Contents lists available at ScienceDirect





journal homepage: www.elsevier.com/locate/apgeochem

Sorption of radiostrontium on various soils



Wolfgang Schulz^{*}, Dharmendra K. Gupta, Beate Riebe, Georg Steinhauser, Clemens Walther

Leibniz Universität Hannover, Institute of Radioecology and Radiation Protection (IRS), Herrenhäuser Str. 2, 30419, Hannover, Germany

ARTICLE INFO

Keywords: Radiostrontium Sorption Soil Pedological characterization of soil Radionuclide mobility

ABSTRACT

The adsorption kinetics of 85 Sr onto three pedologically characterized mineral soils was investigated, namely, one soil from the Chernobyl-Exclusion zone, Ukraine (CEZ-soil), one soil from the dismantling site of a former nuclear research reactor in Germany (DRE-soil) and a sandy reference soil (RefeSol-04A) from the Fraunhofer IME system, Germany. After seven days of treatment with 85 Sr on an overhead shaker, Sr-sorption reached a (temporal) steady state. This timeframe was consistent for all three soils and independent of soil characteristics. From this experiment, maximum K_d values were calculated and compared with the existing literature. They agreed well with predictions made by the co-criterion concept for K_d(Sr) proposed by IAEA. Furthermore, the effect of gamma-sterilization and the consistency of K_d values in soils over longer periods of time is discussed.

1. Introduction

Radiostrontium is of high relevance in the risk assessment of a fission products release into the environment, especially for the medium to long-term assessment. Release scenarios include accidents at nuclear facilities or global fallout from atmospheric nuclear explosions. The two dose-relevant radioisotopes in this timeframe are ⁸⁹Sr ($T_{1/2} = 50.5 d$; fission yield¹: 4.8%) which dominates radiostrontium dose effects in the first months after a release, and ⁹⁰Sr ($T_{1/2} = 28.8$ a; fission yield¹: 5.8%) contributing to dose for decades and fostering its radiological long-term relevance in contaminated areas.

The behavior and potential radiological impact of radionuclides in soils are principally controlled by their chemical form and speciation (Walther and Gupta, 2015). In the case of radiostrontium, the mobility follows the ubiquitously occurring stable Sr, which in turn, is strongly regulated by its highly abundant chemical homologues calcium, and - to a lesser extent - magnesium (Bunde et al., 1997). Under environmental conditions, the alkaline earth elements Sr, Ca and Mg behave chemically similar and exist exclusively in oxidation state + II (Nilsson et al., 1985; Gupta and Walther, 2018). Radiostrontium exhibits higher mobility in soil than other important radionuclides such as ²⁴¹Am, ²³⁹⁺²⁴⁰Pu, and ¹³⁷Cs (Askbrant et al., 1996; Guillén et al., 2015; Gupta et al., 2018a).

The fate of radiostrontium – and its homologues - in contaminated soils is governed by sorption and desorption processes between exchange sites of the soil matrix and the soil-solution. To assess this distribution, the ratio of activity bound to the (immobile) solid phase $(A_m = mass activity density in Bq kg^{-1})$ and the activity in the (mobile) soil-solution $(A_v = volumetric activity density in Bq L^{-1})$ is defined as the distribution ratio (K_d) :

$$K_d = \frac{A_m}{A_\nu} (L \ kg^{-1}) \tag{1}$$

Strictly, the K_d value is defined as the A_m/A_v ratio under thermodynamic equilibrium conditions (IAEA TECDOC 1616 (2009)). However, in the case of radionuclides under environmental conditions, dealing with steady-state thermodynamics is rather the exception than the rule, and the term K_d value is often used in a broader sense as the distribution of activity at a given point in time - with a more or less accurate assumption of the progress of thermodynamical equilibration. Depending on the composition of the contaminated soils, sorption and desorption of radiostrontium to different soil constituents may take place at the surface of different chemical phases in soil (see Fig. 1).

For each of these (equilibrium-) reactions, different sorption kinetics must be assumed, and the observed sorption of a nuclide to a soil is the consequence of different underlying and inter-dependent chemical reactions. These reactions very often did not reach equilibrium yet and in some cases might even be non-reversible. However, in the strontium case, numerous studies have found the sorption of Sr to be fully reversible within the first weeks and months after contamination (Gupta et al., 2018b).

Nowadays, increasing interest is also pointing towards the influence

https://doi.org/10.1016/j.apgeochem.2019.01.001

Received 8 March 2018; Received in revised form 30 December 2018; Accepted 2 January 2019

Available online 03 January 2019

0883-2927/ © 2019 Elsevier Ltd. All rights reserved.

