Doctoral Thesis

Difference in Migration of Radioactive Element Originating from Fukushima Daiichi Nuclear Power Plant Accident: Factors affecting transfer factor of ^{137}Cs from soil to rice and Difference in migration between ^{137}Cs and ^{90}Sr in the Environment

(福島第一原子力発電所事故に由来する放射性元素の移行の相違：土壌からコメへの^{137}Csの移行係数に及ぼす因子と環境中での^{137}Csと^{90}Srの移行の違い)

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Reference Paper

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Contents

Chapter I.

General Introduction

1.1. Background Information

An earthquake that measured 9.0 on a Richter scale hit Fukushima and led to generation of tsunamis which struck north-eastern part of Fukushima on 11th March 2011. The Fukushima Daiichi Nuclear Power Plant (FDNPP) along the Fukushima Pacific Ocean coast lost the ability to cool its 3 functioning reactors due to failure of electric power grid and the generators. Although efforts were made to cool the reactors, there was no progress such that meltdown was experienced and led to hydrogen accumulation followed by explosion as the enthalpy of combustion of hydrogen gas in air was so huge, subsequently radionuclides were expelled into the environment [1].

A big portion of radionuclides was released into the atmosphere via venting and hydrogen explosion while into the sea by leakage of the water from the reactors, finally land through wet and dry deposition [2]. IAEA report singled out most atmospheric releases that took eastward direction to the sea, followed by a few days later in which prominent radionuclides such as: ^{131}I,$^{134+137}$Cs, ^{90}Sr, ruthenium and actinides were directed towards north-western territory and deposited in the soil [3]. Aftermath of the dissipation of these radionuclides and the devastation caused, the people were reallocated and new measures and restriction on foods and water were activated which made people`s lives hard.

Because ^{137}Cs is similar to stable ^{88}Sr in its chemical behaviors, it is readily carried through the environment and food chains [4]. Cesium-137 readily dissolves in water, it can be absorbed by plants and assimilated by animals because it is chemically analogous to potassium and can cause long time internal irradiation [5]. Foods such as rice possess detectable amount of radioactivity which goes into human body via the ingestion pathway. Strontium-90 and $^{134+137}$Cs are the common anthropogenic radionuclides available in food and water [6,7]. Iodine-131 is mainly absorbed by the thyroid gland. In this study we looked at Cesium-137 soil to rice transfer factor in line with soil properties and examined ^{90}Sr distribution in Fukushima soils. The short-lived radioisotope like 1-131 (half-life = 8 d.) was ignored because it was assumed that by the time experiments were being conducted it had already decayed away. Strontium-90 shows greater environmental migration than cesium or the actinides [8] because most of the ^{90}Sr is adsorbed in the easily extractable soil fraction and remains mobile rather than being strongly bound [9].

1.2. Research Objectives

This research focused on the migration and long-term fate of the important fission products, ^{137}Cs and ^{90}Sr in disturbed and undisturbed soils of Fukushima city and Kawauchi village.

The specific objectives were as follows:

Chapter II

To investigate transfer factor of ^{137}Cs from soil to rice plant and to look at physico-chemical properties of soil that might affect transfer factor as follows:

a. influence of exchangeable K^+ and ^{137}Cs on the uptake of Cs^+ in the soil

b. effect of exchangeable cations ($Ca^{2+,}$ Mg^{2+}, K^+ and Na^+) on the uptake of ^{137}Cs in soil

c. assess nature of soil crystals and uptake of radiocesium in the soil

d. observe effect of Fe (II) and Fe (III) on ^{137}Cs uptake in the soil

Chapter III

a. To determine ^{137}Cs, ^{90}Sr concentrations with their coefficient of variation and $^{90}Sr/^{137}Cs$ ratio

b. To identify depth dependence of ^{90}Sr and ^{137}Cs in the core samples

c. To evaluate ^{90}Sr and ^{137}Cs in sediment to soil ratio

1.3. Literature review

1.3.1. Nuclear accidents

The world experienced two major nuclear disasters termed Chernobyl and Fukushima Daiichi Nuclear Power Plant (FDNPP) disasters. Probably FDNPP incident is one of the terrible accidents ever occurred in the world. 11 years on since its happening, its devastation can be seen up to date. However, the UNSCEAR 2020 finding based on 2013 report stated that: "No adverse health effects among Fukushima residents had been documented that were directly due to radiation exposure from the accident at FDNPP [10].

A report by the Nuclear and Industrial Safety Agency (NISA) on 6 June 2011, showed that the following radionuclides were released during the FDNPP accident: ^{134}Cs (about 1.8×10^{16} Bq), ^{137}Cs (about 1.5×10^{16} Bq), and ^{90}Sr (about 1.4×10^{14} Bq).[11]

Cesium-137 in soils of Fukushima has been investigated by several experts in the field [12,13,14]. Further, study by Nabeshi et al. found that besides ^{137}Cs, ^{90}Sr was earmarked as one of the most vital targets radioistopes in FDNPP disaster, mostly as regards to its dose coefficient (higher than ^{137}Cs) and relatively long physical half-life [15]; since when absorbed into the body it accumulates in bone and might lead to bone cancer [16].

1.3.2. Chemical properties of Radiocesium and Radiostrontium

Cesium, Cs, has atomic number 55 and molar mass of 132.905g/mol, melts at 28.44°C while boils at 671°C and its density is 1.93 gcm^{-3}. Cesium belongs to group 1 elements which are all silvery-white except cesium, which is golden yellow in color, and it is chemically similar to potassium and rubidium, discovered in 1860 [17]. It has an ionic radius of 0.167nm and its energy of first ionization is 375.6 kJ/mol. It has 40 isotopes and only ^{133}Cs is stable while three important radioisotopes are ^{135}Cs with half-life of 2.3 million years, ^{137}Cs and ^{134}Cs have half-lives of 30.07 and 2.06 years respectively. Because of its long half-life ,^{135}Cs is much less hazardous than ^{137}Cs or ^{134}Cs [18].

On the other hand, Strontium (Sr) has atomic number of 38 and molar mass of 87.62g/mol, melting point of 777°C and boils at 1377°C and its density is 2.64 gcm^{-3}. It has first ionization energy of 549.2 kJ/mol and has ionic radius of 0.133nm. (https://www.rsc.org/periodic-table/element/38/strontium) [19]. Strontium is a soft silver-white yellowish metallic element that is highly chemically reactive and found in soil. There are four stable isotopes of Strontium: ^{84}Sr, ^{86}Sr, ^{87}Sr, and ^{88}Sr. It has 12 other unstable radionuclides, and the well-known radioactive isotopes are ^{89}Sr and ^{90}Sr. Strontium is chemically analogous to calcium and discovered late 17th century and ^{90}Sr is highly radioactive [20].

Cesium-137 is a significant pollutant because of its large mass production during nuclear fission process and its longer half-life compared to ^{134}Cs [21]. The long-lived ^{137}Cs is an important indicator of radioactive pollution in terrestrial environments. Much of the ^{137}Cs and ^{90}Sr from cold war era decades ago subsequently decayed away. Meanwhile the main constraint has been ^{137}Cs and ^{90}Sr ejected from the FDNPP and the CNPP accidents.

1.3.3. Cesium-137 soil to plant transfer factor

The transfer factor (TF) is defined as the portion of an element in a plant under study to that in the source soil. The TF is a useful tool to predict long-term, chronic exposures and is preferably measured at equilibrium. TFs are essential in hazard monitoring due to transfer of ^{137}Cs to crops through food chain by which evaluation of radiation dose can be estimated based on the amount transferred. Thus, TF is given by:

$$TF = \frac{{}^{137}_{p}Cs(BqKg^{-1}\,, dry\ weight)}{{}^{137}_{s}Cs(BqKg^{-1}\,, dry\ weight)} \quad [22,23]$$

Where ${}^{137}_{p}Cs$ is the amount of ^{137}Cs in plant while ${}^{137}_{s}Cs$ is that in soil, dry weight basis respectively.

Studies conducted previously noted that the plant uptake of radioisotopes in particular ^{137}Cs, relies upon the following physico-chemical properties of soil: soil pH, clay type, exchangeable K^+, Ca^{2+}, organic matter content, particle size distribution and time itself [24,25]. Yamaguchi et al. clarified on soil physico-chemical properties which typically influence Cs^+ transfer [26]. In addition, other researchers verified that exchangeable K^+ inhibit a strong counter-elemental activity for Cs sorption by rice and other plants while that of $^{134+137}$Cs might be influenced by the type of circumstances [27]. Since rice plants grow in flooded fields, they happen to have a plant base uptake of the ^{137}Cs on top of root uptake of which base is the part of the plant immersed in the standing water [28]. Further studies showed that the uptake of radiocesium via the plant base was very efficient in flooded rice plants [29]. However, it would still be vital to assess factors that might determine the ^{137}Cs uptake by plant like oxidation state of the soil by Mössbauer spectroscopy and chemical composition by X-ray diffraction.

1.3.4. Exchangeable cations

Cation exchange capacity is referred to as a measure of the soil's ability to grip positive ions together. It is paramount property affecting soil structure stability, nutrient availability, soil pH and the soil's reaction to fertilizers and other factors [30]. The main cations of concern are calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^+) and potassium (K^+) [31], which are designated as the base cations. Their units are in meq/100 g [32] equivalent to centimoles of charge per kilogram of exchanger (cmol (+)kg^{-1}). The mechanism by which Cs is absorbed up by plant roots are not well understood. However, at minimal K concentration there is envisaged that Cs is taken up by the exchangeable K^+, since K+ strongly undermines Cs sorption [27, 33].

1.3.5. Soil`s oxidation state using Mössbauer spectroscopy

Mössbauer spectroscopy combines the emission and absorption of γ-rays by nuclei in solids and this technique depends on the Mössbauer effect such that some nuclei, while in solid form, can emit and attract γ-rays without energy loss due to recoiling which has been widely applicable in identifying the local electronic structure, magnetic properties, and coordination of iron nuclei in various substances including soil [34,35,36]. The common oxidation states for iron are Fe (II) and Fe (III). Cesium and Sr, happen to have little affinity to adsorb on iron oxidized materials and their hydrolysis potential is very weak, especially Fe II exhibits further immobilization pathways for these radioisotopes [37].

1.3.6. Clay mineral composition of soil using powdered X-ray diffractometer

Powder X-ray Diffractometry (P-XRD) is a technique for measuring and identifying the fine-grained (<2 μm) minerals that are consistently and are the most chemically reactive fraction of soils or sediments [38]. Match software uses the open-access Crystallography Open Database (COD) and proportions are estimates and not generated from retrieved analysis.

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Chapter 2.

Cesium-137 soil to rice transfer factor and soil properties: Fukushima and Kawauchi case study

Reference:
W. C. Bekelesi, T. Basuki, S. Nakashima, Radiation Safety Management Vol. 21 (1–12).

2.1. Introduction

In this research work we monitored the relation between soil properties (soil particle distribution, exchangeable cation and ^{137}Cs, mineral composition, Fe (II), Fe (III) oxidation state and ^{137}Cs TF) by measuring the soil and rice samples from two different paddies in Fukushima prefecture. The results outlined complex factors that might affect the ^{137}Cs released from the soil and its sorption by rice plant, which is critical for assessing the risk of radiation dose through food chain. This work aimed at assessing two different study areas unlike other studies which have only focused on one particular area.

2.2 Materials and Methods

2.2.1. Study area

The samples were taken from two fields: Fukushima city and Kawauchi village. Altogether there were 25 soil and 10 rice samples. The first 5 soil and 5 rice samples collected in Kawauchi were taken from (longitude, latitude: 37.32087, 140.83568; 37.32090, 140.83600; 37.32068, 140.83585; 37.32042, 140.83571; 37.32047, 140.83607 respectively) 20 km away, southwest of FDNPP, on 22 August 2017. The other portion of 20 soil samples and 5 rice samples were gathered from Fukushima city 60 km away, northwest of FDNPP on 23 August 2018. Kawauchi field comprised only of a single paddy (K) while Fukushima consisted of 4 paddies (F1, F2, F3 & F4) （Fig. 1). Each sampling point covered an area of roughly 10 cm x 20 cm ranging from bulk sample of 0-5 cm depth. In order to compare well with Kawauchi‘s (K) only field (F4) was considered in Fukushima city.

