

Binding, fractionation, and distribution of Cs, Co, and Sr in a US coastal soil under saturated and field capacity moisture regimes

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Abstract

Purpose The concerns of the public on safe handling of nuclear energy power facilities have increased due to the recent nuclear plant accidents in Japan and others. Cesium, cobalt, and strontium are a few of the major radionuclides released from nuclear power plant accidents. The objectives of this study are to investigate binding, distribution, fractionation, and transformation of cesium (Cs), cobalt (Co), and strontium (Sr) in a US coastal soil under saturated paste (SP) and field capacity (FC) moisture regimes.

Materials and methods There are four major nuclear power plants in the coast region around the northern Gulf of Mexico where coastal soil often undergoes soil moisture change. A coastal soil was taken from the middle region of these major nuclear power plants and spiked with different concentrations of cesium, cobalt, and strontium salts. The sequential selective dissolution technique was used to investigate the transformation and fractionations of these metals in the coastal soils affected by moisture regime, a key factor in the coastal environment.

Results and discussion The adsorption kinetics showed that both Co and Sr reached the adsorption plateau even after 5 h of adsorption, indicating a fast initial adsorption process in the coastal soil. Cesium, cobalt, and strontium were dominantly presented in the soluble and exchangeable form (EXC) (Cs > Co and Sr), which linearly increased with the addition levels,

possessing the high bioavailability, mobility, and ecotoxicity. Saturated regime significantly reduced the soluble and exchangeable form compared to field capacity moisture regime. **Conclusions** The current study provides the fundamental understanding for designing the cost-effective remediation technology to remediate these metals in coastal soil by targeting on the soluble and exchangeable forms and better prepare the USA for future potentially nuclear power plant accidents.

Keywords Cesium · Coast soil · Cobalt · Fractionation · Redistribution · Strontium

1 Introduction

The most serious pollutants related to nuclear power plant accidents are cesium (Cs), cobalt (Co), strontium (Sr), iodine (I), and some actinides. ¹³⁷Cs is a radioactive pollutant of great concern with a half life of 30.2 years, high bioavailability, and chemical and biological similarity with potassium, an essential element in living organisms. Cs is uniformly distributed among living organisms. Sr behaves similarly with Ca in terrestrial ecosystems and animals and is mostly deposited in the bone systems. Thus, Cs and Sr can be rapidly integrated into the biological cycles and accumulated in various organisms (Gommers et al. 2005). The Chernobyl accident released a huge amount of ¹³⁷Cs, ⁹⁰Sr, ²³⁸Pu, and ²⁴¹Am into surrounding soils (Belarus, Ukraine, and Russia) and even spread through the entire Northern Hemisphere (Gommers et al. 2005; Kashparov et al. 2005). Similarly, radionuclides (¹³⁴Cs, ¹³⁷Cs, ⁶⁰Co, and ¹³¹I) were released during the Fukushima Daiichi nuclear power plant accident in 2011. Radionuclides were dispersed up to 200 km south of the plant in soils and were detected in vegetable, milk, meat, and seawater (Yoshida and Kanda 2012; Yoshida and Takahashi

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2012). ^{137}Cs has heavily contaminated the soils in large areas of eastern and northeastern Japan (Yasunari et al. 2011). The soils around Fukushima and neighboring prefectures have been extensively contaminated with depositions of ^{137}Cs in the Japanese Islands and the surrounding ocean (Yasunari et al. 2011). On the other hand, radionuclides have been reported to be present and be transported in colloids of groundwater of nuclear ground detonation sites such as the Nevada Test Site (Kerstin et al. 1999).

