



## **Studies on the Competitive Sorption of Divalent Metal Ions to Natural Soil Samples Using a Multitracer Technique**

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### **Summary**

Sorption of divalent zinc and/or manganese ions have been investigated on the surface soil samples using a radiotracer technique in order to elucidate competitive sorption processes. Quite different properties appeared among those metal ions used either independently or simultaneously as a tracer. Proton exchange process may be important for the Zn(II) sorption, whereas a solid-solution partition is supposed to control the Mn(II) uptake, when each of them was examined independently as a sorbate. In contrast, simultaneous use of those tracers to a soil suspension had great effects on the result ; the maximum sorption ( $A_m$ ) of Zn(II) increased , and Mn(II) behaved like a sorbate which tends to occupy specific sites of the soil surfaces. Those results indicate that the sorption of minor and/or trace elements to natural soils would not be evaluated only by using a series of single sorbate experimental data.

### **Introduction**

The fate of various pollutants like heavy metals and radionuclides released into the aquatic environment depends on the 'in situ' conditions , such as temperature, pH, redox potential, water flow, existence of scavengers etc. , as well as on the physicochemical properties of the pollutants themselves.

The present authors studied the sorptive behavior of Zn(II) in various natural solid samples including lake and marine sediments by radiotracer technique(1,2). They obtained the results on the zinc sorption which occurs competitively with protons in the aqueous media. There are several candidates of natural solid phases which could be a proton donor or acceptor, such as hydrous iron oxides, clay minerals and also organic substances. Importance of the organic matter as a scavenger of trace elements has been pointed out by many people, and several models have been proposed to predict the fate so far, for

example, by Kinniburgh et al(3). Equilibrium consideration and matrix effects in the solution system are two serious problems to be solved.

The present authors have studied competitive sorption among several divalent metal ions to natural soils using a multitracer technique which is considered to be useful to evaluate relative importance of the sorption without serious matrix effects. This time they will report a result on the sorption of binary systems with Zn-65 and/or Mn-54 as a tracer.

## Experimental

### Reagents and materials

**Soil samples.** The surface soil samples used in this study were collected between June and September 1996 at five different sites around Sapporo City(Hokkaido, Japan).

Figure 1 shows the sampling locations. The samples were dried at 110°C and then ground to a homogeneous powder.

The reagents used were purchased from Wako Pure Chemical Industries(Japan) and were of analytical reagent grade.

Zinc-65 and Manganese-54 were obtained from the Japan Radioisotope Association as chlorides in 0.5M hydrochloric acid. The nominal specific activities for Zn and Mn were 113 and 7.30 MBq/mg, respectively with a radionuclidic and radiochemical purity of 99.00%.

The tracer solutions were prepared by mixing aliquots of either Zn-65 or Mn-54 stock solution and of a standard solution of each metal ion(1g/dm<sup>3</sup>) to yield a specific activity of 2.31GBq/g.

### Instruments

NaI(Tl) scintillation counting system(Aloka ARC301C); x-ray diffractometer(Mac Science MXP); centrifuge(Kokusan Partner 3); ion analyzer(Orion EA940); pH meter(Horiba D-12); mechanical shaker(Yamato Model SA-31); Thermal analyzer(Shimazu DTA-50 and Shimazu TG-50).

### Procedure

The sorption experiments were carried out according to the procedure described by the present authors(1,2) previously. A soil sample(20 mg) was weighed and transferred to a centrifuge tube (10 cm<sup>3</sup>). The total volume of the suspension was adjusted to 10 cm<sup>3</sup> with distilled water. A small amount of Zn-65

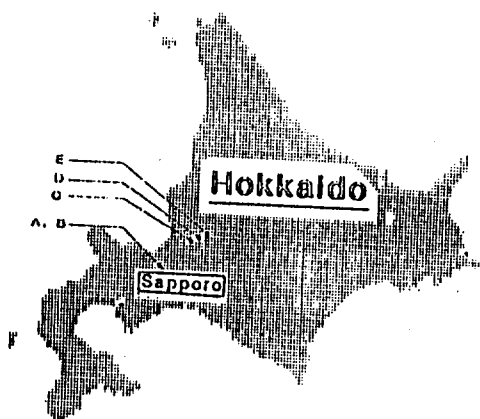


Figure 1 Sampling location of the soils.