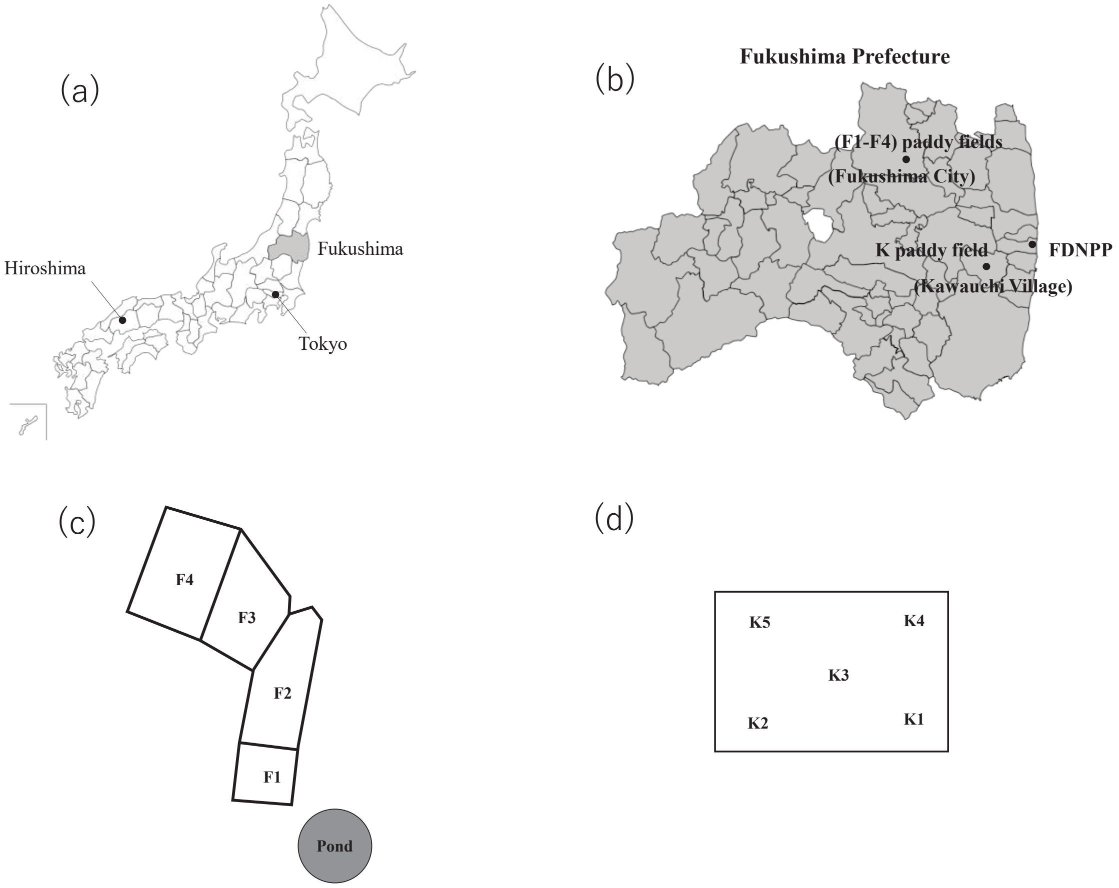

Fig. 1. (a) Fukushima Prefecture, Japan. (b) sampling paddy fields in relation to FDNPP. (c) paddy fields(F1–F4) and a pond of Fukushima. (d) Paddy field (K) in Kawauchi village

2.2.2. Sample preparation and measurement by HPGe detector

Having air dried the soil samples at room temperature for 2 weeks and removal of unwanted materials e.g dead vegetation and large rocks; and the soil was dried sieved through 2mm sieve. The soils were then oven dried at 110°C for 24 hours then packed into the U8 vessel (100 mL, 5 cm height, 5 cm diameter). Likewise, the dried mature rice-grain samples (10 in total) were each also filled into distinct vessel for ^{137}Cs measurement. The activity of ^{134}Cs, ^{137}Cs and ^{40}K in soil were analyzed by Gamma Spectrometry equipped with High Purity Germanium (HPGe) detector and multichannel analyzer (GEM 30-70, ORTEC) at gamma energy peaks of 605, 662 and 1461 keV for ^{134}Cs, ^{137}Cs and ^{40}K, respectively.

The amount of ^{137}Cs was calculated using an equation by Faanu and Darko, 2011 [1]

$$A_{sp} = \frac{N_D \, . \, e^{\lambda_p t_d}}{P \, . \, T_c \, . \eta(E) . \, M_s} \quad \text{.......................} \quad (1), \text{ where:}$$

A_{sp} is the specific activity of radioisotope (Bq/Kg)

N_D is the net counts of radioisotope in the samples,

λ_p is the decay constant of radioisotope,

t_d is the delay time between sampling and measurement,

exp ($\lambda_p t_d$) is the decay correction factor for delay between times of sampling and determination

P is the γ −ray emission probability (γ − ray yield),

η (E) is the absolute counting efficiency of the detector system,

$T_c$is counting time,s; $M_s$is the mass of the sample, kg.

Calibration of gamma spectrometer was done by a set of standard sources (MX033U8PP) produced by the Japan Radioisotope Association. Bekelesi et al.2017 [2] outlined that the purpose of energy calibration is to deploy a relationship between peak positions in the spectrum in relation to the gamma-ray energy of radioisotopes done prior analyzing the samples.

2.2.3. The major transferrable cations (Na^+, K^+, Mg^{2+}, Ca^{2+})

Exchangeable major cations (EMC) referred to as Na^+, K^+, Mg^{2+}, Ca^{2+}) were extracted in each 5g soil sample using 25ml of 1M CH_3COONH_4 (ammonium acetate) at pH 7. The soil samples were then shaked by shaker (EYELA UNI THERMO SHAKER NTS-1300) over 24 h period then centrifuged at 3000 rpm for 10 min. The distillate from each sample was filtered through a 0.45 µm filter paper and the clear solution of each sample was determined instantly by ICP-AES (SPS 3500, Hitachi). To comprehend the exchangeable ^{137}Cs and % of exchangeable ^{137}Cs, ^{137}Cs activity in soil samples were analyzed before and after mixing with 1M ammonium acetate. Cesium-137 radioactivity was analyzed by HPGe detector and the magnitude in ^{137}Cs radioactivity before and after applying 25ml of 1M ammonium acetate was referred to as exchangeable ^{137}Cs.

2.2.4. Calculation of exchangeable K^+

Exchangeable K^+ refers to the exchangeable K^+ divided by total K^+ in soil, based on total activity of ^{40}K in soil measured by HPGe detector. The following expressions were employed:

$$A = \lambda N \text{ .... } (2)$$

where A is activity concentration, λ is the decay constant, s^{-1} and N is number of ^{40}K atoms. We know that:

$$\lambda = \frac{ln2}{t_{1/2}} \text{ .... } (3)$$

where $t_{1/2}$ is half-life of $^{40}K = 1.248 \times 10^9$ yr. $=3.936 \times 10^{16}$ s. Further, mol of ^{40}K using eqn.1 we have:

$$N = N_{\varphi} m \text{ .... } (4)$$

where N_{φ} is Avogadro number $=6.022 \times 10^{23}$ mol^{-1} and m = moles of element (^{40}K). The mass of total K in soil can be calculated related to natural abundance of ^{40}K =0.0117%.

$$Mol\ of\ Total\ K\ =\ mol\ of\ 40K/\ 0.0117\% \text{ .... } (5)$$

Grain size distribution of the soil samples was measured through the horizontal shaking column of 2 mm, 850 µm, 250 µm, 75 µm sieves successively for 2 hours repeatedly.

2.2.5. Mossbauer spectroscopy

Oxidation state of iron in the soil samples was measured by the ^{57}Fe Mössbauer spectroscopy. The analysis was set at 25°C with a ^{57}Co (Rh) radiation source moving in a constant acceleration mode on Wissel MB-500. The Mössbauer characterization conditions were made by least-squares fitting into Lorentzian peaks. The calibration of the spectra was achieved by the six lines of α-Fe, whose center was considered as zero isomer shift.

2.2.6. Powder X-Ray Diffraction

In order to assess the nature of soil composition in Kawauchi village and Fukushima city, soil samples were mounted on glass slides and the structure was determined by X-ray diffraction pattern acquired by Rigaku PXRD using Cu Kα radiation ($\lambda = 1.54059$ Å) at 40 kV and 44 mA, 2θ range from 3 ~ 80°, at 25°C. The P-XRD data of each soil sample was determined by Match software by which the diffraction pattern could be compared with the patterns stored in the ICDD (International Centre for Diffraction Data) PDF database, leading to phase identification. Studies that utilized match software are several [3-5].

2.3. Results and Discussion

2.3.1. Radioisotope`s decay-corrected to the release day

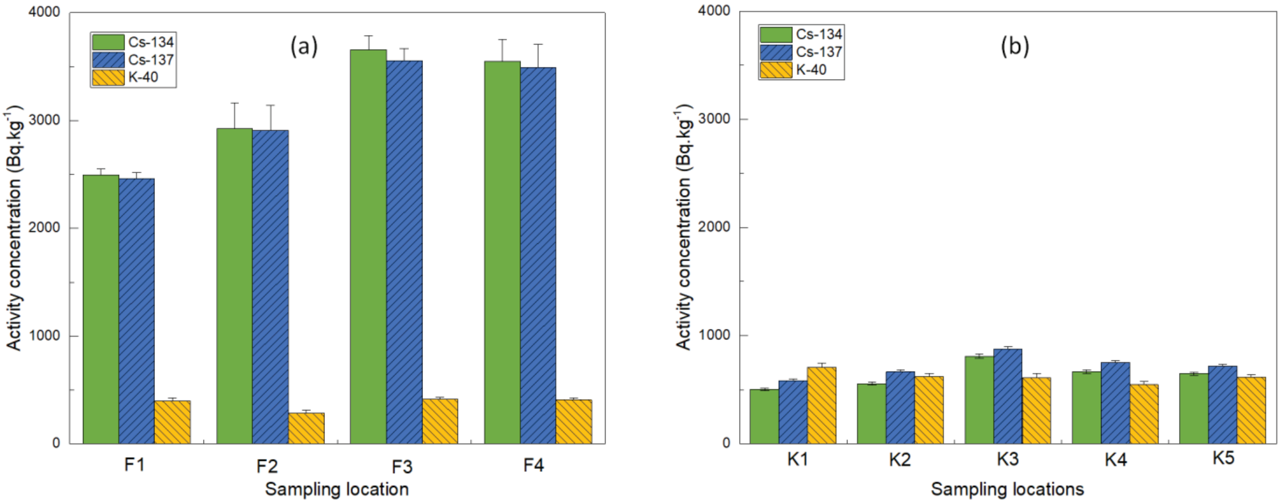

Fig. 2. Radiocesium and ^{40}K concentration of Fukushima (a) and Kawauchi (b) soil decay-corrected to release day. F1 - F4 are rice fields in Fukushima city respectively (Fig. (2a)), while K1 through K5 are sampling points for Paddy field K (Fig 2(b)) in Kawauchi village.

Figure 2(a) and (b) depict the radioactivity concentration decay-corrected to the release day for Fukushima and Kawauchi soils, respectively. In Fig. 2(a) the results of Fukushima soil, ^{134}Cs had a range of 2500 ± 50 - 3660 ± 130 Bq/kg with a mean value of 3160 ± 150 Bq/kg, ^{137}Cs gave values spanning from 2460 ± 60- 3560 ± 110 Bq/kg with mean of 3100 ± 150 Bq/kg, and ^{40}K was from 286 ± 27 - 413 ± 18 Bq/kg with the average of 376 ± 23 Bq/kg. On the other hand, Kawauchi soil (Fig. 2(b)) gave the following results: ^{134}Cs from 505 ± 12 - 810 ± 19 Bq/Kg with average of 638 ± 15 Bq/kg; ^{137}Cs from 583 ± 15 - 877 ± 24 Bq/kg and mean of 720 ± 18 Bq/kg, and ^{40}K from 548 ± 26- 708 ± 37 Bq/kg with average of 622 ± 30 Bq/kg. The results illustrate that the Fukushima soil was more contaminated by ^{137}Cs and ^{134}Cs than Kawauchi soil. One of the explanations to this is probably the difference in the direction of radioactive plume just after the accident or the difference in decontamination activities undertaken in Fukushima prefecture.

2.3.2. Origin of radiocesium in Fukushima prefecture

The release day ratios of ^{134}Cs / ^{137}Cs were as follows, F1: 1.01, F2: 1.01, F3: 1.03 and F4: 1.02 for Fukushima (Fig. 2(a)) while K1: 0.87, K2: 0.83, K3: 0.93, K4: 0.88, K5: 0.90 for Kawauchi (Fig. 2(b)). Nishihara et al. found that the ^{134}Cs / ^{137}Cs ratios of inventories in Units 1 to 3 at the shutdown time (March 11, 2011) were approximated as the topmost for Unit 2 (1.08), the least for Unit 1 (0.94), and intermediary for Unit 3 (1.05) [6]. Komori et al. explained that despite the activity ratio of ^{134}Cs / ^{137}Cs emitted by the accident has been reported to be ~1:1, changes in the activity ratio has arisen in environmental samples, as the ratio varies slightly for each nuclear reactor [7]. Thus, Kawauchi was probably contaminated largely from the unit 1 which was ~ 0.9, while Fukushima from unit 2 and 3 which were ~1. The ratio of ^{134}Cs /^{137}Cs deviation relies on the extent of burn-up of the reactor fuel and the older the rod, the greater the ratio. On the contrary, at Chernobyl NPP, the ratio was ~0.5 - 0.6 while at Fukushima was ~0.9 - 1.0. However, nuclear explosion scarcely produces ^{134}Cs due to the lack of long thermal neutron irradiation [8].

