

# Chemical speciation of heavy metals in the estuarine and tideland sediments

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## Introduction

A brackish-water area including an estuary and a tideland is a very complicated system in which fresh water and seawater are mixed. Accordingly, the distribution, mass transfer and chemical change of elements in their sediments have not been well understood. Yatsu tideland is located at Narashino-city, Chiba Prefecture, Japan. Yatsu tideland was assigned to a conservation area, so people could not enter without admission. Because of it, the sediment of Yatsu tideland is preserved as it was and non-polluted, compared with other estuaries and tidelands. Several studies of estuarine area in the vicinity of big cities were carried out, including Tokyo bay area. But the non-polluted brackish-water area that is located at the vicinity of big cities is rare. Therefore, information on their sediments is significant for comparison with nearby estuarine and tideland areas. In estuarine and tideland sediments under anaerobic condition, sulfate ion from seawater is reduced to hydrogen sulfide. Environmental problem was occurred, because hydrogen sulfide is one of malodorous substances. Hydrogen sulfide reacts with heavy metals(iron and manganese mainly) and is removed from water to the sediments in the forms of sulfide. We have already investigated the chemical states of iron by Moessbauer spectroscopy [1].

In this study, XAFS spectroscopy has been applied to the sediments in order to directly investigate the change in chemical states of manganese with depth.

## Experimental

Sediment samples were collected from the Yatsu tideland which is located in Tokyo bay area. The collected sediments were cut at every 3 cm length immediately, and then porewater was removed by pressure filtration (5 atm, N<sub>2</sub>). Approximately 300mg of each sample was mounted in a sample holder. In order to avoid air oxidation, the sediments were purged with nitrogen gas in oxygen-impenetrable plastic bags. The X-ray absorption measurement was made with synchrotron radiation by using XANES facilities on the beam line 7C, 9A and 12C. The radiation was monochromatized by Si(111) double crystals. The spectra were collected in fluorescence mode using Lytle-type detector at room temperature.

## Results and Discussion

Figure 1 shows the normalized Mn K-XANES spectra of the Yatsu tideland sediments from different depths and standard materials of manganese. According to the comparison with the standard materials, manganese in the sediments existed as mixture of divalent and trivalent components. From the shape of each spectrum at 6.545 keV, MnS was estimated to be rich only in the surface layer, because only the spectrum of the sediment of surface layer has a peak at highest normalised absorption coefficient point of MnS spectra. In our previous research, the vertical distribution of manganese did not show significant variation, but manganese increased a little in the surface layer [1]. According to this fact, it may be imagined that the accumulation of MnO<sub>2</sub>(oxidation number of manganese is four) was generated under an oxidative condition. However, our results clearly show the oxidation state of manganese is not tetravalent. Therefore, it is suggested that manganese in the surface layer reacts with hydrogen sulfide and is accumulated in the form of MnS.

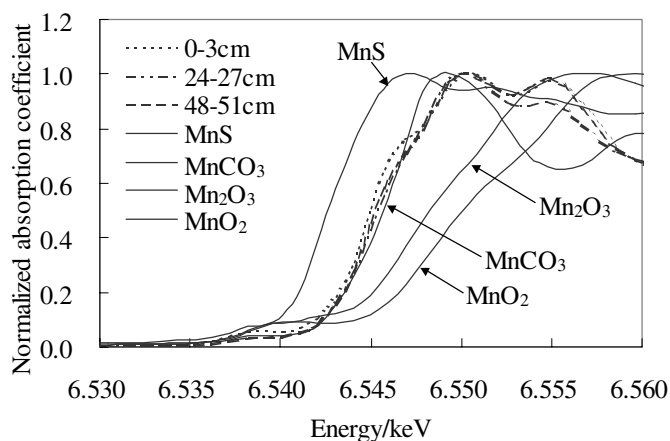


Fig. 1. Normalized Mn K-XANES spectra of the Yatsu tideland sediments and standard materials

## References

- [1] M.Kataoka et al., J. Radional. Nucl. Chem., in press (2002).

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