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Cesium, strontium, and cobalt adsorption and desorption in soils near Korean nuclear facilities: Soil-property dependence and sequential extraction

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Abstract

Remediation planning for decommissioned nuclear sites requires site-specific data on radionuclide retention and release. We evaluated sorption, desorption in water and 0.1 M HNO_3, and sequential extraction of cesium, strontium, and cobalt in actual soils collected near four Korean nuclear facilities. Retention trends were nuclide-specific: cobalt followed surface area and organic matter, strontium followed cation-exchange capacity, and cesium was least soil-dependent. Release differed markedly between washing media: water release varied among soils, whereas acid release was nuclide-controlled (strontium > cobalt > cesium), and half of retained cesium resisted acid. These contrasts call for nuclide- and soil-specific remediation strategies.

Keywords: Cesium, Strontium, Cobalt, Distribution coefficient, Desorption, Sequential extraction

1. Introduction

The decommissioning of nuclear power plants has entered its implementation phase in the Republic of Korea. Kori (KR) Unit 1, the country's first commercial reactor, was permanently shut down in June 2017, and its final decommissioning plan was approved by the Nuclear Safety and Security Commission in June 2025, with completion targeted for 2037. Another nuclear power plant (NPP), Wolsong (WS) Unit 1, was permanently closed in 2019 [1]. Before such sites can be released for other uses, soils that may contain radionuclides such as ^{137}Cs, ^{90}Sr, and ^{60}Co must be assessed and, where necessary, remediated [2]. Total activity concentrations define the degree of contamination, but they do not indicate how strongly the contaminants are bound to the soil or how readily they can be released, either by infiltrating water under natural conditions or by chemical agents during soil washing. Site-specific assessments therefore require information on both the retention and release of specific radionuclides.

Cs, Sr, and Co are predominantly retained by different soil components. Cs is held at non-specific exchange sites and at highly selective frayed-edge and interlayer sites of micaceous clay minerals [3, 4]. The relative contribution of these selective sites to overall Cs retention decreases as Cs loading increases; as a result, Cs sorption depends strongly on concentration and contact history [5–7]. Sr^{2+} ion is retained predominantly by non-selective cation exchange, and competes for binding sites with Ca^{2+} and other major cations [8–10]. Co can be retained via binding to exchange sites, organic matter, and/or Fe–Mn oxides depending on the soil properties and reaction conditions [11, 12]. Consequently, the retention behaviors of Cs, Sr, and Co show different sensitivities to specific surface area (SSA), cation-exchange capacity (CEC), organic matter (OM) content, particle-size

distribution, and mineral composition. Thus, a property associated with strong retention of one ion may have little explanatory value for another.

Retention is commonly quantified by the solid–liquid distribution coefficient (K_d), the ratio of the concentration of a substance sorbed on a solid phase to its equilibrium concentration in the contacting liquid phase, which can vary by several orders of magnitude for a given radionuclide depending on soil characteristics and experimental conditions [13, 14]. Regression relationships based on soil properties such as clay content, pH, and organic carbon content have been developed to predict K_d for environmental assessments [15]. For radiocesium, regression models have identified the radiocesium interception potential (RIP), clay content, and K^+ and NH_4^+ contents as the most relevant soil parameters [16]. Grouping soils by texture, organic matter content, or properties governing radionuclide–soil interactions has also been used to reduce K_d variability [9, 17]. More recently, machine-learning models trained on large data sets have predicted K_d from soil adsorption factors and X-ray fluorescence (XRF) and X-ray diffraction (XRD) data [18, 19]. Site-specific studies, however, usually involve only a few soils, limiting the number of independent between-soil comparisons and precluding reliable training of data-intensive models. For such data sets, a direct comparison of how the soils rank for each radionuclide is more transparent than a statistical model, because the limited number of soils is not concealed by the larger number of individual measurements.

K_d describes the partitioning of ions between soil and liquid under specific sorption conditions, but it does not indicate how much of the retained inventory of ions will be released if the conditions are changed by washing with water or acid solution. Adsorption and desorption are related but distinct processes. Ion release depends on desorption kinetics,

sorption history, the mineral phases to which the ions are bound, and the chemistry of the desorbing solution [5, 20, 21]. Studies therefore frequently characterize sorption and desorption in tandem to evaluate the reversibility of radionuclide sorption in soils, for example by correcting K_d for the reversibly sorbed fraction [22]. Thus, strong retention under sorption conditions does not necessarily imply resistance to desorption during washing with water or a chemical solution. Previously, deionized water and dilute mineral acid solutions have been used as two contrasting washing solutions to study radionuclide release. Water has been used to study release in the absence of added reagents, whereas 0.1 M HNO_3 has been used to create acidic conditions for chemical soil washing [2]. The extent to which soil properties related to retention are also related to release under treatment with deionized water or dilute mineral acid has rarely been examined for Cs, Sr, and Co in the same soils.

Sequential extraction provides information on how elements are held within a substrate by partitioning them into operationally defined fractions using reagents of increasing strength. The classical scheme of Tessier et al. [23] defines partition into five fractions—exchangeable, carbonate-bound, Fe–Mn oxide-bound, organic matter-bound, and residual fractions—with later modifications of this scheme adding a water-soluble step [24]. Sequential extraction has been applied to soils around a research reactor that had been artificially contaminated with stable Cs and Sr [24] and to a coastal soil containing Cs, Co, and Sr [25]. Sequential extraction has also been used to evaluate the washing of Sr- and Cs-contaminated soil near a Korean NPP with Ca- and K-based solutions [26]. The method has also been used in combination with grain-size and mineralogical analyses to interpret the behavior of radioactive and stable Cs in soils in Fukushima [27] and to follow changes

in the distribution of radiocesium and radiostrontium with time and over drying–wetting cycles in mineral and organic soils [28]. More recently, the exchangeable fractions of Sr, Cs, and Co in soils and rocks, estimated from field sampling and batch adsorption experiments using the stable forms of these elements, were related to CEC, potassium feldspar and mica-like clay minerals, and OM content, respectively, and these findings were used to support K_d estimation [29]. Because extractants are not fully selective for their target phases, and because released elements can be redistributed during successive steps, the fractions are operational rather than phase-specific [30, 31]. Evaluations of sequential extraction have therefore relied largely on qualitative comparisons with soil–plant transfer or relative mobility sequences [32, 33]. A remaining question is how reliably operational fractionation corresponds to release measured independently under water and acid treatments for different ions and soils.

The present study applied three complementary approaches—characterization of bulk soil properties, sorption and desorption experiments with deionized water and 0.1 M HNO_3, and sequential extraction—to soil samples collected from four locations in Korea, two near research reactor sites (Korea Research Reactor site in Seoul, SE and HANARO in Daejeon, DJ) and two near NPP sites with permanently shut-down units (Kori, KR and Wolsong, WS unit 1). The soils were experimentally loaded with stable Cs, Sr, or Co as surrogates for the corresponding radionuclides. First, the physicochemical and mineralogical properties of the soils were characterized. The K_d values of the three elements were then determined over a range of initial concentrations, and the amounts released during washing with deionized water or 0.1 M HNO_3 were measured. The soil dependence of retention and release was compared among the ions, and the soil rankings were compared with those of

the bulk soil properties. Finally, the distributions of the elements among six sequential extraction fractions were obtained from the same loaded soils and related to the release data. Previous studies have combined sorption, desorption, or washing with sequential extraction for a single soil or for Cs and Sr only [25, 26, 28]. The present study compares three radionuclide surrogates in four soils collected near Korean nuclear facilities and evaluates where measured water- and acid-induced release agrees with, or departs from, the corresponding operationally defined fractions. The central questions are whether soil properties associated with sorption differ by element, whether strong sorption corresponds to resistance to chemical release, and to what extent sequential extraction helps interpret that release. This study aims to clarify how bulk soil properties relate to the retention and release of three key radionuclide contaminants and to identify which measurements are most informative for element- and soil-specific assessment of remediation options at nuclear facility sites.

2. Experimental

2.1. Soil sampling and characterization

For the sorption, desorption, and sequential extraction experiments, surface soil samples were collected near the Korea Research Reactor in Seoul (37.63°N, 127.08°E; hereafter SE), the Korea Atomic Energy Research Institute (KAERI) in Daejeon (36.42°N, 127.36°E; DJ), the Wolsong NPP (35.70°N, 129.46°E; WS), and the Kori NPP (35.34°N, 129.29°E; KR). Surface soil (0–15 cm) was sampled because this layer is most likely to receive and retain radionuclides released to the environment. Because of security restrictions, the NPP

samples were collected approximately 2.0 km from each facility. At each site, approximately 0.5 kg of soil was collected from each of ten locations to allow for spatial variations within the sampling area, and the subsamples were combined and homogenized into a composite sample weighing approximately 5.0 kg. Plant roots were removed from the combined sample, and then the sample was stored in a polyethylene bag. Prior to use, the soil samples were air-dried at room temperature for 14 days and passed through a 2 mm sieve.

