

As and Pb transportation process in the Red River of Vietnam

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ABSTRACT

To trace transportation system of toxic elements in Red River, major and minor element chemistry of river waters taken from Lao Cai to the river mouth were analyzed. Sample waters were collected in the July to August 2013 (rainy season) and April 2014 (dry season). The concentration of total dissolved components (estimated from EC) was higher in the dry season than in the rainy season due to the evaporation-concentration. Among toxic elements, the total As and Pb concentrations exceeded the WHO standard. The As concentration occasionally exceeded 20 ppb (WHO standard: 10 ppb), and most of those were dissolved phase. Total Pb concentrations were higher than 10 ppb (WHO standard: 5 ppb), and the most of this element behaves with suspended particles. The As concentration is higher in the dry season than the rainy season, while the Pb concentration is much higher in the rainy season than in the dry season. Concentrations of these toxic elements are higher in the main channel than in the branches. Thus, the branch water will be applicable for the alternate water resource for the drinking purpose to the groundwater in Hanoi and other cities.

1. INTRODUCTION

Red River is one of the large rivers originated from Tibet Plateau and runs through the northern part of Vietnam. In Hanoi and surrounding area developed on the Red River delta, people uses groundwater as the main water resource. Shallow groundwaters are occasionally contaminated with As in the Red River delta, and lowering groundwater level in the deep aquifers is threat of water resources in the city area. Riverwater would be an alternate resource, although it has not been effectively used in this area. In this study, riverwater quality was evaluated for a water resource, and the transportation process of As in the Red River was traced.

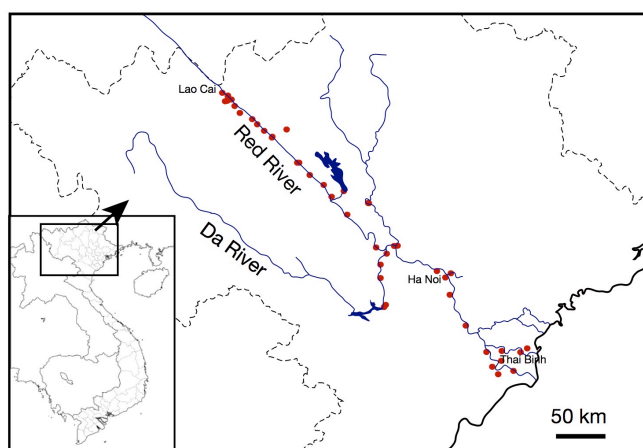


Figure 1 Sampling locations of riverwater in April 2014

2. METHODS

2.1 Sampling of water and sediments

Water was sampled from the Red River on July to August 2013 (28 samples) and April 2014 (45 samples). Sampling locations of the last campaign is in Figure 1. Most of the water samples were taken from the center of the river; from the bridge or using boats, while the others were taken from the shore when no bridge or boats were found. Just after the sampling, water temperature, EC (electric conductivity), DO (dissolved oxygen) and ORP (oxidation-reduction potential) were measured using electrodes. The water samples were bottled in plastic bottles and glass vials with adequate treatments and transported to Japan to analyze in the laboratory. The major and trace components were measured at Osaka City University.

