

Seasonal change of arsenic concentration in groundwater, viewed in sulfur isotopic ratio and related elements

Masako Oono[1]; Harue Masuda[1]; Minoru Kusakabe[2]

[1] Dept. Geosci., Osaka City Univ.; [2] ISEI, Okayama Univ.

Introduction

Naturally arsenic polluted groundwater in the Cenozoic sediments is inferred to be related to biochemical reaction. Seasonal change of the arsenic concentration, major chemistry and sulfur isotope ratios were investigated to estimate the effect of microbiological activity on arsenic release into the groundwater.

Methods

The targeted well, located in the southern part of Osaka Prefecture, was drilled in the Quaternary Osaka Group sedimentary formations. The depth of well is about 50m, and the groundwater level is 2m below the ground surface. The well does not have screens and the groundwater is supplied from the bottom of the well. Stagnant well waters were collected once a month from October, 2001 to June, 2003 from six different depths (0, 1.4, 2.5, 7, 11 and 15.7m) of the well using a vacuum pump. HCl-soluble Fe and As of unfiltered samples are regarded as total concentrations, and those of filtrated samples were dissolved ones. The differences between total and dissolved components are derived from the suspended particles such as iron hydroxides.

Results

In summer, layer stratification is observed in the well water from the surface to 2.5m depth. The layer stratified water is disappeared from autumn to winter.

Total As contents vary in accordance with the total Fe. The total As and Fe concentrations, which collected from 0-2.5m depth, range from 5 to 14ppb and 15 to 37ppm, respectively, from spring to autumn. Those concentrations, which collected from 0-2.5m depths in winter, decrease to 2-5ppb and 3-13ppm, respectively. Total As and Fe concentrations, which collected from 15.7m depth, range from 7 to 16ppb and 27 to 38ppm, respectively, from spring to autumn. These concentrations range from 12 to 13ppb and 33 to 42ppm, respectively, in winter. Fe and As fixed in suspended matters, which collected from 0-2.5m depths are 71-100% and 64-100%, respectively, in the winter time.

ORP varied within the range from -50 to $+110$ mv regardless the depths during the investigation period, except the waters from 0-2.5m depths in the winter, i.e., ORP of the water ranged from $+32$ to $+227$ mv. At that time, total Fe and As were low in those samples. ORP of the water from 15.7m depth ranged from $+98$ to -85 mv in winter.

The concentrations of sulfate and dissolved iron positively correlate with each other, giving the rate of those components to be 2:1. Isotopic ratios of sulfate-sulfur of the water from 0-2.5m depths ranged from $+35$ to $+39.8$ permillage (CDT) from spring to autumn. In winter, sulfur isotopic ratios decreased to $+15.8$ - $+24.1$ permillage (CDT) regardless the depths. Sulfur isotopic ratios of the water from 15.7m depth varied within the range from $+16$ to $+42$ permillage (CDT), which decreased to $+20$ permillage (CDT) also on September 2002. Sulfur isotopic ratios negatively correlate with sulfate concentration.

Discussions

Since the Fe and As fixed in suspended matters give the good linear relationship, As must be absorbed on suspended iron particles. Thus, the As would be released into groundwater when suspended FeOOH decomposed in reducing condition, and vice versa in oxidizing condition.

The large sulfur isotopic ratios would be caused by microorganism activity in the well. Low sulfate concentration and high sulfur isotopic ratios must be caused by active sulfate reduction occurring from spring to autumn. The positive correlation of dissolved iron and sulfate suggests the pyrite oxidation even at 15.7m depth in the winter, since the pyrite oxidation causes the increase of sulfate, and the decrease of sulfur isotopic ratios.

This study demonstrates that concentration of As of this well water is controlled by the precipitation and dissolution of pyrite and iron hydroxide under changing redox reaction controlled by microorganism activity in the groundwater.