The particle-size distribution of each soil was determined by sieving into >500, 200–500, 75–200, and <75 μm fractions. The CEC was determined by a modified version of the sodium acetate method (US EPA Method 9081) [34]. In this method, 1.0 g of soil was mixed with 50 mL of 1 N sodium acetate (pH 8.2) to saturate the soil with Na^+, after which the soil was washed with isopropyl alcohol to remove excess unadsorbed ions. The adsorbed Na^+ was then displaced with 1 N ammonium acetate (pH 7.0). The concentration of displaced Na was determined by atomic absorption spectrometry (AAS). CEC was calculated using Eq. (1).

$$CEC\ \left(\frac{meq}{100g}\right) = \frac{C_{Na}\ \cdot d\ \cdot V_L}{23\ \cdot 10\ \cdot M_{kg}} \qquad (1)$$

where C_{Na} is the concentration of Na^+ in the displacement solution (mg L^{-1}), d is the dilution factor, V_L is the volume of solution (L), 23 is the equivalent mass of Na (mg meq^{-1}), M_{kg} is the mass of the soil sample (kg), and 10 is the factor converting meq kg^{-1} to meq $(100\ g)^{-1}$. CEC values are reported in units of cmol(+) kg^{-1}, which are numerically equal to meq $(100\ g)^{-1}$.

The SSA of each soil was determined by the Brunauer–Emmett–Teller (BET) method from N_2 adsorption isotherms using an ASAP 2420 surface area analyzer (Micromeritics). To determine the moisture content of the sample, soil mass loss was measured after heating at 105 °C. The OM content was estimated from the mass loss on ignition at 550 °C. For qualitative phase identification, XRD patterns were recorded (D8 DISCOVER, Bruker; Cu Kα radiation) after drying for 24 h at room temperature, over a 2θ range of 5–85° with a step size of 0.02°. XRF spectrometry (S2 Ranger, Bruker) was used to determine the major- and trace-element compositions of the soils, which are reported as oxide weight percentages (wt%).

2.2. Batch adsorption experiments and determination of distribution coefficients

Cesium chloride (CsCl) and strontium nitrate ($Sr(NO_3)_2$) were purchased from Sigma-Aldrich (USA) and used to prepare stock solutions, which were serially diluted with deionized water to initial Cs and Sr concentrations of 1, 5, 10, and 30 mg L^{-1}. For Co, a cobalt nitrate ($Co(NO_3)_2$) solution purchased from Sigma-Aldrich (USA) was serially diluted with deionized water to initial Co concentrations of 100, 150, 200, and 250 mg L^{-1}. This higher concentration range was selected because when solutions with lower initial concentrations were exposed to the soil samples, the Co concentrations remaining in solution were below the detection limit of AAS.

For each adsorption experiment, 1.0 g of soil was mixed with 20 mL of a solution containing Cs, Sr, or Co, giving a liquid-to-solid ratio of 20 mL g^{-1}. The three ions were tested separately, and each soil–ion–concentration condition was tested in triplicate. The

suspensions were shaken for 168 h at 120 rpm and 25 °C. The suspensions were then centrifuged, and the supernatants were passed through 0.2 μm syringe filters. The pH values of the filtrates were measured using a pH meter (Orion Star A215, Thermo Scientific). The measured pH in the Co adsorption experiments did not exceed 8; however, pH alone does not rule out precipitation or coprecipitation, and the removal of dissolved Co is therefore interpreted as apparent retention. The Cs and Co concentrations in the filtrates were measured by inductively coupled plasma mass spectrometry (ICP-MS) and AAS, respectively, whereas Sr concentrations were determined by inductively coupled plasma optical emission spectrometry (ICP-OES; Avio 500, PerkinElmer) to avoid potential interference from Ca in AAS. The distribution coefficient was calculated as follows:

$$K_d = \left(\frac{C_0 - C}{C}\right) \times \left(\frac{V}{M}\right) \qquad (2)$$

where C_0 is the initial concentration of the ion (mg L^{-1}), C is the concentration in the filtrate after 168 h (mg L^{-1}), V is the solution volume (L), and M is the soil mass (kg). K_d is expressed in L kg^{-1}, which is numerically equivalent to mL g^{-1}.

2.3. Desorption experiments

To generate samples containing sorbed Cs, Sr or Co, a 35 g portion of each soil (SE, DJ, WS, and KR) was mixed with 350 mL of a 3 mM CsCl, $Sr(NO_3)_2$, or $Co(NO_3)_2$ solution prepared in deionized water (10 mL g^{-1}). The suspensions were shaken at 120 rpm for 168 h at 25 °C to allow adsorption. After sorption, the suspensions were centrifuged and the supernatants were filtered through 0.2 μm polyvinylidene fluoride (PVDF) syringe filters.

The Cs and Co concentrations in the filtrates were determined by ICP-MS, and, AAS, respectively, Sr concentrations by ICP-OES. The ion-loaded soils were then washed with deionized water. The retained inventory (q_0, mg g^{-1}) was calculated from the mass balance:

$$q_0 = (C_i - C_e) \times \left(\frac{V}{M}\right) \qquad (3)$$

where C_i and C_e are the initial and final concentrations in the loading solution (mg L^{-1}), V is the solution volume (L), and M is the soil mass (g). The resulting samples were designated by the element symbol followed by the soil code (e.g., Cs-SE, Sr-SE, and Co-SE). Aliquots from the same prepared batches of loaded soil were used for the desorption experiments (this section) and sequential extraction (Section 2.4). The potential effect of the post-loading water rinse on the inventory used to normalize desorption and extraction recovery requires confirmation from the laboratory records.

For the desorption experiments, 1.0 g of each ion-loaded soil was mixed with 30 mL of either deionized water or 0.1 M HNO_3. The liquid-to-solid ratio was 30 mL g^{-1}, and each soil–ion–desorbent condition was tested in triplicate. The suspensions were agitated on a reciprocal shaker for 24 h at room temperature and then centrifuged, and the supernatants were filtered through 0.2 μm polyvinylidene fluoride (PVDF) syringe filters. Cs and Co concentrations in the filtrates were measured by ICP-MS, whereas Sr concentrations were measured by ICP-OES. The amount released (mg g^{-1}) and the desorption percentage were calculated as follows:

$$Released\ (q_d) = C_d \times \left(\frac{V_d}{m_d}\right) \qquad (4)$$

$$Desorption\ (\%) = \frac{q_d}{q_0} \times 100 = \frac{C_d \times (V_d / m_d)}{q_0} \times 100 \qquad (5)$$

where q_d is the amount released (mg g^{-1}), C_d is the concentration in the desorption solution (mg L^{-1}), V_d is the solution volume (L), m_d is the mass of loaded soil (g), and q_0 is the retained inventory (mg g^{-1}; Eq. 3).

2.4. Sequential extraction

Sequential extraction of Cs, Sr, and Co was performed in triplicate using 1.0 g portions of the ion-loaded soils (Section 2.3) following the six-step procedure described by Bouzidi et al. [24], which is a modified version of the method of Schultz et al. [35]. The procedure partitioned the Cs, Sr, and Co into six operationally defined fractions: water-soluble (F1), exchangeable (F2), organic-associated (F3), carbonate-associated (F4), oxyhydroxide-associated (F5), and residual (F6) (Table S1). A reagent volume of 15 mL per 1.0 g of starting soil (15 mL g^{-1}) was used for steps F1–F5, with the solid residue obtained at the end of each step subjected to the next extraction conditions. The recoveries, calculated as the sum of F1–F6 relative to the retained inventory (q_0), ranged from 85.59% to 113.56% (Table S4).

The water-soluble fraction (F1) was extracted with deionized water for 1 h at room temperature without pH adjustment. The remaining residue was treated with 0.4 M $MgCl_2$ adjusted to pH 5 for 1 h at room temperature to obtain the exchangeable fraction (F2). The organic-associated fraction (F3) was then extracted by mixing with 5–6% NaOCl adjusted to pH 7.5 at 96 °C in two successive treatments of 30 min each. The residue was then subjected to two successive 2 h extractions with 1 M sodium acetate in 25% acetic acid at pH 4 and room temperature to obtain the carbonate-associated fraction (F4). The

oxyhydroxide-associated fraction (F5) was extracted by treatment with 0.04 M hydroxylamine hydrochloride ($NH_2OH \cdot HCl$), adjusted to pH 2 with HNO_3, for 5 h at room temperature. Finally, the remaining solid was digested with a mixture of HNO_3, HCl, HF, and $HClO_4$ at 100 °C until complete dissolution to recover the residual fraction (F6). After each extraction in steps F1-F5, the suspension was centrifuged at 3,500 rpm, and the supernatant was filtered through a 0.2 μm cellulose nitrate membrane. The Sr and Co concentrations in the extracts were determined by AAS, and the Cs concentrations by ICP-MS. Extracted masses were normalized to the initial 1.0 g soil mass and reported in mg g^{-1}. The amount of Cs, Sr, or Co in each fraction was expressed as a percentage of the total amount recovered in F1-F6. The resulting percentages represent reagent-defined pools rather than uniquely identified chemical species or mineral phases.

