Environmental behavior of cesium and strontium in agricultural and forest soil

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Summary

Radionuclides are critical soil contaminants, particularly cesium (Cs-137) and strontium (Sr-90) are harmful due to their high radiotoxicity and metabolic similarity to major soil nutrients (e.g. K^+, Ca^{2+}) (Nisbet, 1993; Alexakhin *et al.*, 2006; Lehto and Hou, 2011). To study the behavior of these contaminants in soil-plant systems is essential to reduce their migration into food chain. Important factors that influence the mobility and plant uptake of radionuclides include soil properties (texture, pH and organic matter), soil management practices (ploughing, disking) and the use of mineral and organic fertilizers. Biochar and digestate are the bioenergy residues that are increasing applied to improve soil properties; however their effect on critical soil contaminants (e.g. radionuclides) is scarcely investigated.

Sorption-desorption behavior of Cs^+ and Sr^{2+} in three different soils was investigated, two soils were of agricultural origin and third one from a forest site. The two organic amendments (biochar and digestate) were applied with typical field application rates (Biochar: 25 t ha^{-1}, digestate: 34 t ha^{-1}). Moreover, the sorption-desorption experiments were carried out at three temperatures (5, 20 and 35°C) to realize the effect of temperature variation. Furthermore, in a lysimeter experiment, we studied the effect of digestate amendment on plant uptake and mobility of Cs-137 and Sr-90 in a silty loam Luvisol.

Sorption experiments showed that amendments with applied rates did not lead to a substantial effect on sorption-desorption of cesium and strontium in opposition to soil texture and land use. The sorption-desorption behavior of the two contaminants was different. Cesium showed highest sorption in arable silty loam soil, followed by forest sandy-clay loam and lowest in arable loamy sand. Strontium sorption was nearly half compared to cesium in all soils with higher sorption in silty loam and almost similar sorption in loamy sand and forest soils. Despite lower soil pH but most likely due to higher clay content and chemical nature of organic matter, Sr retention in forest soil was larger than in amended arable soils. Temperature variation in the range (5-35°C) did not cause a substantial effect on sorption-desorption of the two radionuclides in opposition to the soil type.

Lysimeter results showed that plant uptake of Cs-137 and Sr-90 remained unaffected after digestate amendment with above mentioned applied rate. Furthermore, digestate application failed to induce any effect on vertical mobility of both radionuclides. However, dicotyledonous plant species exhibited higher uptake compared to monocotyledonous plants most likely due to difference in root structure. Hence, the choice of cultivating different plants species on contaminated soils could be helpful to reduce the risk of radionuclides mobility into the food chain.

Kurzfassung

Radionuklide sind gefährliche Bodenschadstoffe, insbesondere Cäsium (Cs-137) und Strontium (Sr-90) sind aufgrund ihrer hohen Radiotoxizität und metabolischen Ähnlichkeit zu Makronährstoffen (z.B. K^{+}, Ca^{2+}) schädlich (Nisbet, 1993; Alexakhin et al, 2006; Lehto und Hou, 2011). Um jedoch die Durchlässigkeit von Cs-137 und Sr-90 in der Nahrungskette zu reduzieren, ist deren Verhalten im Boden-Pflanzen-Systemen zu studieren. Wichtige Faktoren, welche die Mobilität und die Pflanzenaufnahme von RN beeinflussen, sind verschiedene Bodeneigenschaften (z.B. Textur, pH-Wert und organische Stoffe), Bodenbewirtschaftungspraktiken (z.B. Pflügen, Eggen) und der Einsatz von mineralischen und organischen Bodenzuschlagsstoffen. Jedoch wurde der vermehrte Einsatze von Resten aus der energetischen Biomasseverwertung, wie z.B. von Pflanzenkohle und Gärresten bisher kaum im Hinblick auf dessen Wirkung auf die Mobilität von RN im Boden untersucht.

Daher untersuchte ich das Sorptions-Desorptions-Verhalten von Cs^{+} und Sr^{2+} in drei verschiedenen Böden, wobei zwei landwirtschaftlich und ein dritter forstwirtschaftlich genutzt wurden. Den Böden wurden die organischen Bodenzuschlagsstoffe entsprechend gängiger Praxis zugemischt. Um den Einfluss der Temperatur auf das Sorptions-Desorptions-Verhalten zu studieren, wurde die Sorptions-Desorptions-Versuche über einen Temperaturbereich von 5 bis 35°C durchgeführt. Desweiterhin wurde in einem Lysimeterexperiment die Wirkung der Gärreste auf die Mobilität von Cs-137 und Sr-90 in einem schluffig-lehmigen Boden und deren Pflanzenaufnahme studiert.

Die Sorptionsstudie zeigte, dass im Gegensatz zur Bodentexture und der Landnutzung die Zugabe der beiden Bodenzuschlagsstoffe das Sorptions-Desorptions-Verhalten von Cäsium und Strontium nicht wesentlich änderte. Jedoch gab es Unterschiede zwischen den beiden RN. Cäsium wurde vom schluffigen Lehmboden stärker sorbiert als vom Waldboden und dem lehmigem Sand. Strontium wurde weniger stark sorbiert als Cäsium, jedoch auch stärker vom schluffigen Lehm als vom lehmigem Sand und dem Waldböden. Die natürlich gebildete organische Substanz im Waldboden verurschte eine höhere Sr^{2+} Retention als die organische Substanz der landwirtschaftlichen Böden. Über den gesamten Temperaturbereich von 5 bis 35°C wurden kaum Unterschiede in den Sorptions-Desorptions-Verhalten der beiden RN beobachtet.

Die Lysimeterergebnisse zeigten, dass die applizierten Gärreste die Pflanzenaufnahme von Cs-137 und Sr-90 nicht erheblichen änderte. Darüber hinaus hatten die Gärreste keine Auswirkung auf die vertikale Mobilität der beiden Radionuklide, jedoch nahme zweikeimblättrige Pflanzen höhere Mengen auf als einkeimblättrige Pflanzen. Diese Unterschiede in der Aufnahme von RN können höchstwahrschiinlich auf die unterschiedlichen Wurzelstrukturen zurückzuführen. Somit könnte die Pflanzenwahl sehr bedeutend sein, um kontaminierte Böden zu kultivieren und das Risiko der Durchlässigkeit von RN in der Nahrungskette einzuschränken.

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List of Abbreviations

Ads	Adsorption
Ba	Barium
Ba^{2+}	Barium (II)-ion
BET	Brunauer–Emmett–Teller
Ca	Calcium
Ca^{2+}	Calcium (II)-ion
CEC	Cation exchange capacity
Cs	Cesium
Cs^{+}	Cesium (I)-ion
Des	Desorption
FAO	Food and Agricultural Organization of United Nations
FES	Frayed edge sites
H	Hydrogen
H	Hour
IAEA	International Atomic Energy Agency
Mg	Magnesium
Mg^{2+}	Magnesium (II)-ion
Min	Minute
N	Nitrogen
NH_4	Ammonium
NH_4^{+}	Ammonium (I)-ion
NRW	North Rhein-Westphalia
OA	Organic amendment
OM	Oraganic matter

RES	Regular exchange sites
RN	Radionuclides
S	Soil
Sr	Strontium
Sr^{2+}	Strontium (II)-ion
T	Temperature
TC	Total carbon
TDR	Time domain reflectometers
TF	Transfer factors
TN	Total nitrogen
TOC	Total organic carbon
w/v	Weight/volume
w/w	Weight/weight

List of Symbols

$t_{1/2}$	Half life of radioactive substance [T]
Δt	Time interval [T]
Δt_s	Travel time of electromagnetic wave [T]
°C	Celsius (Temperature)
BET	Surface area $[L^2M^{-1}]$
c	Speed of light $[LT^{-1}]$
C_e	Solute concentration at equilibrium $[10^{-3}N10^{-3}L^3]$
C_s	Solute concentration sorbed to soil $[10^{-3}NM^{-1}]$
γ	Gamma radiation [-]
H	Hysteresis index [-]
Ka	Dielectric constant [-]
K_d	Soil water distribution co-efficient $[10^{-3}L^3M^{-1}]$
K_F	Freundlich capacity parameter $[10^{-3}N^{(1-n)}\ 10^{-3}L^nM^{-1}]$
L	Length [L]
n	Freundlich exponent [-]
Σ	Sum of quantities [-]
β	Beta radiation
θ	Volumetric water contnet $[LL^{-3}]$
Ω	Ohm (eletrical resistance) $[ML^2T^{-3}I^{-2}]$

1. General Introduction

1.1 Background

Soil contamination with toxic metals and radionuclides (RN) is a crucial environmental problem that can cause contamination of water bodies and living biomass (Zhu and Smolders, 2000; Alexakhin *et al.*, 2006; Wuana and Okieimen, 2011). Inorganic contaminants (i.e. toxic metals and RN) are more critical as they cannot be biological or chemically degraded like the organic ones, so their toxicity need to be reduced by sorption, phytoremediation and soil-based countermeasures (Nisbet, 1993; Zhu and Smolders, 2000; Tangahu *et al.*, 2011; Wuana and Okieimen, 2011). Thus, immobilization of RN (e.g. Cs-137 and Sr-90) limits their transfer from soil to humans through the food chain.

Cesium is an alkali metal and occurs in the environment as univalent cation. Cs-133 is the only stable isotope out of its 40 known isotopes. Among the three main radioactive isotopes, Cs-137 and Cs-135 are fission products while Cs-134 is an activation product. Cs-137 and Cs-135 are dangerous due to their long half-lives: $t_{1/2}$ = 30 years (Cs-137) and $t_{1/2}$ = $3x10^6$ years (Cs-135) and relatively high fission yields: 6.18% and 6.54% respectively (Choppin *et al.*, 1995; Carbol and Engkvist, 1997; Lehto and Hou, 2011). Cs-137 is a beta emitter decaying (94.6 % E_{max}0.512 MeV β^-) to metastable barium (^{137m}Ba, $t_{1/2}$= 2.6 min) which in turn decays to stable Ba-137 through gamma emission (0.662 MeV γ) and directly to stable barium (5.4 % E_{max}1.174 MeV β^-) (Carbol and Engkvist, 1997; Lehto and Hou, 2011). Strontium is an alkaline earth metal. Due to its high reactivity it is typically found as mineral compounds, celestine ($SrSO_4$) and strontianite ($SrCO_3$) are two basic minerals of strontium (Nilsson *et al.*, 1985). The substantial isotopes of ecological concern are Sr-90 ($t_{1/2}$= 29 years; E_{max} 0.546 MeV β^-) and its daughter, Yttrium (Y-90). Yttrium has a half-life of about 60 h; however, its beta decay (E_{max} 2.274 MeV) intensifies the beta emission of Sr-90 (Lehto and Hou, 2011). Sr-90 and its daughter, Y-90 are the high energy beta radiation sources (Vajda and Kim, 2010; Lehto and Hou, 2011).

Cs-137 and Sr-90 are of particular concern due to their metabolic similarity to potassium (K^+) as well as ammonium (NH_4^+) and calcium (Ca^{2+}), respectively, which can enhance their plant uptake and transfer to humans through the food chain (Nisbet *et al.*, 1993; Zhu and Smolders, 2000; Alexakhin *et al.*, 2006). During nuclear accidents like Chernobyl and Fukushima, large amounts of Cs-137 and Sr-90 were released into the atmosphere (Steinhauser *et al.*, 2014). Furthermore, nuclear weapons testing during the cold war are responsible for a major part of atmospheric radioactive pollution, which includes Cs-137 and Sr-90 (Salbu *et al.*, 2005; Le Roux *et al.*, 2010; IAEA, 2011). The RN accumulated in the atmosphere reach the soil through wet and dry deposition (Clark and Smith, 1988). Knowing the behavior of Cs-137 and Sr-90 in soils is important as soil plays a key role in their migration into water bodies and plants, which ultimately lead their way to humans.

1.2 Rationale

Cesium mobility in soil is governed by different mechanisms like sorption, ion-exchange, and adsorption to iron oxides and organic matter (OM) (Kamel and Navratil, 2002). Factors influencing Cs migration and retention in soils include soil texture, clay mineralogy, soil pH, OM content and exchangeable cations (van Bergeijk *et al.*, 1992; Nisbet *et al.*, 1993; Ehlken and Kirchner, 2002; Rigol *et al.*, 2002; Fuller *et al.*, 2015). Sorption of Cs^+ increases with decreasing size of soil particles, i.e. the smaller particle size the larger sorption (Baeza *et al.*, 1995; Kamel and Navratil, 2002; Giannakopoulou *et al.*, 2007). This is due to the fact that most sorption sites are located on the particle surfaces and as the surface to volume ratio increases, the sorption increases (Baeza *et al.*, 1995; Giannakopoulou *et al.*, 2007). Shenber and Eriksson (1993) studied the effect of various soil fractions (i.e. clay, clay-loam, loamy-sand and sand) on sorption of Cs-134 and respective K_d-values. They reported 3 times higher K_d-values for clay (6189 mL/g) compared to sand (1961 mL/g), while K_d-values of loamy-sand and clay-loam soils were medium (ranging between 3512 mL/g and 4081mL/g). Thus, Cs-137 pollution of sandy soils may cause pollution of water bodies, while reversible sorption of Cs-137 on fine textured soil particles may cause translocation into plants.

Clay textured soil possesses high sorption capacity for Cs^+ compared to sandy and organic soils (Hsu and Chang, 1994; Dumat *et al.*, 1997; Staunton *et al.*, 2002). Cs^+ being a univalent cation has a higher potential for sorption on clay minerals to balance the negative charge on the alumino-silicate structures (i.e. clay minerals) (Cornell, 1993; Comans *et al.*, 1998; Hakem *et al.*, 2000). Sorption of Cs^+ varies with the type of clay mineral and the exchange site (Cornell, 1993; Fuller *et al.*, 2015). Eberl (1980) reported that Cs sorption decreased depending upon the type of clay mineral in the following order: illite> montmorillonite>kaolinite > vermiculite.

The high sorption capacity of clay minerals for Cs^+ is due to the presence of specific bonding sites known as frayed edge sites (FES) which account a small fraction (~1%) of cation exchange capacity (CEC) of soil (Cornell, 1993; Wauters *et al.*, 1994; Dumat *et al.*, 1997). In fact 2:1 illitic clay consists of two tetrahedral Si/Al sheets and a central octahedral (Si/Al/Fe/Mg) sheet, which are held together by monovalent cations (e.g. K^+) placed in space (i.e. interlayer) between sheets (Figure 1.1) (Fuller *et al.*, 2015). Other monovalent and divalent cations (e.g. Cs^+, NH_4^+ and Ca^{2+}) can replace K^+ and alter the particle structure (Fuller *et al.*, 2015). For example, when illite weathers to vermiculite, K^+ is exchanged with Ca^{2+} (Jackson *et al.*, 1952). Sorption of strongly hydrated Ca^{2+} between the layers induces expansion of illite-interlayers (Sawhney, 1966; Jackson, 1968). This results in partially expanded wedge zones between hydrated and dehydrated interlayers known as frayed edges (Nakao *et al.*, 2008). FES can also occur in non-illitic clays (Wampler *et al.*, 2012); however Cs held in these wedge zones is not as strong as in illite (Ohnuki and Kozai, 2013). Since Cs^+ is weakly hydrated compared to K^+, it holds the clay layers more strongly than K^+ (Hird *et al.*, 1996). Consequently, the strongly hydrated cations (Ca^{2+},

Mg^{2+}) which can cause expansion of K^+ held clay layers will not affect the Cs^+ saturated clays (Sawhney, 1966).

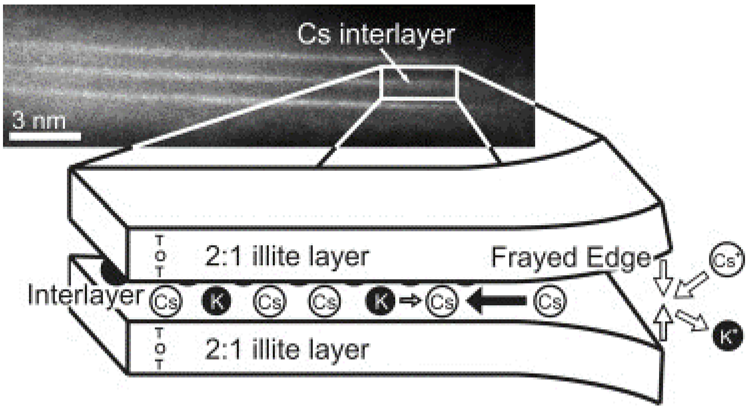

Figure 1.1: Cs fixation into illilte interlayer (frayed edge sites-FES) (Adapted from: (Fuller et al., 2015)).

Another soil compound providing negative surface charge is OM. Thus, OM can retain cations and have an effect on CEC of soils (Kabata-Pendias, 2004). Staunton and Levacic (1999) reported that OM can increase the CEC of the soil. The amount of Cs^+ sorbed on clay will be preferentially higher compared to OM (Baeza *et al.*, 1995; Staunton and Levacic, 1999; Rigol *et al.*, 2002; Staunton *et al.*, 2002). Cesium sorption on OM depends upon the CEC of OM and concentration of Cs and other cations (Dumat *et al.*, 1997; Staunton and Levacic, 1999; Rigol *et al.*, 2002). OM affects Cs sorption directly on regular exchange sites (RES) (i.e. humic acid sites in OM and planar sites in clay) or indirectly retarding its access to FES and preventing its fixation in inner sphere complexes (Dumat *et al.*, 1997; Rigol *et al.*, 1998). Kruyts and Delvaux (2002) postulated that availability of FES directly controls the mobility of cesium, whereas the OM sorption on clay mineral surfaces retards Cs^+ accessibility to clay interlayers (i.e. FES). Furthermore, OM can occupy the planar sites on clays, reducing their sorption capacity (Dumat *et al.*, 1997; Staunton and Levacic, 1999; Staunton *et al.*, 2002). These planar sites on particle surfaces constitute a large part of the sorption capacity of soils (Söderlund *et al.*, 2011). Cesium sorption on OM fractions (e.g. humic acid and humin) is non-specific and is partially or completely reversible (Hsu and Chang, 1994; Rigol *et al.*, 2002; Söderlund *et al.*, 2011).

The pH value provides an estimation of the ion-exchange capacity of the soil, so change in pH can affect the sorption capacity of soil. However, effect of pH on behavior of Cs^+ and Sr^{2+} in literature is controversial (Baeza *et al.*, 1995; Golmakani *et al.*, 2007; Thored, 2010). Wauters *et al*. (1994) described that pH had no direct effect on ion-exchange in a short term Cs^+ availability, however in long term it may enhance Cs^+ fixation. Contrarily, Giannakopoulou *et al*. (2007) while studying the Cs^+ sorption in 4 mineral soils (sandy-loam, loam, clay-loam and clay) observed a highest Cs^+ sorption at a pH value of 8. They attributed this substantial Cs^+ sorption to the maximum negative charge availability on exchange sites at this pH (pH = 8). van Bergeijk *et al* (1992) reported that soil-plant transfer of radiocesium remained unaffected with a pH change from 3.9 to 8.4, while the transfer factor (TF) values of radiostrontium were decreased by a factor of 1.7 with a pH increase from 4.5 to 7.4.

Unlike cesium, strontium is more mobile in mineral soils than in organic soils. It demonstrates faster downward migration in mineral soils compared to Cs (Ivanov *et al.*, 1997; Gastberger *et al.*, 2000). The mobility of Sr in soil mainly depends on the content of exchangeable Ca^{2+}, soil pH and the amount as well as the quality of OM (Sanchez *et al.*, 1988; van Bergeijk *et al.*, 1992; Baeza *et al.*, 1995). Higher amounts of exchangeable Ca^{2+} will lower the migration of strontium in soils due to their analogues behavior (Wiklander, 1964 ; van Bergeijk *et al.*, 1992). In nature, soil weathering causes leaching of Ca^{2+} and Mg^{2+} from exchange sites and replacing them with H^+ ions, resulting in lowering of soil pH (Nilsson *et al.*, 1985). Strontium shows higher mobility in acidic soil due to lack of Ca^{2+} ions on exchange sites. However, in soils with high OM content, Sr mobility is reduced because at low pH humic acids are insoluble which increases Sr retention (Sanchez *et al.*, 1988).

