

The fate of caesium-137 in a soil environment controlled by immobilization on clay minerals

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Abstract

Caesium-137 (^{137}Cs), with its high release rate and long half life, is the most important long-term contributor to environmental contamination of all the radionuclides released by the accident at the Fukushima Dai-ichi nuclear power plant in March 2011. There have been many surveys of the fate of ^{137}Cs in terrestrial environments, especially after the atmospheric nuclear tests of the 1950s and 60s and the Chernobyl accident in 1986. Previous surveys revealed that most of the ^{137}Cs deposited on land remains in the surface soil for decades and that ^{137}Cs rarely exchanges with other cations (atoms that have lost an electron to become positively charged). The immobilization of ^{137}Cs in soil is mostly ascribed to selective adsorption on clay minerals, particularly on illitic minerals. ^{137}Cs is irreversibly retained at the fringe of the layered structure of illitic minerals, called the frayed-edge site, with much higher selectivity than other cations. Comparison of the radiocaesium interception potential (RIP) between soils and clay minerals indicates that the difference in the frayed-edge site capacity is largely dependent on the degree of weathering and the degree of hydroxy-Al interlayering in illitic minerals. Here we investigate the difference in the RIP values between mineral soils to predict the level of contamination of crops grown in ^{137}Cs contaminated fields.

Keywords

Fukushima nuclear disaster, caesium-137, illitic minerals, frayed-edge site, radiocaesium interception potential (RIP)

1. Introduction

The accident at the Fukushima Dai-ichi nuclear plant triggered by the Great Tohoku Earthquake on 11 March 2011 turned our attention to the fate of radionuclides in the terrestrial environment in Japan. The accident caused fission products, such as iodine-131 (^{131}I), ^{134}Cs and ^{137}Cs , to leak from the nuclear reactor into the atmosphere.

Caesium-137 is the most important long-term contributor to environmental contamination because of its high release rate, simulated as 1.3×10^{16} Bq (Chino et al. 2011), and longer half life (30.1 y) when compared with ^{131}I (8 d) and ^{134}Cs (2 y). The results of

environmental gamma-ray dose rate monitoring and the measurement of ^{137}Cs concentration in soil revealed that higher levels of ^{137}Cs were deposited on land to the north west of the Fukushima Dai-ichi nuclear plant than on other areas of Fukushima or other neighboring prefectures. These areas of high ^{137}Cs deposition reflected the *wind* and precipitation patterns during the period when emissions were high.

The widespread dispersion of ^{137}Cs prompted serious concerns about the risk to public health. Consumption of food or water contaminated by ^{137}Cs can expose people internally to radiation and was a cause of concern not just for those living in the highly contaminated areas but also those living further afield. The Japanese Ministry of Health, Labor and Welfare initially set official indices limiting the ingestion of radiocaesium (^{134}Cs plus ^{137}Cs) at levels of 200 Bq L⁻¹ in drinking water and milk and 500 Bq kg⁻¹ in vegetables, cereals and meat (the official indices were later changed to 10 Bq L⁻¹ in drinking water, 50 Bq L⁻¹ in milk and 100 Bq kg⁻¹ in food). Subsequently, the Ministry of Agriculture, Forestry and Fisheries made an official announcement that paddy fields where the concentration of radiocaesium in soils collected from 0-15 cm depth is more than 5000 Bq kg-dry⁻¹ cannot be used for agriculture. As a result of this restriction, the concentration level in rice harvested in Fukushima in autumn 2011 was found to be much lower than 500 Bq kg⁻¹, except for a few irregular cases. Nevertheless, most people tend to avoid purchasing and eating rice or other agricultural products from Fukushima or other neighbor prefectures. This public trend is probably inevitable because the health risks from long-term doses of low-level radiation are difficult to predict. There also seems to be suspicion about the very low transfer rate of ^{137}Cs from soil to crops, which may be derived from insufficient information relating to the dynamics of ^{137}Cs in the soil environment.