^{*} Corresponding author. Gottfried Wilhelm Leibniz Universität Hannover, Institut für Radioökologie und Strahlenschutz (IRS), Herrenhäuser Str. 2, 30419, Hannover, Germany.

E-mail address: schulz@irs.uni-hannover.de (W. Schulz).

 $^{^{1}}$ Cumulative fission yield of $^{235}\mathrm{U}$ with thermal neutrons.



Fig. 1. Distribution of radiostrontium in soil.

that soil-dwelling microorganisms have on the Sr-mobility. Microorganisms have been reported to potentially have mobilizing or demobilizing effects on strontium either through degradation of biomass (Margon et al., 2013), adsorption on the cell walls (Hu et al., 2017) or uptake (Liu et al., 2016). Sterilization by γ -irradiation was shown to not necessarily decrease, but rather increase the sorption of Sr, at least for a while (Dai et al., 2014), rendering the influence of microbial activity on Sr-sorption a very complex and difficult-to-assess subject. Knowledge of the activity distribution between the different phases and the sorption strength to the soil – being a biological habitat itself - is crucial for the prediction of Sr mobility in the geosphere, and the availability for uptake into biota.

Numerous data have been published in the literature, focusing on the sorption kinetics and sorption capacity for Sr to major soil constituents, e.g. clay minerals (Al Attar et al., 2016; Ohnuki and Kozai, 1994), organic matter (Van Bergeijk et al., 1992; Valcke, 1993), sesquioxides (Chiang et al., 2010), and Ca-minerals (Robison et al., 2000; Sengupta et al., 2017). In soils, which consist of a complex mixture of different chemical/mineral phases, the sorption capacity (and thus 'steady-state' K_d) for Sr has been shown to be strongly correlated with the cation-exchange-capacity (CEC) of the concerning soil (Ohnuki, 1994), and to be anti-correlated with the abundance of the main Sr competitors Ca and Mg in the soil-solution ($[Mg]_{SS} + [Ca]_{SS}$)² (Rauret and Firsakova, 1996). Using only CEC and the concentrations of the two main competitors of Sr in soil-solution a strongly simplified equation for the prediction of strontium K_d via the so-called co-criterion concept was derived (Gil-García et al., 2008):

$$K_d(Sr) = \frac{CEC}{([Mg]_{SS} + [Ca]_{SS}2)}$$
(2)

The above equation may seem very simplistic at first, given the fact that many other factors have been reported to interfere with Sr

~ ~ ~

sorption. For instance clay-content of soil, pH (Smičiklas et al., 2015, Baeza et al., 1995), and organic matter content (Valcke, 1993)) have been shown to correlate with Sr-sorption, while the ionic strength (taking into account other potentially competing cations in the soil) has been shown to anti-correlate (Wallace et al., 2012). However, the cocriterion concept indirectly takes into account a large majority of these correlations by using the empirically determined CEC and by focusing only on the two most dominant ionic interferences of Sr in soil, even neglecting the effect of stable Sr completely.

The dominant sorption mechanism to solid soil phases is an outershell sorption of the hydrated Sr^{2+} ion to cation-exchanger sites (Fuller et al., 2016; Yamaguchi et al., 2018). For the majority of mineral soils, sorption to (clay) minerals dominates the sorption to other compartments (Ehlken and Kirchner, 2001). Organic matter and sesquioxides also contribute to sorption, but they become dominant only in soils containing high amounts of these phases (Van Bergeijk et al., 1992; Chiang et al., 2010; Guillén et al., 2015). Though in some studies a significant effect of ageing of Sr was found over some years (Eslava-Gomez and Brown 2013; Rigol et al., 1999), on a short timescale, the sorption of Sr to soils has in general shown to be completely reversible (Al Attar et al., 2016; Noordijk et al., 1992; Corcho-Alvarado et al., 2016).

While the sorption of Sr to pure mineral phases has been shown to typically proceed within hours (Ohnuki and Kozai, 1994; Bilgin et al., 2001), sorption to soils may take up to some days, depending on soil characteristics (Smičiklas et al., 2015). The present work is focused on adsorption kinetics of Sr to three mineral soils. These soils (two from ⁹⁰Sr-contaminated sites of nuclear operations and one reference soil) were selected for plant cultivation experiments aiming at the effect of biological methods on the radionuclide transfer in potatoes and winter rye. After artificial contamination of the soils with ⁸⁵Sr and prior to the beginning of plant growth and biological treatment of the soil with selected fungal strains, a well-defined 'steady' state of Sr-distribution was required. The minimum equilibration time span for this phase was

 $^{^{2}}$ SS = in the soil-solution.

obtained from the Sr-adsorption trend presented in this work.

