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Characterization of Radiocesium Levels and Fractions of ^{137}Cs in Soil Collected from Oguni, Date Using Manual and Instrument Software Calculation Based on Covell Method

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Two core soil samples were collected from Oguni, Date which is located 55 km northwest from the Fukushima Daiichi Nuclear Power Plant accident area to determine the levels of radiocesium using High Purity Ge detector. Radiocesiums are toxic and a major component of nuclear reactions. The total levels of radiocesium in core soil samples for ^{134}Cs is around 34,000 Bq/m^2 and around 160,000 Bq/m^2 for ^{137}Cs. While for the top layer sample of 0-5 cm for ^{134}Cs is around 20,000 Bq/m^2 and around 100,000 Bq/m^2 for ^{137}Cs which is much lower compared to the first record (14 June 2011) of radiocesium deposition of about 300,000 Bq/m^2 at Oguni area. In general, the manual and instrument software calculated results for radiocesium levels showed relative standard deviation of less than 5% for both core samples. The fractions of ^{137}Cs in the top layer soil of the two cores were analyzed and the results were 5 and 3.9% for Fraction I (Exchangeable), 7.1 and 6.4% for Fraction II (Bound to organic matter), and 87.9 and 89.7% for Fraction III (Strongly bound). Compared this result with the previous study done on ^{137}Cs fractions in soil around Oguni area agreed with the observation on its behavior that on a relatively undisturbed soil Fraction I tend to decrease, while Fraction III will increase, and Fraction II will have almost the same percentage value.

Key words: ^{137}Cs fraction, Covell method, FDNPP, Oguni, radiocesium, soil

INTRODUCTION

Nuclear power plants produce many radionuclides during nuclear reactions. $^{239,240}Pu$ (half-life; thousands of years), ^{241}Am (half-life; hundreds of years), ^{137}Cs (half-life; tens of years), and ^{131}I (half-life; days) are some common radionuclides that are produced during nuclear reactions (Rao 2001) which can be measured and characterized. Measurement and detection techniques are based on the scale or amount being measured and on particular radionuclide of concern.

In the event of accidental release of radionuclides from nuclear power plant such as in Chernobyl and Fukushima Daiichi Nuclear Power Plant (FDNPP), immediate assessment on the levels of radionuclides released in the atmosphere is important. Radiocesium, a toxic radionuclide and a major component during nuclear reactions, is one

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of the concerns because it raises great environmental and public health concern for its long range transport via atmosphere (Fan et al. 2014). Radiocesiums (^{137}Cs half-life of 30.17 yr and ^{134}Cs half-life 2.07 yr), are gamma emitters with long half-life. Radiocesiums are strongly retained by clay minerals in soil and can remain in the surface soil for a long time after its deposition (Takeda et al. 2013; Takeda et al. 2014). The mobility of radiocesiums after deposition is low and it poses health risks. This would make radiocesiums readily available for uptake by crops thus may pose health risks to nearby population. Determining and assessing the levels of radiocesiums in soil are very important because many decisions and countermeasures will be based on the level of contamination measured and detected. Science-based data can be used in management decisions such as if the soil is safe for cultivation or not and if it needs to be abandoned or decontaminated. Oguni, Date which is located 55 km northwest from Fukushima Daiichi Nuclear Power Plant (FDNPP) accident and 10 km east of Fukushima City requires continuous assessment and study on the level of radiocesium in soil. Aside from knowing the total radioactivity or level of radiocesium in soil, it is also important to know its behavior and types in soil like how many percent is freely exchangeable to its environment, what percent is bound to organic and strongly bound to soil particles particularly ^{137}Cs which have a long half-life. Knowing this will help the proper authorities in making objective decision in addressing a contaminated area like Oguni, Date.