2.3.3. Kawauchi village and Fukushima city soil Transfer Factor

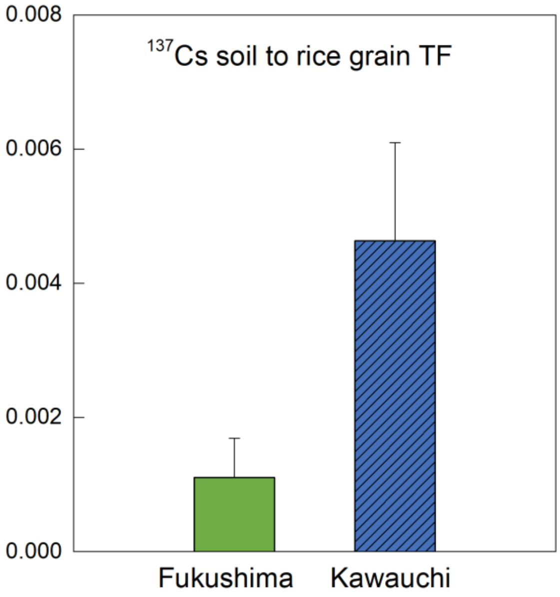

Fig. 3. Cesium-137 average TF in Paddy Fields in Fukushima and Kawauchi.

Cesium-137 activity concentration of dried rice grain decay-corrected to sampling day ranged from 1.1 ± 0.68 - 3.7±1.5 Bq/kg with mean value of 2.6 ±0.82 Bq/kg for Fukushima while Kawauchi samples, Cesium-137 values ranged from 1.4±0.92 - 3.9±0.94 Bq/kg with the average of 2.8±0.83 Bq/kg. Kawauchi showed higher values of ^{137}Cs in rice samples compared to Fukushima`s. Research finding by Hori et al. observed that ^{137}Cs activity concentration for Fukushima rice grain ranged from 0.09~10 Bq/kg [9]. Despite that his result was not compared with any other field, the results for both fields in current study agree with previous research and with time it is anticipated that ^{137}Cs radioactivity would deteriorate even further. Figure 3 displays ^{137}Cs TF of Kawauchi and Fukushima soil which ranged from 0.0021~ 0.0058 with an average value of 0.005 ± 0.001 and from 0.0004~0.0018 with an aggregate of 0.0010±0.0004 for the 5 sampling points each respectively. Figure 3 further shows that the TF of ^{137}Cs is higher in Kawauchi rice field than that of Fukushima in spite of Fukushima city soil deemed more radioactive than that of Kawauchi.

Kawauchi ^{137}Cs TF which is 5 folds greater than that of Fukushima is perhaps associated with exchangeable ^{137}Cs and K^+ in those soils and the difference in soil properties. The greater the exchangeable ^{137}Cs, the more rapid will be the transfer of ^{137}Cs. Exchangeable K^+ being analogous to Cs^+, thus the higher exchangeable K^+ will lead to the lowering of the ^{137}Cs TF [10] .

2.3.4. Exchangeable ^{137}Cs and K^+ in Fukushima city and Kawauchi paddy soil

Figure 4 depict the exchangeable ^{137}Cs and K^+ in Fukushima and Kawauchi soil. Figure 4a portrays effect of treating soil with 1M ammonium acetate at pH 7 as regards ^{137}Cs. The results show that the activity concentration ^{137}Cs for Kawauchi soil before applying ammonium acetate ranged from 369~879 Bq/kg with mean of 620±6.3 Bq/kg while Fukushima soil was from 2160~3140 Bq/kg with an average value of 2640±10 Bq/kg. After ammonium acetate effect Kawauchi`s soil was from 337~700 Bq/kg with the average of 527±4.1 Bq/kg while Fukushima`s ranged from 1980~2940 Bq/kg with the average value of 2330 ±9.7 Bq/kg. Figure 4b describes the aftermath of treating the soil with ammonium acetate on ^{137}Cs in Kawauchi and Fukushima soil such that there was a decline in ^{137}Cs activity concentration for both paddy field soils.

Figures 4 c and d demonstrate that while Fukushima soil contains a lesser percentage of exchangeable ^{137}Cs, it contains a more percentage of exchangeable K^+ in contrast to Kawauchi soil. In other words, it can be simplified that, while exchangeable ^{137}Cs is low and exchangeable K^+ is high in Fukushima soil but the exchangeable ^{137}Cs is high while the exchangeable K^+ is low in Kawauchi soil. Thus, this would explain well the reason behind greater TF for Kawauchi rice in contrast to Fukushima (Figure 3). This finding tallies well with previous studies, example, Kondo et al. and Tsumura et al. explained that ^{137}Cs in plants happen to reduce with lowering exchangeable ^{137}Cs in soil though no clear relationship was found between ^{137}Cs concentration in plants and total ^{137}Cs in soil [11,12]. It has also been indicated that the relationship between exchangeable K^+ and ^{137}Cs concentration in plants show that low exchangeable K^+ increases ^{137}Cs uptake in rice [11,12].

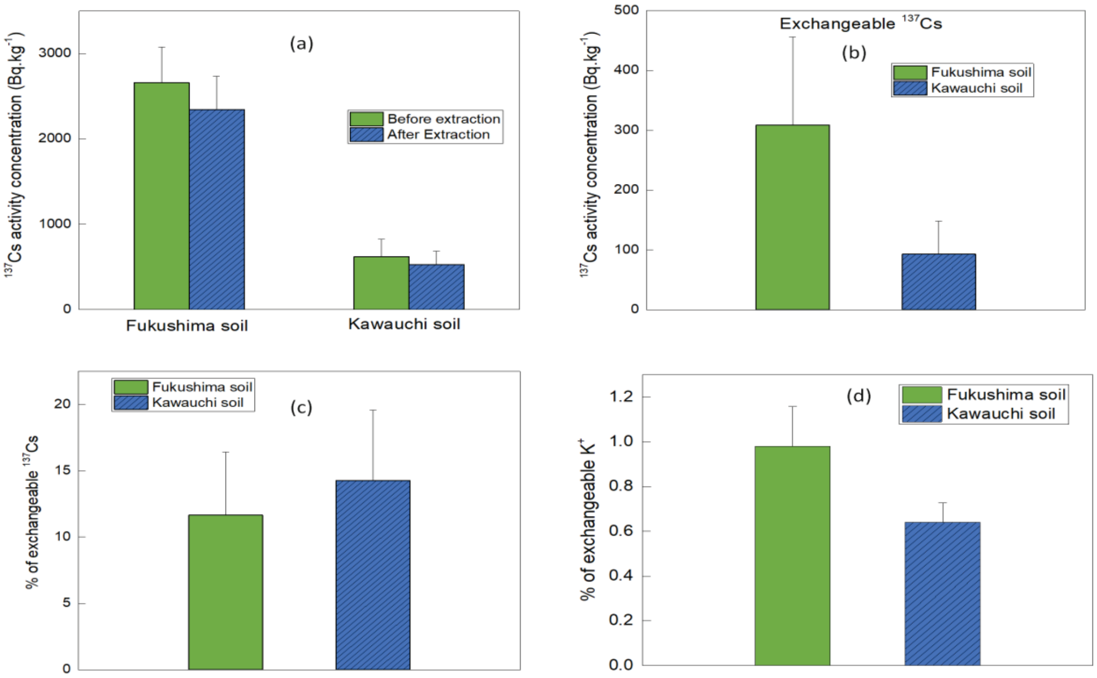

Fig. 4. (a) Effect of ammonium acetate on ^{137}Cs, (b) Amount of ^{137}Cs removed from soil, (c) Rate of exchangeable ^{137}Cs in Fukushima and Kawauchi soil and (d) Rate of exchangeable K^+ in Fukushima and Kawauchi soil.

Figure 5 depicts the exchangeable cations of different soil portions for Fukushima and Kawauchi soil. Na^+ concentration is almost uniform in Fukushima and Kawauchi in soil grain size fragments 75µm<x<850µm while it is a bit higher in size portion of <75 µm (Figure 5a). On the other hand Fig. 5(b) depicts K^+ tend to exhibit greater exchangeable cation in bigger soil sizes of Fukushima soil and Cs is from the same group (Alkali metal element) with K. While K^+ of Fukushima soil is larger for soil grain size of 75µm<x<850µm than Kawauchi soil and higher K^+ in the bigger grain size of Fukushima is perhaps due the fertilizer application contrasting the higher K^+ in the finer grains in Kawauchi which could be probably influenced by nature of clays. Further, it is well established that the greater the K^+ amount the smaller will be the TF [11,13,14]. This is the basis in this research (Figs. 4d and 5b) where Fukushima soils which contain more exchangeable K^+ than Kawauchi soil on average, yet its TF is less than that of Kawauchi. In addition, another contributing factor to this is the magnitude in Mg^{2+} and Ca^{2+} content which is extraordinarily larger than that of Kawauchi which could possibly prevent absorption of ^{137}Cs by rice plants in Fukushima paddy.

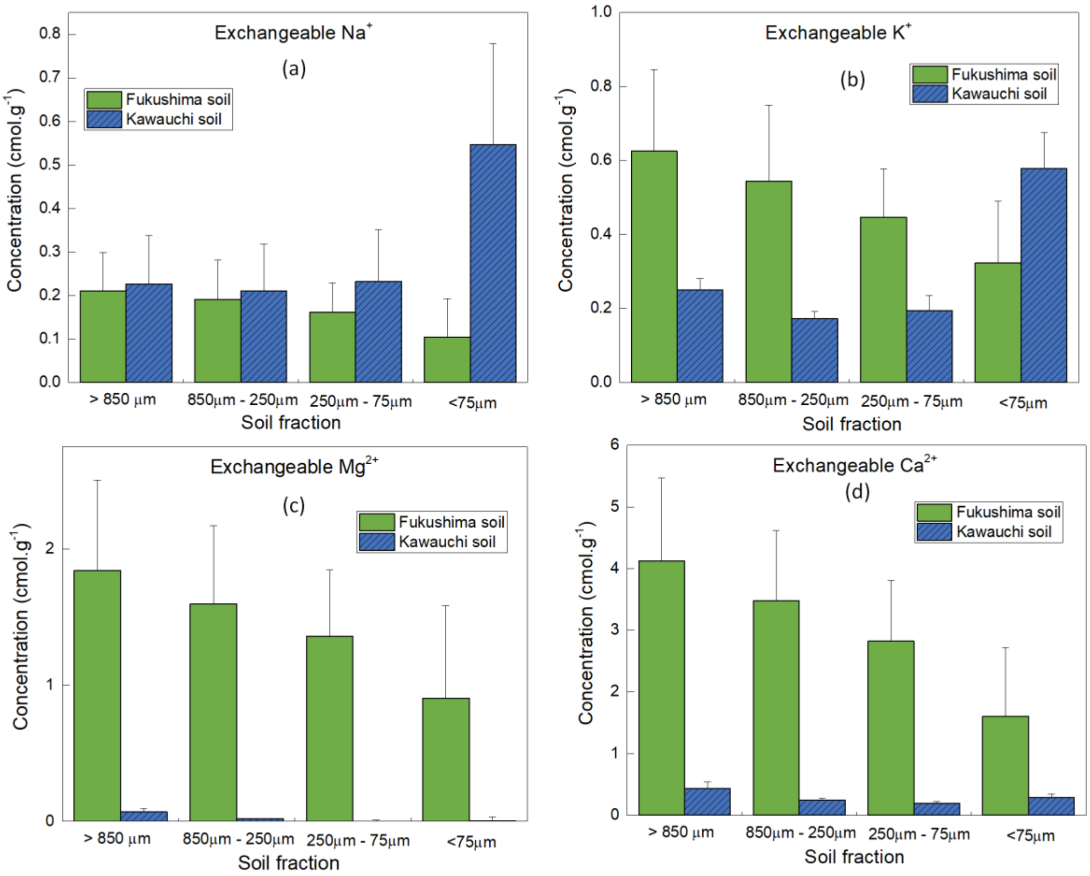

Fig. 5. Exchangeable cations in soil (a) Na^+, (b) K^+, (c) Mg^{2+} and (d) Ca^{2+}.

2.3.5. Soil grain particle size distribution for Fukushima and Kawauchi

Soil grain size distribution of Kawauchi and Fukushima are different (Figure 6). It shows that while Kawauchi has more of <75µm fine particle portions than Fukushima yet a better proportion of fine and medium sand (850-75 µm) which exceeds that of Kawauchi. Nonetheless, the soil with better composition of clay, silt and sand, is easily cemented when mixed with water [15], perhaps this is the case with Fukushima soil.

Moreover, in the current research it was noted that Kawauchi soil contains more silt and clay and less coarse and gravel than Fukushima. Nguyen et al. found that radiocesium is strongly adsorbed to the clay particles of which cesium adsorbed to large sized soil is a bit easily desorbed and absorbed by the rice plant [16]. Tsujimoto et al. reported that the rate of medium sand in soil is one of the contributing factors to determine the transfer of ^{137}Cs from soil to rice plant [17]. Both medium and coarse sand grain particles have large pore sizes which eases ^{137}Cs movement in soil having more fraction of clay and silt in contrast to the sand particles.

However, Kawauchi soil that has more silt and clay contains larger % of exchangeable ^{137}Cs than Fukushima soil that has more fine and medium sands (Figure 4d). Probably this could be associated with difference in mineral composition between the two soils. Other researchers postulated that the ^{137}Cs distribution within the soil layer might be influenced by the adsorption kinetics [18]. The results in the current research depicted that the ^{137}Cs exchangeable rate is hardly described based on the soil grain size migration alone.

