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| Zuwendungsempfänger/ Auftragnehmer: Forschungszentrum Jülich GmbH, Leo-Brandt-Straße, 52428 Jülich | | Förderkennzeichen: 02NUK015E |
| Vorhabensbezeichnung: Verbundprojekt Strahlung und Umwelt: Radionuklide in der Umwelt, ihr Transport in Nahrungsketten zum und im Menschen, Projektteil 2, Work package 2.4 | | |
| Zuordnung zum FuE-Programm: Nukleare Sicherheitsforschung: Strahlenforschung | | |
| Laufzeit des Vorhabens: Von 01.09.2010 bis 30.08.2013 | Berichtszeitraum: 01.09.2011 bis 30.08.2014 | |
| Gesamtkosten des Vorhabens: 140.493,20 € | Projektleiter: Dr. D. Hofmann, Dr. A. E. Berns | |

Schlussbericht

I. Kurze Darstellung zu:

1. Aufgabenstellung

Das Verbundprojekt “Strahlung und Umwelt: Radionuklide in der Umwelt, ihr Transport in Nahrungsketten zum und im Menschen” ist in vier Projekte unterteilt. Das Projekt 2 konzentriert sich auf “Prozesse an den Schnittstellen Pflanzen-Mikroben und den Transport von RN in Pflanzen und in die Nahrungskette”. Das Projekt ist in vier Arbeitspakete unterteilt. Work Package 2.1 bearbeitet den “Einfluss von Biofilmen auf das Migrationsverhalten von Uran und Americium in der Umwelt” und der Fokus des Arbeitspaketes 2.2 sind “Mikrobielle Prozesse der Mobilisierung und Immobilisierung (von Schwermetallen) im Boden.” Arbeitspaket 2.3 befasst sich mit den “Mechanismen der Blattaufnahme von Radionukliden in Pflanzengewebe”.

Das Arbeitspaket 2.4 wird im Institut Agrosphäre (IBG-3), Forschungszentrums Jülich, bearbeitet und befasst sich mit der “Verfügbarkeit von Radionukliden in Böden – Effekte von Bodenmanagement und Klimawandel”. Dieses Arbeitspaket beschäftigt sich mit Fragen der nachhaltigen Nutzung der Böden für die Nahrungs- und Futtermittelproduktion. Hier besteht Bedarf an verbesserten Boden-Management-Systemen.

Im Projekt wird das Verhalten der Radionuklide (RN, Cs-137 und Sr-90) in Bodensystemen desselben Typs mit unterschiedlicher Bodendüngung untersucht. Die Anwendung von Biochar oder Gärrückständen zur Bodenverbesserung einerseits and sinnvoller Anwendung

von Abfällen andererseits verändert die Eigenschaften der organischen Substanz des Bodens sowie die Verfügbarkeit von Nährstoffen/Radionukliden. Darüber hinaus sind extreme Wetterbedingungen auf Grund des Klimawandels zu erwarten die die natürlichen Kohlenstoff- und Nährstoffkreisläufe verändern und sich so in noch unbekannter Weise auf die Mobilisierung von Radionukliden in der Bodenmatrix auswirken mit entsprechendem Einfluß auf den Transfer in die Kulturpflanze.

Bezug zu aktuellen Geschehnissen und zur landwirtschaftlichen Praxis

Das Spektrum der ausgefallenen Radionuklide während des Reaktorunglückes in Tschernobyl (Russland) 1986 war sehr groß. So wurden z.B. ^{95}Zr , ^{95}Nb , ^{106}Ru , ^{137}Cs , ^{134}Cs , ^{90}Sr , verschiedene Jod-Isotope und ^{144}Ce emittiert. Im direkten Umfeld des Reaktors zusätzlich Kernbrennstoffe. Die meisten dieser Radionuklide haben allerdings eine kurze Halbwertszeit. Hinzu kommt, dass die Kernbrennstoffe aufgrund ihrer Geometrie nur in unmittelbarer Nähe des Reaktors im Umkreis von 100 km niedergegangen sind. Anders verhält es sich mit den beiden Radionukliden Cäsium-137 (^{137}Cs) und Strontium-90 (^{90}Sr). Beide besitzen eine Halbwertszeit von ca. 30 Jahren und konnten sich in großem Maße mit den damals vorherrschenden Luftströmen über Nord- und Mitteleuropa ausbreiten. Ein weiterer verheerender Unfall ereignete sich im März 2011 im Kernkraftwerk Fukushima (Japan). Bei diesem Unglück wurden maßgeblich ^{131}I , ^{134}Cs und ^{137}Cs in größeren Mengen und über längere Strecken transportiert.

^{137}Cs und ^{90}Sr sind Radionuklide der ersten bzw. zweiten Hauptgruppe des Periodensystems der Elemente und besitzen ähnliche chemische Eigenschaften wie Kalium und Kalzium. Deshalb wird Cäsium in Böden sehr gut an die mineralische Substanz, insbesondere Dreischichttonminerale, adsorbiert und verbleibt somit lange in den oberen Bodenschichten. Die Mobilität des Strontium hingegen hängt direkt vom Anteil des organischen Kohlenstoffs im Boden ab. Der Abwärtstransport in tiefere Bodenschichten ist somit in der Regel zu vernachlässigen. Auf Ackerböden, Wiesen und Forststandorten sind die oberen 20-30cm die am intensivsten durchwurzelte Zone und enthalten die höchste Fracht an organischer Bodensubstanz.

In den vergangenen Dekaden sind die Mengen an organischen Abfällen beständig gestiegen und erforderten die Entwicklung von kosteneffektiven und umweltfreundlichen Lösungen ihrer Verwertung. Ideal sind dabei Strategien, die Abfallverwertung, Produktion von Bioenergie und nachhaltiges Bodenmanagement verknüpfen. Biogasanlagen produzieren durch Fermentation von organischen Abfällen Gas, das direkt zur Energieerzeugung genutzt wird. Die dabei entstehenden Gärrückstände (feste und flüssige Anteile) zeichnen sich durch hohe Gehalte an Makro- und Mikronährstoffen aus und sind daher hervorragend als Dünger geeignet. Sie führen P und N in beträchtlichem Maße in Ackerböden zurück. Der Eintrag von Nährstoffen und organischem Material kann dabei zu veränderten Sorptionsbedingungen und damit möglicherweise zu verändertem Transport- und Transferverhalten von eingetragenen Radionukliden führen.

Das Sorptionsverhalten der Nuklide unter verschiedenen Düngevarianten und Temperaturen kann relativ einfach in Labor-Batchversuchen ermittelt werden. Belastbare Daten zum Transportverhalten im Boden sowie zum Transfer der Radionuklide in Pflanzen können sinnvollerweise nur in großskaligen Lysimeter-Versuchen erhoben werden.

Im Rahmen der Promotion wurden Laborversuche zum Sorptionsverhalten beider Nuklide sowie 2 Lysimeter-Versuchsansätze im Kontrollbereich des IBG-3 angesetzt. Hierbei wurde untersucht, inwieweit insbesondere die Düngung mit Gärrückständen aus der Biogasherstellung einen Einfluss auf:

- das Sorptionsverhalten der Nuklide im Boden sowie
- das Transportverhalten und den Transfer in die Pflanze hat.

Die Durchführung der Versuche und die erzielten Ergebnisse sind unter II.1 detaillierter dargestellt.

2. Vorraussetzungen, unter denen das Vorhaben durchgeführt wurde

Die wissenschaftliche Betreuung erfolgte durch das Institut Agrosphäre (IBG-3) in der Forschungszentrum Jülich GmbH. Alle Versuche fanden im Kontrollbereich des IBG-3 statt. In der Forschungszentrum Jülich GmbH erfolgten auch die Quantifizierung der Radioaktivität (Geschäftsbereich S - Sicherheit und Strahlenschutz) sowie alle weiteren notwendigen Analysen (IBG-3 und Zentralinstitut für Analytik).

3. Planung und Ablauf des Vorhabens

Das Projekt konnte erst zum 01.09.2011 mit einem Doktoranden besetzt werden. Somit verlängerte sich der Ablauf um zwölf Monate.

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|-------------------|---|
| 09/2011 - 02/2012 | <ul style="list-style-type: none"> - Auswahl und Erwerb geeigneter Biogasfermenter- und Pyrolyserückstände zur Düngung - Erwerb von Radionukliden (Cs-137 und Sr-90) - Erwerb von TDR- und Temperatursonden sowie Tensiometern für Lysimeterversuche; Sensor Kalibrierungen - Literaturübersicht |
| 03/2012 - 08/2012 | <ul style="list-style-type: none"> - Inkubation von Ackerböden (Merzenhausen und Kaldenkirchen) mit Biochar und/ oder Gärrückständen für Laborversuche - Gewinnung eines klassifizierten Waldbodens (Wüstebach) als Referenzprobe - Installation der Lysimetersensoren - Planung und Aufbau von Schutzmaßnahmen zur Handhabung von hochaktiven Nukliden |

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|-------------------|--|
| | <ul style="list-style-type: none"> - Praxistraining mit stabilen Sr-88 und Cs-133-Lösungen - Applikation von Biogasfermenterrückständen auf die Lysimeter |
| 09/2012 – 02/2013 | <ul style="list-style-type: none"> - Planung der Durchführung der Lysimeterkontaminationen - Anschaffung und Aufbau der benötigten Sicherheitsvorkehrungen und Geräte - Verdünnung der hochradioaktiven Stammlösungen - Ansetzen der Applikationslösungen für die Lysimeterversuche - Vorversuche zu Sorptionsexperimenten |
| 03/2013 – 08/2013 | <ul style="list-style-type: none"> - Applikation der Radiotracer Sr-90 und Cs-137 auf die Lysimeter - Aussaat der ersten Frucht (Sommerweizen) - Abgrenzung der Lysimeter zur Verhinderung von Kontaminationsausbreitung - Aufbau Schutzvorrichtung an Lysimeter gegen Eindringen von Tieren - Applikation des konservativen Tracers (KBr) - Beginn der Aufnahme der Lysimeterdaten - Sorptions-/Desorptionsversuche bei Raumtemperatur mit gedüngten und nicht gedüngten Böden |
| 09/2013 – 02/2014 | <ul style="list-style-type: none"> - Ernte Sommerweizen - Bodenprobenahme - Aussaat Zwischenfrucht (Teralife) - Probenvorbereitung Sommerweizen und Boden zur Bestimmung der Transferfaktoren - Sorptions-/Desorptionsversuche bei verschiedenen Temperaturen (5°C und 35°C) - Ernte Zwischenfrucht - Bodenprobenahme |
| 03/2014 – 08/2014 | <ul style="list-style-type: none"> - Aussaat der zweiten Frucht (Hafer) - Teilnahme EGU 2014 (Wien): Präsentation von Sorptions- (Vortrag) und Lysimeterergebnissen (Poster) - Probenvorbereitung charakteristischer Pflanzen der Zwischenfruchtmischung zur Bestimmung der Transferfaktoren - Abschluss und Auswertung der Sorptions-/Desorptionsversuche - Ernte des Hafers |

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|-------------------|---|
| | <ul style="list-style-type: none"> - Bodenprobenahme - Probenvorbereitung Boden und Hafer zur Bestimmung der Transferfaktoren |
| 09/2014 – 05/2015 | <ul style="list-style-type: none"> - Verfassen von zwei Publikationen (Sorptionsversuchen; Lysimeterversuche) - Anfertigen der Dissertationsschrift |

4. Wissenschaftlicher und technischer Stand, an den angeknüpft wurde

Über den Einfluß von Gärrückständen auf das Sorptions- sowie Pflanzentransferverhalten der Radionuklide Cs-137 und Sr-90 in landwirtschaftlichen Böden waren bis dato keine Daten vorhanden.

5. Zusammenarbeit mit anderen Institutionen

Im Rahmen des Projektverbundes gab es regelmäßige Projektbesprechungen und einen intensiven Austausch der Projektpartner zu verschiedensten Themen. Erfahrungen bezüglich Durchführung von Freilandexperimenten, Analytik etc. wurden von der AG Prof. Kothe weitergegeben, Besuche an der Universität Jena und dem Versuchsfeld Gessenwiese intensivierten den Erfahrungsaustausch. Eine direkte Zusammenarbeit kam durch die stark zeitversetzten Starts der Doktorarbeiten nicht zustande. Verschiedene Beteiligte wollen deshalb in einer möglichen dritten Antragsphase schon bei der Konzeption der Versuche intensiv zusammenarbeiten und somit größere Vergleichbarkeit und Interpretationsmöglichkeiten erreichen.

Der Geschäftsbereich S und die Zentrale Analytik des FZJ verfügen über etablierte Analysemethoden (z.T. zertifiziert) zur Quantifizierung von Sr und Cs.

II. Eingehende Darstellung zu

1. der Verwendung der Zuwendung und des erzielten Ergebnisses im Einzelnen, mit Gegenüberstellung der vorgegebenen Ziele

Ergebnisdarstellung in gesondertem Bericht (siehe Anhang I)

2. der wichtigsten Positionen des zahlenmäßigen Nachweises

Der überwiegende Teil der Finanzierung diente der Vergütung des Doktoranden, gefolgt von Kosten für Analysen, Laborverbrauchsmitteln und Dienstreisen.

3. der Notwendigkeit und Angemessenheit der geleisteten Arbeit

Das Thema der Arbeit wurde wissenschaftlich noch nicht bearbeitet, so dass neue Ergebnisse vorgelegt werden konnten. Diese Resultate sind aus radioökologischer Sicht wertvoll, weil hierdurch ein Risikofaktor ausgeschlossen werden kann.

4. des Voraussichtlichen Nutzens, insbesondere der Verwertbarkeit des Ergebnisses im Sinne des fortgeschriebenen Verwertungsplans

Der Nutzen besteht aus radioökologischer Sicht in einer besseren Risikoabschätzung bei der Wirkung von organischen Düngern auf das Sorptions- sowie Pflanzentransferverhalten von Cs-137 und Sr-90.

5. das während der Durchführung des Vorhabens dem ZE bekannt gewordenen Fortschritts auf dem Gebiet des Vorhabens bei anderen Stellen

entfällt

6. der erfolgten oder geplanten Veröffentlichung des Ergebnisses nach Nr. 11

- Khalid Mehmood, Diana Hofmann, Peter Burauel, Harry Vereecken, and Anne E. Berns (2014). “Cesium and strontium sorption behavior in amended agricultural soils.” In: Geophysical Research Abstracts Vol. 16, EGU2014-875, EGU General Assembly, 27 April – 02 May, 2014, Vienna, Austria.
- Khalid Mehmood, Anne E. Berns, Thomas Pütz, Peter Burauel, Harry Vereecken, Myroslav Zoriy, Reinhold Flucht, Thorsten Opitz and Diana Hofmann (2014). “Soil-plant transfer of Cs-137 and Sr-90 in digestate amended agricultural soils- a lysimeter scale experiment.” In: Geophysical Research Abstracts Vol. 16, EGU2014-871-1, EGU General Assembly, 27 April – 02 May, 2014, Vienna, Austria.
- Mehmood K., Hofmann D., Burauel P., Vereecken H., and Berns A.E., (2014).“ Sorption of Cs⁺ and Sr²⁺ after addition of wood-biochar and digestate in two temperate arable soils at different temperatures.” (in preparation)
- Mehmood K., Berns A.E., Pütz T., Burauel P., Vereecken H., Zoriy M., Flucht R., Opitz T., and Hofmann D. “Translocation and plant uptake of Cs-137 and Sr-90 in different crops in digestate amended silty-loam soil- a lysimeter scale experiment.” (in preparation)

III. Erfolgskontrollbericht

1. Beitrag des Ergebnisses zu förderpolitischen Zielen

Förderpolitisches Ziel war die Erhaltung und Förderung des Wissens im Bereich der Radioökologie in Deutschland. Obwohl kein deutscher Kandidat für das Projekt gewonnen werden konnte, konnten durch einen Betreuerwechsel zwei Mitarbeiterinnen mit Vorkenntnissen aus diversen ^{14}C -Projekten gewonnen werden, die sich in diesem Projekt Kenntnisse über den Umgang und die Radioökologie von ^{137}Cs und ^{90}Sr aneignen konnten. Eine Mitarbeiterin plant die Fortführung und Vertiefung dieser Forschung im Bereich dieser Nuklide, um die sehr hohen Kosten zur Etablierung der Freilandlysimeter zur Gewinnung weiterer Daten zu nutzen.