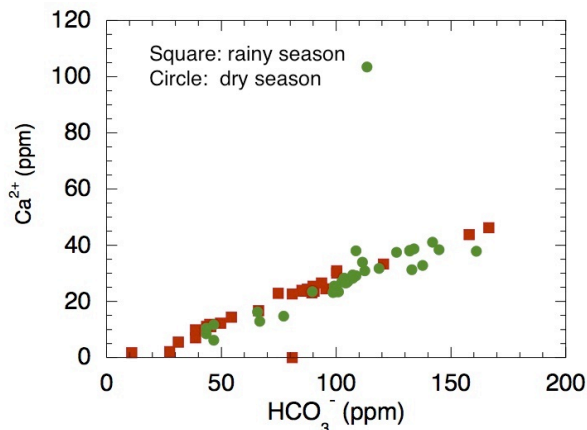


Figure 2 Relationship between HCO_3^- and Ca^{2+} concentrations

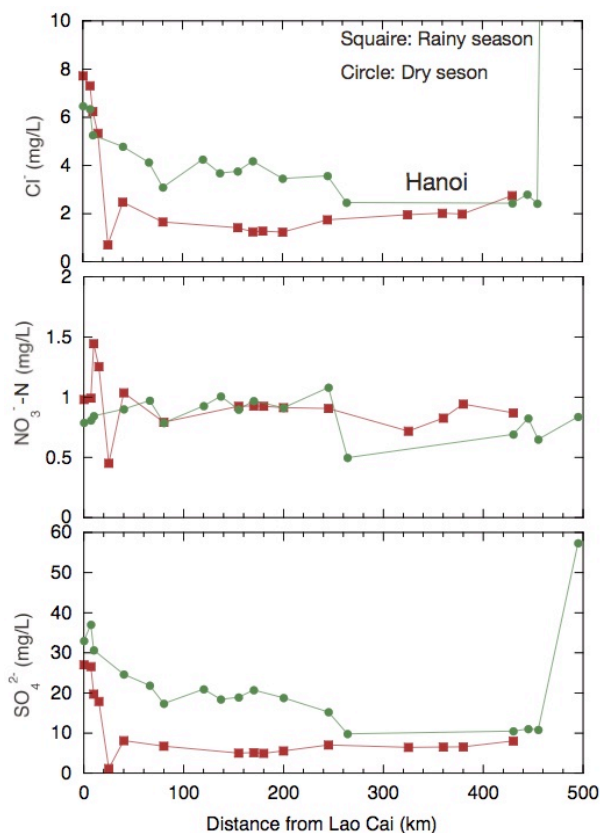


Figure 3 Changes of concentrations of Cl^- , NO_3^- , and SO_4^{2-} of Red River waters with distance from Lao Cai to the mouth

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2.2 Laboratory analyses

Alkalinity was analyzed by titration with HCl, and the other anions were quantified using Ion Chromatography. Among the major cations, Ca and Mg were quantified by EDTA titration, and Na and K were by AAS. Trace elements including As and Pb were quantified by ICP-MS.

Mineralogy of riverbed sediments were determined by XRD, and the major and minor elements were determined by XRF. Total As was analyzed for the solution, which was dissolved in diluted HCl after fusion of the powdered sediments. Sequential chemical extraction was also done for the powdered sediment; the As phases were separated into acid-soluble (carbonates and weakly adsorbed) phase, reducible (Fe-oxyhydroxides and/or Mn oxides) phase, oxidizable (mostly organic and some silicates) phases, and insoluble (silicates and sulfides) phase.

3. RESULTS AND DISCUSSION

3.1 Major water chemistry

Major water chemistry is in general $\text{Ca}^{2+}\text{-HCO}_3^-$ type, and less affected by anthropogenic contamination. Plots of Ca^{2+} and HCO_3^- concentrations are on the regression same between the samples taken in the rainy and dry seasons, indicating simple mixing of $\text{Ca}^{2+}\text{-HCO}_3^-$ type water and diluted water, of which chemistry would be close to that of rainwater (Figure 2). As shown in Figure 3, the highest Cl^- and SO_4^{2-} concentrations were observed at the uppermost main channel at Lao Cai. Although the level of contamination is not serious, the considerable anthropogenic contaminants would be originated from China territory. The concentrations of those components are low between Lao Cai and Hanoi, where inflow from tributaries in Hoang Yen Mountains largely diluted the dissolved components of main channel water. NO_3^- concentration is low compared with the WHO standard (10 mg/L as NO_3^- -N), and most of this component must be derived from cultivated field along the main channel in Vietnam territory.

3.2 As and Pb concentrations of riverwater

Red River water occasionally contains fairly amounts of As and Pb, while the phases of those elements are different. In the rainy season, the highest As concentration is <10 ppb. The concentrations of total As (dissolved and adsorbed ones) and dissolved As are the same within the analytical error, indicating that the most of As is dissolved in the riverwater. The highest concentration of As was 95 ppb (WHO standard: 10 ppb) at the main channel close to Lao Cai in the dry season, however, this high level cannot be explained at present. Except this sample, the highest concentration is about 30 ppb at the uppermost sampling point, and