Furthermore, we compare our obtained results for Sr-K_d with two predictive tools suggested by IAEA (TECDOC 1616), namely the cocriterion concept (see eq. (2)) and the 'texture/OM'-criterion, in which suggestions on the range of Sr-K_d's are made by very roughly classifying the soils as either belonging to the 'Sand group' (> 65% sand < 18% clay), to the 'Clay group' (> 35% clay), to the 'Organic group' (> 20% organic matter) or to the 'Loam group' (all others).

2. Materials and methods

2.1. Selection of soils

In this experiment, we used three different soils: The first soil was taken from a former agricultural field inside the Chernobyl-Exclusion Zone, Ukraine (CEZ-soil), close to the former community of Kopachi village, 5 km south-southeast of the former Chernobyl nuclear power plant. It had been part of an agricultural field of a local farming community and was abandoned in 1986. Soils for the batch experiment were taken from the upper 30 cm and homogenized. The second soil was taken from the construction site of a dismantled nuclear research reactor in Germany (DRE-soil). It was chosen as a soil of interest in the project due to a reported ⁹⁰Sr contamination, found after decommissioning of the reactor. The soil was excavated from roughly 1 m depth, sieved and homogenized. The third soil was a sandy reference soil ("RefeSol-04A") from Fraunhofer IME System, Germany.

2.2. Characterization of soil samples

Determination of soil pH was performed according to DIN EN 15933 (2012), in 0.01 M CaCl₂ solution. For soils of pH > 6.9, an additional analysis of carbonate content (DIN EN ISO 10693 1995 and 2014, respectively) was carried out. Soil carbon was determined via oxygenaided combustion using a CNS analyzer ('Vario EL Cube', Elementar Analysensyteme GmbH). This analysis yielded the total carbon content, which had to be corrected for inorganic carbon content at pH > 6.9. Subsequent to disintegration of organic matter and removal of soluble salts, carbonates, oxides and particle size distribution of the samples were analyzed by wet sieving and sedimentation according to DIN ISO 11277 (2002). Dithionite and oxalate soluble fractions of iron, aluminium, and manganese oxides were extracted using a standard operation procedure based on DIN EN ISO 12782-2 (2012) and DIN EN ISO 12782-3 (2012), respectively, and measured using an inductively-coupled plasma optical emission spectroscopy (ICP-OES) ('iCAP 600', Thermo Scientific, Germany). For the determination of cation exchange capacity (CEC) of the soils, the silver-thiourea method was applied (Dohrmann, 2006). Table 1 summarizes the results of the pedological characterization of the investigated soils.

According to the texture/OM criterion (IAEA TECDOC 1616 (2009)), the CEZ-soil belongs to the "loam-group", whereas DRE-soil and RefeSol-04A belong to the "sand-group". While sesquioxide contents are in the same range for all three soils, contents of silt, clay, and organic matter (OM) differ significantly. The DRE-soil can be classified

as a pure sand soil with very little clay as well as OM content, neutral pH and a low cation-exchange capacity. The history of pedogenesis of this soil is unknown, and the origin possibly anthropogenic (construction sand).

The soil from the vicinity of the Chernobyl nuclear power plant (CEZ soil) can be described as a slightly acidic, very silty sand soil, with very limited content of clay and organic matter, as well as a low CEC. The reference soil used is a slightly acidic, silty sand soil with low clay content, but in comparison to the other two investigated soils (CEZ and DRE); it shows rather high organic matter content and a comparably high CEC.

2.3. Batch experiments

Our experiments aimed at ensuring a complete Sr equilibration in soil, prior to planting in an upcoming plant cultivation experiment. Therefore, untreated (air-dried) soils and a minimum amount of soil solution was used for contamination, just high enough to retract sufficient supernatant water for the subsequent gamma-analysis.

The standard lab procedure involved 0.01 M CaCl₂ solution as a matrix to simulate ionic strength of natural soil solution. In order to assure the same ratio of soil-solution to dry-mass for all three (air dried) soils, the relative content of residual water H₂O_{*rel*} of each soil was determined gravimetrically by drying representative aliquots of the samples at 105 °C until weight constancy was reached. Triplicate batch samples for each individual soil were produced along with a single batch containing no soil (blank standard) for each data point in the following way: An equivalent of 10 g of dry soil (10/(1 - H₂O_{*rel*}))g airdried soil) was weighed into a 50 mL plastic centrifuge vial and supplemented with a CaCl₂ solution ([CaCl₂] = 0.01 M) completing the residual water of the soils to a total soil-solution of 10 ml.