2. Wissenschaftlich-technisches Ergebnis des Vorhabens, erreichte Nebenergebnisse und gemachte Erfahrungen

Es ist von keinem ausgeprägten Einfluß bei Düngung mit Gärrückständen auf das Sorptionsverhalten und den Transfer in die Pflanze der beiden untersuchten Radionuklide auszugehen. Bei Einsatz der Gärrückstände nach den Regeln der guten landwirtschaftlichen Praxis kann daher ein Risikofaktor ausgeschlossen werden.

Ebenso wurde kein erheblicher Einfluß der Temperatur auf das Sorptions- und Desorptionsverhalten der beiden Nuklide festgestellt. Es ist daher unter veränderten klimatischen Bedingungen nicht mit wesentlichen Änderungen im Transferverhalten in die Pflanze zu rechnen.

3. Fortschreibung des Verwertungsplans

i. Erfindungen

keine

ii. Wirtschaftliche Erfolgsaussichten

keine

iii. Wissenschaftliche oder technische Erfolgsaussichten

keine

iv. Wissenschaftliche und wirtschaftliche Anschlussfähigkeit

Bei den bisher durchgeführten Arbeiten, sowohl im vorliegenden Projekt als auch in bisher veröffentlichten Laborstudien, wurde immer nur mit frisch applizierten Radionukliden gearbeitet. Ein langfristiger Einfluß der Alterung auf das Transferverhalten der Radionuklide in Pflanzen konnte bisher im Rahmen der üblichen Förderzeiträumen nicht untersucht werden. Die beschriebenen kontaminierten Lysimeter werden nach Beendigung der vorliegenden Studie weiter betrieben und sollen in den kommenden Jahren Daten zum Langzeitverhalten dieser Radionuklide liefern.

4. Arbeiten die zu keiner Lösung geführt haben

Keine

5. Präsentationsmöglichkeiten für mögliche Nutzer

Keine

6. Die Einhaltung der Ausgaben- und Zeitplanung

Durch den verspäteten Beginn wurde das Vorhaben kostenneutral verlängert. Die Budgetierung entspricht dem Aufwand des Forschungsprojektes.

BMBF-Verbundprojekt Strahlung und Umwelt

Teilprojekt E

Schlussbericht

Environmental behavior of cesium and strontium under the influence of different types of organic matter

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Summary

The effect of organic matter on mobility and plant uptake of cesium and strontium in soil-plant systems has intensively been studied since the Chernobyl accident in 1986. Furthermore, the effect of soil management practices like ploughing, disking and the use of mineral and organic fertilizers on their soil-plant transfer have also been taken into account. However, there are new forms of organic soil amendments like biochar and digestate that are increasingly available due to higher production of bioenergy. The use of biochar and digestate as soil amendments is well recognized for their agronomical benefits (e.g. crop yields); however, the knowledge on their effect on toxic metals and radionuclides mobility in soils is scarce. We used the field (agricultural practice) application rates of these amendments, to probe the immobilization of Cs^+ and Sr^{2+} in regular agricultural soils.

In this PhD work, we adopted two experimental approaches: 1) sorption-desorption experiments and 2) plant uptake and vertical mobility in outdoor lysimeter experiments. In the sorption-desorption experiments, we used three different soils from the region (NRW, Germany), 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. 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. For the lysimeters experiments, the liquid fraction of the digestate (liquor) was used due to higher relevance of competing ions (K^+ , NH_4^+ , Ca^{2+}) in addition to organic fractions. Lysimeters soil contamination was done using chloride salts of Cs-137 and Sr-90. Plant uptake experiments

were conducted with three different plants, summer wheat, summer oat and an Inter-crop (Teralife). Furthermore, soil water sampling was done at three soil depths: 40, 120 cm (using suction cups) and 250 cm (leachate vessels) to probe the vertical mobility of target RN.

In sorption experiments, we observed that applied amendments (with field application rates) did not lead to a considerable 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 silty-loam soil, followed by forest soil and lowest in sandy-loam. Strontium sorption was nearly half compared to cesium in all soils with higher sorption in silty-loam and almost similar sorption in sandy-loam and forest soils. The native organic matter in forest soil led to higher Sr^{2+} retention compared to the applied organic matter (amendments).

In general, temperature variation in the range (5-35°C) did not cause a substantial effect on sorption-desorption of the two radionuclides in opposition to soil type. Furthermore, the effect of temperature variation was quite unpredictable. The two agricultural soils (silty-loam and sandy-loam) showed higher Cs^+ sorption at 5°C in opposition to room temperature (20°C) and 35°C. While the forest soil reflected an opposing trend with slightly higher sorption at 35°C compared to 5 and 20°C, where Cs^+ sorption was nearly similar. Silty-loam soil exhibited higher Cs^+ affinity at 5°C compared to 20 and 35°C. Contrastingly, forest soil showed a decrease in Cs^+ retention with decrease in temperature from 35 to 5°C. Sandy-loam soil reflected higher Cs^+ affinity at room temperature (20°C) compared to 5 and 35°C.

The effect of temperature variation on strontium was similar to cesium in silty-loam soil with slightly higher sorption at 5°C compared to 20 and 35°C. Contrastingly, forest soil showed higher Sr^{2+} sorption at 5 and 35°C compared to room temperature (20°C). Temperature

showed quite erratic changes in Sr^{2+} retention in the different soils. In general, Sr^{2+} sorption hysteresis was higher at 5 and 35°C compared to room temperature (20°C). Forest soil exhibited the highest Sr^{2+} retention, followed by sandy-loam and lowest in silty-loam.

Our lysimeter results showed that the digestate amendment with applied rate (common agricultural practice) does not have a significant effect on soil-plant transfer of the investigated radionuclides. However, in the crops of relevance to the food chain (wheat, oat), the digestate showed a slightly protective effect resulting in lower activities in the grains compared to shoot. Hence, further investigations with higher application rates of used organic amendment would be helpful to assess their effect on radionuclides transfer in soil-plant systems. We could observe clear translocation of radionuclides into different plant parts due to high applied activity in our lysimeter soils. Furthermore, different plant species presented different uptake behavior due to variation in their plant physiology and root architecture. Hence, the choice of cultivating different species on contaminated soils could be helpful to reduce the risk of radionuclides mobility into the food chain.

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1. General Introduction

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 Shaw, 2000; Alexakhin *et al.*, 2006; Wuana and Okieimen (2011)). RN are hazardous soil contaminants, particularly cesium (Cs-134, Cs-137) and strontium (Sr-90) are harmful due to their metabolic similarity to potassium (K^+) and ammonium (NH_4^+), and calcium (Ca^{2+}), respectively, which can enhance their plant uptake and transfer to man 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 RN are released into the atmosphere. Furthermore, nuclear weapons testing during the cold war are responsible for a major part of atmospheric RN pollution. The RN accumulated in the atmosphere reach the soil through wet and dry deposition. Knowing the behavior of these RN in soils is important as soil plays a key role in the migration of RN into water bodies and plants, which ultimately lead their way 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. 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 among the most hazardous RN due to their long half-lives: $t_{1/2} = 30.2$ years (Cs-137) and $t_{1/2} = 3 \times 10^6$ years (Cs-135), high solubility and relatively high fission yields: 6.18% and 6.54% respectively (Grütter *et al.*, 1986). Cs-137 is a beta emitter decaying to metastable Barium (94.6 % $E_{\max} 0.512$ MeV; ^{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).

Strontium is an alkaline earth metal. Due to its high reactivity, it is always found as compounds, the most common strontium compounds are Celestine (SrSO_4) and Strontianite (SrCO_3) (Nilsson *et al.*, 1985). The substantial isotopes of ecological concern are Sr-90 ($t_{1/2}=28.8$ a; $E_{\text{max}} 0.546$ MeV) and its daughter, Yttrium-90. Yttrium has a half-life of about 60 h; however, its beta decay ($E_{\text{max}} 2.274$ MeV) intensifies the beta emission of Sr-90. Sr-90 and its daughter, Y-90, are high energy beta radiation sources.

Cesium mobility in soil is governed by different mechanisms like sorption, ion-exchange, and adsorption to iron oxides and organic matter (Kamel and Navratil, 2002). Factors influencing cesium migration and retention in soils include soil texture, clay mineralogy, soil pH, organic matter content and exchangeable ions (Zygmunt *et al.*, 1998; Cha *et al.*, 2006). Clay minerals possess high sorption capacity for cesium due to their small particle size, larger surface area and chemically active sites (Kim *et al.*, 1996). The high sorption affinity of cesium in clay is attributed to the presence of specific bounding sites known as frayed edge sites (FES) (Sanzharova *et al.*) in illite (Calmon *et al.*, 2009). Cesium is less strongly adsorbed in soils with high organic content, since the organic matter can bind the planar sites of clay and reduces therefore the sorption capacity of clays (Dumat *et al.*, 1997). Kruyts and Delvaux (2002) speculated that the availability of FES directly controls the mobility of Cs-137, whereas the accumulation of organic matter in top soil leads to blocking of FES.

Unlike cesium, strontium is more mobile in mineral soils than in organic soils. It demonstrates faster downward migration in mineral soils compared to cesium (Ivanov *et al.*, 1997b; Gastberger *et al.*, 2000). The mobility of strontium in soil mainly depends on the amount and the quality of organic matter, the content of exchangeable Ca^{2+} and pH. Higher amounts of exchangeable Ca^{2+} and high pH lowers the migration of strontium in soils (Wiklander, 1964). The number of investigations done on Sr-90 is much lower compared to

Cs-137, as Sr-90 needs a laborious and expensive radiochemical separation to quantify its activity (Schimmack *et al.*, 2003; Herranz *et al.*, 2011), while Cs-137 can be directly measured by gamma spectrometry.

The sorption-desorption mechanisms of RN are important to predict their migration behavior and plant availability in soils (Staunton, 1994; Rigol *et al.*, 2002; Giannakopoulou *et al.*, 2012), as soil solution is the medium between the soil components and plant roots. The RN distribution between soil components and the liquid phase is controlled by sorption-desorption reactions (Giannakopoulou *et al.*, 2012). Thus to evaluate the potential risks of RN to living biomass, their sorption behavior needs to be investigated (Bergeijk *et al.*, 1992a; Staunton, 1994; Staunton *et al.*, 2002; Balonov *et al.*, 2010).

A further step to probe the transfer of RN to man through the food chain is to investigate their plant uptake. For this, different approaches can be adopted, ranging from pot- to field experiment. An outdoor lysimeter experiment can provide better simulation of the actual field conditions compared to lab experiments, which are normally done under well controlled conditions but in small scale. The outdoor lysimeter scale experiments are a bridge between lab investigations and full-scale field experiments, while allowing applying RN to undisturbed soil.

Agricultural soil has a fundamental role in human life as it is the main source to meet the growing needs of food and feed production. To maximize crop yields, soil management practices have to be improved. One commonly applied practice to improve soil properties is to add organic matter like manure or compost (Giusquiani *et al.*, 1988). In the last two decades anaerobic bio waste fermentation has proven to be a prime method of recycling. Quickly the residues of this fermentation process were being recognized as valuable

fertilizers. However, as the digestate waste 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 biogas 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).

The development of best uses for organic amendments in agriculture, to improve the soil nutrient and water holding capacities, stands among the top 10 questions related to the future of global agriculture (Pretty *et al.*, 2010). Regarding the effect of organic amendments on contaminants mobility in soil, Beesley *et al.* (2010) reported 30 times higher concentrations of Cu and As after biochar and greenwaste compost application while the concentrations of Zn and Cd significantly decreased with the same treatment. Borchard *et al.* (2012) observed varied sorption of Cu(II) in different biochars before and after composting with farmyard manure while the sorption of SO_4^{2-} was negligible in biochars used either with or without composting.

The main objective of 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. To acquire basic data on sorption behavior of both RN, we conducted sorption-desorption experiments using three different soils from the region (NRW, Germany). In parallel to sorption experiments we probed the fate of radioactive cesium (Cs-137) and strontium (Sr-90) by characterizing their

uptake in different plants in a silty-loam soil with digestate amendment. This work was done using two lysimeters at the lysimeters facility of the Agrosphere institute (IBG-3), Forschungszentrum Jülich (Germany).

2. Experimental approach

2.1 Sorption-desorption experiments

Sorption-desorption experiments were carried out using three soils of different texture and land use. The two arable soils were from intensively used agricultural regions (Merzenhausen and Kaldenkirchen, NRW, Germany), the third soil from a forest region (Wüstebach, Germany). Soil profiles and important physicochemical properties of both arable soils are described (Berns *et al.*, 2008; Garré *et al.*, 2010), the forest soil in (Pätzold and Pütz, 2010). For sorption experiments, soil samples 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 high amounts of native organic matter. Furthermore, the sorption-desorption experiments were carried out at three environmentally relevant temperatures (5, 20 and 35 °C).

2.2 Plant uptake and vertical mobility

2.2.1 Lysimeters set-up

The plant uptake and vertical mobility was investigated using the radioactive chloride salts of cesium (Cs-137) and strontium (Sr-90). The two lysimeters used in this experiment are part of the lysimeter station of Agrosphere (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 V₂A-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 ≤ 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).

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

| Horizon | Depth cm | Sand % | Silt % | Clay % | pH | CEC cmol _c Kg ⁻¹ | Bulk Density 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 |

2.2.2 Lysimeter equipment and instrumentation

The lysimeters were equipped with suction cups and leachate vessels for soil solution sampling, TDRs (Time Domain Reflectometry) and tensiometers for soil water content monitoring and, temperature sensors (PT 100) for soil temperature. The installation of the

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. Additionally, they were sealed (at the installation points) with Sika Flex 252 to avoid the risk of possible leakage of radiochemical contaminated water after application of radionuclides. A sketch of the lysimeter instrumentation and lysimeter after RN application 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.

2.2.2.1 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, K_a of the soil can be determined by Equation 2.1 (Vanderborght *et al.*, 2000).

$$K_a = \left(\frac{c \Delta t_s}{2L} \right)^2 \quad (2.1)$$

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 ' K_a ' was first reported by Topp et al. (1980) and the same expression was used to calculate the volumetric water content:

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

All TDR measurements were carried using a TDR100 system and SDMX 50 multiplexers (Campbell Scientific, Utah, USA). A CR10X data logger (Campbell Scientific, Utah, USA) was used to log the data at 1h intervals.

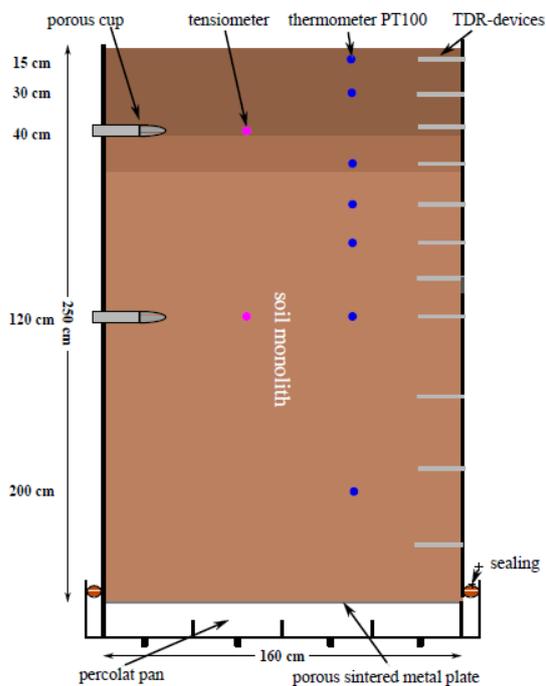


Figure 2.1: a) A sketch of lysimeter instrumentation (used with kind permission of Weihermüller (2005)), b) Lysimeter after radionuclides application.

2.2.2.2 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).

2.2.2.3 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.

2.2.2.4 Suction cups and leachate vessels

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 mobile 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 cm²) is divided into eight segments, each segment having a drainage hole connected to the collection vessel through a plastic pipe. The collection vessels were hermetically closed versus the lysimeter cylinders with a tube sealing (Figure 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).