2.5. Data analysis

K_d, released amounts, and fraction contents are reported as the mean ± standard deviation (SD) of triplicate measurements. Because the soil properties were measured once for each of the four soils, the relationships between retention or release and the soil properties could not be tested statistically: with four soils, even identical rankings give an exact two-sided p value of 0.083 for Spearman's rank correlation coefficient (ρ). Regression models relating the individual measurements to soil properties would also treat replicate and concentration-level observations as independent between-soil information. Instead, the soil dependence of retention and release was described for each ion as follows.

First, the magnitude of the soil dependence was expressed as the coefficient of variation (CV) of the four soil means (sample standard deviation with n - 1 divided by the mean) and as the ratio of the largest to the smallest soil mean. For K_d, the soil mean was the average over the four initial concentrations. Second, the soil ranking of each response was compared with the rankings of SSA, CEC, OM content, and the <75 μm fraction using ρ. These ρ values are reported as descriptive measures of rank agreement (ρ = 1 or -1 for identical or reversed rankings) and not as tests of significance. Non-overlap of mean ± SD ranges was used only as a descriptive indication of separation, not as a formal statistical significance test.

Third, the sequential extraction results were related to the desorption results across the 12 ion–soil combinations. The proportion of the water-soluble fraction (F1) was compared with the desorption percentage in deionized water, and the proportion of the water-soluble and exchangeable fractions (F1 + F2) with the desorption percentage in 0.1 M HNO_3, because F1 uses deionized water, as in the water treatment, and because dilute acid acts largely on the exchangeable pool. Pearson's correlation coefficient (r) and ρ were calculated, and significance was defined as $p < 0.05$. To characterize each ion, the ratio of the desorption percentage to the corresponding fraction proportion was also calculated; a ratio above 1 indicates that acid release exceeds the proportion recovered in the selected operational fractions, but it does not by itself identify the source phase of the released ion. The compared percentages have different normalization bases (initial retained inventory versus total sequentially recovered inventory). Because these correlations combine differences among ions with differences among soils, the soil rankings within each ion

were also compared. All calculations were performed in Python 3.14 using SciPy 1.18.0 [36].

3. Results and discussion

3.1. Physicochemical and mineralogical characteristics of the soils

The four soils differed considerably in SSA, CEC, and OM content (Table 1). SSA decreased in the order KR (17.34 $m^2 g^{-1}$) > WS (12.67 $m^2 g^{-1}$) > SE (2.35 $m^2 g^{-1}$) > DJ (1.80 $m^2 g^{-1}$), whereas CEC followed the order WS (21.88 cmol(+) kg^{-1}) > KR (20.29 cmol(+) kg^{-1}) > SE (9.14 cmol(+) kg^{-1}) > DJ (4.45 cmol(+) kg^{-1}). OM content was highest in KR (6.86%), followed by WS (4.95%), SE (4.59%), and DJ (0.94%). KR and WS thus had greater surface areas and exchange capacities than SE and DJ, indicating a greater capacity for cation retention. However, the observation that the SSA of KR exceeded that of WS but the ranking was reversed for CEC shows that exchange capacity was not determined by surface area alone.

Table 1 Physicochemical properties of the four soils. specific surface area (SSA), BET, cation-exchange capacity (CEC), organic matter (OM) content (loss on ignition)

Soil	SSA ($m^2 g^{-1}$)	CEC (cmol(+) kg^{-1})	OM (%)
SE	2.35	9.14	4.59
DJ	1.80	4.45	0.94
KR	17.34	20.29	6.86
WS	12.67	21.88	4.95

The four soil samples also showed different particle-size distributions (Table S2). The proportion of particles smaller than 75 μm was highest in WS (32.46%), followed by KR

(24.23%), SE (15.18%), and DJ (12.78%). Conversely, the >500 μm fraction accounted for 49.43% of SE, compared with 36.85%, 36.86%, and 22.48% of DJ, KR, and WS, respectively. The observation of higher proportions of fine particles in KR and WS is consistent with these sites showing the highest SSA and CEC values, in agreement with previous findings showing an increase in SSA and CEC with decreasing particle size in fractionated soils [37]. Nevertheless, KR had a larger SSA than WS despite its smaller <75 μm fraction, which suggests additional contributions from its higher OM content and mineral composition. Note that the <75 μm fraction includes particles larger than the conventional clay-size fraction (<2 μm) and therefore should not be interpreted as clay content.

XRF analysis showed that SiO_2 and Al_2O_3 were the principal oxide components of the four soils, with values ranging from 53.98% to 66.65% and from 17.20% to 23.24%, respectively (Table S3). KR had the highest SiO_2 content (66.65%) and lowest Al_2O_3 content (17.20%), whereas WS had the lowest SiO_2 content (53.98%). Fe_2O_3 increased from 4.39% in SE and 4.67% in DJ to 5.44% in KR and 7.62% in WS, and MnO was also highest in WS (0.08%, compared with 0.04–0.05% in the other soils). Fe- and Mn-bearing phases can contribute to Co retention [12]; however, the oxide contents determined by XRF do not distinguish between reactive oxides and elements incorporated into other minerals and cannot be used to quantify the abundance of reactive oxyhydroxides. Thus, the higher Fe_2O_3 and MnO contents of WS do not by themselves indicate greater oxide-associated Co retention, a point examined in Sections 3.3 and 3.6. The CaO contents (2.32–2.66%) varied little among the soils but do not by themselves indicate carbonate abundance, because Ca also occurs in silicate minerals.

The XRD patterns of all four soils contained reflections characteristic of quartz, illite, albite, kaolinite, and muscovite, with KR and WS additionally showing features corresponding to orthoclase (Fig. S1). The presence of illite and muscovite is relevant to Cs retention because micaceous minerals provide sorption sites that are selective for Cs [4, 21]. Illite, for example, has been shown to exhibit high Cs selectivity despite a relatively low CEC, as reflected by its relatively high ratio of RIP to CEC [21]. The low CEC values of SE and DJ are therefore not indicators of a lack of Cs-selective sites. However, qualitative phase identification does not provide information on the abundance or accessibility of such sites.

3.2. Distribution coefficients

The K_d values of Cs, Sr, and Co varied with soil type and initial concentration (Fig. 1). After 168 h, the measured values ranged from 65.00 to 124.09 mL g^{-1} for Cs, from 29.79 to 105.00 mL g^{-1} for Sr, and from 5.64 to 99.19 mL g^{-1} for Co. The partitioning of ions between the solid and solution therefore depended on both the soil characteristics and the loading, indicating that the K_d values should be interpreted as condition-dependent measures of retention rather than intrinsic soil constants. Considering that K_d is the ratio of the amount of ion retained per unit soil mass to the concentration remaining in solution, a decrease in K_d with increasing initial concentration does not necessarily indicate a decrease in the absolute amount adsorbed. Because Co was tested at a higher concentration range (100–250 mg L^{-1}) than Cs and Sr (1–30 mg L^{-1}), and because equal mass concentrations do not represent equal molar loadings, the K_d values are compared among soils for each ion but not among ions.