and/or Mn-54 tracer solutions (both 925 kBq/cm<sup>3</sup>, 1-15 μl) was added to the suspension, which was shaken for 30 min with a mechanical shaker. In order to evaluate the time required for the sorption equilibrium to be reached, the pH change of the soil suspension with time was monitored at 20 °C.

The solid-solution ratio in the whole experiments was set to be 20 mg/10 cm<sup>3</sup> considering the amount of Zn(II) or Mn(II) remaining in the solution after each run to be measured with certain accuracy. After centrifugation, an aliquot (5 cm<sup>3</sup>) of the supernatant solution was pipetted into a vial and the Zn-65 and/or Mn-54 activities of the liquid phase were measured in a NaI(Tl) scintillation counter with the counting efficiencies of 1.31% at γ energy of 1115 keV for Zn-65 and of 3.54% at 835 keV for Mn-54, respectively, where the energy window for counting was set to be 5% for both nuclides. Several standards of known activity were used to evaluate data obtained.

The cation exchange capacity(CEC) of the soil sample was measured electrochemically with an ammonia electrode(Orion 95-10). All the cation exchange sites of a sample in an aqueous suspension were substituted with NH<sub>4</sub><sup>+</sup> ions, and after centrifugation, the residue was treated with 0.1M NaCl solution. The amount of NH<sub>4</sub><sup>+</sup> ions released by the exchange with Na<sup>+</sup> ions was determined electrochemically.

According to the method by Wong et.al.(4), the organic contents of the soil samples were estimated from the weight loss in ignition at 450 °C for 24 hours.

Powder x-ray diffraction analyses were carried out on individual samples to identify the crystalline minerals by a random orientation method.

## Results and discussion

Soils are mixtures of various mineral and organic components which could scavenge toxic trace pollutants discharged to ground surface through atmospheric precipitation and water streams. The scavenging capacity is supposed to be quite different among soils with different physicochemical properties.

Powder x-ray diffraction analyses gave several peaks due to crystalline quartz present in all samples. Some types of clay minerals and also hydrous iron oxides in amorphous state would probably exist in those samples according to the results by Sakaguchi(5).

Table 1 lists the water content(%), weight loss in ignition(%) and ammonia content(mg/100g) of the soils examined. The water and ammonia contents are relatively high in Sample C collected from a peatland(Tsukigata district in Hokkaido).

Radiometric sorption experiments were then carried out on those samples using Zn-65 and /or Mn-54 as a tracer. The metal ions are supposed to compete each other to occupy specific sites on the soil surfaces. Experimental results were summarized in Table 1.

Table 1 Summary of data obtained from all soil samples(A, B, C, D and E).

Sample No	A	B	C	D	E
Water content /%	25.7	35.2	84.5	18.5	24.8
Ignition weight loss /%	10.3	9.0	9.2	3.4	3.7
Ammonia NH <sub>3</sub> g /100g	0.60 <sub>5</sub>	0.90 <sub>3</sub>	2.23 <sub>6</sub>	1.28 <sub>1</sub>	0.57 <sub>9</sub>
Suspension pH	6.99	7.84	4.52	5.45	5.97
CEC /mmo /100g	18.8	7.74	13.3	6.12	10.9
A <sub>m</sub> (Zn) /mmol /100g *	0.34 <sub>8</sub>	0.38 <sub>4</sub>	0.19 <sub>8</sub>	0.18 <sub>3</sub>	0.30 <sub>4</sub>
[Mn] <sub>sol</sub> / [Mn] <sub>aq</sub> /mgcm <sup>-3</sup> *	2.56	11.4	0.68 <sub>1</sub>	1.06	7.27
A <sub>m</sub> (Zn) /mmol/100g(Mn)**	1.50	3.00	2.53	2.00	0.49 <sub>0</sub>
A <sub>m</sub> (Mn) /mmol/100g(Zn)**	0.41	1.28	0.52 <sub>8</sub>	0.58 <sub>7</sub>	0.22 <sub>9</sub>