Here we review the fundamental dynamics of ^{137}Cs as well as the mechanisms behind the dynamics of the soil environment that have been investigated in Japan and other countries after the atmospheric atomic weapon tests and the Chernobyl accident. Particularly, we focus on a specific, negatively charged site in soil that adsorbs ^{137}Cs strongly. This site, called the frayed-edge site, plays a key role in determining the rate of ^{137}Cs transfer from soil to plant. The objective of this paper is to give non-experts of soil science information about 1) the nature of the frayed-edge site, 2) the methods used to evaluate the capacity of this site in soil, and 3) the relationships between soil type and the capacity of this site. Comprehensive understanding of how soil can immobilize ^{137}Cs will give a better prediction of the concentration of ^{137}Cs in crops harvested from a contaminated field, establish a proper strategy to remediate contaminated soils and should, ultimately, reduce public anxiety by showing that many fears are unlikely to become reality (eg. concerns that the high water solubility of $^{137}\text{Cs}^+$ means it will leach from the soil surface down to the groundwater).

2. Dynamics of ^{137}Cs in soil environments

2.1. Transfer of ^{137}Cs from soil surface to water system

Caesium-137 deposited on land tends to remain in the surface soil for decades. Even though more than 40 years have passed since the highest annual deposition of ^{137}Cs was recorded in Japan, caused by the global fallout from atmospheric atomic weapon testing (Komamura et al. 2005), ^{137}Cs has not been detected below a 30 cm depth in soil profiles (eg. Fukuyama and Takenaka 2004), indicating that the migration rate of ^{137}Cs downward would be less than 1 cm yr⁻¹ in soil. The downward migration rate of ^{137}Cs from the soil surface was investigated in Belarus and Sweden after the Chernobyl accident and was calculated as 0.39 to 1.16 cm yr⁻¹ (Belarus; Arapis et al. 1997) and 0.5 to 1.0 cm yr⁻¹ for the first year and thereafter 0.2 to 0.6 cm yr⁻¹ (Sweden; Rosen et al. 1999). Such a low migration rate indicates that ^{137}Cs contamination in groundwater by way of leaching from the soil surface will not occur unless some unforeseen event happens.

Although the migration rate of ^{137}Cs in soil is very slow, it may be mobilized via soil erosion. Most ^{137}Cs deposited on land is retained by fine particles (ie. silt or clay fraction) in soil (Tsukada et al. 2008), which can be dispersed and eroded to a greater extent than coarser fractions (Warrington et al. 2009). Therefore, soil erosion is a primary factor mobilizing ^{137}Cs from the soil surface (Ritchie and McHenry 1990).

The effect from water erosion on mobilizing ^{137}Cs from the soil surface may be significant in Japanese upland forest because of high precipitation and steep slopes. Fukuyama et al. (2005) reported that the ^{137}Cs loss from a headwater catchment in Mie Prefecture, central Japan, increased sharply when maximum rainfall intensity exceeded 30 mm h⁻¹. Transmigration of ^{137}Cs via soil erosion from highly contaminated forest zones in Fukushima may result in a secondary dispersion of ^{137}Cs to downstream water systems.

2.2. Transfer of ^{137}Cs from soil to above-ground biomass: crops and mushrooms

While most of the ^{137}Cs deposited on land remains in the soil surface regardless of soil type, transfer of ^{137}Cs from soil to crops, represented by transfer factor (TF = [^{137}Cs in plant; Bq kg-dry⁻¹]/[^{137}Cs in soil; Bq kg-dry⁻¹]), is dependent on crop type as well as soil type. Tsukada et al. (2002) found the geometric mean of ^{137}Cs TF values for polished rice to be 0.0016 (0.00021 to 0.012, n = 20) by using soils affected by the ^{137}Cs fallout from the atmospheric nuclear testing that mainly occurred in the 1950s and 60s. The ^{137}Cs TF value of 0.0016 means that the concentration of ^{137}Cs in polished rice would be 8 Bq kg⁻¹ when it is grown in soil contaminated by 5000 Bq kg⁻¹ of ^{137}Cs . Polished rice showed relatively low ^{137}Cs TF values compared with those of other crops, such as 0.026 (0.0021 to 0.33, n = 8) for cabbage (Tsukada and Hasegawa 2002) and 0.03 (0.005 to 0.18, n = 8) for potato (Tsukada and Nakamura 1999).