Cesium is primarily found in acidic igneous rock and in argillaceous (clay-containing) sediment with a concentration range of 2 to 10 mg/kg (Reimann and de Caritat 1998). Cesium is relatively active in soils and is easily taken up by plants (Su et al. 2007). When weathering takes place, cesium is strongly absorbed in soils. Hinton et al. (2006) and Nakao et al. (2003) found that micaceous minerals have a high affinity for binding cesium. The average range of cesium in worldwide soils is from 5 to 10 mg/kg (Reimann and de Caritat 1998). Soils in the USA usually contain a range of 0.41 to 5.07 mg/kg of cesium (Govindaraju 1994). The radioactive isotopes ^{134}Cs and ^{137}Cs are the result of nuclear fission in nuclear power plants and nuclear weapon fallout. ^{137}Cs is of great concern because it can be introduced as a by-product of atomic energy production, nuclear weapons testing, the mining and processing of pollucite ore, coal burning, and municipal waste incinerations. The geochemical characteristics of ^{137}Cs are similar to those of the stable Cs. It is strongly absorbed by clay fractions, clay minerals, and organic matter which cause it to move slowly in soil (Tsukada et al. 2008). Fe and Mn sesquioxides also retard the migration of cesium in soil (Arapis et al. 1997; Grin et al. 1999). In alluvial soils, silty soils, the majority of cesium was usually bound to amorphous Fe oxides or organic matter (Kaplan et al. 2005). Roughly a decade following the Chernobyl accident, of the concentration initially measured, about 90 % of ^{137}Cs remained in the top soil layer at the site (Kagan and Kadatsky 1996). The work of Mondini et al. (1995) showed the correlation between the distribution of cesium to the organic matter and cation exchange capacity (CEC). Therefore, cesium was highly concentrated in the top organic soil layer.

The source of cobalt pollution is often from nonferrous metal smelters, coal, and other fuel combustions. Cobalt has siderophilic, iron-loving properties. It is therefore more likely to form minerals with elements such as sulfur, arsenic, and selenium. The geochemical cycle of cobalt is similar to those of iron and manganese and is likely to be associated with many minerals of these metals. When cobalt is in soil, its behavior is reliant on the Mn oxide phase formation (Han 2007). The work of Tani et al. (2003) showed that cobalt has a high capacity to be absorbed by Mn oxides. Cobalt reacts easily with iron and manganese geochemically and biochemically. Han et al. (2002) reported Co concentrations are strongly correlated with contents of Mn oxides and Co

transformation among solid-phase components followed pathways of the Mn oxide (Han et al. 2002; Han 2007).

Strontium is a common element in the Earth's crust, and its concentration ranges from 260 to 370 mg/kg (Reimann and de Caritat 1998). In soils, strontium ranges from 130 to 240 mg/kg (Bohn et al. 1979). Like cesium, it is strongly absorbed by clay materials. Strontium behaves similarly to calcium geochemically and biochemically (Su et al. 2007). It has a lithophilic affinity and is associated with calcium as well as magnesium (Mason 1979). The main sources of strontium pollution are coal combustions, and sulfur mining (Kabata-Pendias and Mukherjee 2007). ^{89}Sr and ^{90}Sr are the results of several nuclear processes (Casacuberta et al. 2013). These radionuclides are the most biologically hazardous to the environment. Radioactive strontium biogeochemically behaves like the stable strontium. ^{90}Sr is also predominantly absorbed by alluvial and organic-rich soils. The speciation of radioactive strontium in various soils shows that easily soluble fractions make up to 90 % of the total content and are likely to occur as organic fractions in the soil solution (Agapkina et al. 1995; Korobova et al. 1998).

Wasserman et al. (2008) reported distribution of spiked ^{137}Cs and ^{60}Co in Brazilian tropical soils among solid-phase components using sequential extraction procedure under field capacity moisture (Wasserman et al. 2008, 2005). They divided both Cs and Co into acidic phase, easily reducible phase, oxidizable phase, alkaline phase, and resistant phase. They found high Cs was present in the alkaline and oxidizable fraction in the three types of soils, while Co distributed depending upon the types of soil. Histosol which contained a high organic matter (8.6 % C) had a high Co in the oxidizable fraction while Ferralsol was high in the acidic and easily reducible fractions and it was dominated in the acidic fraction in Nitisol.

The soil moisture plays an important role in controlling accumulation of soil organic matter and dynamics of reducible oxides (Fe/Mn oxides) in soils (Han and Banin 1996). Han and Banin (1997, 1999, 2000) and Han et al. (2001) reported the moisture strongly affected the distribution and fractionation of trace elements and heavy metals including Cu, Cd, Ni, Zn, Pb, and Cr in arid soils. Solid-phase distribution of these elements finally controlled their bioavailability and ecotoxicity in the ecosystem (Han and Banin 2000). However, the effects of moisture on the binding, fractionation, and distribution of Cs, Sr, and Co in the coastal soils where most of nuclear power plants are located are not well understood.