\* Single sorbate system

\*\* Double sorbate system

**Zn(II) sorption.** Sorption isotherms fit to the Langmuir equation which provides the amount of Zn(II) at the maximum sorption(A<sub>m</sub>) corresponding to 100 percent surface coverage by Zn(II) ions. They were in the range between 0.18 and 1.38 mmol/100g dry soil, and much smaller(< a few %) than the corresponding CEC values of individual samples. Only a part of the total sites for the sorption would be occupied by Zn(II) ions. The A<sub>m</sub> values were positively correlated with the equilibrium pH values of the soil suspensions in all cases. The results indicate that the zinc sorption occurs competitively with protons in the liquid phase.

**Mn(II) sorption.** Divalent manganese ions behaved quite differently from Zn(II) ; almost all Mn(II) ions present in the soil suspension initially disappeared to be with the solid phases. The isotherms for the Mn(II) did not fit to the Langmuir equation. Divalent manganese species may be stable thermodynamically under pH and redox conditions of the present soil solution systems. As predicted from a pε -pH diagram for manganese, Mn(OH)<sub>2</sub> is likely to exist in a soil suspension with pH higher than 7.5. It is in the case of Sample B, where most Mn(II) in the suspension disappeared after the sorption equilibrium. The peatland soil(sample C) with lower pH did not incorporate much amount of Mn(II) from the liquid phase.

**Simultaneous Zn(II) and Mn(II) sorption.** Both tracers were added to a soil suspension simultaneously. The A<sub>m</sub> values for Zn(II) were obtained from the isotherms of individual samples. They were consistently higher than those obtained in the previous systems free from Mn(II), and were much

smaller than the corresponding CEC values in all cases. Manganese ions added to the soil suspension clearly affect the Zn(II) behavior in the sorption process. There seems to be no regularity among the degree of  $A_m$  increases for Zn(II) sorption in the presence of Mn(II). For example, in Sample B with high pH, Mn(II) ions trapped on the soil surfaces may provide additional sites for Zn(II) to occupy. In contrast, the  $A_m$  value of Sample C did not change appreciably regardless whether Mn(II) was present in the system or not.

Peculiar properties also appeared on the Mn(II) sorption, when Zn(II) coexisted in the soil suspension. As in the case of Zn(II) sorption, the Langmuir equation is applicable to fit data obtained for all samples. The result indicates that Zn(II) ions may play a role to make Mn(II) occupy some specific sites of the soil surfaces in order. The  $A_m$  values thus obtained for Mn(II) sorption were much smaller than the corresponding CEC values in all samples.

It seems to be very difficult to evaluate the whole system just as it is, and to make a suitable model to predict the fate of pollutants. However, the present radiometric approach to the zinc and/or manganese sorption may have at least an advantage which is to prevent the results from suffering serious matrix effects often occur in usual techniques.

On the evaluation of the sorption equilibria, there are many data which showed the equilibrium to be far more attained in the real systems. They may be true, as a whole, since a trivial event would cause quite serious problems. It is our approach to deal an edge of the phenomena; to evaluate capacities of the sorption on individual components of various natural samples.

### Conclusion

Divalent zinc and manganese behave quite differently as a sorbate to natural soil samples. It may be partly caused by the  $p\epsilon$ -pH dependence of Mn(II) species in the present soil solution systems. Manganese hydroxide is possibly to be formed in a soil with high pH. In contrast to Mn(II) which is a minor component of soils, there exists some specific sites for Zn(II) ions to be sorbed. They may be ion(proton) exchangeable in character. Those findings suggest that much data are necessary for evaluating the fate of pollutants with certain models.

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