3. Sorption-desorption of Cs^+ and Sr^{2+} in arable and forest soils affected by soil texture, land use and temperature

Abstract

Soil amendments like digestates from anaerobic waste fermentation processes or biochar have gained popularity in the last two decades and are expected to improve soil functions like nutrient storage and availability or water holding capacity. However, their application could also affect the mobility of radionuclides (RN) in soils. We therefore investigated sorption of cesium (Cs^+) and strontium (Sr^{2+}) in two arable soils and, for comparison, in 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 liquor-digestate in separate experiments. The forest soil was kept unamended as organic amendment is not in practice for such soils. Experiments were carried out at different temperatures, 5, 20, and 35°C , to account for 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 the sorption behavior of the investigated RNs in opposition to the soil texture. The silty-loam soil showed the highest sorption affinity for Cs^+ with a 5 times higher sorption K_d compared to the loamy-sand soil and nearly twice as high as sorption in the forest soil. Strontium sorption was nearly half compared to Cs^+ for all three soils with 4 times higher sorption K_d in the silty-loam soil compared to the loamy-sand and forest soils, in which sorption was nearly equally strong. The effect of both amendments on desorption behavior was also negligible compared to the soil texture. Higher amounts of sorbed Cs^+ were retained in the loamy-sand and forest soils compared to the silty-loam soil. Forest soil with a relatively high amount of native organic matter retained the largest amounts of Sr^{2+} compared to arable soils (with and without amendment). We conclude that

the used organic amendments with regular field application rates will not substantially alter the sorption-desorption dynamics of said RN in arable soils.

3.1 Introduction

Radioactive cesium and strontium are harmful due to their metabolic similarities to nutrients (e.g. potassium [K⁺], ammonium [NH₄⁺], calcium [Ca²⁺]), which promotes their availability to plants (Nisbet *et al.*, 1993; Zhu and Smolders, 2000; Alexakhin *et al.*, 2006). Thus, potentially harmful radioactive isotopes of Cs⁺ and Sr²⁺ can reach the food chain (Zhu and Smolders, 2000; Alexakhin *et al.*, 2006; Wuana and Okieimen, 2011), e.g. following a nuclear accident (Desmet and Sinnaeve, 1992; Steinhäuser *et al.*, 2014). The risk associated to RN is due to their radiation emission and not their physico-chemical properties (Keepax *et al.*, 2009).

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; Lloyd and Lovley, 2001; Kirpichtchikova *et al.*, 2006; Cho *et al.*, 2010; Tangahu *et al.*, 2011). Thus the immobilization of RN can limit their transfer from soil to humans through the food chain.

In the environment, land use type affects distribution and availability of Cs⁺ and Sr²⁺ 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.*, 1997a; Zhu and Smolders, 2000). In fact, Shestopalov *et al.* (2003), Ivanov *et al.* (1997a) and Askbrant *et al.* (1996) observed that ploughing homogenized the concentration of radioactive Cs⁺ and Sr²⁺ in plough layers (ca. 25 cm) of arable soils. Contrastingly, forest soils retained more than 95% of Cs-137 in the top 6 cm of soil. 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 later can alter the concentration of major soil nutrients (e.g. K^+ , Ca^{2+} , Mg^{2+}) that affects the availability of Cs^+ and Sr^{2+} (Konoplev *et al.*, 1993; Lembrechts, 1993; Zibold *et al.*, 2009). For example, Lembrechts (1993) reported reduced availability of Cs^+ and Sr^{2+} after application of K-fertilizers, due to a 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, but effects on Cs^+ and Sr^{2+} availability are hardly known.

In soils, factors that influence availability of Cs^+ and Sr^{2+} are multiple and associated to soil texture, organic matter (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 organic matter (Cornell, 1993; Dumat *et al.*, 1997; Staunton and Levacic, 1999). In soils rich in OM, Cs^+ sorption is hence 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; Bergeijk *et al.*, 1992b). Thus, in terrestrial soils that contain clay minerals Cs^+ is preferentially retained, while Sr^{2+} may migrate to deeper soil layers (Ivanov *et al.*, 1997b; Gastberger *et al.*, 2000). However, soils containing considerable amounts of OM (>2 %) can retain Sr^{2+} (Nilsson *et al.*, 1985).

Thus, sorption-desorption mechanisms of Cs^+ and Sr^{2+} are relevant parameters to predict translocation and plant availability of these RNs in soils (Bergeijk *et al.*, 1992b; Staunton, 1994; Staunton *et al.*, 2002; Balonov *et al.*, 2010). In forest soils, the organic matter stems solely from decomposition of autochthonous litter, while arable soils also contain allochthonous OM (e.g. compost, biochar, digestate). As previously mentioned, an established agricultural 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^{2+} in soils, but to our knowledge studies on the effects of these new forms of organic amendments on sorption behavior of Cs^+ and Sr^{2+} in soils are still 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 residues (Cayuela *et al.*, 2010; Tambone *et al.*, 2010; Gell *et al.*, 2011). Biochar is a byproduct 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 have been increasingly applied to agricultural soils with the aim 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). Applications of biochar and digestate can enhance the content of soil

OM, affect the 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 the sorption-desorption behavior of Cs^+ and Sr^{2+} in two arable soils after biochar and digestate application. With the use of soils from different land uses and soil textures we aimed to account for 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. Furthermore, we used field application rates (common agricultural practice) of biochar and digestate to probe 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 performed the sorption study under different environmentally reasonable temperatures (5°C, 20°C and 35°C).

3.2 Material and methods

3.2.1 Chemicals

Cesium chloride (CsCl), strontium chloride hexahydrate ($\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$), calcium chloride (CaCl_2 ; for pre-equilibration and background solutions) and Triethanolamine used for CEC (cation exchange capacity) measurements were all of analytical grade, barium chloride (BaCl_2) was of extra pure quality. All chemicals were purchased from Merck (Darmstadt, Germany). Purified water from a Millipore unit (conductivity: $< 5 \mu\text{S}/\text{cm}$) was used.

3.2.2 Soils and organic amendments

Three contrasting soils were used in this study: i) a clay-silt soil (Orthic Luvisol) from arable land in Merzenhausen, a sandy-loam (Gleyic Cambisol) from arable land in Kaldenkirchen

and a forest soil (Dystric Cambisol; sandy-clay loam) from Wüstebach area. 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). Organic amendments were applied according to 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 liquid fraction of biogas digestate (i.e. liquor) was obtained from an anaerobic digester in Schwalmatal (PlanET Biogastechnik GmbH, Vreden, Germany), operated under mesophilic conditions. The daily feed rate for the digester was 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 under the same conditions but without any treatment. Biochar was sieved to ≤ 2 mm to match the 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 temperatures 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 (Gastberger *et al.*), CEC and plant-available nutrients (Ca²⁺, K⁺, Mg²⁺, NO₃⁻, NH₄⁺). Elemental

analysis, total C and N were performed on milled soil samples (ball mill) using a Vario EL cube (Elementar Analysensysteme GmbH, Hanau, Germany) in CHN-mode. Soil nutrients (Ca^{2+} , K^+ , Mg^{2+}) 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). Plant-available NH_4^+ and NO_3^- were measured in fresh soil samples using ion chromatography (ICS-3000, Dionex, Germany) after extraction with 0.01 M barium chloride solution (Camps *et al.*, 2004). Soil pH was measured in 0.01 M CaCl_2 solution (with a 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 purified water using a TetraCon325 electrode (Proline 197i WTW, Weilheim, Germany). For pH and conductivity, suspensions were shaken on a horizontal shaker for 4 h and centrifuged for 15 min (Allegra 6 KR, Beckman Coulter Inc. CA, USA) at $2804 \times g$ and 20°C . Potential CEC (i.e. adjusted to pH 7) was measured using a modified Mehlich method (Mehlich, 1942). Surface area was measured by N_2 adsorption using BET method with Autosorb 1 (Quantachrome GmbH, Germany).

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 tubes (Oak ridge Nalgene centrifugation tubes, Rochester, NY, USA) for Cs^+ and 50 mL glass centrifugation bottles (Schott, Mainz, Germany) for Sr^{2+} . 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, 4 g dry soil was suspended in 20 mL 1 M CaCl_2 solution (1:5, w/v), shaken on a horizontal shaker for 1 h at room temperature ($20 \pm 2^\circ\text{C}$) and centrifuged (Allegra 6 KR, Beckman Coulter Inc. CA, USA) at $2804 \times g$ (poly-

carbonate tubes) and 1925 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 CaCl₂ solutions respectively, repeating the same procedure as for 1 M CaCl₂.

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 Sr²⁺ five concentration levels (i.e. 0.1, 0.5, 1, 5 and 10 mM) were used, while desorption was tested at two highest concentration levels (10 and 5 mM). A 0.01 M CaCl₂ 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 Sr²⁺ solution were added to centrifugation tubes, shaken and centrifuged as performed during pre-equilibration. Following OECD Guideline no. 106 (OECD, 2000) the sorption kinetic to reach a stable equilibrium was determined in a preceding experiment. A shaking time of 24h was evaluated for Sr²⁺, while for Cs⁺ a shaking time of 72h was applied (Cornell, 1993; Staunton, 1994; Valcke and Cremers, 1994). After centrifugation a 10 mL aliquot was taken to determine Cs⁺ and Sr²⁺ concentration by inductively coupled plasma mass spectrometry (ICP-MS) using either Elan 6100 (Perkin Elmer, Rodgau, Germany) or Agilent 7500 (Agilent Technologies, Boeblingen, Germany). An additional 10 mL aliquot was stored for pH measurement.

For all three steps of the desorption study each time 20 mL of 0.01 M CaCl₂ solution was added to the centrifugation tubes, shaken for 24 h, centrifuged and the supernatant was sampled as described for the 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. We measured pH in all equilibrated solutions using the same method as for incubated soils.

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:

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

Where C_s represents the concentrations of Cs^+ and Sr^{2+} ($mmol\ Kg^{-1}$), respectively, sorbed to the 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 affinity, while the Freundlich exponent (n) reflects non-linearity of a sorption process. 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).

3.3 Results and Discussion

3.3.1 Soil properties after incubation

Depending on land use, soils differed in their pH and organic carbon concentrations (Table 3.2). The forest soil was acidic and showed a higher carbon concentration in comparison to both arable soils, which were slightly acidic (Table 3.2). The lowest carbon concentration was found in the arable sandy-loam soil, which furthermore had the lowest CEC and available K^+ (Table 3.2). Adding biochar and liquor to arable soils did not substantially alter soil pH, CEC and surface area after six months incubation (Table 3.2). Conversely, total C, total N and available nutrient concentrations were affected in arable soils:

- Total C increased with biochar addition, but remained unaffected after liquor addition.
- Total N increased after addition of biochar and liquor.
- Biochar amendment reduced Ca^{2+} availability in both soil; approximately 87% in silty-loam (Me) and about 41% in sandy loam (Ka). Contrastingly Ca^{2+} availability was increased by ~158 % in sandy-loam (Ka) with liquor addition; however in silty-loam (Me) it was not affected
- Depending on soil texture, the effect of biochar and liquor on Mg^{2+} and K^+ availability varied. Mg^{2+} and K^+ concentrations were increased in sandy-loam after biochar addition, while in the silt-loam soil biochar had the opposite effect on K^+ and Mg^{2+} availability. In the silt-loam soil, liquor addition hardly affected Mg^{2+} ; however, K^+ concentration was decreased. In sandy-loam, liquor addition led to an increase in Mg^{2+} while K^+ availability was reduced.

3.3.2 Sorption kinetics

Strontium sorption reached equilibrium within 24h 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 adsorption sites resulting from organic functional groups could lead to a fast adsorption of Sr^{2+} . Ahmadpour *et al.* (2010) observed a very fast (within 5 minutes) Sr^{2+} adsorption on almond green hull (an agricultural waste). In our experiments, in case of mineral soils, where ion-exchange was the dominating sorption mechanism, a fast

equilibration of Sr^{2+} resulted from the replacement of Ca^{2+} by Sr^{2+} at exchange sites, while in forest soil (Wu), the quick Sr^{2+} adsorption could be attributed to the comparatively higher availability of organic matter sites in addition to exchange sites.

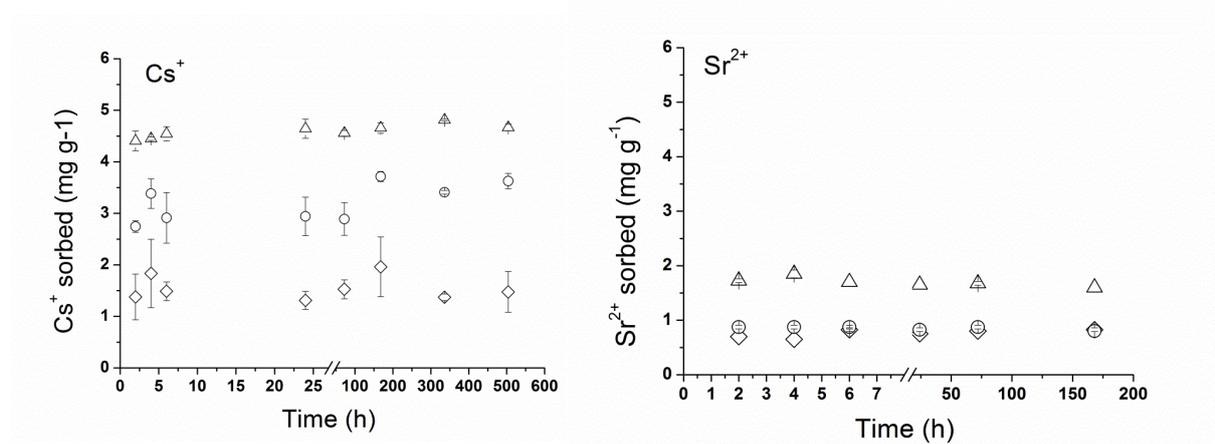


Figure 3.1: Sorption kinetics of Cs^+ and Sr^{2+} in three soils; Δ : silty-loam (Me), \diamond : sandy-loam (Ka) and \circ : forest soil (Wu). Cs^+ sorption for 21 days and Sr^{2+} for 7 days.

Compared to strontium, cesium sorption was non-consistent over time (Figure 3.1). The pre-equilibration with CaCl_2 solutions blocked the regular exchange sites (RES) (Zibold *et al.*, 2009) and sorption proceeded either through exchange with Ca^{2+} ions or in the inner frayed edge sites (Sanzharova *et al.*). Cesium sorption can continue from hours to weeks depending upon the type of soil, its clay mineralogy and organic matter 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 organic matter (OM >80%) compared to the soils with low organic matter (OM < 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, frayed edge sites (Sanzharova *et al.*), causing a slow sorption process (Valcke and Cremers, 1994; Wauters *et al.*, 1994).

Table 3.1: Basic characteristics of the soils under investigation

| Land use | Textural class [†] | Origin | Soil type | Soil texture | | | Field capacity | Available water capacity |
|-------------|-----------------------------|--|------------------|--------------|----------|----------|--------------------|--------------------------|
| | | | | Clay (%) | Silt (%) | Sand (%) | g cm ⁻³ | g cm ⁻³ |
| Arable land | Silt-loam | Merzenhausen (NRW, Germany) (50°55'50"N 6°17'50"E) | Orthic Luvisol | 17 | 79 | 4 | 37 | 21 |
| Arable land | Sandy-loam | Kaldenkirchen (NRW, Germany) (51°18'40"N 6°12'10"E) | Gleyic Cambisol | 4 | 23 | 73 | 23 | 18 |
| Forest | Sandy-clay loam | Wüstebach (NRW, Germany) (50°30'17"N 6°19'56"E) | Dystric Cambisol | 34 | 19 | 47 | 37 | 14 |

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

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 | Ca ²⁺ | Mg ²⁺ | K ⁺ |
|--------------------------|---------|---------------------|-----------------------|----------------------------|------------------|------------------|-------------|-------------|---------------------------|---------------------------|---------------------------|----------------|
| | | | $\mu\text{S cm}^{-1}$ | $\text{m}^2 \text{g}^{-1}$ | | | | | | | | |
| -/- | Biochar | 8.0 | 1031 ± 12 | -/- | -/- | 700 ± 0.2 | 700 ± 0.1 | 5.46 ± 0.05 | 1600 ± .05 ^{+,¢} | 1920 ± .05 ^{+,¢} | 2570 ± .05 ^{+,¢} | |
| -/- | Liquor | 9.3 | 15.7 ± 0.2 | -/- | -/- | -/- | -/- | -/- | -/- | -/- | -/- | |
| -/- | | 6.0 | 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 | |
| Arable land / silt loam | Biochar | 6.2 | 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 | 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 / sandy loam | -/- | 6.2 | 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 | 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 | 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 | 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 | |

OA: Organic amendment, ¢ (Supplier analytical lab), + (EN ISO 11885), £ (n = 2), ¥ (n = 1 & r > 0.99)

3.3.3 Effect of soil texture and land use on sorption-desorption

Cesium

Effect of soil type on sorption

Silty-loam soil (Me) showed a 4-5 times higher sorption capacity for Cs^+ than sandy-loamy (Ka) and nearly twice as high as forest soil (Wu) (K_{Fads} values, Table 3.3). Higher exchange capacities of silty-loam (Me) and forest (Wu) soils compared to sandy-loam (Ka) (CEC values, Table 3.2) led to higher Cs^+ sorption in these soils. Also, the larger surface to mass ratios (BET values, Table 3.2) for these soils provided more ion-exchange sites resulting in higher Cs^+ sorption. The non-linear behavior of the adsorption isotherms (Figure 3.2) shows that a decreasing amount of analyte was sorbed with increasing concentration. This could be associated to the presence of different types of exchange sites in the adsorbent (Dumat *et al.*, 1997). The deviation of the exponent n from unity (Table 3.3) shows the heterogeneity of the adsorption surfaces and indicates a saturation of sorption sites.