Measurement of radioactivity coming from a gamma emitter like ^{137}Cs and ^{134}Cs is performed on a High Purity Germanium (HPGe) detector after proper sample preparation. HPGe usually comes with a software that can do all the analysis and calculation based on the information given like weight, volume, height, counting time, standards used and spectrum software that has a program that uses a particular method for calculation and determination of peak area and net counts. The methods used in photo peak integration are Covell method (Covell 1959), Total Peak Area (TPA) or YULE method (Yule 1972; Yule & Rook 1977), Sterlinski method (Czauderna 1989), and Quittners method (Quittner 1969). The Covell method uses energy channel that have smallest relative standard deviation (Czauderna 1989). The Total Peak Area (TPA) or YULE method oversimplifies the calculation of background counts, making it low and thus increasing its uncertainty (Czauderna 1989). The Sterlinski method is based on the weight of accumulated counts (Czauderna 1989). The Quittners approach employs a non-linear baseline subtraction technique and data points are fitted to second order polynomials using the methods describe by Savitzky and Golay (Czauderna 1989). The Covell method is the most widely used in photopeak integration since it can be easily implemented in the analytical laboratory because calculation of peak areas and standard deviation can be done manually (Heydorn & Lada 1972). Since Covell method is widely used, comparison of results can easily be made against other instrument software that employs the same method.

MATERIALS AND METHOD

Sample Collection and Pre-Treatment

Two core soil samples were collected using a core sampler with a plastic cylindrical container (U-8; 5 cm inner diameter and 30 cm height) on the 14 October 2015 at Oguni, Date with coordinates of N 37.749983°, E 140.566967° (see Figure 1). U-8 container is widely used as soil collector and also as container during measurement of gamma-rays in environmental samples in Japan (Onda et al. 2015). The first core (T core) sample has a height of 23cm, and 30 cm for the second core (A core) sample from the surface. The U-8 container containing the soil sample was removed from the core sampler. The collected soil is left unmixed in the U-8 container and divided into

5 cm thick layer. Each 5cm layer was then dried at 50^{0}C for one week (Tsukada 2008). The dried soil is then passed through 2 mm mesh sieve to remove small pebbles and other unwanted materials.

Sample Analysis

The dried and sieved soil samples were compressed into a plastic bottle (4.5cm x 5.0cm dimension). The weight and height of each sample were measured then analyzed using High Purity Germanium (HPGe) detector connected to a multi-channel analyzer system and counted for 1,800-18,000s depending on the level of radiocesium of each layer.

The fractions of ^{137}Cs in soils were extracted using the sequential extraction method (Tessier et al. 1979) as follows: 1) Extraction 1 (Exchangeable ^{137}Cs), 1 g of top layer (0-5cm) soil sample was weighed and extracted with 10ml of 1M CH_3COONH_4 (pH 7) solution at 20^{0}C and stirred for 1 h. It is then centrifuged for 10 minutes at 4000 rpm and rinsed with ultrapure water. A 0.22 µm membrane filter (Durapore® PVDF Membrane) was used to obtain the extract. 2) Extraction 2 (^{137}Cs bound to organic matter) the rinsed pellet on Extraction 1 was used, added Ultra pure water and heated at 80^{0}C. Then slowly added H_2O_2 (35%) adjusted to pH 2 with HNO_3 for 3 h. Cooled and added 2.5 ml of 3.2 M CH_3COONH_4. It is then centrifuged for 10 minutes at 4000 rpm and rinsed with ultrapure water. A 0.22 µm membrane filter (Durapore® PVDF Membrane) was used to obtain the extract. The supernatant on Extraction 1 and 2 were

