlation was conducted to analyze the relationship between different iron species and water quality parameters monitored during the extreme rainfall event. A significantly positive correlation was observed between the pairs complexed iron-DOC, colloidal iron-DOC, TDI-DOC (Table 1). Thus, DOM may exert great influence upon the concentrations and species of TDI in MHR. In rivers, Fe(II) can be rapidly oxidized to Fe(III) and then precipitate as Fe(III) oxyhydroxides; whereas DOM has high selectivity and affinity for Fe(III), forming steady Fe-DOM complexes, so that DOM can control the solubility and stability of TDI (Nolting et al., 1998). The positive correlation between DOC and TDI was also documented in different works (Wang et al., 2012; Jiann et al., 2013). Furthermore, the species of TDI can be affected by DOM via control of the oxidation and reduction processes; the rate of Fe(II) oxidation may be accelerated by the presence of DOM such as humic acids (Pullin and Cabaniss, 2003). The process of oxidizing Fe(II) is capable of forming both complexed and colloidal iron. The current study provided a full account of how DOC was observed to be positively correlated to complexed and colloidal iron; simultaneously, the dynamics of iron species suggested that the concentration of ionic iron decreased with the rise of DOC values, as well as the complexed and colloidal iron concentrations, after the extreme rainfall process. During the event, the riparian wetlands, which act as indispensable pools of DOM with abundant humic substances in MHR, could convey large quantities of humic substances into the river (Guo et al., 2010), which can accelerate the oxidizing process of ionic iron to form complexed and colloidal iron. Therefore, DOM played an important role in TDI transport and cycling in MHR during extreme rainfall events.

3.3. Potential effects of the impulse flux of TDI to the aquatic ecosystem

Iron has been reported to limit phytoplankton production in open ocean regions and coastal upwelling areas (Blain et al., 2007; Capone and Hutchins, 2013), moreover, organic complexed iron was reported to remain highly bioavailable and to be transported stably in rivers (Chen and Wang, 2008; Pan et al., 2011). Accordingly, TDI flux during the extreme rainfall event (1.2×10^5 tons), which was equal to the annual TDI flux level during 1990–2005 (1.54×10^5 tons, Kulakov et al., 2010) may greatly affect the primary production and relevant ecological processes. Increase of TDI flux was also observed in other studies on rainfall events (Abesser et al., 2006; Cánovas et al., 2008).

An impulse of TDI flux might affect the nutrient cycling in aquatic ecosystems greatly. The redox reaction between Fe(II) and Fe(III) is the principle process in iron cycling in aquatic environments that controls the cycling of other elements, especially nutrient elements, such as phosphorus. It is typical that the oxidization of ionic iron can generate colloidal iron with an average diameter ranging from 0.05 to 0.5 μ m in fresh waters, and the iron colloids remain stable due to their small size and low rate of aggregation and sedimentation (Gunnars et al., 2002). As a result, the iron colloids may transport over a long distance to the estuary and coastal region accompanied by nutrients (Kaplan and Knox, 2004). In the current study, PO₄³⁻-P was observed to be positively correlated to TDI as well as colloidal iron in the event (Table 1). Thus, the impulse flux of TDI may potentially affect the water quality in the estuarine and coastal ecosystems. However, in consideration of the existing data, challenges still remain in identifying how exactly the impulse flux influences the related ecological processes in river, estuarine and coastal ecosystems. To explore its environmental impacts in the future, further research will be needed.

4. Conclusions

This study conducted in the midstream of the Heilongjiang River illustrates that extreme rainfall events are able to increase TDI flux to a great degree and alter the characteristics of its species. TDI concentrations averaged at 1.11 mg/L during the event, with an estimated flux of 1.2×10^5 tons in MHR. Most TDI existed in the form of LMWI; complexed iron was the major species, with the order complexed iron > colloidal iron > ionic iron; DOM had great importance in TDI transport and cycling in

Table 1 – Relationship between iron species and aquatic parameters in extreme rainfall event (n = 35).

	DOC	PO4 ³⁻ -P	Mn
Ionic Fe Complexed Fe Colloidal Fe TDI	N.S. 0.735 ^a 0.474 ^b 0.672 ^a	N.S. N.S. 0.425 ^b 0.409 ^b	N.S. 0.438 ^b N.S. 0.443 ^b
N.C. no significant	correlation		

N.S.: no significant correlation.

^a Correlation is significant at the 0.01 level (2-tailed).

^b Correlation is significant at the 0.05 level (2-tailed).

the period of the extreme rainfall event. The sources of TDI impulse flux owe to the hydrological connection to riparian wetlands and terrestrial runoff. The consequent results, such as the changes in transport and cycling of nutrients as well as related ecological processes, need to be further identified in the future.

Acknowledgments

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