Stable elements – as a key to predict radionuclide transport in forest ecosystems

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Abstract. As the chemical behavior of radiocesium is expected to be almost identical to that of stable Cs, analyses of stable Cs and related stable elements should be useful to understand the long-term behavior of radiocesium and its equilibrium distribution in forest ecosystems. In this study, the concentrations of stable Cs and related alkali and alkaline earth elements in mushrooms, plants and soils were determined by inductively coupled plasma-mass spectrometry (ICP-MS) or inductively coupled plasma-atomic emission spectrometry (ICP-AES). Samples were collected in forests with different contamination levels in Japan, Germany, Finland, Italy, Ireland and Belarus. Vertical distributions in soils, and concentrations in mushrooms and plants were summarized for radiocesium and related stable elements. Relationship between radiocesium and stable Cs in mushrooms and plants, and transfer from soil to vegetation were also discussed. The results indicated that the ratio between radiocesium and stable Cs is useful for judging the equilibrium of deposited radiocesium in different parts of a forest ecosystem. The stable Cs analyses might be also useful to predict the long-term radiocesium contamination of mushrooms and plants.

1. INTRODUCTION

Forest ecosystems tend to accumulate radionuclides such as radiocesium discharged into the atmosphere through nuclear weapons testing and nuclear accidents [e.g. 1-4]. Even more than 10 years after the Chernobyl accident, radiocesium contamination of forest products is high in contrast to agricultural products. High concentrations of radiocesium were observed especially in mushrooms. Since the removal of radiocesium from a contaminated forest is not feasible on a large scale, studies on the distribution and transfer of radiocesium in forest ecosystems are important from radiation protection viewpoint. However, the long-term fate of radiocesium in forest ecosystems is still difficult to predict.

As the chemical behavior of radiocesium is expected to be almost identical to that of stable Cs, analyses of stable Cs and related stable elements should be useful to understand the long-term behavior of radiocesium and its equilibrium distribution. There are many studies on the behavior of major nutrient elements such as K, Mg and Ca in forests [5, 6] and the relationship between radiocesium and K was discussed [7]. However, the data for trace alkali and alkaline earth elements including stable Cs in forest ecosystems are limited, and the relationships among radiocesium, stable Cs and related stable elements are still unclear.

In this study, the concentrations of stable Cs and related alkali and alkaline earth elements were determined by inductively coupled plasma-mass spectrometry (ICP-MS) or inductively coupled plasma-atomic emission spectrometry (ICP-AES) for mushrooms, plants and soils collected in forests with different contamination levels in Japan, Germany, Finland, Italy, Ireland and Belarus. Data of stable elements were compiled together with those of radiocesium. Vertical distributions in soils, concentrations in mushrooms and plants, relationship between radiocesium and stable Cs, and transfer from soil to vegetation were discussed.

2. SAMPLING AND MEASUREMENTS

Twenty-nine mushroom samples belonging to 17 species, 8 plant samples, and soils from different depths were collected from a Japanese pine forest on sandy soil near the coast in Tokai-mura, Ibaraki from 1989 to 1991 [8]. In this forest, most of the radiocesium originates from atmospheric nuclear weapons testing.

Twenty-two mushroom samples belonging to 3 species were collected from forests in Alavus, Kirkkonummi and Kullaa in Finland from 1989 to 1993.

Soil core samples were collected from a pine forest near to Gomel, Belarus, in 1998. This site was not seriously contaminated by the Chernobyl accident. After collecting the organic layers, a core was taken using a 20 cm length and 50 mm diameter corer, and was cut every 1 cm up to 10 cm and every 5 cm thereafter. Four cores were taken inside the sampling site (50 x 50 m^2). Further details of sampling methods in Belarus are given in Schell et al. [9].

A detailed study on the transfer of radiocesium and stable Cs from soil to fungal fruit bodies and green plants was performed at a Norway spruce stand in Hochstadt, Germany. In this site, the soil layers from which certain species of mushrooms take up radiocesium were estimated by using the $^{137}Cs/^{134}Cs$ ratios [10]. Totally 25 soil profiles were randomly taken within an area of about 100 x 100 m^2 of the investigated site in 1993, 1995 and 1996. Four mushroom species were collected every year from 1993 to 1996. It was shown that these species take up radiocesium from different soil horizons. For comparison, samples of a berry plant were also sampled. Further details of sampling methods in Germany are given elsewhere [10, 11].