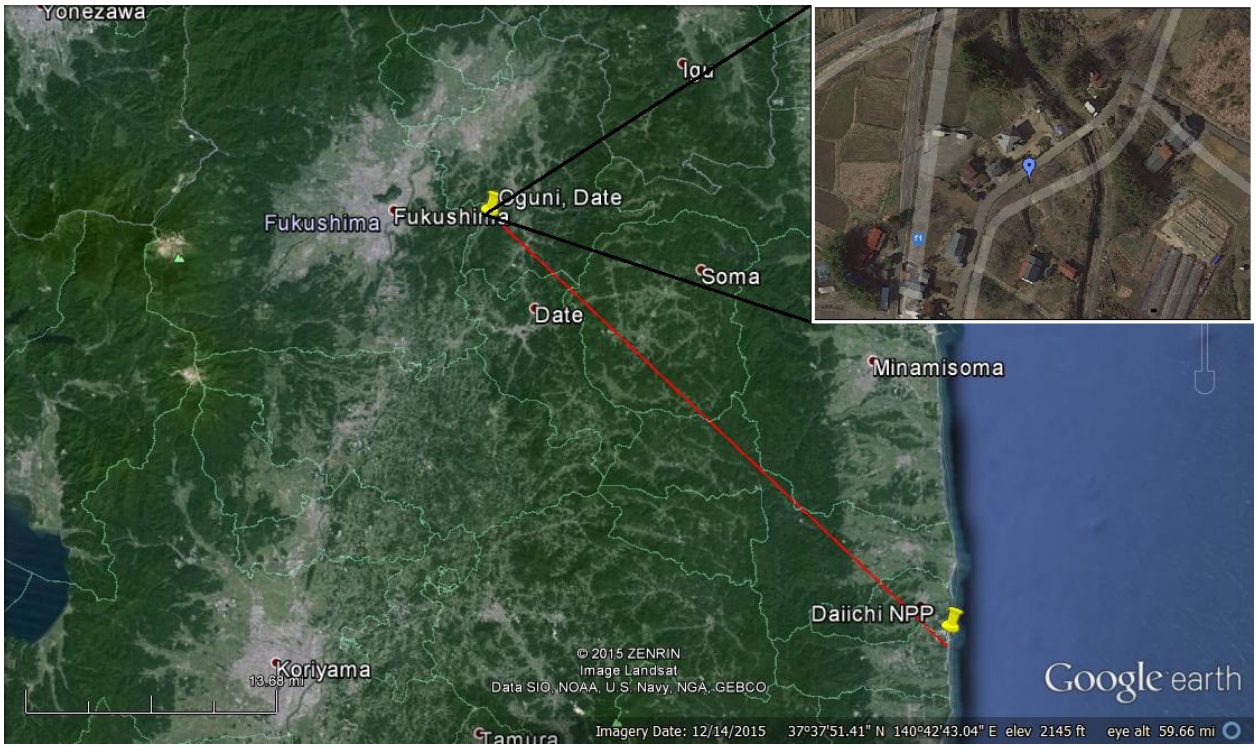

Figure 1. Soil sampling site at Oguni, Date, (N 37.749983°, E 140.566967°) located 55km northwest from FDNPP (Photo credit: Google earth).

analyzed for its ^{137}Cs level using HPGe detector connected to a multi-channel analyzer system and counted for 25,000 to 80,000s.

RESULTS AND DISCUSSIONS

Efficiency Standards and Curve Fitting

The counting efficiency of HPGe detector (Canberra Coaxial HPGe with relative efficiency of ≥30) at energy levels of ^{137}Cs and ^{134}Cs was determined using mixed standard containing nine radionuclides (see Table 1) at heights of 0.5, 1, 2, 3 and 5 cm. The operating software of the instrument is Spectrum Explorer Version 1.74. The result calculated by the software is compared against the result calculated manually both using Covell method.

The amount of radionuclides in the mixed standard was corrected to the time of calibration to reflect the correct efficiency values. The calculated efficiency is then plotted against the energy of radionuclide in all standards (see Figure 4) to compare which standard has the highest efficiency. From this plot you can calculate the efficiency of other radionuclide concern such as ^{134}Cs which is not included in the mixed standards by power curve fitting and using the equation,

$$y = ax^b \quad (1)$$

where x is the energy of ^{134}Cs or of radionuclide curve fitted using power. Then the inverse efficiency of ^{137}Cs, ^{134}Cs or the radionuclide of concern from each standard is curve fitted against standard height using polynomial to obtain the correct efficiency of each sample based on its height (see Figure 5 for inverse efficiency versus standards plot) using the equation from polynomial curve fit,

$$y = ax^2 + bx + c \quad (2)$$

where x is the height of the sample.

