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Uranium distribution in the sediment of the Mianyuan River near a phosphate mining region in China and the related uranium speciation in water

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ABSTRACT

To clarify the mechanisms of uranium distribution in river sediment and its speciation in river water near a phosphate mining region, the sediment and river water in the Mianyuan River in China were investigated. Using linear correlation analysis, it was determined that uranium distribution in upstream sediment is mainly controlled by the adsorption of organic compounds ($R^2_{\text{TOC-U}} = 0.848$), whereas distribution is controlled by physical deposition of albite ($R^2_{\text{Na-U}} = 0.773$) in downstream sediment. In addition, it was determined that Se and As had strong and positive linear correlations with uranium in sediment, regardless of whether it was upstream or downstream sediment. This type of relationship was also found in phosphate ores, which suggests that the ore is the common source of U, Se and As in the sediment. The results of speciation-solubility modelling suggest that no precipitation of uranium minerals occurred in river water and the dominant uranium species in river water included: $UO_2(HPO_4)_2{}^{2-}$, $Ca_2UO_2(CO_3)_3$ and $UO_2(CO_3)_3{}^{4-}$. In addition, our modelling indicated the relative species distribution was mainly affected by the pH and the total phosphate concentration.

1. Introduction

Following the nuclear crisis in Japan (Wang and Chen, 2012), environmental problems involving radionuclide contamination have become a social concern because of the radioactive and toxic effects on human health. Environmental and geochemical studies on the behaviour of uranium in water are important because of its wide presence and harmful effects on organisms (WHO, 2004).

Phosphate ore contains a high amount of radionuclide, such as uranium and thorium (Lakehal et al., 2010). An increasing amount of phosphate ore will be exploited because of agricultural development and the accompanying increasing demand for phosphate fertiliser (Nziguheba and Smolders, 2008). The exploitation of phosphate ore can lead to the migration of uranium, most of which ends up in phosphate fertiliser and becomes a potential contamination source (Yamazaki and Geraldo, 2003; Schipper et al., 2011). Uranium can be transported by river and groundwater (Brown et al., 1998; Katsoyiannis et al., 2006). Finally, uranium in the environment is likely to cause environmental and human health problems. It has been reported that the uranium concentration in the blood of people who work in or live near phosphate mines is higher than that of people in cities (Othman, 1993). Therefore, the study of the uranium distribution in river sediment near a phosphate mining region and the uranium species in the water is important to ensure the safety of the people who live by the river.

Sediment is a good object for the study of the behaviour of uranium in the hydrosphere. The mechanisms of uranium distribution in marine sediment (Kirk et al., 1986; Francois et al., 1993; Chaillou et al., 2002; Zheng et al., 2002) and lake sediment (Chappaz et al., 2010) have already been clarified. The most commonly identified mechanism of uranium accumulation in marine sediments is the reduction of U(VI) from soluble carbonate complex to less soluble U(IV) minerals (Klinkhammer and Palmer, 1991). In lake sediment, the solid phase uranium is mainly bound to organic compounds and the uranium in pore water is found associated with Fe oxyhydroxides (Chappaz et al., 2010). However, there have been a few studies involving uranium distribution in river sediment. Understanding uranium distribution in river sediment is essential for understanding uranium migration in the hydrosphere cycle. The migration of uranium in water can be affected by the adsorption and precipitation of related minerals (Davis et al., 1998, 2004).

