The Distribution Coefficients and Gasification Ratios of [1,2-^{14}C] Sodium Acetate for Various Paddy Soils in Japan

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ABSTRACT

For appropriate safety assessment of the disposal of TRU waste, distribution coefficients (K_d) and gasification ratios of ^{14}C labeled [1, 2-^{14}C] sodium acetate (^{14}C-NaOAc) were determed by batch sorption tests for 85 Japanese paddy soil samples. The soil studied were from four soil types: Andsol; Gley; Gray lowland; and Yellow. The range of K_d values for all soil samples was from 7.5 to 295.2 mL g^{-1}, and the mean value was 105.6 mL g^{-1}. This mean value was higher than that of previous study (1). The high K_d values of the present study could be a result of the properties of the paddy soils. The comparison of K_d values by each soil type revealed statistically significant difference between Andsol and Gray lowland soils ($P < 0.05$). The soil type was one of the factors affecting partitioning of ^{14}C-NaOAc. Gasification ratios ranged from 29.1% to 83.3%, and its mean value was 66.4% of the total ^{14}C-NaOAc added. These results suggest that most of the radiocarbon in ^{14}C-NaOAc will be released from soil into the air as gases. The gasification ratio between soil types was also compared, but no statistically significant differerence was found. Gas production may be controlled by other than physicochemical properties of soil, for expample by factors such as bacterial community. In addition, both the K_d values and the gasification ratios for Gley soil were decreased according to the increase in pH although the underlaying mechanisms for this observation are not clear.

INTRODUCTION

Transuranic (TRU) waste containing radionuclides is generated during the operation and dismantling of reprocessing facilities and mixed oxide (MOX) fuel fabrication facilities. In Japan, this waste broadly equates to long-lived intermediate level waste (ILW) and low level waste (LLW) with significant alpha content. The dominant nuclides contributing to the dose from TRU waste are ^{14}C and ^{129}I. Because these nuclides are long-lived, water-soluble and have very poor sorption properties on soils, they are the key nuclides in safety assessment for geological repositories of TRU waste.

Recently, the possibility of leaching of organic carbon compounds from the simulated hull waste has been reported, and carboxylic acids such as formic acid and acetic acid are dominant forms among the radioactive organic carbon compounds (1). For appropriate safety assessment of the TRU waste, understanding of the behavior of these radioactive carboxylic acids is required. As an indicator of the soil-water partitioning behavior of radionuclides in the soil, distribution coefficients (K_d) are commonly used. Because carboxylic acids can be a carbon source for microorganisms, radiocarbon included in carboxylic acid molecules might be released into the air as gases. Therefore, gasification ratios must also be estimated to understand the behavior of the radioactive carboxylic acids.

Values of K_d and gasification ratios may be influenced by regional climate and soil types, and thus more reliable data on these parameters should be obtained for specific regional environmental conditions. To obtain basic information on the behavior of radioactive carboxylic acids in the environment of Japan, we measured K_d values and gasification ratios for radioactive sodium acetate using agricultural soils which were collected from various parts of Japan. Relationships between soil types and these two parameters were also investigated.

MATERIALS AMD METHODS

Soil Samples

A total of 85 soil samples were collected by using a shovel from paddy fields (top 20 cm) in different parts of Japan and classified into 4 types: Andosol (n = 15), Gley soil (n = 21), Gray Lowland soil (n = 44), and Yellow soil (n = 5). The soil samples were dried at room temperature, and then passed through a 2-mm-mesh-sieve to obtain a homogenous soil. The air-dried soils were stored in polypropylene bottles at room temperature until needed.

Radioactive Tracer Experiment

Each soil sample (0.5 g) in a 50 mL polypropylene tube was contacted with 5-mL of filter-sterilized deionized water spiked with [1, 2-^{14}C] sodium acetate (^{14}C-NaOAc) to an activity of approximately 2 kBq mL^{-1} (a initial slurry sample). The soil slurry was shake-incubated at 25˚C for 7 days in the dark. At the end of the incubation, an aliquot of the slurry was collected and the ^{14}C activity measured. The remainder of the slurry was centrifuged for 10 minutes, and the supernatant was filtered through a 0.2-µm pore size cellulose acetate filter (a filtrate sample). The activities of ^{14}C in the initial slurry, the incubated slurry and the filtrate sample were measured with Tri-Carb-25WTR Liquid Scintillation Analyzer (Packard Instrument Co., Inc., Tokyo, Japan). Figure 1 is a schematic showing the experimental details for treating each sample.