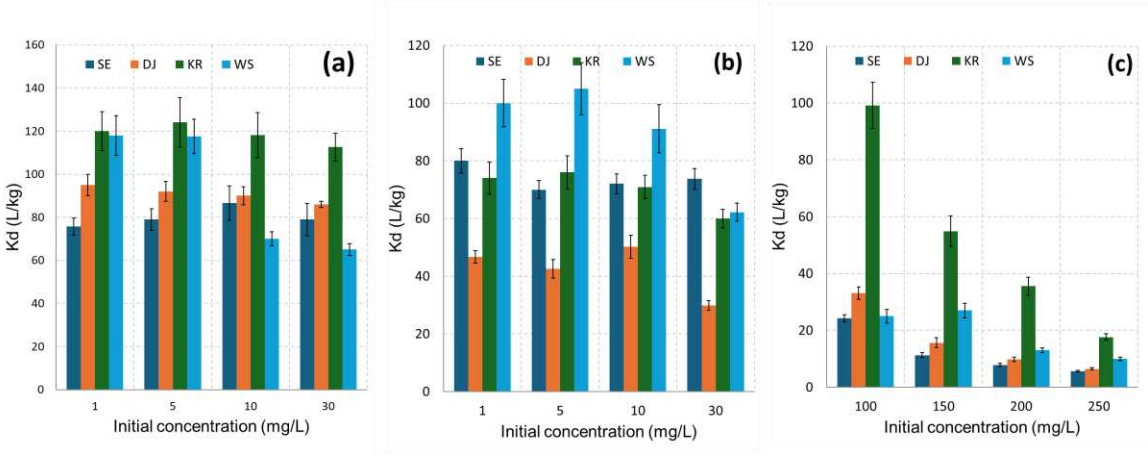


Fig. 1 Distribution coefficients (Kd) of Cs, Sr, and Co in the four soils after 168 h of contact at different initial concentrations: (a) Cs, (b) Sr, and (c) Co. Cs and Sr were tested at 1–30 mg L^{-1} and Co at 100–250 mg L^{-1}. Bars represent the mean, and error bars represent the standard deviation of triplicate measurements

For Cs, KR and WS had the highest K_d values at initial concentrations of 1 and 5 mg L^{-1} (120.00 and 124.09 mL g^{-1} for KR, and 118.00 and 117.55 mL g^{-1} for WS). At 30 mg L^{-1}, the K_d of KR remained high (112.54 mL g^{-1}), whereas that of WS decreased to 65.00 mL g^{-1}. DJ also showed a small decrease, from 95.00 mL g^{-1} at 1 mg L^{-1} to 86.00 mL g^{-1} at 30 mg L^{-1}, and SE varied non-monotonically over a narrow range (75.69–86.61 mL g^{-1}). Consequently, KR showed the highest Cs retention at every concentration, whereas WS fell from second at 1 and 5 mg L^{-1} to lowest at 10 and 30 mg L^{-1}. The decrease in K_d observed with increasing Cs concentration for WS is consistent with the relative contribution from high-affinity sites becoming smaller with increasing loading, as described by multisite models in which highly selective frayed-edge sites dominate at low loadings and less selective exchange sites become increasingly important at higher Cs concentrations [6, 7]. In contrast, the high and nearly constant Cs K_d of KR (112.54–124.09 mL g^{-1}) indicates that its sorption sites were far from saturation over this concentration range. The persistence of relatively high Cs K_d values in DJ, despite the low CEC and SSA

of this soil, suggests that these bulk properties are only weakly related to Cs-selective retention. Because illite and muscovite were identified in all four soils (Fig. S1), their presence alone cannot explain the difference among the soils. The contribution of Cs-selective sites in DJ is discussed together with the fractionation data in Section 3.6.

Sr exhibited a different soil-dependent pattern compared to Cs. For Sr, WS had the highest K_d values at 1–10 mg L^{-1} (91.11–105.00 mL g^{-1}), but K_d decreased to 62.19 mL g^{-1} at 30 mg L^{-1}. DJ consistently showed the lowest Sr retention among the four soils (29.79–50.18 mL g^{-1}). The difference in retention behavior between WS and DJ is consistent with their high and low CEC values, respectively, and with cation exchange being the main mechanism of Sr retention [8, 10]. Nevertheless, SE retained Sr more strongly than KR at three of the four concentrations despite its lower CEC, showing that the complete soil ranking could not be explained by exchange capacity alone. In contrast to the trends observed for Cs and Co, the Sr K_d decreased only moderately with concentration for most soils.

For Co, KR had the highest K_d at every concentration, decreasing from 99.19 mL g^{-1} at 100 mg L^{-1} to 17.61 mL g^{-1} at 250 mg L^{-1}. Similar decreasing trends were observed for SE (from 24.22 to 5.64 mL g^{-1}) and DJ (from 33.13 to 6.44 mL g^{-1}). WS, by contrast, showed a small initial increase from 25.00 to 27.00 mL g^{-1}, followed by a decline to 10.00 mL g^{-1}. Within the different concentration ranges tested, Co showed a pronounced concentration dependence, with K_d decreasing 2.5- to 5.6-fold between 100 and 250 mg L^{-1}. The strong retention observed for KR is compatible with its large SSA and high OM content, although the individual contributions of these properties cannot be separated (Section 3.1). Finally,

WS contained more Fe_2O_3 and MnO than KR but had lower Co K_d values, indicating that bulk oxide composition alone was not a good predictor of Co retention.

3.3. Soil dependence of K_d and comparison with soil properties

The soil dependence of K_d differed markedly among the ions (Table 2; Fig. 2). The CV of the soil-mean K_d among the four soils was 17.2% for Cs, 28.5% for Sr, and 73.6% for Co, and the ratio of the largest to the smallest soil mean increased from 1.48 for Cs to 2.12 for Sr and 4.23 for Co. Thus, the apparent between-soil variation in the concentration-averaged Kd was smallest for Cs and largest for Co under the element-specific concentration ranges tested. This order only partly matches that in global compilations, in which the geometric standard deviation (GSD) of Kd among soils is largest for Co (16) but larger for Cs (7.0) than for Sr (5.9) [14]. Such compilations combine data obtained under different experimental conditions, whereas the present CVs were obtained for the same soils under a single protocol and therefore isolate the effect of the soil. The weak soil dependence of Cs, whose Kd spans five orders of magnitude in compilations (4.3 to 3.8 × 10^5 L kg^{-1}) [14], is consistent with the relatively high loadings used here, at which less selective sites contribute more to sorption [6, 7], and with the presence of micaceous minerals in all four soils (Section 3.1). For Cs, however, the concentration dependence of K_d was soil-specific: K_d decreased by a factor of 1.82 between 1 and 30 mg L^{-1} in WS but changed by 10% or less in SE, DJ, and KR (Section 3.2).

Table 2 Soil dependence of Kd and of the desorption percentages of Cs, Sr, and Co, and rank agreement with soil properties (n = 4 soils). CV, coefficient of variation of the four soil means; Max/min, ratio of the largest to the smallest soil mean; ρ, Spearman's rank

correlation coefficient between the soil means and the soil property, reported as a descriptive measure of rank agreement (with four soils, ρ = ±1 corresponds to an exact two-sided p value of 0.083). Soil means of Kd are averages over the four initial concentrations

Response	Ion	Soil ranking	CV (%)	Max/min	ρ (SSA)	ρ (CEC)	ρ (OM)	ρ (<75 μm)
K_d	Cs	KR > WS > DJ > SE	17.2	1.48	0.8	0.6	0.8	0.6
	Sr	WS > SE > KR > DJ	28.5	2.12	0.4	0.8	0.4	0.8
	Co	KR > WS > DJ > SE	73.6	4.23	0.8	0.6	0.8	0.6
Desorption in water (%)	Cs	SE > KR > WS > DJ	16.0	1.42	0.4	0.2	0.4	0.2
	Sr	DJ > SE > WS > KR	39.4	2.19	−1.0	−0.8	−1.0	−0.8
	Co	WS > SE > DJ > KR	83.9	6.13	−0.2	0.4	−0.2	0.4
Desorption in 0.1 M HNO_3 (%)	Cs	WS > DJ > SE > KR	9.4	1.21	−0.4	0.2	−0.4	0.2
	Sr	SE > WS > DJ > KR	12.2	1.33	−0.4	0.0	−0.4	0.0
	Co	SE > WS > DJ > KR	5.5	1.13	−0.4	0.0	−0.4	0.0

