Contribution of the carboxyl group of acetate to the ^{14}C-containing gas production in agricultural soils

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Abstract
The ^{14}C-containing gas production ratios were determined by batch tests using 142 agricultural (upland and paddy) soil samples. Each of the soil samples was suspended in deionized water containing either [1-^{14}C] sodium acetate or [1,2-^{14}C] sodium acetate and shake-incubated for 7 days. Production ratios, on average, were 68.6% for [1-^{14}C] sodium acetate and 59.1% for [1,2-^{14}C] sodium acetate. From the results, the ^{14}C-containing gas production ratio for [2-^{14}C] sodium acetate was calculated to be 49.6%. The carboxyl group of sodium acetate, therefore, is easily released as gas in Japanese agricultural soils. Land use also affected the ^{14}C-containing gas production. The production ratios of upland soil samples were significantly lower than those of paddy soil samples.

Key Words
Radioactive waste, radiocarbon, carboxyl group, acetic acid, gasification, agricultural soil

Introduction
The demand for nuclear power plants is growing to achieve a low-carbon society. On the other hand, there is increasing concern about potential radioactive contamination of agricultural soils by the promotion of nuclear policies. Thus, understanding of behaviors of radioactive contaminants in agricultural soils is a considerable issue.

Transuranic (TRU) waste containing radionuclides is generated during the operation of reprocessing facilities and mixed oxide (MOX) fuel fabrication facilities. One of the dominant nuclides contributing to the dose from TRU waste is ^{14}C. Recently, it was found that organic ^{14}C-containing compounds such as low molecular weight carboxylic acids are released from metallic TRU waste (Kaneko *et al*. 2003). In a previous study using paddy soils containing [1, 2-^{14}C] sodium acetate, a relatively large amount of the ^{14}C in acetate was released into the air from the soil samples (Ishii *et al*. in press). Although acetate has two carbon atom-containing moieties (methyl and carboxyl groups) in a molecule, there are no data for the gas production ratio of each under the previous experimental conditions. Obtaining the gas production ratios of the ^{14}C bearing methyl and carboxyl groups will provide a better understanding of underlying mechanisms of the ^{14}C behavior. In the present study, the gas production ratios of the ^{14}C-bearing carboxyl group in sodium acetate were determined. In addition, the relationship between gas production ratios and land use such as paddy and upland uses were determined.

Methods
Soil samples
A total of 142 Japanese agricultural soil samples (63 paddy soil and 72 upland soil samples) were collected throughout Japan (Ishikawa *et al*. 2008). The soil samples were dried at room temperature, and then passed through a 2-mm-mesh-sieve to obtain homogeneity. The air-dried soil samples were stored in polypropylene bottles at room temperature.

Radioactive tracer experiments
The carrier-free [1-^{14}C] sodium acetate (specific activity: 2035 MBq/mmol; American Radiolabeled Chemicals, Inc., St. Louis, MO) was diluted to a concentration of 0.9 kBq/mL, and the radioactive solution was filter-sterilized before being added to a 50 mL polypropylene tube with a screw cap closing. In addition, the carrier-free [1, 2-^{14}C] sodium acetate (specific activity: 4070 MBq/mmol; American Radiolabeled Chemicals, Inc., St. Louis, MO) was also used and had a concentration of 1.8 kBq/mL. Each air-dried soil sample was placed in contact with the radioactive solution at a solid-liquid ratio of 0.5 g to 5 mL. This soil suspension was shake-incubated at 25°C for 7 days in the dark. At the end of incubation, a subsample of the soil suspension was collected to measure the activity of ^{14}C. The ^{14}C activities of the subsample were

counted in an Aquasol-2 scintillator (PerkinElmer Japan Co., Ltd., Yokohama, Japan) using a Tri-Carb-25WTR Liquid Scintillation Analyzer (Packard Instrument Co., Inc., Tokyo, Japan). For the soil suspension subsamples, ^{14}C was counted in the gel phase scintillation cocktail. The gas production ratios were determined by the difference between initial and final ^{14}C concentrations. All experiments were triplicated.

pH measurement

Soil solution pH was measured using a pH meter (B-211; Horiba, Kyoto, Japan). To obtain a soil solution, each soil suspension sample was centrifuged at 3,780 × g for 10 min at the end of the incubation. The obtained supernatant was filtered through a 0.2-µm-pore-size cellulose acetate filter.

Results

The production ratios of ^{14}C-containing gas for [1-^{14}C] sodium acetate were determined using 142 agricultural soil samples on day 7 of incubation (Table 1). The mean value of the production ratios was 68.6%. The narrow range between quantile-25% and quantile-75% suggests a small variation for the gas production ratios among agricultural soils although the difference between minimum (F5 sample) and maximum (F61 sample) values was big. Both of these samples were upland soils. Soil characteristics such as particle size, particle density, water content, and carbon content were compared among soil samples but were not special for F5 and F61 samples.

Table 1. Descriptive statistics of ^{14}C-containing gas production ratios (% of total added).