An initial ⁸⁵Sr activity $A_{total} = 500$ Bq was added by pipetting $200\,\mu\text{L}$ of activity standard (0.1 M HCl, $1.4\,\text{mg}\,\text{L}^{-1}$ equalling 8.8×10^{-6} M and corresponding to a total amount of 1.8 nmol stable SrCl₂) that was obtained by diluting an activity standard provided by Physikalisch-Technische Bundesanstalt, Braunschweig. Subsequently, the vials were sealed air-tight, and the solutions were agitated on an overhead shaker (15 rpm). A set of samples (triplicate of each soil + blank standard) was retracted from the overhead shaker after 1, 2, 3, 7, 14, and 28 days, respectively. After 28 days the experiment was ended. After the respective equilibration times, samples were centrifuged for 10 min at 760 g. The supernatant was filtered (Schleicher and Schüll 595 $\frac{1}{2}$; pore size 4–7 μ m) and 1 mL of the filtrated supernatant was pipetted onto a charcoal filter, weighed out and air-dried. Soil solution activity (A_v) was quantified relative to the (decay-corrected) activity measured in the respective blank sample. K_d values were calculated using the formula:

$$K_d = \frac{A_m}{A_v} = \frac{A_{total} - A_v}{A_v}$$
(3)

In a second run of batch experiments, the effect of gamma-sterilization on the sorption process was studied, in order to investigate on the potential role of microorganisms. Therefore, the above-mentioned

Table 1

Pedological characterization of the investigated soils. DRE = Soil from the construction site of a former German research reactor. CEZ = Soil from the vicinity of the former Kopachi-village, 5 km southeast of the Chernobyl nuclear power plant. Ref. = Reference soil ("RefeSol-04A") provided by Fraunhofer IME, Schmallenberg, Germany. CEC = Cation Exchange Capacity (effective). OM = Organic Matter calculated from organic carbon content. Me_o = Oxalate soluble. Me_d = Dithionite soluble. mol_c = charge equivalent amount.

Soil	Texture (DIN ISO 11277)			pH (CaCl ₂)	Sesquioxides		CEC (eff)	OM (C _{org} x 1.72)			
	Clay %	Silt %	Sand %		$\mathrm{Al_o}~\mathrm{g}~\mathrm{kg}^{-1}$	${\rm Mn_o}~{\rm g}~{\rm kg}^{-1}$	${\rm Fe_o}~{\rm g}~{\rm kg}^{-1}$	$\mathrm{Fe}_{\mathrm{d}}~\mathrm{g}~\mathrm{kg}^{-1}$	Fe _o /Fe _d	$\mathrm{mmol}_{\mathrm{c}}\mathrm{kg}^{-1}$	% (weight)
DRE CEZ Ref.	3.3 5.7 2.9	6.3 39.6 8.5	90.4 54.7 88.6	7.4 5.6 5.3	0.42 0.57 1.54	0.06 0.46 0.14	0.56 0.95 0.60	6.71 3.53 2.56	0.08 0.27 0.24	34.4 42.6 71.4	0.16 1.7 4.6

procedure was applied in parallel to both, DRE-soil with and without former gamma sterilization. Gamma sterilization was performed by an external company (Synergy Health Radeberg GmbH), by administering a total dose of 40 kGy using *a* Co-60 source. In this run, pH was measured in-situ after centrifugation and prior to filtration of the supernatant solution.

2.4. Gamma measurements

Gamma-ray measurements of 85 Sr (half-life: 64.8 days) were evaluated using the 514 keV line on a Canberra 131 cm³ co-axial n-type high-purity germanium (HPGe) detector with a relative efficiency of 28% at the 1332 keV 60 Co line, and a resolution of 1.9 keV (at the 1332 keV line). Quantification was achieved relative to a standard solution that was prepared parallel to the measurements but without contact to soil. All measurements were decay-corrected to the same point of time.

2.5. Measurements for stable Ca and Mg

Stable Ca and Mg concentrations were determined in the soil solution after 7 days of equilibration in all three investigated soils (CEZ, DRE and Ref-Soil), measuring triplicate samples diluted in water with an inductively-coupled-plasma mass spectrometer (ICP-MS) with a quadrupole mass analyzer 'iCAP Q' from 'Thermo Fisher Scientific, Germany'. Each measurement was performed in five-fold replicate. Quantification was done using an external ICP-standard. The signals at m/q = 42 amu/e and m/q = 24 amu/e were used to quantify concentrations of the Isotopes ⁴²Ca and ²⁴Mg, respectively. The correlation coefficients of the external calibration were $r^2 = 1.00$ for ⁴²Ca and $r^2 = 1.00$ for ²⁴Mg.

3. Results and discussion

3.1. Batch experiments

Fig. 2 shows the temporal trend of activity distribution in the three soils in the course of the experiment.

