

Arsenic behavior in Quaternary sediments in Osaka Plain

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Naturally arsenic contaminated groundwater have been known in the Quaternary sedimentary formations of Osaka Plain. To clarify the dissolution mechanism of arsenic into groundwater, concentration and fixation process of this element in sediment should be understood. In this study, distribution of arsenic and its chemical forms in shallow sediments are determined. Based on the results, we discuss on the arsenic behavior in sediments and formation mechanism of arsenic contaminated groundwater.

The sample sediments were taken from a 47m deep core drilled at the Taisho High School, Osaka. There are two marine clay layers, Ma12 and Ma13 in this sediment column. The fresh samples were frozen to prohibit oxidation just after the cutting from the core. After freeze drying, the samples were powdered, and separated fine fractions (under 0.3mm) were used for analysis. For determining total arsenic contents, the samples were fused with sodium carbonate and the products was dissolved in hydrochloric acid solution to analyze using an atomic absorption spectrometer. Among 80 samples analyzed total arsenic, selected 12 samples were chemically treated to extract four different forms of arsenic; acid soluble arsenic (carbonate and weakly adsorbed), reducible arsenic (mainly fixed in Fe oxide), organo-arsenic and insoluble arsenic (mainly fixed in pyrite and rarely in silicates), using acetic acid, hydroxyammonium chloride solution, sodium pyrophosphate decahydrate solution, nitric and perchloric acids.

Except for one sample, which was taken from the coarse sand to gravel layers, arsenic content of the studies samples ranges from 0 to 14.5mg/kg. The average content of fine fractions in gravel layers is 2.6mg/kg, that in sands 6.7mg/kg, and that in the marine clays 9.9mg/kg. The arsenic is more concentrated in the marine clays, Ma12 and Ma13, than in the freshwater sediments. Among freshwater sediments, the arsenic content decreases with increasing the grain size.

The proportion of insoluble arsenic to total arsenic contents ranges from 68% to 90% with the average of 80%, which is much higher than those of acid soluble arsenic(average of 9%), reducible arsenic(average of 5%), and organo-arsenic(average of 5%). The reducible arsenic content increases in harmony with the organo-arsenic in the marine clay layers, suggesting that those forms of arsenic are fixed in the sediment by the same process. Since the organo-arsenic compounds are rarely formed inorganically, microbial activity presumably concerns with the formation of reducible and organo-arsenic.

In the Ma13 layer, the total arsenic content is obviously higher in the portions close to the overlying and underlying freshwater sediment layer (8 to 14mg/kg) than those in the middle portion of this layer (6 to 8mg/kg). In the uppermost part of the Ma12, arsenic concentrates more (14.5mg/kg) than in the deeper part. Such an arsenic concentration can be explained in two ways, i.e., clay materials accumulated arsenic under changing the depositional environment from fresh to seawater and vice versa. Or, arsenic, which diffusively moved in pore space, was biochemically accumulated in the parts close to the permeable layers. Since the Ma12 layer is in unconformably contact with the overlying sediments, the secondary accumulation occurred in the sediments is more probable than the primary concentration of the arsenic in the detrital particles.

In the upper part of Ma13 layer, the proportions of reducible arsenic and organo-arsenic are relatively high to that of insoluble arsenic compared with the average proportions. It also suggests the biochemical accumulation of the arsenic in the sediments.