Divalent strontium ions bind to anionic sites of humic and fulvic acids via chelation and complexation, resulting in reduced Sr^{2+} mobility with increase in OM (Saar and Weber, 1982; Sanchez *et al.*, 1988). The knowledge of Sr-90 mobility in soils is scarce if compared to Cs-137, which may be explained by more laborious and expensive radiochemical separation of Sr-90 than required for Cs-137 (Gastberger *et al.*, 2000; Schimmack *et al.*, 2003; Herranz *et al.*, 2011). Thus, distribution of Sr-90 was less investigated after Fukushima accident (Steinhauser, 2014).

Soil solution is the medium between the soil solid phase and plant roots; a profound knowledge about environmental behavior of Cs-137 and Sr-90 is required to predict their plant uptake. Particularly Cs-137 and Sr-90 distribution between soil components and the liquid phase is of interest which is controlled by sorption-desorption reactions in soil (Giannakopoulou *et al.*, 2012). Thus, to evaluate the potential risks of Cs-137 and Sr-90 to living biomass, their sorption behavior needs to be investigated (van Bergeijk *et al.*, 1992; Staunton, 1994; Staunton *et al.*, 2002; Balonov *et al.*, 2010). A further step to probe the Cs-137 and Sr-90 migration to humans through the food chain is to investigate their behavior in soil-plant systems. The vertical mobility of Cs-137 and Sr-90 is an important factor to calculate the external radiation doses to humans since the radiation dose decreases as the Cs-137 and Sr-90 move down in the soil (Forsberg *et al.*, 2000). Further, the mobility of Cs-137 and Sr-90 into soils affect their plant availability and contamination of ground water (Nisbet, 1993; Gastberger *et al.*, 2000; Alexakhin *et al.*, 2006).

The migration of Cs-137 and Sr-90 from soil to plants is assessed by calculating transfer factors (TF) or concentration ratios (CR) by simply dividing the activity in plant part to the activity in soil on dry mass basis (Gerzabek *et al.*, 1998; Ehlken and Kirchner, 2002; Schimmack *et al.*, 2007). The TF or CR values can be used in environmental transfer models to predict mobility of Cs-137 and Sr-90 to humans through the food chain (Zhu and Smolders, 2000; Ehlken and Kirchner, 2002; Lukšienė *et al.*, 2013). However, due to the dependence of soil-plant transfer on multidimensional interacting factors (e.g. soil properties, plant physiology and physiochemical form of RN), it is important to account the TF values for multi soil-plant systems to improve their implementation in radiological and phytoremediation models (Forsberg *et al.*, 2001; Ehlken and Kirchner, 2002; Rigol *et al.*, 2002). Transfer of Cs-137 and Sr-90 in soil-plant systems is influenced by plants species as well as variety and physiochemical properties of radionuclide (Konoplev *et al.*, 1993; Forsberg *et al.*, 2001; Lukšienė *et al.*, 2013; Penrose *et al.*, 2015). The uptake can even vary among different genotypes of the same plants species (Desmet and Sinnaeve, 1992; Kabata-Pendias, 2011). Krouglov *et al* (1997) described that oat (*Avena sativa*) showed the highest contamination of Cs-137 and Sr-90 among the four grain crops (i.e. *Secale cereale, Triticum spec., Hordeum vulgare, Avena sativa*). Alexakhin (1993) reported that selection of crops and varieties can reduce uptake of Cs-137 upto 10 and 4-5 folds respectively. However, to probe such factors causing genotypic variation in RN uptake, plants species need to be grown under similar conditions (e.g. soil type, contamination level and environmental conditions) (Smolders and Merckx, 1993). Both Cs-137 and Sr-90 show a large difference in plant uptake and mobility in mineral soils (Krouglov *et al.*, 1997; Schimmack *et al.*, 2007; Lukšienė *et al.*, 2013). This is due to the fact that Cs binds to clay minerals while Sr is highly available due to lack of interaction to soil clay (Nilsson *et al.*, 1985; Cornell, 1993; Dumat and Staunton, 1999; Sanzharova *et al.*, 2009), conversly Sr^{2+} is less mobile in organic soils due to its strong interaction with OM fractions (Saar and Weber, 1982; Sanchez *et al.*, 1988).

Furthermore, plants can alter chemistry of soil and the soil solution in the rhizosphere (Taiz and Zeiger, 2006), which may also alter mobility of Cs-137 and Sr-90. Additionally, developing large rooting systems enhances plants capability to take up nutrients and elements from a large soil volume (Taiz and Zeiger, 2006). In rhizosphere nutrients and elements reach the root surface either through diffusion governed by concentration gradients or mass flow driven by transpiration (Lasat, 2000; Hopmans and Bristow, 2002). Additionally, when roots grow through the soil they come in direct contact with the soil and intercept nutrients associated with the soil particles (Adler *et al.*, 2009). The soil volume occupied by the roots, nutrients concentration in the soil and the root morphology are the factors which determine nutrients uptake by roots via interception (Adler *et al.*, 2009). The structure of roots differs among different plant species, monocots have fibrous roots while dicots contain a main root axis associated to smaller branched roots (Denny, 2002; Taiz and Zeiger, 2006). The translocation of elements within plants occurs through vascular tissue of plants, consisting of phloem and xylem (Taiz and Zeiger, 2006). The elements taken up by plant roots are moved to the shoot in the conducting cells of xylem via transpiration stream (Denny, 2002; Taiz and Zeiger, 2006).

1.3 Soil management

Another factor affecting distribution of Cs and Sr in soils are agricultural soil management practices, which distribute them physically into other soil layers (e.g. ploughing, disking) and through the addition of competitive elements (i.e. use of fertilizers and soil conditioners) (Lembrechts, 1993; Nisbet, 1993; Nisbet *et al.*, 1993; Camps *et al.*, 2004). Ploughing can reduce stock of Cs-137 and Sr-90, which is available for plant-uptake due to the mixing of top soil containing larger amounts with deeper soil containing initially less amounts of Cs-137 and Sr-90. The use of fertilizers and lime affect the major soil nutrients (e.g. Ca^{2+}, Mg^{2+}, K^+ and NH_4^+) leading to a changing behavior of the soil matrix in terms of ion-exchange. Fertilization with lime and potassium led to a 10 fold lower root uptake of Cs-137 in a spruce forest soil in southern Germany (Zibold *et al.*, 2009), due to higher availability of competing ions.

Although agricultural soils have a fundamental role in human life as it is the main source to meet the growing needs of food and feed production. Soil management practices have to be improved to maximize crop yields. One commonly applied practice to improve soil properties is to add OM like manure or compost (Giusquiani *et al.*, 1988; Senesi, 1989; De Lucia *et al.*, 2013), which may affect mobility of Cs-137 and Sr-90. In the last two decades anaerobic bio-waste fermentation has proven to be a prime method of recycling and its residues (i.e. digestate) were being recognized as valuable soil amendment. However, as the digestate from biogas plants differs not only in its quality from organic fertilizers used so far in agriculture, the behavior of biogas residues and their subsequent nutrient availability will likely differ from that of animal manure (Tani *et al.*, 2006; Zhang *et al.*, 2007; Möller and Stinner, 2009). Furthermore in the last decade the application of biochar as soil amendment has been vastly promoted (Chan *et al.*, 2008; Cayuela *et al.*, 2010; Gell *et al.*, 2011). Biochar is a thermo-chemically decomposed organic material supposed to improve soil properties (Sohi *et al.*, 2010; Jeffery *et al.*, 2011). Both biochar and digestate are anticipated to be increasingly applied to agricultural soils to improve plant productivity (Warnock *et al.*, 2007; Zhang *et al.*, 2007; Jeffery *et al.*, 2011; Teglia *et al.*, 2011) and may affect the mobility of Cs-137 and Sr-90 in amended soil in case of a nuclear accident.

1.4 Objectives

The main objective of current PhD was to investigate the effect of biochar and digestate application on mobility in soil and plant uptake of cesium and strontium in arable soils. Application of biochar and digestate can enhance soil OM, CEC, soil nutrients, pH and surface area of soils (Steiner *et al.*, 2007; Gell *et al.*, 2011; Kookana *et al.*, 2011; Teglia *et al.*, 2011). This in turn, can affect sorption-desorption and plant uptake of Cs-137 and Sr-90 in amended soils due to higher availability of sorption sites (OM sites) and higher concentration of soil nutrients (e.g. K^+, NH_4^+, Ca^{2+}, Mg^{2+}). The use of biochar and digestate as soil amendments is well recognized due to its agronomical benefits; however the knowledge on their effect on toxic metals and Cs-137 and Sr-90 mobility is scarce.

In detail to acquire basic data on sorption behavior of Cs^+ and Sr^{2+}, we conducted sorption-desorption experiments using three different soils from the region (North Rhine-Westphalia, Germany). The two soils were of agricultural origin while third soil was from a forest site. The agricultural soils were amended with field (agricultural practice) application rates of biochar and digestate. By using recommended application rates we intend to probe the immobilization of Cs^+ and Sr^{2+} in typical agricultural soils after biochar and digestate amendment. Moreover the sorption-desorption experiments were conducted on three environmentally relevant temperatures (5, 20 and 35 °C) to account the effect of temperature variation on sorption-desorption dynamics.

In parallel to sorption experiments we investigated the behavior of radioactive cesium (Cs-137) and strontium (Sr-90) by characterizing their uptake in different plants in a silty loam Luvisol with digestate amendment. This work was done using two lysimeters at the lysimeters facility of the Agrosphere institute (IBG-3), Forschungszentrum Jülich, Germany. In contrast to laboratory studies establishing lysimeter experiments are promisingly, because lysimeter studies provide realistic data that are required to simulate environmental behavior of Cs-137 and Sr-90. In brief, lysimeters are large scale leaching column systems, where target material is placed in a container with open surface. The container is provided with a drainage system to collect leachate, with sensors to monitor different physical and chemical properties (e.g. temperature, water content, pH etc.). Thus, lysimeters are powerful instruments to study mobility of nutrients, pesticides, heavy metals, RN in soil-plant systems.

2. Experimental set-up

2.1 Soils

For sorption-desorption experiments we used three contrasting soils: a silty loam soil (Orthic Luvisol) from arable land in Merzenhausen (50°55′50″N 6°17′50″E), loamy sand (Gleyic Cambisol) from arable land in Kaldenkirchen (51°18′40″N 6°12′10″E) and a forest soil (Dystric Cambisol; sandy-clay loam) from Wüstebach (50°30′17″N 6°19′56″E). All sites are located in North Rhine-Westphalia (NRW), Germany. The arable soils were described in (Berns *et al.*, 2008; Garré *et al.*, 2010; Kasteel *et al.*, 2010) and the forest soil in Pätzold and Pütz (2010). The plant uptake experiments were conducted in lysimeters contained with soil monoliths of silty loam soil from the Merzenhausen site.

2.2 Organic amendments

The organic amendments were selected with a view on their use in agricultural practice. Biochar was purchased from Carbon Terra GmbH (Augsburg, Germany), produced via slow pyrolysis (400-450°C) from wood chips. The digestate was obtained from an anaerobic digester in Schwalmtal (PlanET Biogastechnik GmbH, Vreden, Germany), operated under mesophilic conditions. The daily feed rate for the digester was 50 t, consisting of 60 % maize-silage, 4% chicken manure, 20% beef-urine and 16% pig urine (w/w, fresh content). The liquid fraction of the digestate (i.e. liquor) was used in this study to have a better relevance of nutrients competition and a better homogeneous incorporation in soil.

2.3 Lysimeters

The two lysimeters used in this experiment are part of the lysimeter facility of the Agrosphere institute (IBG-3), Forschungszentrum Jülich, Germany. The soil monoliths were excavated in

2001 (Weihermüller, 2005) from a nearby test site, Merzenhausen (10 kM northwest to the Forschungszentrum Jülich) using cylindrical V_2A-vesels with a diameter of 160 cm and a depth of 250 cm. The description of soil properties at the test site Merzenhausen are given in Table 2.1. The soil texture is dominated by silt with approximately 80%, where in turn coarse silt dominates with about 50%. Clay is the second major fraction, ranging from 13 to 23% in different horizons and sand content is $\leq$ 5% in all horizons. A more detailed information about lysimeter excavation, soil types and important physio-chemical soil properties at test site Merzenhausen were described by Weihermüller (2005).

2.3.1 Lysimeters equipment and instrumentation

The lysimeters were equipped with suction cups and leachate pans for soil solution sampling, TDRs (Time Domain Reflectometers) and tensiometers for soil water content monitoring and temperature sensors (PT 100) for soil temperature. The installation of described instruments was originally done by Weihermüller (2005) in 2002. Except for the tensiometers, all instruments (TDRs, PT100, suction cups) were kept at their original location. Tensiometers were removed and installed after refilling and calibration in 2012. The installation points of all sensors were sealed with Sika Flex 252 to avoid the risk of possible leakage of radiochemical contaminated water after RN application. A sketch of the lysimeter instrumentation is shown in Figure 2.1. The lysimeters are placed on a weighing balance with a measuring range of 0 to 12 tons and a resolution of 100 gm^{-2}. The lysimeter cellar is air-conditioned with a reference temperature of the test site Merzenhausen at a depth of 150 cm.

Table 2.1: Selected physio-chemical soil properties for the test site Merzenhausen (lysimeter soil), adopted from Weihermüller (2005). All units based on dry mass, except field capacity (based on saturated soil).

Horizon	**Depth** cm	**Sand** %	**Silt** %	**Clay** %	**pH**	**CEC** $\mathrm{cmol_c Kg^{-1}}$	**Bulk Density** $\mathrm{g\ cm^{-3}}$	**Field Capacity** %
Ap	0 -35	4.7	81.9	13.4	7.1	10.5	1.48	39.2
Al	35-47	3.1	78.9	18.0	7.1	10.5	1.53	42.2
Bt	47-97	2.4	74.9	22.7	7.1	11.9	1.54	39.5
Btv	97-150	2.6	79.4	18.0	7.0	16.3	1.56	39.2
Bv	150-210	2.9	81.1	16.0	6.8	12.5	1.52	38.0
Bcv	210-225	4.5	82.8	12.7	7.6	10.0	1.45	37.1
Cv	225-280	5.0	81.9	13.1	7.6	15.0	1.59	35.0

TDRs

To measure the volumetric water content in soil, each lysimeter was equipped with 22 TDRs probes. TDR works on principle of the measurement of travel time of an electromagnetic pulse through a waveguide (TDR probe) inserted into the soil. From the travel time information, the bulk dielectric constant of the soil is determined, from which soil water content is then inferred (Jones *et al.*, 2002).Soil is composed of air, mineral components, organic particles and water with dielectric constants of 1, 2, 4 and 80 (Farads/meter), respectively. Due to the large difference between the dielectric constant of water (~80) and the constants of the other soil constituents, the travelling speed of electromagnetic pulse varies with water content of the soil. The bulk dielectric constant, Ka of the soil can be determined by Equation 2.1 (Vanderborght et al., 2000).

$$Ka = \left(\frac{c\,\Delta t_s}{2L}\right)^2 \tag{2.1}$$

Where L, is the length of the waveguides [L], Δt_s is the 'travel time' of electromagnetic wave along the TDR rod [T] and 'c' is the velocity of light [LT^{-1}]. The relationship between the volumetric water content 'θ' and the dielectric constant 'Ka' was first reported by Topp et al. (1980) and this expression is used to calculate the volumetric water content:

$$\theta = -5.3 \times 10^{-2} + 2.92 \times 10^{-2}\, K_a - 5.5 \times 10^{-4}\, {K_a}^2 + 4.3 \times 10^{-6}\, {K_a}^3 \tag{2.2}$$

To record TDR measurements, a TDR 100 system and SDMX 50 multiplexers (Campbell Scientific, Utah, USA) were used. A CR10X data logger (Campbell Scientific, Utah, USA) logged the data at 1h intervals.

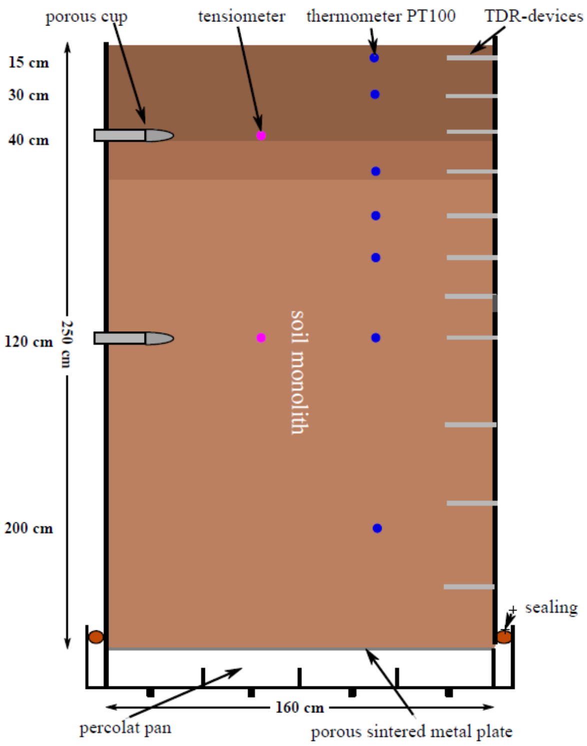

Figure 2.1: A sketch of lysimeter instrumentation [(Weihermüller, 2005): 23].

Tensiometers

The physical force that a root system applies to extract water held in soil is known as matric potential and a tensiometer is the instrument used to measure the matric potential. A tensiometer consists of a sealed plastic tube filled with water, a porous ceramic tip and a vacuum gauge. As the soil dries out, water is sucked out of the ceramic tip, creating a partial vacuum in the tube, readout on the vacuum gauge. Conversely, when soil gets wet by irrigation or rainfall, water is pressed into the ceramic tip and vacuum is reduced. To measure the matric potential in the lysimeter soil, seven tensiometers T4 (Umwelt-analytische Meß-System, München, Germany) were installed (Weihermüller, 2005) horizontally, three at the depth of 40 cm and four at 120 cm. The installed tensiometers were refilled, calibrated and re-installed in 2012. The tensiometers and temperature sensors data was recorded using a DL2e data logger (Delta-T devices, UK).

Temperature sensors

Each lysimeter was provided with six temperature sensors (PT100), three per tensiometer level. The PT100 works on the principle that resistance of a platinum metal changes with temperature. PT100 has a resistance of 100 Ω at 0°C. The metal resistance changes linearly with temperature over a temperature range of 0 to 100 °C.

Suction cups and leachate pans

Soil water sampling at two soil depths (40 and 120 cm) was carried out using seven suction-cups, installed analogues at each depth of tensiometers. The used suction cups consisted of borosilicate glass heads (with 1000 hPa air entry value) 32 mm in diameter and 60 mm long, connected to polyvinyl chloride (PVC) pipes (eco Tech UMS Umwelt-Meß-System, Bonn, Germany). The main advantage of using a suction cup over the other sampling devices is its negligible disturbance to the surrounding soil, so leading to a minor effect on natural percolation. Briggs and McCall (1904) resembled the working of a suction cup to an artificial root system to study the soil water availability to plants as well as its composition. The soil solution sampling with suction cups was done once a month by using a vacuum pump. The soil water collection at the bottom of the lysimeter (250 cm depth) was carried out using eight collection vessels. The total area of lysimeter bottom (2000 cm^2) was divided into eight segments; each segment with a drainage hole was connected to the collection vessel through a plastic pipe. The collection vessels were hermetically closed versus the lysimeter cylinders with a tube sealing (Figure 2.1a) and a suction of 10 cm was applied at the lysimeter bottom to avoid the boundary layer formation. The frequency of percolate collection at the lysimeter bottom varied from once a month to once a week, depending upon the outside weather conditions (precipitation).

2.4 Experiments

2.4.1 Sorption-desorption

Sorption-desorption experiments were carried out using three soils of different texture and land use. The two arable soils were taken from intensively used agricultural regions (Merzenhausen and Kaldenkirchen), the third soil from a forest region (Wüstebach); all sites located in North Rhine-Westphalia (Germany). Soil profiles and important physicochemical properties of both arable soils were described in Berns *et al* (2008) as well as in Garré *et al* (2010) and the forest soil in Pätzold and Pütz (2010). For sorption experiments, soils were taken from the top soil layers (0-25 cm). The arable soils were amended with field application rates (regular agricultural practice) of biochar and digestate while the forest soil was kept unamended to account for the effect of native OM. Furthermore, the sorption-desorption experiments were carried out at three environmentally relevant temperatures 20±2°C (room temperature) and 5±2°C and 35±2°C in a controlled environment incubator shaker G-25 (New Brunswick Scientific Co. Inc., USA).