All three soils showed very similar ⁸⁵Sr adsorption kinetics with maxima after 7 days. This is much slower than the sorption rates reported for pure mineral phases (Ohnuki and Kozai, 1994; Bilgin et al.,



Fig. 2. Development of the activity-distribution of ⁸⁵Sr over 28 days in three different soils. Assuming an equilibration towards a static K_d at constant thermodynamical conditions, the equation $\mathbf{y} = \frac{(ax)}{ax+1}K_d$, was fitted to the data, with the free parameters *a* and K_d using the data analysis software Origin[©] 2016.



Fig. 3. Correlation of Sr-K_d and effective Cation-Exchange-Capacity (CEC). Xerrors indicate the standard deviation of the double-quantification (N = 2) of CEC. Y-error bars indicate the uncertainty of the K_d-parameter, as a result of the fit algorithm (see Fig. 2). The parameters of the linear fit (red line, y = a + bx) are: a = -0.71 ± 0.10 ; b = 0.081 ± 0.002 ; r² = 0.999; χ^2 (reduced) = 0.844. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

2001), where equilibrium was usually reached within hours of agitation. While the CEC of the two mineral soils (DRE-soil and CEZ-soil) can be attributed mainly to the clay-fraction, a stronger influence of organic matter on CEC should be expected for the Ref-soil. However, we found no significant difference in the adsorption kinetics for the three soils. The similarity of the sorption trend of the three different soils might be interpreted as a predominantly diffusion-controlled process, as had been reported elsewhere (Chiang et al., 2010). It should be noted though that other effects, such as an incorporation of strontium into solid phases cannot be excluded based on the retrieved adsorption trend alone. The maximum K_d , however, differs for the three soils. In Fig. 3, the K_d values are plotted against the respective cation-exchange capacities of the soils.

 K_d and CEC correlate linearly in the frame of the experiment in which the sum of Ca and Mg concentrations in solution were very similar for all three soils due to the use of 0.01M CaCl₂ solution (see Table 2). This agrees well with the predictions made by IAEA and others (Rauret and Firsakova, 1996, Gil-García et al., 2008).

The results of the ICP-OES measurements for stable alkaline earth metal ion concentrations in the soil-solution after 7 days of equilibration are summarized in Table 2. The resulting predictions based on the co-criterion, as well as the texture/OM criterion concept as published in IAEA-TECDOC-1616 (2009) are also given and compared to the equilibrium-K_d values found in this work (see Fig. 2).

Comparing the measured K_d-values with the suggested 'predictions' based on the texture/OM criterion we find the presented results to be much lower than the suggested 'best estimate' and in the very low range of suggested values. This is not unexpected due to the use of 0.01 M CaCl₂ solution in the extraction, but it showcases the lack of robustness that the texture/OM criterion offers for the prediction of Sr-K_d and any decision eventually derived. In contrast to the texture/OM criterion, the measured values proved to be remarkably well-predictable by the co-criterion approach using eq. (2).

It should be noted that K_d values reached a maximum after seven days of agitation and showed only a very slight decline in the following three weeks that were part of the experiment (see Fig. 2). This effect was very small (roughly 5% for Ref- and DRE-soil and 1% for CEZ-soil) and not statistically significant in the case of CEZ and DRE soil, yet consistently present for all three soil types. This observation is

Table 2

Results of stable earth-alkaline contents in the soil solution after 7 days of equilibration and resulting predictions for K_d . ¹⁾Predictions taken from IAEA Tecdoc 1616 (2009). Uncertainties (in brackets) based on standard deviation (SD) of triplicate measurements for $[Ca]_{SS}$, $[Mg]_{SS}$ and K_d (this work). Uncertainties of predicted K_d based on error propagation from $[Ca]_{SS}$ and $[Mg]_{SS}$ and CEC.

Soil	[Ca] _{SS} mM	[Mg] _{SS} mM	$K_{\rm d}$ (predicted, co-criterion) $^{1)}$ L kg^{-1}	$\rm K_d$ (predicted, texture/OM)^1) $\rm L~kg^{-1}$	K_d found (this work) L kg ⁻¹
DRE	9.6 [0.4]	0.4 [0.004]	3.4 [0.05]	110 (0.4–2400)	2.1 [0.04]
CEZ	6.9 [2.1]	1.6 [0.5]	5.0 [1.67]	160 (2–2500)	2.7 [0.05]
Refsoil	9.4 [0.07]	1.4 [0.001]	6.6 [0.05]	110 (0.4–2400)	5.1 [0.09]





Fig. 4. Kinetics of the ⁸⁵Sr activity-distribution over 28 days in a sterilized and an unsterilized DRE-soil. Assuming an equilibration towards a static K_d under thermodynamically invariable conditions, the equation: $\mathbf{y} = \frac{(ax)}{ax+1}K_d$, was fitted to the data with the free parameters *a* and K_d using the data analysis software Origin[©] 2016.

inconsistent with the concept of a final thermodynamical K_d and a number of mechanisms may come into consideration here. As the amount of exchange-sites should be rather constant over the period of the experiment we assume that the measured decline was caused by a slow change of thermodynamical conditions inside the gas-tight centrifuge tubes. Such changes - presumably caused by microorganisms – might involve the partial reduction of iron oxide phases and the release of protons, both lowering the availability of sorption sides for Sr.