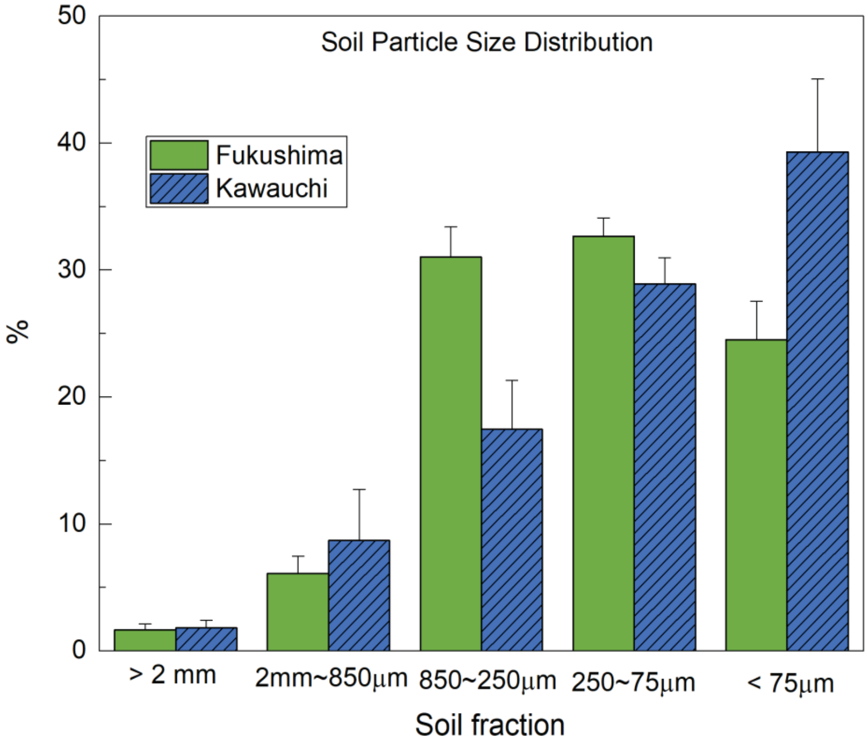

Fig. 6. Grain particle size distribution of Fukushima and Kawauchi soil.

2.3.6. Fukushima and Kawauchi soil Mössbauer spectral data

Fig. (7a) shows that, there was no significant magnetic component (e.g., Fe(II)) in Kawauchi soil in contrast to the other soils from Fukushima (Figure 7b). However Kawauchi`s ratio of Fe(II)/(Fe(III)+Fe(II)) is bigger than that of Fukushima rice field soil and this is contrary to what Nguyen et al. got [16] which depicts the lttle ^{137}Cs transfer when the ratio is big. The differences in Fe (II) and Fe(III) oxidation state explain the degree of difference of the redox potential between the soils. Other researchers revealed that microbially mediated lowering of Fe (III) in chlorite and biotite by *Shewannella oneidensis* MR-1 induces a paramount declining in sorption of both Cs and Sr compared to the abiotic system [19]. Thus, by considering the various factors overall, we ought also to acknowledge the role of magnetic component.

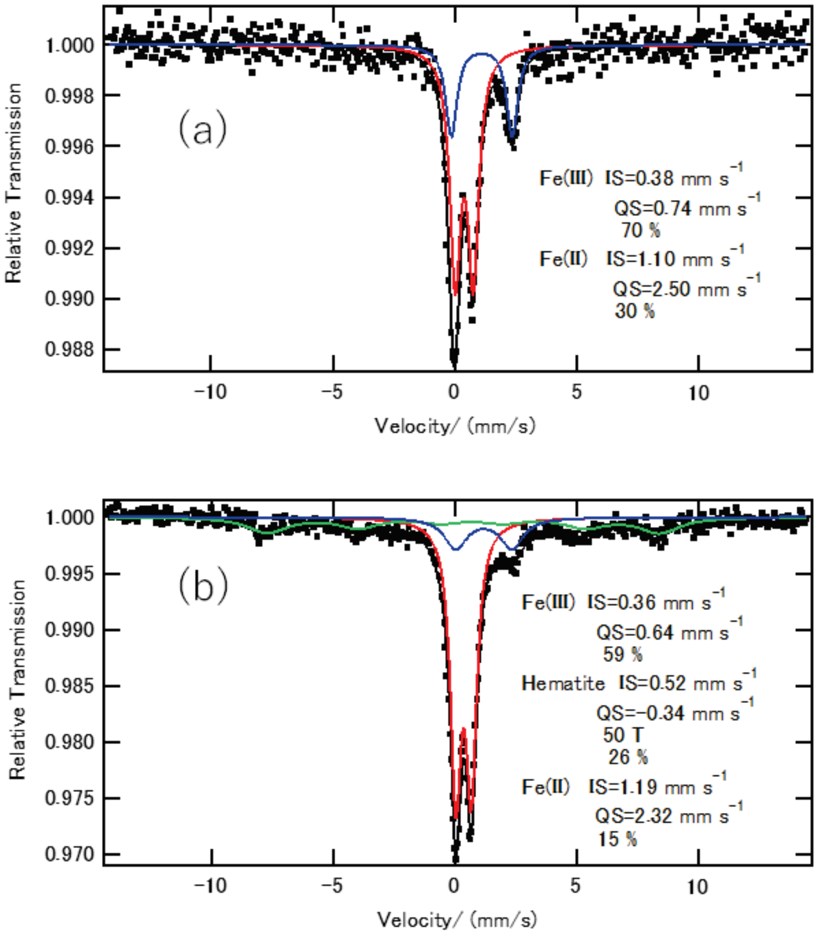

Fig. 7. Mössbauer spectrums for (a) Kawauchi and (b) Fukushima soil.

2.3.7. Powder X-ray diffraction monitoring of the soil samples

Figure 8 depicts diffraction spectral data for Fukushima and Kawauchi soils. Table 1 categorizes the soil composition for Fukushima and Kawauchi in line with powder X-ray diffraction pattern (PXRD) analysis employing Match software [20]. Table 1 shows that despite Kawauchi soil containing more quartz constituents yet it has less mica minerals than Fukushima soil. On the other hand, Fukushima soil composed of more vermiculite, zeolite and phlogopite. Kondo et al. outlined those soils in some parts of Fukushima contained ~ 90% crystalline constituents with some kaolin, vermiculite, mica, zeolite and phlogopite [11].

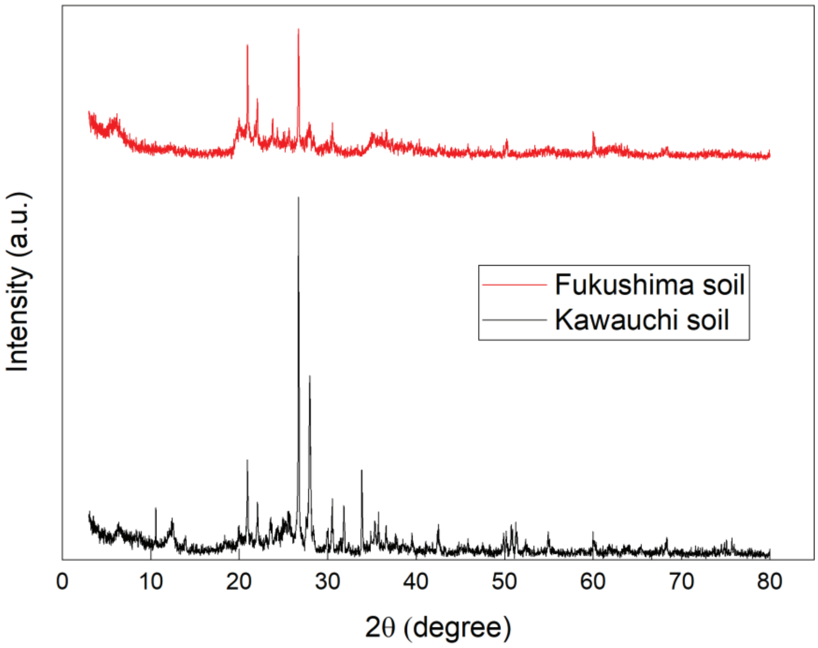

Fig. 8. P-XRD pattern of Fukushima and Kawauchi soil.

Probably Fukushima soil`s ability to retard transfer of $^{137}$Cs is because $^{137}$Cs is adsorbed to the clay particles more strongly than that of Kawauchi the fact that Fukushima soil contains more vermiculite, mica and zeolite than Kawauchi`s. Fujimura et al. showed that the amount of ^{137}Cs in rice plant was lowered by application of potash fertilizer or clays rich in zeolite and vermiculite [21]. Fujimura et al. and Eguchi et al. demonstrated that these minerals impinge the ^{137}Cs distribution in the soil [21, 22]. Furthermore, Nakao et al. interpreted that one essential factor in effective ^{137}Cs adsorption is the presence of rough or weathered edges of some minerals, such as mica, in the soil whose edges catch the radiocesium and prevent its movement. Because hydration enthalpy is small for ^{137}Cs, thus it is easily adsorbed to the

Frayed-edge sites [23]. Further Fujii et al. and others outlined that volcanic soils of Fukushima could essentially be poor in micaceous clays that fix ^{137}Cs remarkably [24, 25]. Generally, the findings in the present study indicate that the availability of mica, phlogopite and zeolite, in Fukushima soil, would probably be a suitable amendment for radiocesium-contaminated rice fields in lessening the ^{137}Cs TF.

Table 1. Powder X-ray diffraction pattern of Fukushima and Kawauchi soil using Match software

Item	Fukushima	Kawauchi
Quartz content	73.2%	80.8%
Micaceous	+++	++
vermiculite	+	-
Zeolite	++	+
phlogopite	++	+
Kaolinite	+++	+++
Aluminium phosphate	+	-

Note: - stands for: little; +, some; ++, common; +++, abundant

2.3.8. How TF, exchangeable cations of Fukushima prefecture, Japan compares with other areas in the World

Table 2 gives summary of TFs for rice grain in the present study in particular Kawauchi and Fukushima and compares with previous studies in various parts of the world. Table 2 depicts that the results are within the range of previously research outcome values both before and after CNPP and FDNPP disasters.

Transfer factors in the present research are smaller compared to those soon after the FDNPP incident [26] and slightly bigger before FDNPP accident [27]. This might be attributed to the fact that fresh deposited ^{137}Cs in soil was in exchangeable form, leading to greater ^{137}Cs sorption by plant which then then became more fixed in soil matrices with time. The concept that TFs before FDNPP accident were smaller than the present research might possibly be due to the ^{137}Cs fall out from nuclear bombardment tests and decayed away, consequently TFs decreased with time than the freshly deposited radiocesium after FDNPP catastrophe. Literature has shown that, contribution of CNPP accident in ^{137}Cs TF of Japan was very little [27].

On the contrary, results obtained from South Korea nuclear power plant displayed the largest TF ever, probably because under pot experimentation most parameters were well under control unlike the rest which were based on field observations. Therefore, we felt it would be inappropriate to draw any conclusion of this study which was based on field samples against the pot experiments.

Table 2. Comparison of TF, exchangeable cations with other studies

Country (Sampling location)	**Experimental condition**	**Instrument**	**TF- Cs-137 (Rice-grain)**	**Exchangeable cations ($cmol.kg^{-1}$)**				**Reference**
				K^+	**Na^+**	**Mg^{+2}**	**Ca^{+2}**	
Japan (Kawauchi)	Brown rice, field observation	HPGe, ICP-AES	0.005(0.0021-0.0058)	0.30	0.30	0.02	0.29	this study
Japan (Fukushima)	Brown rice, field observation	HPGe, ICP-AES	0.001(0.0004 - 0.0018)	0.48	0.17	1.43	3.01	this study
Japan (Fukushima)	Field observation soil	HPGe, ICP-AES	N.A.	0.51	0.18	0.69	6.90	Basuki et al., 2020 [28]
Japan (Fukushima)	Field observation soil	HPGe, ICP-AES	N.A.	0.4	0.1	1.1	5.0	Fujii et al., 2014 [29]
South Korea [a](Kori & Younggwang) [b] (Wolsung NPP)	Rice, pot observation	HPGe, ICP-AES	[a]0.001(0.0012-0.011) [b]0.57(0.022-0.15)	0.81 0.41	1.7 N. A	1.95 2.2	4.52 6.1	Choi et al. 2002, 2011[30, 31]
Japan (Minamisoma)	Rice, field observation	HPGe	0.023(0.019-0.026)	N.A.	N.A.	N.A.	N.A.	Endo et al., 2013 [26]

Country (Sampling location)	**Experimental condition**	**Instrument**	**TF- Cs-137 (Rice-grain)**	**Exchangeable cations ($cmol.kg^{-1}$)**				**Reference**
				K^+	**Na^+**	**Mg^{+2}**	**Ca^{+2}**	
Japan (Fukushima)	Brown rice, field observation	ICP-MS	0.0026	N.A.	N.A.	N.A.	N.A.	Komamura et al., 1994[27]
India (Kaigar)	Rice, field observation	HPGe	0.24(0.07-0.8)	N.A.	N.A.	N.A.	N.A.	Karunakara et al., 2013 [32]
China (Taiwan NPP)	rice, field observation	HPGe	0.0022	N.A.	N.A.	N.A.	N.A.	Lu et al., 2006 [33]
Taiwan (Kaohsiung city)	White rice, field	HPGe	0.13 (0.07–0.27)	N.A.	N.A.	N.A.	N.A.	Wang et al., 1998 [34]
Worldwide	Data gathering	HPGe	0.0083(0.0047-0.012)	N.A.	N.A.	N.A.	N.A.	IAEA, 2010 [35]

2.4. Conclusion

This study has demonstrated that soil to grain ^{137}Cs transfer factor of Fukushima rice field soil is smaller compared to Kawauchi`s paddy soil. The Fukushima paddy soil might restrict sorption of ^{137}Cs by far more by rice plant than Kawauchi soil, though have lower ^{137}Cs activity concentration than Fukushima soil probably due to difference in its soil properties. Both X-ray diffraction pattern of the soils and the ^{57}Fe Mössbauer spectrometry analysis indicated that the soils are different in their composition and Fe (II)/(Fe (III)+Fe(II)) ratios.