2.4.2 Plant uptake and mobility in soil

The plant uptake and mobility in soil was investigated using the radioactive chloride salts of cesium (Cs-137) and strontium (Sr-90). The plant uptake was probed by calculating the transfer factors (TF) for above ground plant parts, i.e.TF-shoot for all plants, additionally TF-grain for cereals (summer wheat and oat). The distribution of applied activity in soil was assessed by soil samples after the harvest of plants and by soil water samples collected in suction cups and leachate pans.

3. Sorption-desorption of Cs^+ and Sr^{2+} in arable and forest soils affected by soil properties, organic amendment and temperature

3.1 Introduction

Radioactive cesium and strontium are harmful due to their metabolic similarities to nutrients (e.g. potassium [K^+], ammonium [NH_4^+], calcium [Ca^{2+}]), which promotes their availability to plant (Nisbet *et al.*, 1993; Zhu and Smolders, 2000; Alexakhin *et al.*, 2006). The chemical behavior of non-active Cs and Sr equals to their radioisotopes (^{137}Cs, ^{90}Sr) (Wild, 1993; Tsukada *et al.*, 2002; Tsukada *et al.*, 2005; Uchida *et al.*, 2009). Thus, potentially harmful radioactive isotopes of Cs and Sr can cause contamination of living biomass (Zhu and Smolders, 2000; Alexakhin *et al.*, 2006), e.g. following a nuclear accident (Desmet and Sinnaeve, 1992; Steinhauser *et al.*, 2014). The risk associated to radionuclides (RN) is hence due to their radiation emission and not their physico-chemical properties (Keepax *et al.*, 2009).

The identical chemical behavior of non-active Cs and Sr to their respective radioisotopes facilitates their use to predict their interaction in soil-plant systems; thus, their availability in soil (Tsukada *et al.*, 2002; Tsukada *et al.*, 2005; Giannakopoulou *et al.*, 2007; Uchida and Tagami, 2007; Kamei-Ishikawa *et al.*, 2008; Uchida *et al.*, 2009) and potential plant uptake (Uchida *et al.*, 2004). Unlike organic contaminants that can be biologically or chemically degraded, inorganic contaminants (e.g. toxic metals and RN) need to be controlled by immobilization using sorption, phyto-remediation and soil-based countermeasures (Nisbet, 1993; Zhu and Smolders, 2000; Tangahu *et al.*, 2011). Thus, to prevent transfer of RN from soil to humans through the food chain, an immobilization of RN is required.

In the environment land use type affects distribution and availability of Cs^+ and Sr^{2+} in soils through mechanical soil preparation (i.e. ploughing) and chemical alteration (e.g. application of fertilizer and organic amendments) (Lembrechts, 1993; Nisbet, 1993; Nisbet *et al.*, 1993; Ivanov *et al.*, 1997; Zhu and Smolders, 2000). In fact, Shestopalov *et al.* (2003), Ivanov *et al.*(1997) and Askbrant *et al.* (1996) observed that ploughing homogenized concentration of radioactive Cs^+ and Sr^{2+} in plough layer (thickness of ca. 25 cm) of arable soils. Contrastingly, forest soils retained more than 95% of Cs-137 in topsoil (ca: 6 cm).

Additionally, land management can affect availability of radioactive Cs^+ and Sr^{2+} isotopes due to application of fertilizers and soil conditioners (e.g. lime; Lembrechts, 1993; Nisbet *et al.*, 1993). The latter can alter concentration of major soil nutrients (e.g. K^+, Ca^{2+}, Mg^{2+}) that affects availability of Cs and Sr (Konoplev *et al.*, 1993; Lembrechts, 1993; Zibold *et al.*, 2009). For example, Lembrechts (1993) reported reduction in transfer factors of Cs^+ and Sr^{2+} after application of lime and K-fertilizer due to change in concentration of competitive cations (K^+, Ca^{2+}) in the exchange complex and soil solution. Moreover, in agriculture the application of organic soil amendments (e.g. compost, biochar, and digestate) is a common practice (Senesi, 1989; Jeffery *et al.*, 2011; Möller and Müller, 2012; Borchard *et al.*, 2014), but effect on Cs and Sr availability are hardly known.

Despite the last, in soils factors that influence availability of Cs^+ and Sr^{2+} are multiple and associated to soil texture, OM, ionic strength and soil pH (Nilsson *et al.*, 1985; Krouglov *et al.*, 1997; Kamel and Navratil, 2002; Sanzharova *et al.*, 2009). Cesium, being a monovalent cation, is sorbed on negatively charged soil components via ion-exchange (Comans *et al.*, 1998; Hakem *et al.*, 2000; Thored, 2010). Additionally, it is well documented that sorption of Cs^+ is stronger to clay minerals than to sesquioxides or OM (Cornell, 1993; Dumat *et al.*, 1997; Staunton and Levacic, 1999). While, in soils rich in OM, Cs^+ sorption is weak due to its lower tendency to form organic complexes (Saar and Weber, 1982; Sanchez *et al.*, 1988). Contrastingly, Sr^{2+}

strongly binds to OM via chelation and complexation (Saar and Weber, 1982; Sanchez *et al.*, 1988), but weakly to clay minerals (Sanchez *et al.*, 1988; van Bergeijk *et al.*, 1992). Thus, in terrestrial soils that contain clay minerals Cs^+ is preferentially retained, while Sr^{2+} may migrate to deeper soil layers (Ivanov *et al.*, 1997; Gastberger *et al.*, 2000). The latter can be limited by considerable amounts of OM (>2 %) that retains Sr^{2+} (Nilsson *et al.*, 1985).

Thus, studying sorption-desorption mechanisms of Cs^+ and Sr^{2+} are important to predict translocation and plant availability of their RN in soils (van Bergeijk *et al.*, 1992; Staunton, 1994; Staunton *et al.*, 2002; Balonov *et al.*, 2010). Particularly, content and origin of OM can differ substantially between arable and forest soils (Eswaran *et al.*, 1993; Guo and Gifford, 2002). In fact, OM found in forest soils remains from decomposition of autochthonous litter, while arable soils can store allochthonous OM (e.g. compost, biochar, digestate). As previously mentioned, an established practice to improve soil properties is the addition of OM (e.g. compost) (Giusquiani *et al.*, 1988; Senesi, 1989; de Leon-Gonzalez *et al.*, 2000; De Lucia *et al.*, 2013).

However, there are new forms of organic soil amendments, namely biochar and digestate that are likely to become more widely available in the future (Borchard *et al.*, 2014) to improve soil quality and crop yields (Sohi *et al.*, 2010; Jeffery *et al.*, 2011; Koide *et al.*, 2011). However, as studied by Valcke and Cremers (1994) natural soil OM can affect sorption of Cs and Sr in soils, but to our knowledge effects of biochar and digestate on sorption behavior of Cs^+ and Sr^{2+} in soils are scarce.

In recent years the concept of biobased economy has risen up to meet the challenges of environmental protection and preserving nature (Gell *et al.*, 2011). For this purpose, production of bioenergy increases, which results in production of large volumes of bioenergy residues (Cayuela *et al.*, 2010; Tambone *et al.*, 2010; Gell *et al.*, 2011). For instance, biochar that is a product of pyrolysis, produced by thermo-chemical decomposition of OM (Cayuela *et al.*, 2010; Gell *et al.*, 2011; Koide *et al.*, 2011), while digestate is the residue of biogas produced via anaerobic digestion of biodegradable wastes (Tani *et al.*, 2006; Zhang *et al.*, 2007; Möller and Stinner, 2009). Both biochar and digestate has been increasingly applied to agricultural soils to increase crop production and associated environmental benefits, e.g. mitigating formation of greenhouse gases (Warnock *et al.*, 2007; Zhang *et al.*, 2007; Jeffery *et al.*, 2011; Teglia *et al.*, 2011). Despite the last, applications of biochar and digestate can enhance content of soil OM, affect cation exchange capacity (CEC), soil pH and nutrient status of amended soils (Steiner *et al.*, 2007; Gell *et al.*, 2011; Kookana *et al.*, 2011; Teglia *et al.*, 2011). This in turn may alter sorption-desorption of Cs^+ and Sr^{2+} in amended soils.

In this study we investigated sorption-desorption behavior of Cs^+ and Sr^{2+} in two arable soils and a forest soil. With the use of soils from different land uses (i.e. forest vs. arable land) and soil textures we aimed to account natural key factors (i.e. soil texture, natural OM, and soil pH) that control sorption-desorption behavior of Cs^+ and Sr^{2+} in these soils. Further, we used common field application rates of biochar and digestate to test their effect on sorption-desorption dynamics of Cs^+ and Sr^{2+} in arable soils. Since temperature may also affect sorption due to change in Gibbs free energy ($\Delta G = - RT \ln K$), we adapted our sorption study to different environmentally reasonable temperatures (5°C, 20°C and 35°C, respectively).

3.2 Material and Methods

3.2.1 Chemicals

Cesium chloride (CsCl), strontium chloride hexa-hydrate ($SrCl_2$* $6H_2O$), calcium chloride ($CaCl_2$), Triethanolamine ($C_6H_{15}NO_3$) and barium chloride ($BaCl_2$) were purchased from Merck (Darmstadt, Germany). Deionized water (conductivity: <5 µS/cm) was used for stock solutions preparation.

3.2.2 Soils and organic amendments

Three contrasting soils were used in this study: a silty loam soil (Orthic Luvisol) from arable land in Merzenhausen (50°55´50″N 6°17´50″E), loamy sand (Gleyic Cambisol) from arable land in Kaldenkirchen (51°18´40″N 6°12´10″E) and a forest soil (Dystric Cambisol; sandy-clay loam) from Wüstebach (50°30´17″N 6°19´56″E). All sites are located in North-Rhine Westphalia (NRW), Germany; basic characteristics of the three soils are presented in Table 3.1. Additionally, the arable soils were described in (Berns *et al.*, 2008; Garré *et al.*, 2010; Kasteel *et al.*, 2010) and the forest soil in Pätzold and Pütz (2010). Biochar was purchased from Carbon Terra GmbH (Augsburg, Germany), produced via slow pyrolysis (400-450°C) from wood chips. The liquid fraction of biogas digestate (i.e. liquor) was obtained from an anaerobic digester in Schwalmtal (PlanET Biogastechnik GmbH, Vreden, Germany), operated under mesophilic conditions. The daily feed rate for the digester was 50 t, consisting of 60 % maize-silage, 4% chicken manure, 20% beef-urine and 16% pig urine (w/w, fresh content).

3.2.3 Soil incubation and chemical analyses

All three soils were collected from the top 25 cm after removing the vegetation and litter layers. The two arable soils were sieved to ≤2 mm and mixed with biochar and liquor and the forest soil was incubated without any treatment. Biochar was sieved to ≤2 mm to equalize particle sizes of soil and added to soil at an application rate of 25 t ha^{-1} (dry mass basis). Liquor was added to soil at an application rate of 34 t ha^{-1}. Each treatment was incubated for six months in triplicate under temperature between 5 and 15°C in 12 L plastic pots and kept moist at their initial field capacity by irrigating once a week using a weight-loss method.

After incubation the soils were characterized for relevant soil parameters: pH, electrical conductivity, total organic carbon (TOC), total inorganic carbon (TIC), total nitrogen, CEC and plant-available nutrients (Ca^{2+}, K^+, Mg^{2+}). Elemental analysis, total C and N were performed on milled soil samples (Ball mill) using a Vario EL cube (Elementar Analysen systeme GmbH, Hanau, Germany) in CHN-mode. Soil nutrients (Ca, K, Mg) were extracted with 0.01 M barium chloride solution (Prost *et al.*, 2013) and the extraction solutions were analyzed with inductively coupled plasma optical emission spectrometry (ICP-OES) (iCAP 6000, Thermo Scientific, USA). Soil pH was measured in 0.01 M $CaCl_2$ solution (soil/solution ratio of 1/5, w/v) with a portable pH-meter (Orion 3-star, Thermo Electron Co., USA) using a glass electrode. Electrical conductivity was measured in de-ionized water using a TetraCon 325 electrode (Proline 197i WTW, Weilheim, Germany). For this, suspensions were shaken on a horizontal shaker for 4 h and centrifuged for 15 min (Allegra 6 KR, Beckman Coulter Inc. CA, USA) at 2524 x g and 20°C. Potential CEC (i.e. adjusted to pH 7) was measured using a modified Mehlich method (Mehlich, 1942). Surface area was measured using Autosorb 1 (Quantachrome GmbH and Co.

KG, Odelzhausen, Germany) by applying Brunauer-Emmett-Teller (BET) equation to multipoint N_2 adsorption isotherms at 343 K.

3.2.4 Pre-treatment for sorption experiments

Pre-equilibration was performed to load sorption surfaces uniformly with Ca^{2+} prior to sorption-desorption experiments. Equilibration was carried out in 50 mL polycarbonate centrifugation bottles (Oak ridge centrifuge bottles, Nalgene, Rochester, NY, USA) for Cs and 50 mL glass centrifugation bottles (Schott, Mainz, Germany) for Sr. Pre-equilibration with $CaCl_2$ solutions was completed in three steps with decreasing concentrations of 1 M, 0.1 M and 0.01 M (OECD, 2000; Borchard *et al.*, 2012). For this, suspensions of 4 g dry soil were suspended in 20 mL 1 M $CaCl_2$ solution (soil/solution rate: 1:5, w/v), shaken on a horizontal shaker for 1 h at room temperature (20±2°C) and centrifuged (Allegra 6 KR, Beckman Coulter Inc. CA, USA) at 2524 x g (poly carbonate tubes) and 1733 x g (glass tubes) for 10 min and 20°C. The supernatant was decanted and discarded and the soil was further equilibrated with 0.1 M and 0.01 M $CaCl_2$ solutions respectively, repeating the same procedure as for 1 M $CaCl_2$.

3.2.5 Sorption-desorption experiments

Experiments were carried out using a batch method, at room temperature (20±2°C) and 5±2°C and 35±2°C in a controlled environment incubator shaker G-25 (New Brunswick Scientific Co. Inc., USA). For sorption experiments of Cs^+ and Sr^{2+} five concentrations levels (i.e. 0.1, 0.5, 1, 5 and 10 mM) were used, while desorption was tested at the highest concentration level (10 mM). A 0.01 M $CaCl_2$ solution was used as background electrolyte in all sorption experiments and as desorption agent.

Following the last pre-equilibration step, 20 mL of Cs or Sr solution (using a soil/solution ratio of 1/5) were added to centrifugation tubes, shaken and centrifuged as performed during pre-equilibration. Regarding OECD Guideline no. 106 (OECD, 2000) a shaking time of 24 h was evaluated for Sr^{2+}, while for Cs^+ a reasonable shaking time of 72 h was applied (Cornell, 1993; Staunton, 1994; Valcke and Cremers, 1994). After centrifugation a 10 mL aliquot was taken to determine Cs and Sr concentration by inductively coupled plasma mass spectrometry (ICP-MS) using either Elan 6100 (Perkin Elmer, Rodgau, Germany) or Agilent 7500 (Agilent Technologies, Boeblingen, Germany). For ICP-MS, quantification was performed by external calibration monitoring isotopes Cs-133, Sr-86 and Sr-88 in addition to Rh-103 as the internal standard. A 10 mL aliquot was stored as backup and for pH measurement. For desorption study 20 mL 0.01 M $CaCl_2$ solution was added to centrifugation bottles, shaken for 24 h, centrifuged and solution was sampled as described for sorption step. Centrifugation tubes were weighed at the start and end of each sorption-desorption step to account for residual solution in the centrifugation tubes.

3.2.6 Data evaluation

The sorption-desorption isotherms were obtained by fitting the data with Freundlich equation (Eq. 3.1) using Origin Pro 8G:

$$C_s = K_F C_e^n \qquad (3.1)$$

Where C_s represents concentration of Cs and Sr (mmol kg^{-1}) sorbed on solid-phase at equilibrium and C_e is the equilibrium solution concentration (mmol L^{-1}). The Freundlich capacity parameter (K_F; ($mmol^{1-n}$ L^n Kg^{-1}) reflects sorption capacity, while the Freundlich exponent (n) reflects non-linearity of a sorption process. The Freundlich isotherm provides a good fit to sorption data on heterogeneous surfaces (Dumat *et al.*, 1997; Shahwan and Erten, 2002). The deviation of parameter n from unity represents surface heterogeneity; the more n is close to unity, the more homogeneous is the sorption surface (Sposito, 1984; Dumat *et al.*, 1997; Staunton and Roubaud, 1997). The non-linear behavior of sorption implies, for $n < 1$ or $n > 1$, the energy barrier for sorption increases or decreases exponentially with increasing fraction of filled sites on the adsorbent, i.e. an increase in initial adsorbate concentration results in decrease in Kd value (Shahwan and Erten, 2002). To assess hysteresis (*H*), ratios of the Freundlich exponents for desorption (n_{des}) and sorption (n_{ads}) were reported (O'Connor *et al.*, 1980; Barriuso *et al.*, 1994; Cells *et al.*, 1998; Sander *et al.*, 2005). To assess how the soils (silty loam, loamy sand and sandy clay loam), amendments (biochar, digestate) and temperature (5, 20 and 35 °C) affected the sorption-desorption of Cs and Sr, we performed non-parametric ANOVAs using PerMANOVA software (Anderson, 2001) with Euclidian distance measure and 4999 permutations. In the case that post hoc pair-wise comparisons were made, the Bonferroni correction was used.

3.3 Results and Discussion

3.3.1 Soil properties after incubation

Soil organic carbon concentrations differed depending on soil types and land uses (Table 3.2). Here, forest soils were extremely acidic and showed higher C concentration in comparison to arable soils, which were moderately acidic (Table 3.2). The lowest C concentration was found in arable loamy sand soil, which further had lowest CEC and available K (Table 3.2). Although biochar additions affect soil pH, CEC and surface area of soils (Crane-Droesch *et al.*, 2013; Mukherjee and Lal, 2013; Mukherjee *et al.*, 2015), respective properties of arable soils used in this experiment remained unaffected within a six months incubation period (Table 3.2).

Obviously, the used biochar application rate of 25 t ha^{-1} was insufficient to affect soil pH, CEC and surface area of both arable soils or properties of biochar and soils were at the same range (Crane-Droesch *et al.*, 2013; Borchard *et al.*, 2014). In the same way, application of liquor hardly affected soil pH, CEC and surface area. Contrastingly, both biochar and liquor altered total C and available nutrient concentrations in arable soils, which is in line with assumptions from (Möller and Müller, 2012; Lorenz and Lal, 2014; Mukherjee *et al.*, 2015) as well as findings by Borchard *et al*. (2014) and Fouda *et al*. (2013).

Table 3.1: Basic characteristics of the soils under investigation

Land use	Textural class†	Soil type	Soil texture			Field capacity
			Clay (%)	Silt (%)	Sand (%)	g cm^{-3}
Arable land	Silty loam	Orthic Luvisol	17	79	4	37
Arable land	Loamy sand	Gleyic Cambisol	4	23	73	23
Forest	Sandy clay loam	Dystric Cambisol	34	19	47	37

† FAO (1990): Guidelines for soil profile description. 3rd Ed. Rome. 70 p

Depending on chemical quality (i.e. stability) of added organic substrate (Cayuela *et al.*, 2010) total C increased after biochar addition, but remained unaffected after liquor application. Both amendments provided sufficient amounts of N, which caused an elevation of total N. Effects on nutrients varied due to type of organic amendment and soil texture. For example biochar amendments reduced Ca availability in arable soils, while additions of liquor increased Ca availability in loamy sand, but not in silty loam (Table 3.2). Further, depending on soil texture the effect of biochar and liquor on Mg and K availability varied strongly (Table 3.2), which may limit integration of biochar and liquor into site specific integrated nutrient management systems.

Table 3.2: Soils characteristics after six months incubation at room temperature (5 -15°C).

