

Elution of radiocesium from soil and sludge

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Elution of radiocesium from soil was studied as a first step for the reduction of external radiation exposure. Three experiments were independently carried out on elution of ¹³⁷Cs with: (I) rainfall, (II) oxidation power of ozone, and (III) chemical reagents. In experiment I, rainfall was simulated by passing deionized water through a soil column, but no elution of ¹³⁷Cs was observed. A sludge sample which was contaminated with the fallout from the Fukushima Daiichi Nuclear Power Plant accident was treated with ozone micro-bubbles and ozone gas in experiment II, but ¹³⁷Cs was not released from the sludge. The oxidation power of ozone had no effects on the elution of ¹³⁷Cs under the present experimental conditions. In experiment III, Good's buffers such as MES (pH6.0) and HEPES (pH 7.5) were used to elute ¹³⁷Cs from soil; however, ¹³⁷Cs eluted into these buffers was below the detection limit. When the soil was soaked with 100 mM KCl and 100 mM (NH₄)₂SO₄, 4.1% and 15.4% respectively, of the total ¹³⁷Cs radioactivity were eluted into these chemical solutions. From these results, it was concluded that 100 mM (NH₄)₂SO₄ was the most effective chemical to elute ¹³⁷Cs from the soil.

Key Words: radiocesium, rain fall, ozone, ammonium sulfate,

1. Introduction

A large amount of radiocesium (¹³⁴Cs and ¹³⁷Cs) was released into the environment by the Fukushima Daiichi Nuclear Power Plant (FDNPP) accident¹⁾. These radionuclides have caused serious contamination onto the soil surface and have emitted gamma rays²⁾. Current residents of the contaminated areas are concerned about radiation exposure resulting from the accident, while former residents who are still remain evacuated are contemplating when it might be safe to return. Techniques for reducing radiation dose, therefore, are highly desirable in speeding up the recovery process.

The local government has tried to remove the surface

soil to reduce external radiation exposure, but this technique has problems such as huge cost, the time involved, disposal of the contaminated soil, and the use of heavy machines, that must be addressed. The authors have suggested that controlling the downward migration of radiocesium in order to avoid ground water contamination might be an effective technique for reducing radiation dose because this technique is simple and has an effect similar to that of deep plowing which inverts the surface soil to deep soil. Furthermore, shielding effect on radiation is also expected as the contaminated surface soil is covered by the non-contaminated deep soil.

The elution of radiocesium from soil has to be

determined as a first step before implementing the downward migration technique. In the present study, the elution of radiocesium from the soil and sedimentation sludge found in drinking water treatment facilities was evaluated by using various solutions such as deionized water (to simulate rain water), potassium chloride, ammonium sulfate, and Good's buffers, and treating water with ozone. Effective chemicals for the elution of ^{137}Cs have been described.

2. Materials and Methods

(1) Experiment I

The effect of rainfall on the elution of ^{137}Cs from soil was determined. The soil, which is a mixture of Akadama soil, Kanuma soil, pumice stone, vermiculite, and cow manure, was purchased at a garden store and was put in nine flowerpots. The volume of soil in each pot was $5.0 \times 10^{-4} \text{ m}^3$ and the surface area was $9.5 \times 10^{-3} \text{ m}^2$. The soil depth was about 80 mm.

The pots were kept on the roof of a five-story building at the National Institute of Radiological Sciences (NIRS) from 11 March to 19 May, 2011. In this way, soil in the nine pots was exposed to the FDNPP fallout for about two months.

Ten and then twenty liters of deionized water without any radiocesium contamination was passed through the soil in each of the three pots at a rate of less than 200 mL min^{-1} to simulate the effect of rain water (Fig. 1). These volumes of deionized water are equivalent to the expected rainfall during a period of 7 months and 17 months, respectively, beginning from March, based on the annual rainfall in Namie-machi which is located inside the evacuation zone. After the deionized water was passed through them, the soil in each of the 10 L pots was separately dried and homogenized; the soil in the 20 L pots was similarly treated. For comparison, soil from three pots without the deionized water supply was also separately dried and homogenized (0 L pots). The radioactivity of ^{137}Cs in the nine homogenized soil samples (three of each type) was analyzed using a germanium detector (Seiko EG&G).

