

Determination of carbon species formed by decomposition of acetate in Japanese paddy soil

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Abstract. For appropriate safety assessment of TRU waste disposal, the dominant chemical species of ^{14}C -gas was studied. $[1,2-^{14}\text{C}]$ sodium acetate was added to flooded paddy soil samples, and the content of ^{14}C in the soil, solution, and the emitted CO_2 gas during incubation period was determined. Recovery ratios of the total ^{14}C activity to the initial ^{14}C activity were 97.9% at day 1, 86.4% at day 3, and 83.5% at day 7 of incubation. The result of the day 1 means that the emitted ^{14}C -gas was almost $^{14}\text{CO}_2$. At day 7 of incubation, about 16.5% of ^{14}C was failed to recover. Even if the unknown ^{14}C was gases other than $^{14}\text{CO}_2$, the dominant chemical species of the emitted ^{14}C -gas will be $^{14}\text{CO}_2$, because the recovery ratio of the $^{14}\text{CO}_2$ was 48.9% (>16.5%). Sodium 2-bromoethane-sulfonate was used to ensure the emission of CH_4 , but there was no effect of the reagent to the recovery ratio of $^{14}\text{CO}_2$. Methane emission may be little under our experimental conditions. These results suggest that the dominant chemical species of the emitted ^{14}C -gas from the flooded paddy soil samples was $^{14}\text{CO}_2$.

1. 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, TRU waste for geological disposal is separated into four groups in accordance with physical properties and the concentration of radioactive materials. Group 2 waste among these four groups includes hull and end piece wastes, which are comprised of the debris and residue from the shearing and dissolution of the spent fuel assemblies. The key nuclide in a geological repository for Group 2 waste is ^{14}C , and leaching of organic ^{14}C compounds from simulated hull wastes has been reported [1]. Because ^{14}C is long-lived and has very little sorption properties, the possible migration of ^{14}C from a TRU repository site to the biosphere through groundwater presents some concern. Therefore, it is necessary to understand the behavior of ^{14}C in the human habitation sphere on the assumption the ^{14}C derived from TRU wastes.

Rice paddy field is an important place to assess the behavior of ^{14}C because rice has long been a staple food in the Japanese diet and people may be exposed to ^{14}C through rice intake. Radioactive tracer experiments with $[1,2-^{14}\text{C}]$ sodium acetate showed that more than 65% of the spiked ^{14}C was released from paddy soil samples into the air as gas forms [2]. Rice plants may assimilate the released ^{14}C depending on chemical species. The chemical species of the released ^{14}C , however, have not been identified yet. This paper will show the dominant chemical species of ^{14}C in gas phase, which was formed by decomposition of acetate by microorganisms in the paddy soil.

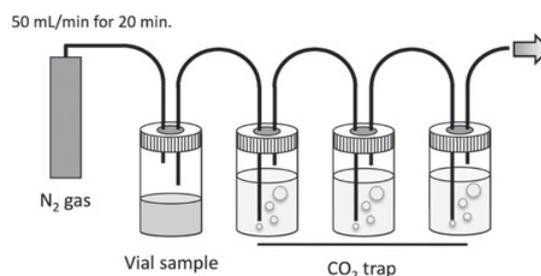
2. MATERIALS AND METHODS

2.1 Soil sample

Paddy soil (Fluvisol) was collected in Shimane prefecture, Japan. The soil sample was air-dried, homogenized, sieved (< 2 mm), and stored in a polypropylene bottle at room temperature until needed. Soil properties were listed in Table 1.

Table 1. Soil properties.

Property	Value
Coarse sand (%)	63
Fine sand (%)	12
Sand (%)	75
Silt (%)	12
Clay (%)	14
Carbon content (g/kg)	16.2
Nitrogen content (g/kg)	1.4

**Figure 1.** Schematic illustration of experimental apparatus.

2.2 Radioactive tracer experiments

The soil sample was contacted with deionized water in a 30 mL glass vial at a solid-liquid ratio of 0.5 g to 5 mL. The vial sample was spiked with [1, 2- ^{14}C] sodium acetate and was sealed with a butyl rubber. Emission of methane during experimental periods was determined by the presence and absence of sodium 2-bromoethane-sulfonate at a final concentration of 10 mM.

The vial sample was incubated with no shake at 25 °C in the dark. The ^{14}C content in solid, liquid, and CO_2 gas phases of the vial sample was determined at the end of incubation. Incubation periods were 1 day, 3 days and 7 days. To determine the ^{14}C content in the solid soil phase, the soil in the vial sample was trapped by filtration on a GF/F filter. About 15 mg of the soil was collected into Combusto-Cone (PerkinElmer, Yokohama, Japan), and it was combusted in 307 Packard sample oxidizer for scintillation counting. The liquid phase of the vial sample was obtained by filtration through a 0.2 μm cellulose acetate filter and then counted for radioactivity in a liquid scintillation counter. A schematic illustration of experimental apparatus for $^{14}\text{CO}_2$ recovery is shown in Figure 1. A head-space gas sample was flushed with N_2 gas at a rate of 50 mL min^{-1} for 20 min. CO_2 gas in the head-space gas sample was trapped by triple sequential traps through Carbo-Sorb E (PerkinElmer, Yokohama, Japan), and the activities of ^{14}C were measured with a Tri-Carb-25WTR Liquid Scintillation Analyzer (Packard, Tokyo, Japan). All the experiments were carried out in triplicate.

