Vertical distribution of soil Fe in typical riparian subzones of the Sanjiang Plain

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ABSTRACT

Sanjiang Plain, in which marshes occupy the largest area of fresh wetlands in China, has historically been considered a key Fe source of the Amur River and the Sea of Okhotsk. Since the 1950s, extensive human activity and wetland reclamation in the Sanjiang Plain has resulted in aggravating fragmentation of marshlands into different hydrological units. In the present study, soil samples were taken from typical riparian subzones of three representative marsh rivers of the Sanjiang Plain (Yalu River, Bielahong River and Naoli River), including the wetland near river (wetland-R), the wetland near a cultivated land (wetland-C) and cultivated land. Soil samples from each riparian subzone were collected vertically every 20 cm from surface to a depth of 1 m and analyzed for total Fe, free Fe oxides, amorphous Fe oxides, acid-soluble Fe(II), water-soluble Fe(II), dissolved carbon (DOC), soil total organic carbon (TOC) and pH. The results showed that the soil total Fe in the 0–60 cm layers increased in the sequence of wetland-R < wetland-C < cultivated land. On the contrary, the soil active ratio of Fe, water- and acid-soluble Fe(II) in the profile decreased in the sequence of wetland-R > wetland-C > cultivated land. These implied that the ability of Fe mobilization and export in the three river basins tended to decrease away from the river. DOC was positively correlated with acid-soluble Fe(II) while negatively correlated with total Fe, indicating that DOC might promote the production of acid-soluble Fe(II) and play a key role in export of Fe from riparian zones to adjacent waters. These findings will be useful to better understand the impacts of natural wetland reclamation in the Sanjiang Plain on the regional environment.

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1. Introduction

Although Fe is abundant in nature, its availability is low due to its insolubility in aerobic circumneutral environments (Sorichetti et al., 2014a,b; Morel and Price, 2003). It has been documented that Fe can act as a limiting micronutrient to the primary productivity in high nitrogen low chlorophyll parts of oceans (Morel and Price, 2003; Han et al., 2011; Planquette et al., 2007; Takeda and Tsuda, 2005; Mills et al., 2004; Schulz et al., 2004), while the land-ocean linkage by Fe transport through rivers might help alleviate the Fe deficiency in ocean ecosystem (Narita et al., 2004; Shiraïwa, 2005; Yoh, 2004). The riverine wetland, which provides a large pool of organic carbon and nutrients, is believed to play a crucial role in export of Fe to rivers (Pan et al., 2010a). This Fe supply may exert control on the dynamics of plankton blooms in neighboring ocean, which in turn affect the biogeochemical cycles of carbon, nitrogen, silicon, and sulfur, and ultimately influence the earth’s climate system (Han et al., 2011; Coale et al., 1996, 2004; Watson et al., 2000; Bishop et al., 2002; Boyd et al., 2007; Cassar et al., 2007; Buesseler et al., 2008).

Sanjiang Plain, occurs in the Amur River Basin, in which marshes occupy the largest area of fresh wetlands in China (Yang et al., 2013). It has historically been considered a key Fe source of the Amur River and even the Sea of Okhotsk in the northwest of North Pacific (Chi et al., 2010; Pan et al., 2010b). The Fe supplied from the Amur River has also been reported to contribute significantly as a Fe source for the Okhotsk Sea ecosystem (Yoshimura et al., 2010). Previous studies showed that the Amur River is one of the 10 longest rivers in the world (4350 km), and its basin covers 2.1 million km². Averaged water discharge from the Amur River is reported to be 11,000 m³ s⁻¹ (Ogi et al., 2001), which is the major source of fresh water to the Okhotsk Sea. The water contains 11 nmol L⁻¹ of dissolved Fe (Nagao et al., 2007). This concentration is four or five orders of magnitude greater than in coastal sea waters, typically assumed to be several nmol L⁻¹ (Lohan and Bruland, 2006). However, Sanjiang Plain has been experiencing extensive human activity and wetland reclamation by construction of numerous artificial drainage ditches since the 1950s (Liu et al., 2005; Wang et al.,

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in typical riparian subzones with different distances to the main watercourse, (2) to explore the activation and mobility of soil Fe in typical riparian subzones, and (3) to evaluate the ability of Fe export to adjacent waters from typical riparian subzones. The anticipated results would help to evaluate the ecological impacts of natural wetland reclamation in riparian zone in the Sanjiang Plain on the neighboring marine environment.