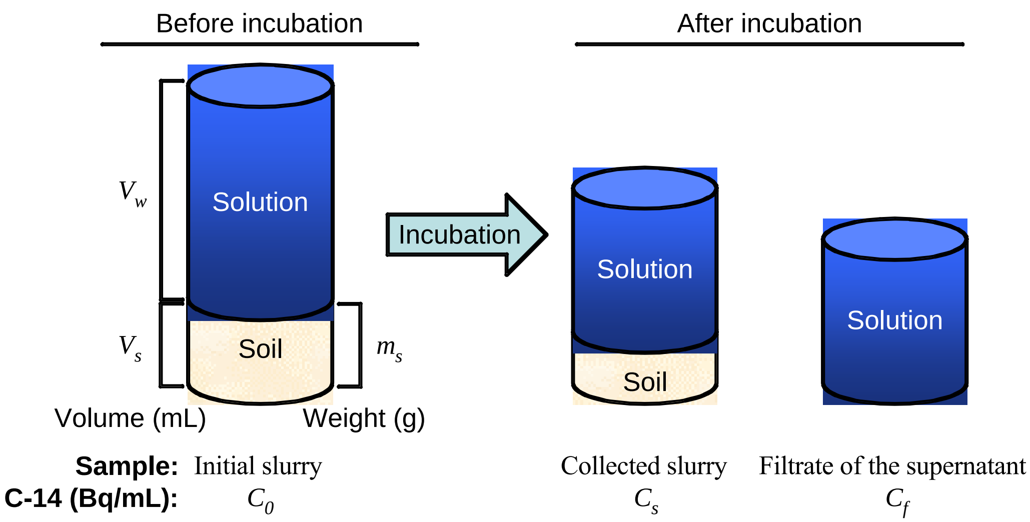

Fig. 1. A frame format of each sample.

The K_d value (mL g^{-1}) was determined by using equation 1 and 2.

$$K_d = \left(\left(V_w + V_s\right)C_s - V_w \cdot C_f\right) \times \frac{1}{m_s} \times \frac{1}{C_f} \qquad \text{(Eq. 1)}$$

$$V_s = m_s \times \frac{1}{\rho_s} \qquad \text{(Eq. 2)}$$

where ρ_s is soil particle density (g cm^{-3}). In this study, the particle density is assumed to be 2.6 g cm^{-3}. This value is the average density of measured values for Japanese paddy soils (n = 63) that included the four types of soil used in this study (unpublished data). The gasification ratio (%) was determined using the values obtained by a liquid scintillation counting system as follows:

$$Gasification\ ratio\ (\%) = \left(\frac{C_0 - C_s}{C_0}\right) \times 100 \qquad \text{(Eq.3)}$$

For the supernatant samples which was obtained after the centrifugation, pH values were measured using a pH meter (B-211; Horiba, Kyoto, Japan).

Statistics

For statistical evaluations of the determined K_d and gasification ratio were analyzed for significant differences by one-way analysis of variance (ANOVA) using Microsoft Excel.

RESULTS AND DISCUSSION

K_d values of ^{14}C-NaOAc for Japanese paddy soils

The K_d values of ^{14}C for Japanese paddy soils were determined (Fig. 2). The values ranged from 7.5 to 295.2 mL g^{-1} and the mean value was 105.6 mL g^{-1}. This mean value was about 10-times higher than that reported by Kaneko et al. (1). They used cement materials as a solid phase sorbent, while in the present study paddy soils were used. Differences in the solid phase, therefore, may result in the higher mean value of K_d in our study. If ^{14}C-NaOAc were to migrate from an underground TRU waste depository to the surface layer on the earth, it would be expected to be retained in soil to a greater extent than in cement.