The order of magnitude difference in ^{137}Cs TF values in the same crops is mainly caused by the difference in soil types. Delvaux et al. (2000) revealed that the TF values obtained by

using the same plant species (ryegrass) and 47 different soils under the same experimental conditions differed by 3 to 4 orders of magnitude. The International Atomic Energy Agency (IAEA) (2010) partitioned the ^{137}Cs TF values of each crop type into those of sandy, loamy and clay soils and revealed that sandy soils tend to show larger TF values than loamy or clay soils. Clay content could be used as a rough indicator to predict the ^{137}Cs TF values for crops. However, Kruyts and Delvaux (2002) showed the ^{137}Cs TF value is not significantly correlated with clay content because soil clay contains several kinds of colloidal particles with different affinity for ^{137}Cs . Therefore it is not only clay content but also clay composition that is important to determine the transferability of ^{137}Cs in soil.

An exceptionally high accumulation of ^{137}Cs was shown in wild mushrooms (eg. Bem et al. 1990). The ^{137}Cs TF values for wild mushrooms previously reported, eg. 9.3 (Tsukada et al. 1998), are much higher than those for crops. Although the ^{137}Cs accumulation mechanisms of wild mushrooms are not fully understood, very high organic matter content or very low clay content of the forest floor may be a key factor in understanding such a high transfer of ^{137}Cs . Kruyts and Delvaux (2002) showed that the ^{137}Cs TF value was significantly and positively correlated with organic matter content in soil and the largest ^{137}Cs TF value was measured in peaty soil (ie. soils mostly composed of organic matter). Rigol et al. (2002) showed that 90-95 per cent of ^{137}Cs was extractable with salt solutions from soils with more than 95 per cent organic matter content, whereas the extraction yield was less than 20 per cent for a soil with 5.9 per cent organic matter content. Thus, an increasing amount of organic matter results in higher mobility of ^{137}Cs in soil, mainly due to the weak retention of ^{137}Cs on organic matter.

3. Selective adsorption of ^{137}Cs on the frayed-edge site of illitic minerals

3.1. Immobilization mechanisms

Caesium-137 behaves as a monovalent cation (a singularly, positively charged ion), $^{137}\text{Cs}^+$, and, therefore, is adsorbed on negatively charged sites in soils. The ^{137}Cs immobilization in soil largely comes from the selective adsorption on a negatively charged site in illitic minerals, a kind of 2:1 clay (ie. clay minerals composed of two parts of tetrahedrally coordinated Si-O sheets, fused to one part of octahedrally coordinated Al-O (OH) sheet) commonly present in soils. A structure model of an illitic mineral is presented in Figure 1. Negative structural charges are created by isomorphic substitution of Si by Al in the tetrahedral sheet or Al by Mg, Fe II in the octahedral sheet. The plane of oxygen ions bonding each side of a 2:1 clay forms a cavity with a radius of approximately 0.13 nm, called a hexagonal cavity. In the presence of nearby isomorphic substitution, a hexagonal cavity attracts cations in the interlayer site of a 2:1 clay.

Large monovalent cations such as K^+ (Ionic radius; 0.133 nm), NH_4^+ (0.143 nm), Rb^+ (0.148 nm) or Cs^+ (0.169 nm) (Eberl 1980; Evans et al. 1983) have relatively low hydration energy so they are easily dehydrated and can make a strong connection to the

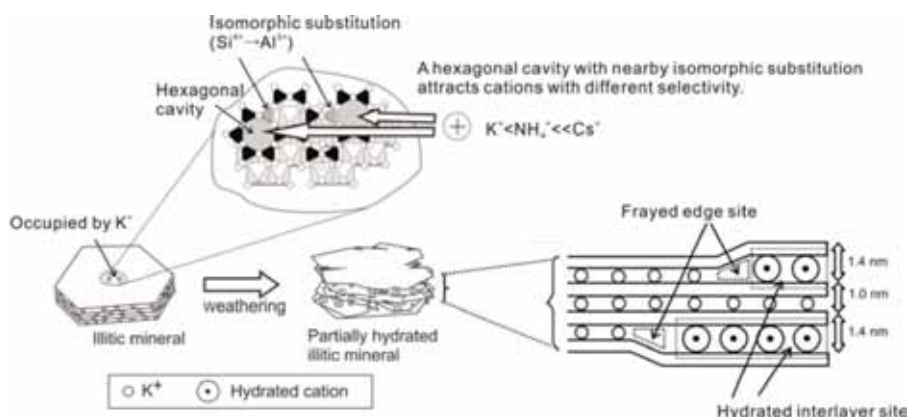


Figure 1. A schematic diagram of illitic minerals forming a frayed-edge site at the outer edge of the interlayer site through weathering

hexagonal cavity without surrounding water molecules (ie. inner-sphere complex) (Sposito 1999). Because K^+ is predominately present compared with NH_4^+ , Rb^+ and Cs^+ , negatively charged hexagonal cavities are normally occupied by K^+ . The 2:1 clay composed of K^+ -fixing layers present in soil is called an illitic mineral (Barré et al. 2007).