With potential "high" risks from nuclear power plant accidents, the safety of nuclear energy is an essential issue for expansion of its use. It is important to prepare the society with better understanding of their environmental fates, interaction with major minerals, and potential into food chain especially in the coastal ecosystems where the soil moisture frequently

changes. Therefore, environmental fates and fingerprints of these pollutants in coastal ecosystems are important topics for risk assessment, nuclear detonation detection, nuclear forensics, anti-terrorism, and better prevention and remediation of possible contaminated sites. The specific research objectives of this study are to investigate binding, distribution, fractionation, and transformation of Cs, Co, and Sr in US coastal soil under various moisture regimes. The ultimate goal of this project is to provide the scientific understanding for further development of the long-term remediation strategy for potential pollution from nuclear power plant accidents in the coasts.

2 Materials and methods

2.1 Location of sampling area

Most of the nuclear power plants are located in the US coastal regions and regions near big rivers and lakes. Around the northern Gulf of Mexico, there are four major nuclear power plants (Joseph M. Farley, Columbia, AL; Waterford Steam Electric Station, Killona, LA; Riverbend Station, St. Francisville LA; Grand Gulf Nuclear Station, Port Gibson, MS). Therefore, we chose a coastal location for soil sampling from the middle region among these four major nuclear power plants. A coastal soil was collected from Moss Point, MS. Moss Point is located in the Grand Bay National Estuarine Research Reserve (NERR) in the northern Gulf of Mexico. This coastal soil is a typical representative soil type of coastal regions in the northern Gulf of Mexico.

2.2 Sample preparation, characterization, and incubation experiment

Soil was air dried and screened through a 1-mm sieve. About 1 kg soil was spiked with different concentrations of cesium, cobalt, and strontium salts. The concentrations were 0, 10, 50, and 200 mg/kg of each metal. The purpose of this study is to simulate the real contaminated fields with multi-elements. For the spiking metals, the appropriate amounts of CsNO_3 , $\text{Co}(\text{NO}_3)_2$, and $\text{Sr}(\text{NO}_3)_2$ were ground and gradually mixed into the soil using a mortar. Each treatment was replicated. The kinetic change among various solid-phase components over the course of 2 months was observed. Han and Banin (1996) reported that the 2-month incubation period provides the soil enough time to reach a quasi-equilibrium of redox reactions. The redox potential and the pH change for the spiked soils were measured with redox electrode and pH combination electrode for 2 months. A subsample was taken for sequential selective dissolution extractions to determine the metal fractionation and solid-phase binding of metals (Table 1). At the same time, subsamples were also sampled

Table 1 Selected soil physicochemical properties

Total element		
Cs	mg/kg	0.53
Co	mg/kg	0.25
Sr	mg/kg	14.17
pH		4.88
Organic matter	%	1.40±0.068
Iron oxides	%	0.31
Manganese oxides	%	0.00015
Total organic nitrogen	%	0.041+0.004
Texture		Silt loam
Clay	%	5
Silt	%	78
Sand	%	17

for determining the soil moisture. Two moisture regimes were employed: saturated paste regime (SP) and field capacity (FC) moisture regime. Saturated paste moisture simulates the soil moisture situation immediately after a storm or rain while field capacity mimics the most moisture scenario of fields a few days after the rain (Han and Banin 1996, 1997, 1999). Soil moisture was kept constant over 2 months.

Soil was characterized according to standard methods. The determination of total organic carbon and nitrogen was performed with a Shimadzu TOC analyzer. Soil texture and particle size analyses were conducted using the hydrometer method (Klute 1986). Free Fe oxides were analyzed by the citrate–bicarbonate dithionite method (Sparks 1996). Fe and Mn in solution were determined with inductively coupled plasma–optical emission spectrometry (ICP-OES). Relevant soil properties of the soil were presented in Table 1.