This research demonstrated that the existence of micaceous minerals, zeolite and vermiculite in Fukushima soil lessen the migration of ^{137}Cs in the soil to rice plant. Further, relatively lower TF of Fukushima soil lies within the slightly lower percentage of exchangeable ^{137}Cs and slightly higher exchangeable K^+ of Fukushima soil than that of Kawauchi soil. In the future research we would like to propose considering how ^{137}Cs transfer factor within the soil layer might be affected by the adsorption kinetics considering 5 folds values TF of Kawauchi compared to Fukushima`s.

2.5. References

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Chapter 3.

Difference of ^{90}Sr and ^{137}Cs Distribution and Migration in Soil and Sediment after the Fukushima Accident

Reference:

BEKELESI, Wiseman Chisale; BASUKI, Triyono; HIGAKI, Shogo and NAKASHIMA, Satoru, Radiation Safety Management Vol. 21 (26–35).

3.1 Introduction

3.1.1. Sr-90 and Cs-137 following Fukushima disaster

Strontium-90 and ^{137}Cs are present in environment aftermath the disasters at Chernobyl Nuclear Power Plant (CNPP) in 1986 and Fukushima Daiichi Nuclear Power Plant (FDNPP) in 2011 and because of the nuclear weapons tests conducted around mid-20th century, which have led to their dispersion all over the world. ^{90}Sr and ^{137}Cs are anthropogenic radionuclides synthesized by fission reaction inside core of the nuclear reactor [1]. Both are hazardous and must strictly be guarded against release into the environment as have intermediate half-lives of 28.7 and 30.2 y, respectively and add to long term doses to human population [2]. These are of concern because of their great quantity of production and also are easily metabolized, being similar to their chemical properties to essential elements such as stable calcium, potassium, respectively [3].

It was reported that ^{90}Sr concentration was about 1/1000 of that of ^{137}Cs in the soil after FDNPP accident [4,5]. However, strontium-90 has longer biological half-life of about 50 years [6] and it is accumulated in the bone than ^{137}Cs which has (about 70 days depending on age) and affect the whole body [7]. Strontium (Sr) migrates in soil columns faster than cesium (Cs) because Sr is chemically easier eluted by rainwater than Cs [8,9].

Regular determination of radiocesium has been conducted by several researchers and the Japanese government in Fukushima Prefecture. However, ^{90}Sr was hardly tackled because the amount released by FDNPP disaster was regarded as minimal, further the procedure for measurement of ^{90}Sr is tedious and requires more time in contrast to that of ^{137}Cs's. Thus, in the database you only have limited results for ^{90}Sr in comparison to ^{137}Cs [9].

Various studies on ^{90}Sr content have only tackled near the soil surface, thus not all ^{90}Sr content present in soil has been accounted for [10]. On the contrary, depth distribution of ^{137}Cs in Fukushima soils has been studied by several researchers [11-13]. Moreover, there have not been any research interested to analyze the ^{90}Sr vertical migration in sediment and horizontal distribution from land to water body.

In the present research, the magnitude in sorption and migration between ^{90}Sr and ^{137}Cs in the soil of disturbed area, Kawauchi (KP) and Fukushima paddy rice fields (FP), and undisturbed area, Lake Ogi valley sediments (LS) and its catchment forestry area (CA), was studied. for the ratio of ^{90}Sr and ^{137}Cs sediment to the soil was used to investigate the horizontal migration difference between ^{90}Sr and ^{137}Cs.

3.2. Methodology

3.2.1. Instrumentation

The sediment and soil samples were determined by three techniques, as follows:, $\gamma -$ Spectrometry equipped with the popular High Purity Germanium (HPGe) detector, Liquid Scintillation and Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) triple quadrupole (QQQ).

3.2.2. Soil and sediment samples

We had 17 samples altogether comprising 10 bulk soil samples, from Fukushima city paddy and Kawauchi village paddy and 4 core soil samples and 3 core sediment samples from Kawauchi`s LS and its CA respectively and were prepared as described in Nguyen et al. [14] and Basuki et al. [11]. The bulk soil samples were taken from 4 corners of rectangular paddies and the center. While the 4 soil core samples and 3 sediment core samples were also collected accordingly. The soil and sediment core samples had to be cut into 2 cm and 1 cm profiles to 10 cm and 5 cm deep, respectively and made 1 composite sample each layer. The soil and sediment samples were then firstly air dried at 25°C for 2 weeks then characterizing soil particles through 2 mm sieve before they were oven dried around 105°C for complete day of 24 h. Table 1 displays sampling area locations [11,15].

Table 1. Various sampling destinations in Fukushima prefecture

Area of sampling	**Sample #**	**Global Positioning System**		**Core sample depth/ cm**	**summary area**
		Longitude	**Latitude**		
The Forest (CA)	1	37.34363	140.90566	0-10	The CA consists of steep slope with deciduous trees
	2	37.34359	140.90571	0-10	
	3	37.34372	140.90567	0-10	
	4	37.34365	140.90559	0-10	
Lake Ogi sediments (LS)	1	37.34362	140.90615	0-5	Lake Ogi valley has no trees
	2	37.34361	140.90613	0-5	
	3	37.34357	140.90623	0-5	
				Surface bulk sample/ cm	
Kawauchi village rice field (KP)	1	37.32087	140.83568	~0-5	The rice field is rectangular, and the samples were taken from all corners plus the middle
	2	37.32090	140.83600	~ 0-5	
	3	37.32068	140.83585	~ 0-5	
	4	37.32042	140.83571	~ 0-5	
	5	37.32047	140.83607	~0-5	
	1	37.72601	140.47479	~ 0-5	The rice field is near a pond for ease
	2	37.72604	140.47471	~ 0-5	

Area of sampling	Sample #	Global Positioning System		Core sample depth/ cm	summary area
		Longitude	Latitude		
Fukushima city rice field (FP)	3	37.72608	140.47477	~ 0-5	of irrigation. Near residential buidings and samples were taken just like in Kawauchi
	4	37.72613	140.47484	~ 0-5	
	5	37.72615	140.47475	~ 0-5	

3.2.3. Cesium-137 analysis by $\gamma - spectrometry$

The sediment and soil samples were loaded into 50 g U8 transparent glass bottles of quantity 100mL, 2.5 cm radius and 5 cm height and were measured by $\boldsymbol{\gamma - spectrometry`s}$ HPGe detector for the ^{137}Cs at γ-energy of 661keV. The instrument was calibrated by standard source (MX033U8PP) produced by Japan Radioisotope Association that comprises several radioisotopes in range of low-high γ-energy emission with different sample thickness. The counting efficiency was computed according to the analyzed value and the standard value. Activity concentration of ^{137}Cs was calculated using expression by Adkupo et al. [16].

3.2.4. Strontium-90 analysis

a. Strontium measurement by Liquid Scintillation Counting (LSC) spectrometry

Comparable to to other methodologies in radiation measurement, the LSC spectrometry is superior to others because radiation can be measured without self /external absorption, thus a precise analysis with higher counting efficiency. A drawback, however, is that quenching might still emerge, a condition that leads to diminishing sample count rate [17].

In this study the quench correction was handled by pipetting 1 mL of 1019 Bq/mL -analytical grade ^{90}Sr standard solution into a set of 6 vials with increasing quenching agent ($FeCl_3$) as follows: 0, 0.02, 0.04, 0.06, 0.08, 0.10 mL, respectively. 10mL of cocktail was then put into each vial. Fig. 1 depicts result showing the relation between spectral index of the external standard (tSIE) or Spectral Quench Parameter of the External Standard SQP(E) and the Counting Efficiency, simply the Ratio of the counts per minute (CPM) to the Disintegration per minute (DPM). This figure was plotted using "IGOR Pro" software for double exponential plus offset curve fitting [18]

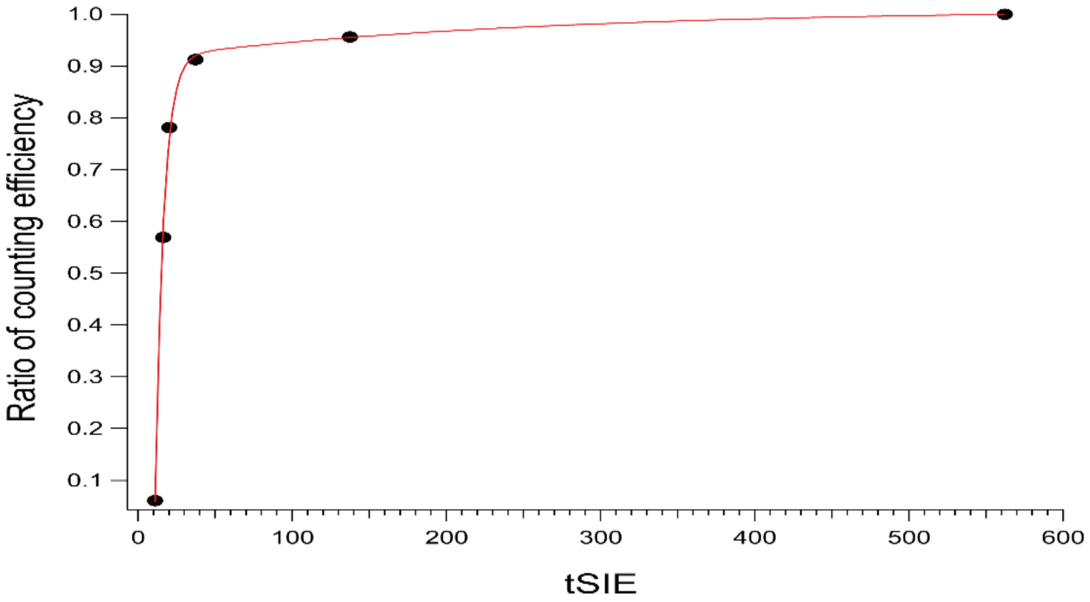


Fig. 1. Ratio of counting efficiency versus tSIE.

After measuring samples for ^{137}Cs, there was need to consider ^{90}Sr analysis suited to radiochemical technique by Maxwell et al. [19] with minor changes (Fig 2) in which Sr yield was done by ICP-MS unlike gravimetric procedure, ^{90}Sr activity was measured by Liquid scintillation not the proportional counter and the soil samples were hardly spiked by ^{90}Sr standard solution. To let go, we ashed the 50 g of soil samples in a furnace at 500°C for 2h then split into 3 equal portions of $\sim 16.7g$ and transferred into 3 Teflon beakers respectively, in order to determine the recovery ratio we added 2 mLof ^{88}Sr carrier ,1003 mg/L to each beaker, summing up to 6ml. We digested each soil and sediment samples in 15mL conc. HNO_3 and 7.5 mL conc. HCl for~ 30 min at ~120°C. We had to increase temperature to ~230°C for 1 hr to dryness. We then switched off the heater and let cool for ~30 min then poured 7 mL conc. HNO_3 into each Teflon beaker and additional 15 mL of 1M HCl for thorough dissolving of the soil. We then transferred liquid phase of each sample into 3 centrifuge tubes, whereby we added 8 mL conc. NH_3 followed by 1 mL of 1.25M $Ca(NO_3)_2$ to avoid ^{40}K interferences and 2 mL of 3.2M $NH_4H_2PO_4$ in order to get rid of Fe(OH)3 and then diluted with deionized water to the 50 mL mark while shaking to homogenize then carried out centrifugation at 3500 rpm for 10 min by KUBOTA KN-70 in which we retained the residue while rejecting the distillate.

We put the collected residue into three equal centrifuge tubes and then filled each with 13 mL of 1.5M HCl followed by 8 mL conc. HF which was diluted to 50 mL mark by 0.01M HCl in order to remove CaF_2. We mixed the samples homogeneously and centrifuged while retaining the residue again. In order to remove silicates and other matrix compounds we then mixed the residue with 7 mL conc. HNO_3 and 1 mL of 3M HNO_3 and 0.25M H_3BO_3 shaked vigorously and added 7 mL 2M Al $(NO_3)_3$ to each tube, followed by shaking then centrifuged 3500 rpm for 10 min in which the residue was rejected this time and maintained the supernatant and then rinsed again the residue with 5mL 3M HNO_3, shaken and centrifuged and then combined the filtrates together and then filtered through 0.45 µm filter paper.