Cesium sorption was nearly half in forest soil (Wu) compared to silty-loam (Me) even with larger CEC and BET values (Table 3.2) and, comparable clay content (Table 3.1). This different behavior of Cs^+ sorption in forest soil (Wu) could be the result of the higher content of SOM and the more acidic soil pH. Cs^+ sorption in mineral soil decreases with increasing amount of SOM as OM can occupy the planar sites on clays, reducing their sorption capacity (Dumat *et al.*, 1997). These planar sites on particle surfaces constitute a large part of the sorption capacity of soils (Söderlund *et al.*, 2011). Additionally, the acidic nature of forest soil caused lower Cs^+ sorption compared to silty-loam. At acidic pH, higher concentration of H^+ ions could lead to a competition with Cs^+ for the available sorption sites. Also, at low pH levels, clay minerals can be dissolved resulting in the destruction of sorption sites leading to a lower Cs^+ sorption (Giannakopoulou *et al.*, 2007).

Effect of amendment on sorption

In opposition to soil texture and land use the effect of amendment on sorption was negligible for both contaminants (Figure 3.2). In case of silty-loam (Me), biochar and digestate did not have a major effect on surface heterogeneity (e.g. creation of new surfaces with different adsorption capabilities) (n values, Table 3.3).

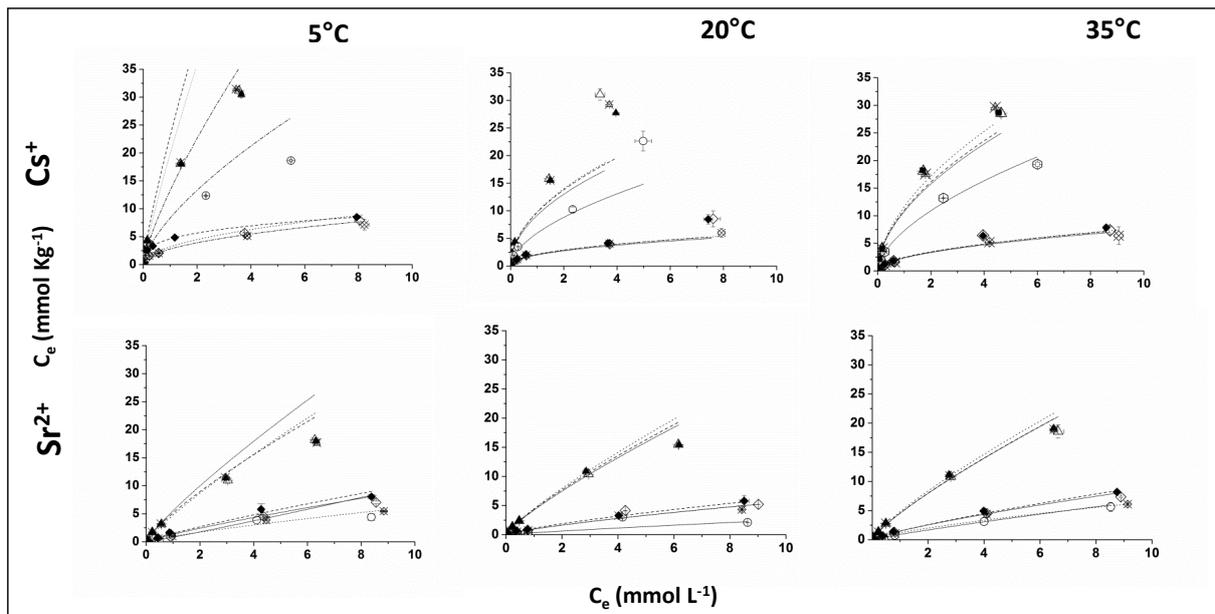


Figure 3.2: Sorption dynamics of Cs^+ and Sr^{2+} at three different temperatures: 5°C, 20°C (room temperature) and 35°C in different soils; silty loam – Me (Δ), sandy loam – Ka (\diamond), forest soil – Wu (\circ). Open symbols: control soils; closed symbols: biochar amended; crossed symbols: liquor (digestate) amended. Data fitted with Freundlich model, $C_s = C_e K^n$, where C_s is analyte concentration in solid phase and C_e is equilibrium solution concentration. Data represents mean \pm one standard deviation (n=3).

Effect of soil type on desorption

The higher Cs^+ retention in sandy-loam (Ka) (H: 0.45, Table 3.3) compared to silty-loam (Me) (H: 0.55, Table 3.3) and the nearly comparable retention of Cs^+ in forest soil (Wu) (H: 0.46, Table 3.3) is contradictory. Principally, the silty-loam soil (Me) and forest soil (Wu) should retain more Cs^+ due to their higher clay contents (17% and 34 % respectively, Table 3.1)

compared to sandy-loam (Ka) with 4% clay. This information contradicts to other investigations (Hsu and Chang, 1994; Dumat *et al.*, 1997; Staunton *et al.*, 2002) which described that clayey soil has a higher capability to retain Cs^+ compared to sandy and organic soils. This is due to the fact that Cs^+ , being a univalent cation, has a higher potential for adsorption on clay minerals to balance the negative charge on the alumino-silicate structures (Cornell, 1993; Comans *et al.*, 1998; Hakem *et al.*, 2000; Thored, 2010). At the clay edges, weathering occurs leading to interlayer expansion with subsequent release of K^+ . This results in formation of specific sites for cations with low hydration energy like Cs^+ and NH_4^+ (Rigol *et al.*, 2002). Organic matter with negative surface charge can also retain cations and have an influence on the CEC of soils (Kabata-Pendias, 2004). However, the amount of Cs^+ sorbed on clay will be preferentially higher compared to OM. Dunigan and Francis (1972) suggested specific interactions of OM based on higher retention of cesium by humic acid.

Effect of amendment on desorption

Cs^+ desorption showed a varying trend with amendment type in different soils; it was more prominent in sandy-loam (Ka) compared to silty-loam (Me) (Figure 3.3). In sandy-loam soil (Ka), biochar led to 35% increase (H: 0.29, Table 3.3) while digestate caused 13% decrease (H: 0.51, Table 3.3) in Cs^+ retention when compared to bare soil (H: 0.45, Table 3.3). Contrarily, in silty-loam soil (Me) both amendments caused ~20% decrease in Cs^+ retention (H: 0.65, biochar amended and H: 0.67, digestate amended; Table 3.3) compared to bare soil (H: 0.55, Table 3.3).

In sandy-loam soil, biochar provided additional sites for sorption on organic matter (TOC: 11.2, Table 3.2) compared to digestate amended and control soils (TOC: 6.7 and 6.3 respectively, Table 3.2). Moreover, lower Ca^{2+} concentration in biochar amended sandy-loam compared to control led to lower competition among different cations (e.g. Ca^{2+} and

Cs⁺) for limited sorption sites (low clay content, 4%, Table 3.1) resulting in higher Cs⁺ retention. Compared to sandy-loam soil, the effect of biochar amendment was less pronounced (TOC values, Table 3.2) in silty-loam. Furthermore, despite a large difference in Ca²⁺ concentrations (Ca²⁺ values, Table 3) in biochar amended silty-loam compared to digestate amended and control soils, the Cs⁺ retention was not affected. Here the Cs⁺ retention was more influenced by K⁺ amount in opposition to organic matter and Ca²⁺ concentration. Lower K⁺ concentrations (K⁺ values, Table 3.2) in amended silty-loam soils compared to the control resulted in lower replacement of K⁺ by Cs⁺ which led to reduced Cs⁺ retention in amended silty-loam soils.

Concerning the role of OM on Cs⁺ sorption in soil, an important question is whether the interaction of Cs⁺ is preferentially controlled by OM or by mineral components. In case of soils with higher amounts of OM, it is well established that cesium fixation is reduced due to a blocking of clay sorption sites by the OM (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 *et al.*, (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 play a role in the higher retention of Cs⁺ in forest soil (Wu) compared to biochar amended silty-loam soil, which has a comparable OM content (Table 3.2).

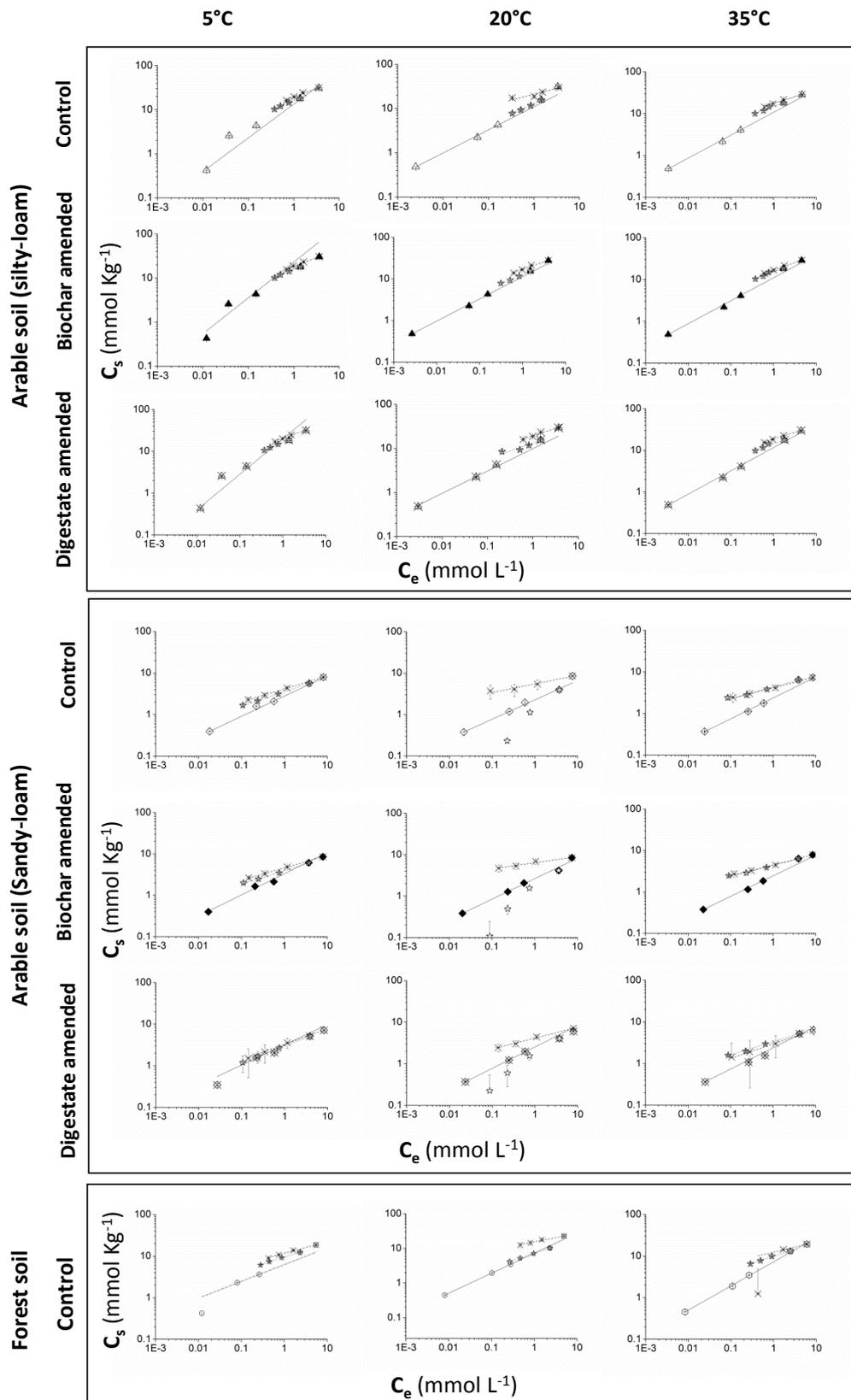


Figure 3.3: Freundlich sorption-desorption isotherms for Cs^+ in different soils at three different temperatures: 5°C, 20°C (room temperature) and 35°C. Δ , \circ , \diamond : sorption, \times : 10mM desorption and \star : 5mM desorption. Data represents mean \pm one standard deviation ($n=3$).

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

| T | Land use/ texture | OA | Sorption | | Desorption 10mM | | | Desorption 5mM | | |
|----|-----------------------------|---------|---|------------------|---|------------------|----------|---|------------------|----------|
| °C | S | | K_{Fads} (mmol ¹⁻ⁿ L ⁿ Kg ⁻¹) | n_{ads} (-) | K_{Fdes} (mmol ¹⁻ⁿ L ⁿ Kg ⁻¹) | n_{des} (-) | H (-) | K_{Fdes} (mmol ¹⁻ⁿ L ⁿ Kg ⁻¹) | n_{des} (-) | H (-) |
| 5 | Arable land / silt loam | -/- | 13.32 \pm 2.25 | 0.76 \pm 0.05 | 19.55 \pm 0.62 | 0.37 \pm 0.03 | 0.49 | 15.85 \pm 0.08 | 0.41 \pm 0.01 | 0.54 |
| | | Biochar | 23.14 \pm 15.11 | 0.81 \pm 0.18 | 18.72 \pm 0.5 | 0.38 \pm 0.02 | 0.47 | 15.67 \pm 0.11 | 0.42 \pm 0.02 | 0.52 |
| | | Liquor | 19.89 \pm 10.01 | 0.85 \pm 0.13 | 20.39 \pm 0.46 | 0.36 \pm 0.03 | 0.42 | 16.01 \pm 0.12 | 0.4 \pm 0.02 | 0.47 |
| | Arable land / sandy loam | -/- | 2.79 \pm 0.08 | 0.49 \pm 0.01 | 4.16 \pm 0.03 | 0.31 \pm 0.00 | 0.64 | 3.56 \pm 0.02 | 0.35 \pm 0.00 | 0.71 |
| | | Biochar | 3.32 \pm 0.28 | 0.51 \pm 0.03 | 4.60 \pm 0.02 | 0.30 \pm 0.00 | 0.58 | 3.93 \pm 0.05 | 0.33 \pm 0.01 | 0.65 |
| | | Liquor | 3.0 \pm 0.42 | 0.49 \pm 0.08 | 3.27 \pm 0.06 | 0.37 \pm 0.01 | 0.76 | 2.97 \pm 0.0 | 0.4 \pm 0.00 | 0.83 |
| | Forest /sandy clay loam | -/- | 6.24 \pm 0.84 | 0.40 \pm 0.03 | 11.71 \pm 0.24 | 0.27 \pm 0.01 | 0.68 | 9.47 \pm 0.08 | 0.32 \pm 0.01 | 0.80 |
| 20 | Arable land / silt loam | -/- | 10.98 \pm 0.26 | 0.50 \pm 0.00 | 21.02 \pm 1.17 | 0.26 \pm 0.06 | 0.55 | 12.93 \pm 0.12 | 0.49 \pm 0.02 | 0.98 |
| | | Biochar | 9.72 \pm 0.77 | 0.51 \pm 0.01 | 17.65 \pm 0.6 | 0.33 \pm 0.03 | 0.65 | 13 \pm 0.1 | 0.44 \pm 0.02 | 0.86 |
| | | Liquor | 9.84 \pm 0.76 | 0.51 \pm 0.01 | 19.31 \pm 0.59 | 0.34 \pm 0.03 | 0.67 | 13.24 \pm 0.46 | 0.37 \pm 0.07 | 0.73 |
| | Arable land / sandy loam | -/- | 2.25 \pm 0.06 | 0.47 \pm 0.00 | 5.47 \pm 0.21 | 0.21 \pm 0.02 | 0.45 | n.a | n.a | n.a |
| | | Biochar | 2.63 \pm 0.1 | 0.50 \pm 0.01 | 6.4 \pm 0.18 | 0.15 \pm 0.01 | 0.29 | n.a | n.a | n.a |
| | | Liquor | 2.54 \pm 0.06 | 0.51 \pm 0.00 | 4.15 \pm 0.09 | 0.26 \pm 0.01 | 0.51 | n.a | n.a | n.a |
| | Forest /sandy clay loam | -/- | 5.95 \pm 0.22 | 0.57 \pm 0.00 | 13.52 \pm 0.47 | 0.26 \pm 0.03 | 0.46 | 6.66 \pm 0.03 | 0.5 \pm 0.00 | 0.89 |
| 35 | Arable land / silt loam | -/- | 10.78 \pm 0.47 | 0.55 \pm 0.00 | 17.71 \pm 0.50 | 0.32 \pm 0.02 | 0.57 | 14.93 \pm 0.35 | 0.36 \pm 0.04 | 0.66 |
| | | Biochar | 11.00 \pm 0.06 | 0.55 \pm 0.01 | 16.95 \pm 0.37 | 0.35 \pm 0.02 | 0.64 | 15.32 \pm 0.48 | 0.36 \pm 0.05 | 0.66 |
| | | Liquor | 11.64 \pm 0.64 | 0.56 \pm 0.64 | 18.67 \pm 0.33 | 0.32 \pm 0.02 | 0.57 | 14.54 \pm 0.43 | 0.34 \pm 0.05 | 0.60 |
| | Arable land / sandy loam | -/- | 2.35 \pm 0.14 | 0.50 \pm 0.02 | 4.13 \pm 0.08 | 0.26 \pm 0.01 | 0.52 | 4.33 \pm 0.11 | 0.29 \pm 0.02 | 0.56 |
| | | Biochar | 2.45 \pm 0.13 | 0.50 \pm 0.02 | 4.47 \pm 0.09 | 0.26 \pm 0.01 | 0.52 | 4.37 \pm 0.09 | 0.26 \pm 0.02 | 0.53 |
| | | Liquor | 2.39 \pm 0.10 | 0.51 \pm 0.01 | 2.95 \pm 0.05 | 0.35 \pm 0.01 | 0.68 | 3.33 \pm 0.04 | 0.31 \pm 0.01 | 0.61 |
| | Forest /sandy clay loam | -/- | 7.29 \pm 0.32 | 0.58 \pm 0.01 | 12.40 \pm 1.78 | 0.25 \pm 0.1 | 0.42 | 9.86 \pm 0.08 | 0.32 \pm 0.01 | 0.56 |

