2 Cesium (^{137}Cs and ^{133}Cs) and Alkali Metals K and Rb

Cesium is an alkali metal and a member of the alkali family in the same group as lithium, sodium, potassium, rubidium, and francium. Stable cesium (^{133}Cs) is the only naturally occurring isotope of cesium and presents in the crust in small amounts. There are a number of artificial radioactive isotopes of cesium. Radioactive cesium (^{137}Cs) is produced in nuclear fission reactions and is of special interest.

Cesium (^{137}Cs and ^{133}Cs) and Alkali Metals K and Rb in Forest Soil and Fungi

Radiocesium (^{137}Cs) has been released into the environment by nuclear weapons testing in the 1950s and 1960s, the Chernobyl accident in 1986, and from the Fukushima Daiichi Nuclear Power Plant (FDNPP) in 2011. As ^{137}Cs has a long half-life of 30 years and high fission yield, it is still a critical fission product. The study of the cesium radioisotope ^{137}Csis important, as the production and emission rates are much higher than other radioisotopes, and as the cesium compounds being water soluble, it moves easily and spreads in the environment, and can result in significant damage to living cells. The results obtained in several experimental studies conducted in Swedish forest ecosystems and peatlands are presented here, along with a discussion on the behavior of cesium isotopes (^{137}Cs and ^{133}Cs) and their counterparts potassium (K) and rubidium (Rb) in the "soil fractions-soil fungi transfer" system.

The bioavailability of radionuclides controls the ultimate exposure of living organisms and the ambient environment to these contaminants. Thus, the understanding of bioavailability of radionuclides is a key issue in the field of radioecology, both conceptually and methodologically. Soil-fungi-plant transfer is the first step by which ^{137}Cs enters food chains in forest ecosystems.

The behavior of ^{137}Cs in forest ecosystems differs substantially from other ecosystems, due to the abundance of fungal mycelia in soil, which contribute to the persistence of Chernobyl radiocesium in the upper horizons of forest soils (Vinichuk & Johanson, 2003). In the microbial biomass in boreal forest soil, fungi are dominant. The mycelium of both saprotrophic and mycorrhizal soil fungi has a central role in both breaking down organic matter and in the uptake of nutrients from soil into plants via the formation of symbiotic mycorrhizal associations (Read & Perez-Moreno, 2003). The mycelium mobilizes nutrients from organic substrates through the action of extracellular catabolic enzymes, thus facilitating nutrient uptake into the host plant (Leake & Read, 1997), and are efficient at taking-up and accumulating microelements (Smith & Read, 1997). As a result, the fruit bodies of fungi are able to accumulate significant amounts of trace elements, both metals and metalloids. This ability also results in the accumulation of non-essential elements and radionuclides, particularly ^{137}Cs, and can have important consequences for the retention, mobility, and availability of these elements in forest ecosystems (Steiner et al. 2002).

The uptake of radiocaesium by fungi is variable and affected by the fungi's environment. Many fungal species accumulate more ^{137}Cs than vascular plants do, and ^{137}Cs activity concentrations in many fungi are 10 to 100 times higher than in plants (Rosén et al. 2011), indicating their substantial contribution to ^{137}Cs cycling in forest systems.

Fungi are principally important in radiocesium migration in nutrient poor and organic rich soils of forest systems (Rafferty et al. 1997). The presence of single strains of saprotrophic fungi in organic matter considerably enhances the retention of Cs in organic systems, with ≈ 70% of the Cs spike being strongly (irreversibly) bound (remains non-extractable) (Parekh et al. 2008), compared to only ≈ 10% in abiotic (sterilized) systems.

Generally, fungal mycelium contains a substantial amount of radiocesium: up to 50% of the total ^{137}Cs may be located within the upper 0-10 cm layers in Swedish and Ukrainian forest soils (Vinichuk & Johanson, 2003, Vinichuk et al. 2004). In terms of the total radiocesium within a forest ecosystem, fungal sporocarps contain a relatively little and may only account for about 0.5 % (McGee et al. 2000) or even less − 0.01 to 0.1% (Nikolova et al. 1997) of the total radiocesium deposited within a forest ecosystem. Based on the calculation of the total vegetation biomass and through relationships between fungal biomass in both sporocarps and mycelia in soil, the total ^{137}Cs activity located in fungi is estimated as 0.1% in bog, 2% in pine swamp, and 11% in forest (Vinichuk et al. 2013). However, these estimates are based on the assumption that radionuclide concentration in fungal sporocarps is similar to of the concentration in the fungal parts of mycorrhizae (Nikolova et al. 1997). Although activity concentration in sporocarps is probably higher than in mycelium (Vinichuk & Johanson, 2003, Vinichuk et al. 2004), sporocarps constitute only about 1% of the total mycelia biomass in a forest ecosystem. Due to the high levels of ^{137}Cs in sporocarps, their contribution to the internal dose in humans may be high through consumption of edible mushrooms (Kalač, 2001). Consequently, the consumption of sporocarps of edible fungi (Skuterud et al. 1997), or of game animals that consume large quantities of fungi with high ^{137}Cs contents (Johanson & Bergström, 1994), represents an important pathway through which ^{137}Cs enters the human food system. However, ^{137}Cs activity concentration in edible fungi species has neither decreased since the late 1990s (*S. variegatus*) nor significantly increased (*Cantharellus* spp.) (Mascanzoni, 2009; Rosén et al. 2011).

Although fungi are important for ^{137}Cs uptake and migration in forest systems, the reasons and mechanisms for the magnitude higher concentration of

radiocesium in fungi than in plants remains unclear (Bystrzejewska-Piotrowska & Bazala, 2008). In addition to radiocesium, fungi effectively accumulate potassium (K), rubidium (Rb) and stable cesium (^{133}Cs) (Gaso et al. 2000), and the concentrations of ^{137}Cs, ^{133}Cs, and Rb in fungal sporocarps can be one order of magnitude higher than in plants growing in the same forest (Vinichuk et al. 2010b).

The chemical behavior of the alkali metals, K, Rb, and ^{133}Cs can be expected to be similar to ^{137}Cs due to similarities in their physicochemical properties, e.g. valence and ion diameter (Enghag, 2000). Potassium is a macronutrient and an obligatory component of living cells, which depend on K+ uptake and flux to grow and maintain life. Although potassium is not a permanent structural organic component of plants, potassium uptake is usually higher than any other macronutrient. In radioecology, cesium is assumed to behave similarly to potassium. There is evidence fungi cannot distinguish between cesium and potassium, therefore, cesium can occupy potassium-binding sites when potassium is deficient (Zichner, 2000). As it accumulates within cells, potassium is the most important ion for creating membrane potential and excitability.

Radioactive (^{137}Cs) and stable (^{133}Cs) cesium and K are assumed to assimilate in a similar fashion with the elements passing through the biological cycle together (Chao et al. 2008). The influx of Cs into cells and its use of K transporters are reviewed by White & Broadley (2000), and potassium transport in fungi is reviewed by Rodr ǵuez-Navarro (2000).

Rubidium (Rb) is another rarely studied alkali metal, which is consistently biomagnified in diverse food webs (Campbell et al. 2005) and may be an essential trace element for organisms, including fungi. This element accumulates in large amounts in certain fungal species (Campos et al. 2012), and fungal fruit bodies

have substantially higher Rb concentrations than plants (Yoshida & Muramatsu, 1998). The concentrations of K, Rb, and ^{133}Cs have been analyzed in fungal sporocarps (Baeza et al. 2005; Vinichuk et al. 2010b; 2011a) and a relation between the uptake of Cs and K has been found (Bystrzejewska-Piotrowska & Bazal, 2008). The content of K, Rb, and ^{133}Cs in the fungi's environment appears important and radiocesium uptake in fungi is affected by the presence of K, Rb, and ^{133}Cs (Gyuricza et al. 2010; Terada et al. 1998).

However, there is scarce information on the concentration and distribution of Rb in fungi, particularly in the mycelial part, and its behavior in food webs originating in the forest. Rubidium is often used in studies on K uptake, as it appears to emulate K (Marschner, 1995): both K and Rb have the same uptake kinetics and compete for transport along concentration gradients in different soil and organisms compartments (Rodr ́guez-Navarro, 2000). However, in fungal sporocarps, the relationships between these alkali metals and ^{137}Cs, when taken up by the fungi, and the underlying mechanisms are insufficiently understood, as Cs does not always have high correlation with K, and it is suggested there is an alternative pathway for Cs uptake into fungal cells (Yoshida & Muramatsu, 1998).

The correlations between ^{137}Cs and these alkali metals suggest the mechanism of fungal uptake of ^{133}Cs and ^{137}Cs is different from K, and that Rb has an intermediate behavior between K and ^{133}Cs (Yoshida & Muramatsu, 1998). However, this interpretation is based on a few sporocarp analyses from each species, and comprising different ectomycorrhizal and saprotrophic fungal species. In spite of the fact that fungal accumulation of ^{133}Cs is reported as species-dependent, there are few detailed studies of individual species (Gillet & Crout, 2000), and the variation in ^{137}Cs levels within the same genotype of fungal sporocarps can be as large as the variation among different genotypes (Dahlberg et al. 1997).

Another way of interpreting and understanding the uptake and relations between ^{137}Cs, ^{133}Cs, K, and Rb in fungi is to use the isotopic (atom) ratio ^{137}Cs/^{133}Cs. Although ^{133}Cs and ^{137}Cs are the same chemically, atom abundance and isotopic disequilibrium differ, and among other factors, the uptake of ^{133}Cs and ^{137}Cs by fungi depends on whether equilibrium between the two isotopes is achieved. Within forest ecosystems, equilibrium between stable ^{133}Cs and ^{137}Cs in the bioavailable fraction of soils is reported (Karadeniz & Yaprak, 2007), but in cultivated soils, equilibrium between fallout ^{137}Cs and stable ^{133}Cs among exchangeable, organic bound and strongly bound fractions has not reached, even 20 years after most of the ^{137}Cs was deposited on the soils (Tsukada, 2006).