3. RESULTS AND DISCUSSION

3.1 Dominant chemical species of ^{14}C gas

Figure 2 shows the recovery ratios of ^{14}C at the end of incubation. The recovery ratio at the day 1 of incubation was $97.9 \pm 2.5\%$. This result means that the chemical species of the released gas from the vial sample was carbon dioxide. The unrecovered ^{14}C was increased with incubation periods. However, even the lower recovery ratio at the day 7 of incubation was $83.5 \pm 10.6\%$. That is, about 16.5% of ^{14}C was failed to recover. Because the recovery ratio of the $^{14}\text{CO}_2$ was $48.9 \pm 11.9\%$, the dominant chemical

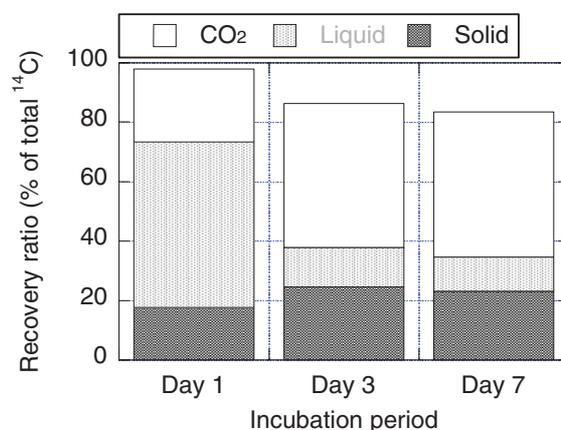


Figure 2. Recovery ratios of ^{14}C in solid and liquid phases and $^{14}\text{CO}_2$ gas.

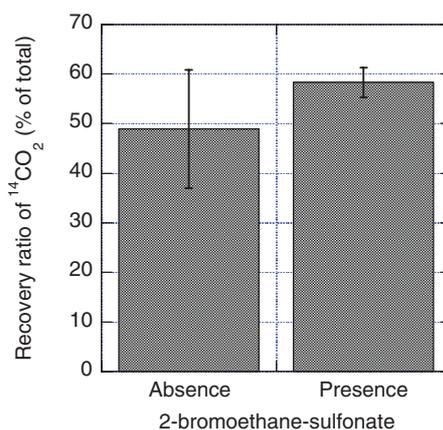


Figure 3. Effects of sodium 2-bromoethane-sulfonate on the recovery ratios of $^{14}\text{CO}_2$.

species of the released gas would be carbon dioxide if 16.5% of ^{14}C were a chemical species other than carbon dioxide. Carbon dioxide can diffuse into the plant leaf through the stomata. The behavior of $^{14}\text{CO}_2$ in paddy fields must be attention.

3.2 Generation of methane

Paddy fields are a source of methane emission [3], and thus generation of methane gas under our experimental conditions were determined. At the day 7 of incubation, effects of sodium 2-bromoethane-sulfonate, which is a specific inhibitor of methanogens, were investigated (Fig. 3). No differences were observed for $^{14}\text{CO}_2$ emission between the presence and absence of that reagent (*t*-test, $P > 0.05$), suggesting little methane emission during the experimental periods. 16.5% of ^{14}C which was failed to recover at the day 7 of incubation may contain ^{14}C -gases other than CO_2 and CH_4 . These ^{14}C -gases other than $^{14}\text{CO}_2$ be diluted and dispersed in the atmosphere.

4. CONCLUSION

Dominant chemical species of ^{14}C containing gas, which derived from [1, 2- ^{14}C] sodium acetate, were determined. The following conclusions were drawn in the present study.

1. Dominant chemical species of ^{14}C containing gas is carbon dioxide.
2. The content of the ^{14}C -gases other than $^{14}\text{CO}_2$ may increase with incubation time.
3. Methane emission is little under our experimental conditions.

The $^{14}\text{CO}_2$ emitted from paddy fields will be assimilated by rice plants through photosynthesis. Rice straw will plow back next year, and thus the assimilated ^{14}C may be recycled in paddy ecosystem. It should be very careful to clarify ^{14}C cycles in paddy ecosystem for the safety of geological disposal of TRU waste.

Acknowledgments

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References

- [1] S. Kaneko, H. Tanabe, M. Sasoh, R. Takahashi, T. Shibano, S. Tateyama, *Mat. Res. Soc. Symp Proc.* 757, 621 (2003).
- [2] N. Ishii, H. Koiso, H. Takeda, S. Uchida, *J. Nucl. Sci. Technol.* 47, 238 (2010).
- [3] M. Prather, R. Derwent, D. Ehhalt, P. Fraser, E Sanhueza, X. Zhou, in *Climate Change 1994*, edited by J.T. Houghton et al. (Cambridge U. Press, 1995), pp. 73-126.