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

Strontium

Effect of soil type on sorption

Compared to cesium the sorption of strontium was nearly half in all soils (Figure 3.2). Silty-loam (Me) demonstrated 4-5 times higher Sr^{2+} sorption compared to sandy-loam (Ka) and forest (Wu) soils (K_{Fads} values, Table 3.4). In mineral soils, higher amounts of strontium are located in silt and sand fractions compared to clay (Nilsson *et al.*, 1985). A larger amount of silt (~4 times) in silty-loam (Me) compared to sandy-loam (Ka) and forest soil (Wu) (Table 3.1) resulted in higher sorption of Sr^{2+} in silty-loam (Me). However, forest soil (Wu) with approximately 8-times higher clay content (Table 3.1) compared to sandy-loam (Ka), showed similar sorption capacity to the sandy soil. This leads to the conclusion that Sr^{2+} interaction in mineral soils is less affected by clay as is the case for Cs^+ , also reported by other investigators (Bergeijk *et al.*, 1992b). The effect of sand fraction on Sr^{2+} sorption was negligible. The sandy-loam soil (Ka) with approx. 1.5 times higher sand fraction compared to the forest soil (Wu) (Table 3.1) exhibited a comparable sorption than the latter. So, in our results, the silt fraction played a dominant role in Sr^{2+} sorption. Moreover, the Freundlich linearity parameter n_{ads} was close to unity (Table 3.4), indicating homogeneity of adsorption surfaces for Sr^{2+} .

Effect of amendment on sorption

Strontium sorption was more influenced by soil texture and land use compared to the type of amendment (Figure 3.2). Surprisingly, despite an approx. 50 % increase in OM content (TOC values, Table 3.2) after biochar amendment, the Sr^{2+} sorption behavior in silty-loam did not change. Contrarily, in sandy-loam soil (Ka), an 87% increase in OM after biochar amendment tended to increase Sr^{2+} sorption. Moreover, the concentration of competing ions (Ca^{2+}) also affects Sr^{2+} sorption due to competition for available sorption sites. In sandy-

loam soil, digestate amendment caused 158% increase in Ca^{2+} concentration, resulting in lower Sr^{2+} sorption in digestate amended soil. However, the effect of Ca^{2+} concentration seems less effective in biochar amended soils. In silty-loam soil, 87% lower Ca^{2+} concentration after biochar amendment compared to control (Ca^{2+} values, Table 3.2), did not improve sorption capacity of silty-loam soil. Comparing the sorption trends in the two mineral soils, it can be speculated that organic matter and competing cations (Ca^{2+}) have higher influence on Sr^{2+} sorption in soils with low silt content (sandy-loam soil). However, when the concentration of the mineral component responsible for Sr^{2+} sorption (silt) is higher (silty-loam), the effect of OM and competing ions becomes less significant.

Effect of soil type on desorption

The forest soil (Wu) showed larger sorption affinity for Sr^{2+} compared to silty-loam (Me) and sandy-loam (Ka), (H values, Table 3.4). Among the two mineral soils, the sandy soil reflected a slightly higher affinity for Sr^{2+} compared to the silty soil. Higher retention of Sr^{2+} in forest soil (Wu) compared to mineral soils is in agreement with other investigations (Bergeijk *et al.*, 1992b; Sanzharova *et al.*, 2009). In mineral soils, Sr^{2+} sorbs on exchange sites and is easily displaced by competing ions like Ca^{2+} (Nilsson *et al.*, 1985; Sanzharova *et al.*, 2009). While in organic soils, Sr^{2+} is bound to organic matter fractions, e.g., fulvic and humic acids, through chelation and complexation and is not displaceable by competing ions (Saar and Weber, 1982; Sanchez *et al.*, 1988). A slightly higher retention of Sr^{2+} by sandy-loam compared to silty-loam reflects the lower capability of silt to retain Sr^{2+} (despite its higher capacity for Sr^{2+} sorption).

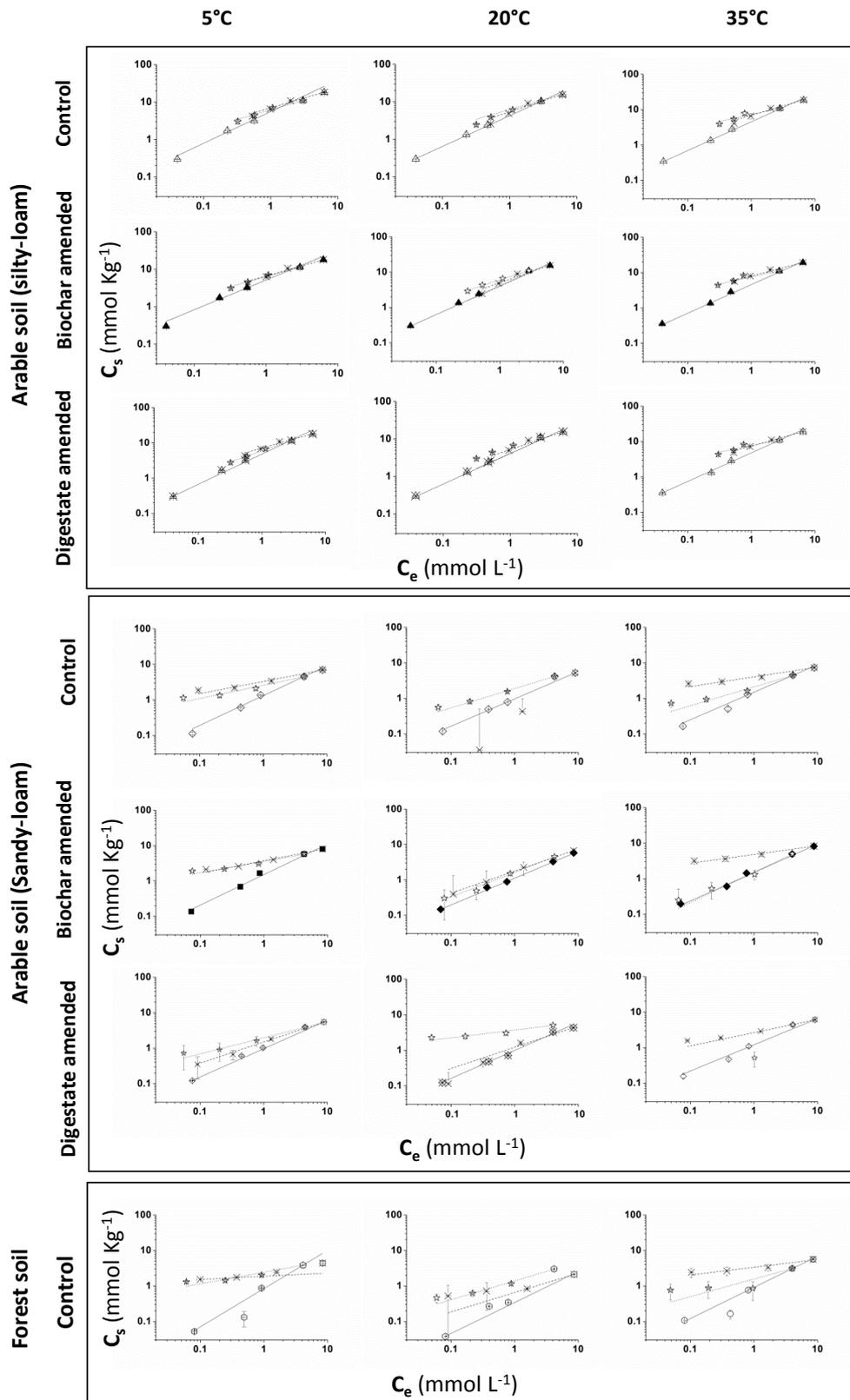


Figure 3.4: Freundlich sorption-desorption isotherms for Sr^{2+} in different soils at three different temperatures: 5°C, 20°C (room temperature) and 35°C. Δ , \circ , \diamond : sorption, \times : 10mM desorption and \star : 5mM desorption. Data represents mean \pm one standard deviation (n=3).

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

| T | Land use/ texture | OA | Sorption | | Desorption 10mM | | | Desorption 5mM | | |
|--------------------------|-----------------------------|-----------------|---|-------------------------|---|-------------------------|-----------------|---|-------------------------|----------|
| $^{\circ}\text{C}$ | | | K_{Fads} ($\text{mmol}^{1-n} \text{L}^n$ Kg^{-1}) | n_{ads} (-) | K_{Fdes} ($\text{mmol}^{1-n} \text{L}^n$ Kg^{-1}) | n_{des} (-) | H (-) | K_{Fdes} ($\text{mmol}^{1-n} \text{L}^n$ Kg^{-1}) | n_{des} (-) | H (-) |
| 5 | Arable land / silt loam | -/- | 5.55 ± 0.77 | 0.85 ± 0.07 | 7.00 ± 0.57 | 0.53 ± 0.05 | 0.62 | 6.21 ± 0.29 | 0.52 ± 0.05 | 0.61 |
| | | Biochar | 5.16 ± 0.55 | 0.80 ± 0.06 | 6.56 ± 0.58 | 0.55 ± 0.05 | 0.69 | 6.38 ± 0.22 | 0.54 ± 0.04 | 0.67 |
| | | Liquor | 4.80 ± 0.31 | 0.85 ± 0.02 | 7.08 ± 0.61 | 0.51 ± 0.06 | 0.60 | 5.92 ± 0.14 | 0.62 ± 0.02 | 0.73 |
| | Arable land / sandy loam | -/- | 1.32 ± 0.10 | 0.84 ± 0.06 | 3.31 ± 0.21 | 0.34 ± 0.04 | 0.40 | 2.58 ± 0.16 | 0.37 ± 0.04 | 0.44 |
| | | Biochar | 1.52 ± 0.13 | 0.86 ± 0.08 | 3.74 ± 0.19 | 0.36 ± 0.03 | 0.42 | 3.58 ± 0.19 | 0.32 ± 0.04 | 0.37 |
| | | Liquor | 0.97 ± 0.02 | 0.80 ± 0.00 | 1.50 ± 0.06 | 0.59 ± 0.02 | 0.74 | 1.96 ± 0.11 | 0.45 ± 0.04 | 0.56 |
| Forest /sandy clay loam | -/- | 0.84 ± 0.08 | 1.08 ± 0.06 | 1.88 ± 0.2 | 0.09 ± 0.05 | 0.08 | 2.43 ± 0.17 | 0.33 ± 0.05 | 0.31 | |
| 20 | Arable land / silt loam | -/- | 4.25 ± 0.19 | 0.82 ± 0.02 | 5.41 ± 0.78 | 0.59 ± 0.09 | 0.72 | 6.21 ± 0.29 | 0.52 ± 0.05 | 0.63 |
| | | Biochar | 4.05 ± 0.18 | 0.82 ± 0.02 | 4.96 ± 0.69 | 0.64 ± 0.09 | 0.78 | 6.01 ± 0.13 | 0.58 ± 0.0 | 0.71 |
| | | Liquor | 4.06 ± 0.14 | 0.82 ± 0.01 | 5.19 ± 0.72 | 0.61 ± 0.09 | 0.74 | 4.1 ± 0.29 | 0.79 ± 0.07 | 0.96 |
| | Arable land / sandy loam | -/- | 0.96 ± 0.03 | 0.77 ± 0.02 | n.a | n.a | n.a | 1.88 ± 0.07 | 0.54 ± 0.03 | 0.70 |
| | | Biochar | 1.64 ± 0.07 | 0.70 ± 0.03 | 1.77 ± 0.07 | 0.62 ± 0.02 | 0.88 | 1.11 ± 0.05 | 0.76 ± 0.02 | 1.08 |
| | | Liquor | 0.99 ± 0.04 | 0.79 ± 0.02 | 1.2 ± 0.17 | 0.6 ± 0.07 | 0.76 | 3.69 ± 0.19 | 0.22 ± 0.04 | 0.28 |
| Forest / sandy clay loam | -/- | 0.34 ± 0.04 | 0.87 ± 0.04 | 0.65 ± 0.01 | 0.55 ± 0.01 | 0.63 | 1.38 ± 0.1 | 0.53 ± 0.06 | 0.61 | |
| 35 | Arable land / silt loam | -/- | 4.51 ± 0.17 | 0.81 ± 0.02 | 6.88 ± 0.56 | 0.53 ± 0.05 | 0.65 | 7.27 ± 0.48 | 0.39 ± 0.07 | 0.48 |
| | | Biochar | 4.55 ± 0.15 | 0.81 ± 0.02 | 7.99 ± 0.32 | 0.47 ± 0.03 | 0.58 | 7.53 ± 0.36 | 0.4 ± 0.0 | 0.49 |
| | | Liquor | 4.77 ± 0.17 | 0.81 ± 0.02 | 7.4 ± 0.28 | 0.51 ± 0.02 | 0.63 | 7.62 ± 0.48 | 0.36 ± 0.07 | 0.44 |
| | Arable land / sandy loam | -/- | 1.48 ± 0.06 | 0.78 ± 0.04 | 4.03 ± 0.25 | 0.27 ± 0.03 | 0.35 | 2.09 ± 0.18 | 0.53 ± 0.06 | 0.68 |
| | | Biochar | 1.48 ± 0.10 | 0.8 ± 0.05 | 4.78 ± 0.18 | 0.25 ± 0.02 | 0.31 | 1.49 ± 0.17 | 0.85 ± 0.09 | 1.06 |
| | | Liquor | 1.19 ± 0.22 | 0.74 ± 0.08 | 2.65 ± 0.00 | 0.38 ± 0.00 | 0.51 | n.a | n.a | n.a |
| Forest /sandy clay loam | -/- | 0.91 ± 0.06 | 0.88 ± 0.04 | 3.35 ± 0.25 | 0.22 ± 0.04 | 0.25 | 1.56 ± 0.37 | 0.50 ± 0.17 | 0.19 | |

T: Temperature; S: Soil; OA: Organic amendment; K_{F} : Freundlich capacity parameter; n: Freundlich linearity parameter, H: Hysteresis index

Effect of amendment on desorption

The effect of amendments on Sr^{2+} desorption in silty-loam soil (Me), was similar to sorption (negligible effect). In sandy-loam soil (Ka), digestate amendment tended to decrease Sr^{2+} retention following a similar trend to sorption. Surprisingly, biochar which led to an increased Sr^{2+} sorption in sandy-loam, here showed an opposing trend with decreased Sr^{2+} retention in biochar amended soil. Lower retention of Sr^{2+} in digestate amended sandy-loam could be due to higher availability of competing ions (Ca^{2+}). While lower affinity of Sr^{2+} in biochar amended sandy-loam (Ka) compared to forest soil (Wu), is probably due to difference in origin of organic matter.