Land use / soil texture	OA†	pH$_{CaCl2}$	Conductivity	BET‡	CEC§	TOC¶	TC#	TN††	Available nutrients		
									Ca^{2+}	Mg^{2+}	K^{+}
			µS cm^{-1}	m^{2}g^{-1}	cmol$_{c}$ Kg^{-1}		g Kg^{-1}			mg Kg^{-1}	
-/-	Biochar	8.0 ± 0.0	1031 ± 12.5	-/-	-/-	700 ± 0.2	700± 0.1	5.46 ± 0.05	1600 ± 0.05††	1920 ± 0.05††	2570 ± 0.05††
-/-	Liquor	9.3 ± 0.0	15.7 ± 0.2	-/-	-/-	-/-	-/-	-/-	-/-	-/-	-/-
Arable land / silty loam	-/-	6.0 ± 0.2	206.3 ± 3.1	10.3	11.4 ± 0.3	10.4 ± 0.02	11.9 ± 0.05	1.05 ± 0.02	900	130	275
	Biochar	6.2 ± 0.0	197.3 ±4.1	10.6	11.1 ± 0.0	15.6 ± 0.08	17.0 ± 0.09	1.14 ± 0.03	120	33	17
	Liquor	6.4 ± 0.0	290.7 ± 3.3	10.5	11.2 ± 0.1	11.0 ± 0.01	12.3 ± 0.05	1.19 ± 0.02	860	115	175
Arable land / loamy sand	-/-	6.2 ± 0.1	97.3 ± 3.3	1.9	5.1 ± 0.3	6.3 ± 0.08	6.5 ± 0.1	0.59 ± 0.0	1680	110	94
	Biochar	6.1 ± 0.0	87.0 ± 3.3	2.3	4.8 ± 0.4	11.8 ± 0.05	11.9 ± 0.05	0.64 ± 0.01	990	120	240
	Liquor	5.7 ± 0.1	208.0 ± 1.4	1.9	5.3 ± 0.1	6.7 ± 0.01	6.9 ± 0.02	0.71 ± 0.02	4350	190	290
Forest / sandy clay loam	-/-	4.2 ± 0.1	106.3 ± 8.2	25.6	14.7 ± 0.4	17.9 ± 0.01	18.0 ± 0.0	1.75 ± 0.04	4190	165	210

† Organic amendment, ‡ Surface area determined by Brunauer–Emmett–Teller theory (n = 1, r > 0.99), § Cation exchange capacity (n = 2), ¶ Total organic carbon, # Total carbon, ††external laboratory (EN ISO 11885).

3.3.2 Sorption kinetics

Strontium sorption reached equilibrium within 24 h and exhibited this behavior up to day 7 (Figure 3.1). The pre-equilibration of soils with $CaCl_2$ solutions led to the saturation of exchange sites with Ca^{2+} ions, resulting in fast equilibration of Sr^{2+} with Ca^{2+} via ion-exchange. This fast ion exchange process was also witnessed by Rani and Sasidhar (2012) while investigating Sr^{2+} sorption on Kaolinite rich clays. In case of organic soils, high availability of sorption sites resulting from organic functional groups could lead to a fast sorption of Sr^{2+}. Ahmadpour *et al. (2010)* reported a fast (within 5 minutes) Sr^{2+} sorption on almond green hull (an agricultural waste).

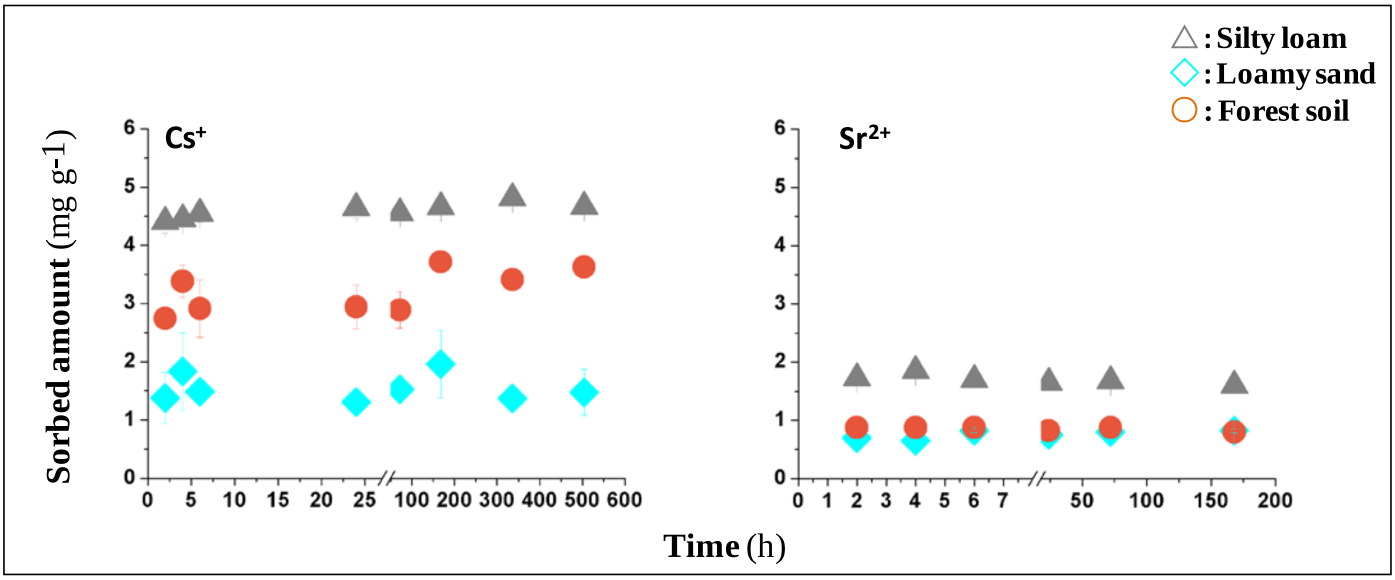

Figure 3.1: Sorption kinetics of Cs$^+$ and Sr^{2+} in three soils. Cs$^+$ sorption for 21 days and Sr^{2+} for 7 days.

Compared to strontium, cesium sorption was non-consistent over time (Figure 3.1). Cesium sorption can continue from hours to weeks depending upon the type of soil, its clay mineralogy and OM content (Cornell, 1993; Valcke and Cremers, 1994; Staunton and Levacic, 1999). Valcke and Cremers (1994) noted a fast sorption (within hours) of radiocesium in soils with high OM content (>80%) compared to the soils with low

OM amount (< 40%) where it took 2-3 weeks to accomplish the sorption. In organic soils, a fast ion-exchange occurs on regular exchange sites (RES) particularly at humic acid sites while in mineral soils with low OM content, cesium sorption occurs in specific sites, FES (Sanzharova *et al.*, 2009), causing a slow sorption process (Valcke and Cremers, 1994; Wauters *et al.*, 1994).

Cesium sorption is a two-stage process, a fast sorption occurring on external sites followed by a slow, diffusion controlled sorption, occurring in internal sites (Sawhney, 1966; Cornell, 1993). In the context of long shaking times causing irregularities in K_d values of Cs^+ sorption, Cornell (1993) concluded the following reasons: 1) weathering of mineral particles generating more sites for sorption, 2) phase changes in clay minerals, leading to new products with different CEC values, 3) possible formation of colloidal particles and cesium sorption on them and 4) dissolution of these colloids with the release of adsorbed cesium. Staunton and Roubaud (1997) used short shaking times of 2 h on illite and montmorillonite clay minerals considering a short contact period of 2 h is enough for ion exchange and longer equilibration times can cause interferences particularly in case of illite. In our soils, mineral fractions are the dominating species for Cs^+ sorption causing an unstable kinetic behavior as reported by other investigators (Cornell, 1993; Valcke and Cremers, 1994).

3.3.3 Effect of soil type, organic amendment and temperature on sorption-desorption

Soil textures and land uses affected sorption behavior of Cs^+ and Sr^{2+} substantially, but application of biochar and liquor had negligible effects on sorption in arable soils (Figure 3.2, Table 3.5). Moreover, varying temperature did not affect ($p<0.05$; Table 3.5) sorption of both Cs^+ and Sr^{2+}. Further, desorption of Cs^+ and Sr^{2+} was governed by soils, but their effect decreased with number of desorption steps, while simultaneously effect of organic soil amendments increased (Table 3.6). The effects of temperature on desorption of Cs^+ and Sr^{2+} were negligible, but interaction between temperature and soil properties increased within desorption sequence (Table 3.6).

Cesium

Sorption of Cs^+ followed non-linear behavior (Freundlich equation, Figure 3.2) due to heterogeneity of sorption surfaces indicated by Freundlich exponents (i.e. n; Table 3.3; (Dumat *et al.*, 1997). Surface heterogeneity caused saturation of high affinity sorption sites with Cs^+ at lower concentration levels, which decreased potential Cs^+ affinity at higher concentration levels (Dumat *et al.*, 1997; Staunton and Roubaud, 1997). Sorption capacity (K_{Fads}) differed between soil textures, which was 4 to 5 times higher for silty loam soil from arable land than for loamy sand from arable land and nearly twice as high as than those of sandy clay loam soil from forest (Table 3.3, Figure 3.2).

Particularly, the higher CEC of silty loam soil and sandy clay loam soil compared to loamy sand (Table 3.2) led to higher Cs^+ sorption in these soils. Surprisingly, sandy clay loam from forest with larger CEC and BET values and comparable clay content to silty loam from arable land (Table 3.1 & 3.2), exhibited a lower sorption capacity. This distinct behavior of Cs^+ sorption in forest soil could be the result of higher soil OM concentration, which can inhibit sorption of Cs^+ on planar sites of clay minerals due to competition with soil organic carbon moieties (Dumat *et al.*, 1997; Dumat and Staunton, 1999; Rigol *et al.*, 2002). Additionally, the acidic nature of forest soil caused lower Cs^+ sorption compared to silty loam from arable land (Giannakopoulou *et al.*, 2007). At acidic pH, higher concentration of H^+ ions could compete with Cs^+ for the available sorption sites. Also, at low pH levels, there is possibility of dissolution of clay minerals with destruction of sorption sites leading to a lower Cs^+ sorption (Giannakopoulou *et al.*, 2007). Thus, rather soil properties and related land uses affected sorption of Cs^+ than nature of applied OM.

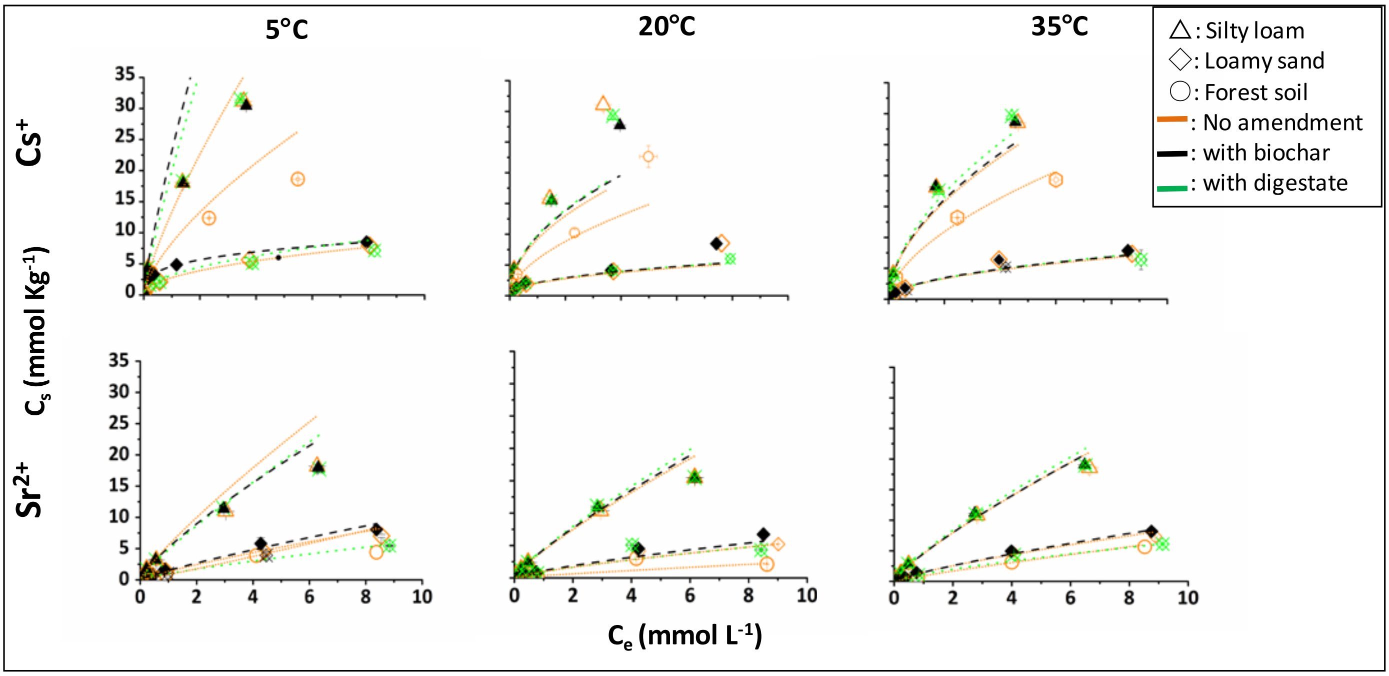

Figure 3.2: Sorption dynamics of Cs^+ and Sr^{2+} at three different temperatures: 5, 20 (room temperature) and 35°C in different soils. Data fitted with Freundlich model ($Cs = Ce\ K^n$), Cs is the analyte concentration in solid phase, Ce is the equilibrium solution concentration. Data represents mean ± one standard deviation (n=3).

Retention capacity of Cs^+ was substantially governed by soils, but in arable soils influenced by soil amendment (Tables 3.3 & 3.6). Silty loam soil and sandy clay loam soil retained more Cs^+ due to their higher clay content (170 g_{clay} kg^{-1} and 340 g_{clay} kg^{-1} respectively, Table 3.1) compared to clay poor loamy sand soil (40 g_{clay} kg^{-1}). The latter is in line to other investigations (Hsu and Chang, 1994; Dumat *et al.*, 1997; Staunton *et al.*, 2002), which clearly showed that soils rich in clay minerals provide higher capability to retain Cs^+ than coarse textured sandy soil and organic soils (Cornell, 1993; Comans *et al.*, 1998; Hakem *et al.*, 2000; Thored, 2010). Soil OM can also sorb Cs^+; however amount of Cs^+ sorbed on clay will be preferentially higher (Dumat and Staunton, 1999; Staunton and Levacic, 1999; Rigol *et al.*, 2002). However, reversibility of sorbed Cs^+ might be affected by soil OM due to competitive sorption on clay minerals, which our results suggest by decreasing effect size of factor soil (i.e. different clay contents) in comparison to increased proportion of effect size of factor organic amendment within desorption sequence (Table 3.6).

While considering the role of OM on Cs$^+$ sorption in soil, an important question is whether the interaction of Cs$^+$ is controlled by OM or by mineral components. In case of soils with higher amounts of OM, it is well established that radiocesium fixation is reduced due to a lack of clay content (Dumat and Staunton, 1999; Rigol *et al.*, 2002). Some authors reported that cesium fixation is governed by mineral components (Cremers *et al.*, 1990) not by OM (Carlsen *et al.*, 1984). Staunton (2002) assumed that the nature of OM and its interaction with the mineral components is as important as the amount of OM. Judging from our data, the nature of OM seems to a play a role in slightly retention of Cs$^+$ in the forest soil compared to biochar amended silty-loam soil (Figure 3.2, Table 3.3) which has a comparable OM content (Table 3.2).

In principle, sorption and desorption of Cs$^+$ in soils can be affected by temperature due to alteration of specific sorption on clay minerals (Cornell, 1993; Hadadi *et al.*, 2009; Yıldız *et al.*, 2011). However, in our study effect of temperature on Cs$^+$ sorption was negligible but interaction between soil types (i.e. soil texture and organic amendment) and temperature changed within successive desorption (Tables 3.3 & 3.6). In general Cs sorption was higher at 5°C compared to higher temperatures (20 and 35°C) in arable soils, while forest soil reflected an opposing trend to arable soils.

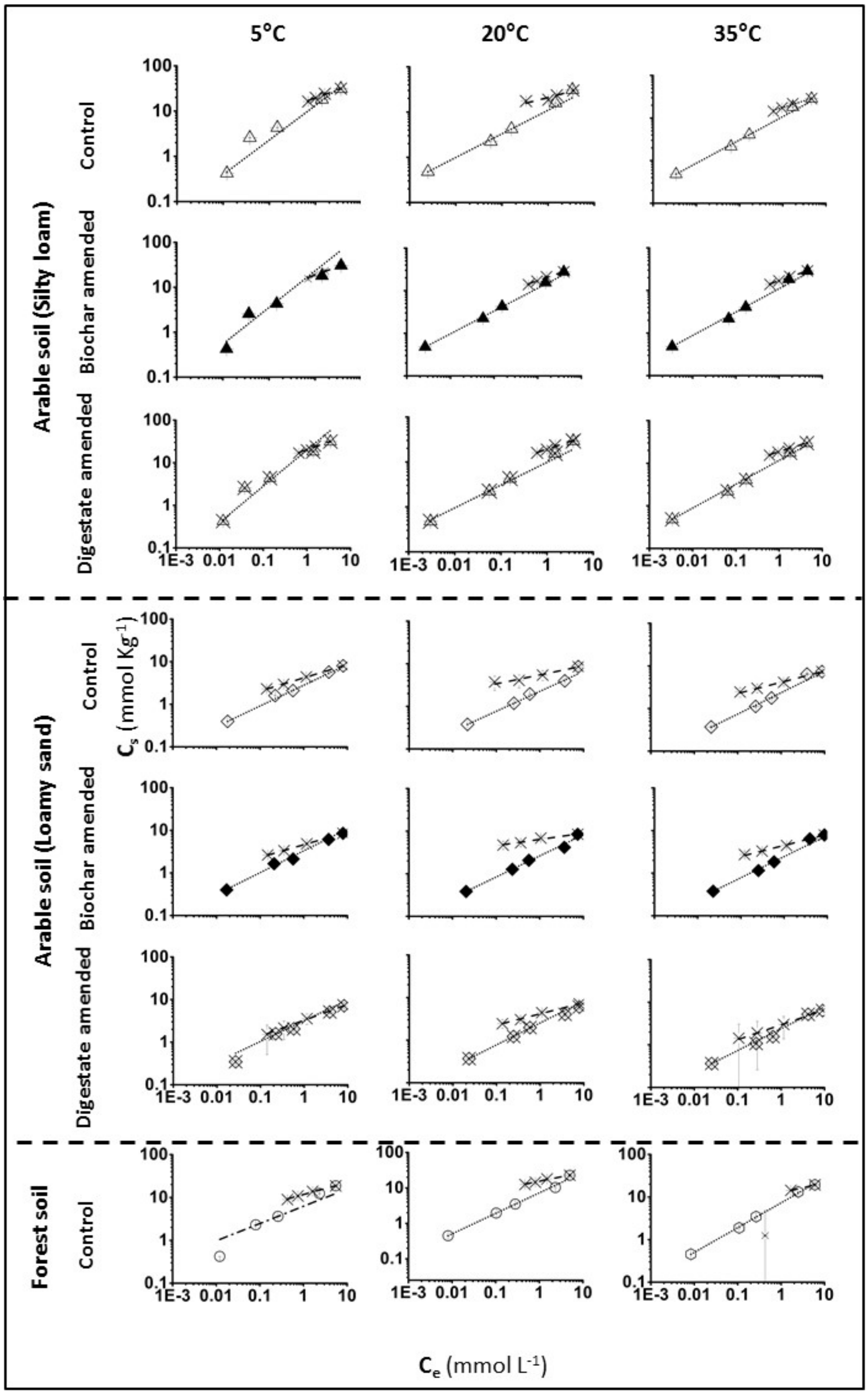

Figure 3.3: Freundlich sorption-desorption isotherms for Cs$^+$ in different soils at three temperatures. Δ , ◊ and ○ represents sorption while x stands for desorption (10mM). Data fitted with Freundlich model (Cs = Ce K^n), Cs is the analyte concentration in solid phase, Ce is the equilibrium solution concentration. Data represents mean ± one standard deviation (n=3).

Table 3.3: Parameters (± standard error) of the Freundlich isotherm for Cs^+ sorption-desorption isotherm and hysteresis index.