(2) Experiment II

The effect of oxidation power of ozone on the elution of ^{137}Cs from sedimentation sludge was determined. Sludge was taken from a drinking water treatment facility

Table 1 The elemental composition of the sludge.

Element	Conc.* (mg/g)	Element	Conc.* (mg/g)	Element	Conc.* (mg/g)
Al	95.24	K	6.85	Sr	0.00
Ca	2.67	Mg	1.84	Ti	2.41
Cu	0.09	Mn	3.05	Zn	0.30
Fe	38.91	Na	6.12		

*Conc.: concentration



Figure 1. Photograph showing the deionized water supply setup.



Figure 2. Bubbling ozone gas through the sludge.

in Saitama Prefecture. It had a ^{137}Cs concentration of $4.2 \text{ kBq kg}^{-1}\text{-dry}$. The elemental composition of the sludge is listed in Table 1.

a) Ozone micro-bubble water

Fifteen grams of the sludge was mixed with 18 mL of deionized water in a 50 mL centrifugation tube, and the sludge-water sample was further separately mixed with one of the following as eluate: deionized water or 3 ppm ozone micro-bubble water (OMBW). The volume of the added eluate was 15 mL. Each tube with a sample for elution was manually shaken 150 times. After shaking,

each tube was allowed to stand for several minutes and then the supernatant was collected to determine the elution efficiency of ^{137}Cs . The procedure beginning with the addition of each of eluate to the collection of the supernatant was repeated six times. The supernatant first collected had a volume of 10 mL while the second and subsequent collections had volumes of 15 mL each. The collected supernatant (total 85 mL) was filtered through Sterivex-GP (Millipore) to remove small particles. The radioactivity of ^{137}Cs in the filtrate was analyzed using a germanium detector (Seiko EG&G). The elution ratio of ^{137}Cs was determined as follows:

$$\text{Elution ratio (\%)} = \left(\frac{^{137}\text{Cs in the solution}}{^{137}\text{Cs in the sludge}} \right) \times 100$$

b) Ozone gas bubbling

In order to elute ^{137}Cs , bubbling of the sludge by ozone gas was also carried out (Fig. 2). Thirty grams of the sludge in a 250 mL bottle was soaked in 150 mL deionized water. Ozone gas (46.3 g m^{-3}) was bubbled through this sludge sample at 3.3 liters per minute for 30 minutes. A similar sludge sample was also treated with bubbling oxygen gas as a control experiment. The collection of the supernatant, filtration, and the determination of ^{137}Cs radioactivity were performed using the same procedure as described above.

(3) Experiment III

Elution of ^{137}Cs from soil by using various chemical solutions was investigated. Chemical solutions used were 1 mM and 100 mM KCl, 1 mM and 100 mM $(\text{NH}_4)_2\text{SO}_4$, 10 mM 2-morpholinoethanesulfonic acid (MES; pH 6.0), and 10 mM 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES; pH7.5). MES and HEPES are commonly used as buffering agents in biology and biochemistry and are known as Good's buffers.

Soil from the surface layer (0-1cm) was collected from the NIRS campus on 6 April, 2011. The measured radioactivity of ^{137}Cs was $2.9 \times 10^3 \text{ Bq kg}^{-1}$ -dry soil. Fifty grams of the soil was soaked with 200 mL of each chemical solution, and then mixed well by hand. The soil-solution sample was incubated at 25°C in the dark without shaking. To determine the elution of ^{137}Cs , the supernatant of the soil-solution sample was collected four times during the experimental period, and the

radioactivity of ^{137}Cs in the supernatant was analyzed using a germanium detector (Seiko EG&G). This experiment was repeated two times.