Interlayer sites in “unweathered” illitic minerals are non-hydrated with a 1.0 nm thickness and, therefore, not accessible for other cations incorporated into soil. Those at the outer edge of the illitic layer, however, release K^+ and are hydrated or expanded to a 1.4 nm thickness through weathering processes and so become accessible for other cations. The intermediate part between a non-hydrated and a hydrated interlayer site, called as a frayed-edge site, is not accessible for hydrated cations but accessible for easily dehydrated cations (ie. K^+ , NH_4^+ , Rb^+ and Cs^+). Because Cs^+ has the lowest hydration energy among these cations (Eberl 1980), it can be preferentially adsorbed on the frayed-edge site.

The capacity of the frayed-edge site in 47 soils collected from selected European countries (Austria, Belgium, Germany, Ireland, Italy and Sweden) – including sandy to clay soils with variable physical and chemical properties – was estimated as 0.013 to 4.861 mmol kg^{-1} (Delvaux et al. 2000). The radiocaesium contamination level of 5000 Bq kg^{-1} , above which agricultural activity is prohibited in Fukushima, corresponds to about 10^{-8} mmol kg^{-1} , assuming that radiocaesium is totally ^{137}Cs . This trace concentration of ^{137}Cs as a molar basis is much smaller than the estimated capacity of the frayed-edge site. Therefore, the frayed-edge site capacity should be sufficient to immobilize ^{137}Cs deposited on land by the Fukushima accident.

3.2. Quantitative estimates of the frayed-edge site in soil

Quantification of the frayed-edge site using a simple chemical adsorption-desorption experiment, such as determining the cation exchange capacity (CEC), has proven to be difficult. The main reason for this is the frayed-edge site is not accessible for hydrated cations

but can irreversibly adsorb monovalent cations with low hydration energy (ie. K^+ , NH_4^+ , Rb^+ and Cs^+) with the formation of an inner-sphere complex.

After the Chernobyl accident, Cremers et al. (1988) obtained a quantitative indicator of the frayed-edge site from the solid/liquid distribution coefficient of Cs and concentration of K in solution. This indicator, the radiocaesium interception potential (RIP), is now widely accepted by many researchers in Europe as a quantitative index of the frayed-edge site to fix ^{137}Cs in soils (eg. Smolders et al. 1997; Waegeneers et al. 1999; Delvaux et al. 2000). It is described as

$$RIP \equiv K_d^{Cs} \cdot mK = K_c^{FES}_{(Cs-K)} \cdot [FES] \quad (\text{mol kg}^{-1}) \quad (1)$$

where K_d^{Cs} is the solid/liquid distribution coefficient of Cs ($L \text{ kg}^{-1}$), mK is the K concentration in solution (mol L^{-1}), $K_c^{FES}_{(Cs-K)}$ is the selectivity coefficient of Cs against K in the frayed-edge site, and $[FES]$ is the amount of the frayed-edge site in soil (mol kg^{-1}). As $K_c^{FES}_{(Cs-K)}$ is a constant, then $K_d^{Cs} \cdot mK$ is regarded as proportional to the amount of the frayed-edge site.

Two experimental conditions are prerequisite to make Equation 1 valid. First, exchangeable sites must be masked from Cs and K with silver thiourea to assume Cs and K adsorption occurs only on the frayed-edge site. Based on this assumption, Cs-K exchange reaction on the frayed-edge site can be expressed as

$$[K_{FES}] + mCs = [Cs_{FES}] + mK \quad (2)$$

where $[K_{FES}]$ (or $[Cs_{FES}]$) is the amount of K (or Cs) adsorbed on the frayed-edge site (mol kg^{-1}), and mK (or mCs) is the concentration of K (or Cs) in solution (mol L^{-1}). As this reaction is an ion exchange between monovalent cations, the selectivity coefficient (ie. $K_c^{FES}_{(Cs-K)}$) can be expressed as