2.3 Adsorption kinetics and isotherms

For the adsorption kinetics studies, two initial concentration 10 and 50 mg/L Cs, Co, and Sr was studied with 0.01 M sodium nitrate (NaNO_3). A gram of soil was placed in each 50-mL Teflon centrifuge tube with 10 and 50 mg/L initial concentrations of these three metals. Twenty-five milliliters of solution was added to all of the samples. The kinetic times for each concentration were as follows: 10 min, 30 min, 1 h, 2 h, 4 h, 1 day, 2 days, 3 days, 1 week, 2 weeks, 1 month, and 2 months. After the samples were shaken for the appropriate times (their extraction time), the samples were centrifuged for 10 min at 23 °C and 8000 rpm. The samples were analyzed using ICP-OES for Co and Sr and inductively coupled plasma mass spectrometry (ICP-MS) for Cs. Based on the kinetics studies, the adsorption of these three metals reached the equilibrium after 1–2 days (discussed later). Therefore, the adsorption isotherms were measured for 2 days of reaction.

2.4 Metal fractionation with selective sequential dissolution procedures

The subsamples were extracted with the selective sequential dissolution procedures described below. After each extraction, the supernatant liquid was decanted and filtered through a 0.45- μm filter. The centrifugation-decantation steps are the same for all extractions. The soil residue of an extraction was used for the subsequent extraction until the last extraction is completed. The protocol for the solid-phase distribution of this study followed the protocol of Han et al. (2004, 2006, 2007):

Soluble plus exchangeable metals (EXC)—This fraction includes soluble plus exchangeable fraction on the surface of clay, minerals, and organic matter. Twenty-five milliliters of a 1-M NH_4NO_3 solution (pH adjusted to 7.0 with NH_4OH) were added to about 1 g of dry soil in a 50-mL Teflon centrifuge tube, and the mixture was shaken for 30 min at 25 °C and then centrifuged. The supernatant liquid was decanted and filtered.

Metals bound to carbonates (CARB)—This fraction extracts metals bound to carbonates. Twenty-five milliliters of a 1-M $\text{CH}_3\text{COONa}-\text{CH}_3\text{COOH}$ at pH 5.0 were added to the residual from the previous extraction. The suspension was mixed and shaken for 6 h.

Metals mostly bound to easily reducible oxides (ERO)—This fraction mainly targets metals bound to easily reducible oxides such as Mn oxides (Shuman 1982). Twenty-five milliliters of a 0.3-M $\text{NH}_2\text{OH}+0.01\text{ M HCl}$ solution (pH 2.0) were added to the soil residue and shaken for 30 min. This acid could attack some organic matter, resulting in underestimating the organically bound metal. Fortunately, this attack is less serious after the exchangeable fraction extraction.

Metals bound to organic matter (OM)—This fraction mainly targets metals bound to soil organic matter and microbes (Tessier et al. 1979; Han et al. 2004). Three milliliters of a 0.01-M HNO_3 and 5 mL of 30 % H_2O_2 were added to the soil residue. The mixture was digested in a water-bath at 80 °C for 2 h. An additional 2 mL of 30 % H_2O_2 were added, and the mixture was heated for an hour. Fifteen milliliters of a 1-M NH_4NO_3 solution were then added, and the sample was agitated for 10 min.

Metals bound to amorphous iron oxides (AmoFe)—This fraction extracts metals bound to amorphous iron oxides. Twenty-five milliliters of a 0.2-M oxalate buffer solution (0.2 M $(\text{NH}_4)_2\text{C}_2\text{O}_4-0.2\text{ M H}_2\text{C}_2\text{O}_4$ at pH 3.25) were added to the soil residue and the sample shaken in the dark for 4 h (Shuman 1982).

Metals bound to crystalline iron oxides (CryFe)—This fraction extracts metals bound to crystalline iron oxides. Twenty-five milliliters of 0.04 M $\text{NH}_2\text{OH.HCl}$ in a 25 % acetic acid solution were added to the soil residue and the sample digested in a water-bath at 97–100 °C for 3 h.

Metals in the residual fraction (RES)—4 M HNO_3 extract metals within crystal structures of primary and secondary minerals as well as the residual metals from the incomplete extraction of previous fractions (mostly from the organically bound metals, such as humin bound metals). Twenty-five milliliters of 4 M HNO_3 were added to the residue, and the sample was digested in a water-bath at 80 °C for 16 h.

