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Enrichment and mechanisms of heavy metal mobility in a coastal quaternary groundwater system of the Pearl River Delta, China

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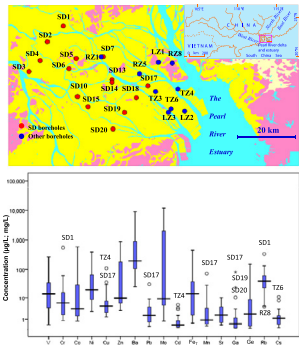
HIGHLIGHTS

- Heavy metals enriched in sedimentary organic matter, carbonate and Fe-Mn oxides.
- Heavy metal mobility is significantly influenced by hydrogeochemical conditions.
- Mobility of V, Ba, Cr, Rb and Cs is related to organic matter decomposition.
- Mobility of Co, Ni, Cu, Zn, Pb and Cd is due to reducing dissolution of Fe-Mn oxides.
- Mobility of Co, Ni, Cu, Ba, Zn, Pb, Cd, Mn, Sr and Ga may be due to ion exchange.

GRAPHICAL ABSTRACT



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ABSTRACT

The risks posed by heavy metal mobilization strongly depend on the pathways that the metals follow, with the sediment-water pathway representing a direct risk to groundwater contamination. Monitoring and sequential extraction experiments in the laboratory generally have limitations with respect to understanding the mechanisms of heavy metal mobilization in the field. The Quaternary coastal groundwater system of the Pearl River Delta, China was chosen as the study area to understand heavy metal enrichment and mobility. Heavy metals including V, Cr, Co, Ni, Cu, Zn, Ba, Pb, Mo, Cd, Sr, Ga, Ge, Rb, and Cs in both sediments and groundwater were analyzed. Geochemical parameters including Fe_2O_3, MnO, sedimentary organic matter, and carbonate content as well as hydrochemical parameters including K^+, Na^+, Ca^{2+}, Mg^{2+}, NH_4^+, SO_4^{2-}, Cl^-, HCO_3^-, pH, TDS, and dissolved organic carbon were also measured. The enrichment of heavy metals in the solid sediment phase as well as the mobilization mechanisms of heavy metals in groundwater are discussed as informed by Pearson's correlation analysis. Hydrochemical analyses demonstrated that the mobility of V, Ba, Cr, Rb, and Cs is closely related to the decomposition of buried sedimentary organic matter; the mobility of Co, Ni, Cu, Zn, Pb, and Cd is closely linked with the reductive dissolution of Fe–Mn oxides; and the mobility of Co, Ni, Cu, Ba, Zn, Pb, Cd, Mn, Sr and Ga is probably controlled by ion exchange processes. This study demonstrates that heavy metal mobility in the field is not entirely consistent with the potential mobility as indicated by sediment analysis, due to the complicated hydrogeochemical conditions in the groundwater system, and suggests that comprehensive geochemical and hydrochemical studies are useful ways to understand the mobility mechanisms of heavy metals in the field.

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1. Introduction

The environmental fate of heavy metals in a groundwater system (e.g., mobility, bioavailability) depends not only on their total content and distribution in the solid phases to which they are bound (Ure and Davidson, 2001) but also on the specific hydrogeochemical conditions of the groundwater system. Heavy metals bound to various solid phases in sediments/soil can be released into groundwater via a range of physical-chemical processes (e.g., desorption, dissolution, ion-exchange), and these releasing processes can be influenced by physical-chemical conditions of the groundwater system, such as pH, salinity, and cation exchange capacity (Tack and Verloo, 1995; Appelo and Postma, 2005; Skrbic and Djurisic-Mladenovic, 2010).

Many studies have been carried out to understand the mobility mechanisms of heavy metals in groundwater systems. For example, simulation experiments have been carried out in the laboratory to study the influences of specific factors, such as pH, salinity, and evaporation, on heavy metal mobility (Acosta, Jansen, Kalbitz, Faz, and Martínez-Martínez, 2011; Wang and Mulligan, 2013; Lima, Safar, and Loch, 2014), and sequential extraction experiments have been widely employed to understand the speciation and mobility of heavy metals in sediments (Gomez Ariza, Giraldez, Sanchez-Rodas, and Morales, 2000; Kraus and Wiegand, 2006; Ho, Swennen, Cappuyns, Vassilieva, Van Gerven, and Tran, 2013). However, laboratory experiments generally have limitations with respect to evaluating the fate of heavy metals in groundwater systems. Simulation experiments in the laboratory are often carried out to evaluate only one or two specific influencing factors, but real situations in the field can be much more complicated by a series of physical-chemical parameters that simultaneously affect the mobility processes of heavy metals. In addition, the mobility of heavy metals in the field is a result of interactions between the sediments/soil and groundwater, and these interactions can be influenced by various hydrogeochemical processes. However, sequential extractions can only be used to help to understand the potential mobility of heavy metals in sediments (Long, Hu, Fang, Wu, and Shen, 2009; Relic, Dordevic, Popovic, Jadranin, and Polić, 2010; Kumar, Furumai, Kurisu, and Kasuga, 2013).