Tree samples were collected in a mixed forest in Italy and commercial stand in Ireland. One representative tree was selected for each forest and different parts of the tree were sampled. 90 years old Norway Spruce (*Picea abies*) was sampled in September 1996 in Italy, and 43 years old Sitka Spruce (*Picea sitchensis*) was sampled in 1998 in Ireland.

All samples were dried and milled. Each sample was placed in a plastic bottle and concentrations of ^{137}Cs, ^{134}Cs and ^{40}K were determined by counting with a Ge-detector. The decay correction was made as to May 1986. Details for the radiocesium determination have been described by Muramatsu et al. [12] and Rühm et al. [10, 11].

Mushroom and plant (0.2 - 0.4 g) and soil (0.1 g) samples were digested in Teflon™ PFA pressure decomposition vessels with acids (HNO_3, HF and $HClO_4$). A microwave digester was used for heating the samples. After digestion, the samples were evaporated to dryness. Then, the residues were dissolved in 1 - 2% HNO_3 to yield the sample solutions. Trace elements (Rb, Cs, Sr and Ba) were measured by ICP-MS (Yokogawa Analytical Systems, PMS-2000). Major elements (Na, K, Mg and Ca) were determined by ICP-AES (Seiko Instruments, SPS7700). Duplicate sample preparation and measurement have been done for each sample. Several standard reference materials were used to validate the analytical procedure. Details for the analyses have been described by Yoshida and Muramatsu [13].

3. RESULTS AND DISCUSSION

3.1 Vertical distributions in soils

Vertical distributions of stable Cs and ^{40}K in forest soils in Japan, Belarus and Germany were compared with those of radiocesium (**Figure 1**). The concentration of radiocesium is high in the organic layers and decreased with depth in the following mineral layers. At present, this maximum in the organic layers is typical for natural ecosystems and has been reported by many researchers after the Chernobyl accident. On the other hand, the concentrations of stable Cs were almost constant in the mineral layers and were lower in the organic layers. Vertical distributions of ^{40}K were similar to those of stable Cs. These facts indicate that the main source of stable Cs is mineral itself and the contribution of the atmospheric deposition is negligible.

The radiocesium/stable Cs ratios in mineral layers were mostly depend on the radiocesium concentration, and were decreased with depth. However, the ratios in the organic layers were not so varied. The detailed distributions of radiocesium and stable Cs in the organic layers had been studied in Hochstadt, Germany (**Figure 1**)[14]. In the figure, the vertical profiles are shown for Chernobyl-derived ^{134}Cs, for ^{137}Cs due to weapons fallout (^{137}Cs-f), and for stable Cs. The ^{137}Cs-f was calculated using an isotopic ratio of $^{137}Cs/^{134}Cs$ = 1.75 for Chernobyl cesium on 1 May 1986 [15]. The profile for ^{134}Cs shows a maximum in the Of and Oh layers, being lower in the litter layer and the mineral horizons, as reported in many papers. The profile for ^{137}Cs-f shows different characteristics. The ^{137}Cs-f increases from about 7 Bq/kg in the litter layer to about 100 Bq/kg in the Ah layer. The similar increase can be seen for stable Cs for the organic layers including the Ah horizon. The ^{137}Cs-f/stable Cs ratios were almost constant from litter to Ah horizons, indicating that fallout ^{137}Cs is now well mixed with stable Cs in the organic layers in this forest. In the B horizon, stable Cs concentration reaches about 3 ppm. In this layer, stable Cs may be enclosed in mineral particles, in contrast anthropogenic ^{137}Cs. For this reason, differences in the stable Cs and ^{137}Cs profiles are understandable for this horizon. As will be discussed later, however, stable Cs is unlikely to be enclosed in bedrock particles in the organic horizons L, Of, and Oh in this forest.

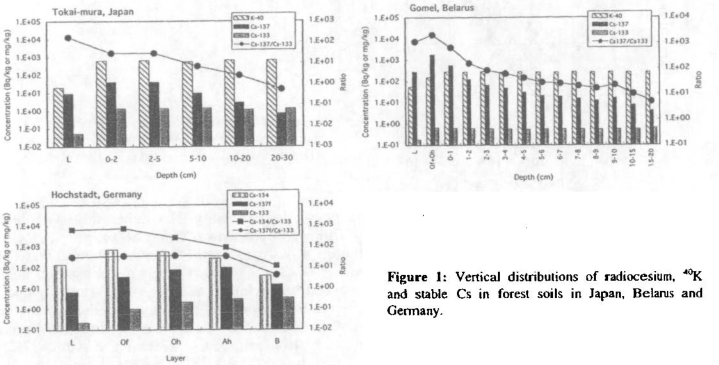

Figure 1: Vertical distributions of radiocesium, ^{40}K and stable Cs in forest soils in Japan, Belarus and Germany.