The mechanisms involved in nutrient uptake by fungi in forest soils, in particular, the role of fungi in ^{137}Cs transfer between soil and fungi require better understanding. Although transfer of radioactive cesium from soils to plants through fungi is well researched, there is still limited knowledge on the transfer of stable ^{133}Cs and other alkali metals (K and Rb) through fungi. However, alkali metals have a potential role in predicting radiocesium behavior, and there is a relationship between ^{133}Cs and other alkali metals (K and Rb) during uptake by fungi (Vinichuk et al. 2011b).

To be able to explore the mechanisms governing the uptake of radionuclides (^{137}Cs), data are required on the uptake of stable isotopes of alkali metals (K, Rb, ^{133}Cs) by fungal species, and the behavior of the three alkali metals K, Rb, and ^{133}Cs in bulk soil, fungal mycelium, and sporocarps. Therefore, an attempt was made to quantify the uptake and distribution of the alkali metals in the soil-mycelium-sporocarp compartments, and to study the relationships between K, Rb, and ^{133}Cs in the various transfer steps (Vinichuk et al. 2010a, 2010b, 2011a, 2011b). The sporocarps of ectomycorrhizal fungi *Suillus variegatus* were analyzed to determine whether i) Cs (^{133}Cs and ^{137}Cs) uptake was correlated

with K uptake; ii) intraspecific correlation of these alkali metals and ^{137}Cs activity concentrations in sporocarps was higher within, rather than among, different fungal species; and, iii) the genotypic origin of sporocarps affected uptake and correlation.

K, Rb and ^{133}Cs Concentrations in Soil Fractions and Fungal Compartments

From the concentrations of K, Rb, and stable cesium (^{133}Cs) in soil fractions and fungal compartments, the bioconcentration ratio (BCR) at each step of transfer in the soil-fungi system can be calculated, and differences in uptake between elements and their relationships can be determined. This may be the main reason for the different K, Rb, and ^{133}Cs concentrations observed in sporocarps of various fungal species (Vinichuk et al. 2011b). The concentrations of K, Rb, and ^{133}Cs in bulk soil are similar to those found in rhizosphere fraction, although the values for all three elements are slightly higher in the rhizosphere fraction (Table 2.1).

Table 2.1 *Mean concentrations of K, Rb, and ^{133}Cs (mg kg^{-1} DW±standard deviation) in soil fractions and fungi[1] (Vinichuk et al. 2010b, 2011b).*

Element	Bulk soil	Rhizosphere	Soil root interface	Fungal mycelium	Fruit bodies
K	642±215^{a}	899 ±301^{a}	3 215±843^{b}	2 867±728^{b}	43 415±20 436
Rb	3.9±2.7^{a}	5.4±4.4^{a}	6.8±1.7^{a}	13.8±6.9^{b}	254±274
^{133}Cs	0.3±0.2^{a}	0.4±0.3^{a}	0.2±0.05^{a}	0.8±0.8^{a}	5.7±7.1^{b}

[1]Means within rows with different letters (a or b) are significantly different ($p < 0.001$).

Potassium concentrations are higher in both the soil-root interface and fungal mycelium fractions than in the bulk soil and rhizosphere fraction. Fungal sporocarps accumulate much greater amounts of K, Rb, and ^{133}Cs than mycelium. For example, K concentrations in fungal sporocarps collected from the same plots

where soil samples and mycelium were extracted are about 15 times higher than K concentrations found in mycelium (Vinichuk et al. 2010b). The concentrations of Rb in fungal sporocarps are about 18-fold higher than in corresponding fungal mycelium, and those of ^{133}Cs are about 7-fold higher (Table 2.1).

Thus, potassium concentration increases in the order bulk soil < rhizosphere < fungal mycelium < soil-root interface < fungal sporocarps and is higher in the soil-root interface fraction and fungi than in bulk soil. The high concentrations of K in fungal sporocarps may reflect a demand for this element as a major cation in osmoregulation and that K is an important element in regulating the productivity of sporophore formation in fungi (Tyler, 1982).

Rubidium in mycelium is about 3.5-fold higher than in bulk soil and about 2.5-fold higher than in rhizosphere: the concentrations of Rb increase in the order bulk soil < rhizosphere < soil-root interface < fungal mycelium < fungal sporocarps and are slightly higher in the soil-root interface fraction than in bulk soil. Thus, fungi appear to have high preference for Rb, as the accumulation of Rb by fungi, and especially fungal sporocarps, is well pronounced. Rubidium concentrations in sporocarps are more than one order of magnitude higher than in mycelium extracted from soil of the same plots where fungal sporocarps are sampled. Fungi have the ability to accumulate Rb: mushrooms accumulate at least one order of magnitude higher concentrations of Rb than plants growing in the same forest (Yoshida & Muramatsu, 1998).

Concentrations of stable cesium vary among soil fractions but the differences are not significant (Vinichuk et al. 2010b). Stable ^{133}Cs is generally evenly distributed within bulk soil, rhizosphere, and soil-root interface fractions, indicating no ^{133}Cs enrichment in these forest compartments. Thus, cesium concentrations increase in the order soil-root interface < bulk soil < rhizosphere <

fungal mycelium < fungal sporocarps, and are only significantly higher in fungal sporocarps, than in bulk soil. Concentrations of ^{133}Cs in sporocarps are nearly one order of magnitude higher than concentrations of ^{133}Cs in soil mycelium.

The behavior of radioactive ^{137}Cs appears similar to ^{133}Cs: the activity concentrations of ^{137}Cs increase in the order soil < mycelium < fungal sporocarps (Vinichuk & Johanson, 2003; Vinichuk et al. 2004). The differences between fungal species in their preferences for uptake of radioactive ^{137}Cs or stable ^{133}Cs may reflect the location of the fungal mycelium relative to the location of cesium within the soil profile (Rühm et al. 1997). Unlike ^{137}Cs, stable ^{133}Cs originates from soil; therefore, the amount of unavailable ^{133}Cs in soil, compared to the total amount of ^{133}Cs, is presumably higher than that of ^{137}Cs. As a result, stable ^{133}Cs is less available for uptake, as it is contained in mineral compounds and is difficult for fungi or plants to access: the concentration ratio of stable ^{133}Cs in mushrooms is reported to be lower than for ^{137}Cs (Yoshida & Muramatsu, 1998). The difference in behavior between naturally occurring and radioactive forms of ^{133}Cs may also derive from their disequilibrium in the ecosystem (Horyna & Řanad, 1988).

Concentration Ratios of K, Rb, and ^{133}Cs in Soil Fractions and Fungi

The concept of bioconcentration ratios (BCR, defined as the concentration of the element (mg kg^{-1} DW) in a specific fraction or fungi divided by the concentration of the element (mg kg^{-1} DW) in bulk soil) is widely used to quantify the transfer of radionuclides from soil to plants/fungi. This approach allows the estimation of differences in uptake of the elements. The elemental concentration ratio has a similar pattern to their content in the respective fraction, but the enrichment of all three elements in fungal material is more evident, particularly in sporocarps (Table 2.2).

Table 2.2 *Bioconcentration ratios in bulk soil, mean values±standard deviation). Adapted from Vinichuk et al. (2010b).*

Element	Rhizosphere	Soil root-interface	Fungal mycelium	Fruit bodies
K	1.7±0.4	6.1±1.9	5.1±1.4	68.9±23.1
Rb	1.3±0.4	2.7±1.1	3.9±1.1	122.7±172.2
Cs	1.1±0.5	0.8±0.3	2.1±0.9	39.7±67.6

Thus, for all three alkali metals, the levels of K, Rb, ^{133}Cs, and ^{137}Cs in sporocarps are at least one order of magnitude higher than the levels in fungal mycelium (Table 2.2, Vinichuk et al. 2010b). The concentration ratios for each element vary considerably among fungal sporocarps of sampled species. The saprotrophic fungus *Hypholoma capnoides* grown in boreal forest has the lowest values and the mycorrhizal fungus *Sarcodon imbricatus* has the highest. The concentration ratios of sporocarps (mg kg^{-1} DW in fungi)/(mg kg^{-1} DW in bulk soil) are presented in Table 2.3.

Sarcodon imbricatus accumulates nearly 100 000 Bq kg^{-1} of ^{137}Cs, giving TF values (defined as ^{137}Cs activity concentration (Bq kg^{-1} DW) in fungi divided by ^{137}Cs deposition (kBq m^{-2})) of about 22 (Vinichuk & Johanson, 2003). The sporocarps of *Sarcodon imbricatus* have distinctively higher bioconcentration ratios of Rb and ^{133}Cs than other species that have been analyzed. The mycorrhizal fungus *Cantharellus tubaeformis*, which grows on living or rotten wood, is another species with relatively high concentration ratios, particularly for K and Rb and accumulates several tens of thousands Bq kg^{-1} of ^{137}Cs (Kammerer et al. 1994). Among the fungi with moderate concentration ratios for each element are *Boletus edulis*, *Tricholoma equestre*, *Lactarius scrobiculatus* and *Cortinarius* spp.

