Research Group for Interfacial Reaction Field Chemistry

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The research objectives of this group are to explore novel chemical reactions of aqueous species of elements including actinides at liquid-solid interfaces on minerals, cells of microorganisms, and their hybrid system and elucidate those reaction mechanisms in order to contribute to environmental chemistry, actinide chemistry, and waste treatment. Using our knowledge and experience on minerals and microorganisms, we have worked on contamination of the environment with radionuclides by the Fukushima Daiichi Nuclear Power Plant accident.

In the year of 2015, we studied 1) reactions of lanthanides in a binary system where cells of fungi oxidize Mn(II) and consequently MnOx forms [1], 2) profiles of ^{137}Cs in sediments deposited after the the Fukushima Daiichi Nuclear Power Plant (FDNPP) accident [2], and 3) bacterial dissolution of ^{137}Cs from the soil contaminated by the FDNPP accident [3].

Mn(II)-oxidizing fungus releases biomolecules combine specifically with tetravalent lanthanides

Microorganisms have high sorption capabilities for lanthanides. They sorb lanthanides on their cell surfaces and sometimes precipitate lanthanides as phosphate on the cell surfaces. The effect of their biological response on lanthanides migration in the environment is however yet to be clarified. *Acremonium strictum* KR21-2 is a Mn(II)-oxidizing fungus. This fungus was cultured in a nutrient medium containing Mn(II)SO_4. The concentration of Mn(II) in the aqueous phase decreased with increasing number of cells and black particles (MnO_x) precipitated during the culture. When lanthanides were introduced to the nutrient medium before the culture of cells, most of the lanthanides were sorbed on cells in 24 h, and then Ce was preferentially desorbed. The desorbed Ce increased with increasing precipitation of MnO_x. Most of the desorbed Ce was associated with a biomolecule produced by the active fungus. X-ray absorption near edge structure (XANES) analysis suggested that the Ce associated with the biomolecule was in the tetravalent oxidation state. The Ce-binding biomolecule was not associated with any other trivalent lanthanides tested or with Fe. The biomolecule had an apparent molecular weight of *c.a*. 4700 Dalton in size, and it contains saccharides that differed from those non-nuclide-specific organic substances released from resting cells. When trisodium citrate and lanthanides were introduced to the nutrient medium before the culture of cells, neither desorption of Ce nor release of this biomolecule occurred. When citrate was present, the sorption of lanthanides on cells decreased with increasing the concentration of citrate. This result strongly suggests that the release of the biomolecule was stimulated by the sorption of lanthanides on the fungus cells. This would be an adaptive response of fungi to lanthanides.

Depth distribution of radioactive cesium in sediments deposited on a sandbar after the FDNPP accident

The sediments deposited on a sandbar from the surface to 20 cm in depth was collected in the Abukuma River to elucidate the history of ^{137}Cs derived from the FDNPP accident. The concentrations of ^{137}Cs in the size-fractioned sediment samples and bulk sediment samples were analyzed. The deepest sediment layer (18-20 cm) contained the highest concentration of ^{137}Cs, which indicates that soils with a lower ^{137}Cs concentration were transported and deposited on the sediment having a higher ^{137}Cs concentration (Fig.1). The upper sediment layer with a lower ^{137}Cs concentration might have been transported from upstream areas, which suggests a decrease of the radioactivity level in the provenance areas of the sediments. The three sediment layers at 4-6 cm, 16-18 cm and 18-20 cm had similar grain size compositions and similar relations between grain size and concentration of ^{137}Cs although the concentrations of bulk ^{137}Cs were different from each other. Therefore the decrease in ^{137}Cs concentration in the bulk of the upper layers is not due to the change in the grain size composition but due to a decrease in the radioactivity in the catchment area. These results demonstrate that sediment layers deposited on a sandbar retaine the cumulative history of the fluvial transport of radiocesium after the FDNPP accident.

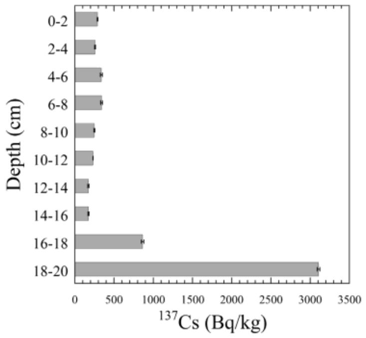

Fig. 1 Concentrations of ^{137}Cs in sediments deposited on a sandbar in the Abukuma River

Bacterial dissolution of ^{137}Cs from the soil contaminated by the FDNPP accident

An endemic Japanese deciduous tree, *Eleutherococcus sciadophylloides* (Franch. et Sav), accumulates high concentrations of ^{137}Cs and Mn from soil. Root endophytic bacteria were isolated from this tree and their siderophore production was evaluated via chrome azurol S (CAS) Fe and CAS Al assays. Among the isolated 463 strains, 107 (23.1%) strains produced siderophores. Using eight strains that showed high siderophore production, desorption of ^{137}Cs, Mn, Fe and Al by the bacterial culture filtrates from ^{137}Cs-contaminated soil collected in Fukushima was examined after decomposing the soil organic matter using hydrogen peroxide. The desorption of ^{137}Cs and Mn was concomitant with desorption of Al and Fe and decrease of pH. These results strongly suggest that the root endophytic bacteria of *E. sciadophylloides* produce the siderophores that solubilize ^{137}Cs and Mn in the rhizosphere, making the solubilized ^{137}Cs and Mn ions easier for this tree to absorb from the rhizosphere.

References

[1] Q. Yu *et al*., Geochim. Cosmochim. Acta, **174**, 1, (2016).
[2] K. Tanaka *et al*., J. Environ. Radioactiv., **150**, 213 (2015).
[3] K. Yamaji *et al*., J. Environ. Radioactiv., **153**, 112 (2016).