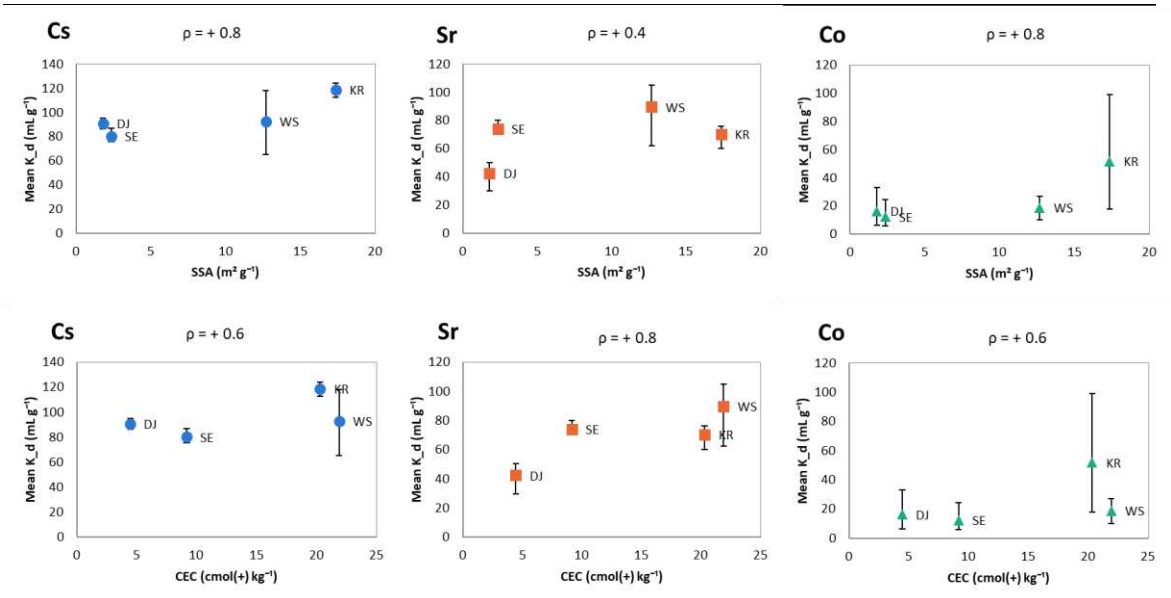


Fig. 2 Soil-mean Kd of Cs, Sr, and Co plotted against the specific surface area (SSA; upper panels) and cation-exchange capacity (CEC; lower panels) of the four soils. Symbols show the mean over the four initial concentrations, and bars show the range (minimum–maximum) over these concentrations. ρ is Spearman's rank correlation coefficient between the soil-mean Kd and the soil property (n = 4), reported as a descriptive measure of rank agreement

The soil ranking of Co K_d was KR > WS > DJ > SE, both when averaged over the four concentrations and at 150–250 mg L^{-1}. This ranking agreed with those of SSA and OM content ($\rho = 0.8$), the only difference being the order of the two low-SSA soils, DJ and SE, whose Co K_d values differed by less than 5 mL g^{-1} at 150–250 mg L^{-1}. KR, which had the largest SSA (17.34 m^2 g^{-1}) and OM content (6.86%), showed Co K_d values 1.8–4.9 times those of the other soils at every concentration. In contrast, WS had the highest Fe_2O_3 and MnO contents and a CEC similar to that of KR, but its Co K_d was 25–49% of that of KR at 100–200 mg L^{-1}. Co retention therefore corresponded more closely to accessible surface and organic matter than to exchange capacity or bulk oxide composition, although SSA and OM content cannot be separated with the present soils.

For Sr, the soil ranking WS > SE > KR > DJ agreed most closely with those of CEC and the <75 μm fraction ($\rho = 0.8$), and less with those of SSA and OM content ($\rho = 0.4$). The clearest contrast was between WS and DJ, which had the highest and lowest CEC (21.88 and 4.45 cmol(+) kg^{-1}) and the largest and smallest <75 μm fractions (32.46% and 12.78%), and whose mean Sr K_d values differed by a factor of 2.1 (89.6 vs. 42.3 mL g^{-1}). This pattern is consistent with cation exchange being the main mechanism of Sr retention [8, 10] and with the previous finding that Sr K_d is described with lower variability by a cofactor based on the ratio of CEC to the Ca and Mg concentrations in the soil solution than by soil texture groups [9]. The departure from complete rank agreement arose from SE, which retained Sr more strongly than KR at three of the four concentrations despite its lower CEC, indicating that factors other than bulk exchange capacity, such as competing cations in the soil solution, also affected Sr retention.

Cs showed the weakest soil dependence among the three ions. KR had the highest Cs K_d at every concentration (112.54–124.09 mL g^{-1}), 1.02–1.31 times that of the next-highest soil. The ranking of the other soils, however, changed with concentration: at 1 and 5 mg L^{-1}, the ranking was KR > WS > DJ > SE, which matched the rankings of SSA and OM content except for the order of DJ and SE, whereas at 10 and 30 mg L^{-1}, WS fell to the lowest position (KR > DJ > SE > WS). The rank agreement between the soil-mean Cs K_d and SSA (ρ = 0.8) therefore reflects the consistently high K_d of KR and the low-concentration data for WS rather than a consistent dependence on surface area. The decrease in the Cs K_d of WS with increasing concentration is consistent with multisite behavior, in which highly selective frayed-edge sites dominate at low loadings and less selective exchange sites become increasingly important at higher concentrations [6, 7]. Because such selective sites account for only a small part of the total exchange capacity, typically less than 1–2% of the CEC [4, 6], Cs retention is governed by the abundance of these sites rather than by bulk CEC or SSA [3], as illustrated by WS and KR, which had similar CEC values (21.88 and 20.29 cmol(+) kg^{-1}) but differed in Cs K_d by a factor of 1.7 at 30 mg L^{-1}. The relatively constant Cs K_d of DJ, which had the lowest SSA and CEC, is discussed together with its large residual Cs fraction in Section 3.6.

Overall, the soil properties associated with K_d were ion-specific. Co K_d followed SSA and OM content, Sr K_d followed CEC and the fine-particle fraction, and Cs K_d depended on concentration in a soil-specific manner that was not captured by bulk properties. These associations partly agree with a recent study of soils and rocks, in which the exchangeable fractions of Sr, Cs, and Co were related to CEC, potassium feldspar and mica-like clay minerals, and OM content, respectively [29]; the association for Sr is consistent with those

findings and that for Cs is compatible with them, whereas Co retention in the present soils corresponded to SSA as well as to OM content. However, SSA was positively correlated with CEC (r = 0.93) and OM content (r = 0.81), and CEC with the <75 μm fraction (r = 0.95), because KR and WS had higher values of all four properties than SE and DJ (Table S1 and S2). Combined with the small number of soils, this covariation means that the rank agreements identify the most consistent indicator for each ion rather than establishing causal relationships.

3.4. Desorption results

The release of Cs, Sr, and Co from the loaded soils was compared between deionized water and 0.1 M HNO_3 after 24 h of contact (Section 2.3). For all four soils, desorption of Cs, Sr, and Co was substantially greater with 0.1 M HNO_3 than with water (Fig. 3; Table S5). Water released 0.194–0.244 mg g^{-1} of Cs, 0.067–0.116 mg g^{-1} of Sr, and 0.011–0.047 mg g^{-1} of Co, corresponding to desorption percentages of 6.04–8.56%, 5.41–11.86%, and 0.85–5.23%, respectively. In contrast, 0.1 M HNO_3 released 1.003–1.585 mg g^{-1} of Cs, 0.704–1.020 mg g^{-1} of Sr, 0.538–0.781 mg g^{-1} of Co, corresponding to desorption percentages of 42.45–51.46%, 63.77–84.58%, and 53.90–61.15%, respectively. The mean desorption percentages across the four soils increased from 6.94% to 45.13% for Cs, from 7.49% to 75.01% for Sr, and from 2.47% to 58.59% for Co when water was replaced by acid solution. The ranking of the ions also differed between the two desorbents. With water, the mean desorption percentages followed the order Sr (7.49%) > Cs (6.94%) > Co (2.47%), whereas with 0.1 M HNO_3, the fractional release followed the order Sr > Co > Cs for every soil. Thus, Co, which was the least mobile ion in water, was released more extensively than

Cs under acid treatment, indicating that the resistance of a ion to release by water does not predict its resistance to release by acid.