Table 2.3 *Elemental bioconcentration in fungi for fungal sporocarps. Adapted from Vinichuk et al. (2010b).*

Sampling plots according to Vinichuk et al. (2010b)	Species	Concentration ratios		
		K	Rb	^{133}Cs
4	Boletus edulis	62.7	77.4	37.4
6	*Cantharellus tubaeformis*	1045	110	15.5
7	*Cortinarius armeniacus*	67.5	69.6	19.2
5	*C. odorifer*	71.8	70.9	34.7
8	*C. spp.*	90.9	157.2	14.8
8-10	*Hypholoma capnoides*[1]	26.6	13.1	6.9
1	*Lactarius deterrimus*	29.9	17.2	2.6
3	*L. scrobiculatus*	67.8	26.2	3.7
6	*L. trivialis*	77.5	126.9	52.2
5-7	*Sarcodon imbricatus*	102	676	259
2	*Suillus granulates*	58.6	41.4	14.7
10-11	*Tricholoma equestre*	66.6	75.4	15.4

[1]Saprophyte, all other analyzed fungal species are ectomycorrhizal (Vinichuk et al. 2010b)

Thus, the levels of K, Rb, ^{133}Cs, and ^{137}Cs in sporocarps are at least one order of magnitude higher than the levels in fungal mycelium, indicating biomagnification through the food web in forest ecosystems. The saprotrophic fungus *Hypholoma capnoides* has the lowest CR values and the mycorrhizal fungus *Sarcodon imbricatus* has the highest CR values.

Relationships between K, Rb, and ^{133}Cs in Soil and Fungi

Although correlation analysis may be not definitive, it is a useful approach for elucidating similarities or differences in uptake mechanisms of cesium (^{137}Cs and ^{133}Cs), K, and Rb: close correlation between elements indicates similarities in uptake mechanisms. However, no significant correlations between K in soil and in either mycelium ($r = 0.452$, ns) or in sporocarps ($r = 0.338$, ns) have been identified, and sporocarp Rb and ^{133}Cs concentrations are unrelated to soil

concentrations. However, in mycelium both elements are correlated with soil concentrations (Rb: r=0.856, p=0.003; Cs: r=0.804, p =0.009). The K:^{133}Cs ratio in soil and fungal components has the following pattern: the K:Cs ratio in mycelium is closely positively correlated (r=0.883, p=0.01) to the K:^{133}Cs ratio in soil (Figure 2.1a), but is relatively weak and not-significantly correlated to soil in fungal sporocarps. There is a close positive correlation (r=0.946, p =0.001) between the K:Rb ratio in soil and in fungal mycelium (Figure 2.1b): this relationship is also apparent between soil and sporocarps, but is weak and non-significant (r=0.602, ns: Figure 2.1b). No significant correlations have been identified among the concentrations of the three elements in fungi, soil pH, or soil organic matter content (data not shown).

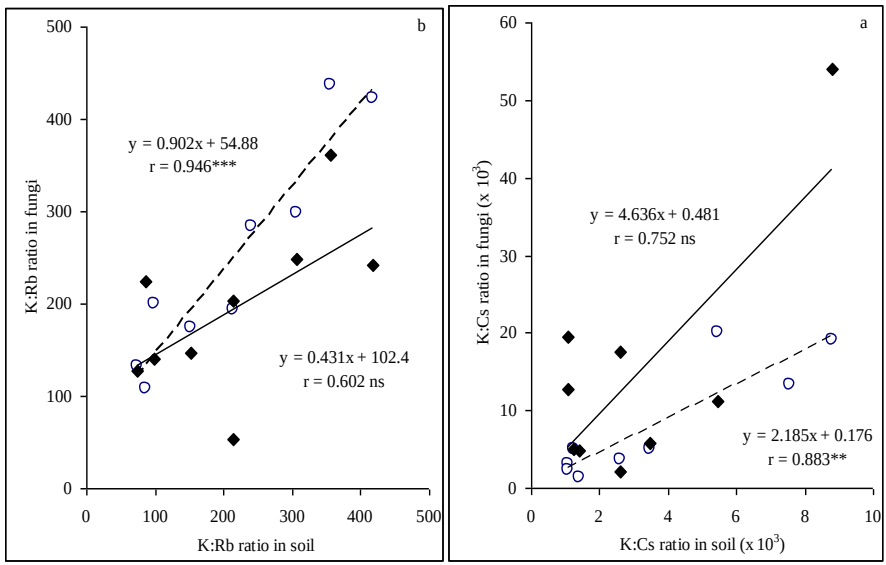

Figure 2.1 *Ratio of (a) K:^{133}Cs and (b) K:Rb in fungal sporocarps (♦, solid line) and soil mycelium (○, dotted line) in relation to the soil in which they are growing (Vinichuk et al. 2010b). ** p=0.01, *** p=0.001.*

In an attempt to estimate the relationships between the concentrations of K, Rb, and ^{133}Cs in soil, mycelia, and fungal sporocarps, the competition between

these elements in the various transfer steps has been investigated (Vinichuk et al. 2010b). The lack of a significant correlation between K in soil and in either mycelium or sporocarps indicates a demand for essential K within fungi, regardless of the concentration of this element in the soil. Irrespective of fungal species, K concentration in fungi appears to be controlled within a narrow range (Yoshida & Muramatsu, 1998), and supports the claim K uptake by fungi is self-regulated through internal nutritional requirements of the fungus (Baeza et al. 2004).

In fungal sporocarps, when there is no relationship between uptake of Cs and K, Rb concentrations are related to concentrations of stable Cs, and the concentrations of K and Rb only moderately related (Table 2.4).

Table 2.4 *Correlation coefficients among K, Rb, and Cs concentration in fruit bodies of fungi.*

	K	**Rb**
Rb	0.51*	
Cs	0.26	0.91**

* P < 0.05, ** P < 0.01

The relationships observed between K:Rb and K:^{133}Cs ratios in fungal sporocarps and soil mycelia, with respect to the soil in which they are growing (Figure 2.1), also indicate differences in fungal uptake of these alkali metals. Although correlation analyses are not the best tool for analyzing uptake mechanism, the closest positive correlations between K:Rb ratios in fungal mycelium and in soil indicate similarities in the uptake mechanism of these two elements by fungi, although the relationships between K:^{133}Cs ratios in soil mycelium and in soil are less pronounced. Yoshida & Muramatsu (1998) suggest there may be an alternative pathway for ^{133}Cs uptake into cells and the mechanism of ^{133}Cs uptake by fungi is similar to that for Rb, as ^{133}Cs does not have good

correlation with K. The high efficiency of Rb uptake by fungi indicates Rb, but not ^{133}Cs, eventually replaces essential K, due to K limitation (Brown & Cummings, 2001), and Rb has the capacity to partially replace K, whereas ^{133}Cs does not (Wallace, 1970, and references therein). Forest plants apparently discriminate between K^+ and Rb^+ in soils, and a shortage of K^+ favors uptake of the closely related Rb^+ ion (Nyholm & Tyler, 2000), whereas, increasing K^+ availability in the system decreases Rb^+ uptake (Drobner & Tyler, 1998). These results provide new insights into the use of transfer factors or concentration ratios.

The Isotopic (Atom) Ratios ^{137}Cs/K, ^{137}Cs/Rb and ^{137}Cs/^{133}Cs in Fungal Species

The isotopic ratios of ^{137}Cs/K, ^{137}Cs/Rb, and ^{137}Cs/^{133}Cs in the fungal sporocarps belonging to different species have been used to interpret the distribution of ^{137}Cs and the alkali metals in fungi and to provide better understanding of the uptake mechanisms. Measurements of trace levels of stable ^{133}Cs can provide information about the biological behavior of ^{137}Cs and to obtain better estimates, the isotopic ratios for fungal sporocarps have been calculated by Vinichuk et al. (2011b) and compared with estimates calculated in similar studies by Yoshida & Muramatsu (1998). The mean values of isotopic ratios of ^{137}Cs/K, ^{137}Cs/Rb, and ^{137}Cs/^{133}Cs in the fungal sporocarps, and range and correlation coefficients between concentration ratios ^{137}Cs/^{133}Cs and K, Rb, and ^{133}Cs are presented in Table 2.5.

The activity concentrations of ^{137}Cs in fungal sporocarps are about 13 to 16 orders of magnitude lower than mass concentrations of K, 10 to 13 orders of magnitude lower than mass concentrations for Rb, and 8 to 9 orders of magnitude lower than mass concentrations for ^{133}Cs. In fungal sporocarps collected in Sweden, isotopic (atom) ratios are two-three orders of magnitude lower than in

fungal sporocarps collected in Japan, which reflects the level of ^{137}Cs concentrations in mushrooms. The median value for all fungi species is 4 151 Bq kg^{-1} DW in Swedish forests and 135 Bq kg^{-1} DW in Japanese forests. The isotopic (atom) ratios of ^{137}Cs/K, ^{137}Cs/Rb, and ^{137}Cs/^{133}Cs vary in both datasets and appear independent of specific species of fungi. These ratios might reflect the isotopic ratios in the soil horizons from which radiocesium is predominantly taken up and be a possible source of the variability in isotopic ratios in fungal fruit bodies. Rühm et al. (1997) used the isotopic ratio ^{134}Cs/^{137}Cs to localize fungal mycelia in *in situ* species; alternatively, the isotopic (atom) ratio ^{137}Cs/^{133}Cs can be used to localize fungal mycelia *in situ*. However, this approach is only appropriate for organic soil layers, which contain virtually no or very little clay mineral to which cesium can bind. The isotopic ratios ^{137}Cs/^{133}Cs in fruit bodies of fungi are similar to the ratios found in organic soil layers of forest soil (Rühm et al. 1997; Karadeniz & Yaprak, 2007).