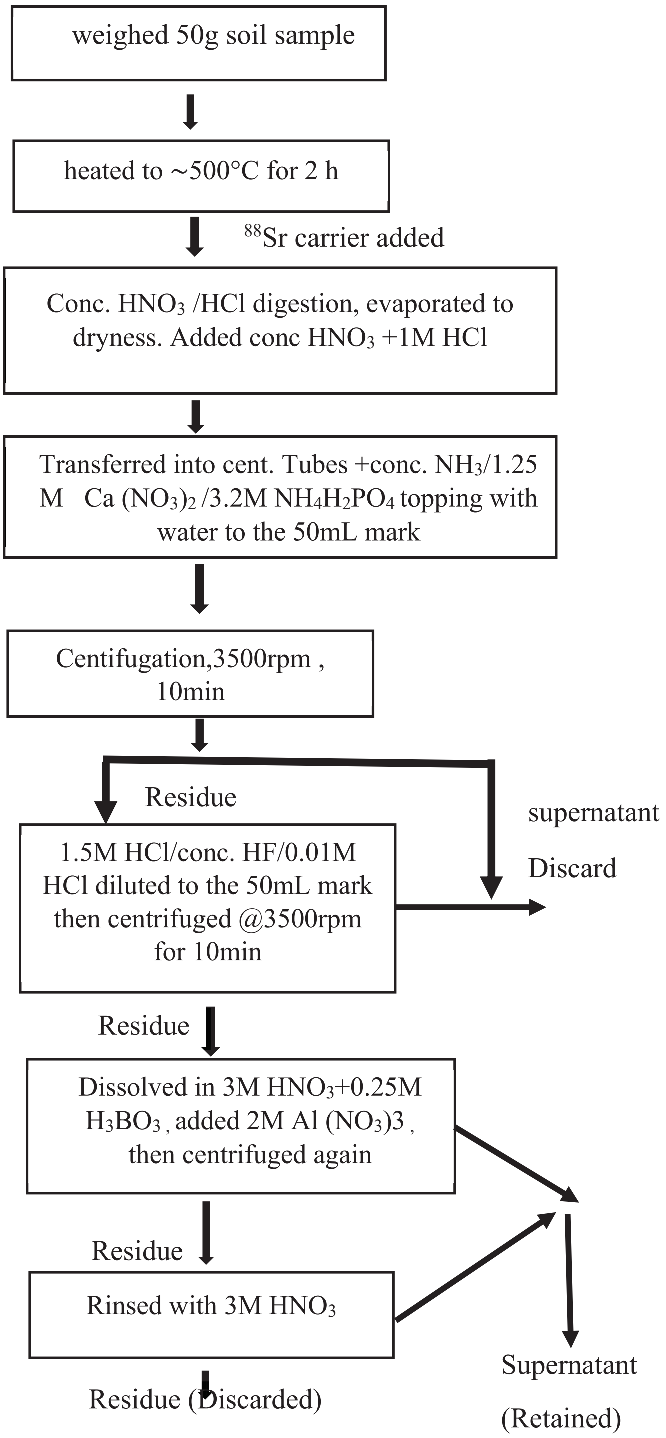


Fig. 2. Strontium-90 determination modified from Maxwell et al. [19]

b. Strontium extraction via Sr-resin technology

Sr -Resin (Eichrom) which comprises 4,4′′(5′′)-di-t-butylcyclohexano 18-crown-6 (crown ether) and its derivatives in 1-octanol was applied with very selective complexing environment for Sr ions. We loaded the columns packed with 2ml cartridges of 50-100 µm Sr resin each while connected to a vacuum pump.

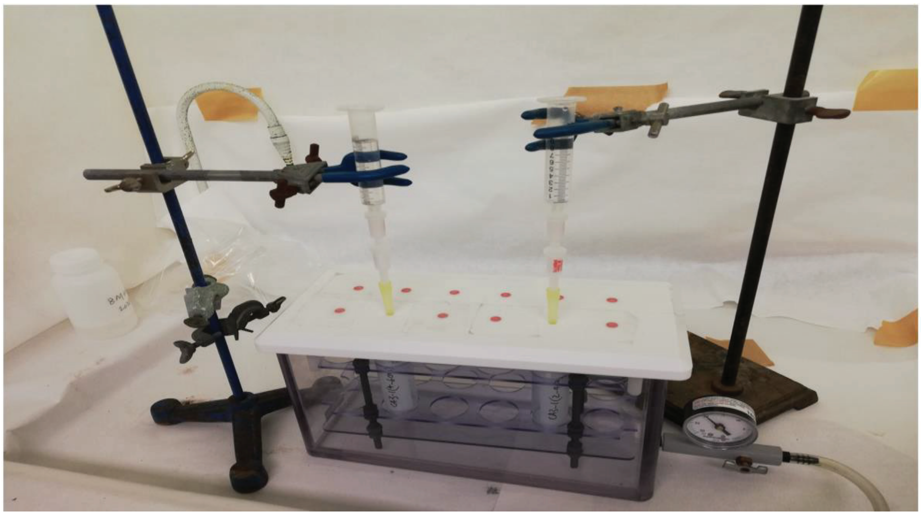


Fig. 3. Strontium affinity towards Sr-resin.

Before transferring the sample into the columns, they were conditioned with 10ml 8 M HNO_3. After passing the filtered sample through the conditioned columns we rinsed gently with 15mL 8M HNO_3 until it all passed through because Howitz et al. noted that Sr sorption coefficient at such high concentration of HNO_3 towards Sr-resin is ∼90%[20]. We then rinsed again with 10 mL, a mixture of 3M HNO_3 and 0.05M oxalic acid because there is also a possibility of tetravalent actinides retention by the columns and oxalic acid acts as a competitive complexing agent that suppressed actinides retention then added 10 mL 8M HNO_3 in order to get rid of Barium impurities.

We eluted ^{90}Sr by 18 mL 0.05M HNO_3 while1mL of the eluant was pipetted and mixed with 10mLcocktail namely Insta Gel Plus ,Perkin Elmer Inc which we left aside for more than 18 days (≥ 448 hr) roughly after 3 weeks to reach ^{90}Sr-^{90}Y secular equilibrium and then analyzed using Liquid Scintillation Counter (Tri-carb 2910TR, Perkin Elmer Inc) The other portion, 1 mL of each sample was measured immediately by ICP-MS triple quadrupole (QQQ) for Sr recovery ratio.

c. Measurement of ^{90}Sr via its daughter ^{90}Y during secular equilibrium

Strontium-90 is a pure β^- emitter and during its decay to granddaughter ^{90}Zr via ^{90}Y a neutron gets converted to proton in each case thus Y-39, Zr-40 respectively and there is also dissipation of energy. Secular equilibrium (SE) is simply the decay in which the daughter half-life ($t_{1/2}$) is much lower than that of the parent by magnitude of $\sim$10,000 (Fig. 4)

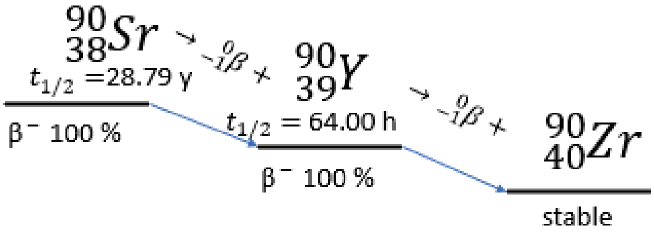


Fig. 4. Strontium-90 decay series to grand-daughter stable Zirconium-90

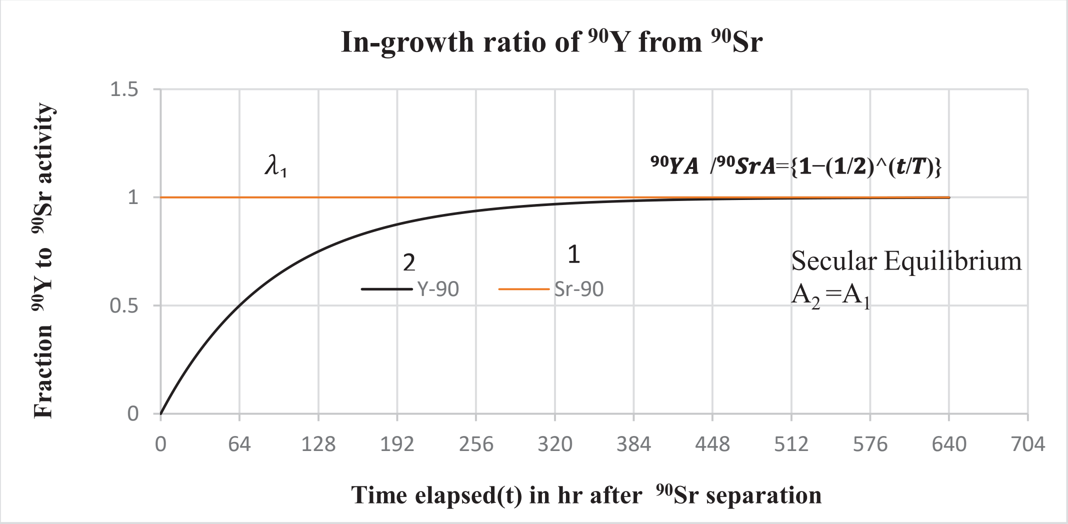


Fig. 5. Secular equilibrium for ^{90}Sr-^{90}Y.

Fig. 5 shows SE in which after 3 weeks rate of formation of the daughter is given by:

$$\frac{dN_2}{dt} = \lambda_1 N_1 - \lambda_2 N_2 \qquad (1)$$

and $\lambda_1 N_1$- $\lambda_2 N_2$ at time (t) is the sum of the rate of formation of daughter from the parent and the rate of decay of the daughter respectively [21,22]

after integrating with respect to time(t) on both sides

$$\Longrightarrow \lambda_2 N_2 = \lambda_1 N_1^0 \, (1 - e^{-\lambda_2 t}) \qquad (2)$$

Thus, overall activity of the daughter at any elution time during SE is given by:

$$\lambda_2 N_2 = \lambda_1 N_1^0 \, [1 - \left(\tfrac{1}{2}\right)^n] = \lambda_1 N_1^0 \, [1 - \left(\tfrac{1}{2}\right)^{\frac{t}{T}}] \qquad (3)$$

n being number of half-lives, ⇒ n = $\frac{t}{T}$, t is time from elution and T is the $t_{1/2}$of daughter radionuclide.

By substitution ^{90}Sr, ^{90}Y for parent, daughter in eq.3 above, then

$$^{90}\mathrm{Y}_A = {}^{90}\mathrm{Sr}_A\{1 - \left(\tfrac{1}{2}\right)^{\frac{t}{T}}\} \qquad (4)$$

d. Determination of ^{90}Sr via ^{90}Y using LSC

Having eluted strontium, the ^{90}Sr concentration was analyzed via its daughter ^{90}Y by the liquid scintillation counter after 3 week`s radioactive SE was established between ^{90}Sr and ^{90}Y and each sample was determined for 72,000 s.

In order to find the amount of ^{90}Sr in the soil and sediment samples was calculated by equation (4) and to obtain the specific activity concentration of ^{90}Sr in soil and sediment samples we used the following equation:

$$^{90}\mathrm{Sr}_C = \frac{90\mathrm{Sr}_A}{r \times M_s} \qquad (5)$$

where $^{90}\mathrm{Sr}_C$ is the specific activity concentration of ^{90}Sr in soil (Bq/kg), related to *r*, the recovery ratio of stable ^{88}Sr and M_s, the dry weight of soil sample (kg).

We calibrated the equipment (LSC) by measuring 4 liquid samples with initial ^{90}Sr standard solution of concentration: 0.00, 0.10, 0.20, 0.40 Bq, respectively in similar condition. The Sr-90 standard reference solutions (SR010) were calibrated using Japan calibration service system (JCSS). Fig 6 is a calibration curve with good linearity between activity (dpm) and cpm. We really applied a conversion factor [Bq/cpm] of ~ 0.0089.