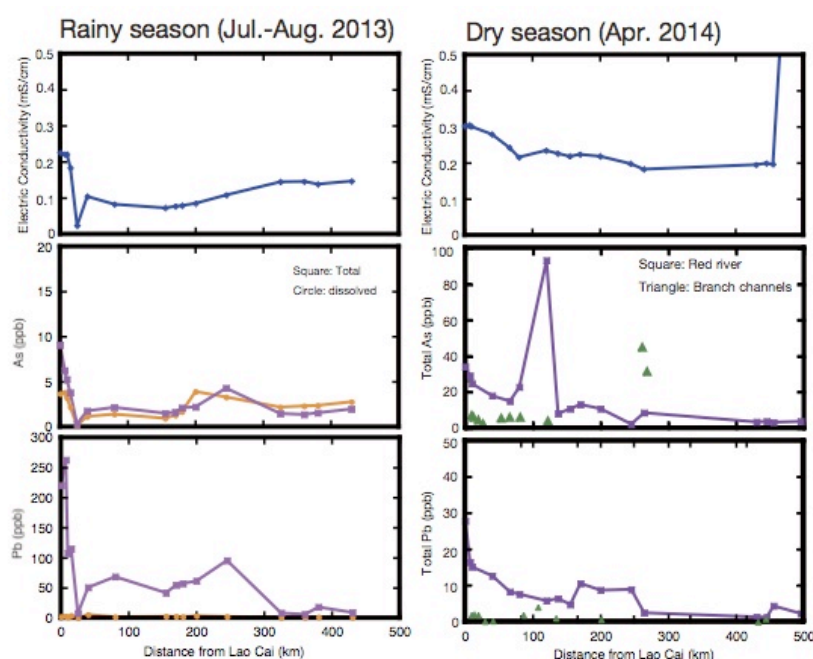


Figure 4 Changes of EC and concentrations of As and Pb along Red River from Lao Cai to the mouth. Give attention to the differences of concentration ranges of As and Pb between the dry and rainy seasons. More detailed description is in the text.

the concentration decreased toward downstream in the dry season. It is notable that the As concentration is higher in the main channel than in the tributaries. EC (electric conductivity) is higher in the dry season than in the rainy season, thus, the As concentration increases due to evaporation and condensation as similar to the other dissolved components such as Cl^- .

Total Pb concentration is higher in the rainy season, and the maximum concentration was 250 ppb (WHO standard: 0.5 ppb). The Pb concentrations are the highest in the uppermost locations in the rainy and

dry seasons. The concentration decreased drastically toward downstream, and it was <1 ppb in the downstream from Hanoi. Dissolved Pb concentration is always less than WHO standard. Thus, it is clear that the Pb is transported with suspended particles.

3.3. As in riverbed sediments

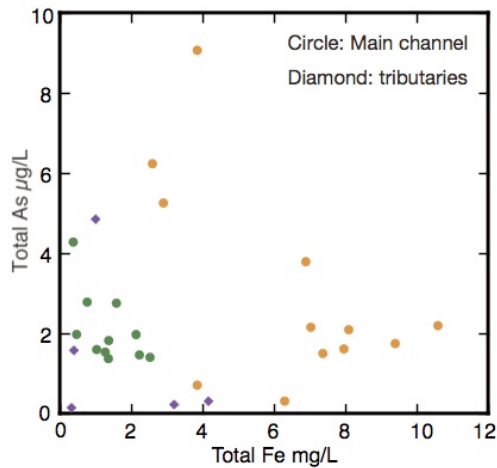


Figure 5 Relationship between total concentrations of Fe and As of waters of Red River and tributaries in Vietnam territory

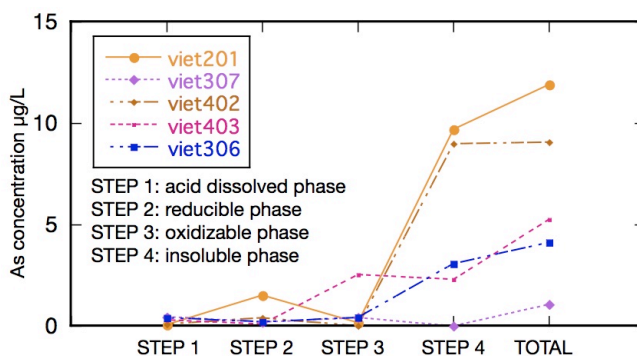


Figure 6 Arsenic concentrations of chemically separated phases in the Red River sediments

actively flowing water. However, As concentration is occasionally higher than the WHO standard. Although the total Pb concentration is also high, this element is easily removed from the water via precipitation since it is adsorbed onto the suspended matters. The As is largely transported with detrital As-bearing mineral(s) in the Red River, and probably causes As polluted groundwater in the delta developed on the downstream. Waters of tributaries in Vietnam territory are not seriously polluted and less contaminated with As and Pb. Those can be used for the supply waters in the city area instead of groundwater.

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Total As of the water samples is of dissolved and acid-soluble components. The latter would mostly be the adsorbed As on the suspended particles. Total Al and Fe of the water samples are derived from acid-soluble suspended particles, similar to the Pb. While, the As concentration did not have positive relationship to those of Al and Fe (Figure 5, only the relationship between Fe and As are shown), consistent with the abundant soluble phase of As in the riverwater. On the other hand, sequential chemical extraction analysis documented that the As in the riverbed sediments were fixed in abundantly insoluble phase(s) (Figure 6), such as silicates and sulfides. At present, the host mineral phase of As is not clear, however, clay minerals including chlorite are one of the candidate

minerals. As concentration of riverbed sediments is 10^3 times higher than that of riverwater, and we can conclude that the abundant As is transported in the Red River by detrital As-bearing minerals.

4. CONCLUSIONS

Waters of Red River generally are diluted Ca^{2+} - HCO_3^- dominant chemistry, which are characteristics of