2. Methods and materials

2.1. Research area description

The Sanjiang Plain (43°49′55″–48°27′40″N, 129°11′20″–135°05′26″E) is located in the northeastern region of Heilongjiang Province, China. The total plain area is 10.89 × 10^6 ha (Liu et al., 2013). It has a typical continental monsoon climate; summer is short, warm and rainy while winter is long and cold. Average temperatures range from −18 °C in January to 21–22 °C in July, with a frost-free period of 120–140 days. Annual precipitation ranges from 500 to 650 mm, with 60% taking place from June to September. It is an alluvial plain with an altitude of <200 m in major parts and most of the rivers at the area have riparian wetlands supporting meadow and marsh vegetation (Guo et al., 2008). Carex lasiocarpa and Calamagrostis angustifolia are dominant and their coverage is up to 80–90%. Other plant communities...
mainly include *Prundo phragmites, Querns mongolica, Populus davidiana–Betula platyphylla–Q. mongolica, C. angustifolia meadow* and *Betula fruticosa–Miscellaneous meadow* (Liu et al., 2013).

The study was performed in the basins of Yalu River, Bielahong River and Naoli River, which are the three representative marsh rivers in the Sanjiang plain. In each riparian zone, three typical subzones with different distances to the main watercourse were selected as sampling sites, covering the wetland-R, wetland-C and cultivated land (Fig. 1). *P. phragmites* and *C. angustifolia* are dominant in the wetlands. The cultivated lands were converted from wetlands by planting soybean about ten years ago.

### 2.2. Soil samples collection

In August 2008, soil samples were collected vertically at depth of 0–20, 20–40, 40–60, 60–80 and 80–100 cm, with three replicates at each sampling site. Before being transported to laboratory, the soil cores were wrapped with thin wall plastic films and stored at 0–4 °C to prevent Fe oxidation.

### 2.3. Analytical methods

After transport to laboratory, samples were then analyzed for total Fe, free Fe oxides, amorphous Fe oxides, acid-soluble Fe(II), water-soluble Fe(II), and dissolved carbon (DOC). In addition, soil total organic carbon (TOC) and pH values were also measured. Soil general properties of sample sites were tabulated in Table 1.

Acid-soluble Fe(II), water-soluble Fe(II), DOC and soil moisture content were determined with fresh soil. Acid-soluble Fe(II) and water-soluble Fe(II) were extracted by 0.5 M hydrochloric acid solution and deionized water, respectively. Both of the extracts were determined by phenanthroline colorimetry using a Spectord 50 spectrophotometer (Analytik Jena AG, Jena, Germany) (Thompson et al., 2006). To determine the concentration of DOC, 10 g of soil was shaken with 30 mL of deionized water (1:3 w/v soil-to-solution ratios) for 2 h on a horizontal shaker with a constant temperature of 25 °C. A mixed sample was centrifuged at 3000 rpm for 10 min and then filtered through a 0.45 μm polytetrafluoroethylene filter. The quantity of DOC in the extract was analyzed by Multi C/N 2100 Analyzer (Analytik Jena AG, Jena, Germany). Soil moisture content was determined by drying the soil at 110 °C for 24 h.

Another set of subsamples were loosely disaggregated to facilitate air-drying at 20 °C, and passed through a 2-mm mesh sieve to remove larger particles and vegetation remains. The soil pH values was determined with a soil:water ratio of 1:2.5 by using Elico Digital EC meter.