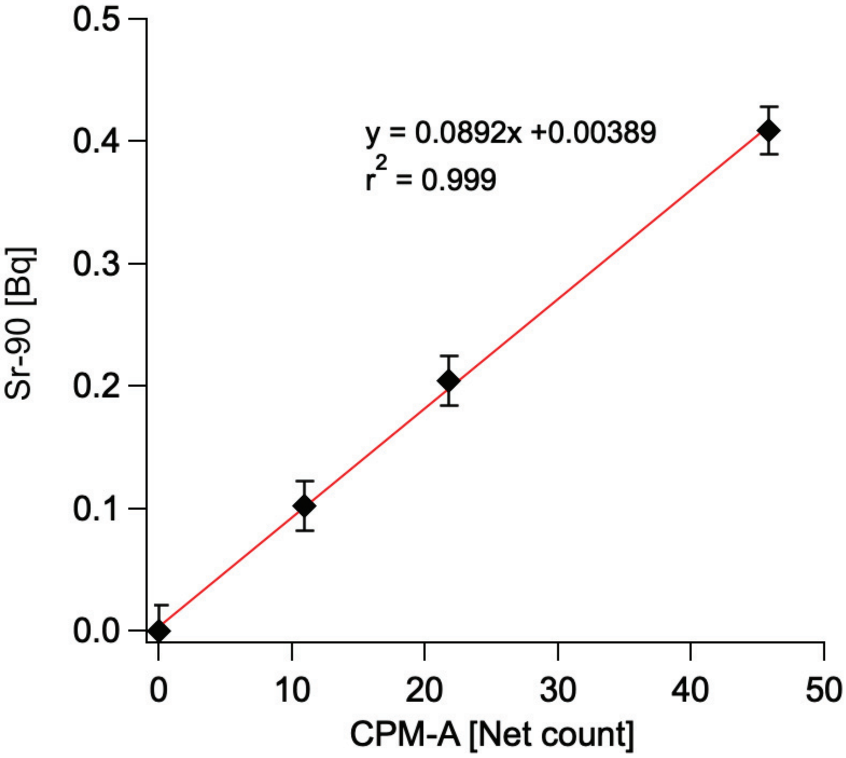


Fig. 6. LSC calibration curve of ^{90}Sr

e. The Minimum Detectable Activity (MDA)

A minimum detectable activity (MDA) is meant to be a good indication to scrutinize the analysis outcome of a given radiometric technique. Currie [23], solved MDA using:

$$\text{MDA (Bq kg}^{-1}) = \frac{2.71+4.65\sqrt{B}}{C_t \times \varepsilon \times r \times M_s} \qquad (6)$$

where B is the background count, C_t is counting time, ε is counting efficiency of ^{90}Y by liquid scintillation counter, r is recovery ratio by ICP-MS, and M_s is sample mass. In our study got the MDA mean value of ~ 0.49 ± 0.21 Bq/kg. Konno and Takagai arrived at the detection limit of ~0.2 Bq/Kg [24] while ~0.41Bq/Kg was found by Maxwell et al. [19].

f. The recovery yield by Inductively Coupled Plasma -Mass Spectrometry

An ICP-MS/MS triple quadrupole (QQQ) (Agilent 8800, Agilent Technologies Inc.) was the main equipment that we used to obtain stable strontium-88 concentration in order to correct the activity concentration of ^{90}Sr as regards to the Sr recovery yield. ICP-MS QQQ technology combined with the incorporation of a reaction cell, have ensured its application to rapid analysis of Sr [25] in various environmental matrices. We calibrated the ICP-MS before running the samples by stable ^{88}Sr.

The calibration graph demonstrated remarkable linear fit line with $R^2 = 0.9998$ (Fig 7).

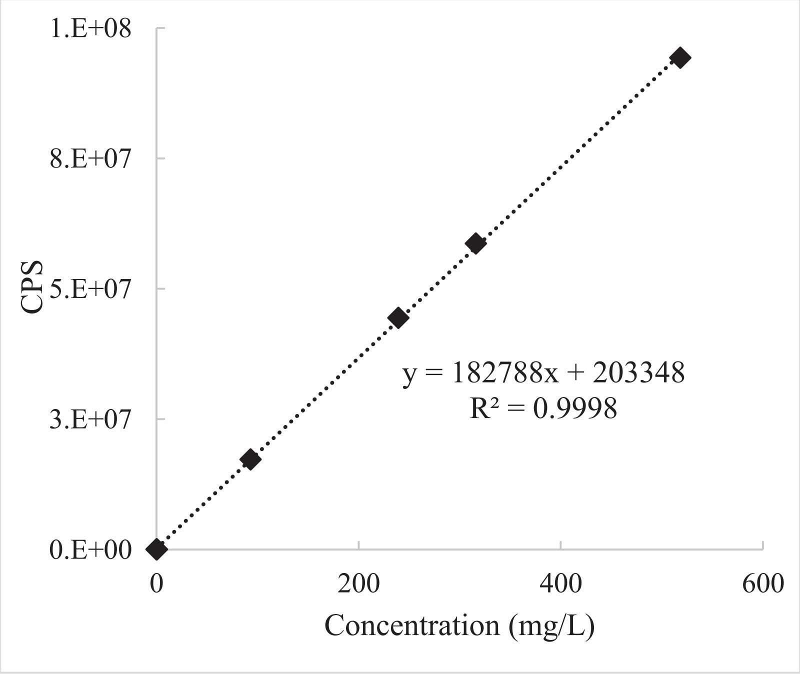


Fig. 7. CP-MS calibration curve ^{88}Sr.

The results calculated on each sample were related to the initial amount of stable strontium in order to find the recovery ratio (r) in equation (5) and (6). We obtained the ICP-MS recovery ratios in a range of 14 - 67% with an aggregate of ~37% relying upon the sample. We found the total ^{90}Sr activity concentration in soil and sediment samples from LSC determined result in relation to each sample`s recovery ratio of stable ^{88}Sr.

3.3. Results and Discussion

3.3.1. Stable Strontium-88 recovery ratio

We obtained Sr recovery ratio values correction by mass spectrometry after Sr extraction via Sr-resin from 14 - 67% with the average value of 34 % which scattered for various samples. The mean value was in a good agreement with the reported values. For example, Sasaki et al. outlined that the values for Sr recovery ratio correction employing mass spectrometry by the on-line extraction chromatography was ~ 30% in average and also scattered depending on the samples [26]. In addition, Vajda and Kim compiled recovery ratios analyzed using several Sr analysis procedures globally and they found that ICP-MS happen to give higher chemical yields than the average gravimetry [27].

The Sr recovery ratio may portray the magnitude in characteristics for each soil and sediment sample. We got the average values with standard deviations as follows: 0.21±0.05, 0.51±0.11, 0.27±0.11, and 0.36±0.05 for FP, KP, LS, and CA, respectively. The corresponding coefficient of variation were 0.23, 0.22, 0.25, and 0.15, respectively. It portrayed that Fukushima and Kawauchi paddy soil demonstrated a different Sr recovery ratio.

3.3.2. Migration of ^{90}Sr and ^{137}Cs in Fukushima, Kawauchi rice fields, Lake Ogi and its forestry catchment area

Figure 8 depicts the migration of ^{137}Cs and ^{90}Sr corrected to sampling date, March 15th, 2018 for Kawauchi paddy, Lake Ogi and its catchment forestry area and August 23rd, 2017 for Fukushima rice field. Fig.8 shows there is a rough correlation between ^{90}Sr and ^{137}Cs concentrations. Five soils for FP , KP show the almost same ^{137}Cs concentrations in each paddy, respectively while they demonstrate extensively distributed ^{90}Sr concentrations in each paddy. Other researchers noted that the ^{90}Sr concentrations before FDNPP disaster were in the range of ~0.2- 20.4 Bq/kg in Fukushima prefecture [24]. Based on Fig.6 the ^{90}Sr at KP might be due to the global fall out. However, forestry area shows relatively high values for both ^{137}Cs and ^{90}Sr concentrations. The rough correlation in Fig. 6 deviates from original point (0, 0) which might relate to the global fallout of ^{90}Sr unlike its counterpart, ^{137}Cs which is not verified in the Fig. 8. Such trend is observed in the literature [28].

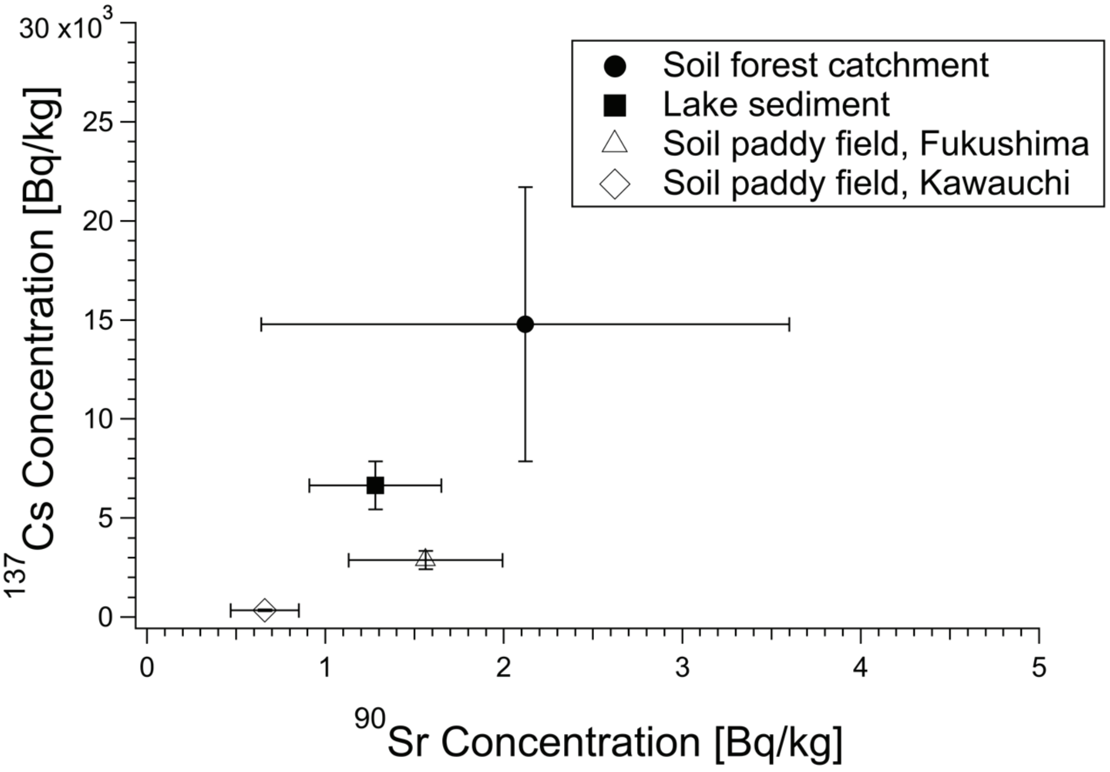


Fig 8. Stontium-90 and Cesium-137 in Fukushima, Kawauchi Paddy rice fields, Lake Ogi and its forestry catchment area.

Table 2 gives the mean ^{137}Cs and ^{90}Sr activity concentrations and their coefficient of variations and ^{90}Sr/^{137}Cs ratios. Cesium-137 concentration happen to fall in the order: CA>LS>FP>KP with aggregate value of 14,781±6,921, 6668±1220, 2882±461, 347±49 Bq/kg, respectively, while ^{90}Sr in the areas differ slightly from ^{137}Cs as follows:

CA>FP>LS>KP with average value of 2.12±1.48, 1.56±0.28, 1.28±0.37, 0.66±0.19 Bq/kg, appropriately. The results outline that the forestry areas are still proportionately highly contaminated with ^{137}Cs and ^{90}Sr, while decontamination activities conducted in Fukushima led to the lowering of contamination as regards to Kawauchi paddy field.

Table 2. Average Cesiym-137 and Strontium-90 concentrations and their CF and ^{90}Sr/^{137}Cs ratio

Parameter	FP	KP	LS	CA	LS/
Sample # (n)	5	5	3	4	
Mean ^{137}Cs (Bq/kg)	2882	347	6,668	14,781	0.45
StDev (Bq/kg)	412	44	1,220	6,921	
CF	0.14	0.13	0.18	0.47	
Mean ^{90}Sr (Bq/kg)	1.56	0.66	1.28	2.12	0.60
StDev (Bq/kg)	0.43	0.19	0.37	1.48	
CF	0.28	0.29	0.29	0.70	
Ratio (^{90}Sr/^{137}Cs)	0.00054	0.0019	0.00019	0.00014	
Uncertainty (^{90}Sr/^{137}Cs)	0.00017	0.00061	0.000066	0.00012	

Table 2 outlines ^{90}Sr/^{137}Cs ratio ranges from 0.0001 to 0.0019 with a mean value of 0.0007±0.0005 and ^{90}Sr is moderately low. Further, the coefficient of variation for ^{90}Sr (0.28, 0.29), that is greater than that for corresponding recovery yield (0.23, 0.22), is remarkably big in contrast to ^{137}Cs (0.14, 0.13) for Fukushima and Kawauchi paddy. However the CF for ^{90}Sr (0.29, 0.70), which is greater than that of the corresponding recovery ratio (0.26, 0.15), is also greater than that of ^{137}Cs (0.18, 0.47) for LS and CA, correspondingly. The results mean that the transportation of ^{90}Sr is more influenced by external factor.

The ^{90}Sr/^{137}Cs ratios in Table 2 are paramount in deciphering sources of radioactive releases and clues of environmental behaviors of these radionuclides. Studies of annual average values of ^{90}Sr/^{137}Cs activity ratios of deposition samples from 1980 -1985 showed values from 0.43 - 0.77, probably as a result of Chinese Nuclear weapons test in 1980s [29]. The ^{90}Sr/^{137}Cs ratio obtained in Japan-Tsukuba after CNPP accident in 1986 was ~ 0.0094 while in March 2011 aftermath of FDNPP accident, ^{90}Sr/^{137}Cs ratio at Tsukuba diminished to ~ 0.0002-0.003 [30]. Thus, the current study ratio ^{90}Sr/^{137}Cs of 0.0007 ± 0.0005 shows that the source of ^{90}Sr might be due to nuclear weapons test as well as FDNPP accident.

Table 3 categorizes ^{90}Sr and ^{137}Cs and their ratio in current research and previous studies in Fukushima prefecture. The table depicts that currently findings fall within the expected values of results, for example Sahoo et al . [4] noted that ^{90}Sr concentration ranged from 3-23 Bq/kg while ^{137}Cs from 700-110,000Bq/kg while ^{90}Sr/^{137}Cs ratio was from 0.0002-0.004 , within the range of current study. The source of ^{90}Sr has been inferred to be probably due to consequences of previous nuclear disasters and the nuclear weapons tests in 1950`s by America and Russia. This is verified in the study done by Konno and Takagai [24] before and after FDNPP incident and the latest research outlined the decreased ^{90}Sr results with range from ~0.5-5 Bq/kg perhaps pointing to nuclear weapons tests and FDNPP disasters. ^{90}Sr determined in agricultural foods was much minimal in contrast to that determined in soil for other studies and the present study.