The experiments described above were repeated with a gamma-sterilized DRE-soil and another batch of (unsterilized) DRE-soil in parallel (Fig. 4). 3

No significant difference in the adsorption trend or in the (maximum) K_d was observed in the comparison of sterilized vs. unsterilized soil. In the case of the sterilized soil, the K_d continuously increased (as opposed to a minute decline after 7 days), however the range of uncertainties does not allow to give a conclusive statement on the effect of gamma-irradiation and microbial influence.

In this experiment, we also carefully monitored the development of pH for each data point (see Fig. 5).

The pH values measured decreased slightly over time, which might explain the partial desorption of Sr in the later stage of the experiment (see Fig. 4). However, both, K_d and pH time evolution are very similar for gamma-sterilized and non-sterilized soil. We thus conclude, that microbiological activity was not primarily responsible for this

Fig. 5. Time evolution of pH in DRE-soil over the course of the experiment. Error bars indicate standard deviations (SD) within triplicates.

development neither by reduction of reducible iron nor by exudation of protons. Also the uptake of strontium by microorganisms seems negligible. The case of potential adsorption on the cell walls of microorganisms, however is hard to assess, as these sorption-sites might stay intact for a while after irradiation (Dai et al., 2014) and a slow decomposition of dead biological matter may well be present in both the sterilized and the unsterilized samples. It should also be noted that the experiment was continued at non-sterile conditions, rendering contamination with microorganisms at a later stage quite plausible.

In any case, the ongoing change of pH throughout the experiment emphasizes the fact that the concept of a 'final K_d ' value in a soil – being a complex geochemical admixture as well as a biological habitat – can be rather elusive over longer time periods.

4. Conclusions

Strontium adsorption on soils has been shown to proceed rather fast. The kinetics were surprisingly little affected by differences in the soil characteristics insinuating no big differences in the sorption kinetics of Sr to the different soil phases contributing to CEC, which might be explained by the kinetics being predominantly diffusion-controlled. While Sr-sorption may be a very fast process when applied to pure suspended phases, in the case of contamination of real soils even under continuous agitation, an equilibration time of one week should be allowed before the process of Sr adsorption can be expected to be in a 'steady-state'. A longer equilibration time did not lead to a further increase in K_d values. In contrast, a minute decline of K_d values was observed over the following weeks, which probably reflects the changing thermodynamical conditions in the gas-tight, non-sterile plastic tubes. This explanation is supported by the slow decline of pH in the samples that were measured over the following weeks.

The use of a 0.01M CaCl₂ solution as the liquid phase lead to

 $^{^{3}}$ A data point for sampling after 14 days was retrieved, but was discarded in the graph because the execution of the analytical procedure turned out to be erroneous. For the discussion of this data point, see supplementary material.

comparably low Sr-K_d values. This effect was well predicted by the cocriterion concept suggested for the estimation of Sr-K_d values, while - in this particular case of comparably high Ca-concentration- the prediction of K_d values solely based on the texture/OM criterion leads to an overestimation by almost two orders of magnitude. We therefore strongly suggest to use the co-criterion concept over the texture/OM concept, whenever the needed data for CEC and ([Mg]_{SS} + [Ca]_{SS}) can be retrieved or estimated well enough.

Acknowledgements

The authors are thankful to Ms. Hilal Alemdar for her strong support during lab work at IRS, Hannover, especially with the pedological characterization. This work was conducted as a part of the BioVeStRa project, funded by the German Federal Ministry of Education and Research (BMBF) under the Grant No. 02S9276D.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.apgeochem.2019.01.001.

