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Migration behavior of [1, 2–^{14}C] sodium acetate in a flooded soil

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Abstract. For appropriate safety assessment of TRU waste disposal, gasification ratios and distribution coefficients (K_d) of ^{14}C labeled [1, 2-^{14}C] sodium acetate were determined by batch experiments for a Japanese paddy soil sample. Approximately 60% of the total added C-14 was released from the flooded paddy soil into the air as gas forms during 7 days shake-incubation periods. In the present study, the paddy soil was contacted with deionized water and well water, and the lower gasification ratio was found for the well water sample. The similar result was observed for the K_d values. Values of K_d varied from 51 to 138 mL g^{-1}. The lower values were observed when the soil was contacted with well water. When the microorganisms in the samples were killed by glutaraldehyde, both gasification ratios and K_d values were nearly zero. These results suggested that microorganisms responsible for the behavior of C-14 in biosphere. In addition, water characteristics such as dissolved ions, pH and electrical conductivity would affect the gasification ratio and the K_d values.

1. INTRODUCTION

Transuranic (TRU) waste containing some radionuclides is generated during the operation of reprocessing facilities and mixed oxide (MOX) fuel fabrication facilities. The dominant nuclides contributing to the dose from TRU waste are iodine-129 and carbon-14. They are the key nuclides in safety assessment for a geological repository 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]. The C-14 decays with its half-life of approximately 5700 years, and the organic C-14 is soluble and has very poor sorption properties on solids. These characteristics have raised the concern of the transport of organic C-14 from an underground TRU waste depository to the biosphere of human habitation. For appropriate safety assessment of the TRU waste, understanding of the behavior of organic C-14 in the biosphere is required. As an indicator of the soil-water partitioning behavior of radionuclides in the soil, distribution coefficient (K_d) is commonly used. In addition, organic C-14 can be decomposed and transferred to gas forms by microorganisms. Gasification ratios must also be estimated to understand the behavior of organic C-14.

In the present study, we estimated K_d values and gasification ratios of C-14 from C-14 labeled sodium acetate and studied the contribution of water characteristics and microorganisms.

2. MATERIALS AND METHODS

2.1 Soil sample

In December 1991, soil was collected from the top 13 cm of a paddy field in Saga Agricultural Experiment Station, Japan. The soil sample was air-dried, homogenized, sieved (<2 mm), and stored in a polypropylene bottle at room temperature until needed.

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2.2 Radioactive tracer experiments

The soil sample was contacted with deionized water (DIW) or well water (WW) in a 50 mL polypropylene tube at a solid-liquid ratio of 0.5 g to 5 mL (initial suspension). Ion contents in the WW solution are showed in Table 1. Initial pH of DIW and WW were 5.5 and 8.5, respectively. The acidic pH of DIW is due to dissolved CO_2. For the study on the effect of microorganisms existing in the DIW solution and the WW solution, both solutions were filter-sterilized. These solution samples were spiked with [1, 2-^{14}C] sodium acetate (^{14}C-NaOAc) before the contact with the soil sample.

Table 1. Ion contents in WW.

Anion	Conc. (mg/L)	Cation	Conc. (mg/L)
F^-	0.15 ± 0.04	Na^+	11.36 ± 0.04
Cl^-	21.21 ± 0.14	NH_4^+	0.07 ± 0.01
NO_2^-	0.42 ± 0.00	K^+	2.30 ± 0.00
NO_3^-	7.07 ± 0.06	Mg^{2+}	7.02 ± 0.03
SO_4^{2-}	8.23 ± 0.09	Ca^{2+}	34.23 ± 0.20

The suspension of the soil was shake-incubated at 25 °C for 7 days in the dark. At the end of the incubation, an aliquot of the suspension (incubated suspension) was collected for the measurement of C-14. The remainder of the suspension was filtered to separate into the solid phase and the liquid phase. The activities of C-14 were measured with a Tri-Carb-25WTR Liquid Scintillation Analyzer (Packard Instrument Co., Inc., Tokyo, Japan).

