Chemical States of Stable Zn and Aging Effect of $^{65}$Zn in the Soil

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The amount of stable Zn and the specific activity (S.A.) of $^{65}$Zn in DTPA extract were pursued as a function of time after the administration of $^{65}$Zn to Tanashi volcanic ash soil and Naka-gawa alluvial soil to investigate chemical states of Zn in the soils and also aging effect of $^{65}$Zn introduced to the soils.

There were at least 3 kinds of Zn pools, i.e., rapid exchange pool (pool A; possibly soil solution), exchange pool (pool B; several tens of days are needed to attain isotopic exchange equilibrium), and very slow exchange pool (pool C; several thousand days are needed to reach isotopic exchange equilibrium).

The aging effect was not clearly observed because $^{65}$Zn introduced into the soil remained in an available fraction (in pool A and B) for relatively long days.

INTRODUCTION

Zn is one of the essential elements for crops. Therefore, it is of importance to know chemical state of the element in the soil. The relevant radioisotope, $^{65}$Zn, is one of the important induced radionuclides and was found in the environment after nuclear explosion tests.

When this radionuclide is introduced into the soil, the nuclide enters into human body through the crops. The amount of $^{65}$Zn transferred from soil to crops may be limited by its physical decay, amount of stable Zn concerning isotope dilution and aging effect, that is, day-by-day transformation of the nuclide into non-available form by the crops if it remains in the rhizosphere for long period.

This paper reports on the chemical states of Zn and the aging effect of $^{65}$Zn in the soil.

MATERIALS AND METHODS

Soil Preparation

Tanashi volcanic ash soil and Naka-gawa alluvial soil were used. Main difference of chemical properties between the 2 soils is that cation exchange capacity and humus content are higher in Tanashi soil than in Naka-gawa soil. After the soils were air-dried and screened, each 400 g was put in an acryl container with a cap. $^{65}$Zn (27.4 µCi) was administered into the
container with 20 μg of Zn and 200 μg of Ca as chlorides. The soil in the container was moisture-saturated with 270 ml of deionized water in case of Tanashi soil and 180 ml for Naka-gawa soil. The soil was mixed by a glass lod for 5 minutes. After being covered with the cap and shaken horizontally for 24 hours, the container without the cap was allowed to stand in a well ventilated room (temperature 22–28°C). When the soil was air-dried, the deionized water was added to the soil to moisture content of about 80% at 20–35 days interval.

**Extraction Procedure**

Sometimes, about 8 grams of soil was taken up and shaken for 48 hours to extract Zn and $^{65}$Zn with 16 ml of DTPA extractant containing 0.005M diethyltriamine pentaacetic acid in 0.1M triethanolamine buffer and 0.01M CaCl$_2$\textsuperscript{1,2}. The extract was obtained by centrifugal force at 1500 gravity for 5 minutes, followed by filtration with No. 5C filter paper.

**Analytical Procedure**

Activity of $^{65}$Zn was measured by a well-type scintillation counter. Zn was determined by atomic absorption spectrophotometry.

**RESULTS AND DISCUSSION**

Fig. 1 shows the log plot of DTPA extractable Zn as a function of time after $^{65}$Zn administration. By wet digestion with conc. HNO$_3$-HClO$_4$-H$_2$SO$_4$ to obtain a total amount of Zn,
105 and 78.0 ppm of Zn were solubilized from Tanashi soil and Naka-gawa soil, respectively. As can be seen from the figure, DTPA extractable Zn was a very little in comparison with the total Zn. There were no significant and regular variations of the DTPA extractable Zn during the experimental period though some fluctuations were observed. Boawn\textsuperscript{3)} also reported that Zn concentration in DTPA and 0.1N HCl extractable fractions was almost constant for over 5 years when Zn was not fertilized.