3. Results and Discussion

(1) Elution by annual rainfall

The concentration of ^{137}Cs in the 0 L pot sample type was compared to those for the 10 L and the 20 L sample types (Table 2). No difference was observed between the 0 L pot type and the 10 L pot type and between the 0 L pot type and the 20 L pot type although a decrease in ^{137}Cs content was expected for those through which deionized water had been passed. These results suggest that the downward migration of ^{137}Cs aided by rainfall is quite small. The shielding effect by rainfall is ineffective because radiocesium remained in the surface layer, as evident from our experiment.

Table 2 The concentration of ^{137}Cs in the three homogenized soil sample types.

Deionized water (L)	Concentration* (Bq/kg dry)	P value (t-test)**
0	447 ± 19	
10	421 ± 196	> 0.05
20	487 ± 113	> 0.05

*The results are presented as the mean value of three independent replicates +/- standard deviation.

** The concentrations of ^{137}Cs in the 10 L and the 20 L sample types were compared to that for the 0 L pot sample type .

Table 3 The radioactivity of ^{137}Cs and elution ratio by treatment with deionized water and OMBW.

Elution	^{137}Cs in the sludge (Bq)	^{137}Cs in the solution (Bq)	Elution ratio (%)
Deionized water	63	DL*	< 2.4
OMBW	63	DL*	< 2.4

* DL: detection limit.

Table 4 The activity of ^{137}Cs in the sludge and the solution.

Bubbling	^{137}Cs in the sludge (Bq)	^{137}Cs in the solution (Bq)	Elution ratio (%)
Oxygen	126	DL*	< 1.0
Ozone	126	DL*	< 1.0

* DL: detection limit.

Table 5 Elements which were easy to elute by ozone gas bubbling.

Element	O ₃ /O ₂ *	Element	O ₃ /O ₂ *	Element	O ₃ /O ₂ *
Be-9	6.0	Ag-107	72.2	Ho-165	2.8
Cr-53	5.3	La-139	4.2	Tm-169	3.6
Ni-60	32.1	Ce-140	3.1	Hf-178	21
Cu-63	4.0	Pr-141	4.2	Th-232	6.4
Y-89	4.4	Tb-159	3.0	U-238	57.3
Zr-90	199.2	Dy-163	11.5		

*O₃/O₂: the ratio of the concentration of dissolved elements in O₃ gas sample to that in O₂ gas sample.

(2) Elution by treating water with ozone and ozone micro-bubbles

Sedimentation sludge from drinking water treatment facilities is generated every day. Over time, increasing in the storage amount of the radioactive contaminant sludge is a concern, especially in the Kanto and Tohoku areas. Decreasing the amount of sludge wastes that must be specially handled, by eluting radiocesium from them, is desirable. So the authors have investigated a technique for elution of radiocesium from the sludge by using the oxidation power of ozone.

Table 3 shows the elution ratio of ¹³⁷Cs by treatment with deionized water and OMBW. The radioactivity of ¹³⁷Cs was under the detection limit for both samples. Elution of ¹³⁷Cs was difficult even for the strong oxidation power of OMBW under the experimental conditions. No elution by the addition of deionized water supported the results of the first experiment for the effect of rainfall.

The sludge was bubbled with oxygen and ozone gas. Table 4 shows the radioactivity of ¹³⁷Cs in the sludge and

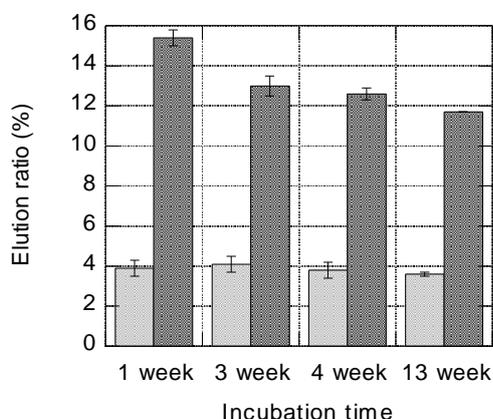


Figure 3. Elution ratios of ¹³⁷Cs for the 100 mM KCl (gray bars) and 100 mM (NH₄)₂SO₄ (black bars) samples.

in the solution. Even for ozone bubbling, elution of ¹³⁷Cs was under the detection limit. From the results of the OMBW and the ozone bubbling experiments, it was concluded that oxidation by ozone was not an effective method to elute ¹³⁷Cs from the sludge.