T	Land use/ soil texture	OA	Sorption			Desorption			H
°C			K_{Fads}	n_{ads}	R^2	K_{Fdes}	n_{des}	R^2	
			(mmol^{1-n} L^n Kg^{-1})	(-)	(-)	(mmol^{1-n} L^n Kg^{-1})	(-)	(-)	(-)
5	Arable land / silty loam	-/-	13.32 ± 2.25	0.76 ± 0.05	0.88	19.55 ± 0.62	0.37 ± 0.03	0.99	0.48
		Biochar	23.14 ± 15.11	0.81 ± 0.18	0.56	18.72 ± 0.5	0.38 ± 0.02	0.99	0.47
		Liquor	19.89 ± 10.01	0.85 ± 0.13	0.63	20.39 ± 0.46	0.36 ± 0.03	0.98	0.42
	Arable land / loamy sand	-/-	2.79 ± 0.08	0.49 ± 0.01	0.99	4.16 ± 0.03	0.31 ± 0.00	0.99	0.64
		Biochar	3.32 ± 0.28	0.51 ± 0.03	0.97	4.60 ± 0.02	0.30 ± 0.00	1.00	0.58
		Liquor	3.20 ± 0.42	0.49 ± 0.08	0.92	3.27 ± 0.06	0.37 ± 0.01	0.99	0.76
	Forest /sandy clay loam	-/-	6.24 ± 0.84	0.40 ± 0.03	0.93	11.71 ± 0.24	0.27 ± 0.01	0.99	0.68
20	Arable land / silty loam	-/-	10.98 ± 0.26	0.52 ± 0.00	0.99	21.02 ± 1.17	0.26 ± 0.06	0.88	0.55
		Biochar	9.72 ± 0.77	0.51 ± 0.01	0.99	17.65 ± 0.6	0.33 ± 0.03	0.98	0.65
		Liquor	9.84 ± 0.76	0.51 ± 0.01	0.99	19.31 ± 0.59	0.34 ± 0.03	0.97	0.67
	Arable land / loamy sand	-/-	2.25 ± 0.06	0.47 ± 0.00	0.99	5.47 ± 0.21	0.21 ± 0.02	0.96	0.45
		Biochar	2.63 ± 0.1	0.50 ± 0.01	0.99	6.40 ± 0.18	0.15 ± 0.02	0.96	0.29
		Liquor	2.54 ± 0.06	0.51 ± 0.00	0.99	4.15 ± 0.09	0.26 ± 0.01	0.99	0.51
	Forest /sandy clay loam	-/-	5.95 ± 0.22	0.57 ± 0.00	0.99	13.52 ± 0.47	0.26 ± 0.03	0.97	0.46
35	Arable land / silty loam	-/-	10.78 ± 0.47	0.55 ± 0.00	0.99	17.71 ± 0.50	0.32 ± 0.02	0.98	0.57
		Biochar	11.00 ± 0.06	0.55 ± 0.01	0.99	16.95 ± 0.37	0.35 ± 0.02	0.99	0.64
		Liquor	11.64 ± 0.64	0.56 ± 0.01	0.99	18.67 ± 0.33	0.32 ± 0.02	0.99	0.57
	Arable land / loamy sand	-/-	2.35 ± 0.14	0.50 ± 0.02	0.98	4.13 ± 0.08	0.26 ± 0.01	0.99	0.52
		Biochar	2.45 ± 0.13	0.50 ± 0.02	0.99	4.47 ± 0.09	0.26 ± 0.01	0.99	0.52
		Liquor	2.39± 0.10	0.51 ± 0.01	0.98	2.95 ± 0.05	0.35 ± 0.01	0.99	0.68
	Forest /sandy clay loam	-/-	7.29 ± 0.32	0.58 ± 0.01	0.99	12.40 ± 1.78	0.25 ± 0.10	0.65	0.42

T: Temperature; OA: Organic amendment; K_F: Freundlich capacity parameter; n: Freundlich linearity parameter, H: Hysteresis index

Silty loam soil showed higher Cs^+ sorption at 5°C compared to room temperature (20°C) and 35°C (Table 3.3). The effect was more pronounced in amended soils due to altered affinity, which was shown by almost doubled K_{Fads} values if compared to the control soil (Table 3.3). Loamy sand soil followed a similar trend to silty loam for Cs^+ sorption; however the effect was not as prominent as in silty loam. Contrasting to arable soils, sandy clay loam soil from forest exhibited slightly higher Cs^+ sorption at 35°C compared to 5 and 20°C, where it was nearly equal (K_{Fads} values, Table 3.3).

Cs^+ retention was elevated at 5°C, but reduced at 35°C when compared to 20°C in silty loam soil, while in loamy sand and forest soils, the trend was opposite. Non-amended and amended silty loam soils presented a 12 to 37% higher hysteresis at 5°C compared to the corresponding hysteresis at 20°C (H values, Table 3.3); however, the effect of temperature variation from 35 to 20°C was negligible. Forest soil presented an opposing trend to silty loam soil with lower Cs^+ retention with decrease in temperature (H values, Table 3.3). Loamy sand soil showed drastic changes in hysteresis with temperature variation. Control and digestate amended loamy sand soils presented ~13-25% increase in hysteresis from 35 to 20°C but a 42-50% decrease in hysteresis from 20 to 5°C. Biochar amended loamy sand soil showed highest variation with temperature change, with ~44% increase in hysteresis from 35° to 20°C and about 100% reduction in hysteresis with decrease in temperature from 20°C to 5°C.

In literature, a varying trend of Cs^+ sorption with change in temperature was described (Cornell, 1993; Hadadi *et al.*, 2009; Yıldız *et al.*, 2011). A decrease in Cs^+ sorption was reported by Cornell (1993) on montmorillonite, chlorite and kaolinite with increase in temperature from 20 to 80°C. Contrastingly, Yildiz*et al.*, (2011) observed an increase in thermodynamic parameters with increasing temperature (5-25°C) for Cs^+ sorption on bentonite, kaolinite and zeolite. Also, Hadadi *et al.*, (2009) noted an increase in Cs^+ sorption K_d on vermiculite with increase in temperature from 25 to 95°C. The variation in Cs^+ sorption with changing temperature could be attributed to difference in soil texture and its clay mineralogy. In our results, mineral soils followed a similar trend to Cornell (1993). However an opposing behavior of forest soil (Wu) compared to mineral soils could be due to difference in its clay mineralogy and origin of OM.

Strontium

Compared to Cs^+, sorption capacity of Sr^{2+} was nearly half in all soils (Figure 3.2). Moreover, the Freundlich linearity parameter *n* was close to unity (Table 3.4), indicating homogeneity of sorption surfaces for Sr^{2+}, which indicates that Sr^{2+} interaction in mineral soils is less affected by clay content (Sanchez *et al.*, 1988; van Bergeijk *et al.*, 1992) as previously shown from Cs^+ (Cornell, 1993; Dumat *et al.*, 1997; Staunton and Levacic, 1999). Thus, even larger CEC and BET in forest soil (Table 3.2), Sr^{2+} sorption capacities were lower than those found for arable soils. In detail, silty loam soil from arable land demonstrated 4 to 5 times higher Sr^{2+} sorption compared to loamy sand from arable land and sandy clay loam from forest area (Table 3.4). This implies that Sr^{2+} being a di-valent cation had limited accessibility to sorption sites in clay accessible for mono-valent cations (e.g. Cs^+) (Sawhiney, 1972). Yet, soils explained majority of Sr^{2+} sorption variability, despite any addition of organic material (Table 3.5).

Additions of biochar and digestate failed to affect sorption of Sr^{2+} substantially (Table 3.5). Surprising, despite a ~50 % increase in OM (TOC values, Table 3.2) after biochar application, Sr^{2+} sorption in silty loam soil was not affected. Contrarily a ~90 % increase in OM content with the same amendment (biochar) led to an increase in sorption capacity of loamy sand. In fact in silty loam soil, the number of OM sorption sites were reduced due to possible interaction between OM and clay and silt fractions (Dumat *et al.*, 1997; Cheshire *et al.*, 2000). Contrastingly, in loamy sand the lack of interaction between OM and sand particles led to the higher availability of OM sites for Sr sorption. Moreover, increase in Ca^{2+} concentration in loamy sand after digestate addition decreased the Sr^{2+} sorption due to competition for the available sorption sites. Similar to our results, Rani and Sasidhar (2012) and Bunde *et al* (1997) also reported lower Sr^{2+} sorption with increasing Ca^{2+} concentration in soil. However, the effect of Ca^{2+} content was less effective in biochar amended soils. In silty loam soil, a decrease in Ca^{2+} concentration after biochar amendment (Ca^{2+} values, Table 3.2), did not affect sorption capacity of silty loam soil.

Desorption of Sr^{2+} was largely affected by soils (Table 3.4), which were reduced in arable soils due to organic amendments (Table 3.4 & 3.6). Compared to arable soils the acidic nature of forest soil contributed to higher retention of Sr^{2+} (van Bergeijk *et al.*, 1992; Baeza *et al.*, 1995; Sanzharova *et al.*, 2009). At low pH, where humic acids are insoluble, Sr^{2+} interaction with OM is strong compared to typical ion-exchange reaction resulting in higher Sr^{2+} retention (Sanchez *et al.*, 1988). In mineral soils, Sr^{2+} sorbs on exchange sites and is easily displaced by competing cations (e.g. Ca^{2+}) (Nilsson *et al.*, 1985; Sanzharova *et al.*, 2009), which explained larger effect size of soil compared to organic amendment within desorption sequence (Table 3.6). Soil organic material bounds Sr^{2+} through chelation and complexation (Saar and Weber, 1982; Sanchez *et al.*, 1988), which explains lasting effect on Sr^{2+} retention (Table 3.4 & 3.6).

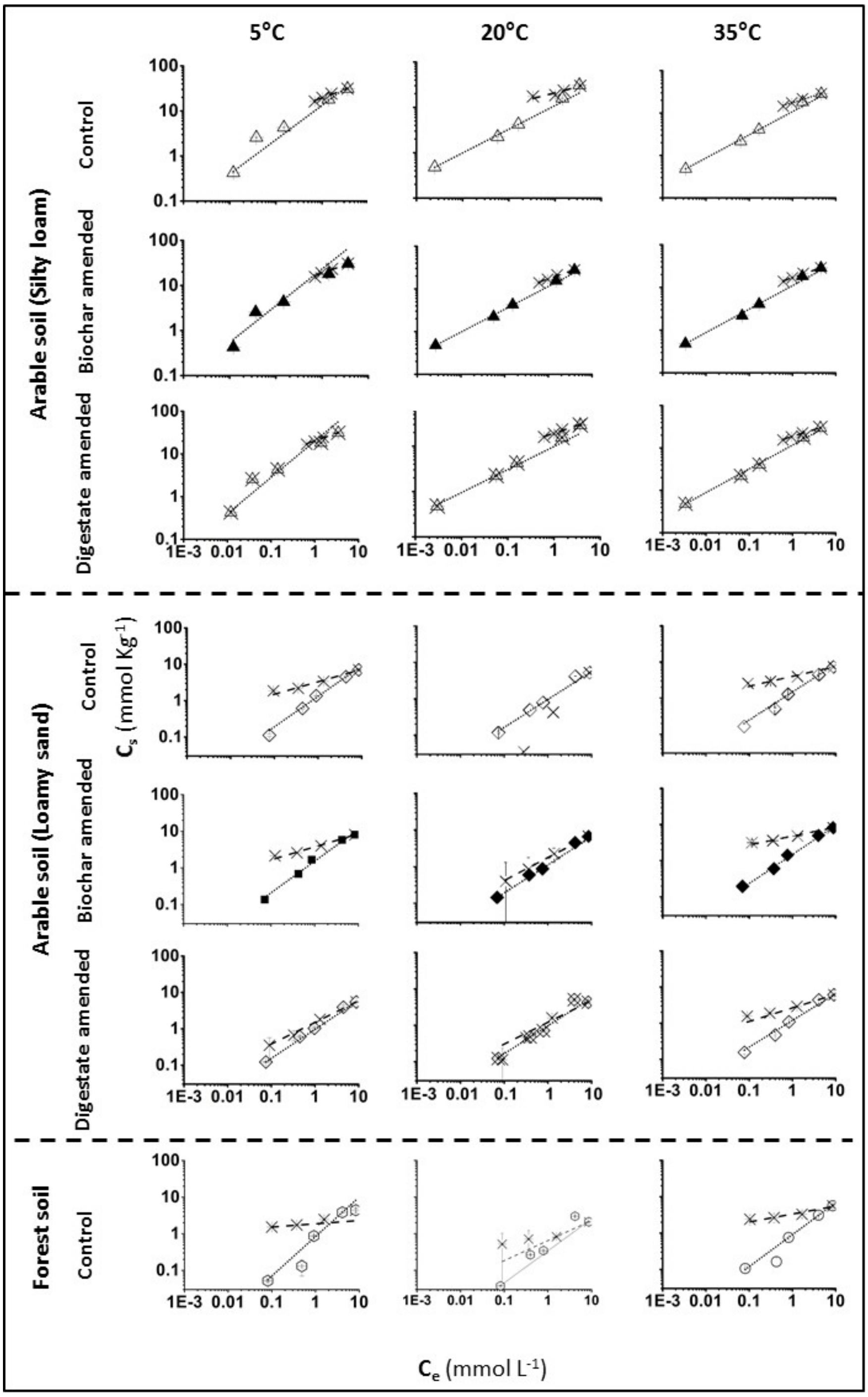

Figure 3.4: Freundlich sorption-desorption isotherms for Sr^{2+} in different soils at three temperatures. Δ , ◊ and ○ represents sorption while x stands for desorption (10mM). Data fitted with Freundlich model (Cs = Ce K^n), Cs is the analyte concentration in solid phase, Ce is the equilibrium solution concentration. Data represents mean ± one standard deviation (n=3).

Table 3.4: Parameters (± standard error) of the Freundlich isotherm for Sr^{2+} sorption-desorption isotherm and hysteresis index.

T	Land use/ soil texture	OA	Sorption			Desorption			H
°C			K_{Fads}	n_{ads}	R^2	K_{Fdes}	n_{des}	R^2	
			(mmol^{1-n} L^n Kg^{-1})	(-)	(-)	(mmol^{1-n} L^n Kg^{-1})	(-)	(-)	(-)
5	Arable land / silty loam	-/-	5.55 ± 0.77	0.85 ± 0.07	0.95	7.00 ± 0.57	0.53 ± 0.05	0.98	0.62
		Biochar	5.16 ± 0.55	0.80 ± 0.06	0.96	6.56 ± 0.58	0.55 ± 0.05	0.99	0.69
		Liquor	4.80 ± 0.31	0.85 ± 0.02	0.98	7.08 ± 0.61	0.51 ± 0.06	0.97	0.60
	Arable land / loamy sand	-/-	1.32 ± 0.10	0.84 ± 0.06	0.97	3.31 ± 0.21	0.34 ± 0.04	0.97	0.40
		Biochar	1.52 ± 0.13	0.86 ± 0.08	0.95	3.74 ± 0.19	0.36 ± 0.03	0.99	0.42
		Liquor	0.97 ± 0.02	0.80 ± 0.00	1.00	1.50 ± 0.06	0.59 ± 0.02	1.00	0.74
	Forest /sandy clay loam	-/-	0.84 ± 0.08	1.08 ± 0.06	1.00	1.88 ± 0.20	0.09 ± 0.05	0.31	0.08
20	Arable land / silty loam	-/-	4.25 ± 0.19	0.82 ± 0.02	0.99	5.41 ± 0.78	0.59 ± 0.09	0.95	0.72
		Biochar	4.05 ± 0.18	0.81 ± 0.02	0.99	4.96 ± 0.69	0.64 ± 0.09	0.95	0.78
		Liquor	4.06 ± 0.14	0.82 ± 0.01	1.00	5.19 ± 0.72	0.61 ± 0.09	0.95	0.74
	Arable land / loamy sand	-/-	0.96 ± 0.03	0.77 ± 0.02	0.99	n.d	n.d	n.d	n.d
		Biochar	1.12 ± 0.06	0.76 ± 0.02	0.98	1.76 ± 0.07	0.62 ± 0.02	0.99	0.82
		Liquor	0.97 ± 0.05	0.77 ± 0.04	0.99	1.21 ± 0.17	0.60 ± 0.07	0.99	0.78
	Forest /sandy clay loam	-/-	0.34 ± 0.04	0.87 ± 0.04	0.90	0.65 ± 0.01	0.55 ± 0.01	1.00	0.63
35	Arable land / silty loam	-/-	4.51 ± 0.17	0.81 ± 0.02	1.00	6.88 ± 0.56	0.53 ± 0.05	0.98	0.65
		Biochar	4.55 ± 0.15	0.81 ± 0.02	0.99	7.99 ± 0.32	0.47 ± 0.03	0.99	0.58
		Liquor	4.77 ± 0.17	0.81 ± 0.02	0.99	7.40 ± 0.28	0.51 ± 0.02	1.00	0.63
	Arable land / loamy sand	-/-	1.48 ± 0.06	0.78 ± 0.04	0.99	4.03 ± 0.25	0.27 ± 0.03	0.98	0.35
		Biochar	1.48 ± 0.10	0.80 ± 0.05	0.96	4.78 ± 0.18	0.25 ± 0.02	0.99	0.31
		Liquor	1.19 ± 0.22	0.74 ± 0.08	1.00	2.65 ± 0.00	0.38 ± 0.00	1.00	0.51
	Forest /sandy clay loam	-/-	0.91 ± 0.06	0.88 ± 0.04	0.98	3.35 ± 0.25	0.22 ± 0.04	0.88	0.25

T: Temperature; S: Soil; OA: Organic amendment; K_F: Freundlich capacity parameter; n: Freundlich linearity parameter, H: Hysteresis index

In line with findings for Cs^+ (see above) temperature had small effects on Sr^{2+} sorption and desorption in the studied soils and their treatments amended with biochar and digestate (Tables 3.4, 3.5 & 3.6), which is in line with findings of Ahmadpour *et al*. (2010). However, depending on clay mineralogy an elevated Sr^{2+} affinity may occur (Rani and Sasidhar (2012)) as indicated by significant interaction between soil type and temperature (Table 3.4 & 3.6). In general, Sr^{2+} retention was low at room temperature (20°C) compared to 5°C and 35°C in three soils in absence of any amendment.

Temperature did not induce a considerable impact on Sr^{2+} retention in silty loam soil after amendments. However, in biochar and digestate amended loamy sand, Sr hysteresis was either decreased (35°C to 20°C) or increased (20°C to 5°C) when compared to room temperature (H values, Table 3.4). Sr^{2+} showed a varying desorption trend at different desorption levels in amended soils when compared to control. In unamended soils, temperature effect decreased in sequential desorption steps; however in amended soils, temperature showed a drastic increase from desorption level 1 to 2 followed by a decrease from desorption level 2 to 3 (Table 3.6). Moreover, in unamended soils, the interaction between soils and temperature was higher at 5 and 35 °C compared to room temperature (20 °C). While in amended soils, the interaction among main factors (soil, organic amendment and temperature) reflected an increase in successive desorption levels.

Table 3.5: Effect strength (i.e. η^2 provides a value that describes percentage of explained variability) of factors soil, organic amendment and temperature on sorption of Cs^+ and Sr^{2+}. Three soils (i.e. arable silt loam, arable loamy sand, forest sandy clay loam) and three amendments (i.e. no amendemnt as control treatment, biochar and digestate amendmemt) were used. Data were split into two data sets consisting of all soils without organic amendment and arable soils with organic amendment. Statistics were performed using MANOVA (software PerMANOVA, see also Anderson et al. 2001).

Arable and forest soils without organic amendment

Source	η^2_{Cs}	η^2_{Sr}
Soil (S)	$94_{2,282}$***	$94_{2,328}$***
Temperature (T)	$2_{2,6}$***	$2_{3,10}$***
TxS	$1_{4,1}$	$1_{4,1}$

Arable soils with organic amendment

Soil (S)	$97_{1,2649}$***	$94_{1,7089}$***
Organic amendment (OA)	$0_{2,1}$	$1_{2,64}$**
Temperature (T)	$1_{2,19}$***	$1_{2,10}$***
TxS	$0_{2,4}$*	$0_{2,1}$
SxOA	$0_{2,3}$	$1_{2,7}$**
TxSxOA	$0_{4,1}$	$0_{4,1}$

F statistics is indicated and shows degree of freedom and F value, level of significance is indicated as ***$p<0.001$, **$p<0.01$ and *$p<0.05$.

Table 3.6: Effect strength (i.e. η^2 provides a value that describes percentage of explained variability) of factors soil, organic amendment and temperature on successive desorption of Cs^+ and Sr^{2+} (i.e. three successive desorption steps). Three soils (i.e. arable silt loam, arable loamy sand, forest sandy clay loam) and three amandments (i.e. no amendemnt as control treatment, biochar and digestate amendmemt) were used. Data were split into two data sets consisting of all soils without organic amendment and arable soils with organic amendment. Statistics were performed using MANOVA (software PerMANOVA, see also Anderson et al. 2001).