	Category of sample		
Statistic	All	Upland	Paddy
Mean	68.6	66.3	71.4
Median	70.9	69.5	71.7
Minimum	4.6	4.6	61.0
Maximum	81.5	81.5	81.0
Quantile-25%	66.1	64.6	68.6
Quantile-75%	74.5	74.8	74.3
Number of samples	142	79	63

The effect of land use on the production ratios of ^{14}C-containing gas was determined (Table 1). The production ratios of upland soil samples were significantly lower than those of paddy soil samples (*t*-test, $P<0.01$). Because a previous study indicated that the production of ^{14}C-containing gas was negatively correlated with soil pH (Ishii *et al*. in press), the pH values of soil solutions were compared between the upland soil and the paddy soil samples (Figure 1). For the upland soil samples, the range of pH values was wide, and the median pH value was high compared with that for the paddy samples. The mean values of pH were 6.6 for upland and 6.2 for paddy soil samples, and the difference was significant (*t*-test, $P<0.01$). The pH values for 20 of 79 upland soil samples were more than 7.0, and the mean value of the gas production ratios for these samples was 58.5%. The ^{14}C-containing gas production will be controlled by soil pH. This control may be explained by the solubility of CO_2. It is well known that the maximum total amount of CO_2 that may dissolve in water is a function of pH. If the released ^{14}C-containing gas is CO_2, more $^{14}CO_2$ gas will be dissolved in the liquid phase with increasing pH.

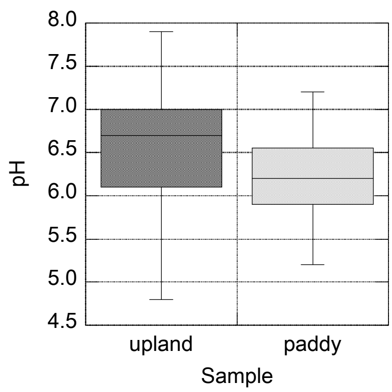

Figure 1. Box and whisker plots illustrating the range of the pH of upland and paddy soil samples.

1 – 6 August 2010, Brisbane, Australia. Published on DVD.

In the present study, the production ratios of the ^{14}C-containing gas were also determined by using [1,2-^{14}C] sodium acetate, which has ^{14}C in both carboxyl and methyl groups in the molecule. The slope of the regression line (Figure 2, dashed line) was similar to that of the solid line. This means that the behavior of ^{14}C in acetate is similar for [1-^{14}C] sodium acetate and [1,2-^{14}C] sodium acetate.

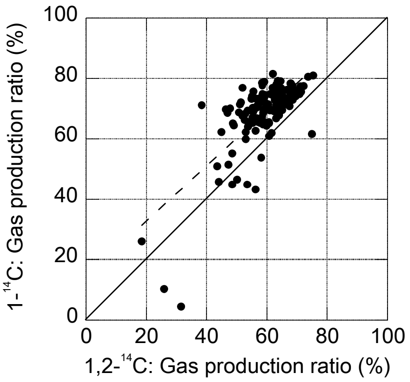

Figure 2. Correlation of ^{14}C-containing gas production ratios between [1,2-^{14}C] sodium acetate and [1-^{14}C] sodium acetate. The solid and the dashed lines show "y = x" and the regression line, respectively. The regression equation for the scattered points was given by y = 0.92x + 14.4, and the correlation coefficient (*r*) was 0.72 (n = 142).

Most of the points were above the solid line (Figure 2), suggesting that the gas production ratios for [1-^{14}C] sodium acetate are higher than those for [1,2-^{14}C] sodium acetate. The ^{14}C in carboxyl group will be easily released as gas. The mean values of the ^{14}C-containing gas production ratios were 68.6% for [1-^{14}C] sodium acetate (Table 1) and 59.1% for [1,2-^{14}C] sodium acetate, and the difference in the ratio was significant (*t*-test, $P<0.01$). From those values, the ^{14}C-containing gas production ratio for [2-^{14}C] sodium acetate was calculated to be 49.6%. In a future study, it must be experimentally confirmed whether the ^{14}C-containing gas production ratios are really low for [2-^{14}C] sodium acetate.

Conclusion
The production ratios of ^{14}C-containing gas from [1-^{14}C] sodium acetate were determined. Of the two types of carbon moieties in sodium acetate, the ^{14}C of the carboxyl group was released as gas at high production ratios. The gas production ratios were negatively correlated with the pH values of soil solutions. In the comparison between paddy and upland soil samples, the gas production ratios of the paddy samples were higher than those of upland soil samples. The high values of gas production ratios of the paddy soil samples can be explained by the low pH of the paddy samples. The position of ^{14}C in the acetate and the pH of soil solutions are important parameters for the behavior of ^{14}C of acetate in agricultural soils. The production ratios of the ^{14}C-containing gas from [2-^{14}C] sodium acetate will next be determined to assure the relationship between the position of the C in the acetate and the gas production ratio in a planned future study.

Acknowledgment
This work has been partially supported by the Agency for Natural Resources and Energy, the Ministry of Economy, Trade and Industry (METI), Japan.

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