

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

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Introduction

Naturally arsenic polluted groundwater occurs mainly in the Cenozoic sediments. Biochemical reaction is supposed to play an important role for such an arsenic dissolution into the groundwater from the sediments. In order to elucidate the participation of microbial activity in the arsenic behavior in aquitard, seasonal change of the arsenic concentration, major chemistry and sulfur isotopes of the groundwater in the south of Osaka Prefecture were investigated.

Methods

The targeted well was drilled in the Quaternary Osaka group. Bottom of the well is about 50m depth, and the groundwater level is 2m below the surface. The well is not used very often. Thus, the well water would be stagnant especially in the shallower depths. During October, 2001 to January, 2002, water samples were collected from six different depths of the well using a vacuum pump. The sampling depths were about 0, 1.4, 2.5, 7, 11 and 15.7m. After measuring temperature, pH, Eh and alkalinity in the field, arsenic and other dissolved components were analyzed in the laboratory. Sulfate in the groundwater was collected as barium sulfate, which was converted to sulfur dioxide to determine sulfur isotope ratios.

Results and discussions

The well water is characterized to contain high total iron, and arsenic contents vary in accordance with the total iron. Total arsenic and iron concentrations of the surface waters range from 2.4 to 8ppb and 3 to 19.6ppm, respectively. Ferrous ion of the deeper water is about 30ppm. Total arsenic and iron concentrations, which collected from 0-2.5m depths in December, decrease to 2ppb and 4.5ppm respectively, while those of the deeper water does not change.

Total arsenic and ferrous ion concentrations in January increase to 6ppb and 30-35ppm, and the difference of concentrations by depth get smaller. These of surface water in April and March are 13ppb and 39ppm, which are higher than those of deeper depth. In June, total concentrations of arsenic and ferrous ion of surface water are smaller than those of deeper depths. Distribution of the concentration of total arsenic and ferrous ion in June are same those of October and November 01.

The concentration of total iron in surface water is higher than the ferrous ion by 10ppm in April. The difference must be particulated FeOOH. Total arsenic of samples positively correlates with total iron concentration, suggesting that FeOOH adsorbs arsenic.

ORP is high at the surface of groundwater, and decreases with depth. For the most part of investigation period, it ranges from -50 to -110mV. But it shows +30mV in December, 01 and +200mV in December, 02, when total arsenic and iron concentrations suddenly decrease. ORP shows -60mV in January, indicating that the water become more reductive than in the December.

Stable isotopic ratio($^{34}\text{S}/^{32}\text{S}$) of sulfate-sulfur varies in the range from +25.9 to +32.7 permil(CDT). Those of the surface water are from +25.9 to +28.4 permil in the October and November, 01, while the deeper samples show larger values, ranging from +26.4 to +35.9 permil. Sulfur isotopic ratio did not change at all depths in the December (+32-+32.5 permil). The minimum ratios were recorded in the January, 02 ranging from +12.6 to +15.1 permil. The isotopic values increase in the April ranging from +32.6 to +32.9 permil, suggesting that the pyrite in the sediment was the source of the sulfur.

The concentration of sulfate ion in the surface water, increases from 14ppm during the most of the year to 27.8ppm in the January, 01, when the sulfur isotopic ratio decrease. The other sources than the pyrite, such as aerosol and fertilizer would contribute to change sulfur isotopes of this month. Total arsenic, iron, and sulfur isotopic ratio show maximum in the April, probably because high decomposition rate of pyrite in the sediment. However, biological concentration is still not clear to the arsenic release from the pyrite into the groundwater.