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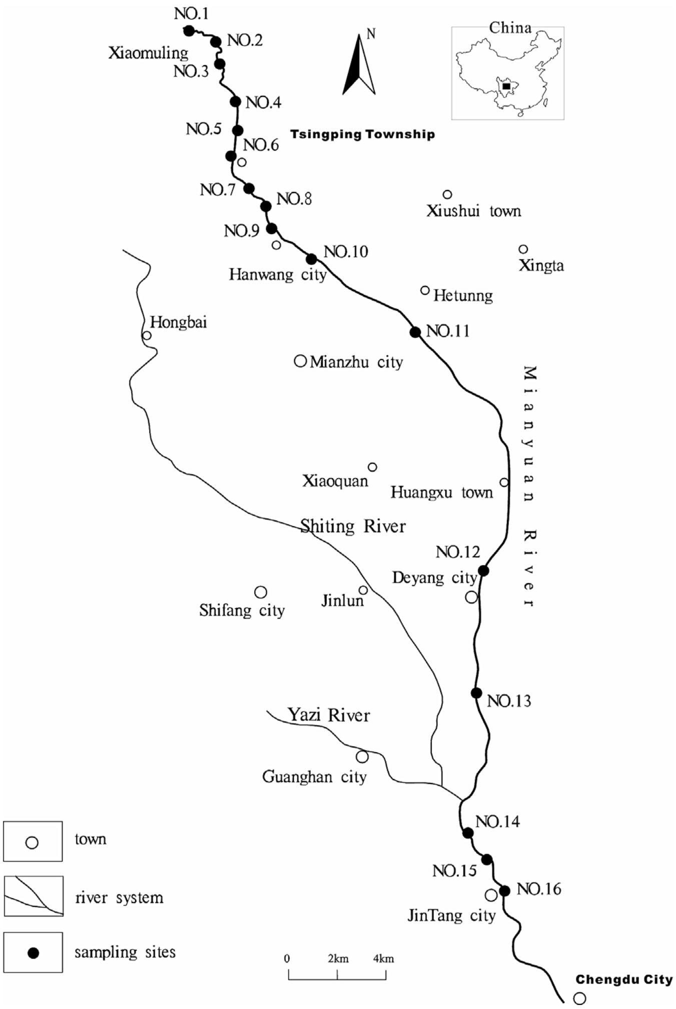

Fig. 1. Location of the sampling sites along the *Mianyuan* River.

The adsorption of uranium by ferrihydrite (Payne et al., 1996; Fox et al., 2006), goethite (Guo et al., 2009), quartz (Fox et al., 2006), hematite (Murphy et al., 1999) and zirconium oxophosphate (Almazan-Torres et al., 2008) has been studied using batch experiments and modelling (Missna et al., 2003; Almazan-Torres et al., 2008). Our specific goals were to understand the mechanisms of uranium distribution in river sediment near a phosphate mining region and to clarify the speciation of uranium in the river water.

2. Materials and methods

2.1. Study area and sampling

The Mianyuan River is located in the northwest of Sichuan Province in China (Fig. 1). It flows through phosphate mining regions (No. 2 and No. 4 in Fig. 1) that were nearly destroyed by the WenChun Earthquake in 2008. River sediment and water were sampled from upstream (No. 1 to 6) to downstream (No. 7 to 16) sites. The location of the sampling sites is presented in Fig. 1. After being filtered through a cellulose acetate membrane with a pore size of 0.45 μm, 2 ml of HCl (1:1) were added to the water sample (2 l) and a matching sample was also collected, but no acid was added. Only clay sediment (approximately 2.5 kg) was selected at each site. At special sites (e.g., dammed lakes sites No. 3 and No. 7, which appeared after the earthquake), parallel sediment samples were collected and the averaged results were used. Site No. 6 was near Tsingping township, which was selected as the dividing point between the upstream and downstream regions (Site No. 6 was classified as being upstream) because Site No. 6 is the dividing point between the mining region and the inhabited area. Site No. 10 is in front of a destroyed dam. Site No. 12 is an artificial lake. Sites No. 14, 15 and 16 are located near farmlands. The local season was spring and the weather was sunny when we collected the water and sediment (without rain) samples. Moreover, the Yazi River and Shiting River (Fig. 1) were completely dried up.

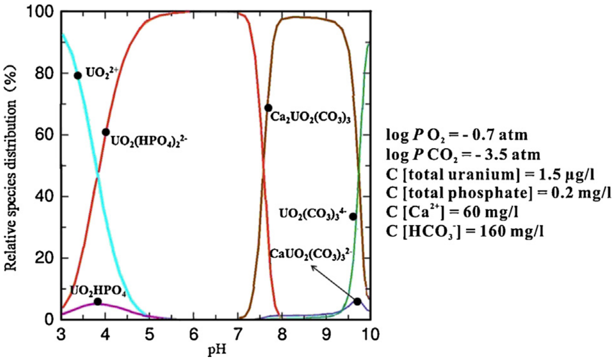

Fig. 2. Relative species distribution of uranium in river water as a function of pH (Only species with a maximum percentage exceeding 5% are plotted).