The K_d values (mL g^{-1}) were determined using the values obtained by a liquid scintillation counting system as follows:

$$K_\mathrm{d} = \left(\frac{C_s - C_n}{C_n}\right) \times \frac{V}{W} \tag{1}$$

where C_s and C_n are the concentration of C-14 (Bq mL^{-1}) in the incubated suspension and in the liquid phase sample, respectively, V is the volume of the solution (mL), and W is the dry weight of the soil (g). In the present study, the volume of the soil in the incubated suspension was ignored because the volume is negligible to the volume of the liquid phase.

Gasification ratios (%) were also determined as follows:

$$\text{Gasification ratio} = \left(\frac{C_0 - C_s}{C_0}\right) \times 100 \tag{2}$$

where C_0 is the concentration of ^{14}C (Bq mL^{-1}) in the initial suspension, and C_s is the C-14 concentration in the incubated suspension.

For the supernatant samples which were obtained after the centrifugation, pH values were measured using a pH meter (B-211; Horiba, Kyoto, Japan). Horiba's Compact EC meter (Twin Cond B-173) was used for measuring electrical conductivity (EC).

2.3 Statistics

For statistical evaluations of the determined K_d and gasification ratio were analyzed for significant differences by student's t-test using Microsoft Excel. All the experiments were carried out in triplicate.

3. RESULTS AND DISCUSSION

3.1 Gasification ratio

Prior to the estimation of the gasification for the soil-solution samples, the contribution of microorganisms in the DIW solution on the gasification ratio was estimated. When ^{14}C-NaOAc was added to the DIW solution, the concentration of C-14 in the DIW solution was decreased from 1.7 to 0.9 kBq mL^{-1}during the shake-incubation period of 7 days, but no decrease was observed for the filter-sterilized DIW solution (data not shown). The results suggest that microorganisms in the DIW solution have the ability of releasing C-14 as gas.

When the soil sample was contacted with the DIW solution, the gasification ratio was 68.5 ± 1.8% (Fig. 1). For the filter-sterilized DIW samples, the ratio was 69.5 ± 0.4%, and there was no significant difference in the ratio between both samples. Microorganisms existing in the DIW solution were able to release C-14 into the air, but the elimination of microorganisms by the filter-sterilization had no effects on the gasification ratio. Soil microorganisms would be a better contribution to the gasification of C-14.

To confirm the contribution of soil microorganisms to C-14 gasification, microorganisms in the soil-DIW samples were completely killed by the addition of glutaraldehyde (final concentration: 2%). The gasification ratios for the glutaraldehyde-treated samples were 5.4 ± 3.8% (data not shown).

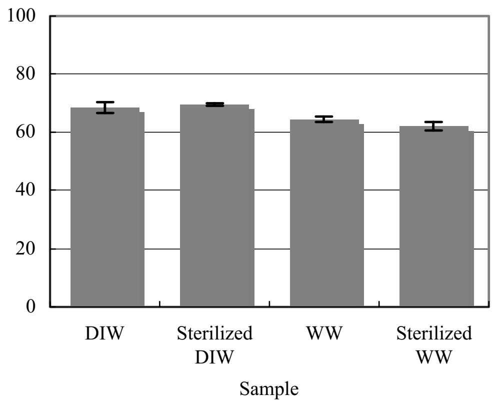

Figure 1. Gasification radios of the C-14 from ^{14}C-NaOAc for DIW, WW, and their filter-sterilized samples. Values represent the means and standard deviations of triplicate experiments.

The gasification ratio was also estimated for the WW samples, and the value was 64.4 ± 0.9% (Fig. 1). The difference in the ratio was only 4% between the DIW and the WW sample, but the difference was significant ($P < 0.05$). Water characteristics would be one of the factors affecting the gasification ratio. The significant low gasification ratio could be explained by the initial alkaline pH of the WW sample. If the C-14 was released as carbon dioxide, C-14 gas can be dissolved into alkaline solutions more easily than into acidic solutions. As the result, the gasification ratio becomes low.

For the WW samples, there was no effect of the filter-sterilization on the gasification ratio (Fig. 1). The gasification ratio for the filter-sterilized WW samples was 62.0 ± 1.4%, and difference in the gasification ratio between the WW sample and the filter-sterilized sample was not significant.

From these results, it was found that more than 60% of the total C-14 added are released as gas under our experimental conditions and that the release is caused by soil microorganisms. The gasification ratio of C-14 would also be affected by water characteristics such as pH.