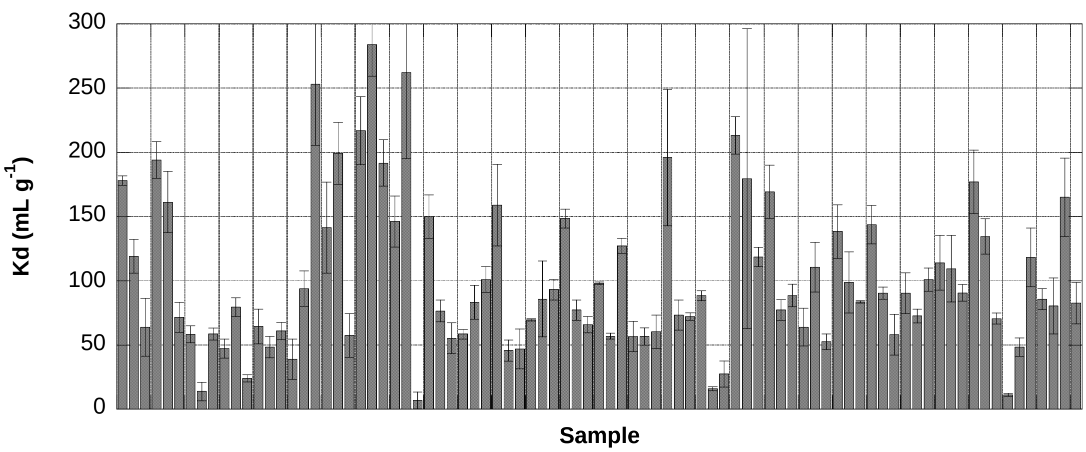

Fig. 2. K_d values of ^{14}C-NaOAc for all soil samples. Error bars are standard deviation (n = 3).

Physicochemical properties, which affect K_d values (2), are different among soil types. In the present study, four types of soils were used for the determination of K_d, and the K_d value of each soil type was compared (Table I). Mean values of K_d were in order of Andosol > Gley soil > Gray lowland soil > Yellow soil, and a statistically significant difference was seen between Andsol and Gray lowland soil (ANOVA, $P < 0.05$). The type of soil, therefore, was one of the factors affecting partitioning of the ^{14}C from ^{14}C-NaOAc between the water and the soil.

Table I. Statistics of K_d for each soil type

Statistics	Soil type			
	Andosol	Gley soil	Gray lowland soil	Yellow soil
Mean	145.8	109.6	92.6	82.8
SD	82.7	59.7	47.5	63.0
Median	152.0	97.9	80.6	61.2
Max	295.2	263.1	221.6	156.0
Min	40.8	16.9	12.0	7.5
Quantile-25%	74.7	82.9	60.9	49.4
Quantile-75%	201.6	149.6	114.3	140.1
number	15	21	44	5

Gasification ratio of ^{14}C-NaOAc for Japanese paddy soils

In addition to sorption behavior of ^{14}C-NaOAc, gas generation is another important parameter for safety assessment of TRU waste because a TRU repository will produce gas through processes such as microbial action for organic wastes. In the present study, the gasification ratios for Japanese paddy soil were also determined (Fig. 3). Gasification ratios were relatively high, and the mean value was 66.4% of the total ^{14}C-NaOAc added, and the ratios ranged from 29.1% to 83.3%. These results suggest that most of the radiocarbon in ^{14}C-NaOAc would be released from soils into the air as gases. It was thought that gas production rates are relatively low and that gas is expected to be dispersed and that this pathway would not contribute significantly to dose levels (3), however, results of the present study much higher gas generation rates in the laboratory study. It definitely appears that some of the ^{14}C in ^{14}C-NaOAc did change to gasses such as CO_2 and CH_4 in a surface soil within a short period of time. Dissipation pathway of ^{14}C gasses and its rate deserves further research.

The correlation between K_d values and gasification ratios were investigated, but no significant relationship was found under the present experimental conditions.

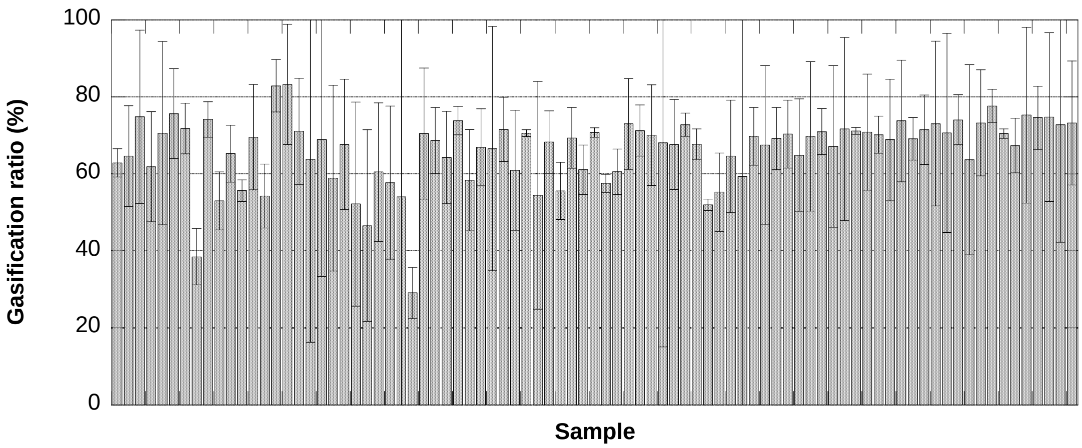

**Fig. 3. Gasification ratios of ^{14}C-NaOAc for all soil samples.
Error bars are standard deviation (n = 3).**

The gasification ratio of each soil type was also compared (Table II). Mean values of the ratio were in order of Gray lowland soil > Gley soil ≥ Andosol > Yellow soil. There were only slight differences in gasification ratios among soil types, and no statistically significant difference was found. Physicochemical properties of each type of soil could not affect the gasification ratio. The soils used in the present study were air-dried, and thus bacterial species diversity may be similar among soil types. It is necessary to investigate relationships between gasification ratios and bacterial species compositions or bacterial activity in soil samples.

