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Trace metals in estuaries in the Russian Far East and China: Case studies from the Amur River and the Changjiang

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HIGHLIGHTS

- High dissolved Fe and Mn, and low suspended solids occur in the Amur River.
- Elevated suspended solids and pH, and low dissolved metals, occur in the Changjiang.
- Fe removal from, and Cd and Mn transfer to solution, are usual in Amur River estuary.
- Increase of dissolved trace metals occur in the Changjiang estuary.
- River composition controls the behavior of metals in estuaries and fluxes to the sea.

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ABSTRACT

This paper compares the distributions of dissolved and particulate forms of Mn, Fe, Ni, Cu, Zn, Cd, and Pb in the estuaries of the largest rivers in East Asia: the Amur River and the Changjiang (Yangtze River). High suspended solid concentrations, elevated pH, and relatively low dissolved trace metal concentrations are characteristics of the Changjiang. Elevated dissolved Fe and Mn concentrations, neutral pH, and relatively low suspended solid concentrations are characteristics of the Amur River. The transfer of dissolved Fe to suspended forms is typical in the Amur River estuary, though Cd and Mn tend to mobilize to solution, and Cu and Ni are diluted in the estuarine system. Metal concentrations in suspended matter in the Amur River estuary are controlled by the ratio of terrigenous riverine material, enriched in Al and Fe, and marine biogenic particles, enriched in Cu, Mn, Cd, and in some cases Ni. The increase in dissolved forms of Mn, Fe, Ni, Cu, Cd, and Pb compared with river end-member is unique to the Changjiang estuary. Particle–solution interactions are not reflected in bulk suspended-solid metal concentrations in the Changjiang estuary due to the dominance of particulate forms of these metals. Cd is an exception in the Changjiang estuary, where the increase in dissolved Cd is of comparable magnitude to the decrease in particulate Cd. Despite runoff in the Amur River being lower than that in the Changjiang, the fluxes of dissolved Mn, Zn and Fe in the Amur River exceed those in the Changjiang. Dissolved Ni, and Cd fluxes are near equal in both estuaries, but dissolved Cu is lower in the Amur River estuary. The hydrological and physico-chemical river characteristics are dominated at the assessment of river influence on the adjoining coastal sea areas despite differences in estuarine processes.

1. Introduction

The watersheds of China and the Russian Far East have diverse geological and geomorphological characteristics, climates, and landscapes, and make a significant contribution to global water and biogeochemical cycles at the land–sea interface. Watersheds in China and the Russian Far East collectively cover a wide latitudinal range, from tropical to sub-polar areas, and river runoff from these regions thus provides a considerable portion of the dissolved and suspended matter delivered to the northwest Pacific and Arctic oceans (Meybeck and Ragu, 1997; Zhang, 2002). Large rivers in East Asia include, but are not limited to the Changjiang (Yangtze River) and Amur River, which are ranked 4th and 16th in the world in terms of discharge, (Meybeck and Ragu, 1997). Their runoff is one of the factors that control biological production and water quality within large coastal areas of the East China Sea, Yellow Sea, Sea of Japan/East Sea, and Okhotsk Sea (Zhang, 2002; Lin et al., 2005; Nishioka et al., 2007; Fan and Huang, 2008; Nishioka et al., 2011).

Suspended solids, trace metals (e.g., Mn, Fe, Ni, Cu, Zn, Cd, and Pb), and plant nutrients (e.g., N, P, and Si) have different concentrations in river and seawater. Thus, the transformation of river runoff in estuarine

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zones significantly modifies the net fluxes of chemical elements delivered by rivers to adjacent coastal environments (Gordeev and Lisitsyn, 1978; Edmond et al., 1985; Bewers and Yeats, 1989; Statham, 2012).

There are a number of studies that have documented the chemical composition of Chinese rivers and their estuaries (Zhang et al., 1988; Huang et al., 1992; Zhang and Huang, 1993; Zhang et al., 1999; Wang and Liu, 2003; Koshikawa et al., 2007; Müller et al., 2008; Zhang et al., 2008). Compared with rivers of the Russian Far East and Arctic watersheds, most large Chinese rivers drain into densely populated areas. Intensive land-use in these watersheds is accompanied by increased weathering and erosion, and higher suspended matter loads in rivers. The monsoon climate and abundance of loess in some Chinese watersheds result in high background suspended solid loads. Historically, trace metal concentrations in suspended solids in large Chinese rivers were lower than in European rivers, and similar to other large minimally-disturbed aquatic systems (e.g., the Amazon and Orinoco rivers). This illustrates the effect of weathering products (e.g., soils) on elevated suspended solid loads in Chinese rivers (Zhang, 2002). The distribution of particulate trace metals, along with salinity gradients, is relatively stable in Chinese estuaries compared with European estuaries where particulate element concentrations tend to decrease with salinity growth (Zhang and Liu, 2002).

Dissolved trace metal concentrations in large Chinese rivers are, on average, comparable with less-disturbed rivers in Europe and North America (Zhang, 2002; Koshikawa et al., 2007; Müller et al., 2008). However, mobilization to solution is an important feature of dissolved trace metals in Chinese estuaries, and the behavior of dissolved trace elements is more diverse than for particulate forms (Zhang, 1995; Wang and Liu, 2003; Koshikawa et al., 2007). Dissolved Fe, for example, transfers readily to solution in the extremely turbid Huanhe estuary (Zhang, 1995), while in other estuaries (including the Changjiang estuary), flocculation and coagulation processes prevail (Sholkovitz, 1976; Edmond et al., 1985; Koshikawa et al., 2007).

