Coupling of ICP-MS and Multitracer Technique as a New Method to Investigate Dynamics of Various Elements in Soil-water System

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Coupled application of multitracer method for the sorption experiments and ICP-MS for leaching experiments was proposed as a new method to study the dynamics of various elements in soil–water systems. This method enables us to obtain reversibility and the time required to attain the steady-state simultaneously for various elements in soil–water system. An example of the results obtained by this method was shown for the case of Co in this letter.

Soil contamination, either from natural or anthropogenic source, is widely found in the world for various elements such as for As, Co, and Cr.[1–3] However, further study is still needed to understand the detailed mechanism of reactions in soil-water systems for various elements, since the reactions in soil-water systems are complex. In particular, studies on dynamics of the trace elements in soil–water system should be an important issue in addition to studies under equilibrium condition.

To understand further the reactions and dynamics in soil–water systems, we proposed in this letter to couple both leaching experiments using ICP-MS (inductively-coupled plasma mass spectrometry) and sorption experiments using multitracer technique[4–7] (Figure 1). By the coupling of the two methods, we could study how the difference in initial states of the elements can affect their soil–water distributions. In this study, soil–water distributions of various ions were conducted in both directions, that is, starting from ions in soil (leaching experiments) and from dissolved ions (sorption experiments). At first, leaching experiments were conducted by ICP-MS for the stable isotopes originally contained in the soil. On the other hand, multitracer technique was used in the sorption experiments. Multitracer contains many radioisotopes in a solution generated by nuclear fragmentation reaction by heavy-ion bombardment.[4,5] This technique enables us to detect simultaneously a number of elements in the system. Multitracer solution we used in this experiment contained radionuclides of ^{7}Be, ^{48}V, ^{51}Cr, ^{54}Mn, ^{58}Co, ^{59}Fe, ^{65}Zn, ^{74}As, ^{75}Se, ^{83}Rb, ^{85}Sr, ^{88}Y, ^{88}Zr, and ^{103}Ru. Added multitracer does not influence the reactions of elements initially involved in soil, since the concentration of each element in multitracer solution is less than 10^{-12} M order. Therefore, results of sorption and leaching experiments can be compared directly. In this letter, we showed the results mainly for Co as an example of the application. Cobalt is of interest from environmental radiochemistry, since the radionuclide ^{60}Co is an important activation product of metals in nuclear facilities and also a common nuclide used in nuclear sciences.[8]

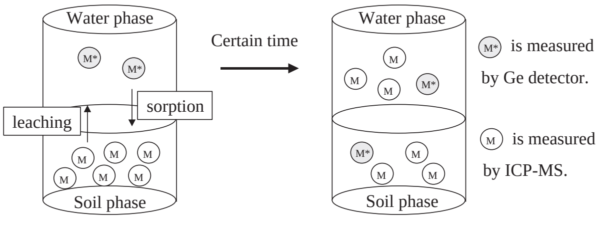

Figure 1. Schematic figure of sorption and leaching experiments for an element M using ICP-MS and multitracer analyses. M* denotes the radioisotope of M. Note that the concentration of M* is much smaller than that of M.

The sorption and leaching experiments were conducted based on a method in literature.[9,10] Soil sample was from paddy field in National Institute of Agro-Environmental Science, Tsukuba, Japan. The soil sample was air-dried, homogenized, and sieved (2 mm). Major element compositions of the soil were reported in Takahashi et al.,[10] while Co abundance was 93.5 mg/kg. For the leaching experiments, 20 g of the soil were put into 50 mL styrene tube with Milli-Q water containing 0.010 M NaCl as supporting salt. To observe leaching of elements under various redox conditions, the amount of water in the soil was varied, noted as water saturation ratio (Ws) hereinafter. The Ws value was defined as the volume ratio of water and soil in the system, where $W\text{s} = 0\%$ is the moisture content in the soil at 110 °C.[10] Similar experiments were conducted for the sorption experiments, where multitracer was added in the system. These samples were incubated at 20 °C for 28 d in both experiments. Eh was measured by a platinum electrode designed for Eh measurement in soil water (Fujiwara Sci., EHS-120). In the leaching experiments, the concentrations of Co, As, Zn, Fe, Mn, Rb, and Sr were measured by ICP-MS (VG, PQ-3) using Ge and In as internal standards. In the sorption experiments, the abundances of all radioisotopes in the solution were analyzed simultaneously by a Ge semiconductor detector (SEIKO EG&G).