Table 2.5 *Isotopic (atom) ratios of ^{137}Cs/K, ^{137}Cs/Rb, ^{137}Cs/^{133}Cs, correlation coefficients between isotopic ratios ^{137}Cs/^{133}Cs and mass concentrations of K, Rb, and ^{133}Cs in fungal sporocarps. The result of the comparison between our data (Vinichuk et al. 2011b, Sweden) and data from Yoshida & Muramatsu (1998), Japan.*

Data set	**n**	**Isotopic ratios**		
		^{137}Cs/K	**^{137}Cs/Rb**	**^{137}Cs/^{133}Cs**
Vinichuk et al. (2011b), Sweden	12	14.4(1.54−45.4) x10^{-13}	7.8(0.55−30.9) x10^{-10}	4.9(0.30−15.1) x10^{-8}
Yoshida & Muramatsu (1998), Japan	29	5.2(0.15−23.0) x10^{-16}	3.4(0.14−18.2) x10^{-13}	4.1(1.53−5.94) x10^{-9}
		Correlation coefficients		
		^{137}Cs/^{133}Cs:K	**^{137}Cs/^{133}Cs:Rb**	**^{137}Cs/^{133}Cs:^{133}Cs**
Vinichuk et al. (2011b), Sweden	12	0.25	−0.35	−0.31
Yoshida & Muramatsu (1998), Japan	29	0.12	0.39	0.26

[1]n = number of sporocarps analyzed

The relationships observed between the concentration ratios ^{137}Cs/^{133}Cs and K, Rb, and ^{133}Cs in fungal sporocarps vary widely and are inconsistent (Table 2.5).

The concentration of K, Rb, and ^{133}Cs in sporocarps appears independent of the ^{137}Cs/^{133}Cs isotopic ratio, suggesting differences in fungal uptake of these alkali metals and complex interactions between fungi, their host, and the environment.

K, Rb, and Cs (^{137}Cs and ^{133}Cs) in Sporocarps of a Single Species

Most results presented in this Chapter are already published (Vinichuk et al. 2011a), and based on sporocarp analysis of different ectomycorrhizal and saprotrophic fungal species. As fungal accumulation of ^{137}Cs is suggested to be species-dependent (Kammerer et al. 1994) ^{137}Cs activity concentration and mass concentration of K, Rb, and ^{133}Cs in fungal sporocarps belonging to the mycorrhizal fungus *Suillus variegatus* were analyzed. Sporocarps were collected in the forest area located in Harbo (Heby county), about 40 km north-west of Uppsala in central Sweden (N 60°08′; E 17°10′). *S. variegatus* form *mycorrhiza* with Scots pine and predominantly occur in sandy, acidic soils. This fungus has a marked ability for accumulating radiocesium (Dahlberg et al. 1997) and, as it is an edible mushroom, the high radiocesium content presents some concern regarding human consumption.

The concentrations of K (range 22.2-52.1 g kg^{-1}) and Rb (range 0.22-0.65 g kg^{-1}) in sporocarps of *S. variegatus* vary within relatively narrow ranges, whereas, the mass concentration of ^{133}Cs has a range of 2.16 to 21.5 mg kg^{-1} and the activity concentration of ^{137}Cs ranges from 15.8 to 150.9 kBq kg^{-1}. Both ^{133}Cs and ^{137}Cs have wider ranges than K or Rb within sporocarps from the same genotype or across a combined set of sporocarps (Table 2.6, Vinichuk et al. 2011a). The means the ^{137}Cs/^{133}Cs isotopic ratio in the combined set of sporocarps was 2.5 x 10^{-7} (range 8.3 x 10^{-8} to 4.4 x 10^{-7}). The ^{137}Cs/Cs isotopic ratios from identified genotypes were site-genotype dependent: the ratio values

of genotypes at site 4 were about two-times higher than the ratios of genotypes at site 2 (Table 2.7, Vinichuk et al. 2011a).

Similarly, in another study (Vinichuk et al. 2004), the concentrations of K in sporocarps of *S. variegatus* were not related to the concentrations of ^{137}Cs (r=0.103) or ^{133}Cs (r=−0.066) in a combined data set (Figure 2.2: c, b). However, the concentrations of K and Rb were significantly correlated in the combined dataset (r=0.505, Figure 2.2: a).

Table 2.6 *Potassium, rubidium and cesium (^{133}Cs) mass concentrations and ^{137}Cs activity concentrations in sporocarps of S. variegatus (DW) from identified and unknown genotypes, where n = number of sporocarps of each genotype analyzed, M = mean, SE = standard deviation, CV = coefficient of variation. Adapted from Vinichuk et al. (2011a).*

Site-genotype[1]	n	K			Rb			^{133}Cs			^{137}Cs		
		g kg^{-1}		%	g kg^{-1}		%	mg kg^{-1}		%	kBq kg^{-1}		%
		M	SD	CV	M	SD	CV	M	SD	CV	M	SD	CV
Sporocarps with identified genotypes													
2-1	8	30.6	8.06	26.4	0.47	0.12	24.7	12.1	4.23	35.1	67.3	35.1	52.2
2-2	6	28.0	6.99	25.0	0.50	0.07	13.8	16.6	2.19	13.2	75.9	23.2	30.6
4-3	4	28.5	2.13	7.5	0.39	0.16	4.0	6.6	0.44	6.7	68.9	11.7	17.0
4-4	3	33.6	8.60	-	0.30	0.04	-	3.0	0.60	-	39.1	9.38	-
4-5	2	38.9	2.40	-	0.36	0.02	-	3.8	0.04	-	35.7	28.2	-
4-6	2	35.2	8.84	-	0.37	0.11	-	3.7	2.16	-	26.8	8.54	-
7-7	5	33.7	5.79	17.2	0.34	0.06	17.9	6.7	0.80	12.0	71.4	9.30	13.0
6-8	2	25.4	1.34	-	0.31	0.03	-	8.7	2.16	-	63.3	18.3	-
Sporocarps with unknown genotypes													
	19	33.4	6.69	20.0	0.38	0.08	20.3	7.7	1.97	25.5	66.0	21.3	32.3
Combined set of sporocarps (identified and unknown genotypes)													
	51	31.9	6.79	21.3	0.40	0.09	23.6	8.7	4.36	50.1	63.7	24.2	38.0

[1]Site numbering according to Dahlberg et al. (1997), the second figure is a running number of the study's different genotypes according to Vinichuk et al. (2011a).

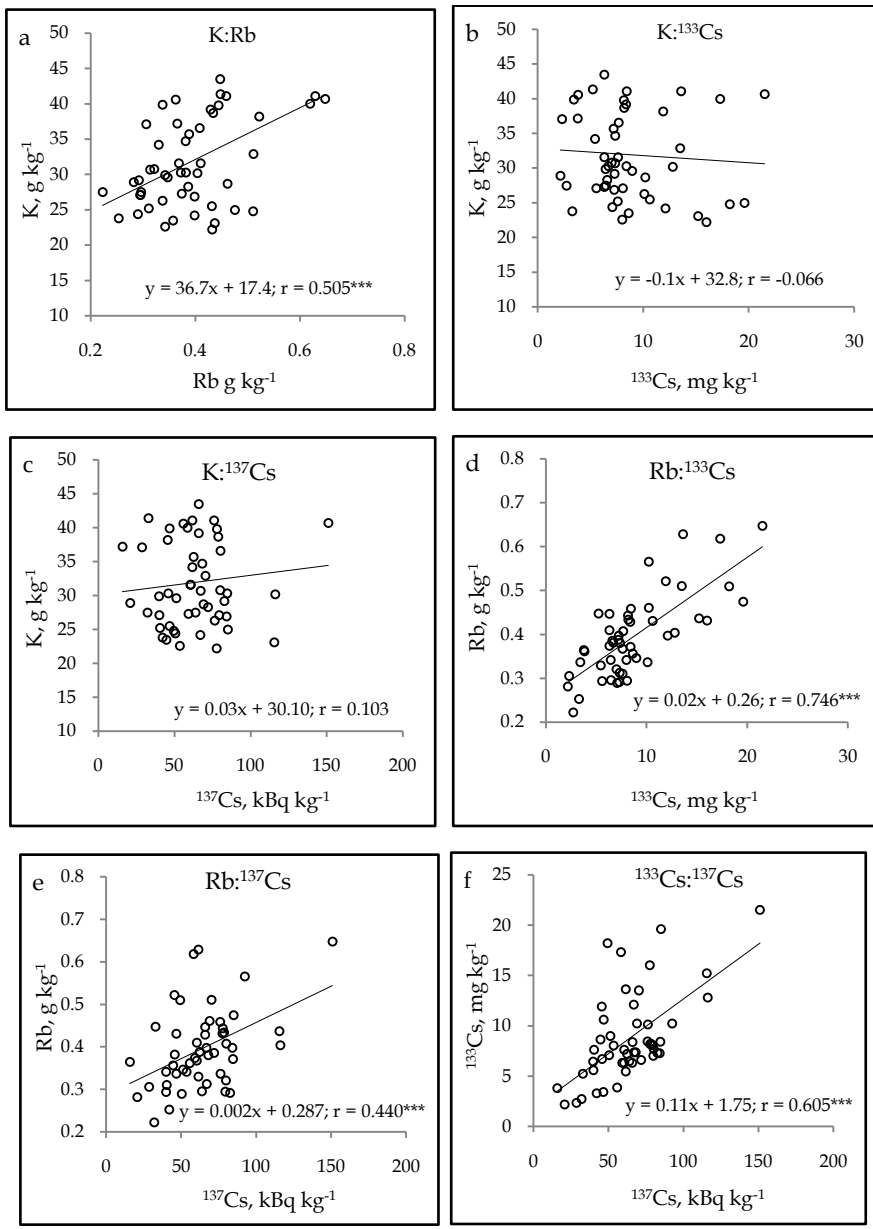

Figure 2.2 *Relationship between ^{137}Cs and K, Rb, and ^{133}Cs concentrations in sporocarps in the combined set of all S. variegatus sporocarps (a-f). K:Rb (a); K:^{133}Cs (b); K:^{137}Cs (c); Rb:^{133}Cs (d); Rb:^{137}Cs (e); and, ^{133}Cs:^{137}Cs (f). *** p=0.001.*

Rubidium is strongly correlated with stable ^{133}Cs (r=0.746) and moderately correlated with ^{137}Cs (r=0.440) and K (r=0.505: Figure 2.2: d, e, a). Both ^{133}Cs and ^{137}Cs were significantly correlated in the combined dataset (Figure 2.2: f).