Total Metals (TOT)—The concentrations of total metals were determined in soils digested with 4 M HNO_3 . The digestion procedure for the determination of the total metals is the same as the RES fraction above.

2.5 Measurement of Cs, Co, and Sr in solution

The ICP-OES (Perkin Elmer OPTIMA 3300 DV model) and the ICP-MS (Varian 820-MS ICP Mass Spectrometer) were employed to determine the metal concentrations in the extracts. The ICP-OES was used for the analyses of Co, Sr, Fe, and Mn and the ICP-MS was used for the analysis of Cs in all extracts, and for Co and Sr at the low concentrations as well as for all metals in 1 M NH_4NO_3 extracts (Fraction 1 and 4). Multi-element standards containing Co and Sr were made to the following concentrations: 0.02, 0.05, 0.1, 0.5, 1, and 2 mg/l and those for Fe and Mn up to 5 mg/l for ICP-OES, while for ICP-MS, 0.02, 0.05, 0.1, and 0.5 mg/l of Cs, Co, and Sr were used.

2.6 Quality assurance

In order to ensure that the methodology chosen is properly executed and effective, 4 M HNO_3 was used to extract metals from standard soil samples from the National Institute of Soil and Technology (SRM 2710, Montana soil with highly elevated trace element concentrations, and SRM 2711a, Montana soil with moderately elevated trace element concentrations). If the protocol for this experiment produces similar results to the certified values, the method is valid and effective for this study.

Two standard reference materials (SRM) were used to validate the analytical methods. Validity was being based on whether the NIST values provided fall within the range provided by the 95 % confidence interval of the experimental values. Table 2 summarized the recoveries of Cs, Co, and Sr from two NIST standard soils with 4 M HNO_3 extraction. The mean and standard deviation of each experimental measurement was provided. Based on the 95 % confidence interval, a range was created. If the NIST value fell within the range, the result was considered acceptable. Likewise, the coefficient of variance was calculated. Values that were below the coefficient of variation (CV) $\pm 20\%$ were considered acceptable.

Acceptable values for cesium were observed with both soils, but none of the NIST values for Cs were certified since only one method was used to measure the concentration. The

Table 2 Summary of the recoveries of Cs, Co, and Sr from two NIST standard soils with 4 M HNO₃ extraction

Elements	Soil	Measured values		Range	NIST values		CV %
		Mean	σ		Mean	σ	
Cs	2710	85.8		85.07	107		-20.5
	2711a	6.21	0.83	5.65–6.77	6.7	0.2	-7.31
Co	2710	8.73	3.13	6.62–10.83	10		12.73
	2711a	11.45	0.91	10.84–12.06	9.89	0.18	-15.75
Sr	2710	247.6	58.29	208.4–286.7	330		-24.98
	2711a	129.7	14.82	119.7–139.6	242	10	-46.43

concentrations obtained from SRM 2710 and SRM 2711a for cobalt were favorable. Although cobalt had similar concentrations as the NIST concentration reported for SRM 2710, none of the values provided for Cs, Co, or Sr were certified. Neither of the strontium concentrations obtained with 4 M HNO₃ extract from the standard soils agreed with the NIST values. This discrepancy in Sr may be due to less complete dissolution of 4 M HNO₃ used for the present study. 4 M HNO₃ could not completely dissolve the silicon/aluminum minerals in soils and may not extract those inside the lattice structure of the minerals.

3 Results and discussion

3.1 Adsorption kinetics and isotherms of Co and Sr on US coastal soil

The adsorption kinetics of Co and Sr on the soil was performed at room temperature (Fig. 1 and Table 3). Kinetic data showed that both Co and Sr reached the adsorption plateau even after 5 h of adsorption and then little changed at both 10 and 50 mg/L initial concentrations. The adsorption isotherm data were predicted with both Freundlich and Langmuir models. In general, the Langmuir model gave the better fitting (R^2) for both Co and Sr. Both models indicated Co and Sr had similar adsorption capacity on the current coastal soil. However, Co had much higher adsorption affinity as indicated by the intensity parameter and adsorption energy parameters (Table 2). This observation was in agreement with previous studies on adsorption of ⁶⁰Co and ⁸⁵Sr on other regional soil/groundwater systems (Seliman et al. 2010) and on stable isotope (Welp and Brümmer 1999). It was found that soils had higher adsorption affinity for Co than Sr.