3.3.4 Effect of temperature on sorption-desorption

Cesium

Effect on sorption

Silty-loam soil (Me) showed higher Cs^+ sorption at 5°C compared to higher temperatures, 20°C (room temperature) and 35°C. Moreover, the sorption in amended soils was more influenced by changes in temperature, yielding K_{Fads} values almost double to the non-amended soil (Table 3.3). Sandy-loam soil (Ka) followed a similar trend to silty-loam for Cs^+ sorption; however the effect was not as prominent as in silty-loam. Contrasting to mineral soils, forest soil (Wu) 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).

In literature, a varying trend of Cs^+ sorption with change in temperature was described (Cornell, 1993; Hadadi *et al.*, 2009; Yildiz *et al.*, 2011). A decrease in Cs^+ adsorption 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 (T° range?) 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 (T° range). The variation in Cs^+ sorption with changing temperature could be attributed to differences in soil texture and its clay mineralogy. In our results, mineral soils followed a similar trend to Cornell (1993). The opposing behavior of forest soil (Wu) compared to mineral soils could be due to differences in its clay mineralogy and the composition of organic matter.

Effect on desorption

The effect of temperature on Cs^+ affinity varied with the type of soil and amendment. Silty-loam soil (Me) presented 11-14% higher hysteresis at 5°C (H: 0.49, Table 3.3) compared to the corresponding hysteresis at 20°C (H: 0.55) and 35°C (H: 0.57) (Table 3.3) for the non-amended soil. The trend was similar in biochar amended silty-loam with ~27% higher hysteresis at 5°C (H: 0.47, Table 3.3) compared to higher temperatures; (H: 0.65, 20°C and H: 0.64, 35°C; Table 3.3). However, digestate amended silty-loam soil exhibited a varying trend with ~17% decrease in hysteresis from 35 to 20°C (H: 0.57 and 0.67 respectively, Table 3.3) and a 37% increase in hysteresis index from 20 to 5°C (H: 0.67 and 0.42 respectively, Table 3.3). The forest soil (Wu) presented an opposite trend to silty-loam soil (Me), lower Cs^+ retention with decrease in temperature. In forest soil (Wu), the hysteresis index was decreased (~47%) from 20°C (H: 0.46) to 5°C (H: 0.68); however, for a temperature change from 35°C (H: 0.42) to 20°C (H: 0.46), the decrease in hysteresis was low (~9%).

Sandy-loam soil (Ka) showed drastic changes in hysteresis with temperature variation. The non-amended sandy-loam soil presented ~11% increase in hysteresis with decrease in temperature from 35°C (H: 0.52) to 20°C (H: 0.45), while the hysteresis was reduced (~42%) from 20°C (H: 0.45) to 5°C (0.64). Biochar amendment exhibited ~44% increase in hysteresis

from 35°C (H: 0.52) to 20°C (H: 0.29) and about 100% reduction in hysteresis with decrease in temperature from 20°C (H: 0.29) to 5°C (H: 0.58). Digestate amendment showed a similar trend to biochar with ~25% increase in hysteresis from 35°C (H: 0.68) to 20°C (H: 0.51) and about 50% decrease in hysteresis with change in temperature from 20°C (H: 0.51) to 5°C (H: 0.76).

Strontium

Effect on sorption

Temperature had quite diversified effects on Sr^{2+} sorption in different soils, more prominent in soils of different origin than the type of amendment (Figure 3.4). Silty-loam soil (Me) followed a similar trend to Cs^+ sorption with slightly higher sorption at 5°C (~ 1.2 times) compared to higher temperatures (20 and 35°C) (K_{Fads} , Table 3.4). However, forest soil (Wu) showed higher sorption (~ 2.5 times) at 5 and 35°C compared to room temperature (20°C). Sandy-loam non-amended soil showed a similar trend to forest soil (Wu) with 1.5 times higher Sr^{2+} sorption at 5 and 35°C compared to room temperature (20°C). However, in amended sandy-loam soils, temperature did not lead to a comparable difference in Sr^{2+} sorption.

Higher Sr^{2+} sorption in forest soil compared to silty-loam at 5°C could be due to differences in OM and clay minerals in both soils. Sr^{2+} sorption is more influenced by OM and silt fractions and less by clay content (Nilsson *et al.*, 1985; Bergeijk *et al.*, 1992b). However, the type of OM could influence Sr^{2+} sorption. In the context of effect of temperature on Sr^{2+} sorption in clays, Rani and Sasidhar (2012) reported an increase in Sr^{2+} sorption with increasing temperatures (T°range) on kaolinite-rich clays. In another study, Ahmadpour *et al.*, (2010) did not observe any effect of temperature variation (10, 20 and 30°C) on Sr^{2+}

sorption on almond green hull (an agricultural waste). So, it could be speculated that the only parameter leading to higher Sr^{2+} sorption in forest soil is its clay mineralogy as other soil fractions like silt, sand and even OM will be less affected by this temperature variation.

Effect on desorption

The effect of temperature variation on Sr^{2+} affinity is erratic and shows no clear trend. In general hysteresis was higher both at 5 and 35°C compared to room temperature (20°C) (Figure 3.4). Forest soil (Wu) exhibited highest Sr^{2+} retention, followed by sandy-loam (Ka) and lowest in silty-loam (Me) (H values, Table 3.4). Among the two mineral soils, sandy-loam (Ka) displayed a slightly higher retention of Sr^{2+} compared to silty-loam (Me) at 5 and 35°C, while at room temperature the difference was not significant (H values, Table 3.4).

The effect of temperature variation in amended soils was similar to the non-amended soil (higher hysteresis at 5 and 35°C compared to 20°C) in silty-loam soil (Me). Temperature variation led to drastic changes in amended sandy-loam soils. Biochar amended sandy loam showed a decrease in hysteresis from 35°C (H: 0.31) to 20°C (H: 0.88) and an increase in hysteresis from 20°C (H: 0.88) to 5°C (H: 0.42) (Table 3.4). Digestate amendment in sandy-loam caused a decrease in hysteresis from 35°C (H: 0.51) to 20°C (H: 0.76) while the temperature variation from 20 to 5°C did not affect the hysteresis index (H values, Table 3.4).

3.4 Conclusion

Compared to soil texture and land use, the applied amendments with field application rates had no significant effects on the sorption behaviors of cesium and strontium. The trend was similar for desorption, where differences were more prominent in soils of different origin than differently amended soils. This suggests that amendments applied with the

recommended rates (common agricultural practice) will most likely not affect the soil-plant transfer of the target contaminants. The two contaminants showed a distinct behavior in sorption-desorption dynamics. Cesium showed highest sorption in silty-loam (Me), followed by forest soil (Wu) and lowest in sandy-loam (Ka) in agreement with other investigations. Compared to cesium, strontium sorption was nearly half in all soils with higher sorption in silty-loam (Me) and almost similar sorption in both sandy-loam (Ka) and forest soils (Wu). The native organic matter in forest soil (Wu) had a higher influence on Sr^{2+} retention compared to the applied organic matter (amendments). Decrease in temperature (20 to 5°C) led to higher Cs^+ sorption in silty-loam (Me), while in forest soil (Wu) and sandy-loam (Ka), temperature effect was hardly quantifiable. Cesium showed higher hysteresis in sandy-loam (Ka) and forest soils (Wu) compared to silty-loam (Me) at room temperature, while at 5°C, the trend was just opposite. The effect of temperature on strontium sorption was almost negligible compared to cesium. Sr^{2+} desorption was quite varied at different temperatures with higher retention at 5 and 35°C compared to room temperature (20°C).

4. Plant uptake and vertical mobility of Cs-137 and Sr-90 in digestate amended silty-loam soil - a lysimeter scale experiment

Abstract

Plant uptake and vertical mobility of Cs-137 and Sr-90 are of great concern due to their accessibility to humans through the food chain. Biogas digestate has gained popularity as organic amendment in agriculture due to its high organic matter and nutrient content. In the present study, we investigated the plant uptake and vertical mobility of Cs-137 and Sr-90 in a silty-loam soil after digestate amendment. The experiment was conducted in lysimeters with three different crops, summer wheat, summer oat and an intercrop - Teralife. Digestate was applied following the common agricultural practice with a rate of 34 t/ha. The soil contamination was done using chloride salts of both radionuclides, with a final soil contamination level of $\sim 65 \text{ MBq m}^{-2}$ for Cs-137 and $\sim 18 \text{ MBq m}^{-2}$ for Sr-90 in the top 2 cm soil. The results indicate that the biogas digestate (with applied rates) did not have a major effect on the plant uptake of the two radionuclides. However, the different plant species showed a difference in uptake. Weed plants showed a higher uptake compared to the main crop plants (wheat/oat). Due to the high applied activity in soil, a clear translocation of activity was observed in different plant parts. The grains contained less activity than the shoots for both RN. Sr-90 exhibited an 80-100 times higher plant uptake and translocation compared to Cs-137. The results for soil samples collected at different soil depths (0-5, 5-10, 10-15, 15-20 cm) indicated that most of the applied activity was retained in the top soil layers. Furthermore, the percolate samples (suction cups at the 40 cm depth) did not show any activity, confirming the lower vertical mobility of both RN. We conclude that biogas digestate applied

according to the common agriculture practice will not affect the plant uptake and mobility of Cs-137 and Sr-90 in arable soils.

4.1 Introduction

Cs-137 and Sr-90 pose a long term threat to human populations due to their relatively long half-lives and, in the case of Sr-90, high radio-toxicity (Sanzharova *et al.*, 2009). The behavior of these radionuclides (RN) in soils plays a key role in their release into groundwater and their uptake in plants, which leads their way to humans through the food chain (Zhu and Shaw, 2000; Wuana and Okieimen, 2011). Plants take up elements from soil directly via roots or absorb them by above ground parts (e.g. leaves) from air (Kabata-Pendias, 2011). Root uptake is considered the dominant pathway and also more relevant when dealing with soil-borne radioactive contamination. Our understanding of root uptake of plants is mainly based upon the studies of nutrients uptake (e.g. K^+ , Ca^{2+}) (Kabata-Pendias, 2011).

Important factors influencing the mobility of cesium and strontium in soils are soil texture, organic matter, pH and concentration of competing ions (K^+ , NH_4^+ , Ca^{2+}) (Nilsson *et al.*, 1985; Krouglov *et al.*, 1997; Kamel and Navratil, 2002; Sanzharova *et al.*, 2009). For cesium, both the organic as well as inorganic ingredients of soil show affinity and restrict its downward migration, clay minerals can adsorb and fix cesium in frayed edge sites (FES); also cesium can compete for ion-exchange in organic soils (Cornell, 1993; Dumat *et al.*, 1997; Staunton and Levacic, 1999). However, Cs^+ interaction with organic matter is weak, so in organic soils it is easily bioavailable (Saar and Weber, 1982; Sanchez *et al.*, 1988). The strong cesium sorption to clay minerals is due to the small hydration energy of Cs^+ ion that enables its access to clay interlayers, FES sites in illitic clays (Wauters *et al.*, 1994; Hakem *et al.*, 2000; Larsson, 2008). Contrastingly, strontium is weakly sorbed to clay minerals but can be strongly sorbed by

organic matter (OM) (Sanchez *et al.*, 1988; Bergeijk *et al.*, 1992b). Strontium sorbed via ion-exchange (Sanzharova *et al.*, 2009) can be displaced by competing cations (e.g. Ca^{2+}) from the exchange sites (Nilsson *et al.*, 1985) while Sr^{2+} bound to OM fractions like humic and fulvic acids via chelation and complexation is not easily bioavailable (Saar and Weber, 1982; Sanchez *et al.*, 1988).

The radionuclide distribution in the soil is affected by the type of soil, land use, soil water content, climatic conditions and the soil management practices (Nisbet *et al.*, 1993; Ivanov *et al.*, 1997a; Forsberg *et al.*, 2000; Zhu and Shaw, 2000). Askbrant *et al.* (1996) observed that 95 % of Cs-137 was available in the top 6 cm in undisturbed soddy podzolic sandy soils while in cultivated soils, RN were nearly homogeneously distributed in the top 25 cm soil in Chernobyl affected regions of Belarus, Ukraine and Russia. In another study, Shestopalov *et al.* (2003) reported a higher mobility of Cs-137 compared to Sr-90 in peaty soils; however, in soddy-podzolic sandy soil, migration rate of Cs-137 was comparatively low. Agricultural practices affect the soil-plant transfer of RN by physical dilution (ploughing, disking) and through the addition of competitive elements (use of fertilizers and soil conditioners) (Lembrechts, 1993; Nisbet, 1993; Nisbet *et al.*, 1993; Camps *et al.*, 2004) . Ploughing can reduce the RN pool available for plant-uptake due to the mixing of top soil containing larger amounts of RN with deeper soil containing less RN. The use of fertilizers and lime affect the major soil nutrients (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 (e.g. K^+ , NH_4^+).

Soils compose the long term reservoir for RN in terrestrial ecosystems and the methodologies employed to reduce the migration of RN into the food chain are mostly

applicable at the soil level. Root uptake of RN occurs from the soil solution and so the higher the concentration of RN in soil solution, the greater its concentration in the plant. Countermeasures intended to reduce RN plant uptake should therefore be targeted at either reducing the concentration of RN, or increasing the concentration of competitive ions in soil solution. The main competing elements for cesium and strontium are potassium/ammonium and calcium respectively. Bogdevitch (1999) observed a decrease in radiocesium uptake by oat grain with increasing K^+ content in soddy podzolic soils. A decrease in transfer of Sr-90 into seeds of winter rye with varying concentrations of exchangeable calcium was reported by Kashparov (2001) in their experiments on different soils in Chernobyl affected areas. The uptake of strontium is generally inversely related to the amount of exchangeable calcium in soil, the higher the concentration of exchangeable calcium in soil the lower the Sr^{2+}/Ca^{2+} ratio and the lower the Sr^{2+} uptake (Carini, 1999, 2001).

Sustainable agriculture implies the adoption of organic agriculture together with the use of improved crops breeding. Biogas digestate is a bio-energy derived organic amendment; it is the residue of biogas produced via anaerobic digestion of biodegradable wastes (Tani *et al.*, 2006; Zhang *et al.*, 2007; Möller and Stinner, 2009). Digestate is promoted to be applied in agricultural soils to improve plant productivity. Enhanced bio-energy production to meet the challenges of sustainability will produce larger volumes of digestates (Tambone *et al.*, 2010; Gell *et al.*, 2011). This requires better management of these materials to truly benefit from their environmental (greenhouse gas emissions and waste management) and agronomical (crop production, soil sustainability) advantages. Hence, it is necessary to assess the impacts of these amendments on retention/immobilization of soil contaminants, soil-water quality and functions of microbial community. To our knowledge the influence of digestate

amendment on the mobility in soil and plant uptake of Cs-137 and Sr-90 has not been accounted for so far.

4.2 Material and methods

4.2.1 Lysimeters preparation

The basic information about the two lysimeters and their instrumentation has been described in chapters 2.2.1 (lysimeters set-up) and 2.2.2 (lysimeter equipment and instrumentation). To avoid the problem of activity analysis (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. Further, each lysimeter was divided into two halves by inserting a metallic plate to a depth of 30 cm of the top soil (Figure 4.1). With this physical separation, one half of each lysimeter was used for organic amendment and the other half for control.