References

- Al Attar, L., Al-Oudat, M., Safia, B., Abdul Ghani, B., 2016. Ageing impact on the transfer factor of 137Cs and 90Sr to lettuce and winter wheat. J. Environ. Radioact. 164, 19–25.
- Askbrant, S., Melin, J., Sandalls, J., Rauret, G., Vallejo, R., Hinton, T., et al., 1996. Mobility of radionuclides in undisturbed and cultivated soils in Ukraine, Belarus and Russia six years after the Chernobyl fallout. J. Environ. Radioact. 31 (3), 287–312.
- Baeza, A., del Rio, M., Jimenez, A., Miro, C., Paniagua, J., 1995. Relative sorption of ¹³⁷Cs and ⁹⁰Sr in soil: influence of particle size, organic matter content and pH. Radiochim. Acta 68, 135–140.
- Bilgin, B., Atun, G., Keçeli, G., 2001. Adsorption of strontium on illite. J. Radioanal. Nucl. Chem. 250 (2), 323–328.
- Bunde, R.L., Rosentreter, J.J., Liszewski, M.J., Hemming, C.H., Welhan, J., 1997. Effects of calcium and magnesium on strontium distribution coefficients. Environ. Geol. 32, 219–229.
- Chiang, P.N., Wang, M.K., Huang, P.M., Wang, J.J., Chiu, C.Y., 2010. Cesium and strontium sorption by selected tropical and subtropical soils around nuclear facilities. J. Environ. Radioact. 101, 472–481.
- Corcho-Alvarado, J.A., Balsiger, B., Sahli, H., Astner, M., Byrde, F., Röllin, S., Holzer, R., Mosimann, N., Wüthrich, S., Jakob, A., Burger, M., 2016. Long-term behavior of 90Sr and 137Cs in the environment: case studies in Switzerland. J. Environ. Radioact. 160 (Suppl. C), 54–63.
- Dai, Q., Zhang, W., Dong, F., Yulian, Z., Wu, X., 2014. Effect of γ-ray radiation on the biosorption of strontium ions to baker's yeast. Chem. Eng. J. 249, 226–235.
- DIN EN 15933, 2012. Schlamm, behandelter Bioabfall und Boden-Bestimmung des pH-Werts. Deutsche Fassung, November 2012. (in German).
- DIN EN ISO 10693, 2014. Bodenbeschaffenheit–Bestimmung des Carbonatgehaltes– Volumetrisches Verfahren (ISO 10693:1995). Deutsche Fassung, Juni 2014. (in German).
- DIN EN ISO 12782-2, 2012. Bodenbeschaffenheit-Parameter zur geochemischen Modellierung der Elution und Speziation von Bestandteilen in Böden und Materialien–Teil 2: Extraktion von kristallinen Eisenoxiden und -hydroxiden mittels Dithionit. Fassung, September 2012. (in German).
- DIN EN ISO 12782-3, 2012. Bodenbeschaffenheit–Parameter zur geochemischen Modellierung der Elution und Speziation von Bestandteilen in Böden und Materialien–Teil 3: Extraktion von Aluminiumoxiden und -hydroxiden mittels Ammoniumoxalat/Oxalsäure. Fassung, September 2012. (in German).
- DIN ISO 11277, 2002. Bodenbeschaffenheit-Bestimmung der Partikelgrößenverteilung in Mineralböden - Verfahren mittels Siebung und Sedimentation. Fassung, August 2002. (in German).
- Dohrmann, R., 2006. Cation exchange capacity methodology II: a modified silver-thiourea method. Appl. Clay Sci. 34, 38–46.
- Ehlken, S., Kirchner, K., 2001. Environmental processes affecting plant root uptake of radioactive trace elements and variability of transfer factor data: a review. J. Environ.

Applied Geochemistry 101 (2019) 103-108

Radioact. 58, 97-112.