Table 2.7 *^{137}Cs/^{133}Cs isotopic (atom) ratios in sporocarps of S. variegatus from identified genotypes, with unknown genetic belonging, and the two combined groupings, x10^{-7}. M = mean, CV = coefficient of variation. Adapted from Vinichuk et al. (2011a).*

Parameters	Site-genotype[1]								Unidentified genotypes	Combined set of sporocarps
	2-1	2-2	4-3	4-4	4-5	4-6	7-7	6-8		
M	1.67	1.43	3.16	3.95	2.86	2.43	3.27	2.24	2.62	2.50
CV (%)	97.1	36.4	10.4	5.1	78.1	29.5	9.2	3.9	20.0	34.6

[1]Site numbering according to Dahlberg et al. (1997), the second figure is a running number of the study's different genotypes according to Vinichuk et al. (2011a).

The ^{137}Cs/^{133}Cs isotopic ratio in the combined dataset was not correlated to K concentration, but correlated moderately and negatively with both ^{133}Cs (r=−0.636) and Rb (r=−0.500) concentrations (Figure 2.3: a, c, b).

Thus, the study of *S. variegatus* revealed no significant correlation between ^{133}Cs mass concentration or ^{137}Cs activity concentration and the concentration of K in sporocarps, either within the whole population or among the genotypes.

Potassium, ^{133}Cs, and ^{137}Cs within the four genotypes were also not correlated, with one genotype exception (Table 2.8). This exception was conditional due to one single value. Three of four sporocarp genotypes analyzed had high correlation between K and Rb: the fourth was only moderately correlated (Table 2.8).

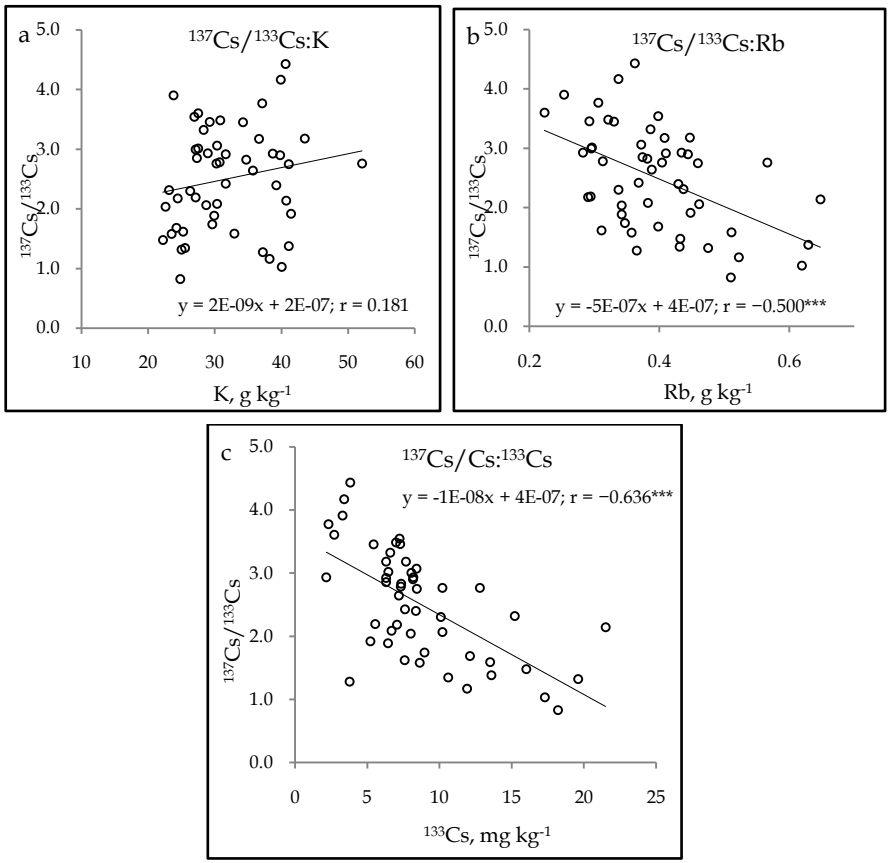

Figure 2.3 *Relationship between the ^{137}Cs/^{133}Cs isotopic (atom) ratios (x10^{-7}) and K, Rb, and ^{133}Cs mass concentrations in the combined set of S. variegatus sporocarps, (a) ^{137}Cs/^{133}Cs:K; (b) ^{137}Cs/^{133}Cs:Rb; and, (c) ^{137}Cs/^{133}Cs:^{133}Cs. *** p=0.001.*

The correlations between ^{137}Cs and K and Rb and ^{133}Cs in the four genotypes were inconsistent (Table 2.8). Potassium, Rb, ^{133}Cs, and ^{137}Cs were correlated in genotype 2-1 (due to one single value), whereas, no or negative correlations were found between the same elements/isotopes for the other three genotypes. In two (2-2 and 4-3) of four genotypes, the ^{137}Cs/^{133}Cs isotopic ratio was not correlated with ^{133}Cs, K, or Rb; however, there was a negative correlation with

Rb in one genotype (2-2) and positive correlation with ^{133}Cs in another (4-3) (Table 2.8.).

Mass concentration of ^{133}Cs and activity concentration of ^{137}Cs have different relations in fungal sporocarps. In three of four genotypes, there was a high correlation, two of which were significant (r=0.908** and r=979*), but there was no correlation in the fourth genotype (r=−0.263, Table 2.8), whereas, correlation between ^{137}Cs and ^{133}Cs within the whole population was only moderate (r=0.605*** Figure 2: f).

Table 2.8 *Correlation coefficients between concentrations of potassium, rubidium, and cesium (^{133}Cs and ^{137}Cs) in genotypes of S. variegatus with more than four sporocarps (Vinichuk et al. 2011a).*

	^{137}Cs	K	Rb	^{133}Cs
Genotype2-1 (8 sporocarps)				
K	0.502			
Rb	0.626*	0.966***		
^{133}Cs	0.908**	0.745*	0.837**	
^{137}Cs/^{133}Cs		−0.172	−0.058	0.240
Genotype2-2 (6 sporocarps)				
K	−0.472			
Rb	−0.658	0.928**		
^{133}Cs	−0.263	−0.138	0.159	
^{137}Cs/^{133}Cs		−0.352	−0.608	−0.586
Genotype4-3 (4 sporocarps)				
K	−0.531			
Rb	0.177	0.696		
^{133}Cs	0.979*	−0.569	0.182	
^{137}Cs/^{133}Cs		−0.488	0.163	0.930
Genotype 7-7(5 sporocarps)				
K	−0.562			
Rb	−0.472	0.987**		
^{133}Cs	0.699	−0.528	−0.404	
^{137}Cs/^{133}Cs		−0.115	−0.155	−0.345

* p=0.05; ** p=0.01; *** p=0.001

The data obtained for *S. variegatus* supports results from other studies (Ismail, 1994; Yoshida & Muramatsu, 1998) on different species of fungi; suggesting cesium (^{137}Cs and ^{133}Cs) and K are not correlated in mushrooms. Thus, correlation analysis may be a useful, although not definitive, approach for determining similarities or differences in the uptake mechanisms of cesium (^{137}Cs and ^{133}Cs) and K.

The concentration of K in sporocarps appears independent of the ^{137}Cs/^{133}Cs isotopic ratio in both the whole population (Figure 2.2) and among the genotypes, with one exception (Table 2.8). The lack of correlation between ^{137}C (or ^{133}Cs) and K in fungi may be due to the incorporation of K being self-regulated by the nutritional requirements of the fungus, whereas, incorporation of ^{137}Cs is not self-regulated by the fungus (Baeza et al. 2004).

Although K and cesium (^{133}Cs and ^{137}Cs) concentrations did not correlate within *S. variegatus*, both K^+ and Cs^+ ions may compete for uptake by fungi. In experiments under controlled conditions and with sterile medium (Bystrzejewska-Piotrowska & Bazala, 2008), the competition between Cs^+ and K^+ depends on Cs^+ concentration in the growth medium and on the path of Cs^+ uptake. The addition of monovalent cations of K^+, Rb^+, and NH_4^+ reduces the uptake of Cs by the hyphae of basidiomycete *Hebeloma vinosophyllum* grown on a simulated medium (Ban-Nai et al. 2005). Radiocesium transport by arbuscular mycorrhizal (AM) fungi decreases if K concentration increases in a compartment only accessible to AM (Gyuricza et al. 2010), and a higher Cs: K ratio in the nutrient solution increases uptake of Cs by ectomycorrhizal seedlings (Brunner et al. 1996). A noticeable (20-60%) and long-lasting (at least 17 years) reduction in ^{133}Cs activity concentration in *in situ* fungal sporocarps after a single K fertilization of 100 kg ha^{-1} in a Scots pine forest is reported by Rosén et al. (2011).