As the risks posed by mobilization of heavy metals strongly depend on the pathways that the heavy metals follow, understanding the sediment/soil-water pathways that pose direct risks of groundwater contamination is essential to groundwater management in coastal groundwater systems. There is growing concern regarding heavy metal contamination in groundwater in coastal aquifers (Leung and Jiao, 2006; Huang, Huang, Jiao, and Chen, 2007; Upadhyaya, Survaiya, Basha, Mandal, Thorat, Haldar, Goel, Dave, Baxi, Trivedi, and Mody, 2014), many of which are used as drinking water resources; coastal aquifers are also important links for terrestrial and marine biogeochemical cycles (Moore, 1999; Slomp and Van Cappellen, 2004).

This study aimed to understand the enrichment and mobility mechanisms of heavy metals in a coastal Quaternary groundwater system by undertaking both geochemical and hydrochemical studies on sediment and groundwater samples. A multivariate statistical method was employed in the analysis and informed the discussion. Geochemical and Pearson's correlation analyses were used to assess the enrichment of trace elements in various solid sediment phases.

The coastal Quaternary groundwater system of the Pearl River Delta (PRD), China, was chosen as the study area. Geochemical, hydrochemical, and hydrogeological conditions of this coastal aquifer-aquitard system have been well documented (Wang and Jiao, 2012; Wang, Jiao, and Cherry, 2012; Wang, Jiao, Cherry, and Lee, 2013). Heavy metal contamination in shallow groundwater in the PRD has been studied (Huang, Sun., Zhang, Chen, and Liu, 2013), but the enrichment and risks of heavy metal contamination in the coastal Quaternary groundwater system in the PRD remain unclear. Runoff from PRD estuaries contains large amounts of heavy metals and metalloids (SOAPRC, 2009) and intensive interactions have been identified between the river water and the groundwater in the PRD estuary (Liu, Dai, Chen, Huh, Wang, Li, and Charette, 2012). Therefore, groundwater in the PRD Quaternary aquifer is believed to be one of the potential sources of heavy metals in the river runoff and the coastal waters. This results of this study will contribute to a greater understanding of the enrichment of heavy metals in the sediments and groundwater, and the possible mobility mechanisms of heavy metals in the PRD region.

2. Geological and hydrogeological settings

The PRD is located in the coastal area of the South China Sea (Fig. 1A). The Pearl River drainage basin in the delta plain is largely covered by late Quaternary sediments, and locally the bedrock formed during Cambrian to Tertiary outcrops (Long, 1997).

The formation and evolution of the PRD is due to a series of sea level variations in the late Quaternary, and many studies have been carried out to understand the associated formation processes of the delta (Huang, Li, Zhang, Li, and Qiao, 1982; Wu, Ren, Bao, Lei, and Shi, 2007; Yim, Hilgers, Huang, and Radtke, 2008; Zong, Yim, Yu, and Huang, 2009). It has been suggested that the late Quaternary stratigraphic units of the PRD are generally composed of four sedimentary sequences (Zong, Yim, Yu, and Huang, 2009), including two terrestrial units, named T1 and T2, and two marine units, named M1 and M2 (Fig. 1B). The unit at the bottom is the old terrestrial sediments (T2), mainly composed of sand and gravel. T2 was widely distributed in palaeo-valleys prior to the when the last transgression occurred in the late Pleistocene. A layer of old marine sediments (M2), mainly composed of silt and clay, was deposited above T2 during the last transgression in the late Pleistocene. The upper part of the old marine sediment M2 was weathered due to low sea level through the last glacial period. Concurrently, a younger terrestrial unit was distributed along palaeo-river channels. The terrestrial sediments are mainly composed of sand and gravel. The weathered old marine sediments and the younger terrestrial sediments constitute T1. During the early Holocene, the PRD experienced large-scale transgression, and this rapid rise in sea level resulted in a layer of younger marine sediment (M1) comprised of silt and clay. The thickness of T1 varies from 5 to 20 m. Fig. 1B shows the four sedimentary units and the calibrated ^{14}C ages as per previous studies (Huang, Li, Zhang, Li, and Qiao, 1982; Li, Qiao, Zheng, Fang, and Huang, 1991; Zong, Yim, Yu, and Huang, 2009).

The fine texture of silt and clay makes M1 and M2 the effective aquitards in the PRD groundwater system, and the widely distributed sand and gravel T2 forms the basal aquifer. The river network is extensively developed in the delta plain area (Fig. 1A). The elevation of the PRD plain is about 6–9 m above sea level (asl) in the north and about 1–2 m asl in the coastal area (GHT, 1981). Because the gentle topographic slope of the plain is toward the southeast coast, and shallow groundwater table in the delta follows the topography, driving the shallow groundwater flow toward the coast. Based on the distribution of equipotential lines of the basal aquifer, regional groundwater flow directions are also toward the southeast coast (Wang, Jiao, Cherry, and Lee, 2013) and quite similar to that of the shallow groundwater flow.

3. Field and laboratory methods

3.1. Sediment and groundwater sample collection

A total of 24 hydrogeological boreholes were drilled in the PRD region and their locations are shown in Fig. 1A. A rotary drilling method was used, and sediment samples were collected from the center part of the drilling cores at different depths immediately after drilling. Temporary wells were installed after borehole drilling. Well development was fully carried out, and groundwater samples were collected when pumping water became clear. Groundwater samples of the basal aquifer were collected from boreholes with the prefix 'SD' (marked in red in Fig. 1A). However, groundwater from the other nine boreholes (marked