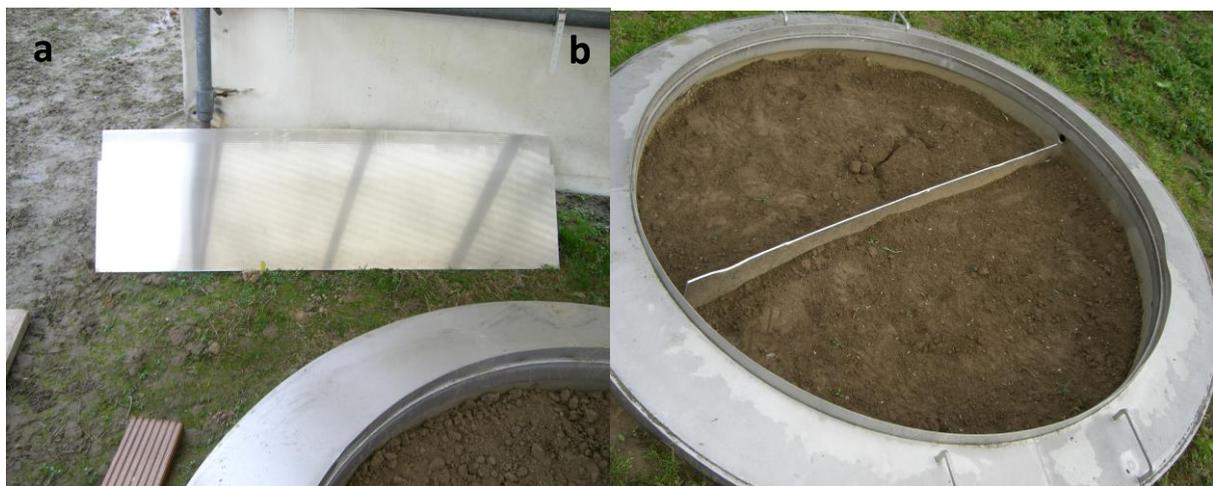


Figure 4.1: Metallic plate insertion in lysimeter top soil; a) metallic plate (45 cm in height), b) plate after insertion: 30 cm in soil and 15 cm above soil.

4.2.1.1 Digestate application

Biogas digestate was obtained from a biogas plant in Schwalmatal (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). The liquid fraction of digestate (liquor) was used in this experiment to have a higher relevance of nutrients competition (in addition to organic fractions) and better homogeneous incorporation.

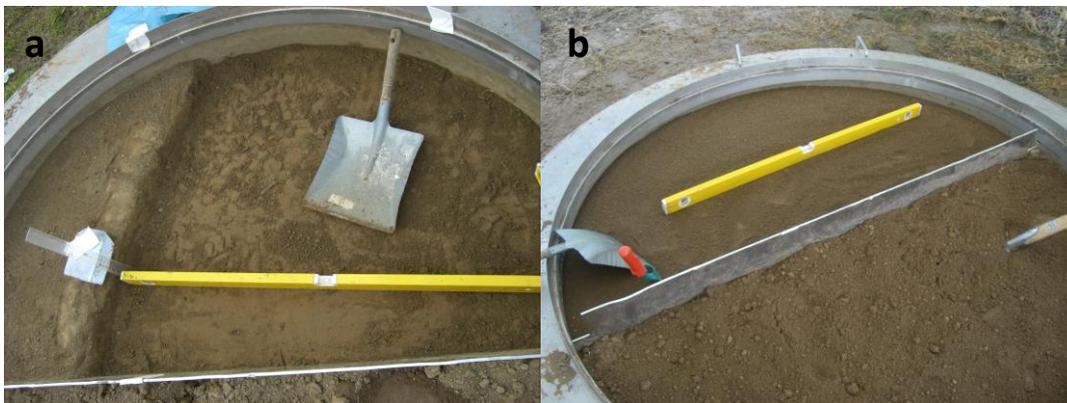


Figure 4.2: Digestate application in lysimeter soils; a) removal of top 5 cm soil, b) mixed soil spreading.

Digestate application was done in Oct, 2012. For this, the top 5 cm of soil were removed with a spade, mixed with digestate in a concrete mixer and spread over the lysimeter surface (Figure 4.2). Before spreading the mixed soil onto the lysimeter, the lower soil, 6-15 cm was ploughed manually with a spade (to reduce the compaction effect during plate insertion). Digestate application was carried out in reference to field practice (personal communication with the farmer) with an application rate of 34 ton/ha, and mixing in top 5 cm or 25 cm. 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 positioned at 25 cm depth.

4.2.1.2 Radionuclides application

Radionuclides 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 both parts of each lysimeter were removed; 1/3 of soil was spread directly over the seeds (to protect seeds from birds) and 2/3 of soil was used for RN mixing. The removed soils were sieved through a 4 mm mesh before RN mixing. To avoid an initial adsorption of RN on soil organic matter, 100 g of soil from both parts of each lysimeter were combusted at 600°C for 24 hrs.

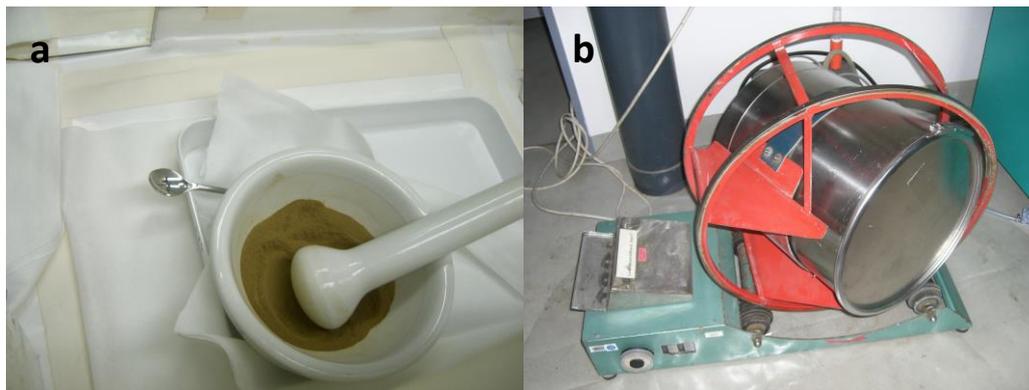


Figure 4.3: Radionuclides mixing; a) Ceramic bowl for initial mixing of 100 g combusted soil b) Drum hoop mixer for mixing of 100 g contaminated soil to the remaining 30 Kg soil.

In a first step, these 100 g of soil were spiked drop wise with ten milliliters of RN solution (with an approximate activity of 44 MBq for Cs-137 and 30 MBq for Sr-90) and left for drying overnight. The next day, these 100 g of soil were manually ground and mixed in a ceramic bowl using a pestle. 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 (Figure 4.3). The contaminated soil was spread over the 1 cm non-contaminated soil. So, the

summer wheat seeds were under a depth of approximately 3.5 to 4 cm which was close to the recommended practice of 4-5 cm.

4.2.1.3 Application of water tracer- KBr

To assess the movement of water in lysimeter soil, a conservative water tracer (Potassium Bromide (KBr)) was applied. For this, a molar solution of Potassium Bromide was prepared by dissolving 119 g of KBr in one liter of de-ionized water. From this, an aliquot of 315 mL was applied on each part of both lysimeters using a hand sprayer to have an application rate of 25.17 g/m² of bromide. The hand sprayer was weighed before and after the application to determine the actual amount applied.

4.2.2 Sowing and harvesting of plants

4.2.2.1 Summer wheat

Summer wheat was sown in March, 2013. Seed sowing was carried out following the recommendations in agricultural practice in the region (NRW, Germany). Considering the late sowing and small scale plantation, a seed rate of 500 seeds/m² (24 g /m²) was chosen. Seeds were sown with a row-row distance of 9 cm. For this, each semi-circle of lysimeter was divided into eight rows of varying lengths and eight seed aliquots were prepared depending upon the length of each row. The seeds were placed manually in each row to a depth of about 1 cm and with an approximate distance (seed-seed) of 2 cm. Later the seeds were covered with 1 cm non-contaminated soil and 2 cm of contaminated soil removed at the time of RN application as described in chapter 4.2.1.2 (Radionuclides application).

For summer wheat, in the unamended part a nitrogen deficiency (Figure 4.4 a) was observed. Hence, a nitrogen fertilizer KAS (N content 27%) was applied with an application rate of 50 Kg/ha. Summer wheat was harvested in August 2013. The plants were cut approximately 2

cm above ground to avoid an external surface contamination of the plants and the cutting tool (scissor). The roots were not collected to reduce the exposure time to high activity (~ 65 MBq/m²) needed to collect the large number of roots.



Figure 4.4: Summer wheat; a) Nitrogen deficiency effect on wheat (left) in unamended part, b) Ripened wheat covered to avoid birds' accessibility to grain.

4.2.2.2 Inter-crop Teralife

Following the summer wheat harvest an intercrop, Teralife, was sown in September 2013. For this, the lysimeter soils were ploughed manually (using a garden spade) to a depth of 15 cm and the seeds were spread manually with a seed rate of 5 g/m². Teralife was harvested in December 2013 using a garden scissor. For Teralife roots extraction was not possible due to a variety of plant species (Figure 4.5).

4.2.2.3 Summer oat

Summer oat was sown in February 2014 adopting a similar procedure as for summer wheat with a seeds rate of 300 seeds/m². Preliminary soil ploughing was 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. Due to the lower seeds density (300 seeds/m²) compared to summer wheat, the roots of summer oat could also be collected at the harvest in July 2014 (Figure 4.6).



Figure 4.5: Teralife plants, before and after harvest.

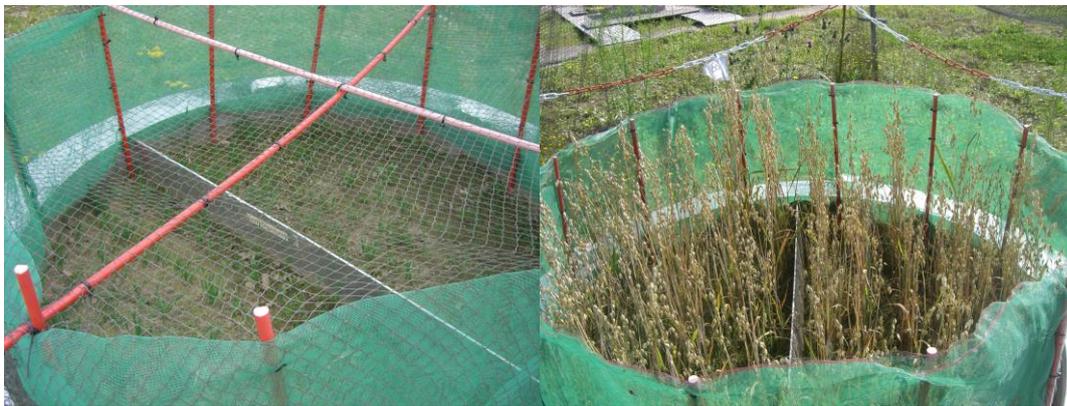


Figure 4.6: Summer Oat; a) after sowing, b) before harvest.

4.2.4 Soil water sampling and analysis

Soil water was sampled at three soil depths: 40 cm, 120 cm (both with suction cups) and 250 cm (leachate vessels). Suction cups sampling was done by using a vacuum pump (vacuum: 940 mbar) operating in non-continuous mode. The soil water at the lysimeter bottom (250 cm depth) was collected under natural drainage condition (no vacuum). The frequency of percolate collection by suction cups was once a month, however the percolate collection at lysimeter bottom (250 cm) varied from once a month to once a week depending upon the weather conditions (precipitation). The collected soil water samples were analyzed for bromide concentration and activity. Activity analysis (Cerenkov) was done with liquid scintillation counting (LSC) (LSC; Tri Carb, 2500 TR, Canberra Packard, Dreieich, Germany) by

adding 10 mL of Ultima Gold (Perkin Elmer) as LSC cocktail to a 5 mL sample. Bromide concentration was determined by HPLC (Jasco GmbH, Germany) with a UV detector, UV 2075 (Jasco GmbH, Germany) (UV 310 nm) and a Hamilton PRPX110 HPLC column (pore size 7 μm , 150 mm length, 4.6mm ID) using para Hydroxybenzoic acid (4mM) plus 2.5% Methanol (with 1N NaOH, pH: 8) as mobile phase.

4.2.5 Soils and plants analyses

Soil samples and plants were dried at 105 °C for 24 h. The dried soils were sieved (≤ 2 mm) to remove the plant parts and to homogenize the soil. The plants were cut (using a garden scissor) to reduce their size for sample preparation. For wheat and oat, the seeds were separated from the stalk by pressing the stalk manually. The shoot was threshed in a lab scale thresher. Cs-137 activity was determined 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 digested in 200 mL of 5M concentrated HNO_3 , using a heating bath for about 30 min. The digested solution was filtered (cellulose filter) and diluted to 500 mL with deionized water. Later, a 10 mL aliquot was analyzed with a low- level Beta counter, FHT 770T (Thermo Fischer Scientific, USA).

4.3 Results and Discussion

4.3.1 Plant uptake and translocation- summer wheat and oat

In general, the effect of the digestate amendment on the RN uptake was less pronounced than the plant type (Figure 4.7). In general, the weed plants showed a higher uptake compared to the main crops (wheat/oat) (Figures 4.7 and 4.8). Due to the high applied activity (Cs-137: $\sim 65 \text{ MBq m}^{-2}$, Sr-90: 18 MBq m^{-2}), a clear translocation of the activity was

recorded in different plant parts; grain resulted in lower activity values compared to shoots for both RN. The two RN showed a distinctively varied behavior in plant uptake, Sr-90 exhibited a ~ 80 higher uptake and translocation compared to Cs-137 (Figure 4.7).

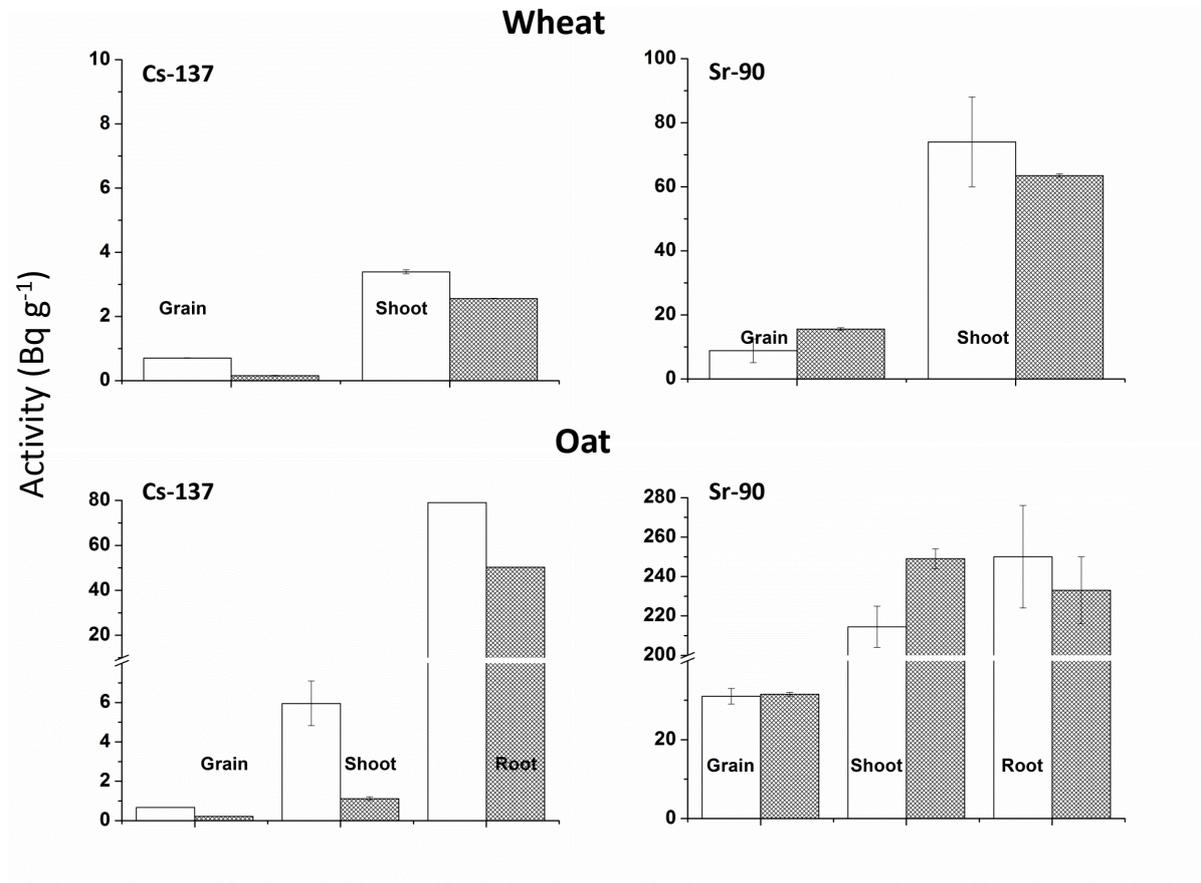


Figure 4.7: Plant uptake and translocation in summer wheat and oat. Open symbol (\square): no amendment; closed symbol (\blacksquare): digestate amended. Error bars indicate standard deviation about the mean of duplicate plant samples ($n=2$).