Table 1. Details of radionuclide in the standards.

Radionuclide	Energy (keV)	Half-life (day)	Radiation rate (%)	Channel
Cd-109	88.0	453.0	3.8	175.8
Co-57	122.1	271.6	85.6	243.8
Ce-139	165.9	137.2	79.9	331.2
Cr-51	320.1	27.7	10.2	639.6
Sr-85	514.0	64.9	99.3	1027.4
Cs-137	661.6	11012.1	85.0	1322.7
Mn-54	834.8	312.2	100.0	1668.9
Y-88	898.0	106.6	94.3	1795.2
Co-60	1173.2	1924.2	100.0	2345.5
Co-60	1332.5	1924.2	100.0	2663.9
Y-88	1836.0	106.6	99.3	3670.8

Figure 2. Mixed efficiency standards made from Al_2O_3 with heights of 0.5, 1, 2, 3, and 5 cm to address the issue on geometry made by the Japan Radioisotope Association.

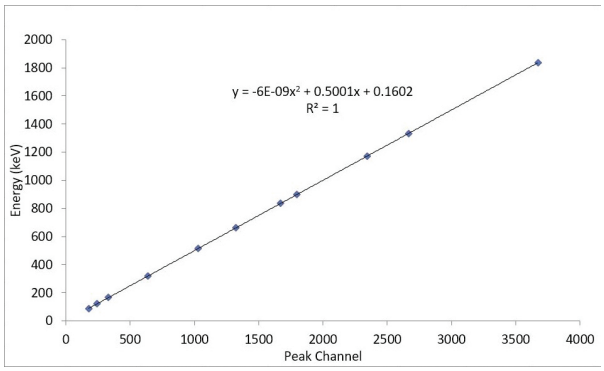

Figure 3. Radionuclide energy vs. peak channel (peak channel is the channel number with the highest peak), the equation $y = ax^2 + bx + c$ is used to obtain the energy on a given peak channel(x).

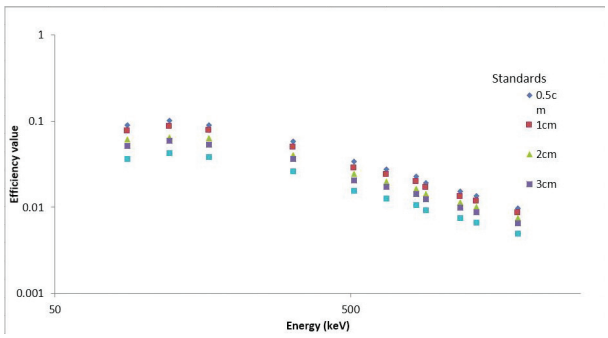

Figure 4. Plot of the efficiencies of radionuclides at five different heights against energy using logarithmic scale. The figure shows that the standard at the lowest height has the highest efficiency.

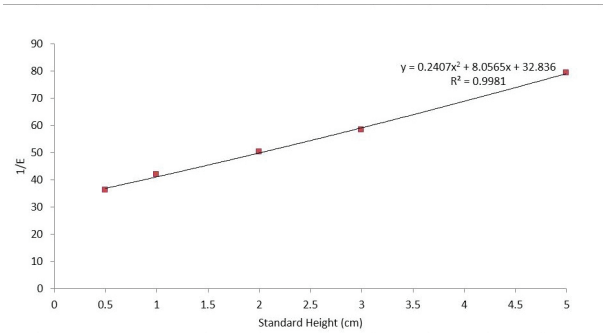

Figure 5. ^{137}Cs plot of its inverse efficiency vs heights of mixed standards. The plot is curve fitted using polynomial to get the value for the formula $y = ax^2 + bx + c$, where x is the sample height and y is the calculated efficiency which addresses the geometry issue.