The remaining subsamples were air-dried and then ground to pass through a 0.149-mm sieve for analysis of the contents of total Fe, free Fe oxides, amorphous Fe oxides and TOC. The total Fe was measured by an Aanalyst 200 flame atomic absorption spectrophotometer (PerkinElmer Inc, Massachusetts, America) after sodium carbonate fusion digestion. The free Fe oxides was extracted by sodium hydrosulfite–sodium citrate–sodium bicarbonate at pH 7.0, and determined by phenanthroline colorimetry (Analytik Jena AG, Jena, Germany) (Schwertmann and Murad, 1990). The amorphous Fe oxides was extracted by acidified ammonium oxalate at pH 4.0, and determined by phenanthroline colorimetry (Analytik Jena AG, Jena, Germany) (Campbell and Schwertmann, 1984). TOC was determined by dry combustion, using TOC 5000A autoanalyzer (Shimadzu Corp, Kyoto, Japan).

### 2.4. Data analysis

Statistical analyses were performed using SPSS 19.0 (SPSS Inc, Chicago, USA). One-way analysis of variance (ANOVA) was employed to compare the differences of test parameters between different riparian subzones and between different soil layers. In analyses where P is <0.05, the factor tested and the comparisons were considered statistically significant. Pearson correlation analysis was performed to analyze the relationships between total Fe and acid-soluble Fe(II) and soil organic carbon to further reveal the distribution pattern of total Fe and acid-soluble Fe(II) as affected by soil organic carbon. Graphics and data fitting were performed using Sigmaplot 12.0 (Systat Software Inc, California, USA).

### 3. Results

#### 3.1. Soil total Fe

In the riparian zone, the soil total Fe in the profile above 60 cm increased in the sequence of wetland-R < wetland-C < cultivated land. Taking Yalu River basin as an example, in the 20–40 cm soil layer, the soil total Fe concentrations in cultivated land (44.7 g kg⁻¹) and wetland-C (28.0 g kg⁻¹), were higher than that in wetland-R (19.9 g kg⁻¹). Soil total Fe in wetland-R increased remarkably with depth below 40 cm while its contents were relatively stable in wetland-C (Fig. 2).
3.2. Free Fe oxides

In all three sample locations, the contents of soil free Fe oxides above 80 cm in the profiles decreased in the sequence of cultivated land > wetland. Taking Yalu River basin as an example, in the 0–20 cm soil layer, the free Fe oxides concentration in cultivated land (9.6 g kg⁻¹) was higher than that in wetland-R (2.6 g kg⁻¹). By comparing the soil free Fe contents in the wetlands with different distances away from the main watercourse, similar vertical distribution trends of soil free Fe were found in wetland-R and wetland-C (Fig. 3).

3.3. Active ratio of Fe

In the three river basins, the active ratios of Fe (the ratio of amorphous Fe oxides to free Fe oxides) in the profiles decreased in the sequence of wetland-R > wetland-C > cultivated land. Significant differences were found among the three riparian subzones. Taking Yalu River basin as an example, in the 0–20 cm soil layer, the active ratios of Fe in cultivated land (38.7%) and wetland-C (72.1%) were lower than that in wetland-R (78.6%) (Fig. 4).

3.4. Water- and acid-soluble Fe(II)

Both water- and acid-soluble Fe(II) contents in the profiles decreased in the sequence of wetland-R > wetland-C > cultivated land. In the profiles of wetland, the acid soluble Fe(II) were high in the topsoil layer, while water soluble Fe(II) showed high concentrations in 60–100 cm layers. Especially in the wetland-R of the Yalu River basin, the water-soluble Fe(II) was 51.9% lower in the topsoil layer than in the 40–60 cm layer. Furthermore, the concentrations of water soluble Fe(II) were remarkably lower than the contents of acid soluble Fe(II) (Figs. 5 and 6).