The relation between ^{137}Cs and K, and Rb and ^{133}Cs within S. *variegatus* (Figure 2.2) was similar to earlier findings on different species of fungi (Yoshida & Muramatsu, 1998). Rubidium concentration in sporocarps was positively correlated with ^{133}Cs and ^{137}Cs, but generally negatively correlated with ^{137}Cs/^{133}Cs isotopic ratio, i.e. a narrower ^{137}Cs/^{133}Cs ratio in sporocarps results in higher Rb uptake by fungi. This ratio may reflect the soil layers explored by the mycelia (Rühm et al. 1997). Fungi have a higher affinity for Rb than for K and cesium (Ban-Nai et al. 2005; Yoshida & Muramatsu, 1998), and Rb concentrations in sporocarps can be more than one order of magnitude greater than in mycelium extracted as fungal sporocarps from soil in the same plots (Vinichuk et al. 2011a). Soil mycelia consist of numerous fungal species and the intraspecific relationships between soil mycelia and sporocarps has not yet been estimated; however, the development of molecular methods with the ability to mass sequence environmental samples in combination with quantitative PCR may enable these analyses to be conducted.

In terms of ^{133}Cs and ^{137}Cs behavior, there would be no biochemical differentiation, but differences in atom abundance and isotopic disequilibrium within the system. Fungi have large spatiotemporal variation in ^{133}Cs and ^{137}Cs content in sporocarps of the same species and different species (de Meijer et al. 1988), and the variation in K, Rb, ^{133}Cs, and ^{137}Cs concentrations within a single genotype appear similar, or lower, than the variation within all genotypes. The results for ^{137}Cs and alkali elements in a set of samples of *S. variegatus*, collected during the same season and consisting of sporocarps from both different and the same genotype, indicate the variability in concentrations is similar to different fungal species collected in Japan over three years (Yoshida & Muramatsu, 1998).

The relatively narrow range in K and Rb variation and the higher ^{133}Cs and ^{137}Cs variations may be due to different mechanisms being involved. The differences in correlation coefficients between ^{137}Cs and the alkali metals varied among and within the genotypes of *S. variegatus*, suggesting interspecific and intrapopulation variation in the uptake of K, Rb, stable ^{133}Cs and, ^{137}Cs and, that their relationships can be explained by factors other than genotype identity. As the variability in ^{137}Cs transfer depends on the sampling location of fungal sporocarps (Gillett & Crout, 2000), the interaction factors for *S. variegatus* might include the spatial pattern of soil chemical parameters, heterogeneity of ^{137}Cs fallout, mycelia location, and heterogeneity due to abiotic and biotic interactions increasing over time (Dahlberg et al. 1997).

Within the combined set of sporocarps, the concentration of Rb and ^{137}Cs activity concentration in *S. variegatus* sporocarps were normally distributed but the frequency distribution of ^{133}Cs and K was not: asymmetry in ^{137}Cs frequency distributions is reported in other fungal species (Baeza et al. 2004; Ismail, 1994). According to Gillett & Crout (2000), the frequency distribution of ^{137}Cs appears species dependent: high accumulating species tend to be normally distributed and low accumulating species tend to be log-normally distributed. However, lognormal distribution is the default for concentration of radionuclides and is unlikely to be a species-specific phenomenon, as it also occurs in soil concentrations; implying normal distribution is not expected, even if large set of samples are analyzed.

Possible Mechanisms of ^{137}Cs and alkali Metals Uptake by Fungi

There is a lack of information about the mechanisms involved in the uptake and retention of radionuclides by fungi, and there are few studies of uptake mechanisms and affinity for alkali metals in fungi are scarce, although some

results are reviewed by Rodríguez-Navarro (2000). Fungal fruit bodies can be characterized by high ^{137}Cs, ^{133}Cs, and Rb concentrations and low calcium (Ca) and strontium (Sr) concentrations, compared to plants (Yoshida et al. 1998). In a laboratory experiment with a wood-inhabiting mushroom *Pleurotus ostreatus* (Fr.) Kummer Y-l (Terada et al. 1998), ^{137}Cs uptake by mycelia decreases as the concentration of ^{133}Cs, K, or Rb in the media increases, and K uptake by mycelia decreases as the concentration of ^{133}Cs increases. In an experiment with pure cultures of mycorrhizal fungi (Olsen et al. 1990) some species preferred Cs to K. In experiments with yeast (Conway & Duggan, 1958), K had preference over Cs and the affinity for alkali metal uptake decreased in the order $K^+ < Rb^+ < Cs^+$ then Na^+ and Li^+, with a relative ratio of 100:42:7:4:0.5. Fungi (mycelium and sporocarps) have higher affinity for uptake of Rb and K than for Cs, and based on the CR values for fungal sporocarps (Table 2.3), alkali metals can be ranked in the order $Rb^+ > K^+ > Cs^+$, with a relative ratio of 100:57:32, which is within the range of 100:88:50 derived by Yoshida & Muramatsu (1998).

It is likely that the affinity for an alkali metal depends on the nutritional status of the organism. The mycorrhizal species *Sarcodon imbricatus* is efficient in accumulating K, Rb, and Cs: mean elements CR for fungal sporocarps of this species are 102, 676, and 259 respectively (Vinichuk et al. 2010b). Likewise, Tyler (1982), reports a mean CR for Rb in litter decomposing fungus *Collybia peronata* of 41, and a mean CR for Rb of over 100 in *Amanita rubescens*, which is mycorrhizal with beech (*Fagus sylvatica* L.). However, lower ^{40}K content for mycorrhizal species is reported by Römmelt et al. (1990), which means mycorrhizal species do not necessarily accumulate alkali metals more efficiently than saprotrophic ones.

Fungal accumulation of stable and radioactive cesium appears to be species-dependent, although it is affected by local environmental conditions. The

variation in concentrations of stable and radioactive cesium in fungi of the same species is generally larger than the variation between different species (de Meijer et al. 1988) and the variation in ^{137}Cs levels within the same genet of *S. varegatus* is as large as within non-genet populations of the species (Dahlberg et al. 1997). This suggests both interspecific and intrapopulation variation in the uptake of K, Rb, stable ^{133}Cs, and ^{137}Cs, and that their relationships can be explained by factors other than genotype identity (Vinichuk et al. 2011a). There is about two orders of magnitude variation in Cs uptake, with the highest CR value in e.g. *S. imbricatus* (256) and the lowest in *Lactarius deterrimus* (2.6) (Vinichuk et al. 2010b).

Cs (^{137}Cs and ^{133}Cs), K and Rb in *Sphagnum* Plants

Peatlands are areas where remains of plant litter have accumulated under waterlogged and generally nutrient-poor habitats, particularly temperate and boreal bogs in the northern hemisphere. Bogs are ombrotrophic, i.e. all water and nutrient supply to the vegetation is from aerial dust and precipitation; this results in an extremely nutrient-poor ecosystem that is often dominated by peat mosses (*Sphagnum*). *Sphagnum*-dominated peatlands with some groundwater inflow (i.e. weakly minerotrophic 'poor fens') are almost as nutrient poor and acid as true bogs. *Sphagnum* plants grown on such bogs absorb and retain substantial amounts of fallout-derived radiocesium. The radioactive cesium isotope ^{137}Cs is transferred within raised bogs there is relatively high ^{137}Cs bioavailability to bog vegetation and mosses (Bunzl & Kracke, 1989; Rosén et al. 2009).

The transfer of ^{137}Cs within a peatland ecosystem is different from transfer in forests. In nutrient-poor but organic-matter-rich forest soils, the vertical migration rate of ^{137}Cs is low, but bioavailability is often high, particularly for

mycorrhizal fungi (Olsen et al. 1990; Vinichuk & Johansson, 2003; Vinichuk et al. 2004; 2005). This is partly due to extensive fungal mycelium counteracting the downward transport of ^{137}Cs (Rafferty et al. 2000), which results in a slow net downward transport of ^{137}Cs in the soil profile.

In *Sphagnum*-dominated peatlands, *Sphagnum* peat is virtually clay mineral free organic matter, which also lacks fungal mycelium. The downward migration of ^{137}Cs in *Sphagnum* peat is expected to be faster than in forest soil; however, Cs is continuously translocated towards the growing apex of the *Sphagnum* shoots, where it accumulates.

The chemical behavior of radiocesium in raised bog is assumed to be similar to that of stable ^{133}Cs and other alkali metals, i.e. K, Rb, which have similar physicochemical properties (Rosén & Vinichuk, 2009; Vinichuk et al. 2010a). In *Sphagnum*, the relationships between K, Rb, and Cs and whether Cs follows the same pathways as K are not clearly understood.

The influence of alkali metals (K, Rb, ^{133}Cs) on ^{137}Cs distribution and cycling processes in peatlands has not been well studied. Plant species growing on peat have varying capacities for influencing uptake and binding of radionuclides, but there is a lack of systematic study covering all the dominant species of *Sphagnum* peatlands and their competition for radionuclides and nutrients. The important role of *Sphagnum* mosses in mineral nutrient turnover in nutrient-poor ecosystems, in particular their role in ^{137}Cs uptake and binding, necessitates clear understanding of the mechanisms involved.

Therefore, the ^{137}Cs activity concentration and mass concentration of K, Rb, and ^{133}Cs were analyzed within individual *Sphagnum* plants (down to 20 cm depth) and the results were published in collaboration with Professor H. Rydin (Vinichuk et al. 2010a). The distribution of Cs (^{133}Cs and ^{137}Cs), K, and Rb in

the uppermost capitulum and subapical segments of *Sphagnum* mosses were compared to determine the possible mechanisms involved in radiocesium uptake and retention within *Sphagnum* plants.