Total Radiocesium Level

Every 5 cm layer of sample weighing from 13.7 - 50.7 g and 0.8 - 3.4 cm for its heights is counted on HPGe to measure the net counts per second. The Net Counts and error of each sample were acquired manually based on Covell method and compared with the counts obtained by the instrument software. The equation for obtaining net counts is,

$$N = X - Y - Z \qquad (3)$$

where, N is net counts of the peak area, X is gross count in the peak area, Y is background counts from the left side, and Z is the background counts from the right side of the peak area (see Figure 6 for peak area determination scheme, Czauderna 1984). The error is calculated as the square root of the sum of all counts,

$$\sigma = \sqrt{(X + Y + Z)} \qquad (4)$$

The radioactivity of the sample is calculated using the equation,

$$A = (Nc - Nb) / (W \times E \times R) \qquad (5)$$

where A is the radioactivity, Nc is the sample net counts per second, Nb is background count per second, W is the weight of the sample, E is the efficiency, and R is the relative abundance. The manual and instrument software calculated levels of radiocesium based on Covell method for T and A core sample is summarized in Tables 2 and 3. In general, the results for radiocesium levels of manual and instrument software calculated showed relative standard deviation (RSD) of less than 5% except for ^{134}Cs having 5.7% at 15-20 cm and 6.7% at 10-15 cm layer for T and A core, respectively. The results for both calculations have no significant difference and either can be used for reporting. The Total radioactivity or level of ^{137}Cs and ^{134}Cs in the core sample can be calculated by multiplying the radioactivity measured on each layer by its weight, then

Table 2. Summary of manual and instrument software calculated radiocesium levels for T core soil based on Covell method.

T Core						
	^{137}Cs levels (Bq/kg)			^{134}Cs levels (Bq/kg)		
Layer (cm)	**Manual**	**Software**	**%RSD**	**Manual**	**Software**	**%RSD**
0-5	7,138 ± 88	7,148 ± 88	0.1	1,531 ± 38	1,554 ± 39	1.1
10-May	3,445 ± 48	3,514 ± 49	1.4	729 ± 20	745 ± 21	1.5
15-Oct	515 ± 8	523 ± 9	1.1	111 ± 4	115 ± 4	2.5
15-20	116 ± 4	120 ± 4	2.4	24 ± 2	26 ± 2	5.7
20-23	185 ± 6	187 ± 6	0.8	37 ± 3	39 ± 3	3.7
Level (Bq/m$^{2)}$						
Top layer		[a]104,694 ± 524			[a]22,458 ± 113	
Total core		[a]159,841 ± 569			[a]34,132 ± 133	

Note: RSD=relative standard deviation; a - calculated using manual result only.

Table 3. Summary of manual and instrument software calculated radiocesium levels for A core soil based on Covell method.

A Core						
	^{137}Cs levels (Bq/kg)			^{134}Cs levels (Bq/kg)		
Layer (cm)	**Manual**	**Software**	**%RSD**	**Manual**	**Software**	**%RSD**
0-5	5,150 ± 68	5,062 ± 67	1.2	1,052 ± 29	1,046 ± 29	0.4
5-10	1,835 ± 28	1,795 ± 24	1.6	369 ± 11	367 ± 10	0.4
10-15	161 ± 5	161 ± 5	0.0	30 ± 2	33 ± 2	6.7
15-20	442 ± 6	433 ± 6	1.5	95 ± 3	95 ± 3	0.0
20-25	644 ± 8	633 ± 8	1.2	143 ± 3	141 ± 3	1.0
25-30	209 ± 5	216 ± 6	2.3	46 ± 3	49 ± 3	4.5
Level (Bq/m$^{2)}$						
Top layer		[a]98,201 ± 491			[a]20,062 ± 101	
Total core		[a]166,360 ± 539			[a]34,125 ± 120	

Note: RSD=relative standard deviation; a - calculated using manual result only.

divided by the height and diameter of sample per layer. The sum of radioactivity of each layer is the resulting total level of ^{137}Cs and ^{134}Cs in terms of Bq/m^2 per area. The total ^{137}Cs level measured and calculated is around 160,000 Bq/m^2 and around 34,000 Bq/m^2 for ^{134}Cs respectively for T and A core samples. The level for top layer (0-5 cm) is around 100, 000 Bq/m^2 for ^{137}Cs and around 20,000 for ^{134}Cs which are much lower compared to the first record (14 June 2011, Saito et al. 2015) of 300,000 Bq/m^2 for surface soil sample of 5 cm at Oguni, Date.