2.2. Analysis and modelling

2.2.1. River water

The pH, Eh and temperature of river water were in situ analysed. The primary water sample (added HCl) was used to measure the concentrations of metals. The acid-free sample was used to measure the concentrations of anions. Concentrations of K, Na, Ca and Mg were measured using an inductively coupled plasma atomic emission spectrometer (ICP-AES; 6300 Radial, Thermo Fisher Scientific). The precision was 1.1% and accuracy 2.0%. The concentration of U were measured using inductively coupled plasma mass spectrometry (ICP-MS; X Serier II, Thermo Fisher Scientific). The precision and accuracy ranged from 2.2% to 4.0%. The concentration of total phosphate (TP) in water was measured using spectrophotometry. The precision was 2.5% and the accuracy 3.2%. The concentrations of SO_4^{2-}, NO_3^-, NO_2^- and Cl^- were measured using ion chromatography (IC Metrohm 883). The precision and accuracy ranged from 2.3% to 5.0%. The concentrations of HCO_3^- and CO_3^{2-} were measured using the volumetric method; the precision and accuracy ranged from 2.1% to 8.2%.

2.2.2. Sediment

All the sediments were dried, crushed and sieved with a 200 mesh sieve. Large particles and rotted plants were removed. Briefly, sediment samples were digested with HNO_3, $HClO_4$ and HF. After evaporation, the residues were redissolved in a 0.2 N HNO_3 solution. The contents of Ba, CaO, total Fe_2O_3, K_2O, MnO, Al_2O_3, Cr, MgO, Na_2O, P_2O_5, V_2O_5 and Zn in the sediment were measured using ICP-AES and fluorescence spectrometry (XRF-1500, Shimadzu). The precision and accuracy ranged from 0.21% to 5.2%. The contents of Pb, Cd, U and Th in the sediment were measured using ICP-MS. The precision and accuracy ranged from 0.8% to 7.3%. The contents of As and Se were measured using atomic fluorescence spectrometer (AFS). The precision and accuracy ranged from 0.2% to 4%. The content of total organic carbon (TOC) in the sediment was measured using a Carbo Erba analyser. The precision and accuracy were 2.2% and 5.2%, respectively. The sediment chemical analysis result is presented in Appendix A. The primary mineralogical constituents of all sediments were identified using X-ray diffraction (XRD).

2.3. Modelling

The speciation of uranium in water is important to environmental impact and bioavailability (Cheng et al., 2010; Rossiter et al., 2010; Simon et al., 2011; Laurette et al., 2012). In addition, the precipitation of minerals from water can affect the uranium distribution in sediment. Based on the results of our analysis, the uranium speciation distribution and saturated indices of minerals in water were calculated with the software PHREEQC (Parkhurst and Appelo, 1999) using the MINTEQ database (Alison et al., 1991). Moreover, the thermodynamic parameters of important reactions were updated according to the latest reports in the literature (Table 1). The filtered solutions were clean and we assumed that no minerals were supersaturated. The saturation index (SI) was calculated by comparing the chemical activities of the dissolved ions of the mineral (ion activity product, IAP) with their solubility product (Ksp). In equation form, $SI = \log(IAP/Ksp)$. Minerals tend to be precipitated when $SI > 0$, whereas they tend to be dissolved when $SI < 0$ (Parkhurst and Appelo, 1999). This type of modelling has been widely used in many aqueous systems (Sandino and Bruno, 1992; Arnold et al., 2011). Fig. 2 shows the relative species distribution of uranium in water as a function of pH and was drawn according to the major composition of the river water.

3. Results

Uranium displayed strong positive linear correlations with Se, As, Cr, Cd, Ba, Zn and TOC in the upstream sediment (Table 3). In