3.2 Elemental composition of mushrooms and plants

After the Chernobyl accident, high concentration of radiocesium in mushrooms were reported in many papers. However, data for stable elements, which can be discussed with the radiocesium concentration are limited for wild mushrooms. In order to compare the elemental composition between mushroom and plant, alkali and alkaline earth elements and ^{137}Cs were analyzed for 29 mushroom and 8 plant samples collected in a pine forest in Tokai-mura, Japan [8]. The highest median concentration in mushrooms (mg/kg-dry) was found for K (27200) followed by Mg (1050), Na (1000), Ca (389), Rb (87.6), Ba (5.12), Sr (2.88) and Cs (1.01). For plants, the highest median value was found for Ca (16300) followed by K (8860), Mg (1800), Na (802), Sr (70.8), Ba (11.1), Rb (9.35) and Cs (0.043). The median concentrations of ^{137}Cs were 135 Bq/kg-dry for mushrooms and 3.8 Bq/kg-dry for plants. In comparison with the elemental composition of plants, the mushroom composition could be characterized by the high ^{137}Cs, Cs and Rb concentrations and low Ca and Sr concentrations. Higher accumulations of Cs and Rb, and lower accumulation of Sr in mushrooms than those in plants were also observed from cultivation experiments in flasks using radiotracers [16, 17].

3.3 Equilibrium in biological cycle

Correlations between ^{137}Cs and stable Cs for mushrooms collected from 5 different forests in Finland, Germany and Japan are summarized in **Figure 2**. The data for mushrooms collected from a pine forest in Rokkasho-mura, Aomori, Japan reported by Tsukada et al. [18] are also plotted in the figure. A good correlation between ^{137}Cs and stable Cs was observed for each site independently, although several different species of mushrooms are included. This finding suggests that mushrooms take up ^{137}Cs together with stable Cs. The ^{137}Cs/stable Cs ratios were fairly constant for samples collected at the same site. The

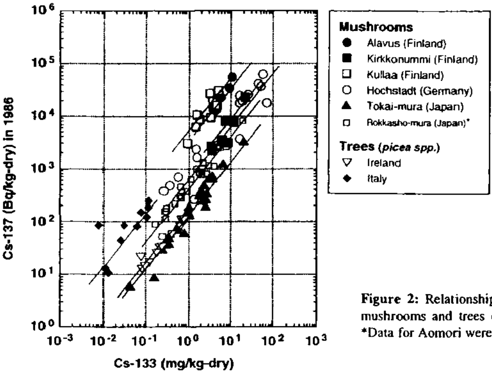

Figure 2: Relationship between stable Cs and ^{137}Cs in mushrooms and trees collected from 8 different forests. *Data for Aomori were reported in Tsukada et al. [18].

results for different sites, however, showed different degrees of variability. The highest ratio was obtained at Kullaa (^{137}Cs/stable Cs = 5100 ± 1900 Bq/mg), followed by Alavus (4000 ± 800 Bq/mg), Hochstadt (990 ± 470 Bq/mg), Kirkkonummi (800 ± 260 Bq/mg), Rokkasho-mura (430 ± 120 Bq/mg) and Tokai-mura (150 ± 40 Bq/mg). A good correlation between ^{137}Cs and stable Cs was also observed in plant samples collected from different parts of trees in Irish and Italian forests as shown in the same figure.

The ^{137}Cs/stable Cs ratio might be a useful criterion for judging the equilibrium of deposited ^{137}Cs to stable Cs in a forest ecosystem. Standard deviation of the ^{137}Cs/stable Cs ratio was low in Japanese forests (Rokkasho-mura: 28%, Tokai-mura: 27%), in which most ^{137}Cs originated from the global fallout. This finding suggests that ^{137}Cs, mainly deposited onto the forest ecosystem during the 1960s, has already attained a dynamic equilibrium within the soil-mushroom system and is now cycling together with stable Cs. The almost constant ^{137}Cs/Cs ratios observed for tree samples collected in the same site suggests that the distribution of ^{137}Cs in trees is similar to that of stable Cs more than 10 years after the Chernobyl accident. The standard deviation of the ^{137}Cs/stable Cs ratio was high in Hochstadt, Germany (48%), indicating that the ^{137}Cs/stable Cs ratio is still changing in the system. A detailed study on the transfer of radiocesium from organic soil horizons to mushrooms in Hochstadt (**Figure** 3) showed that the ^{134}Cs/stable Cs ratio in mushrooms reflected the ratios of those soil layers, from which the corresponding mushroom species takes up ^{134}Cs [14].