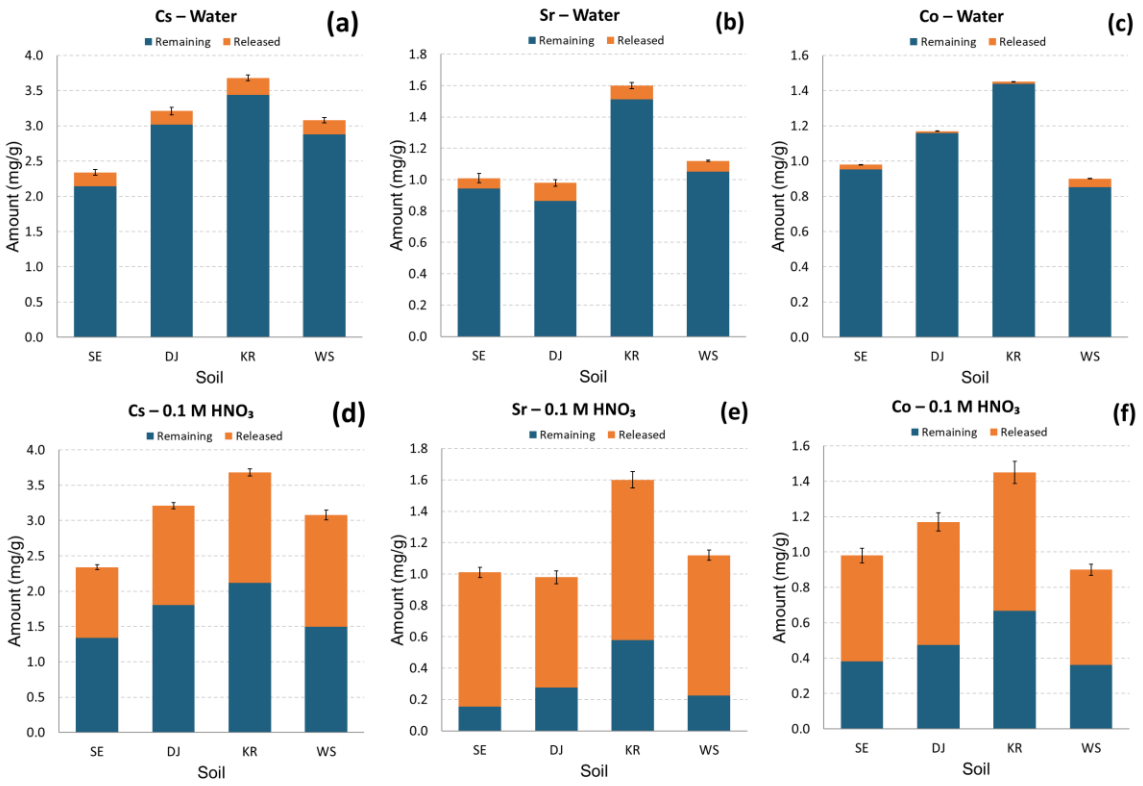


Fig. 3 Desorption of Cs, Sr, and Co from the four soils using (a–c) deionized water and (d–f) 0.1 M HNO_3 after 24 h at room temperature. Each bar shows the retained inventory (q_0) divided into the released and remaining amounts (mg g^{-1}). The corresponding desorption percentages are listed in Table S5. The same loaded soils, and hence the same q_0, were used for both treatments. Error bars represent the standard deviation of the released amounts in triplicate measurements

For Cs, acid desorption was highest for WS (51.46%), with SE, DJ, and KR showing similar values (42.86%, 43.74%, and 42.45%, respectively). Thus, 48.54–57.55% of the retained Cs inventory was not released during the 24 h treatment with 0.1 M HNO_3. This incomplete release is consistent with the retention of part of the Cs at frayed-edge and interlayer sites of 2:1 clay minerals, from which Cs is not readily displaced by ion exchange [4, 21, 38]. Slow desorption kinetics may also contribute, because Cs desorption from illite

can continue over periods much longer than 24 h [5]; the fraction not released within 24 h must not be equated with a permanently non-desorbable fraction.

In all of the soil samples treated with 0.1 M HNO_3, Sr showed the highest desorption percentage among the three elements, with the desorption percentage decreasing in the order SE (84.58%) > WS (79.84%) > DJ (71.86%) > KR (63.77%). The observation of low levels of Sr desorption in water but high levels of desorption in acid is consistent with the retention of Sr mainly as hydrated, outer-sphere complexes on exchange sites. Unlike Cs, which forms inner-sphere complexes at frayed-edge and interlayer sites of micaceous minerals [4, 21], outer-sphere Sr complexes are readily affected by changes in pH and ionic strength [10, 38]. Hence, the protons in 0.1 M HNO_3 displaced a larger proportion of Sr than of Cs from the exchange sites. The behavior of Co, which is controlled by different retention mechanisms, is discussed below.

Co also showed pronounced desorption in acid solution. Although KR released the largest absolute amount of Co (0.781 mg g^{-1}), it had the lowest desorption percentage (53.90%) because its retained Co inventory was larger. The distinct behavior of absolute amount and desorption percentage shows that released mass and fractional release should be considered together when comparing treatment responses among soils. The desorption percentages of Co for the four soils subjected to acid treatment varied over only a narrow range (53.90–61.15%). Acid-enhanced release may involve proton competition, surface protonation, and dissolution of susceptible host phases. Because Co extraction in acid solution depends on soil buffering and the resulting solution pH [12], differences in the final extraction pH among the four soils may have contributed to the observed soil-dependent release. The present measurements cannot separate ion displacement from

dissolution-mediated release; complementary evidence, such as dissolved host-element concentrations or characterization of the treated solids, would be required to distinguish between these mechanisms.

Overall, 0.1 M HNO_3 mobilized substantial proportions of all three elements, although Cs consistently showed the highest resistance to acid treatment. The present findings are consistent with the previous observation that soil washing removes Sr and Co more readily than Cs, because Cs has a high affinity for soil components [2].

3.5. Soil dependence of release and comparison with soil properties

In contrast to K_d, the soil dependence of release depended strongly on the desorbent (Table 2). In water, the CV of the desorption percentage among the four soils was 16.0% for Cs, 39.4% for Sr, and 83.9% for Co, whereas in 0.1 M HNO_3 it was only 9.4%, 12.2%, and 5.5%, respectively. Thus, the soil type affected release mainly under mild conditions, whereas under acidic conditions release was determined largely by the ion, and the order Sr > Co > Cs was the same in every soil (Section 3.4).

In water, the largest soil differences were observed for Co, for which the desorption percentage ranged from 0.85% in KR to 5.23% in WS, and the mean ± SD ranges of all soil pairs except DJ and KR were distinct. Co release in water showed no consistent rank agreement with SSA, CEC, OM content, or the <75 μm fraction ($|\rho| \leq 0.4$); these soil differences are examined using the fractionation data in Section 3.6. Sr release in water was highest in DJ (11.9 ± 2.1%), and the soil ranking (DJ > SE > WS > KR) was exactly the reverse of the rankings of SSA and OM content ($\rho = -1.0$) and nearly the reverse of

that of CEC ($\rho = -0.8$). This is consistent with weaker retention of Sr in the soil with the fewest surface and exchange sites, as also indicated by the lowest Sr K_d of DJ (Section 3.3). In contrast, Cs release in water varied little among the soils (6.04–8.56%), and the mean ± SD ranges of all four soils overlapped (Fig. 3; Table S5).

In 0.1 M HNO_3, the soil differences were small but not absent. For Cs, WS released a larger proportion (51.5 ± 2.2%) than the other three soils (42.45–43.74%), whose ranges overlapped. For Sr, SE and WS (84.58% and 79.84%) released larger proportions than DJ (71.86%), which in turn released more than KR (63.77%). For Co, the ranges of all four soils overlapped (53.90–61.15%). None of these rankings agreed consistently with those of SSA, CEC, OM content, or the <75 μm fraction ($|\rho| \leq 0.4$). KR, which had the largest retained inventories of all three ions (3.68, 1.60, and 1.45 mg g^{-1} for Cs, Sr, and Co, respectively), showed the lowest desorption percentages of all three ions in acid but released the largest absolute amounts of Sr and Co. Thus, a larger retained inventory was accompanied by a larger proportion of ions that resisted acid treatment (Fig. 3).

Overall, release in water depended on both the ion and the soil, whereas release in 0.1 M HNO_3 was controlled mainly by the ion. This dominance of ion identity under acidic conditions is consistent with the observation that radionuclide characteristics are a major factor in determining the degree to which soils at nuclear facility sites can be decontaminated [2]. This contrast between retention and release extends the finding of Gil-García et al. [22], who reported for 30 Spanish soils that radiostrontium extraction yields were systematically higher than those of radiocesium and that sorption reversibility could not be predicted from sorption data. In the present soils, the soil sensitivity of retention (CV of Kd, 17–74%) largely disappeared under acid treatment (CV of release, 5–12%),

indicating that the soil properties used to estimate retention cannot be used directly to predict acid-washing performance. Except for Sr in water, none of the bulk soil properties showed a consistent rank agreement with release, and the operational distribution of the retained ions is therefore examined in Section 3.6.

3.6. Sequential extraction

Sections 3.3 and 3.5 compare the retention and release of the ions with bulk soil properties, but they do not indicate how the ions are held within the soils. This section uses the sequential extraction results (Fig. 4; Table S4) to explain the differences in release among the ions and soils. The recoveries of the six fractions relative to the retained inventories were 86–114% (Table S4), and the fractions are expressed as percentages of the total recovered amount. Note that the sequential extraction was performed on soils loaded at 3 mM, which corresponds to higher concentrations than those used in the K_d experiments for Cs and Sr (1–30 mg L^{-1}) but lies within the range used for Co (3 mM ≈ 177 mg L^{-1}); the fractionation at lower loadings may therefore differ. The fractions may also change with aging: in podzolic soils, the exchangeable fraction of radiostrontium decreased by 20–25%, and that of radiocesium decreased two- to threefold after nine months of drying–wetting cycles [28], and the exchangeable fractions of stable Sr, Cs, and Co in field soils and rocks, although determined by a different approach, were mostly well below 20% [29]. The present fractions therefore represent freshly loaded conditions and are likely to overestimate the mobile pools of aged contamination.