The specific activity (S.A.) of $^{65}$Zn in the DTPA extract was plotted in a log diagram\textsuperscript{4)}, as shown in Fig. 2. The S.A. decreased relatively rapidly during 50 days after administration of $^{65}$Zn, followed by an extremely slow decrease. Moreover, the S.A. in the extract was tremendously higher than that in the wet digestion fraction. This fact suggests that the administered $^{65}$Zn was diluted by a small portion of soil native Zn, which might be a labile form of Zn, though different by soils. In addition, present result indicates that the aging effect hardly occurred because $^{65}$Zn introduced into the soil remained in an available form for relatively long days. Just after $^{65}$Zn is introduced into the soil, the radioisotope will be diluted immediately by Zn in the soil solution. After that, the $^{65}$Zn will be transferred to solid phase. There are three possible reactions between $^{65}$Zn in soil solution and Zn in solid phase of the soil, that is, isotopic exchange reaction, cationic exchange reaction, and the irreversible reaction. Among them, we took isotopic exchange reaction as the most promising reaction under the condition of chemical equilibrium attainment among the Zn pools, deducing from the fact presented in Fig. 1.

Table 1 shows the list of the regression lines and the corresponding correlation coefficients,
Table 1. Regression lines and coefficients of correlation expected from log plot of S.A. in DTPA extract

<table>
<thead>
<tr>
<th>Component</th>
<th>Days point after $^{65}$Zn administration</th>
<th>Tanashi soil</th>
<th>Naka-gawa soil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fast</td>
<td>(1) 11, 13, 20</td>
<td>$y = 0.697 - 5.65 \times 10^{-3} t$</td>
<td>$y = 0.982 - 8.43 \times 10^{-3} t$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>($r = 0.958^*$)</td>
<td>($r = 0.958^*$)</td>
</tr>
<tr>
<td></td>
<td>(2) 11, 13, 20, 48</td>
<td>$y = 0.656 - 2.99 \times 10^{-3} t$</td>
<td>$y = 0.887 - 1.72 \times 10^{-3} t$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>($r = 0.972^{**}$)</td>
<td>($r = 0.723$)</td>
</tr>
<tr>
<td>Slow</td>
<td>(1) 20, 48, 77, 104, 158, 275, 299</td>
<td>$y = 0.544 - 2.31 \times 10^{-4} t$</td>
<td>$y = 0.815 - 1.09 \times 10^{-4} t$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>($r = 0.785^*$)</td>
<td>($r = 0.843^*$)</td>
</tr>
<tr>
<td></td>
<td>(2) 48, 77, 104, 158, 275, 299</td>
<td>$y = 0.513 - 1.24 \times 10^{-4} t$</td>
<td>$y = 0.813 - 1.09 \times 10^{-4} t$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>($r = 0.906^*$)</td>
<td>($r = 0.805^*$)</td>
</tr>
</tbody>
</table>

$^{**}$significant at 1% level, $^*$significant at 5% level.

which are calculated from the log plot data. As shown in the table, regression line (2) is more suitable than (1) to express the fast component of Tanashi soil because of the higher correlation coefficient, while regression line (1) is better than (2) in Naka-gawa soil. As to the slow component, regression line (2) is more suitable than (1) also because of the higher correlation coefficient on Tanashi soil, while the line (1) is better than (2) on Naka-gawa soil. In addition to soil solution (pool A), the day-by-day variations of the S.A. in the DTPA extracts shown in Fig. 2 represents that there are the other two Zn pools. These are an exchange pool (pool B) in which several tens of days are needed to attain isotopic exchange equilibrium, and a very slow exchange pool (pool C) in which several thousand days are needed to attain isotopic exchange equilibrium.

In conclusion, there are at least three Zn pools in the soils from the isotopic exchange point of view. The amount of a radionuclide transferred from soil to crops is limited by physical decay, the extent of isotope dilution and aging effect if the nuclide remains in the rhizosphere. The physical half-life of $^{65}$Zn is 244 days (about 8 months). However, the period from seedling to harvest is almost within 6 months. If $^{65}$Zn is administered into the soil at the seedling period, more than half of the nuclide remains at the harvest. Isotope dilution is sometimes expected though different by soils and the aging effect was not observed because $^{65}$Zn introduced into the soil remained in an available form for considerably long days.

REFERENCES