Desorption level	Source	Arable and forest soil without organic amendment (OA)		Arable soils with organic amendment	
		η^2_{Cs}	η^2_{Sr}	η^2_{Cs}	η^2_{Sr}
Step 1	Soil (S)	$81_{2,47}$***	$39_{2,27}$***	$55_{1,81}$***	$40_{1,46}$***
	Organic Amendment	-/-	-/-	$3_{2,2}$	$3_{2,2}$
	Temperature (T)	$2_{2,1}$	$9_{2,6}$**	$6_{2,4}$*	$0_{2,0}$
	S x T	$1_{4,0}$	$39_{4,14}$***	$4_{2,3}$	$12_{2,7}$***
	S x OA	-/-	-/-	$5_{2,3}$*	$3_{2,2}$
	OA x T	-/-	-/-	$1_{4,0}$	$6_{4,2}$**
	S x T x OA	-/-	-/-	$1_{4,0}$	$5_{4,2}$
Step 2	Soil (S)	$14_{2,3}$	$55_{2,21}$***	$19_{1,14}$***	$8_{1,9}$***
	Organic Amendment	-/-	-/-	$10_{2,4}$*	3_{2},1
	Temperature (T)	$15_{2,3}$	$5_{2,2}$	$2_{2,1}$	$13_{2,7}$***
	S x T	$30_{4,3}$**	$15_{4,3}$	$2_{2,1}$	$28_{2,15}$***
	S x OA	-/-	-/-	$3_{2,0}$*	$2_{2,1}$
	OA x T	-/-	-/-	$11_{4,0}$	$6_{4,1}$
	S x T x OA	-/-	-/-	$4_{4,1}$	$7_{4,2}$
Step 3	Soil (S)	$8_{2,1}$	$13_{2,3}$*	$5_{1,4}$*	$2_{1,2}$
	Organic Amendment	-/-	-/-	$11_{2,5}$**	$11_{2,5}$**
	Temperature (T)	$9_{2,2}$	$3_{2,1}$	$5_{2,2}$	$8_{2,3}$*
	S x T	$30_{4,3}$*	$34_{4,3}$**	$6_{2,3}$	$2_{2,1}$
	S x OA	-/-	-/-	$11_{2,5}$**	$11_{2,5}$**
	OA x T	-/-	-/-	$12_{4,3}$*	$11_{4,3}$*
	S x T x OA	-/-	-/-	$11_{4,3}$*	$12_{4,3}$*

F statistics is indicated and shows degree of freedom and F value, level of significance is indicated as ***$p<0.001$, **$p<0.01$ and *$p<0.05$.

3.4 Conclusion

The applied amendments with field application rates did not change the sorption behavior of cesium and strontium while the effect of soil texture and land use was more pronounced. The trend was similar for desorption, where differences were more prominent in soils of different origin than by added amendments. However, the two radionuclides showed a distinct behavior in sorption-desorption dynamics. Cesium showed highest sorption in arable silty loam soil, followed by forest soil and lowest in arable loamy sand. Strontium sorption was nearly half compared to cesium in all soils with higher sorption in silty loam and almost similar sorption in loamy sand and forest soils. Strontium retention was higher in forest soil compared to the arable soils (with and without organic amendment); presumably this was the result of difference in nature of OM. In general, temperature did not cause a substantial effect on sorption-desorption of the investigated radionuclides, however some variations were observed. Silty loam soil presented higher sorption and affinity for Cs^+ at 5°C compared to higher temperatures (20 and 35°C) contrasting to forest soil where the trend was just opposite. Cesium sorption in loamy sand was least affected by temperature change. Temperature showed erratic changes in Sr^{2+} sorption and affinity in different soils. In general, Sr^{2+} sorption and affinity was higher at 5 and 35°C compared to room temperature (20°C). We conclude that organic amendments with applied rates will not affect the soil-plant transfer of investigated radionuclides. Furthermore, temperature variation in the range 5-35°C will not influence the sorption-desorption dynamics of the two radionuclides.

4. Mobility and plant uptake of Cs-137 and Sr-90 in digestate amended silty loam Luvisol - a lysimeter experiment

4.1 Introduction

The radionuclides (RN) Cs-137 and Sr-90 released from nuclear power plants accidently pose a long term threat to human populations due to their high radio-toxicity and long half-lives of 30 and 28 years, respectively (Sanzharova *et al.*, 2009; Vajda and Kim, 2010). The interaction of these RN with soil constituents affect their release into groundwater, uptake in plants and thus, and ultimately their access into humans through the food chain (Zhu and Smolders, 2000; Alexakhin *et al.*, 2006). Plants can absorb elements from air by above ground plant parts (e.g. leaves) and take them up from soil via their roots (Kabata-Pendias, 2011). Root uptake is considered the dominant pathway with regard to soil-borne radioactive contamination. In contrast to metal nutrients (e.g. K^+, Ca^{2+}) the uptake of RN is less investigated (Kabata-Pendias, 2011); however, it show similar chemical behaviour (Kabata-Pendias, 2011).

The root uptake of RN is influenced by a number of abiotic and biotic factors that include chemical behavior of RN, soil properties (soil texture, OM, pH, and concentration of competing ions), land use and plant species (Konoplev *et al.*, 1993; Forsberg *et al.*, 2001; Lukšienė *et al.*, 2013; Penrose *et al.*, 2015), but effects of soil amendments (e.g. biochar and digestate) were so far hardly considered.

The mobility of Cs in soil is affected by organic and inorganic soil components (Cornell, 1993; Dumat *et al.*, 1997). Clay minerals sorb Cs in frayed edge sites (Cornell, 1993; Fuller *et al.*, 2015), but interaction with soil OM is weak. Thus, in soils with high organic content majority of Cs is mobile (Saar and Weber, 1982; Sanchez *et al.*, 1988). In contrast, Sr is reversibly sorbed via ion-exchange to soil minerals like silt and clay but can be strongly bound to OM via chelation and complexation (Nilsson *et al.*, 1985; Sanchez *et al.*, 1988; van Bergeijk *et al.*, 1992; Sanzharova *et al.*, 2009). Thus, RN mobility in soils is mainly governed by soil properties, but land use and plants can modify mobility and distribution of RN in soils as well.

4. Mobility and plant uptake of Cs-137 and Sr-90 in digestate amended silty loam Luvisol - a lysimeter experiment

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The distribution of RN in the soil is affected by land use and soil management practices (Nisbet, 1993; Ivanov *et al.*, 1997; Forsberg *et al.*, 2000; Zhu and Smolders, 2000; Forsberg *et al.*, 2001). Askbrant *et al* (1996) observed that 95 % of Cs-137 remained in the upper-top soil (0 to 6 cm) in undisturbed sandy Podzol, while cultivation of adjacent soil mixed Cs-137 nearly homogeneously within the top 25 cm soil. Thus, agricultural practices affect distribution and bioavailability of RN by physical dilution like ploughing and disking (Lembrechts, 1993; Nisbet, 1993; Nisbet *et al.*, 1993; Camps *et al.*, 2004).

Cultivation of crops requires commonly use of fertilizers and lime that alter concentration of major soil nutrients (Ca^{2+}, Mg^{2+}, K^+, NH_4^+), which may cause a mobilization of competitive ions. As an example fertilization with lime and dolomite led to a 10 fold lower root uptake of Cs-137 in a Luvisol covered by spruce (*Picea spec.*) forest in southern Germany due to addition of competitive calcium and magnesium (Zibold *et al.*, 2009). Camps *et al* (2004) reported decrease in TF of radiostrontium in peat and podsolic soils after ploughing plus reseeding and for radiocesium with additional effect of K fertilization. Beside the use of mineral fertilizers, the application of organic amendments (e.g. compost, biochar, digestate) can also affect the mobility of RN in soil due to alteration of soil nutrient concentrations and the soil OM content and composition.

A soil organic amendment with increasing significance is digestate, which is the residue from anaerobic biogas production from organic biomass and wastes (Tani *et al.*, 2006; Zhang *et al.*, 2007; Möller and Stinner, 2009; Tambone *et al.*, 2010; Gell *et al.*, 2011). Digestates contain nutrients and OM, and is used therefore to improve soil properties (Tani *et al.*, 2006; Möller and Stinner, 2009; Tambone *et al.*, 2010). Hence, it is necessary to assess the impacts of this amendment on behavior of soil constituents and RN and their incorporation into plants.

Moreover, the distribution of RN in soil will affect the plant uptake depending upon the root system. Further, the capability of a plant to develop an extensive root system differs between monocotyledons and dicotyledons, which may affect their uptake of RN (Denny, 2002; Taiz and Zeiger, 2006). Monocotyledones have fibrous root system while dicotyledons contain a main root axis and branched smaller roots (Denny, 2002; Taiz and Zeiger, 2006). Dicotyledones with stronger roots could have higher accessibility to RN in deeper soil layers resulting in higher plant uptake (Materechera *et al.*, 1991). Gerzabek *et al* (1998) reported ~6 times higher uptake of Cs-137 in dicotyledonous (mustard, sugar beet, potato) compared to monocotyledons species (wheat, maize, rye grass). After uptake the translocation of RN within plants is maintained by transpiration stream and occurs through vascular tissue of plants (Taiz and Zeiger, 2006), which can affect RN distribution in the plant. Although soil application of digestates is beneficial for agricultural production, their effect on contaminants (e.g. Cs-137 and Sr-90) is less investigated.

The accidental releases from nuclear power plants can cause soil contamination of RN and can reach the food chain. So, the parameters that influence the RN mobility in soil and their plant uptake like ploughing, disking and the use of organic amendments need to be investigated. The main objective of this study was to investigate the effect of digestate amendment on the mobility in soil and plant uptake of Cs-137 and Sr-90 by characterization of transfer factors (TF) as a function of plant and radionuclide. The effect of soil physical treatment (e.g. ploughing) on RN distribution and the plant uptake was also accounted for, which is rarely studied with such high activities of artificially applied RN.

4.2 Material and Methods

4.2.1 Chemicals

RN (Cs-137 and Sr-90) were obtained as chloride salts from Russia through Chemotrade GmbH (Düsseldorf, Germany). Potassium bromide (KBr) was purchased from Merck (Darmstadt, Germany).

4.2.2 Digestate

Digestate was obtained from a biogas plant in Schwalmtal (PlanET Biogastechnik GmbH, Vreden, Germany). The digester was operated under mesophilic conditions with a daily feed rate of 60 % maize-silage, 4% chicken manure, 20% beef-urine and 16% pig urine (w/w, fresh content). Only, the liquid fraction of digestate (i.e. liquor) was used in this experiment for better homogeneous incorporation.

4.2.3 Lysimeters preparation

The two lysimeters used in this experiment are part of the lysimeters facility of the Agrosphere institute (IBG-3), Forschungszentrum Jülich (Germany). The soil monoliths were excavated in 2001 (Weihermüller, 2005) from a nearby test site, Merzenhausen (10 kM northwest to the Forschungszentrum Jülich) using cylindrical V_2A-vesels with a diameter of 160 cm and a depth of 250 cm. The description of soil properties at the test site Merzenhausen (i.e. lysimeter soils) are given in Table 4.1. A more detailed information about lysimeter excavation, soil types and important physio-chemical soil properties at the test site Merzenhausen were described by Weihermüller (2005). To avoid the problem of activity analysis (i.e. beta radiation separation from Cs-137 and Sr-90 when both RN are applied together), one lysimeter was specified for Cs-137 and the second for

Sr-90. Each lysimeter was divided into two halves by inserting a metallic plate to a depth of 30 cm of the top soil (Figure 4.1a). With this physical separation, one half of each lysimeter was used for digestate amendment and the other half for control. Main lysimeter work activities are summarized in Table 4.3.

Table 4.1: Selected physio-chemical properties of lysimeter soil, adopted from Weihermüller (2005). All units based on dry mass, except field capacity that based on water saturated soil.

Horizon	**Depth**	**Sand**	**Silt**	**Clay**	**pH**	**CEC**	**Bulk Density**	**Field Capacity**
	cm	%	%	%	-	$cmol_c k^{-1}$	$g\ cm^{-3}$	%
Ap	35	4.7	81.9	13.4	7.1	10.5	1.48	39.2
Al	47	3.1	78.9	18.0	7.1	10.5	1.53	42.2
Bt	97	2.4	74.9	22.7	7.1	11.9	1.54	39.5
Btv	150	2.6	79.4	18.0	7.0	16.3	1.56	39.2
Bv	210	2.9	81.1	16.0	6.8	12.5	1.52	38.0
Bcv	225	4.5	82.8	12.7	7.6	10.0	1.45	37.1
Cv	+280	5.0	81.9	13.1	7.6	15.0	1.59	35.0

Each lysimeter was equipped with seven suction cups and eight percolate collection pans for soil solution sampling. The suction cups were installed horizontally, three at the depth of 40 cm and four at the depth of 120 cm. The used suction cups consisted of borosilicate glass heads (with 1000 hPa air entry value) 32 mm in diameter and 60 mm long, connected to polyvinyl chloride (PVC) pipes (eco Tech UMS Umwelt-Meß-System, Bonn, Germany). The soil water collection at the bottom of the lysimeter (250 cm depth) was carried out using special stainless steel collection pans. The total area of lysimeter bottom (2000 cm^2) was divided into eight segments, each segment having a drainage hole connected to the collection vessel through a plastic pipe. The collection pans were hermetically closed versus the lysimeter cylinders with a tube. The installation of the described equipments was originally done by Weihermüller (2005) in 2002. However, the installation points were resealed with Sika Flex 252 to avoid the risk of possible leakage of radiochemical contaminated water after application of RN.

4.2.3.1 **Digestate application**

Digestate application was done in September 2012. The top 5 cm of soil were removed and the underlying soil (6-15 cm) was ploughed manually. Digestate was mixed into the removed soil in a concrete mixer and mixed soil was spread over the lysimeter surface. The soil of the control half was also mixed in the concrete mixer without amendment addition and placed on the lysimeter surface. We used the top 5 cm soil for digestate mixing for an easier handling and uniform mixing in the concrete mixer. Also ploughing of the lysimeter soil below 15 cm bore a risk of damaging the first set of sensors. Important characteristics of lysimeter soils before and after digestate amendment are summarized in Table 2.

Figure 4.1: a) Metallic plate insertion in lysimeter top soil, b) Soil removal for digestate mixing.

Table 4.2: Relevant soil parameters before and after digestate amendment. Data represents mean ± standard error of duplicate samples (n: 2).

Soil	pH$_{CaCl2}$	BET	CEC	TOC	TC	TN	Ca^{2+}	Mg^{2+}	K^{+}
		m^{2}g^{-1}	cmol$_c$ kg^{-1}		-------------------g kg^{-1}---------------			--------mg kg^{-1}--------	
Control	6.5 ± 0.00	9.6	9.9 ± 0.4	9.9 ± 0.03	10.6 ± 0.00	0.97 ± 0.00	4070	175	250
Amended	6.6 ± 0.00	9.1	10.2 ± 0.2	11.6 ± 0.04	12.4 ± 0.00	1.23 ± 0.00	1730	135	200

4.2.3.2 **Radionuclides application**

RN application to the lysimeter soils was done simultaneously with the summer wheat sowing in March 2013. For this, the top 3 cm of soil from each lysimeter was removed and sieved through a 4 mm mesh. Wheat seeds were spread (24 g/m^2) manually and one third of the sieved soil was spread directly over the seeds (to protect seeds from birds). Two third of the sieved soil was used for RN mixing.

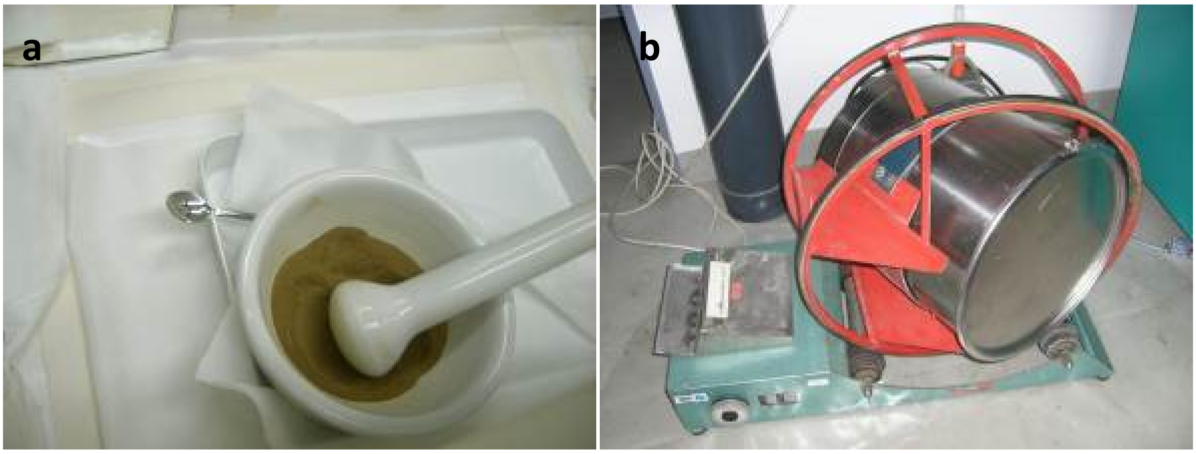

Figure 4.2: RN mixing; a) Ceramic bowl for initial mixing of 100 g combusted soil b) Drum hoop mixer for mixing of 100 g contaminated soil to the remaining top 2 cm soil.

To avoid an initial sorption of RN on soil OM, 100 g of soil from each part of both lysimeters were first combusted at 600°C for 24 h. The combusted soils were spiked drop wise with ten milliliters of RN solution (i.e. approximate activity of 65 MBq for Cs-137 and 18 MBq for Sr-90) and left for drying overnight in a fume hood. The following day, these soils were manually ground and mixed in a ceramic bowl using a pestle (Figure 4.2a). The contaminated soil was then mixed in a drum hoop mixer in several steps in which the amount of soil was gradually increased to the remaining top 2 cm soil (~ 32 Kg) (Figure 4.2b). The contaminated soils were spread over respective lysimeter halves. As a result of this procedure the wheat seeds were covered by 4 cm soil which was close to the recommended practice.

4.2.3.3 **Application of conservative tracer- KBr**

To assess the movement of water in lysimeter soil, a conservative water tracer (Potassium Bromide) was applied with an application rate of 25 g/m^2 of bromide using a hand sprayer. The hand sprayer was weighed before and after the application to determine the actual amount applied.

4.2.4 Sowing and harvesting of plants

Sowing and harvesting of plants were carried out following the practice in the region (North Rhine-Westphalia, Germany). Related agricultural practices such as use of pesticides and fertilizers and use of irrigation in dry periods were restricted to the minimum. Major lysimeter work activities including cultivation of plants and soil sampling are summarized in Table 4.3. Summer wheat (*Triticum aestivum;* Saaten Union GmbH,Isernhagen HB, Germany) was sown in March, 2013. Considering the late sowing and small scale plantation, a seed rate of 500 $seeds/m^2$ (24 g/m^2) was chosen. Seeds were placed manually with a row-row distance of 9 cm and a seed- seed distance of ~2 cm. Summer wheat was harvested at maturity in August 2013. The plants were cut approximately 2 cm above the soil surface.

Terralife - Rigol TR® (Deutsche Saatveredelung AG, Lippstadt, Germany) was sown in September 2013. First, the lysimeter soils were ploughed manually to a depth of 15 cm to simulate the common practice in agriculture. The seeds were spread manually with a seed rate of 5 g/m^2. Terralife® was harvested in December 2013. Summer oat (*Avena sativa*; Berthold Buaer, Obertraubling, Germany) was sown in February 2014 adopting a similar procedure as for summer wheat with a seed rate of 300 seeds/m^2. Preliminary soil ploughing was again done manually using a garden spade to a depth of 15 cm. The seeds were placed manually to a depth of 5 cm and with a row-row distance of ~13 cm. Oat plants were cut 2 cm above the soil surface in July 2014.

4.2.5 Soil water sampling and analysis

Soil water was sampled at three soil depths: 40 cm, 120 cm (suction cups) and 250 cm (percolate collection pans). Suction cups sampling was done once a month by using a vacuum pump. The percolate collection at lysimeter bottom varied from once a month to once a week depending upon the outside weather conditions. The collected soil water samples were analyzed for bromide concentration and radioactivity. Activity analysis was done with liquid scintillation counting (LSC) (LSC Tri Carb, 2500 TR, Canberra Packard, Dreieich, Germany) by adding 10 mL of Ultima Gold scintillation cocktail (Perkin Elmer) to 5 mL sample. Bromide concentration was determined by HPLC (Jasco GmbH, Gross-Umstadt, Germany) with a PRPX100 HPLC column (CS-Chromatographie Service GmbH, Langerwehe, Germany) (125 mm x 3 mm x 10 µm) using an aqueous solution of 4 mM para Hydroxybenzoic acid plus 2.5% Methanol (adjusted to pH 8) as mobile phase with a flow rate of 1 mL min^{-1}. Bromide was detected at 310 nm with a UV detector (Jasco GmbH, Gross-Umstadt, Germany).