The *Sphagnum* plants were growing in a small peatland (Palsjömossen) within a coniferous forest in eastern central Sweden, about 35 km NW of Uppsala (60°03′40″N, 17°07′47″E): the peatland area sampled was open and *Sphagnum*-dominated. A weak minerotrophic influence was indicated by the dominance of *Sphagnum papillosum*, and the presence of *Carex rostrata*, *Carex pauciflora*, and *Menyanthes trifoliata* (fen indicators in the region). The area mostly built by *Sphagnum fuscum* was dominated by dwarf-shrubs such as *Andromeda polifolia*, *Calluna vulgaris*, *Empetrum nigrum* and *Vaccinium oxycoccos*. Sampling was within a 25 m^2 low, flat 'lawn community' (Rydin & Jeglum, 2006) totally covered by *S. papillosum*, *S. angustifolium* and *S. magellanicum* with an abundant cover of *Eriophorum vaginatum*. The water table was generally less than 15 cm below the surface: surface water had a pH of 3.9-4.4 (June 2009).

Samples of individual *Sphagnum* shoots that held together down to 20 cm were randomly collected in 2007 (May and September) and 2008 (July, August and September). Thirteen samples of *Sphagnum* plants were collected and analyzed; three sets in 2007 and 10 sets in 2008. Each sample consisted of approximately 20-60 individual *Sphagnum* plants (mostly *S. papillosum*, in a few cases *S. angustifolium* or *S. magellanicum*). In the laboratory, the fresh, individual, erect, and tightly interwoven *Sphagnum* plants were sectioned into 1 cm (0-10) or 2 cm (10-20 cm) long segments down to 20 cm from the growing apex. The ^{137}Cs activity concentrations were measured in fresh *Sphagnum* segments. Thereafter, the samples were dried at 40 ℃ to constant weight and analyzed for K, Rb, and ^{133}Cs.

The activity concentration (Bq kg^{-1}) of ^{137}Cs in plant samples is determined by calibrated HP Ge detectors. The analysis of *Sphagnum* segments for K, Rb, and Cs is performed by a combination of ICP-AES (K concentration) and ICP-SFMS (^{133}Cs and Rb concentration) techniques at ALS Scandinavia AB, Luleå, Sweden. The detection limits were 200 mg kg^{-1} for K, 0.04 mg kg^{-1} for ^{133}Cs, and 0.008 mg kg^{-1} for Rb. Relationships between K, Rb, and ^{133}Cs concentrations in different *Sphagnum* segments were determined by Pearson correlation coefficients. All statistical analyses were with Minitab (© 2007 Minitab Inc.) software.

Distribution of Cs (^{137}Cs and ^{133}Cs), K, and Rb within *Sphagnum* Plants

The concentration of Cs (^{137}Cs and ^{133}Cs) and alkali metals K and Rb in different segments of *Sphagnum* plants provide information on differences in their uptake, distribution, and relationships. The averaged ^{137}Cs activity concentrations in *Sphagnum* segments are presented in Figure 2.4. Within the upper 10 cm from the capitulum, ^{137}Cs activity concentration in *Sphagnum* plants was about 3350 Bq kg^{-1}, with relatively small variations. Below 10-12 cm, the activity gradually declined with depth and in the lowest segments of *Sphagnum*, ^{137}Cs activity concentration was about 1370 Bq kg^{-1}.

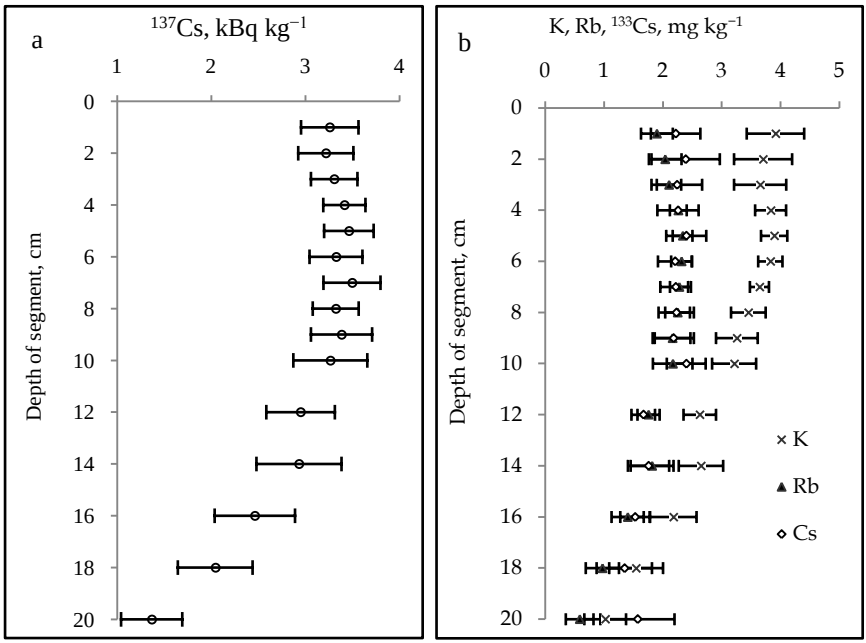

Figure 2.4 *^{137}Cs and alkali metals in Sphagnum: (a) average ^{137}Cs activity concentration (kBq kg^{-1}) in Sphagnum segments (+/− SE, n=13); (b) average concentrations of K (scale values should be multiplied by 10^{3}), Rb (x10^{1}), and ^{133}Cs (x10^{-1}) (mg kg^{-1}) in Sphagnum segments (+/− SE, n=4). Adapted from Vinichuk et al. 2010a).*

For individual samples, K concentrations ranged between 508 and 4970 mg kg^{-1} (mean 3096); Rb ranged between 2.4 and 31.4 mg kg^{-1} (mean 18.9), and ^{133}Cs ranged between 0.046 and 0.363 mg kg^{-1} (mean 0.204): averaged concentrations of K, Rb, and ^{133}Cs in *Sphagnum* segments are presented in Figure 2.4b. Concentrations of Rb and ^{133}Cs were constant in the upper 0-10 cm segments of *Sphagnum* moss and gradually declined in the lower parts of the plant length; whereas, the concentration of K decreased with increasing depth below 5 cm. Generally, the distribution of all three alkali metals was similar to ^{137}Cs, but with a weaker increase of Rb towards the surface. The ^{137}Cs activity concentrations had the highest coefficient of variation (standard deviation divided

by the mean) in *Sphagnum* (43%). The coefficients of variation were 35% for K, 35% for Rb, and 37% for ^{133}Cs concentrations.

Two important features affect the distributions of K, Rb, ^{133}Cs, and ^{137}Cs in a *Sphagnum*-dominated peatland. Firstly, this type of peatland is extremely nutrient-poor, and only a few plant and fungal species producing small fruit bodies can grow and no mycorrhiza, except ericoid mycorrhiza, exist. Secondly, the upper part of the stratigraphy is composed of living *Sphagnum* cells that selectively absorb mineral ions from the surrounding water, and the binding of K, Rb, and ^{133}Cs can be at exchange sites, both outside and inside the cell.

The distribution of ^{137}Cs within *Sphagnum* plants is similar to stable K, Rb, and ^{133}Cs. The ^{137}Cs activity concentrations and concentrations of K, Rb, and ^{133}Cs are highest in the uppermost 0-10 cm segments of *Sphagnum* (in the capitula and the subapical segments) and gradually decrease in older parts of the plant. Such distribution can be interpreted as dependent on the living cells of capitula and living green segments in the upper part of *Sphagnum*. Similar patterns of K distribution within *Sphagnum* plants are reported (Hájek, 2008). The ^{137}Cs appears to be taken up and relocated by *Sphagnum* plants in similar ways to the stable alkali metals, as concentrations of K, Rb, and ^{137}Cs activity concentrations in *Sphagnum* segments (Figure 2.4.) are similar to the depth of about 16 cm, and display a slightly different pattern in the lower part of the plant.

Mass Concentration and Isotopic (Atom) Ratios between ^{133}Cs, K, Rb, and ^{133}Cs, in Segments of *Sphagnum* Plants

Ratios between mass concentrations of all three alkali metals and ^{137}Cs activity concentrations, i.e. ^{133}Cs:^{137}Cs, K: ^{137}Cs, Rb: ^{137}Cs, and ^{133}Cs:^{137}Cs are constant through the upper part (0-16 cm) of *Sphagnum* plants (Figure 2.5). The

K:Rb ratio is higher in the uppermost (0-2 cm) and the lowest (18-20 cm) parts of the plant (Figure 2.5).

However, the isotopic (atom) ratios between ^{137}Cs activity concentrations and mass concentrations of alkali metals, i.e. ^{137}Cs/K, ^{137}Cs/Rb, and ^{137}Cs/^{133}Cs have a different pattern of distribution through the upper part (0-20 cm) of *Sphagnum* plants (Figure 2.6).

