

Diversity of microbial metalloid transformation pathways and its geochemical implications

*Natsuko Hamamura¹, Sathoshi Mitsunobu²

1.Dept. Biology, Faculty of Science, Kyushu University, 2.Faculty of Agriculture, Ehime University

Arsenic (As) and antimony (Sb) are both naturally occurring toxic elements and are considered to be priority pollutants of interest by the USEPA. Although the concentrations of these toxic metalloids in natural systems are generally low ($\sim 15 \mu\text{g g}^{-1}$ As and $<1 \mu\text{g g}^{-1}$ Sb in soils [1]), the elevated levels of As and Sb have been released via natural processes and human activities. Antimony is commonly associated with As in the environment and both elements have similar chemistry and toxicity. Antimony and arsenic can exist in four oxidation states (-III, 0, III and V), while they are mainly found in two oxidation states, trivalent (III) and pentavalent (V) in natural systems. Antimonate [Sb(V)] and arsenate [As(V)] are the thermodynamically stable species in aerobic environments and occur primarily as H_2AsO_4^- and HAsO_4^{2-} , or $\text{Sb}(\text{OH})_6^-$. In anaerobic environments, the dominant solution species of antimonite [Sb(III)] and arsenite [As(III)] occur as the neutral $\text{Sb}(\text{OH})_3^0$ and $\text{As}(\text{OH})_3^0$ at the environmentally relevant pH range. As(III) and Sb(III) are considered more toxic than As(V) and Sb(V) [1].

Despite its toxicity, microorganisms have developed mechanisms to tolerate and utilize these elements for respiratory metabolism. Although many microorganisms have been identified to catalyze As transformations, we have just begun to unveil the full diversity of microbial processes associated with As and Sb geochemical cycling in the environment. In this study, we characterized metalloid transformation pathways associated with As and Sb-impacted environments. The presence of indigenous microbial populations capable of metalloids transformation was examined by using both molecular approach targeting As functional genes and cultivation approach. The genes coding for arsenite oxidase (*ainA*), which catalyzes the oxidation of As(III) coupled to O_2 reduction, have been recovered from soils from mine tailing. Successful cultivation of various As(III)-oxidizing bacteria confirmed the microbial attribute in As oxidation. In contrast, diverse sequences of anaerobic arsenite oxidase (*arx*) and arsenate respiratory reductase (*arr*) genes were detected from the As impacted lake sediments, while no *ain* genes were recovered. The anaerobic arsenite oxidase, Arx, is known to catalyze arsenite-oxidation coupled to nitrate reduction or photosynthesis. Consistent with the molecular analysis, an anaerobic arsenite-oxidizing nitrate reducer and an arsenate-reducing bacterium were isolated from the lake sediments. The indigenous microbial population associated with Sb transformation was also identified by successful cultivation of aerobic Sb(III)-oxidizing *Pseudomonas*- and *Stenotrophomonas*-related isolates from the mine tailing soils. In addition, anaerobic enrichment cultures capable of reducing Sb(V) were also obtained, in which the precipitation of antimonite as antimony trioxide was observed.

This study revealed the diversity and distribution of microbial metalloid redox metabolisms associated with the polluted environments, indicating their contribution to the speciation and mobility of As and Sb *in situ*.

[1] M. Filella, N. Belzile, Y.-W. Chen. Earth Sci. Rev. 57:125-176. (2002)

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