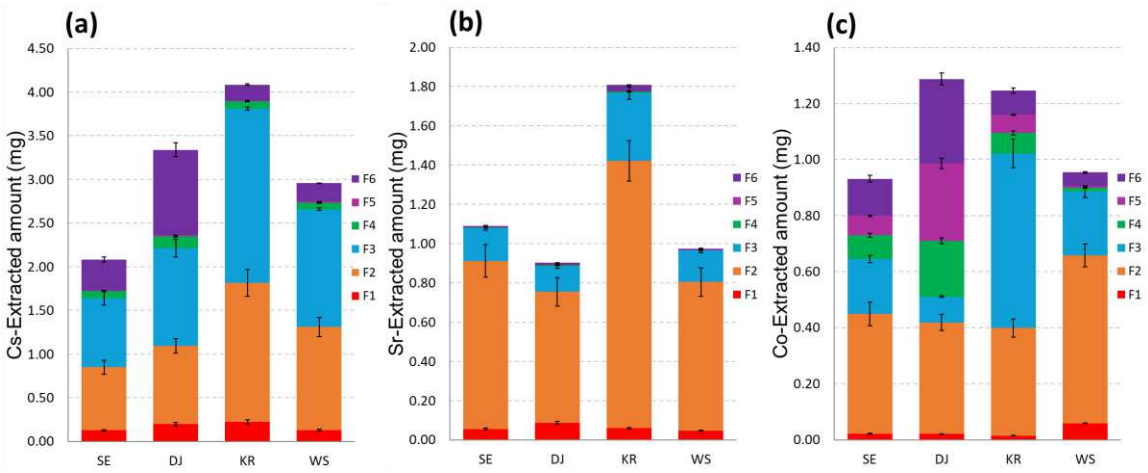


Fig. 4 Operational distributions of Cs, Sr, and Co among the six sequential extraction fractions in SE, DJ, WS, and KR soils. Amounts are expressed per unit soil mass (mg g^{-1}), and error bars indicate standard deviations of triplicate measurements. The corresponding percentages of the summed amounts recovered in F1–F6 are given in Table S4. F1, water-soluble; F2, exchangeable; F3, organic-associated; F4, carbonate-associated; F5, oxyhydroxide-associated; F6, residual

The fractionation differed systematically among the ions. Averaged over the four soils, the water-soluble and exchangeable fractions (F1 + F2) accounted for 82.1% of recovered Sr, 45.5% of Co, and 40.5% of Cs, whereas the residual fraction (F6) followed the reverse order: 1.2% of Sr, 12.3% of Co, and 14.7% of Cs. The mean acid-desorption percentages followed the same order as the mobile fractions: Sr (75.01%) > Co (58.59%) > Cs (45.13%; Section 3.4). The organic-associated fraction (F3) was also large for Cs (33.5–48.7%) and Sr (14.4–19.0%), despite neither element having a strong affinity for OM. Because the NaOCl extractant used to obtain F3 supplies a high Na^+ concentration at 96 °C, part of F3 for these elements probably reflects displacement by Na^+ exchange rather than organic association, which underlines the operational nature of the fractions. In addition, because Mg^{2+} is a weak competitor for Cs, the $MgCl_2$ step (F2) probably underestimated the exchangeable Cs, so that part of this pool was recovered only in the F3 step.

Fig. 5 compares the desorption percentages with the operationally mobile fractions for each ion–soil combination. Because the water treatment and F1 both use deionized water, and because dilute acid acts largely on the exchangeable pool, an overall correspondence between release and these fractions is expected. Across the 12 ion–soil combinations, the desorption percentage in water was correlated with the F1 proportion ($r = 0.93$, $\rho = 0.73$) and that in 0.1 M HNO_3 with the F1 + F2 proportion ($r = 0.82$, $\rho = 0.76$; all $p < 0.01$), although these correlations mainly reflect differences among the ions. The ions differed, however, in whether their release was confined to these pools or extended beyond them, and these differences define the desorption characteristics of each ion. Previous evaluations of sequential extraction compared the operational fractions mainly with soil–plant transfer or relative mobility sequences [32, 33], or fractionated Cs and Sr only or a single soil [24, 25, 28]. In the present study, release measured independently on the same loaded soils provided a direct benchmark for the operational fractions of three elements in four soils: a ratio of acid release to the F1 + F2 proportion close to 1 indicates that these fractions accounted for the acid-mobilizable pool, whereas a ratio above 1 indicates that acid also mobilized Co or Cs beyond these fractions. As shown below, the same extraction scheme performed differently for Sr, Co, and Cs.

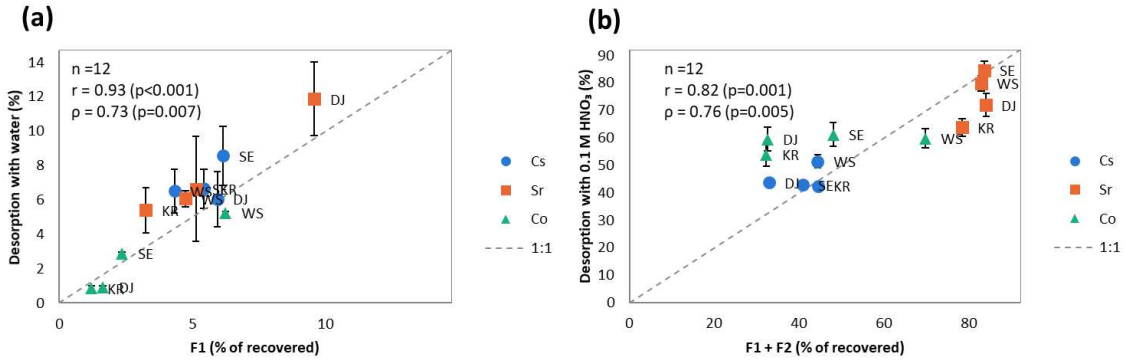


Fig. 5 Relationship between the sequential extraction fractions and desorption for the 12 ion–soil combinations: (a) proportion of the water-soluble fraction (F1) versus the desorption percentage in deionized water, and (b) proportion of the water-soluble and exchangeable fractions (F1 + F2) versus the desorption percentage in 0.1 M HNO_3. Fractions are expressed as percentages of the total amount recovered in F1–F6. Symbols denote ions, labels identify soils, and error bars represent the standard deviation of triplicate desorption measurements. The dashed line indicates a 1:1 relationship; points above the line indicate release exceeding the corresponding fraction. r, Pearson's correlation coefficient; ρ, Spearman's rank correlation coefficient

Sr was held predominantly in the exchangeable fraction (F2 = 74.3–78.3%), and its fractionation was nearly identical in the four soils. Its acid release (63.77–84.58%) was close to or below the F1 + F2 proportion (ratio of 0.81–1.01), indicating that acid removed mainly exchangeable Sr. The predominance of exchangeable Sr agrees with sequential extraction of artificially contaminated soils around a research reactor, in which Sr was recovered mainly in the water-soluble and exchangeable fractions [24], and with a US coastal soil, in which 75% of the Sr added at a high loading was exchangeable [25]; the present ratios further show that this pool accounted quantitatively for the acid release of Sr. Sr release was therefore governed by ion exchange. In water, the soil ranking of release (DJ > SE > WS > KR) matched that of the F1 proportion exactly and was the reverse of the rankings of SSA and OM content (Section 3.5). In acid, release was lowest from KR and DJ (ratios of 0.81 and 0.86), in which part of the exchangeable Sr was not displaced within 24 h. Because only 0.5–2.3% of the recovered Sr was in the residual fraction, the Sr remaining after acid treatment (15.4–36.2%) is attributed mainly to incomplete exchange rather than to a strongly bound pool.