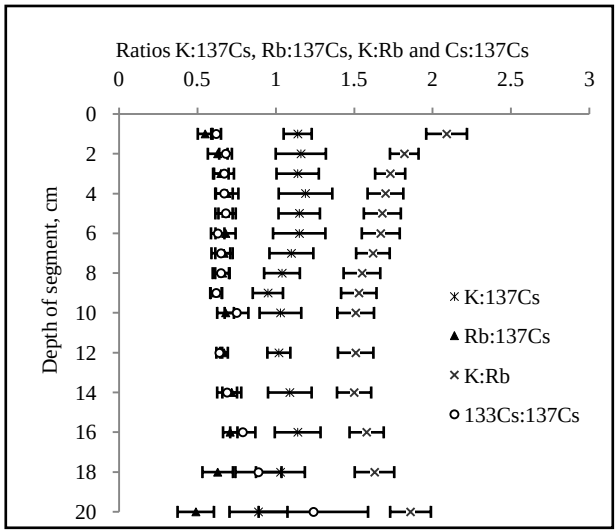

Figure 2.5 *Ratios between K:^{137}Cs, Rb:^{137}Cs (scale values should be multiplied by 10^{-2}), K:Rb (x10^{2}), and ^{133}Cs:^{137}Cs (x10^{-4}) in Sphagnum segments. Calculations based on concentrations in mg kg^{-1} for stable isotopes and Bq kg^{-1} for ^{137}Cs (+/– SE, n=13 for ^{137}Cs; n=4 for each of K, Rb, and ^{133}Cs) (Vinichuk et al. 2010a).*

The ^{137}Cs/K ratio is relatively narrow through the upper part (0-16 cm) of *Sphagnum* plants and wider with increasing depth, whereas, the ^{137}Cs/^{133}Cs ratio is constant throughout the upper part (0-12 cm) of *Sphagnum* plants and becomes narrower in the lower (14-20 cm) parts. The ^{137}Cs/Rb ratio is constant through the middle part (4-16 cm) of *Sphagnum* plants and somewhat narrower in the uppermost (0-4 cm) and lowest (16-20 cm) parts (Figure 2.6).

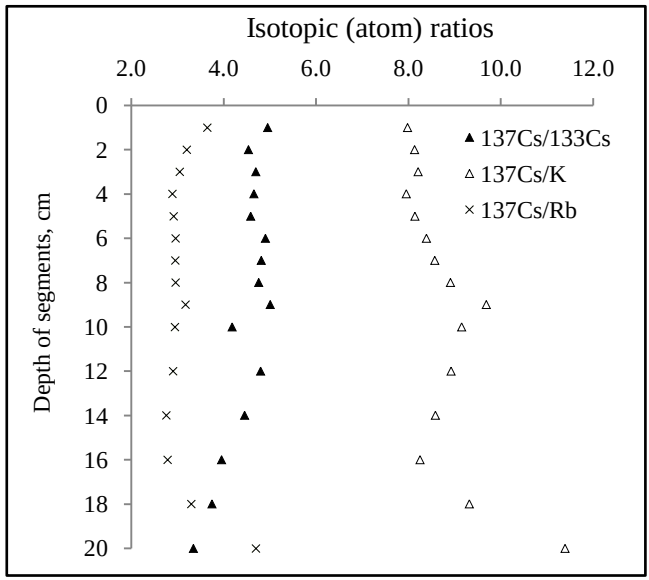

Figure 2.6 *Isotopic (atom) ratios ^{137}Cs/K (scale values should be multiplied by 10^{-12}), ^{137}Cs/Rb (x 10^{-09}), and ^{137}Cs/^{133}Cs (x10^{-07}) in Sphagnum segments. Calculations based on ^{137}Cs activity concentrations and mass concentrations of K, Rb, ^{133}Cs (Eq. 2) (mean values, n=4 for each of ^{137}Cs, K, Rb, and ^{133}Cs) (Vinichuk et al. 2010a).*

The distribution of the isotopic (atom) ratios between ^{137}Cs activity concentrations and mass concentrations of alkali metals K and Rb through the upper part (0-20 cm) of *Sphagnum* plants are probably conditioned by at least three processes. These include physical decay of ^{137}Cs atoms with time; attainment of equilibrium between stable ^{133}Cs and ^{137}Cs in the bioavailable fraction of peat soil; and, the relation between cesium (^{133}Cs and ^{137}Cs), K, and Rb when taken up by the *Sphagnum* plant.

Relationships between ^{133}Cs, K, Rb, and ^{133}Cs in Segments of *Sphagnum* Plants

The relationships between ^{133}Cs, K, Rb, and ^{133}Cs in separate segments of *Sphagnum* plants provide a tool for future investigation of the uptake

mechanism. There are close positive correlations between K, Rb, and ^{133}Cs mass concentrations and ^{137}Cs activity concentrations in *Sphagnum* segments (Table 2.9). The highest correlation is between ^{137}Cs activity concentrations and Rb mass concentrations (r=0.950; p=0.001) and correlation between K and Rb mass concentrations (r=0.952; p=0.001) in 10-20 cm length of *Sphagnum* plants; however, ^{137}Cs and K have a weaker correlation only when the upper 0-10 cm part of *Sphagnum* plants are analyzed (r=0.562; p=0.001). There is no, or negative correlation between^{137}Cs/^{133}Cs isotope (atom) ratios and mass concentrations of alkali metals (K, Rb, and ^{133}Cs) (Table 2.9).

Table 2.9 *Correlation coefficients between concentrations of potassium, rubidium, and cesium (^{133}Cs and ^{137}Cs) in Sphagnum segments (*** p=0.001) (Vinichuk et al. 2010a).*

	^{137}Cs	K	Rb	^{133}Cs
0-10 cm length				
K	0.562***			
Rb	0.893***	0.632***		
^{133}Cs	0.840***	0.792***	0.802***	
^{137}Cs/^{133}Cs	–	−0.262	0.270	−0.157
10-20 cm length				
K	0.856***			
Rb	0.950***	0.952***		
^{133}Cs	0.645***	0.651***	0.664***	
^{137}Cs/^{133}Cs	–	0.122	0.219	−0.401

The marked decrease in ^{137}Cs activity concentration below 14 cm (Figure 2.4a) raises the question as to what depth the 1986 Chernobyl horizon was when the sampling was done. A peat core was sampled in May 2003 at Åkerlännа Rönmosse, an open bog about 14 km SW of Pålsjömossen, by van der Linden et al. (2008). Detailed dating by ^{14}C wiggle-matching indicates the Chernobyl horizon was then at a depth of 17 cm. Depth-age data estimates a linear annual peat increment of 1.3 cm yr^{-1} over the last decade (R^2=0.998), indicating the Chernobyl horizon

would be at about 23 cm deep when the ^{137}Cs sampling was done in 2007/2008. Even if there are uncertainties in applying data from different peatlands, the Chernobyl horizon should be at, or below, the lowest segments sampled. Thus, ^{137}Cs has migrated upwards, although no downward migration could be tested (Vinichuk 2010a).

The relatively unchanged ^{137}Cs/K, ^{137}Cs/Rb, and ^{137}Cs/^{133}Cs isotopic (atom) ratios in the upper 0-14 cm part of Sphagnum plant and the noticeable widening below 14-16 cm supports this assumption. Upward migration of ^{137}Cs has been previously reported (Rosén et al. 2009). Similarly, the majority of ^{137}Cs from nuclear bomb testing in 1963 was retained in the top few centimeters of *Sphagnum* peat 20 years later, but with a lower peak at the level where the 1963 peat was laid down (Clymo, 1983).

Mechanisms of ^{137}Cs and Alkali Metals Uptake by *Sphagnum* Plants

Presumably, ^{137}Cs is bound within capitula, living green segments, and dead brown segments of *Sphagnum* plants. According to Gstoettner and Fisher (1997), the uptake of some metals (Cd, Cr, and Zn) in *Sphagnum papillosum* is a passive process as the living and dead moss accumulate metal equally. For a wide range of bryophytes, Dragović et al. (2004) found ^{137}Cs is primarily bound by cation exchange, with only a few percent occurring in biomolecules. *Sphagnum* mosses have remarkably high cation exchange capacity (Clymo, 1963), and according to Russell (1988), a high surface activity of *Sphagnum* is related to its high cation exchange capacity, which ranges between 90-140 meq/100 g. In a water saturated peat moss layer, water washes (1 L de-ionized water added to a column of with a volume of 1.4 L) removed about 60% of K from *Sphagnum* (Porter B. Orr, 1975), indicating this element was held on cation exchange sites. In turn, the desiccation of living moss usually causes cation leakage from cell cytoplasm, during which

most of the effused K^+ is retained on the exchange sites and reutilized during recovery after rewetting (Bates, 1997).

However, this is not necessarily the case for ^{137}Cs, as ^{137}Cs has a weaker correlation with K, especially in the uppermost parts of the plant, which means ^{137}Cs uptake can be somewhat different from that of K. Even within the same segments of the plant, ^{137}Cs activity concentrations have higher variation than K concentration. An even stronger decoupling between ^{137}Cs and K is observed in the forest moss *Pleurozium schreberi*, in which ^{137}Cs is retained more in senescent parts (Mattsson & Lidén, 1975). However, the close correlations found between Rb and ^{137}Cs suggest similarities in their uptake and relocation: similar observations are reported for fungi (Vinichuk et al. 2010b; 2011a; 2011b).

Although some lower parts of *Sphagnum* plants are still alive and able to create new shoots, as they are still connected to the capitulum (Högström, 1997), much of lower stem is dead. Thus, the decrease in ^{137}Cs activity concentration in plant segments below 10 cm indicates a release of the radionuclide from the dying lower part of *Sphagnum* and internal translocation to the capitulum.

The mechanism of radiocesium and alkali metal relocation within *Sphagnum* is probably the same active translocation as described for metabolites by Rydin & Clymo (1989). Although external buoyancy-driven transport (Rappoldt et al. 2003) could redistribute ^{137}Cs, field evidence suggests buoyancy creates a downward migration of K (Adema et al. 2006); thus, this mechanism appears unlikely. Likewise, a passive downwash and upwash (Clymo & Mackay, 1987) cannot explain accumulation towards the surface.