Assessing soil properties governing radiosamarium sorption in soils: Can trivalent lanthanides and actinides be considered as analogues?

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ABSTRACT

The interaction of radiosamarium (RSm), represented here by the [151]Sm isotope, a trivalent lanthanide radioisotope of particular concern due to its presence in radioactive waste, was evaluated in 30 soils with contrasting characteristics by determining sorption and desorption parameters. Solid-liquid distribution coefficients (K_d) were in the range of 10^2–10^5 L kg^{-1} and desorbed fractions were always <2%, which demonstrated that RSm was, in general, strongly and irreversibly sorbed in soils. The statistical analyses performed allowed us to identify pH, specific surface area (BET) and soil organic matter content as the soil properties controlling RSm sorption in the soils. From these, the sorption mechanisms responsible for the RSm-soil interaction are suggested. Two models, a multiple linear regression with BET and pH, and a partial least square regression-based model, were successfully developed and externally validated enabling to accurately predict K_d (RSm) values directly from soil properties. It was also evidenced that RSm and Am sorption is controlled by the same soil properties, and that K_d (RSm) values can be successfully predicted through the application of prediction models calibrated with Am data. Thus, the chemical analogy among trivalent actinides and trivalent lanthanides in terms of soil interaction and the feasibility of using interchangeably K_d data of both element families to predict their interaction in soils was demonstrated.

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1. Introduction

Increasing amounts of waste containing radioactive elements are being generated by some industrial activities. Given that radioactive waste represents a potential hazard to the environment and human health, safe waste management systems are crucial. Considerable progress has already been achieved in the safe disposal of radioactive waste in near-surface and deep geological repositories, which isolate it from the environment, even in the long term (NAGRA, 1988; NEA, 2000; NEA, 2008). Nevertheless, the potential emission of radionuclides (RNs) into the environment should always be considered, especially in the event of a nuclear accident or the malfunction of waste-storage facilities, and it is therefore essential that the derived risk can be assessed within decision support systems. Radioactive risk assessment is based on the parameterisation and quantification of the processes governing the mobility of RNs among ecosystems and their subsequent transfer to biota and eventually to human beings. In terrestrial radioactive contamination episodes, risk assessment is often based on the development and application of reactive transport models for porous media, which require reliable input data for those parameters that describe the behaviour of RNs in the target matrices (IAEA, 2001). In this context, a key

process to be parameterised is the interaction of RNs in soils, as this environmental compartment governs the transfer of RNs to other compartments and to the food chain (IAEA, 2009). The solid-liquid distribution coefficient (K_d) of RNs is a frequently used parameter in this context, since its quantification makes it possible to estimate RN retention in soils and its subsequent mobility (EPA, 1999; IAEA, 1994). However, since soils are heterogeneous materials with different physicochemical properties that affect the sorption of RNs, K_d values for a given RN can range within several orders of magnitude. Thus, the proposal of a single K_d value as the input data for models cannot be used as a scientifically based option (unless only conservative estimations are pursued), since K_d variability may jeopardise its reliability for risk assessment purposes. Alternatively, K_d variability may be reduced by grouping K_d values according to general soil properties that may affect the sorption of the target RN (such as texture or organic matter content) (IAEA, 2009), or by deriving K_d values from correlations with selected soil properties when the mechanisms governing RN interaction are ascertained.

While the interaction mechanisms for a limited number of RNs, including radiocaesium, radiostrontium and uranium, have been ascertained (Gil-García et al., 2009a; Vandenhove et al., 2009), less is known about lanthanides and actinides, for which there are scarce sorption data and a lack of knowledge regarding their interaction in soils (Gil-García et al., 2009b). In the particular case of samarium (Sm), this