$$K_c^{FES}_{(Cs-K)} = ([Cs_{FES}] \cdot mK) / ([K_{FES}] \cdot mCs) \quad (3)$$

Second, the amount of Cs adsorbed on the frayed-edge site (ie. $[Cs_{FES}]$) must be minimized using carrier-free ^{137}Cs so it can be assumed the amount of K adsorbed on the frayed-edge site (ie. $[K_{FES}]$) is identical to the amount of the frayed-edge site (ie. $[FES]$ in Eq. 1). Based on this assumption, Equation 3 becomes

$$K_c^{FES}(Cs-K) (Cs \rightarrow 0) = K_d^{Cs} \cdot mK / [FES] \quad (4)$$

Equation 1 is thus formed by transposing the denominator on the right-hand side to the left in Equation 4.

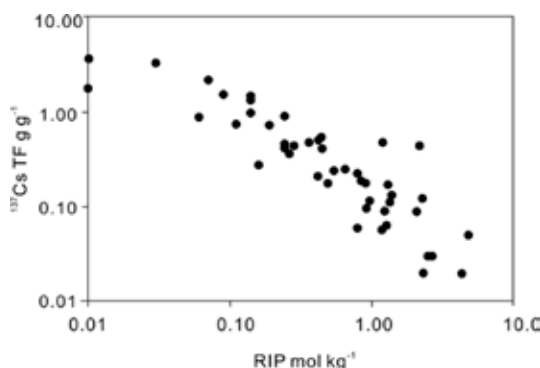


Figure 2. Relationship between ^{137}Cs transfer factor (TF) and the radiocaesium interception potential (RIP) in soil
Source: authors, using data from Delvaux et al. 2000

The method of Cremers et al. (1988) was followed by Wauters et al. (1996), in which the silver thiourea for masking exchangeable sites could be successfully replaced with specific Ca/K ratio in solution (ie. $0.1 \text{ mol L}^{-1} \text{ CaCl}_2 + 0.5 \text{ mmol L}^{-1} \text{ KCl}$) to make the method more easily applicable. Because the average $K_c^{\text{FES}}_{(\text{Cs-K})}$ value is considered as about 1000 (Brouwers et al. 1983; Wauters et al. 1996), the RIP divided by 1000 can approximate the hypothetical frayed-edge capacity in soil. The RIP can be a reliable indicator to predict the ^{137}Cs TF value, which is supported by a significant negative correlation between the ^{137}Cs TF value and the RIP value obtained by Delvaux et al. (2000) using 47 soils with widely varying properties, as shown in Figure 2.

3.3. Variations in RIP value dependent on soil conditions

What causes variance in the RIP value between soils? Although a positive correlation between RIP value and clay content could be shown for selected soil samples (Waegeneers et al. 1999) (Figure 3), it is not a direct relationship. The primary factor determining the RIP value is the amount of illitic minerals in the soil. Illitic minerals are normally concentrated in the clay fraction (Dultz 2000), therefore the clay content may be indirectly related to the RIP value.

A significant positive relationship between the RIP and the total K in soil clay – an index of the amount of illitic minerals – was shown in Thailand's soils (Nakao et al. 2009a). Comparison of the RIP value between pure clay minerals also revealed a clear difference in the value between illitic minerals and other negatively charged materials in soil. The RIP values of “unweathered” illitic minerals, $10\text{--}15 \text{ mol kg}^{-1}$ (Nakao et al. 2008; Delvaux et al. 2001), were much higher than those of other clay minerals, such as kaolinite ($0.006 \text{ mol kg}^{-1}$) and montmorillonite (0.1 mol kg^{-1}) (Nakao et al. 2008). Furthermore, peaty soils containing more than 90 per cent organic matter had an RIP value of less than 0.02 mol kg^{-1} (Sanchez et al. 1999), corresponding to the fact that organic matter does not retain ^{137}Cs

