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Assessment of heavy metal pollution in Red River surface sediments, Vietnam

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ABSTRACT

Surface sediment samples were collected from upstream down to the subaqueous delta of the Red River in Vietnam to assess heavy metal pollution. Sediment Cr and V concentrations are strongly correlated with Al, Fe, Mn and total organic carbon concentrations, as well as particle size, suggesting that these two metals are derived primarily from natural sources and enriched in the fine fraction of sediments. In contrast, Cu, Cd, Pb, Ni and Zn concentrations show weaker correlations with particle size, with very high concentrations observed at several sites in the upper reach of the river, pointing to anthropogenic input as a possible source of these heavy metals. Enrichment factors (EF) of Cu, Cd, Pb, Ni and Zn suggest that heavy metal pollution is present in sediments with significantly high values in the upstream. The data analysis indicates that Cd, Cu and Pb are the dominant pollutants in the Red River, with their concentrations reaching moderate to serious pollution levels.

Heavy metal pollution in many river systems of the world is a common environmental problem due to rapid population growth, industrialization and economic development (Förstner, 1981; Hudson-Edwards et al., 2001; Staley et al., 2015). River sediments tend to be the repository of heavy metals which are potential secondary source of metal pollutants to the overlying aquatic systems (Adams et al., 1992). Heavy metals are non-degradable and toxic, and as such, heavy metal pollution in river sediments is drawing global attention (Soares et al., 1999; Fu et al., 2012; Shafie et al., 2014; Nan et al., 2016).

Water pollution in Vietnam has been increasing over the last 30 years. In particular, downstream reaches of rivers, lakes and canals in urban areas are the most polluted (WEPA, 2011). The Red River, which originates from China, is the second largest river in Vietnam. The Red River has two major tributaries, the Da River and the Lo River, which have their head sources in China (Fig. 1). It plays an important role in the economic, cultural and social life of the Vietnamese people. With a population density varying from 80 to >1000 inhabitants/km^2 in different sectors of its watershed, the Red River system is a typical example of a subtropical system experiencing rapid increasing population pressure (Le et al., 2010). Driven by urbanization, industrialization and the intensified use of agrochemicals, a large amount of waste water containing heavy metals is discharged into the Red River system. For example, arsenic concentration in the Red River in Hanoi exceeded the WHO provisional guideline value of 10 μg/L (Berg et al., 2001). Heavy metal pollution is therefore becoming a critical issue in the Red River water management. Understanding the status of heavy metal pollution in the Red River is critical for remediating pollutants in the environment. There have been several heavy metal pollution studies in the Red River delta (Ho and Egashira, 2000; Phuong et al., 2010; Thuong et al., 2013). Coastal environmental research requires knowledge about the source, transport and fate of the contaminant in the riverine, estuarine and coastal system. However, a source-to-sink analysis for heavy metal pollution in the Red River sediments is still quite limited. In this study, heavy metal distributions in the Red River sediments are investigated from its upper reach down to the subaqueous delta. The purpose of this study is to gain a better understanding of environmental status of the Red River due to sediment heavy metal pollution.

The catchment of the Red River is dominated by Paleozoic sedimentary rocks together with metamorphic and igneous rocks distributed along the main stream and in the Lo River basin (Borges and Huh, 2007). The river basin is within a subtropical monsoon climate region with a mean annual rainfall of 1590 mm. The wet season (May–October) accounts for 85–95% of the total annual rainfall. Mean annual temperature in the upstream region ranges from 14 to 16 °C in winter to 26–27 °C in summer, and 17 to 30 °C in the delta area, which is slightly higher than that in inland (Le et al., 2007). Thao River, which is the main stream of the Red River in the upstream, is the major source of sediments. Contribution of sediments from the Da River is minor due to the closure of the Hoa Binh Dam in 1989 (Fig. 1). According to the

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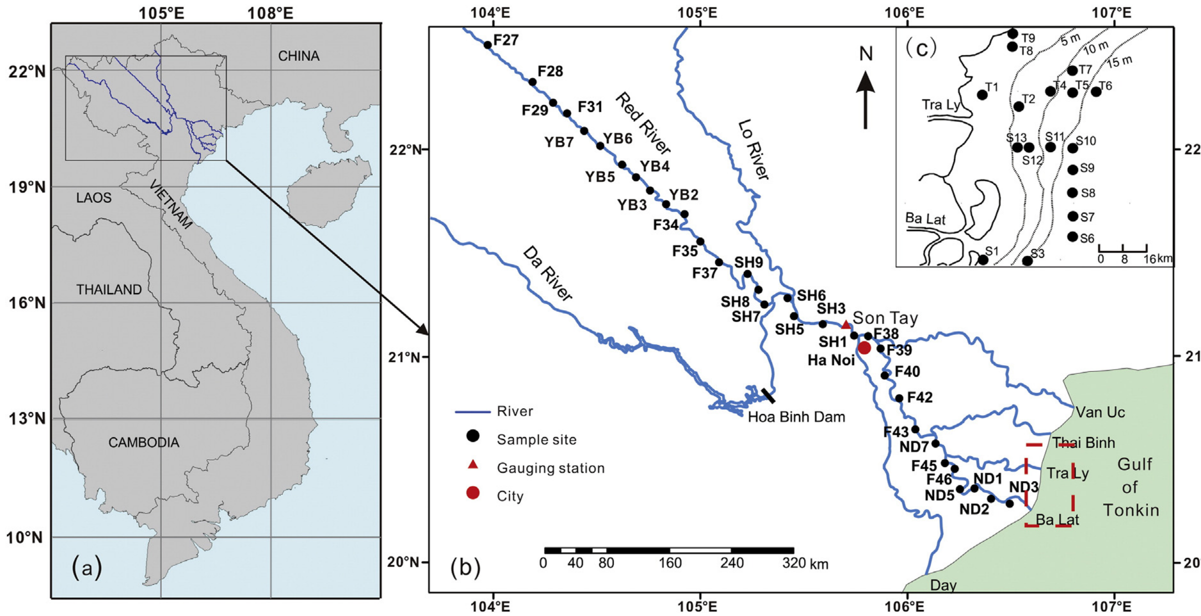

Fig. 1. Map of the study area (a), with the sampling sites detailed in (b). The inset map in (b), map (c), shows the sampling sites in the subaqueous delta.