- Fuller, A.J., Shaw, S., Peacock, C.L., Trivedi, D., Burke, I.T., 2016. EXAFS study of Sr sorption to Illite, Goethite, Chlorite, and mixed sediment under hyperalkaline conditions. Langmuir 32, 2937–2946.
- Gil-García, C.J., Rigol, A., Vidal, M., 2008. New best estimates for radionuclide solid–liquid distribution coefficients in soils, Part 1: radiostrontium and radiocaesium. J. Environ. Radioact. 100, 690–696.
- Gomez, A.E., Brown, J., 2013. Determination of root uptake to vegetables grown in soil contaminated for twenty-five years. https://www.gov.uk/government/uploads/ system/uploads/attachment_data/file/337136/HPA-CRCE-047_for_website.pdf, Accessed date: 30 December 2018.
- Guillén, J., Baeza, A., Corbacho, J.A., Munoz-Munoz, J.G., 2015. Migration of ¹³⁷Cs, ⁹⁰Sr, and ²³⁹⁺²⁴⁰Pu in Mediterranean forests: influence of bioavailability and association with organic acids in soil. J. Environ. Radioact. 144 (Suppl. C), 96–102.
- Gupta, D.K., Walther, C., 2018. Behaviour of Strontium in Plants and the Environment. Springer, USA.
- Gupta, D.K., Deb, U., Walther, C., Chatterjee, S., 2018a. Strontium in the ecosystem: transfer in plants via root system. In: Gupta, D.K., Walther, C. (Eds.), Behaviour of Strontium in Plants and the Environment. Springer, Germany, pp. 1–18.
- Gupta, D.K., Schulz, W., Steinhauser, G., Walther, C., 2018b. Radiostrontium transport in plants and phytoremediation. Environ. Sci. Pollut. Res. 25, 29996–30008.
- Hu, W., Dong, F., Yang, G., Peng, X., Huang, X., Liu, M., Zhang, J., 2017. Synergistic interface behavior of strontium adsorption using mixed microorganisms. Environ. Sci. Pollut. Res. 25, 22368–22377.
- IAEA, 2009. Quantification of Radionuclide Transfer in Terrestrial and Freshwater Environments for Radiological Assessments. TECDOC-1616. IAEA, Vienna.
- Liu, M., Dong, F., Zhang, W., Nie, X., Sun, S., Wei, H., Luo, L., Xiang, S., Zhang, G., 2016. Programmed gradient descent biosorption of strontium ions by *Saccaromyces cervisiae* and ashing analysis: a decrement solution for nuclide and heavy metal disposal. J. Hazard Mater. 314, 295–303.
- Margon, A., Mondini, C., Valentini, M., Ritota, M., Leita, L., 2013. Soil microbial biomass influence on strontium availability in mine soil. Chem. Speciat. Bioavailab. 25 (2), 119–124.
- Nilsson, K., Jensen, B.S., Carlsen, L., 1985. The migration chemistry of strontium. European Applied Research Reports 7 (1) 1985.
- Noordijk, H., Van Bergeijk, K.E., Lembrechts, J., Frissel, M.J., 1992. Impact of ageing and weather conditions on soil-to-plant transfer of radiocesium and radiostrontium. J. Environ. Radioact. 15, 277–286.
- Ohnuki, T., 1994. Sorption characteristics of strontium on sandy soils and their components. Radiochim. Acta 64, 237–245.
- Ohnuki, T., Kozai, N., 1994. Sorption characteristics of radioactive cesium and strontium on smectite. Radiochim. Acta 66/67, 327–331.
- Rauret, G., Firsakova, S., 1996. The Transfer of Radionuclides through the Terrestrial Environment to Agricultural Products, Including the Evaluation of Agrochemical Practices. EUR 16528 EN, European Commission, Luxembourg.
- Rigol, A., Roig, M., Vidal, M., Rauret, G., 1999. Sequential extractions for the study of radiocesium and radiostrontium dynamics in mineral and organic soils from Western Europe and Chernobyl areas. Environ. Sci. Technol. 33, 887–895.
- Robison, W.L., Conrado, C.L., Hamilton, T.F., Stoker, A.C., 2000. The effect of carbonate soil on transport and dose estimates for long-lived radionuclides at a U.S. Pacific test site. J. Radioanal. Nucl. Chem. 243, 459–465.
- Sengupta, P., Sanwal, J., Mathi, P., Mondal, J.A., Mahadik, P., Dudwadkar, N., Gandhi, P.M., 2017. Sorption of Cs and Sr radionuclides within natural carbonates. J. Radioanal. Nucl. Chem. 312, 19–28.
- Smičiklas, I., Jović, M., Šljivić-Ivanović, M., Mrvić, V., Čakmak, D., Dimović, S., 2015. Correlation of Sr²⁺ retention and distribution with properties of different soil types. Geoderma 253–254, 21–29.
- Valcke, E., 1993. The Behavior Dynamics of Radiocesium and Radiostrontium in Soils Rich in Organic Matter. Phd-Thesis. Katholieke Universiteit Leuven, Belgium.
- Van Bergeijk, K.E., Noordijk, H., Lembrechts, J., Frissel, M.J., 1992. Influence of pH, soil type and soil organic matter content on soil-to-plant transfer of radiocesium and strontium as analyzed by a nonparametric method. J. Environ. Radioact. 15, 265–276.
- Wallace, S.H., Shaw, S., Morris, K., Small, J.S., Fuller, A.J., Burke, I.T., 2012. Effect of groundwater pH and ionic strength on strontium sorption in aquifer sediments: implications for ⁹⁰Sr mobility at contaminated nuclear sites. Appl. Geochem. 27 (8), 1482–1491.
- Walther, C., Gupta, D.K., 2015. Radionuclides in the Environment: Influence of Chemical Speciation and Plant Uptake on Radionuclide Migration. Springer, Germany.
- Yamaguchi, A., Tanaka, M., Kurihara, Y., Takahashi, Y., 2018. Local structure of strontium adsorbed on 2:1 clay minerals and its comparison with cesium by XAFS in terms of migration of their radioisotopes in the environment. J. Radioanal. Nucl. Chem. 317 (1), 545–551.