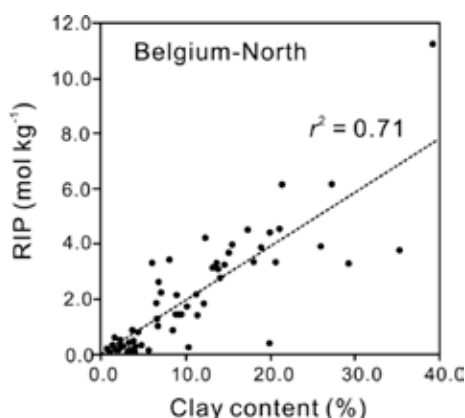


Figure 3. Scatterplot of the radiocaesium interception potential (RIP) and the clay content for soils collected from northern Belgium
Source: authors, using data from Waegeneers et al. 1999

strongly. Vandebroek et al. (2012) compared the RIP values between soils classified into 12 different groups based on the soil classification system of the World Reference Base for Soil Resources (WRB), an international and comprehensive classification system (International Union of Soil Sciences Working Group WRB 2007). They found that the average RIP value of ferralsols (highly weathered tropical soils) was 0.4 mol kg⁻¹, much lower than those of illitic minerals. This result is appropriate because soil clays in ferralsols are mostly composed of kaolinite with only small amounts of illitic minerals.

Weathering (the breaking down of minerals) causes a large variation in the RIP value of illitic minerals. Expansion of the non-hydrated interlayer occurs randomly at the outer edge of illitic minerals through weathering, multiplying the amount of frayed-edge site in a mass of illitic minerals. This was confirmed by an increase in the RIP value of silt-sized illite from 4.3 mol kg⁻¹ to 10.5 mol kg⁻¹ after continuous extraction of K from the illitic structures (Figure 4). Nakao et al. (2009a) showed that the RIP values per a mass of illitic minerals in Indonesian soils were significantly larger than those in Thai soils, which can be explained by the greater degree of weathering of illitic minerals in Indonesia. Thus, a higher degree of weathering of illitic minerals results in a larger RIP value in soil.

Frayed-edge sites formed by the expansion of the non-hydrated interlayer in illitic minerals may be occluded by hydroxy-Al polymers in acidic soil environments. In moderately acidic conditions (a soil pH of 4.0-5.0), as found in most Japanese forest soils, hydroxy-Al polymers are formed and intercalated into the expanded interlayer of illitic minerals (Figure 5a). This occlusion largely decreases the accessibility of the frayed-edge site to ¹³⁷Cs (Maes et al. 1999), causing much smaller RIP values in soil clays than those expected from the amount of illitic minerals (Nakao et al. 2009b). In strongly acidic soil conditions (ie. pH < 4.0), hydroxy-Al polymers are not stable; they are monomerized as Al³⁺, which is exchangeable with other cations. In such conditions, the RIP value is particularly high because hydroxy-Al

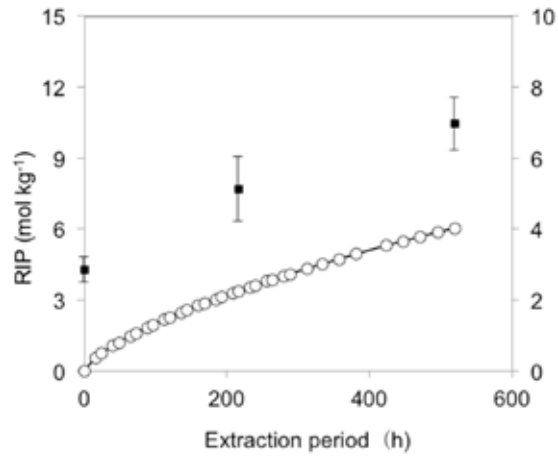
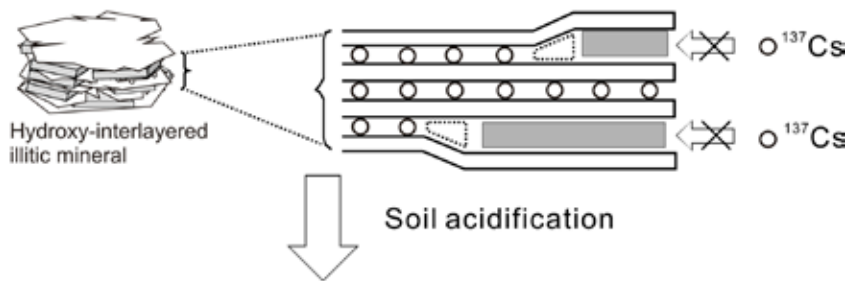


Figure 4. Amount of K extracted from silt-sized illite with time (h) and the RIP values of silt-sized illite after being subjected to K extraction for a given time

(a) Moderately acidic condition (pH = 4.0-5.0)



(b) Strongly acidic condition (pH < 4.0)