The concentration of dissolved elements after the bubbling was analyzed with ICP-MS. It was found that some elements were easier to elute by ozone gas bubbling than by oxygen gas bubbling (Table 5). Among the 17 elements listed in Table 5, eight elements are rare earth elements. The bubbling by ozone gas may be useful for the elution of rare earth elements.

(3) Elution by chemicals

To determine the effect of pH on the elution of ¹³⁷Cs, MES and HEPES were used, but no elution of ¹³⁷Cs was observed. The elution of ¹³⁷Cs was not influenced by pH in the 6.0 to 7.5 range.

Effects of KCl and (NH₄)₂SO₄ on the elution of ¹³⁷Cs were next considered. ¹³⁷Cs was only detected in the supernatant when the soil was soaked with 100 mM KCl and 100 mM (NH₄)₂SO₄. The elution of ¹³⁷Cs depended on the concentrations of KCl and (NH₄)₂SO₄ because no elution of ¹³⁷Cs was found for the 1 mM KCl and 1 mM (NH₄)₂SO₄ samples.

Figure 3 shows the elution ratio of ¹³⁷Cs with the addition of 100 mM KCl and 100 mM (NH₄)₂SO₄. The elution ratio for 100 mM KCl was constant (from 3.6 to 4.1%) during the experimental period. For 100 mM (NH₄)₂SO₄, the elution ratio of ¹³⁷Cs decreased from 15.4% to 11.7% with time. The decrease was due to the decrease in the concentration of ammonium in the sample as ammonium is an important source of nitrogen for heterotrophic bacteria³.

The maximum ratio of 15.4% for the 100 mM (NH₄)₂SO₄ sample was found one week after the commencement of the experiment. This result suggests that by spraying 100 mM (NH₄)₂SO₄ on the ground surface it is possible to promote the elution and the downward migration of ¹³⁷Cs from the surface layer. The reduction of external radiation exposure from ¹³⁷Cs, therefore, would be reduced by the shielding effect from the surface soil. However, the impact of 100 mM (NH₄)₂SO₄ on the environment such as ground water contamination, transfer to plants, biological disturbance and so on, must be considered before this can be used practically.

4. Conclusions

The elution of ^{137}Cs from the soil and sludge was studied as a first step for reduction of external radiation exposure from this radionuclide. The maximum elution was observed when contaminated soil was soaked with 100 mM $(\text{NH}_4)_2\text{SO}_4$. The second most effective chemical is 100 mM KCl. The elution and downward migration of ^{137}Cs was enhanced, and the surface layer also offered shielding to the deeper layers from radiation by ^{137}Cs . Similar results were also observed for ^{134}Cs although these data have not been presented here. For practical use of these chemicals, the penetration depth of ^{137}Cs , shielding effects on the radiation from the ^{137}Cs , impact on the environment from using these chemicals, and their cost-effectiveness must be first studied.

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References

- 1) Chino, M., H. Nakayama, H. Nagai, H. Terada, G. Katata, H. Yamazawa, Preliminary estimation of release amounts of ^{131}I and ^{137}Cs accidentally discharged from the Fukushima Daiichi Nuclear Power Plant into the atmosphere, *Journal of Nuclear Science and Technology*, **48**, 1129-1134, 2011.
- 2) Ishii, N., K. Tagami, H. Takata, K. Fujita, I. Kawaguchi, Y. Watanabe, S. Uchida, Deposition in Chiba Prefecture, Japan, of Fukushima Daiichi Nuclear Power Plant fallout, *Health Physics*, (in press).
- 3) Keil, R. G., D. L. Kirchman, Contribution of dissolved free amino acids and ammonium to the nitrogen requirements of heterotrophic bacterioplankton, *Marine Ecology Progress Series*, **73**, 1-10, 1991.