The digestate amendment led to a decrease in Cs-137 uptake in all plants, the effect was more prominent in oat. Moreover, Cs-137 translocation was also affected by amendment, reflecting lower activity in grain compared to shoot in both crops (wheat, oat) (Figure 4.7). The effect of digestate amendment on Sr-90 uptake and translocation varied in different plants. In wheat grain, digestate caused an increase in Sr-90 translocation (nearly double),

while in oat grain, the effect was negligible. Digestate presented an opposing effect in Sr-90 translocation in the shoots of two crops (wheat and oat); Sr-90 uptake was decreased (~14%) in wheat shoot while in oat shoot, it was increased (~18%) after digestate amendment (Figure 4.7).

Generally the higher uptake of strontium compared to cesium is due to its higher availability. In mineral soils, Sr^{2+} interaction is less influenced by clay compared to other soil fractions (silt, organic matter) (Sanchez *et al.*, 1988; Bergeijk *et al.*, 1992b), increasing its plant availability. Comparatively, Cs^+ is strongly sorbed to clay minerals (Cornell, 1993; Dumat *et al.*, 1997; Staunton and Levacic, 1999) which reduces its plant availability.

4.3.2 Plant uptake in Teralife and weed plants

In Teralife, plant uptake varied with plant species and the radionuclide. In general, the uptake was much higher (~80-100 times) for Sr-90 compared to Cs-137 (Figure 4.8). Digestate amendment led to a decrease (nearly 5 times reduction) in Cs-137 uptake in *Lupinus L.*, while for the other three plants (*Trifolium L.*, *Avena L.* and *Phacelia Juss.*) the effect was not significant. Sr-90 uptake was decreased by 13-17 % in *Lupinus L.* and *Trifolium L.* while it increased by 69% in *Phacelia Juss.* after digestate amendment. Among different plant species, *Lupinus L.* and *Trifolium L.* showed the most pronounced response to the amendment while *Avena L.* displayed the lowest plant uptake and least response to organic amendment for both RN.

In the case of the weeds, digestate amendment presented a considerable reduction in plant uptake for both RN. Digestate led to 5-7 times decrease in Cs-137 uptake in *Sonchus L.* (~80% reduction) and *Matricaria recutita L.* (~86% reduction) and about 42% reduction in *Chenopodium L.* Similarly, Sr-90 uptake was decreased by ~13% in *Trifolium squarrosum L.*

while for *Chenopodium L.*, the effect was negligible. Moreover, digestate effect on Sr-90 uptake in *Sonchus L.* and *Matricaria recutita L.* and Cs-137 uptake in *Trifolium squarrosum L.* was not comparable due to the non-availability of plants in non-amended part of respective lysimeter.

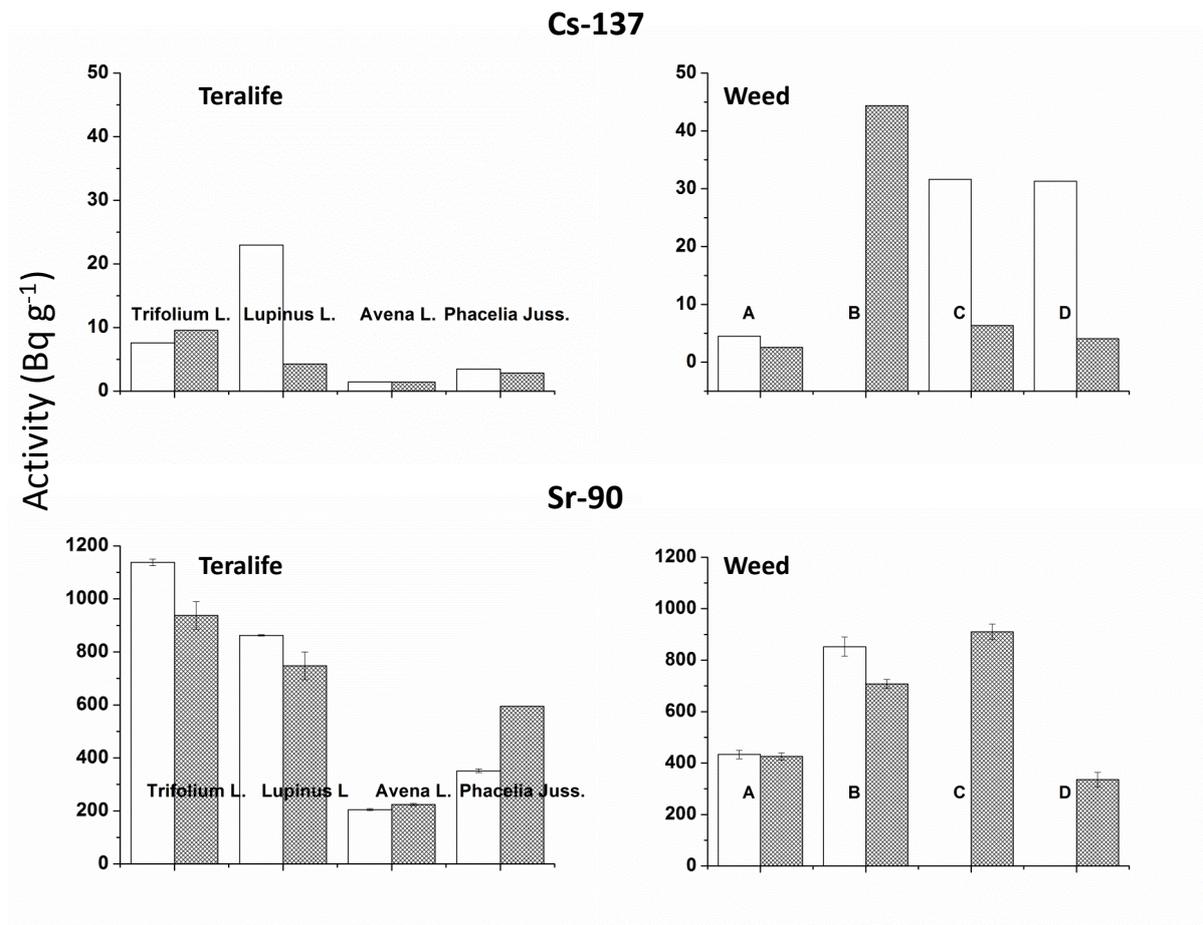


Figure 4.8: Plant uptake in Teralife and weed plants. A: *Chenopodium L.*, B: *Trifolium squarrosum L.*, C: *Sonchus L.*, D: *Matricaria recutita L.* Open symbol (□): no amendment; closed symbol (▨): digestate amended. Error bars indicate standard deviation about the mean of duplicate plant samples (n=2).

4.3.3 Vertical mobility

The contaminated soil was spread in the top 2 cm. However, in the unamended part of the Cs-137 lysimeter, the top soil got mixed into deeper soil layers (10-15 cm) due to an animal intrusion (mouse problem) (Figure 4.9). In general, most of the applied activity was observed

in the top soil layers (0-15 cm) in non-amended and amended soils for both radionuclides. Cs-137 with nearly 3-times higher applied activity ($\sim 65 \text{ MBq m}^{-2}$), compared to Sr-90 ($\sim 18 \text{ MBq m}^{-2}$), did not reflect a considerable difference to Sr-90 mobility. This is due to the fact that in mineral soils, cesium is quickly sorbed to clay minerals, reducing its availability. Contrarily, Sr-90 is less influenced by clay but could retain in the silt fraction in mineral soils. A considerable amount of clay (13%) and high silt content ($\sim 80\%$) in the top lysimeter soil (0-35 cm) (Table 2.1) led to lower vertical mobility of Cs-137 and Sr-90 in our experiment.

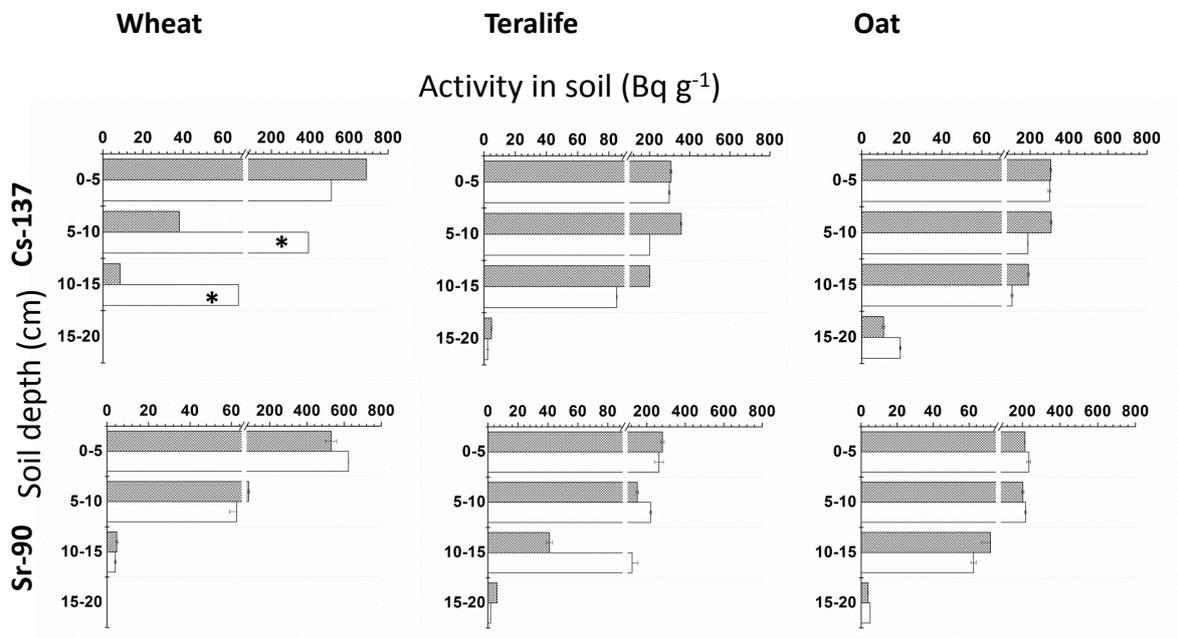


Figure 4.9 Vertical mobility of Cs-137 and Sr-90 after three consecutive crops: 1) summer wheat, 2) Teralife and 3) summer oat. Initial (applied) activities: Cs-137 $\sim 65 \text{ MBq m}^{-2}$, Sr-90 $\sim 18 \text{ MBq m}^{-2}$. *Physical disturbance (mouse problem) causing Cs-137 migration to deeper soil (10-15 cm). Open symbol (□): no amendment; closed symbol (■): digestate amended. Error bars indicate standard deviation about the mean of duplicate soil samples ($n=2$).

Comparing the RN mobility after wheat harvest, Sr-90 showed a slight higher mobility ($\sim 14\%$) in the digestate amended part compared to the unamended part. For Cs-137, this comparison was not possible due to the accidental physical disturbance of the soil. Following the wheat harvest, the soils were ploughed to a depth of 15 cm to sow the next crops, so the

RN were then evenly distributed in the top 15 cm in all lysimeter halves. The manual ploughing (using garden spade) showed a nearly homogeneous mixing in the top 10 cm soil for both RN while in 10-15 cm mixing was not so homogeneous (more obvious in Sr-90 in Teralife, Figure 4.9). This is due to fact that manual ploughing of highly contaminated soil gets a bit complicated. Both RN did not show any vertical mobility into deeper soil layers (15-20 cm) after the harvest of Teralife and Oat. Furthermore, no activity was recorded in the suction cups samples (40 cm depth), confirming the low mobility of both RN. However, the conservative water tracer (bromide) was found in soil water samples collected in suction cups, indicating that the water flow in the lysimeter was not compromised. As no vertical mobility of both RN was observed in deeper soil layers (below 20 cm), the effect of environmental parameters (water content, temperature) on vertical migration could not be evaluated.

4.4 Conclusion

Digestate amendment with rates according to common agricultural practice did not lead to marked effect on soil-plant transfer of the investigated radionuclides (RN). However, in the crops of higher relevance to food chain (wheat, oat), digestate reflected a slightly protective effect resulting lower activities in grains compared to shoot. Hence, further investigations with higher application rates of used organic amendment are necessary to probe the RN plant availability in agricultural soils in the long run. High applied activity in our lysimeter soils helped to trace RN mobility into different plant parts. Furthermore, different plant species presented different uptake behavior due to variation in their plant physiology and root architecture. So, the variation in plant species could be helpful to reduce the risk of RN mobility into food chain.

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18. Kurzfassung

The effect of organic matter on mobility and plant uptake of cesium and strontium in soil-plant systems has intensively been studied since the Chernobyl accident in 1986. Furthermore, the effect of soil management practices like ploughing, disking and the use of mineral and organic fertilizers on their soil-plant transfer have also been taken into account. However, there are new forms of organic soil amendments like biochar and digestate that are increasingly available due to higher production of bioenergy. The use of biochar and digestate as soil amendments is well recognized for their agronomical benefits (e.g. crop yields); however, the knowledge on their effect on toxic metals and radionuclides mobility in soils is scarce. We used the field (agricultural practice) application rates of these amendments, to probe the immobilization of Cs⁺ and Sr²⁺ in regular agricultural soils.

In this PhD work, we adopted two experimental approaches: 1) sorption-desorption experiments and 2) plant uptake and vertical mobility in outdoor lysimeter experiments. In the sorption-desorption experiments, we used three different soils from the region (NRW, Germany), 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. 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. For the lysimeters experiments, the liquid fraction of the digestate (liquor) was used due to higher relevance of competing ions (K⁺, NH₄⁺, Ca²⁺) in addition to organic fractions. Lysimeters soil contamination was done using chloride salts of Cs-137 and Sr-90. Plant uptake experiments were conducted with three different plants, summer wheat, summer oat and an Inter-crop (Teralife). Furthermore, soil water sampling was done at three soil depths: 40, 120 cm (using suction cups) and 250 cm (leachate vessels) to probe the vertical mobility of target RN.

In sorption experiments, we observed that applied amendments (with field application rates) did not lead to a considerable 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 silty-loam soil, followed by forest soil and lowest in sandy-loam. Strontium sorption was nearly half compared to cesium in all soils with higher sorption in silty-loam and almost similar sorption in sandy-loam and forest soils. The native organic matter in forest soil led to higher Sr²⁺ retention compared to the applied organic matter (amendments).

In general, temperature variation in the range (5-35°C) did not cause a substantial effect on sorption-desorption of the two radionuclides in opposition to soil type. Furthermore, the effect of temperature variation was quite unpredictable. The two agricultural soils (silty-loam and sandy-loam) showed higher Cs⁺ sorption at 5°C in opposition to room temperature (20°C) and 35°C. While the forest soil reflected an opposing trend with slightly higher sorption at 35°C compared to 5 and 20°C, where Cs⁺ sorption was nearly similar. Silty-loam soil exhibited higher Cs⁺ affinity at 5°C compared to 20 and 35°C. Contrastingly, forest soil showed a decrease in Cs⁺ retention with decrease in temperature from 35 to 5°C. Sandy-loam soil reflected higher Cs⁺ affinity at room temperature (20°C) compared to 5 and 35°C. The effect of temperature variation on strontium was similar to cesium in silty-loam soil with slightly higher sorption at 5°C compared to 20 and 35°C. Contrastingly, forest soil showed higher Sr²⁺ sorption at 5 and 35°C compared to room temperature (20°C). Temperature showed quite erratic changes in Sr²⁺ retention in the different soils. In general, Sr²⁺ sorption hysteresis was higher at 5 and 35°C compared to room temperature (20°C). Forest soil exhibited the highest Sr²⁺ retention, followed by sandy-loam and lowest in silty-loam.

Our lysimeter results showed that the digestate amendment with applied rate (common agricultural practice) does not have a significant effect on soil-plant transfer of the investigated radionuclides. However, in the crops of relevance to the food chain (wheat, oat), the digestate showed a slightly protective effect resulting in lower activities in the grains compared to shoot. Hence, further investigations with higher application rates of used organic amendment would be helpful to assess their effect on radionuclides transfer in soil-plant systems. We could observe clear translocation of radionuclides into different plant parts due to high applied activity in our lysimeter soils. Furthermore, different plant species presented different uptake behavior due to variation in their plant physiology and root architecture. Hence, the choice of cultivating different species on contaminated soils could be helpful to reduce the risk of radionuclides mobility into the food chain.

19. Schlagwörter

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18. abstract

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