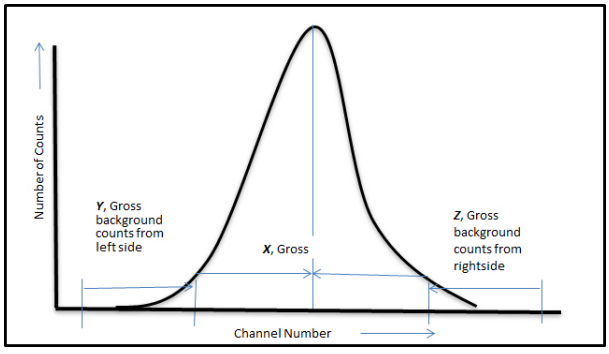

Figure 6. Peak area determination scheme.

Fractions of ^{137}Cs in Soil

The amount of ^{137}Cs fractions in the top surface layer (0-5cm) of T core soil sample are 360 ± 20 Bq/kg for exchangeable cesium (Fraction I), 500 ± 40 Bq/kg for Organic bound ^{137}Cs (Fraction II) and 6,280 ± 100 Bq/kg for strongly bound to soil particle (Fraction III). While for A core soil sample it is 200 ± 20, 330 ± 30, and 4,620 ± 80 Bq/kg of ^{137}Cs respectively for Fractions I, II and III. In terms of percentage value, Fraction I is 5 and 3.9%, Fraction II is 7.1 and 6.4% and Fraction III is at 87.9 and 89.7% respectively for T and A soil samples. The summary of percentage ^{137}Cs fractions are described in Figure 7 compared with the data from the published report of Tsukada (2014) for the year 2012 and 2013 whose sampling area (N 37.731236°, E 140.558617°) is estimated 2 km away. The result on this study showed

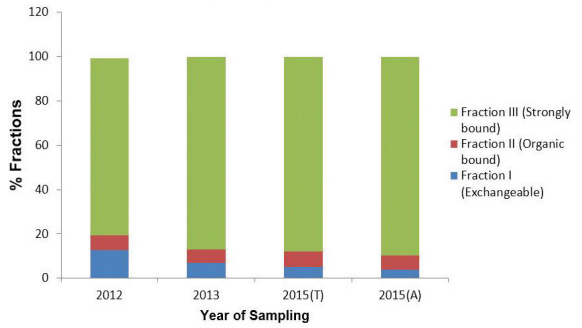

Figure 7. Percentage fractions of ^{137}Cs in top surface soil, 2015(T) and 2015(A) are data from this study, 2012 and 2013 from previous study of Tsukada (2014).

good agreement with that of Tsukada (2014) in terms of ^{137}Cs fractions in soil. On a relatively undisturbed soil, Fraction I tend to decrease over time while Fraction III will increase, and Fraction II will have almost the same percentage value.

CONCLUSIONS

The results of total radiocesium levels for the two core soil samples collected at Oguni, Date are around 160,000 and 34,000 Bq/m^2 for ^{137}Cs and ^{134}Cs respectively. The top layer (0-5cm) soil samples are around 100,000 and 20,000 for ^{137}Cs and ^{134}Cs respectively. The result on this study is significantly lower compared to the first record (14 June 2011) of radiocesium deposition on surface soil sample of 5 cm which is around 300,000 Bq/m^2. The decrease can be attributed to the effort of the management in the Fukushima to decontaminate the area. There is no significant difference in the results of manual and software based calculation which indicated either method can be used. Results on the percentage value of ^{137}Cs fractions in soil agreed with the observation from previous study that on a relatively undisturbed soil, Fraction I exchangeable tends to decrease over time, while Fraction III strongly bound increases and Fraction II organic bound is almost constant.

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