3.5. Relations of DOC and soil Fe

In the three river basins, the DOC content in the 20–40 cm layers in the riparian soil profile increased in the sequence of cultivated
land < wetland (Fig. 7). The correlation analyses showed that DOC were negatively correlated with total Fe ($r = 0.444$, $p < 0.01$) while positively correlated with acid-soluble Fe(II) ($r = 0.522$, $p < 0.01$) (Fig. 8).

4. Discussion

4.1. DOC

DOC is a mixture of hydrophilic and hydrophobic groups. The hydrophilic fraction is comprised of carbohydrates, carboxylic acids and protein/peptides, while the hydrophobic fraction includes humic and aromatic components and polyphenols (Wang et al., 2015b). The higher DOC in the wetland than in cultivated land indicated that the wetland was the main source of organic carbon in the riparian zone. When hydrologically connected to surface flow, wetlands would export DOC to receiving waters (Sharifi et al., 2013), acting as a primary source of humic substances to adjacent rivers.
is beneficial to the transport of Fe to aquatic systems because DOC is shown to be a medium of transport for other elements including Fe (Canário et al., 2008).

4.2. Soil total Fe

Our results showed that total Fe contents in the upper soil layers were lower in wetland than that in cultivated land. The upper layers of wetland contained abundant organic matter (Table 1), which promoted the activation of soil Fe and significant amounts of Fe might be subject to vertical and horizontal transportation, and eventual export into the adjacent river waters. In the cultivated land, much soluble Fe was deposited in the soil profile, where good aeration occurred due to a lower groundwater level and artificial disturbances, preventing the mobilization and export of soil Fe.

A comparison of soil Fe between the two types of wetlands showed that the vertical distribution of total Fe became more balanced and less variable with increasing the distance from the river. The results were consistent with the previous study (Wang et al., 2003). It may be related to the different pedohydrological regime between the wetlands. The hydrogeological conditions in wetland-C caused more frequent interaction between soil and water in the soil profile, which would promote the migration of soil Fe in the whole profile.

In addition, the high DOC content in the topsoil of wetland-R might also contribute to the leaching of soil Fe, which was implied by the significant negative relationship between soil total Fe and DOC. This is consistent with the findings of previous studies which have suggested that soil organic matter might have the ability to increase the solubility and mobility of Fe (Lovley and Woodward, 1996; Liptzin and Silver, 2009). One reason was that DOC had the ability to form soluble Fe-organic complexes with ferric iron. The complexes could contribute significantly to total soluble Fe in soil solution and make it more mobile (Lindsay, 1991). Another reason was that during the degradation of organic matter in soils, electrons and other reducing agents were released to the surrounding soil. This biological process enhanced the reducing condition and remarkably raised the solubility of ferrous iron (Lindsay, 1991). Moreover, DOC could be involved in the transport of electrons from Fe(III) reducers to Fe(II) oxide to simulate the reduction of Fe (Lovley, 1997).

4.3. Free Fe oxides

The abundance of free Fe oxides was considered as an important index to reflect the degree of soil weathering. Weathering could be influenced by soil temperature and moisture content. In addition, weathering and erosion rates would also be promoted by farming practices. The higher abundance of free Fe oxides in the cultivated land in current study revealed that the impact of reclamation might promote the formation of free Fe oxides by modifying the soil weathering rate.

The similar trends of free Fe oxides distribution in the wetland-C and wetland-R suggested that reclamation activities had no significant effect on the soil weathering rate of adjacent wetland. In topsoil, the content of free Fe oxides was lower in the wetland-R than in the wetland-C, possibly due to the difference in soil total Fe content in the two wetlands.

4.4. Active ratio of Fe

Fe oxides can exist in soils in various forms. The less crystallized the Fe oxides, the more readily reducible by microbes (Lovley, 1997). Therefore, amorphous Fe oxides were considered as the most form of reactive Fe oxides in numerous soil environments (Chen and Barak, 1982). The active ratio of Fe was identified as a measure of the proportion of amorphous Fe oxides in total Fe oxides, which could better reflect the effects of land use change on the mobility of soil Fe oxides (Blume and Schwertmann, 1969).