Food and Agriculture Organization classification system, soils in the upper basin of the Red River are typically Acrisols and Ferrasols (Gong, 1999), and the river is named after the red color of the eroded laterite soils. At present, the main outlet of the Red River is the Ba Lat mouth, which releases 38% of the fluvial sediment (Fig. 1) (Duc et al., 2007). Geomorphologically, the subaqueous delta is divided into an erosional shoreface zone (water depth <5 m), a delta front at the Ba Lat mouth, and a prodelta zone (water depth 5–30 m) (van den Bergh et al., 2007). Sand dominates in the shoreface zone, while silt and clayey silt are dominant in the delta front and prodelta zone, respectively (Duc et al., 2007).

A total of 50 surface sediment samples were collected using a plastic sampler or a grab sampler between 2007 and 2015 (Fig. 1). In 2007, fourteen samples were collected at Sites F27–F31, and F38–F46 on the river bank along the main channel of the Red River, and eighteen surface sediment samples were collected in the subaqueous delta, respectively. In 2014, sixteen samples were collected at Sites SH1, SH3, SH5–SH9, ND1–ND3, ND5 and ND7. Six samples were collected at Sites YB2–YB7 in 2015. All the sediment samples were dried at 40 °C, then disaggregated prior to the analysis. Sites F27–F38 are located in the upper and middle sections of the Red River. Downstream below Site F39, the river branches into several distributaries, which belong to the Red River delta plain. Sites S1, T1, T8 and T9 are within the shoreface zone (<5 m), while the other sites (i.e., S3, S6–S13, T2 and T4–T7) are in the pro-delta zone (>5 m).

For heavy metal analysis, sediment samples were digested using a mixture of concentrated HF–$HClO_4$–HNO_3 acids, following the method described in Zhang et al. (2009). The samples were then analyzed for Cd, Cu and Pb concentrations using a graphite furnace atomic absorption spectrometer (Perkin Elmer A Analyst 800), and for Al, Fe, Cr, Mn, Ni, V and Zn concentrations using Inductively Coupled PlasmaOptical Emission Spectrometer (iCAP™ 7400 ICP-OES Analyzer). The reagent blanks were monitored throughout the analysis. China Stream Sediment Reference Material (GSD9, now named GBW07309), issued by the General Administration of Quality Supervision, Inspection and Quarantine of the People's Republic of China, was analyzed along with the samples for quality assurance purposes. The analytical results of metal concentrations for GSD9 were within the range of the certified values and the analytical precision was better than 10% based on the replicate analysis for each batch of samples. Total organic carbon (TOC) was determined by titration with $FeSO_4$ after digestion with $K_2Cr_2O_7$–H_2SO_4 solution (Lu, 2000). Data on particle size distributions of the samples are cited from work done by Nguyen et al. (2016).

Table 1
Heavy metal concentrations in sediments of the Red River, Vietnam (unit % for Al and Fe, while mg·kg^{-1} for the other elements).

	Al	Fe	Mn	Cd	Cr	Cu	Ni	Pb	Zn	V	Reference
	%		mg·kg^{-1}								
Red River sediment											
Min-Max	2.62–8.92	1.51–5.66	258–1240	0.06–1.40	23.88–113.08	20–332	12–122	27–188	40–287	46–140	
Mean ± SD	6.30 ± 1.71	3.76 ± 0.99	806 ± 236	0.35 ± 0.27	85.71 ± 23.75	83 ± 55	38 ± 17	66 ± 28	127 ± 50	97 ± 27	
Red River bank	6.06 ± 1.67	3.84 ± 1.05	826 ± 262	0.46 ± 0.28	81.69 ± 25.40	98 ± 63	37 ± 20	68 ± 32	127 ± 57	88 ± 21	This study
Subaqueous delta (<5 m)	3.92 ± 0.07	2.08 ± 0.04	474 ± 144	0.08 ± 0.02	59.91 ± 10.27	26 ± 5	21 ± 4	32 ± 5	64 ± 8	61 ± 10	
Subaqueous delta (>5 m)	7.58 ± 0.06	4.07 ± 0.02	856 ± 59	0.18 ± 0.04	102.29 ± 4.75	63 ± 11	44 ± 3	71 ± 7	144 ± 12	126 ± 8	
Soil, Red River delta				0.21	137.22	58.14		45.89	109.14		Phuong et al. (2010)
Suspended sediment	9.85	5.46		0.59	160	94	100	129	179		Gaillardet et al. (1999)
Ba Lat estuary				0.4	66.95	73.49		81.59	134.38		Nguyen et al. (2011)
Cam River	5.36 ± 0.87	3.62 ± 0.35	827 ± 94		90 ± 11	82 ± 16	38 ± 6	92 ± 15	178 ± 31		Ho et al. (2013)
Upper Continental Crust	8.04	3.5	600	0.098	35	25	20	20	71	60	Taylor and McLennan, 1995

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