3.2 Distribution coefficient

After the release of C-14 as gas forms, about 40% of the total C-14 added was remained in the soil suspension samples. Values of K_d were determined using the remaining C-14 in the soil suspension samples. For the DIW sample, the value of K_d was $138 \pm 24\,\mathrm{mL\,g^{-1}}$ (Fig. 2). This value was more than 10-times higher than the previously reported [1]. Cement materials were used as a solid phase sorbent in the previous study, while the paddy soil was used in the present study. Differences in the solid phase may result in the significant different in the K_d value.

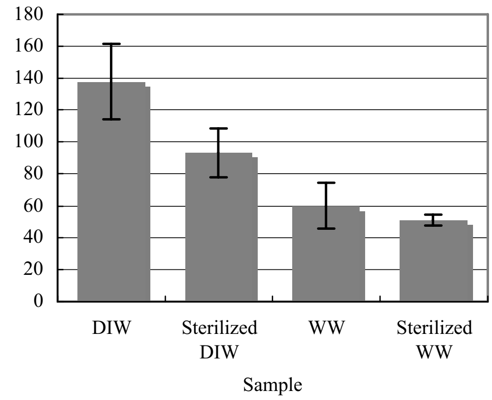

Figure 2. K_d Values of the C-14 from ^{14}C-NaOAc for DIW, WW, and their filter-sterilized samples. Values represent the means and standard deviations of triplicate experiments.

When the soil sample was contacted with the filter-sterilized DIW solution, the K_d value was $93 \pm 15\,\mathrm{mL\,g^{-1}}$ (Fig. 2). There were no differences in K_d values between both samples. The K_d value would be affected by soil microorganisms rather than by microorganisms in DIW.

To confirm the contribution of soil microorganisms to the K_d value, glutaraldehyde was added to the soil-DIW samples (final concentration: 2%). The K_d values of the samples were nearly zero (data not shown). These results suggested that soil microorganisms were responsible for the partitioning of C-14 to solid phase. The relatively high K_d values in the present study may be caused by microbial assimilation of C-14 because the assimilated C-14 by soil microorganisms was partitioned to solid phase.

Soil is not always contacted with the same quality of water, and thus the soil sample was also contacted with the WW solution. The obtained K_d was $60 \pm 14\,\mathrm{mL\,g^{-1}}$ (Fig. 2), and the value was significantly lower than that of the DIW sample ($P < 0.01$). The result suggests that water quality is one of the factors affecting K_d. Yasuda (1994) reported that K_d values of radionuclides decreased according to the increase in EC. In other words, the total amount of dissolved ions in the solution affects K_d values of radionuclides. In the present study, EC of the WW samples was $0.25\,\mathrm{mS\,cm^{-1}}$ at the end of the shake-incubation, and the value is about 2.5-times higher than that of the DIW samples. The K_d of C-14 from ^{14}C-NaOAc may also be controlled by the ions in the solution. In addition, the pH of the DIW samples and the WW samples were 5.5 and 8.5, respectively. Because K_d is often influenced by pH [3], the effect of pH on the K_d values of C-14 deserves further research.

When the soil sample was contacted with the filter-sterilized WW solution, a decreasing trend in K_d was observed (Fig. 2) although there was no significant difference between the WW samples and the filter-sterilized WW samples.

4. CONCLUSION

Gasification ratios and distribution coefficients of C-14, which derived from [1, 2-^{14}C] sodium acetate, were determined. The following conclusions were drawn in the present study.

1. Gasification ratios and K_d values depended on microbial activity. Both values were nearly zero when the microorganisms were completely killed by glutaraldehyde.
2. The range of gasification ratio was from 62.0% to 69.5%. More than 60% the total added C-14 was released into the air as gas forms under our laboratory conditions.
3. The range of K_d was from 51.1 to 137.6 mL g^{-1}. These values were higher than that of previous study [1].
4. Water characteristics such as dissolved ions, pH, and CE also affected both the gasification ratios and the K_d values.

It seems that the organic C-14 compound was ingested and assimilated by microorganisms, and then a part of the ingested C-14 was released as gas forms. Soil microbes are the key organisms in safety assessment for a geological repository of TRU waste.

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