

# **Biogenic Manganese Crust and Zinc Uptake in the River mixed with Groundwater**

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Manganese oxides are known to be found in various aqueous environments, such as deep-sea floors, lakes, and mine wastewater. In most of these environments, microbial involvement has been suggested, and heavy metals such as Co, Ni, and Zn are reported to be concentrated in those manganese oxides. We found extensive crust of manganese oxide on the concrete wall of a canal located in several km downstream of the junction entering groundwater into the main river within the Aso caldera in the volcanic area, southwest Japan. The crust is mainly composed of todorokite (hydrated manganese oxide mineral) with 20~30 wt % Mn concentration, which is comparable to that of deep-sea manganese nodules. In addition, Co, Ni, and Zn are more enriched than the surrounding soil and several manganese-oxidizing bacteria and fungi are also found in the crust. Geochemical condition of the river water mixed with groundwater in the canal could affect the biogeochemical transformation of manganese and heavy metals. In order to understand the microbial manganese oxidation process and metal uptake in this environment, we conducted both a field experiment at the canal and a laboratory experiment.

We placed plastic test pieces in the waterway where river water had been flowing for two and a half years. As a result, the amount of manganese deposited on the test piece increased linearly with time. The amount and the type of manganese-oxidizing microorganisms changed sequentially. The amount of zinc in the deposit on the test piece also shows a gradual increase in the latter half of the test.

A manganese-oxidizing fungus isolated from the wall crust was cultured on non-woven fabric and it was placed in a column, where simulated river water with manganese continuously flowed. Manganese oxide formation and zinc uptake were confirmed in the presence of 0.15 mM Zn. The results show that the microbial manganese oxidation and zinc uptake was successfully reproduced at laboratory. Combination of the field and laboratory results suggest that manganese oxide formed by the interaction between dissolved manganese and microorganisms affects the dynamics of manganese and zinc in the river-groundwater mixture.