Table 4.3: Chronological schedule of lysimeter preparation, radionuclide as well as digestate application, cultivation of plants and their harvest as well as soil sampling.

Day	month/year	Activity	Method
0	09/12	Application of digestate	Top 5 cm soil in concrete mixer
180	03/13	Application of radionuclides	Top 2 cm soil in drum hoop mixer
		Sowing of summer wheat	Seed rate: 500 seeds/m^2
			Seed depth: 4 cm
187	03/13	Application of conservative tracer (KBr)	Hand sprayer (25 g/m^2)
260	06/13	Weed removal	by hand
		Application of nitrogen fertilizer	by hand, KAS (N content: 27%)
344	08/13	Wheat harvest	Plants were cut 2 cm above soil
		1st soil sampling	Humax auger, 0-15 cm
350	09/13	Manual ploughing	Spade, 0-15 cm
		Sowing of TerraLife – Rigol TR®	Seed rate: 25 g/m^2
			Seed depth: 4 cm
445	12/13	Harvest of TerraLife®	Plants were cut 2 cm above soil
526	02/14	2nd soil sampling	Humax auger, 0-20 cm
527	02/14	Manual ploughing	Spade, 0-20 cm
		Sowing of summer oat	Seed rate: 300 seeds/m^2
			Seed depth: 4 cm
594	05/14	Weed removal	by hand
		Application of nitrogen fertilizer	by hand , KAS (N content: 27%)
673	07/14	Oat harvest	Plants were cut 2 cm above soil
680	07/14	3rd soil sampling	Humax auger, 0-20 cm

4.2.6 Soil and plants sampling and analyses

Soil samples were collected using Humax auger to a depth of 15 cm after wheat harvest and upto 20 cm after Terralife® and oat harvest, respectively. In total 11 soil corers were collected from each lysimeter half. Each sampled soil core was further sub-divided into 3-4 parts depending upon the sampling depth (0-5, 5-10, 10-15 and 15-20 cm). The corresponding depth horizons of the 11 soil cores were mixed and aliquots from these mixtures were used to assess the Cs-137 and Sr-90 activities in the soil.

Soil samples and plants were dried at 105°C for 24 h. The dried soils were sieved (≤ 2 mm) to remove the roots and to homogenize the soil. The plants were cut up small using scissors. For wheat and oat, ears were separated from the stalk and were threshed in a lab scale thresher. Cs-137 activity was measured in dried soil and plant samples with a Gamma spectrometer using Ortec detectors (p-type) D6 GEM-65195-P Poptop (65% efficiency) or D7 GEM-65195-P Poptop (40% efficiency). For Sr-90, a 5 g soil or plant aliquot was boiled in 200 mL of 5M HNO_3 for about 30 min using a sand bath. The digested solution was filtered through a cellulose filter (pore size: 0.45 µm) and diluted to 500 mL with deionized water. A 10 mL aliquot was analyzed with a low- level Beta counter (FHT 770T, Thermo Fischer Scientific, USA). Data were presented as means plus their standard errors.

4.2.7 Transfer factors

Different expressions for calculating transfer factors (TF) are used in literature including complete plant or individual plant parts (e.g. TF- root, TF- shoot and TF- grain) (Krouglov *et al.*, 1997; Gerzabek *et al.*, 1998; Ehlken and Kirchner, 2002; Schimmack *et al.*, 2007; Lukšienė *et al.*, 2013; Qi *et al.*, 2015). We calculated two TFs: *i*) soil to shoot (i.e. TF-shoot) for all plants and *ii*) soil to grain (i.e. TF-grain) for cereals only. TF values were determined on dry mass basis by dividing the RN activity in plant part (shoot/grain) to the total activity in top 15 cm (wheat) or 20 cm (Terralife® and oat) of the soil. Determined TFs were presented as means and their standard errors.

$$TF = \frac{activity\ in\ shoot\ or\ grain\ (Bq\ g^{-1})}{activity\ in\ soil\ (Bq\ g^{-1})}$$

4.3 Results and Discussion

4.3.1 Distribution of applied RN in soil

After RN application into upper top 2 cm of soil columns, majority of RN remained in the top soil during first cropping season (Figure 4.3 & A-1, Appendix). However, soil management practices such as ploughing mixed RN into deeper soil layers and rooting zones, which may affect their plant uptake (Konoplev *et al.*, 1993; Camps *et al.*, 2004).

Although no tillage systems are today used in agriculture, ploughing is still common in agriculture practice (Hill, 1990; Pedro and Silva, 2001). It can cause mixing of contaminants into deeper soil layers as observed in our work after ploughing (Figure 4.3 & A-1, Appendix). Despite ploughing, both RN showed negligible migration into soil layers deeper than 15 cm (Figure 4.3 & A-1, Appendix), while applied conservative tracer (i.e. bromide) migrated into deeper soil layers as observed in suction cups samples at 40 cm depth (Figure 4.4). In spite of having vertical migration potential, in our study Cs-137 and Sr-90 remained in top soil due to chemical and physical mechanisms. In mineral soils Cs^+ is sorbed on FES of clay minerals and OM, but sorption on FES of clay minerals is stronger than reversible sorption on OM (van Bergeijk *et al.*, 1992; Cornell, 1993; Dumat and Staunton, 1999; Sanzharova *et al.*, 2009). Contrastingly, Sr^{2+} is less sorbed to clay minerals than Cs^+, but OM can retain Sr^{2+} in soil due to chemical (e.g. complexation and chelation) and physical mechanisms (e.g. occludation) (Nilsson *et al.*, 1985; Sanchez *et al.*, 1988; van Bergeijk *et al.*, 1992).

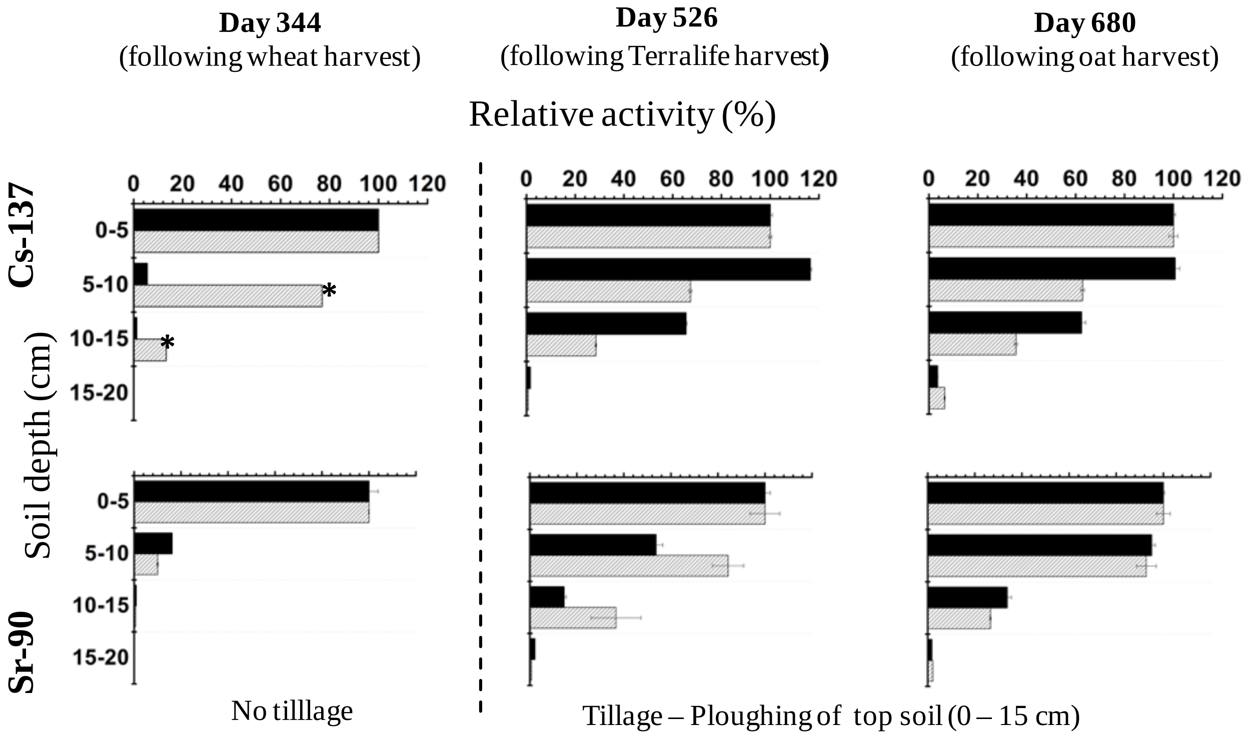

Figure 4.3: Distribution of applied Cs-137 and Sr-90 after no tillage cultivation of summer wheat and cultivation of Terralife® and summer oat after ploughing up to a soil depth of 15 cm. Data are shown as relative values compared to activity measured in upper top soil (0 to 5 cm). Relative value (%) = (activity in soil depth /activity in upper top soil)*100. Control soils are indicated by grayish columns while black columns present results from soils amended with digestate. Data are shown as means and standard error.*Physical disturbance (i.e. mouse intrusion).

Further, the limited vertical mobility of Cs-137 and Sr-90 is in agreement with Bréchignac *et al* (2001), who observed nearly homogeneous distribution of both RN in first 20 cm of soil. However, Cline and Rickard (1972) reported that Sr migrated into subsoil below ploughing horizon, while Cs was immobile due to strong sorption of Cs on soil particles. So, in our soils, a considerable amount of clay and high silt content (Table 4.1) led to a lower vertical migration of both RN. However, the digestate amendment (with applied rate) did not change the RN mobility in investigated soil. Beside our results any comparison between soils contaminated with Cs-137 and Sr-90 may be biased due to pedo-turbation (mouse intrusion) in Cs-137 enriched soils during first cropping season.

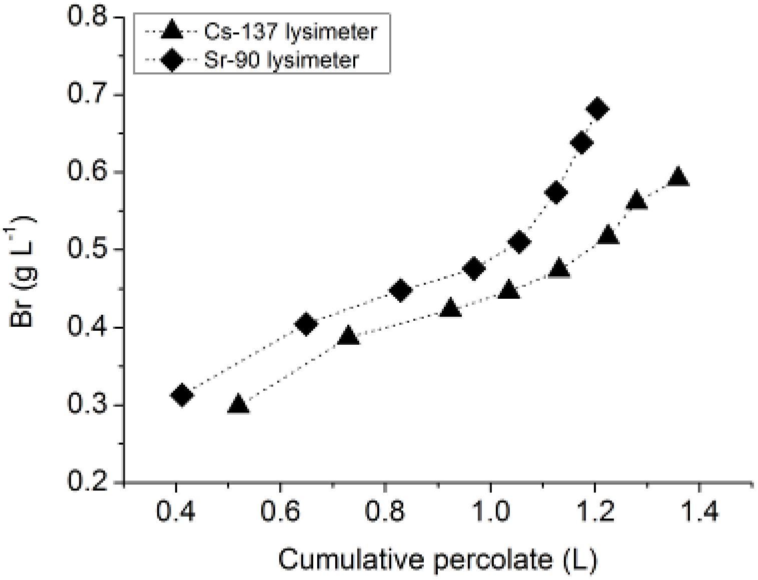

Figure 4.4: Soil columns enabled water percolation, which was proven by using a conservative tracer (i.e. bromide). Bromide was measured in a soil depth of 40 cm, which indicated descendent water percolation. Data are presented as cumulative elution curves.

4.3.2 Transfer of RN into plants and their distribution

Digestate amendments reduced Cs-137 uptake into plants on average by 55 ± 11% and depicted in reduced TF (Figure 4.5 & Table 4.4). Contrastingly, digestate had variable effect on Sr-90 uptake by plant with increased and decreased uptake of Sr-90 (Figure 4.5; Table 4.4). Consequently, additions of digestate to silty-loam Luvisols faciliate production of plant biomass less contaminated with Cs-137, but Sr-90 uptake remained unchanged (on average 4 ± 6%). However, due to multiple uptake of

Sr-90 in comparison to Cs-137 (Tables 4.4 & 4.5) a net reduction of nuclear hazard is scarcely to be expected.

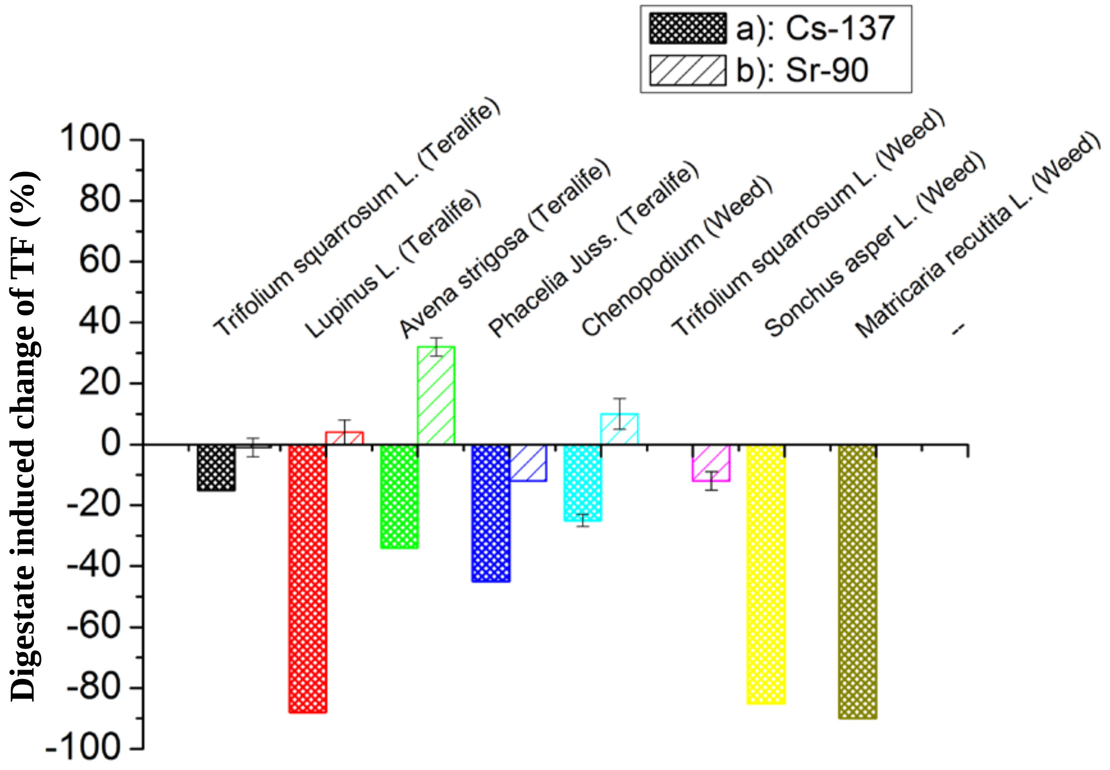

Figure 4.5: Digestate induced change of transfer factors in Terralife® and weed plants. Relative data were calculated as follows: Change (%) = ((Digestate treatment – Control)/Control)*100) and are shown as means and their standard error.

Uptake of Cs-137 through monocotyledones and dicoltyledones remained unaffected after digestate application, but uptake of Sr-90 differed between monocotyledones and dicotyledones (Figure 4.5). Uptake of Sr-90 through monocotyledones increased substantially after digestate application, while Sr-90 TF of dicoltyledones were variable (Figure 4.5, Table 4.4). Despite the latter total uptake of Sr-90 by monocotyledons was smaller than those of dicotyledons (Table 4.4), which may be a result of their different root systems. Dicotyledons have stronger and more branched roots than monocotyledons enhancing their capability to access nutrients and RN in soils and thus, larger root uptake (Taiz and Zeiger, 2006; Rich and Watt, 2013). The latter attracted research to investigate use of several cover crops (e.g. *Lupinusalbus* L., *Sonchus* L., *Matricariarecutita* L.) for their use as phyto-remediation (Yoon *et al.*, 2006; Masarovičová *et al.*, 2010; Fumagalli *et al.*, 2014). Thus, despite a larger increase in Sr-90 uptake by monocotyledons from digestate amended silty-loam Livisol, dicotyledons took up multiple amounts of Sr-90 from both Luvisol treatments (e.g. control and digestate amended).

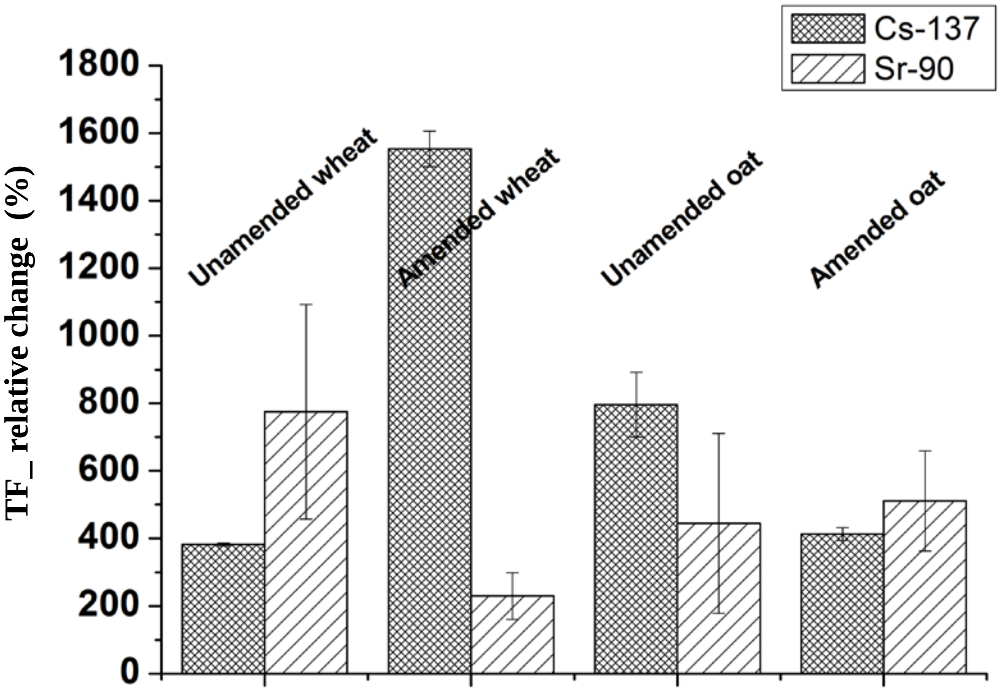

Figure 4.6: Relative change of grain and shoot TF due to digestate amendment (shown as mean and their standard error). This graph shows differences in percentage between TFs investigated for grain and shoot, i.e. TF of shoot in relation to grain.

Table 4.4: Transfer factors of Cs-137 and Sr-90 for total above ground biomass of Terralife® and weed plants cultivated on silty-loam Luvisol and treatments amended with digestate. Data represents mean ± standard error of duplicate samples (n=2).

Plant type	Plant group	Plant species	Cs-137		Sr-90	
			Unamended	Amended	Unamended	Amended
Terralife®	Dicoltyledone	*Trifoliumsquarrosum L.*	0.013 ± 0.000	0.011 ± 0.000	1.97 ± 0.045	1.95 ± 0.077
	Dicoltyledone	*Lupinus L.*	0.039 ± 0.000	0.005 ± 0.000	1.49 ± 0.026	1.56 ± 0.077
	Monocotyledone	*Avenastrigosa*	0.002 ± 0.000	0.002 ± 0.000	0.35 ± 0.010	0.47 ± 0.006
	Dicoltyledone	*Phacelia Juss.*	0.006 ± 0.000	0.003 ± 0.000	2.34 ± 0.005	2.07 ± 0.000
Weed	Dicoltyledone	*Chenopodium*	0.005 ± 0.000	0.003 ± 0.000	0.63 ± 0.01	0.69 ± 0.04
	Dicoltyledone	*Trifoliumsquarrosum L.*	-/-	0.054 ± 0.000	1.64 ± 0.06	1.44 ± 0.03
	Dicoltyledone	*Sonchus asper L.*	0.052 ± 0.001	0.008 ± 0.000	-/-	1.85 ± 0.05
	Dicoltyledone	*Matricariarecutita L.*	0.051 ± 0.001	0.005 ± 0.000	-/-	0.68 ± 0.04

Table 4.5: Transfer factors of Cs-137 and Sr-90 for stem and grain for oat (*Avena sativa*) and wheat (*Triticum aestivum*) cultivated on silty-loam Luvisol and treatments amended with digestate. Data represents mean ± standard error of duplicate samples (n=2).