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is a trivalent lanthanide whose radioisotopes may be present in radioactive waste as a result of ^{235}U nuclear fission during nuclear fuel burn-up (GRS, 2012; Magill et al., 2003). In addition, higher levels may be found in some radioactive waste due to spent nuclear fuel reprocessing (GRS, 2012; IAEA, 2004). Among all Sm radioisotopes, the medium-lived beta emitter ^{151}Sm ($T_{1/2}$ = 90 years) is of paramount importance when analysing nuclear waste disposal safety, since it is expected to be one of the main contributors in low- and intermediate-level waste to the medium-term external dose (100–500 years) (Rego et al., 2011; SKB, 1997). Furthermore, Sm can be considered as a chemical analogue for actinides that are relevant in the context of radioactive waste management, including curium (Cm) and americium (Am), due to their similar chemical properties, such as ionic radii, coordination number and oxidation state. In fact, stable lanthanide isotopes have been used as actinide surrogates in order to study their interaction with matrices such as engineered barrier materials, rocks and clay minerals (Krauskopf, 1986; McCarthy et al., 1998; SKB, 1995, 1997). Although a few studies have tested the similarity between lanthanides and actinides in terms of their sorption in geological materials (Lee et al., 2006), there have been no quantitative studies that have tested the suitability of using lanthanides as chemical analogues of actinides for interaction studies in soils.

The main objective of this work was to study the interaction of radiosamarium (RSm), represented here by the ^{151}Sm radioisotope, in a collection of soils with contrasting edaphic properties aiming to: 1) identify the soil properties that govern RSm sorption and desorption in soils; 2) construct and validate models to predict K_d (RSm) data in soils from soil properties, and 3) demonstrate the suitability of using trivalent lanthanides (Ln(III)) as surrogates for trivalent actinides (Ac(III)), or vice versa, for sorption studies in soils.

2. Materials and methods

2.1. Soil samples and sample characterisation

A collection of 30 soil samples was used for the present study. Most were natural and agricultural soils included in the Spanish radioactive monitoring network and collected as part of a sampling campaign conducted within a previous study (Gil-García et al., 2008). Furthermore, in order to ensure that the soils had a range of edaphic properties as wide as possible, some peat soils from wet meadows in Ukraine, Belarus and the United Kingdom were also included in the study. All soil samples were taken from the surface layer (0–10 cm), air-dried, sieved through a 2 mm mesh, homogenised with a roller table and stored in plastic bottles until analysis. Then, an extensive physico-chemical characterisation of soil samples was carried out. The cation exchange capacity (CEC) was determined as the sum of exchangeable bases plus the exchangeable acidity obtained by displacement with BaCl$_2$-triethanolamine solution buffered at pH 8.2 (Burt, 2004). The loss on ignition (LOI) content was determined as the loss of soil weight by ashing 2 g of each soil sample (previously oven-dried overnight at 110 °C) at 450 °C for 16 h in a muffle furnace. Organic carbon (C$_{org}$) content was determined in the samples pre-treated with 2 mol L^{-1} HCl to eliminate carbonates by Thermo EA 1108 (ThermoScientific, Italy) elemental analyser using tin capsules and V$_2$O$_5$ as additive (ISO, 1995). The carbonate (CaCO$_3$) content was determined by using the calcimeter Bernard method (Müller and Gastner, 1971). Particle size distribution was determined by the pipette method (Burt, 2004) and the specific surface area of soils (BET) was determined by N$_2$ adsorption after degasification at 100 °C (Fagerlund, 1973). The iron and manganese amorphous contents (Fe$_{amorph}$ and Mn$_{amorph}$, respectively) were quantified by means of ascorbate extraction (Kotska and Luther, 1994), whereas the content of aluminium amorphous content (Al$_{amorph}$) was determined by extraction with acid oxalate under darkness (Carter and Gregorich, 2006).