3.2 Metal fractionation and distribution among solid-phases in the US coastal soils

The metal fractionation and their distribution among solid-phase components in the coastal soil were presented in Figs. 2, 3, and 4. Overall, the CV% between the sum of the

fractions and the total contents Cs, Co, and Sr were mostly $\leq 20\%$. At 200 mg/kg treatment levels, the average CV% for Co was $17.3 \pm 4.8\%$ and $22.2 \pm 5.7\%$ for the SP and FC moisture, respectively. The average CV% for Co was $-21.0 \pm 13\%$ and $-3.4 \pm 14\%$ for SP and FC, respectively. Sr CV% was 7.82 ± 11 and $18.1 \pm 8.8\%$ for two moistures, respectively. The CV% increased with the decrease in the treatment levels and the control due to the low concentrations of these elements.

In general, Cs, Co, and Sr behaved differently when they entered the coastal soil. Cs was mostly presented in the EXC fraction. With time, Cs was rapidly transferred and redistributed into the RES and other solid-phase components such as CARB, ERO, AmorFe, and CryFe fractions (Fig. 2).

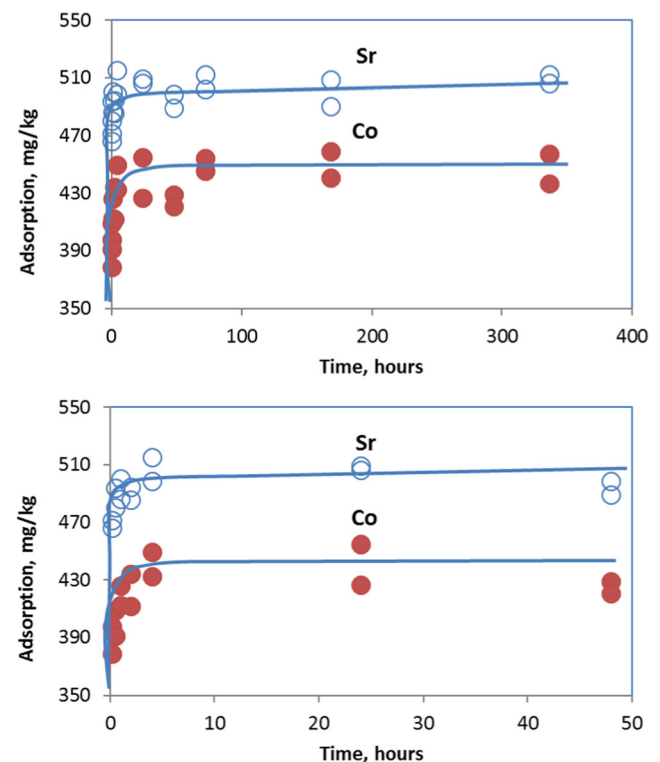


Fig. 1 Adsorption kinetics of Co and Sr on a coastal soil (mg/kg) at 50 mg/L initial concentrations with time (hours) (Cs data not available due to unaccess to the ICP-MS at the time)

Table 3 Parameters of adsorption isotherms of Co and Sr on a US coastal soil with Freundlich and Langmuir models

Model	Parameters				
Freundlich	Kf	n	R^2	Sample no.	
	(Capacity)	(Intensity)			
	Co	93.3	1.72	0.74	6
	Sr	84.0	1.27	0.69	6
Langmuir	Qo	b		Sample no.	
	(Maximum adsorption capacity)	(Adsorption energy)			
	Co	172	1.81	0.93	6
	Sr	189	1.43	0.97	6