Co showed different behavior. It was the least released by water (0.85–5.23%), consistent with its small water-soluble fraction (1.2–6.2%). The soil ranking of water release (WS > SE > DJ > KR) matched that of the F1 proportion exactly, and WS, which

had the largest F1 (6.24%) and F2 (63.32%) proportions, released the most. In acid, however, the release of Co exceeded the F1 + F2 proportion in SE, DJ, and KR by factors of 1.28–1.83, suggesting that acid mobilized Co beyond the amount represented by the initial water-soluble and exchangeable operational fractions. This comparison does not establish which additional fractions were depleted. This excess was largest in DJ, in which the carbonate- and oxyhydroxide-associated fractions (F4 + F5) accounted for 36.8% of the recovered Co and acid release (59.55%) exceeded the F1 + F2 proportion (32.46%) by 27 percentage points, and in KR, in which the organic-associated fraction (F3) accounted for 50.20% and the excess was 22 percentage points. Because the acetate step also extracts ions specifically sorbed on clays, organic matter, and Fe–Mn oxides [12], the F4 fraction in DJ is better regarded as a weakly bound, specifically sorbed pool than as strictly carbonate-bound Co. Co was therefore strongly retained against water but readily released by acid. A contribution from additional pools is plausible, although not directly verified; this may help explain why the acid-desorption percentage varied little (53.90–61.15%) despite large differences in the F1 + F2 proportion (32.2–69.6%). The acid release of Co (53.90–61.15%) was lower than the approximately 65–100% recovered with 0.1 M HCl from eight soils by Jović et al. [12], who also found that Co desorption by dilute acid depended on soil type and was lowest in calcareous soils. The large organic-associated fraction in KR and the carbonate- and oxyhydroxide-associated fractions in DJ may account for part of this difference.

Cs showed a third pattern. Its water release varied little among the soils (6.04–8.56%), and its soil ranking did not follow that of the F1 proportion ($\rho = 0.4$). Its acid release (42.45–51.46%) was the lowest of the three ions and was close to or moderately above the

F1 + F2 proportion (ratio of 0.96–1.33), so that about half of the retained Cs remained after acid treatment in every soil. Thus, the Cs extracted in F3, which probably includes Cs displaced by the high Na^+ concentration in the NaOCl step, and in F6 (33.5–48.7% and 4.7–29.4% of the recovered Cs, respectively) was largely not mobilized by 0.1 M HNO_3. This acid-resistant pool is consistent with Cs held at frayed-edge and interlayer sites of micaceous minerals [4, 21], from which Cs is displaced by high concentrations of competing cations but not readily by protons. Cs is therefore characterized by a low soil dependence of release and a large acid-resistant fraction, which limits the effectiveness of acid washing for Cs-contaminated soils. This behavior contrasts with that in a US coastal soil, in which Cs showed the highest soluble and exchangeable proportion among the three ions [25]; in the present soils, all of which contained micaceous minerals (Section 3.1), Cs had the smallest F1 + F2 proportion (32.8–44.4%). The residual Cs fraction (4.7–29.4%) was also much smaller than in Fukushima soils, in which radioactive Cs was found predominantly in the strong-acid extract and the residue [27]. Because the present soils were freshly loaded at high concentrations, the acid-resistant fraction of Cs in aged field contamination is likely to be larger than the approximately 50% observed here.

The fractionation also helps to interpret the soil dependence of K_d. Co K_d corresponded most closely to SSA and OM content (Section 3.3). KR, which had the largest SSA and OM content and the highest Co K_d at every concentration, also had the largest organic-associated Co fraction (F3 = 50.20%). This suggests that the high Co retention of KR involved organic and organomineral surfaces. Although NaOCl can also dissolve carbonates out of sequence [35], meaning that a portion of F3 may include carbonate-associated Co, the high OM content of KR supports a predominantly organic association.

Sr K_d corresponded most closely to CEC and the fine-particle fraction. The Sr fractionation was almost identical in the four soils (F2 = 74.3–78.3%); hence, the twofold difference in Sr K_d between DJ (mean 42.3 mL g^{-1}) and WS (89.6 mL g^{-1}) did not arise from a difference in the mode of retention but more likely from differences in the number of accessible exchange sites. This interpretation is consistent with the positive correlation between the exchangeable Sr fraction and CEC observed for diverse soil and rock media [29].

For Cs, DJ, which had the lowest SSA and CEC, had the highest residual Cs fraction (F6 = 29.36%), and its Cs K_d decreased only slightly with increasing concentration (from 95.00 to 86.00 mL g^{-1}). This pattern is consistent with a contribution from selective sites on micaceous minerals that are not quantified by bulk properties [6, 7] and with the highest K2O content of DJ among the four soils (Table S3). In the absence of orthoclase reflections, a micaceous contribution is plausible, but bulk K2O cannot uniquely identify its mineral host. Because the abundance of Cs-selective sites was not quantified, this interpretation remains qualitative. Similarly, in Fukushima soils, Cs remaining in the extraction residue was concentrated in the silt and clay fractions and associated with micaceous minerals [27]. However, the acid-desorption percentage of Cs was similar in soils with very different residual fractions (4.69–29.36%), and the concentration-dependent decrease in Cs K_d cannot be resolved by fractionation at a single loading. Describing these features would require site-specific information, such as the radiocesium interception potential and the solution chemistry during extraction.

Overall, sequential extraction identified distinct desorption characteristics for the three ions. Sr release was confined to the exchangeable pool; Co was strongly retained against

water, but its acid release exceeded the water-soluble and exchangeable pools in three of the four soils; and Cs release was close to or moderately above the water-soluble and exchangeable pools, leaving about half of the retained Cs in the organic-associated and residual fractions. The fractionation also linked the soil dependence of K_d to organic-associated retention for Co and to differences in exchange capacity within a nearly constant mode of retention for Sr. These element-specific agreements and departures between the operational fractions and the measured release, obtained for the same loaded soils, could not have been identified from sequential extraction or desorption experiments alone.

4. Conclusions

This study combined soil characterization, batch sorption and desorption experiments, and sequential extraction to examine the retention and release of Cs, Sr, and Co in soils collected near four Korean nuclear facilities. Unlike compilations of Kd obtained under different experimental conditions and sequential extraction studies evaluated against plant transfer or mobility sequences, the present study made two comparisons for the same soils under a single protocol: the soil dependence of retention versus that of release, and the operational fractions versus independently measured release. K_d depended on both the soil and the initial metal ion concentration, and the soil dependence differed markedly among the metal ions, with CVs of the soil-mean K_d of 17% for Cs, 29% for Sr, and 74% for Co. The soil ranking of Co K_d agreed with those of SSA and OM content, and that of Sr K_d with those of CEC and the fine-particle fraction, whereas Cs K_d remained highest in KR at every concentration but decreased sharply with concentration in WS, consistent with, but not direct proof of, a concentration-dependent contribution of selective Cs sites in WS.

Compared to treating the soils with water, treatment with 0.1 M HNO_3 led to substantially greater release of all three metal ions, and the fractional release under acid treatment decreased in the order Sr > Co > Cs for every soil. Release in water differed among the soils, particularly for Co and Sr, whereas release in acid varied little among the soils (CV of 5–12%). Sequential extraction identified distinct desorption characteristics: Sr acid release was broadly consistent with its predominantly exchangeable fraction; Co was strongly retained against water but showed acid release exceeding F1 + F2 in three soils; and about half of the retained Cs remained after 24 h of acid treatment, without direct identification of the post-treatment solid-phase distribution. Thus, the soil properties that controlled retention did not control acid release, and sequential extraction accounted for the acid release of Sr, underestimated that of Co, and assigned a large fraction of Cs to an operational step (F3) that was not mobilized by acid.

The present results show that the soil properties relevant to retention and release are metal ion-specific. As a result, no single bulk property can describe the behavior of Cs, Sr, and Co together. When assessing remediation options for nuclear facility sites, SSA and OM content are useful indicators of Co retention and CEC and the fine-particle fraction of Sr retention, whereas Cs requires additional mineralogical information such as the abundance of illite and the radiocesium interception potential. For washing-based remediation, the tested acid treatment released the largest fraction of Sr, a substantial fraction of Co, and the smallest fraction of Cs. These laboratory removal fractions do not by themselves establish field-scale washing performance. Because aging decreases the exchangeable fractions of radiocesium and radiostrontium [28], the acid-washing efficiencies obtained for freshly loaded soils are likely to be upper limits for aged

contamination. Because only four soils were examined, these associations should be tested using soils from additional sites. Furthermore, because the present work used stable elements at concentrations far above those of ^{137}Cs, ^{90}Sr, and ^{60}Co in contaminated soils, the Cs, Sr, and Co probably saturated the high-affinity sites on soil particles, particularly in the case of Cs binding to frayed-edge sites, and the Kd values reported here cannot be applied directly to trace-level radionuclides. Furthermore, deionized water does not reproduce site-specific groundwater or saline conditions; competing major ions, soil buffering, and contact time may modify both retention and release. Sequential extraction fractions are operational and do not directly identify the phases depleted by acid washing.

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Competing interests

The authors declare no competing interests.

Data availability

The data supporting the findings of this study are available from the corresponding author upon reasonable request.

Author contributions

In-Ho Yoon: Writing – original draft, Writing – review & editing, Supervision, Visualization, Methodology. Sunyoung Park – Investigation. Haein Kim - Conceptualization, and Ilgook Kim - Formal analysis

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Supplementary information

The online version contains supplementary material (Tables S1–S5 and Fig. S1).

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