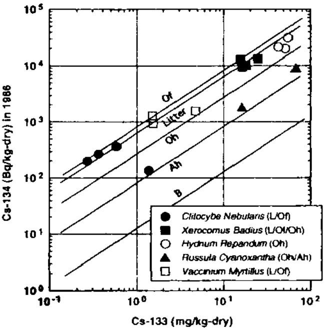

Figure 3: Relationship between stable Cs and ^{134}Cs in different mushroom and plant samples collected in Hochstadt, Germany. Straight lines correspond to ^{134}Cs/stable Cs ratios measured in different soil horizons.

The estimated total deposition of ^{137}Cs from Chernobyl accident and global fallout is the highest in Italian forest (38.7 kBq/m^2) and the lowest in Japanese forest (Tokai-mura). A positive correlation between the total deposition of ^{137}Cs and the ^{137}Cs/stable Cs ratio was observed for the different sites (**Figure 4**), indicating that the difference between the ratios of different sites is partly attributable to the different deposition levels of ^{137}Cs. Using this relationship, the ^{137}Cs concentration in mushroom might be predicted within an order of magnitude, if the data of total deposition and the stable Cs concentration are presented. However, different concentrations of stable Cs in soil and different forest types (e.g. vegetation, geology, soil type) might also affect the ^{137}Cs/stable Cs ratio. Relatively low ^{137}Cs/stable Cs ratios in trees might be attributable to the dilution effect with stable Cs storage in tree biomass or uptake of Cs with low ^{137}Cs/stable Cs ratio from the deeper soil layer.

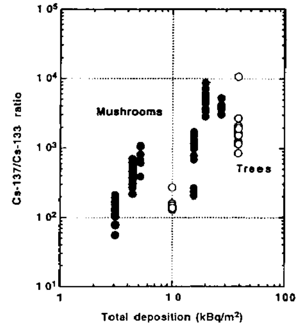

Figure 4: Relationship between total deposition of ^{137}Cs and ^{137}Cs/stable Cs ratio in vegetation.

3.4 Transfer from soil to vegetation

In order to discuss the transfer of radiocesium and stable Cs from soil to mushroom (plant), the tentative transfer factors defined as "median concentration in mushrooms on a dry weight basis" divided by "concentration in the surface 0 - 5 cm soil on a dry weight basis" were calculated for mushrooms collected in a Japanese pine forest in Tokai-mura, both for ^{137}Cs and stable Cs. The values were 3.9 for ^{137}Cs and 0.8 for stable Cs [8]. The transfer factor of ^{137}Cs was higher than that of stable Cs. The surface 0 - 5 cm soil in this forest is a mixture of organic materials and minerals (sand). Stable Cs is originally contained in the mineral components and this stable Cs is difficult for plants and mushrooms to take up. Tsukada et al. [18] also reported higher average transfer factor for ^{137}Cs than stable Cs in 21 different species of mushrooms collected in a pine forest in Rokkasho-mura.

On favorable conditions, e.g. in case of organic horizons with a low content of mineral material, the physico-chemical properties of stable Cs and radiocesium are expected to be similar. For the forest at Hochstadt, Germany, transfer factors for ^{134}Cs and stable Cs were calculated for four different mushroom species and one species of green plants. Transfer factors were explicitly related to the soil layers, from which the corresponding species takes up radioactive ^{134}Cs and ^{137}Cs [14]. Most species take up ^{134}Cs from organic layers (L, Of and/or Oh). The resulting transfer factors for stable Cs were close to the corresponding transfer factors for ^{134}Cs, indicating that bio-availabilities of Chernobyl ^{134}Cs and stable Cs are similar. There will be no significant future change (aging effect) of the bio-availability of radiocesium in the organic layers at this site.

Recent developments of analytical method using ICP-MS have provided much information on the behavior of trace elements, which are related to radionuclides in forest ecosystems. The radiocesium/stable Cs ratio is useful for judging the equilibrium of deposited radiocesium in different parts of a forest ecosystem. The stable Cs analyses might be also useful to predict the long-term ^{137}Cs contamination of mushrooms and plants. We are currently studying samples collected in 4 different forests with different contamination levels in Belarus. This study is expected to yield comprehensive information of radiocesium and stable cesium and their interrelation in the whole forest ecosystem.

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