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Evaluation of zinc speciation in combined sewer sediments and road dusts with fluorescent XAFS analysis

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Introduction

In urban area, road runoff and human sewage are treated in same sewer pipes. In case of heavy rain enough to over the capacity of waste water treatment plant, a part of untreated sewage water which are called combined sewer overflow (CSO) are discharged into public water. It is believed that combined sewer sediments and road dusts are one of the main loads of CSO pollution[1].

Though it is thought that heavy metal behavior, such as toxicity, mobility and bioavailability, is mainly governed by its speciation, only total zinc was added to environmental criteria for conservation of aquatic organisms standpoint in 2003. In this study, in order to get information regarding zinc speciation, those of combined sewer sediments and road dusts were measured with XAFS analysis.

Experiments

Combined sewer sediments were taken from pipe of combined sewer system and separated sewer sediments were also collected for comparison. Road dusts were collected at heavy traffic street. Combined sewer sediments and road dusts were fractionated into four fractions (250-2000, 106-250, 63-106, and less than 63 μm). The sample was put into polyethylene clear bags and shielded from air. XAFS spectra at the Zn K-edge were taken in the fluorescence mode with 19 solid-state detector using station BL-12C at KEK-PF. All experimental procedures were performed at ambient temperature. The software REX 2000 ver. 2.3 was used to fit the spectra of the reference species to that of the samples. The distribution of each zinc speciation was refined for each reference spectrum in the liner combination fit (LCF) of XANES. The residual value (R) was calculated using the following equation.

$$R = \frac{\Sigma(XANES_{Measured} - XANES_{Calculated})^2}{\Sigma(XANES_{Measured})^2}$$

Results and discussion

The spectra of combined sewer sediments and separated sewer sediments were similar (Fig. 1). However, those of sewer sediments and road dusts were different. It suggested that the partial concentration of zinc speciation of sewer sediments were different form road dusts. From the results of LCF (Fig. 2), the main zinc speciation in sewer sediments were ZnS and $ZnCO_3$, and that in road dusts was $ZnCO_3$. Since ZnO and $ZnSO_4$ exhibited in road dusts were not observed in combined sewer sediments and ZnS exhibited in combined sewer sediments were not observed in road dusts, transformation into ZnS probably proceeded in combined sewer sediments.

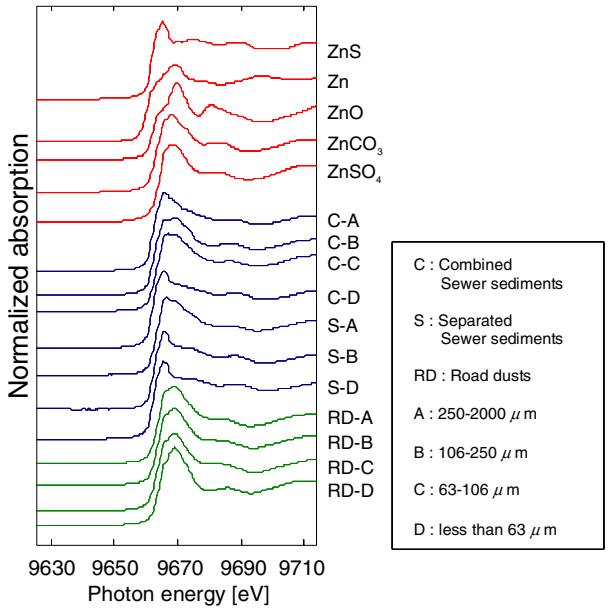

Fig.1 Normalized Zn K-edge XANES spectra of reference materials, combined sewer sediments, separated sewer sediments and road dusts

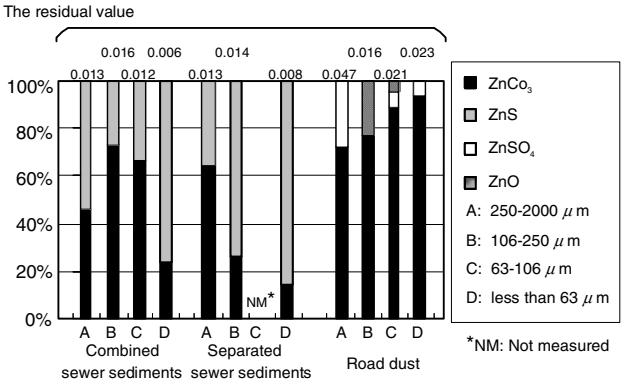

Fig. 2 The distribution of each zinc speciation by LCF in combined sewer sediments, separated sewer sediments and road dusts

References

[1] Gromaire M. C. et al., *Water Research*, 35, 521-533, 2000..

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