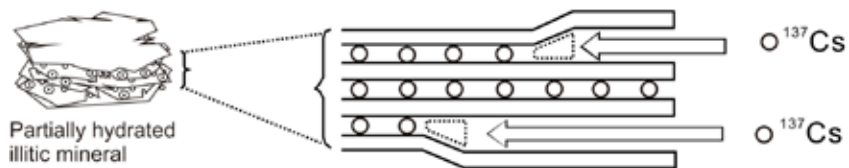


Figure 5. Schematic diagrams of illitic minerals intercalated by hydroxy-Al polymers in their expanded interlayer sites at pH 4.0-5.0, followed by the decreasing accessibility of ^{137}Cs to the frayed-edge site (a). At strongly acidic soil condition, the hydroxy-Al polymers can be monomerized, enabling ^{137}Cs to access the frayed-edge site (b)

polymers do not prevent ^{137}Cs accessing frayed-edge sites inside of an expanded interlayer of illitic minerals (Nakao et al. 2009b) (Figure 5b).

In normal circumstances, smectite (a kind of 2:1 clay with expandable interlayer sites), does not adsorb ^{137}Cs selectively but markedly increases in RIP value after potassium saturation and wet-dry repetitions. Vandenhove et al. (2003) showed a significant decrease in the ^{137}Cs TF value by adding K-saturated smectite (bentonite) in an experimental pot. They ascribed the decrease to the formation of “pseudo-illite” in an expandable interlayer site of smectite through wet-dry repetitions during the pot experiment. Subsequently, Degryns et al. (2004) investigated the effect of K-saturation and wet-dry repetitions at 50°C on RIP values and showed that the RIP yield by this method is up to 99 mol kg⁻¹, much higher than the RIP value of illitic minerals.

This knowledge can be applied to Japanese soils to understand the potential transfer of ^{137}Cs to crops. In general, as paddy soils in Japanese lowland contain smectite in their clay fraction, this treatment may be used without addition of bentonite to reduce the ^{137}Cs transfer from soil to crops. However, it should be noted that the Cs-selective site created by this treatment was degraded under K-deficient conditions. Nakao et al. (2011) showed that although K_d values of Cs for smectitic soils became four to 10 times larger than the original K_d values after potassium saturation and wet-dry repetitions, the K_d was decreased to near the original value after a continuous K leaching experiment. Thus, the “pseudo-illite” created by this method may not persistently function as a ^{137}Cs selective site in soil under leaching conditions. Further research is required to understand whether this approach is can be used practically as a countermeasure to reduce the transfer of ^{137}Cs from soil to crops.

4. Conclusion

All soils that do not have high organic matter content contain illitic minerals that absorb Cs with higher selectivity than other cations, resulting in very low mobility of ^{137}Cs in the soil environment. The strong adsorption of ^{137}Cs in illitic minerals occurs at the frayed-edge site, where ^{137}Cs is large enough to fit the hexagonal cavity without the need for surrounding water molecules to fill the cavity (ie. the inner-sphere complex). Differences in the frayed-edge site capacity of mineral soils causes different ^{137}Cs TF values, which should be investigated to predict the contamination level of crops grown in ^{137}Cs contaminated fields.

Comparing the RIP values of soils and clay minerals indicated that the difference in the capacity is largely dependent on the composition of clay minerals in the soil. In particular, the degree of weathering and hydroxy-Al interlayering in illitic minerals govern the magnitude of RIP values. The status of illitic minerals is established by a combination of geological, climatic and chronological factors, which means we should consider the relationship between soil clay mineralogy and soil formation processes to predict the ^{137}Cs dynamics in soil.

Sano et al. (2010) reported that 2:1 clays are dominant in a wide variety of paddy soils in Fukushima. Geological factors may greatly influence the clay mineralogy because most of the soils in Fukushima are developed from green tuff, sandstone, mudstone and granites, which originally include illite (mica) and smectite. Although the ^{137}Cs fixing ability of Fukushima's soils has not widely been investigated, we can postulate that the ability would be relatively high in this region and, therefore, the transfer of ^{137}Cs from soil to crops might not occur to any great extent. The determination of RIP values for a wide variety of soils in Fukushima is required to clarify their ^{137}Cs fixing ability before such information can be used to establish effective strategies to remediate the ^{137}Cs contaminated soils.

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