In addition, the solutions obtained after equilibrating the soil samples with deionised water under the same conditions as those of the

RSm sorption tests (see Section 2.2.1) were also characterised in terms of: pH, dissolved organic carbon (DOC) and dissolved inorganic carbon (DIC), and concentration of major cations (Ca, Mg, K and Na). The DOC content was measured using a Total Organic Carbon analyser (Shimadzu TOC-5000 A) (Shimadzu, Japan) with a previous acidification with HCl to a pH of 3 to remove the carbonates in solution. The DIC content was calculated as the difference between the total carbon content, determined as the DOC but without the acidification step, and the DOC content. The concentration of major cations was determined by inductively coupled plasma optical emission spectrometry (ICP-OES) (Thermo-Jarrell Ash 25 and Perkin Elmer Optima 3200 RL, USA). The following emission lines were used (nm): Ca: 315.887 and 317.933, Mg: 279.077 and 285.213, K: 766.490, and Na: 330.237. The detection limits of ICP-OES were 0.1 mg L^{-1} for Ca and Mg, 1 mg L^{-1} for K, and 5 mg L^{-1} for Na. Table 1 summarises the main characteristics of the soil samples. Most variables presented a wide range of values, which confirmed that the selected soil samples represented varying soil scenarios. Detailed characterisation data concerning the 30 soil samples analysed are also available in Tables S1 and S2 in Supporting Information (SI).

2.2. Quantification of ^{151}Sm sorption and desorption parameters

2.2.1. Batch sorption and desorption tests

Batch sorption experiments were applied in triplicate to the 30 soil samples to quantify K_d (RSm) values. The sorption test procedure consisted of mixing 2 g of each dried soil sample (m) with 49 mL of double-deionised water in 80 mL polypropylene centrifuge tubes and shaking the suspensions for 16 h using an end-over-end shaker at 60 rpm. Afterwards, each resulting suspension was spiked with 1 mL of a solution containing ^{151}Sm and stable Sm at the same concentration level (custom solution from Eckert and Ziegler, Germany). The suspensions, which contained 50 mL (V) of the spiked contact solution with a known initial ^{151}Sm activity concentration of approximately 10^5 Bq L^{-1} (C_i), were equilibrated again for 24 h and centrifuged (12,880g, 30 min, 10 °C) using a Beckman J2-HS centrifuge with a JA14 rotor (Beckman, Ireland). The supernatants were decanted off, filtered through 0.45 μm nylon syringe filters and the ^{151}Sm activity concentration determined (see Section 2.2.2). The K_d (RSm) values, which correspond to the ratio between the ^{151}Sm activity concentration

Table 1
Summary of soil characteristics.

Variable	Code	Unit	Min.	Max.	GM[a]
Related to soil solid phases					
Clay fraction (wrt. initial soil weight)	Clay	%	0.3	47.4	10.4
Sand fraction (wrt. initial soil weight)	Sand	%	4.1	84.5	27.9
Calcium carbonate content	CaCO$_3$	%	0.2	51	5.0
Organic carbon	C$_{org}$	%	0.2	41	3.3
Loss on ignition	LOI	%	1.4	78	9.6
Aluminium amorphous content	Al$_{amorph}$	mg kg^{-1}	73	2725	471
Iron amorphous content	Fe$_{amorph}$	mg kg^{-1}	56	19,668	852
Manganese amorphous content	Mn$_{amorph}$	mg kg^{-1}	11	4018	251
Cation exchange capacity	CEC	cmol$_c$ kg^{-1}	19	140	44
Specific surface area	BET	m^2 g^{-1}	0.4	47	3.9
Related to the supernatant[b]					
pH	pH	–	3.9	9.9	6.6
Dissolved inorganic carbon	DIC	mg L^{-1}	1	139	9
Dissolved organic carbon	DOC	mg L^{-1}	1	290	26
Ca	Ca	mg L^{-1}	4	444	43
Mg	Mg	mg L^{-1}	2	17	5
K	K	mg L^{-1}	1	12	4
Na	Na	mg L^{-1}	0.2	93	2.0

[a] GM = geometric mean.

[b] Solutions obtained after equilibrating the soil samples with deionised water under the same experimental conditions as applied in the sorption tests.