For the sorption experiments, the fraction remaining in solution of each element (R_{S}) was obtained from the percentage of the amount of each radionuclide in water relative to the total amount introduced in the system. For the leaching experiments, because of the presence of various components as host phases of trace elements in soil, concentrations in "active phase" in the soil were experimentally determined based on sequential extraction procedure.[11,12] The procedure can identify abundance of each element in such phases as Mn and Fe oxides, organic matters, carbonates, exchangeable ions, and insoluble residues. We use the sum of concentrations in all the phases but the residual phase as the concentrations in the active phase, which was 3.98 mg/kg for Co. For the leaching experiments, R_{L} was defined as the fraction of each element leached into water relative

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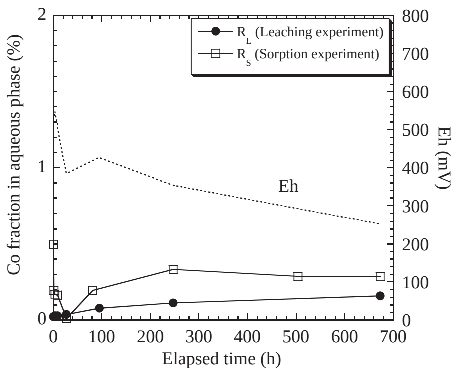

Figure 2. Comparison of R_S and R_L values for Co with Eh depending on elapsed time for incubation time at Ws (water saturation ratio) = 200%. Uncertainties of R_L and R_S are smaller than the sizes of the symbols.

to that in the active phase. When R_S is similar to R_L, it is suggested that the reaction of the element with the active phase is reversible in the soil–water system.

We have obtained the leaching and sorption behavior for Mn, Fe, Co, Zn, As, Rb, and Sr. The R_S and R_L values at $W\text{s} = 200\%$ were compared for Co as an example in Figure 2 accompanied with Eh variation over time. Initial R_S value for Co must be 100%, while initial R_L must be 0%. As the elapsed time increased, Eh value decreased due to the development of reducing condition in the soil. The R_S value decreased until after 30 h, which turned into the increasing trend after that. The R_L values for Mn and Fe increased with time, showing the dissolution of Mn and Fe oxides during the development of the reducing condition. The R_L value for Co monotonously increased with time as Eh decreases. In our sequential extraction experiments, 62.0% of Co was in Mn and Fe oxides relative to total Co in the active phase. Therefore, the increase of R_S and R_L values for Co can be ascribed to the dissolution of Mn and Fe oxide phases. Finally, R_S and R_L became similar for Co around 0.2%, which suggests that the sorption–leaching equilibrium can be attained within about 600 h in the soil–water system for Co. Figure 3 shows comparison of R_S and R_L at various Ws for Co. The Eh value decreased with increasing Ws in soil, which shows that the redox condition became reductive at larger Ws, since the increase in water amount diminish oxygen supply into soil. As reducing condition developed, R_L and R_S values increased for Co. As Ws increased, R_L and R_S values also increased for Fe, Mn, and As, but did not change very much for Zn (data not shown). This strongly suggests that Co and As were dissolved in a soil solution by the dissolution of Fe and Mn oxides containing a large amount of Co and As, as reported in many studies.[12–14]

The fact that R_S and R_L showed similar values for Co in Figures 2 and 3 is interesting, considering the complex reactions in soil. These results strongly suggest that the reaction of Co with the active phase is reversible and that Co entering into a soil–water system will reach a steady-state within a relatively short period. By the present method, it is expected that a time needed for each element to be incorporated into a stable phase in soil can be discussed. In this study, the agreement of R_S and R_L values was observed for Co, but not for Zn. Such a difference will be an important issue for the future study, which must be related to the difference in the reactions that govern behavior of Co and other elements in soil.

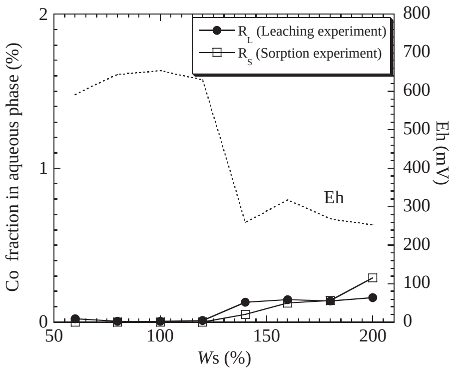

Figure 3. Comparison of R_S and R_L values with Eh for Co depending on the Ws (water saturation ratio) in soil after the incubation for 28 d. Uncertainties of R_L and R_S are smaller than the sizes of the symbols.

In this study, it was suggested that the coupling of sorption experiments using multitracer technique and leaching experiments using ICP-MS can give insights into the reversibility and the time required to attain the steady-state for various elements in soil–water systems. Multitracer contains more than 30 elements as available elements,[5] while ICP-MS is established as a multi-elemental analytical method. Therefore, the similar results for a variety of elements can be obtained by the simultaneous applications of the two methods, as we have shown for Co in this letter. The information on various elements including many toxic elements by the present method will contribute to the understanding of their reactivities and dynamics in soil–water systems.

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