Plant species	Plant parts	Cs-137		Sr-90	
		Unamended	Amended	Unamended	Amended
Avena sativa	grain	0.001 ± 0.000	0.0003 ± 0.0000	0.06 ± 0.00	0.06 ± 0.00
	shoot	0.010 ± 0.001	0.0014 ± 0.0000	0.41 ± 0.02	0.51 ± 0.01
	Σ	0.011 ± 0.001	0.0017 ± 0.0000	0.47 ± 0.02	0.57 ± 0.01
Triticum aestivum	grain	0.001 ± 0.000	0.0002 ± 0.0000	0.01 ± 0.00	0.03 ± 0.00
	shoot	0.004 ± 0.000	0.0035 ± 0.0000	0.11 ± 0.01	0.10 ± 0.00
	Σ	0,005 ± 0.000	0,0037 ± 0.0000	0,12 ± 0.02	0,13 ± 0.00

The two cereals (i.e. wheat and oat) showed different uptake of Sr-90 (Figure A-2, Table 4.5), which is in line with investigations of Kruglov *et al.* (1997) and Qi *et al.* (2015). Oat took up larger amounts of Sr-90 than wheat (Figure A-2, Table 4.5), which is in line to previous findings and resulting suggestions to use oat to remedite soil contaminated with heavy metals and radionuclides (Krouglov *et al.*, 1997; Ebbs and Kochian, 1998; Han *et al.*, 2013; Qi *et al.*, 2015). Within plant Cs is more uniformly distributed than Sr (Russell, 1963), which is confirmed by our results (Table 4.5).

Despite the latter, stem of wheat and oat contained more Cs-137 and Sr-90 than grain of respective plants (Figure A-2, Table 4.2). This is in line with previous findings of Gerzabek *et al* (1990) who recorded lower Cs-137 activities in grains compared to straw (i.e. 1.8-times and 4.2-times lower for barley and wheat, respectively). While, Rasmusson *et al* (1963) measured multiple (i.e. up to 7.6-times) Sr-89 activity in stem of barley and wheat if compared to their grains. Assuming lack of alteration caused by for instance digestate application these ratios would remain stable. However, TF ratios changed during our study (Figure 4.6), but cultivation of different plant species (i.e. wheat and oat) and different soil management strategies (i.e. no tillage and tillage) override effect caused by digstate application (Figure 4.6).

4.4 Conclusion

On average Cs-137 uptake was reduced after digestate application while uptake of Sr-90 was variable with no uptake by dicotyledons and an increased uptake by monocotyledons. Neither digestate nor tillage changed the vertical mobility; however, ploughing affected the RN distribution within the plough layer. Further investigations with higher application rates of digestate and with longer study periods are necessary to realize its effect on critical soil contaminants mobility into food chain. Lower activities in grain compared to shoot postulate that the consumption of fruits from above ground plant parts will be less harmful when the growing of grain crops is unavoidable in highly contaminated soils. The higher uptake in cover crops and weed plants compared to main crops reflects the advantage of using cover crops for phytoextraction and in reducing the RN mobility to humans through the food chain.

5. Synopsis

5.1 Extended summary

Radioactive cesium and strontium are critical environmental contaminants due to their hazardous radiation effects and relatively long half-lives (Sanzharova *et al.*, 2009; Lehto and Hou, 2011). Analogues behavior of Cs^+ and Sr^{2+} to macro soil nutrients (e.g. K^+ and Ca^{2+}) increases the risk of their migration to humans through the food chain (Nisbet *et al.*, 1993; Zhu and Shaw, 2000). Their mobility in soils and uptake by plants has intensively been studied since Chernobyl accident in 1986. In soils factors that influence availability of Cs^+ and Sr^{2+} are multiple and associated to soil texture, OM, ionic strength and soil pH (Nilsson *et al.*, 1985; Krouglov *et al.*, 1997; Kamel and Navratil, 2002; Sanzharova *et al.*, 2009). Moreover, land use type affects distribution and availability of Cs^+ and Sr^{2+} in soils through mechanical soil preparation (i.e. ploughing) and chemical alteration (e.g. application of fertilizer and organic amendments; Lembrechts, 1993; Nisbet, 1993; Nisbet *et al.*, 1993; Ivanov *et al.*, 1997; Zhu and Shaw, 2000). Although, the effect of important soil parameters (e.g. texture, pH and OM), soil management practices (ploughing, disking) and the use of mineral and organic fertilizers on their soil-plant transfer has largely been investigated, effects of biochar and digestate amendments on Cs and Sr availability are hardly known. We used common field (i.e. agricultural practice) application rates of these amendments to probe the immobilization of Cs^+ and Sr^{2+} in regular agricultural soils.

In current PhD work, we adopted two experimental approaches: 1) sorption-desorption experiments and 2) plant uptake and vertical mobility in outdoor lysimeters experiment. In the sorption-desorption experiments, we used three different soils from temperate region in Germany (North Rhine- Westphalia), two soils from intensively used agricultural sites and the third soil from a forest site. The two organic amendments were obtained keeping in view their application in agricultural practice. We used liquid fraction of digestate (i.e. liquor) due to higher relevance of competing ions (i.e. K^+, NH_4^+, Ca^{2+}) in addition to organic fractions. Furthermore, the sorption-desorption experiments were conducted at three environmentally relevant temperatures (5, 20 and 35°C) to assess the effect of temperature variation on sorption-desorption. The two lysimeters used in this project were undisturbed soil monoliths of silty loam soil, 2.5 m long and 1.6 m in diameter. Lysimeters soil contamination was done using chloride salts of Cs-137 and Sr-90. Plant uptake experiments were conducted with two cereals, summer wheat and oat and an inter-crop (i.e. Terralife® seed mixture). To probe the vertical mobility, soil was sampled after each harvest at different soil depths (0-5, 5-10, 10-15 and 15-20 cm). Furthermore, soil water sampling was done at three soil depths: 40, 120 cm (using suction cups) and 250 cm (leachate pans) to probe the vertical mobility of target radionuclides.

5.1.1 Effect of soil properties and temperature on sorption-desorption

The mobility and retention of Cs^+ and Sr^{2+} in soils is affected by the soil properties (i.e. texture, pH, OM and concentration of competing cations), its land use and soil management practices (Lembrechts, 1993; Nisbet, 1993; Nisbet *et al.*, 1993; Ivanov *et al.*, 1997; Zhu and Smolders, 2000). Biochar and digestate are increasingly applied to agricultural soils for higher crop yields and associated environmental benefits like mitigating greenhouse gases emissions and waste management (Tani *et al.*, 2006; Warnock *et al.*, 2007; Zhang *et al.*, 2007; Jeffery *et al.*, 2011; Teglia *et al.*, 2011). Application of biochar and digestate can enhance soil OM, cation exchange capacity (CEC), soil nutrients, pH and surface area of soils (Steiner *et al.*, 2007; Gell *et al.*, 2011; Kookana *et al.*, 2011; Teglia *et al.*, 2011). This in turn, can affect sorption-desorption dynamics in amended soils due to higher availability of sorption sites (OM sites) and competition with relevant soil nutrients (e.g. K^+, NH_4^+, Ca^{2+}, Mg^{2+}).

We investigated sorption of cesium (Cs^+) and strontium (Sr^{2+}) in two arable and one forest soil. Arable soils (i.e. silty loam and loamy sand) were amended with 25 t ha^{-1} of wood-biochar and

34 t ha^{-1} of digestate, while forest soil was kept unamended. Experiments were carried out at different temperatures, 5, 20 and 35°C to account the temperature effects on sorption dynamics according to Gibbs free energy change ($\Delta G = -RT\ln K$).

The applied amendments did not lead to a significant effect on sorption behavior of investigated RN in opposition to the soil texture and land use. Silty loam soil showed highest sorption capacity for Cs^+ with 5 times higher sorption compared to loamy sand and almost double to the forest soil. Strontium sorption was nearly half compared to Cs^+ for all soils with 4 times higher sorption in silty loam compared to loamy sand and forest soils, where it was nearly equal. The effect of amendments on desorption behavior was negligible compared to effects of soil texture and land use. Forest soil with native OM retained highest Sr^{2+} compared to arable soils (with and without amendment). Temperature change in the investigated range (5-35°C) did not cause a significant effect on sorption-desorption of the two RN. Statistical analysis revealed that soils were the main source of data variability in sorption-desorption of both contaminants. We conclude that used organic amendments with regular field application rates will not alter the sorption-desorption dynamics of said RN in arable soils.

5.1.2 Plant uptake and mobility of Cs-137 and Sr-90 in soil

The empirical models predicting the soil-plant transfer of RN are mostly based on transfer factors. These models encounter limitations due to poorly documented variabilities in TF values, coming from variability in plant species under consideration and also due to the complexity and diversity of the soils. So, there is need to get experimental data for different soil-plant systems to validate the results from empirical models. Our lysimeters results make some contribution in the existing knowledge on the subject that could be used to predict the behavior of investigated RN in related soil-plant systems.

5. Synopsis

We investigated mobility and plant uptake of Cs-137 and Sr-90 in artificially contaminated silty loam soil using typical field application rate of digestate (34 t ha^{-1}). The experiment was conducted in large outdoor lysimeters (⌀ = 1.6 m, height = 2.5 m) with two grain crops (i.e. summer wheat and oat), their accompanying weeds, and an intercrop (i.e. Terralife$^{®}$ seed mixture). Soil contamination was done with chloride salts of both RN, with a final soil contamination level of ~65 MBqm^{-2} for Cs-137 and ~18 MBqm^{-2} for Sr-90 in the top 2 cm soil. Soil sampling was done at four different depths (0-5, 5-10, 10-15, 15-20 cm). The results showed that uptake varied with the type of plant and the radionuclide. Cover crops (i.e. Terralife®) and weeds showed higher uptake compared to main crops (i.e. wheat, oat). The vertical mobility of both RN was unchanged after digestate amendment and tillage; however, ploughing affected the RN distribution in the plough layer. Both RN was retained in the top 20 cm soil. As result we suggest to use weed plants and Terralife$^{®}$ for phytoremediation of contaminated soils and thereby to reduce the mobility of investigated RN to humans.

5.2 Synthesis

5.2.1 Final conclusions

The type of radionuclide and the soil properties (i.e. soil texture, nature of OM and land use) were the main parameters controlling the behavior of investigated RN. The organic amendments with applied rates failed to change the sorption-desorption behavior of the two RN leading to the assumption that amendments applied with the recommended rates may not affect the soil-plant transfer of the target RN. Furthermore, it infers that the two bioenergy residues (i.e. biochar, digestate) produced in different process conditions will behave differently in soils.

The behavior of two RN was distinctive in sorption-desorption as well as in plant uptake. Cesium sorption was highest in silty loam soil, followed by forest soil and lowest in loamy sand.

5. Synopsis

Compared to cesium, strontium sorption was nearly half in all soils with higher sorption in silty loam and almost similar sorption in loamy sand and forest soils. Forest soil showed highest affinity for Sr^{2+}, followed by loamy sand and lowest in silty loam. Higher retention of Sr^{2+} in forest soil compared to amended soils (e.g. biochar amendment) clues that nature of OM may have higher influence on RN affinity than the relevant amount.

Temperature variation in the range (5-35°C) did not lead to a substantial effect on sorption-desorption of both RN. Further, temperature effect interacted with the type of soil and the radionuclide. Sorption and affinity of Cs^{+} was higher at 5°C compared to 20 and 35°C in silty loam soil while in forest soil the trend was just opposite and loamy sand was unaffected by this temperature change. Strontium showed erratic changes with temperature variation in different soils. Sorption of Sr^{2+} was higher at 5 and 35°C compared to room temperature (20°C). However, the impact of temperature on RN sorption in soils may be important to be considered on the long-term due to increasing mean soil temperatures most likely caused by global warming (Grillakis *et al.*, 2016).

Plant uptake varied with the type of plant and the radionuclide. Cs-137 uptake was reduced in dicotyledons after digestate application, surprisingly an increase in Sr-90 uptake was observed in monocotyledons. The vertical migration of both RN was remained unaffected after digestate amendment and ploughing; however tillage affected the RN distribution in the plough layer. The lower RN activities in edible plant parts (e.g. grain) compared to non-edible parts (stem) gives the possibility of growing grain crops on contaminated soils when their cultivation is unavoidable. The higher RN uptake in Terralife® and weed plants compared to main crops provides advantage of cultivating cover crops to reduce RN mobility into food chain in addition to their use to conserve, accumulate and recycle OM and plant nutrients.

5.2.2 Outlook

5.2.2.1 Sorption-desorption

Studying sorption-desorption mechanisms of RN is an important parameter to predict their vertical migration and plant availability in soils of different origin and land uses. With the use of typical field application rates of organic amendments, we simulated the conditions of regular agriculture practice. However, to realize the long term effects of these amendments, more studies with different application rates (i.e. dose-response study) and with longer incubation periods (i.e. long-term agricultural field experiments) are necessary. The difference in RN affinity in soils that contain native and amended organic matter needs further research to explore the mechanisms of binding RN with organic compounds, which is required to manage RN-enriched/contaminated soils. Temperature variation (5-35°C) had no significant effects on sorption-desorption behavior of studied radionuclides. Further investigation with wide temperature ranges should be included to simulate whole variability of environmental conditions at regional and global scale.

5.2.2.2 Plant uptake and mobility in soil

Digestate amendment with applied rate of 34 t ha^{-1} affected plant uptake of the two RN. Further investigations with higher application rates (i.e. dose-response experiments) are required to assess mechanistic effects of this type of soil organic amendment on RN mobility in soil-plant systems. In present work, both RN did not show any vertical mobility into deeper soil layers (i.e. deeper than 15 cm). Continuation of this experiment under the same working conditions (i.e. lysimeters exposed to natural conditions, ploughing) may change the RN mobility in future. A slow vertical mobility of Cs-137 and Sr-90 into deeper soil layers (>40 cm) is expected, then the continuing data monitoring through TDRs, tensiometers and temperature sensors can be used to assess the long-term effects of environmental parameters (e.g. temperature, water content) on studied RN which can be helpful in refining model predictions. Outdoor lysimeter experiments provided a clue on effect of natural and controlled environmental conditions on RN behavior in soil. Thus, a more logical approach for investigating soil contaminants mobility into food chain should link laboratory investigations to actual field practice through lysimeters experiments/field trials. Different plants species exhibited different uptake of the two RN. Therefore, variation in plant species could be a valuable tool in phyto-extraction of RN from contaminated soils. Higher uptake of investigated RN in Terralife® and weed plants compared to grain crops suggests investigating plant uptake of critical soil contaminants in cover crops to reduce RN mobility into food chain.

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7. Appendices

7.1 Appendix A-1

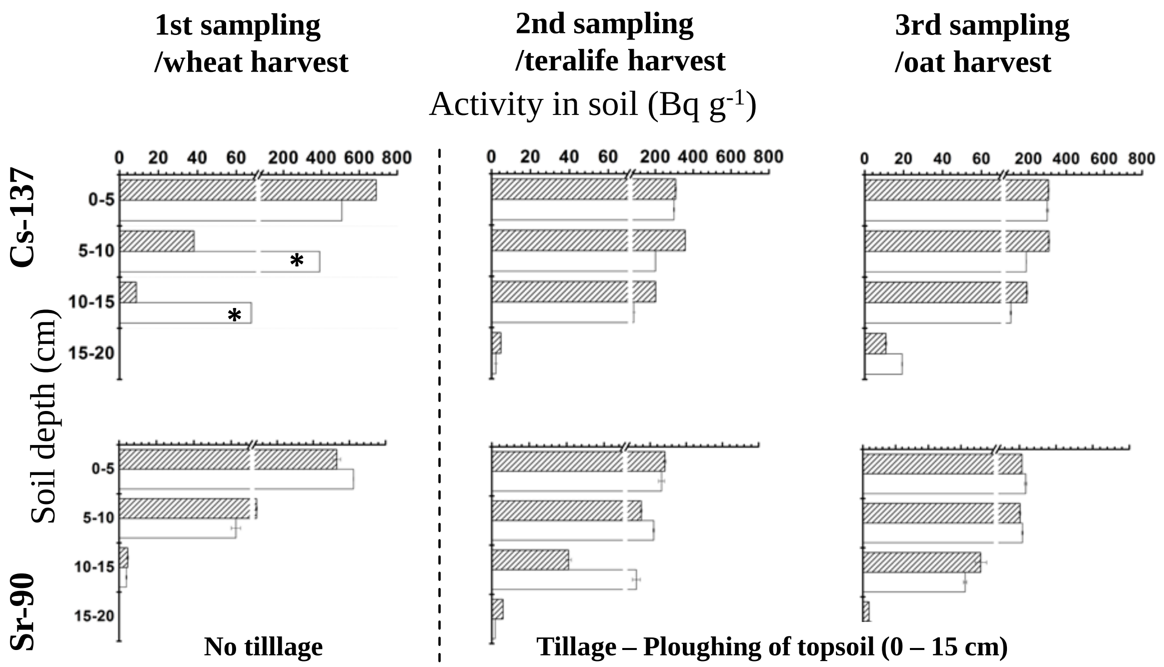

Figure A-1. Distribution of applied RN after summer wheat, Terralife® and summer oat harvest. Control soils are indicated by open columns while grayish columns present results from soils amended with digestate. Data are shown as means and their standard error (n=2). *Physical intrusion (mouse problem).

7.2 Appendix A-2

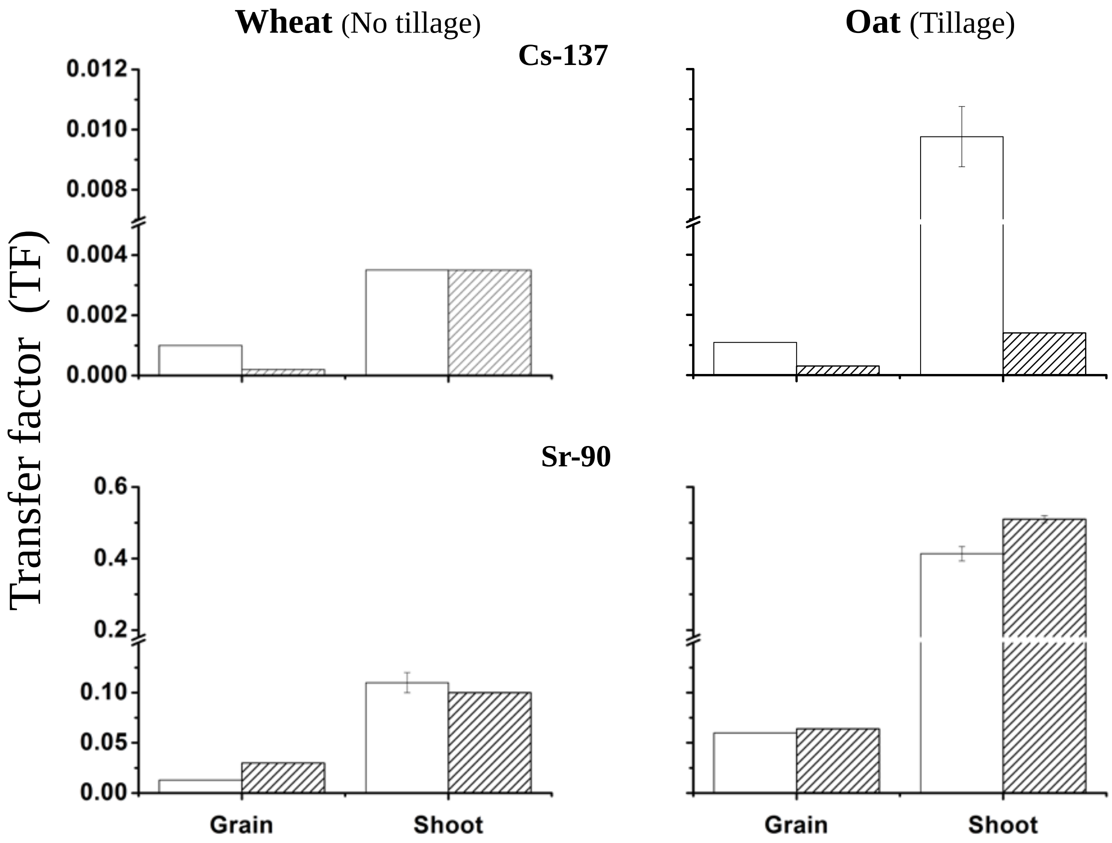

Figure A-2. Transfer factors (i.e. soil to shoot/grain) in summer wheat and summer oat. Control soils are indicated by open columns while grayish columns present results from soils amended with digestate. Data are shown as means and their standard error (n=2).