Table II. Statistics of *gasification ratio* for each soil type

	Soil type			
Statistics	Andosol	Gley soil	Gray lowland soil	Yellow soil
Mean	66.4	66.5	67.0	60.0
SD	10.8	6.7	7.2	19.3
Median	67.7	67.5	69.5	70.5
Max	83.3	74.9	75.7	74.2
Min	46.6	52.0	38.5	29.1
Quantile-25%	59.2	63.9	63.7	53.0
Quantile-75%	72.4	71.1	71.5	73.3
number	15	21	44	5

Correlation coefficients between pH and both K_d and gasification ratio

Because the behavior of chemical compounds is often influenced by pH, the pH values of the flooded samples were measured after the end of shake-incubation. Pearson's product-moment correlation coefficients between pH and both K_d and gasification ratio are summarized in Table III. Coefficients for all the soils taken together were significant between pH and both parameters (K_d, $P < 0.01$; Gasification ratio, $P < 0.05$).

Table III. Pearson's product-moment correlation coefficients between pH and both K_d and gasification ratio

Soil type	K_d		Gasification ratio		pH	
	r	*P* value	r	*P* value	Mean	SD
All soils	-0.511	0.000	-0.219	0.044	6.4	0.5
Andsol	-0.301	0.276	0.154	0.584	6.4	0.4
Gley soil	-0.704	0.000	-0.505	0.019	6.3	0.7
Gray lowland soil	-0.579	0.000	-0.285	0.061	6.4	0.5
Yellow soil	-0.677	0.209	-0.330	0.587	6.2	0.6

For each soil type, the pH values negatively correlated with the K_d values. For example, for both Gley soil and Gray lowland soil *P* was less than 0.01 even though the changes in the pH values were slight. Significant correlations were also found between the pH and the gasification ratio of Gley soil ($P < 0.05$). The decrease in K_d values according to the increase in pH may be explained by electrochemical reactions of ^{14}C-NaOAc, but it is not quite clear for the decrease in the gasification ratios for Gley soil although the contribution of bacteria is suspected. For appropriate safety assessment of the TRU waste it is necessary to find the controlling factors of the K_d value and the gasification ratio of ^{14}C-NaOAc.

CONCLUSION

Distribution coefficients and gasification ratios of [1, 2-^{14}C] sodium acetate for 85 Japanese paddy soils were determined. The soil samples were four soil types as follows: Andsol, Gley soil, Gray lowland soil, and Yellow soil. The values of K_d and gasification ratio were also compared by soil types. The following conclusions were drawn in the present study.

1. The range of K_d was from 7.5 to 295.2 mL g^{-1}, and the mean value was 105.6 mL g^{-1}. This mean value was about 10-times higher than that of previous study (1).
2. Mean values of K_d were in order of Andsol > Gley soil > Gray lowland soil > Yellow soil. Statistically significant difference was only observed between Andsol and Gray lowland soil.
3. The range of gasification ratio was from 29.1% to 83.3%, and the mean value was 66.4%.
4. Mean values of gasification ratio were in order of Gray lowland soil > Gley soil ≥ Andsol > Yellow soil. No statistically significant difference was found.
5. Statistical analysis of the data indicated that the pH values negatively correlated with K_d values. Also the gasification ratios for Gley soil were decreased according to the increase in pH.

These findings should contribute to a more reliable assessment of the safe disposal of TRU waste.

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REFERNCES

1. S. KANEKO, H. TANABE, M. SASOH, R. TAKAHASHI, T. SHIBANO and S. TATEYAMA, "A Study on the Chemical Forms and Migration Behavior of Carbon-14 Leached from the Simulated Hull Waste in the Underground Condition" Mat. Res. Soc. Symp Proc. 757: 621-6. (2003)
2. Y. NAKAMARU, K. TAGAMI and S. UCHIDA, "Distribution coefficient of selenium in Japanese agricultural soils" Chemosphere. 58: 1347-54. (2005)
3. A. HOOPER, W. R. ALEXANDER, J. MATHIESON and M. SHIOTSUK, "Review of intrernational progress I transuranic and long-lived intermediate level waste disposal" ICEM05-1377. (2005)