Release of arsenic by organic acids from damped sediments originally deposited in the Shinaki Dam receiving neutralized sulfate-rich acidic river water (Yukawa river), Gunma, central Japan

[a,b]Yamaguchi K E, [a]Yoshino T, [a]Tanaka E

The Yukawa River, originating from the Kusatsu-Shirane volcanic district, Gunma Prefecture, in the central part of Japan, is rich in sulfate because of natural oxidation of sulfide minerals in its source hot spring area and becomes acidic with pH as low as 2. Neutralization has been done on the Yukawa River water for nearly fifty years by adding pulverized $CaCO_3$ in suspension at its mid-downstream. The Shinaki Dam was constructed to precipitate and store the treated sediments for assurance of water quality, because water flowing out of the dam eventually merges to the Tone River system, supplying drinking water to Tokyo area. However, the sediments have been filling the dam with unexpected speed. The sediments are now dredged and transported to nearby mountains for damping by local government. Those sediments are expected to contain significant amount of As, because of its high concentration in the Yukawa River (up to 10 mg/L) and co-precipitation with $Fe(OH)_3$ produced by increase of pH from ~2 to ~5 through neutralization. Arsenic is an harmful element to living organisms and a ubiquitous element in hot springs in volcanic district. Once released from the damped sediments, arsenic would cause serious environmental and helth problems. Thus, chemical stability of the damped sediments needs to be guaranteed; however, environmental acids such as acid rain and organic acids would dissolve $Fe(OH)_3$ to release adsorbed arsenic. It is therefore important to investigate the stability of the damped sediments by attack of acids mentioned above. We performed a series of laboratory experiments to assess how much arsenic was released with time by leaching the sediments from the Shinaki Dam after addition of various reagents organic acids (acetic, oxalic, formic, and citric acids, each with 0.1M and 0.01M concentrations) and natural organic acids produced in soils collected nearby the dam. We used ICP-MS for measurement of As and other metal concentration and ICP-AES for Fe, Al, and Ca. We confirmed that almost all As in the sediments (~0.5 wt.%) were released by the leaching within three days. Formic and oxalic acid was found to be the most effective media to liberate As. Because temporal changes in the concentrations of As and Fe in leachate were found to be similar, we suggest that nearly all As in sediments was adsorbed on the Fe(OH)3 and releases by its dissolution by added organic acids. The results of this study have important implications for how we should treat the sediments in the Shinaki dam for water quality assurance.

[a] *Geochemical Laboratory, Department of Chemistry, Faculty of Science, Toho University, Chiba, Japan (kosei@chem.sci.toho-u.ac.jp)*
[b] *NASA Astrobiology Institute*