Our study indicated that the active ratio of Fe in the whole profile tended to be lower away from the river. The results on free Fe oxides and active ratio of Fe suggested that reclamation could promote the weathering of soil, while retarded the formation of amorphous Fe oxides. The active ratio of Fe was remarkably higher in the wetland-R than in the wetland-C, which was mainly due to their differences in hydrogeological conditions. We inferred that three reasons were responsible for the differences in active ratio of Fe among the three riparian subzones. First, compared with cultivated land and wetland-C, the wetland-R had a longer flood period which greatly restricted the movement of oxygen into soil pore-space. Then the regions would become partially anaerobic which could promote the microbial dissimilatory reduction of Fe(III) and inhibit crystallization of Fe oxides (Lovley, 1991; Lindsay, 1991). Next, crystalline Fe was converted into amorphous Fe in submerged soil which could significantly increase the concentration of the latter (Kumar, 1981). This process, probably through hydration, is also mediated by microorganisms (Wahid and Kamalam, 1993). Further, migration of soil amorphous Fe oxides from cultivated land and wetland-C to wetland-R along the hydraulic gradient of the riparian zone could also contribute to the higher active ratio of Fe in the wetland-R.

4.5. Water- and acid-soluble Fe(II)

In the three river basins, the soil active ratio of Fe, water- and acid-soluble Fe(II) in the profiles decreased in the sequence of wetland-R > wetland-C > cultivated land, indicating that the ability of Fe mobilization and export tended decrease way from the river.

As an active component, water-soluble Fe(II) is sensitive to change of soil environment and can directly reflect the soil redox conditions and emergent climate events (Zou et al., 2009). In current study, soil water-soluble Fe(II) in deep layers might be contributed by Fe(II) leaching from upper layers and in situ Fe(III) reduction associated with gleyization. It can be verified by the characteristic gleyic color patterns found in the 60–80 cm wetland soil layers.

Soil acid-soluble Fe(II) in wetland, including Fe oxides and Fe-organic particle, can be used to characterize the potential migration ability of Fe in the soil (Pan et al., 2010b). Previous studies have revealed that most of the dissolved ferric Fe is present as organic Fe complexes in surface waters (Pan et al., 2010b; Powell and Donat, 2001). Therefore, high DOC concentrations in riparian wetlands in this study would be of great benefit to transport of Fe and other elements in rivers and estuaries (Ross and Sherrell, 1999; Sholkovitz and Copland, 1981). In addition, the significant positive relationship between acid-soluble Fe(II) and DOC suggested that different soil DOC undoubtedly contributed to the observed differences in the mean concentration of soil acid-soluble Fe(II) among different soil profiles.

5. Conclusion

The reclamation of wetland in the Sanjiang Plain resulted in aggravating fragmentation of wetlands, which influenced spatial distribution, mobilization and export of soil Fe. The wetland reclamation reduced the activity of soil Fe due to a lower groundwater level and artificial disturbances, preventing the mobilization and export of soil Fe, while the different hydrogeological conditions in the wetland-R and wetland-C also caused differences in fractionation and migration of soil Fe. As a result, the soil total Fe in the profile above 60 cm increased in the sequence of...
wetland-R → wetland-C → cultivated land; the soil active ratio of Fe, water- and acid-soluble Fe(II) in the profiles decreased in the sequence of wetland-R → wetland-C → cultivated land. It indicated that the ability of Fe mobilization and export in the three river basins tended decrease away from the river. The correlation analyses showed that DOC were positively correlated with acid-soluble Fe(II) while negatively correlated with total Fe, implying that DOC might promote the production of acid-soluble Fe(II) and play a key role in export of Fe from riparian zone to adjacent waters.

Considering that the Sanjiang Plain encompasses numerous natural freshwater wetlands, large scale field observations and controlled experiments are needed in further study to fully understand the behaviors of soil iron in riparian zones and to quantify the flux of dissolved iron from the Sanjiang Plain to the Amur River. It is hoped this article will stimulate further research in this area.

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