Previous studies have also documented chemical processes in estuaries in the Russian Far East, including the Amur River estuary (Shulkin, 2006; Dudarev et al., 2009). Rivers in the Russian Far East primarily drain through mountainous and forested areas, and the population is low compared with China. For example, forested and vegetated land in the Russian portion of the Amur River watershed (54% of the watershed surface area) covers 792,500 km^2 compared with 395,000 km^2 in the Chinese portion of the watershed (Ganzey et al., 2007). When Russian rivers flow through populated areas, the anthropogenic impact on watersheds is localized and concentrated around settlements. Vast wetlands also occur in the downstream reaches of many rivers in the Russian Far East. For example, wetlands and lakes in the Amur River basin cover 150,000 km^2, and two-thirds of this area is contained in the Russian part of watershed (Ganzey et al., 2007).

Suspended solid concentrations in rivers of the Russian Far East have significant seasonal variability, but the annual average tends to be appreciably lower than for Chinese rivers. The annual average in the Amur River, for example, is 72 mg/L (Gaillardet et al., 1999) compared with about 500 mg/L in the Changjiang (Yang et al., 2006). Trace metal concentrations in suspended solids in rivers of the Russian Far East lie within the same range as those observed in Chinese rivers, but elevated concentrations are found in tributaries and in small rivers where there is significant anthropogenic disturbance (Shulkin et al., 2007; Chudaeva and Chudaev, 2011).

Concentrations of dissolved trace metals in large rivers of the Russian Far East are low compared with contaminated rivers in Europe and North America, but comparable with large Chinese rivers. Dissolved Mn, and especially Fe, are the exceptions, with concentrations one order of magnitude higher than in Chinese rivers (Shulkin, 2006; Chudaeva and Chudaev, 2011). The elevated concentrations of dissolved Fe in Amur River runoff has led to a hypothesis that this watershed plays a leading role in the supply of Fe to marine ecosystems in the Okhotsk Sea, as well as the adjacent northwest Pacific Ocean (Nishioka et al., 2007).

The distribution of trace metals in estuaries of the Russian Far East is dependent on river end-members. For example, when Mn, Zn, Cu, and Cd concentrations are elevated in suspended solids, there is mobilization/desorption of these metals to solution (Gordeev et al., 1983; Shulkin and Bogdanova, 1984). The transfer to the suspended forms at the salinity growth prevails for the dissolved Fe regardless the concentrations in river waters (Shulkin, 2006). The next major controlling factors on the distribution of trace metals are dynamic conditions within an estuary, which define the residence time of water and suspended matter in areas of intermediate salinity.

The aims of this paper are: (1) to highlight the features of trace metal geochemistry in river runoff in the Russian Far East and East China, using the Amur River and the Changjiang as case studies; (2) to compare the distribution of dissolved and suspended trace metals in the estuaries of these rivers; and (3) to identify the main reasons for similarities and differences in trace metal behavior in estuaries in East China and the Russian Far East, and compare trace metal behavior in these estuaries with other global river systems.

2. Environmental setting

2.1. Amur River and estuary

The Amur River is the largest river in the Russian Far East, with an annual water discharge of 344 km^3, and a watershed that covers an area of 1.8555×10^6 km^2 distributed between Russia (54%), China (44%), and Mongolia (2%). The Russian portion of the Amur basin is mainly forested, while grassland and semi-arid areas dominate the Chinese part of watershed. Uneven population distribution is another peculiarity of the Amur River basin. In China, the basin is home to more than 67.5 million people, which is almost 10 times higher than the Russian part of the basin, which has 7.1 million people. The population density in the northern watershed, in the Russian Khabarovsk and Amursk provinces, does not exceed 2.3 persons/km^2, which is more than an order of magnitude lower than in the Chinese Heilongjiang and Jilin Provinces where the population density is 83–151 persons/km^2. In the low part of the Amur River basin, there are a number of villages but only two cities, Komsomolsk-on-Amur and Nikolaevsk, with populations of around 20,000. This population distribution influences the flux of chemical substances into the river in the upper and middle reaches of the Amur River. Downstream from Khabarovsk, the river drains along a distance of around 1000 km through a sparsely populated and forested area, with a wide swampy flood plain. These wetlands play an important role as natural filters for the removal of pollutants from terrestrial sources upstream, and can also act as a reductive environment, releasing Fe and Mn downstream.

The hydrological regime of the Amur River is characterized by a distinct discharge minimum of 1500–4500 m^3/s from December until April, when the river and estuary are covered by ice. Snowmelt in spring results in an increase in water discharge: from 13,800–19,500 m^3/s in May to 17,700–27,300 m^3/s in June. In mid-summer, water discharge tends to decrease (Fig. 1), but in some years, heavy typhoon rains in August and September can lead to flooding with a maximum monthly discharge of 36,000 m^3/s (Anon, 1986). Between 2005 and 2012, there were no typhoon-induced floods in the downstream reaches of the Amur River, but in summer 2013 high rainfall caused an unprecedented summer flood.

The Amur River estuary consists of Amur Liman, the adjacent south Sakhalin Bay, and northern Tatar Strait (Fig. 1). Salinity decreases significantly in these areas due to river dilution of estuarine waters. The central part of the estuary is Amur Liman; a vast shallow water area (about 5000 km^2) situated between the Russian mainland and Sakhalin Island. The average water depth in Amur Liman is 2.5 m only.