

## Chemical speciation of manganese in the estuarine and tideland sediments

Masaki KATAOKA\*<sup>1</sup> and Motoyuki MATSUO<sup>2</sup>

<sup>1</sup>Graduate School of Science, The University of Tokyo,  
3-8-1 Komaba, Meguro-ku, Tokyo 153-8902, Japan

<sup>2</sup>Graduate School of Arts and Sciences, The University of Tokyo,  
3-8-1 Komaba, Meguro-ku, Tokyo 153-8902, Japan

### Introduction

Environmental monitoring of estuarine and tideland areas, which have decreased by urbanization in Japan recently, receives much attention in these days. Furthermore a brackish-water area such as an estuary and a tideland is a very complicated system in which fresh water and seawater are mixed. Accordingly, the migration of substance and chemical reaction in the estuarine and tideland sediments have not understood yet. Arakawa-river is one of the big rivers which pass densely populated area and inflow to Tokyo Bay. 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 several heavy metals and is removed from water to the sediments in the forms of sulfide. In this study, XAFS spectroscopy has been applied to sediments in order to directly investigate the change in chemical states of manganese with depth.

### Experimental

We collected sediments vertically in Arakawa-river which is located at the east part of Tokyo and the river is assumed to be polluted with human activities. The collected sediments were cut at every 3-5 cm length immediately, and then porewater was extracted 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 Arakawa-river sediments from different depth and standard materials of manganese. According to the comparison with 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 normalized absorption coefficient point of MnS spectrum. The vertical distribution of manganese in Arakawa-river sediments increased a little in a surface layer. This fact suggests that manganese accumulation in a surface layer was made by MnS. Additionally, this tendency was also observed in the sediments of Yatsu tideland which is non-polluted area [1] [2]. However, it has been supported that manganese in the surface of the sediments existed as the form of MnO<sub>2</sub>, since sediments in a surface layer becomes relatively oxidative condition. The spectrum of the sediments of a surface layer is obviously different from that of MnO<sub>2</sub>.

Therefore, it is considered that the surface manganese accumulated in the sediments, which is produced by the reaction with hydrogen sulfide, presents in the form of MnS, and this reaction is not influenced by the anthropogenic contribution.

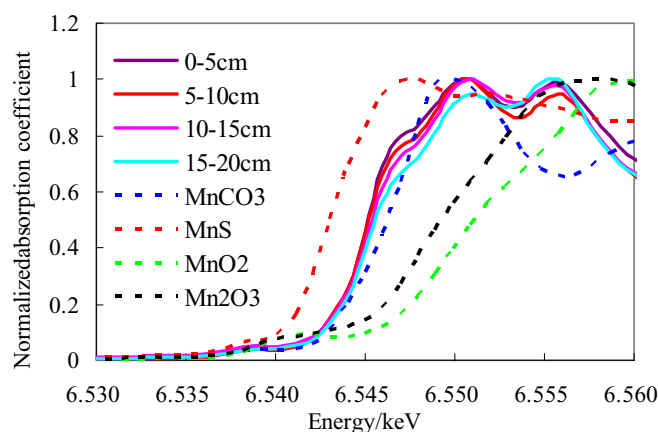


Fig. 1. Normalized Mn K-XANES spectra of the Arakawa-river sediments and standard materials

### References

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\*kataokai@dolphin.c.u-tokyo.ac.jp