Table 3. concentration of ^{90}Sr and ^{137}Cs and ^{90}Sr/^{137}Cs ratio comparable to other studies

Location	Strontium-^{90}	Cesium-^{137}	^{90}Sr/^{137}Cs	Reference
Fukushima	0.47-4.63	14,780.97	0.0001-0.0019	current study
Fukushima	9-38			[25]
Fukushima*a	0.2 – 20.41			[24]
Fukushima*b	0.37-80.8		0.001	[24]
Fukushima	3-23.3	700-1.1x10^5	0.0002-0.004	[4]
Fukushima			0.001-0.0042	[5]
Fukushima*c	0.0047–0.31	0.055-80	0.003	[31]
Fukushima			0.0013 ± 0.0006	[32]

*^{a} Before FDNPP accident *^{b} After FDNPP accident *^{c} Agricultural products

a. Strontium-90 and Cesium-137 Depth dependence

Following their discharge on the soil surface, the radioisotopes move downwards. The rate of migration can easily be approximated based on the depth profile of the radioisotope in relation to time taken. These depth profiles were obtained by monitoring the various portions of sample cores obtained from forestry catchment area and Lake Ogi valley.

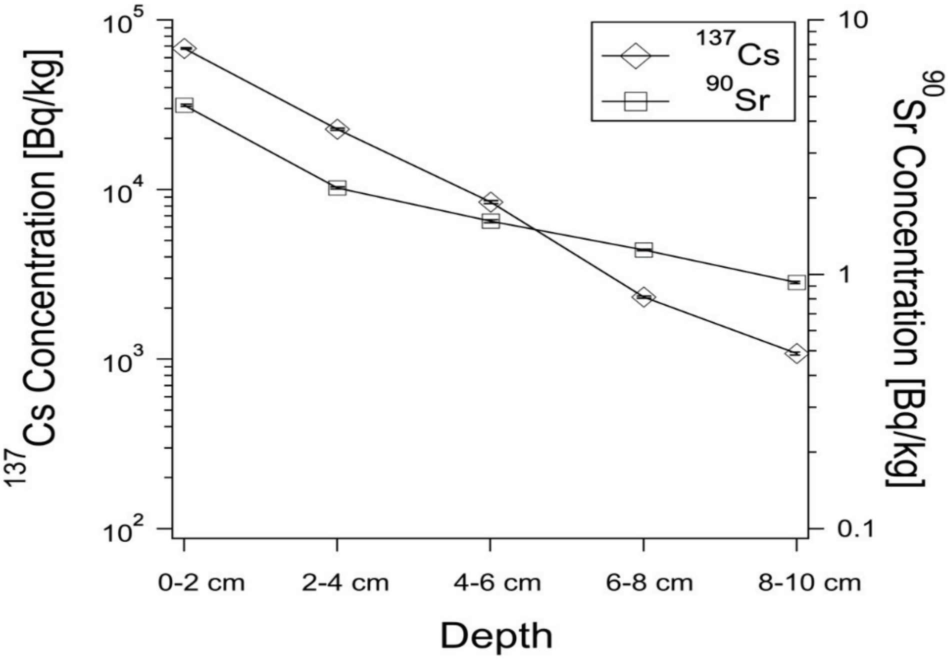


Fig. 9. Depth reliance of ^{90}Sr and ^{137}Cs at the forestry area.

Figure 9 indicates activity concentration of ^{90}Sr,^{137}Cs at Catchment Forestry area in relation to depth. It shows that both Cesium-137 and ^{90}Sr activity concentrations decrease exponentially with the depth. However, the vertical profile between the two happen to be distinguished with ^{90}Sr faster vertical migration than that of ^{137}Cs. It is clear to notice that Cesium-137 concentration lowered from 67,900 to 1,100Bq/kg giving a 1.6 % ratio at 8-10 cm depth, while ^{90}Sr decreased greatly from 4.63 to 0.93 Bq/kg outlining 20% ratio at the depth of 8-10 cm. The strong sorption of ^{137}Cs by soil profile has been reported by Konopleva et al. [33] who directed that, 19 years after the CNPP disaster, almost over 50% of the Chernobyl-derived ^{137}Cs adsorbed in the upper 10-cm layer in German forestry soil; and Koarashi et al. [13] observed that at a Japanese cedar plantation even after 38 years had elapsed after nuclear weapons tests, yet the traces of ^{137}Cs remained in the topmost 5 cm layer of the mineral soil.

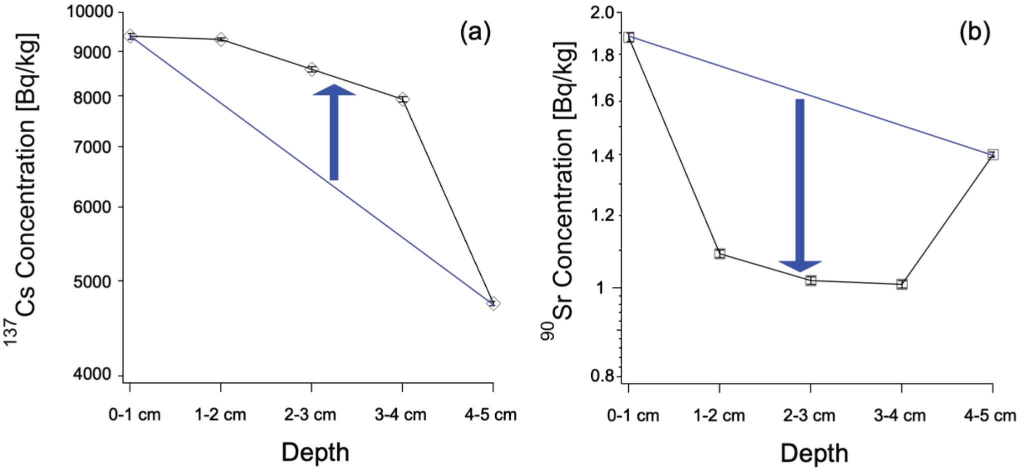


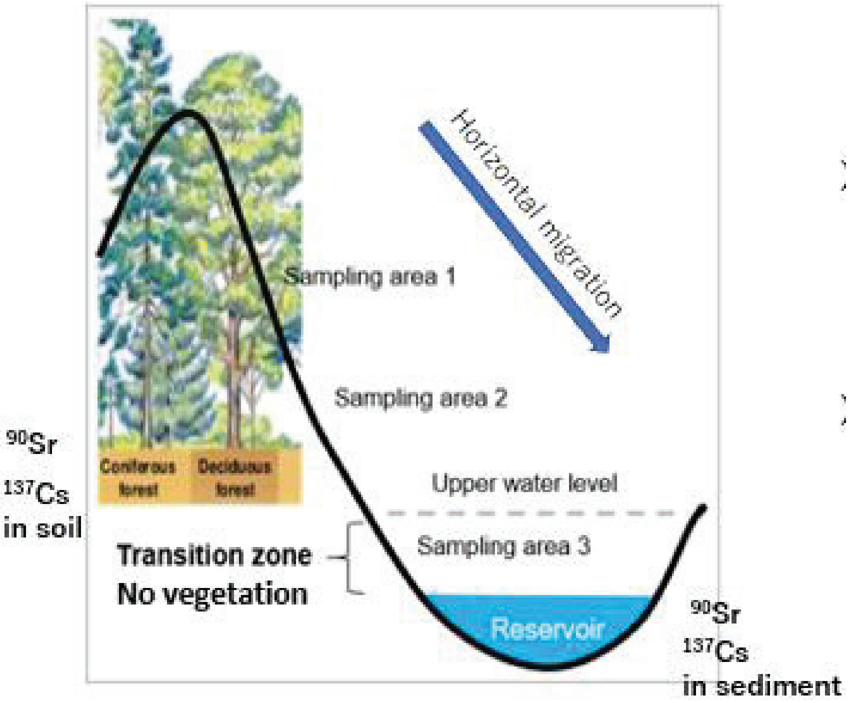
Fig 10. Cesium-137 (a) Strontium -90 (b) depth dependence at Lake Ogi.

Depth dependence of ^{137}Cs and ^{90}Sr at Lake Ogi is shown in Fig. 10 which portray exponential change is interfered for both ^{137}Cs and ^{90}Sr. The shift is interchangeably opposite between the two, with upward convex for ^{137}Cs, while downward for ^{90}Sr. An explanation for this could be probably that the surface sediments became relatively uniform by the disturbance near (0~4 cm) surface while Cesium-137`s strongly adsorbed to the sediment becomes uniform, while ^{90}Sr weakly adsorbed to sediment re-dissolves to the lake water. The re-dissolved ^{90}Sr is adsorbed to the sediment again at (0~1 cm) depth. Thus, the sediment at (0~1 cm) has remarkably greater ^{90}Sr in contrast to the rest. Cesium is preferably adsorbed by ion exchange and its sorption is different from that of strontium because of its large cation, with very minimal hydration energy, which implies that the electrostatic attraction between it and the clay is more preferred than strontium [34, 35].

b. Sediment to soil ratio of ^{90}Sr and ^{137}Cs

Table 2 and Fig.11 display the ^{90}Sr and ^{137}Cs in sediment to soil ratio and it shows that the LS/CA ratio of ^{90}Sr (0.60) is greater than that of ^{137}Cs (0.45). This implies that there was more proportion of ^{90}Sr deposited in sediment than that of ^{137}Cs and this might relate to ^{90}Sr faster horizontal migration than ^{137}Cs.

The application of sediment to soil ratio to predict the transfer of Cs has been reported by Basuki et al. [11]. The outcome of relatively faster horizontal distribution of ^{90}Sr than that of ^{137}Cs was matched well with vertical migration in soil of these two radioisotopes which might be regulated by their interaction behavior with the soil component. Other researcher proposed that clay minerals rich in phyllosilicate, due to their interlayer or frayed edge sites, such that Cs^+ on these sites is irreversibly adsorbed, making Cs^+ desorption from soil with such clay difficult [36]. Bekelesi et al.2022 found that Fukushima soil contains some micaceous minerals, the subset of phyllosilicates [15]. The comparatively less interaction of ^{90}Sr with soil component than that of ^{137}Cs might lead to ^{90}Sr washing by run-off water or melting snow.



Modified from Basuki et al., 2020 [11].

Fig. 11. LS/CA ratio, 0.45 (^{137}Cs) and 0.60 (^{90}Sr).

3.4. Conclusion

In this research the rough correlation between Strontium-90 and Cesium-137 concentrations was obtained. The relation deviates from original point (0, 0) which implies the global fallout of ^{90}Sr. The coefficient of variation for ^{90}Sr is greater than that of ^{137}Cs for Fukushima city and Kawauchi village rice field. In addition, the coefficient of variation for ^{90}Sr is bigger than that of ^{137}Cs for Lake Ogi and its forestry catchment area. The results portray that the distribution of ^{90}Sr is influenced by external factor to great extent. ^{90}Sr infiltrates deeper than ^{137}Cs in the soils of catchment forest and sediment to soil ratio of ^{90}Sr is bigger compared to that of ^{137}Cs, signifying ^{90}Sr more swift horizontal migration than ^{137}Cs. Exponential change for both ^{137}Cs and ^{90}Sr is mostly impeded near the surface (0 -4 cm) depth for the sediment. Probably the surface sediments become nearly uniform by the disruption near the surface (0~4 cm) deep. ^{137}Cs strongly adsorbed to sediment becomes uniform, while ^{90}Sr weakly adsorbed to sediment re-dissolves to the lake water. The re-dissolved ^{90}Sr is adsorbed to the sediment again at (0~1 cm) depth. Thus, the sediment at (0~1 cm) depth happen to exhibit higher ^{90}Sr concentration than that of deeper sediment layer. The ^{90}Sr/^{137}Cs ratio for soil and sediment samples ranged from 0.0001-0.0019 with mean value of 0.0007±0.0005 that is quite in a good agreement with some previous results.

3.5. References

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Chapter 4.

General Conclusion

In the first study by assessing the two rice fields (Fukushima city and Kawauchi village), and by investigating the relation among soil properties, ^{137}Cs migration and transfer factor (TF) of ^{137}Cs from soil to rice plant, it was observed that Transfer factor (TF) of ^{137}Cs from soil to rice in study area of Kawauchi is larger than that of Fukushima and TF of ^{137}Cs from soil to rice was shown to be influenced by the soil characteristics. It was noted that Fukushima soil tends to have more micaceous clays and has less percentage of exchangeable ^{137}Cs and high percentage of exchangeable K^+ which retard sorption of Cs-137 which inhibit migration of Cs-137 into the rice plants than that of Kawauchi soil

The second research showed different migration behavior between ^{90}Sr and ^{137}Cs. ^{90}Sr penetrated more deeply vertically in soil layer than ^{137}Cs, and furthermore, the higher sediment to soil ratio of ^{90}Sr than that of ^{137}Cs indicated that ^{90}Sr was easier to migrate horizontally.

Both these findings on factors affecting the TF as well as the difference of ^{90}Sr and ^{137}Cs migration might be useful information for reducing the Cs-137 uptake by rice plant and in assessing their radiation risk to the population and environment respectively.

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