However, more than 90 % of Cs was still in the soluble and exchangeable (EXC) even after 2 months of reaction period at the high level (200 mg/kg). This indicates the high bioavailability of added Cs in the coastal soil, resulting in its potential high bio-transfer and bioaccumulation in plants and crops (Wasserman et al. 2008). Mondini et al. (1995) showed the correlation between the distribution of cesium to the organic matter and cation exchange capacity (CEC). Cesium behaves similarly with K in the ecosystems and is easily absorbed by higher plants and microorganisms. Bunzl et al. (1998) reported that ^{137}Cs in the organic layers was present throughout all solid-phase fractions although mainly in the clay mineral

fractions. Wasserman et al. (2008) found that the spiked ^{137}Cs was dominated in the oxidizable and alkaline fractions (equivalent to the organic matter bound and iron oxide bound fractions) in Brazilian histosol with 8.6 % organic C and was mostly present in the alkaline (iron oxide/organic matter fraction) in Ferralsol with 4.9 % iron oxide.

Co was rapidly distributed among EXC, CARB, and OM fractions (Fig. 3). With the time, Co was transferred from the EXC and CARB fractions into the OM fraction. At the low loading level such as 10 mg/kg, added Co was mostly bound to CARB and OM fractions, while in the higher loading levels (200 mg/kg), Co was dominated in the EXC fraction (>60 %)

Fig. 2 Distribution of Cs among solid-phase components in soils treated with CsCl_2 at 10 and 200 mg/kg levels under saturated paste (SP) and field capacity (FC) moisture regimes

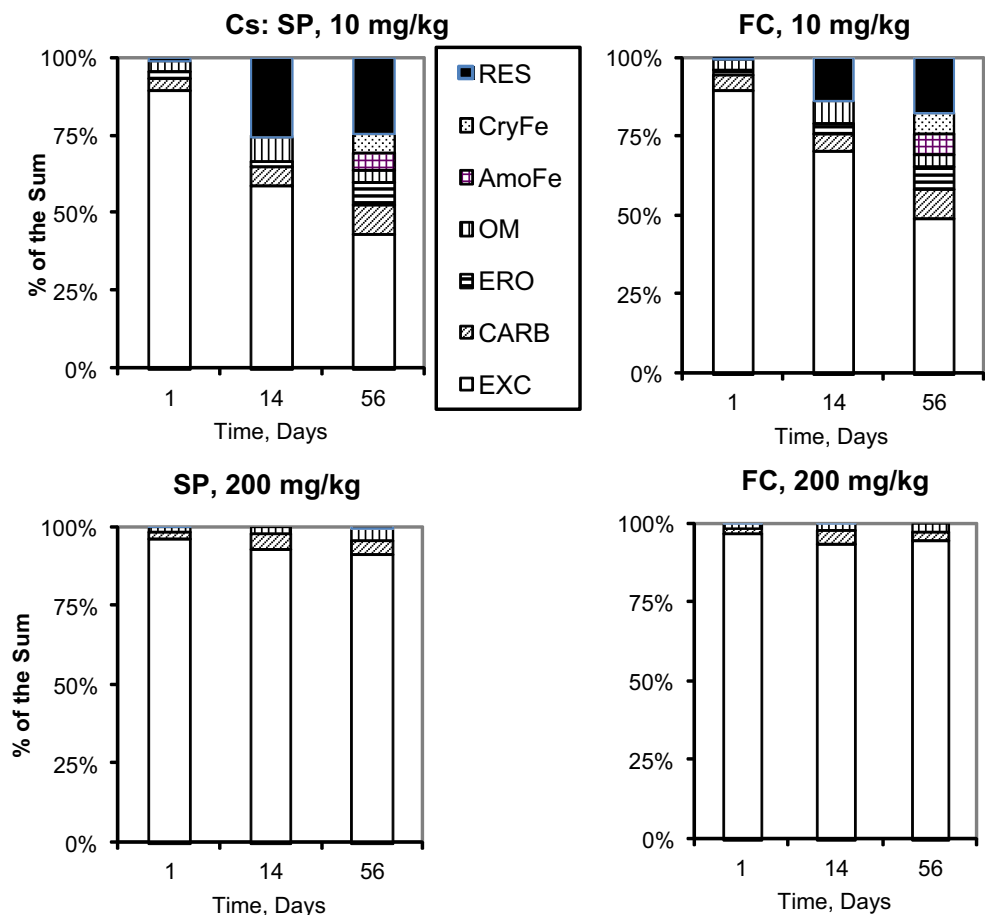
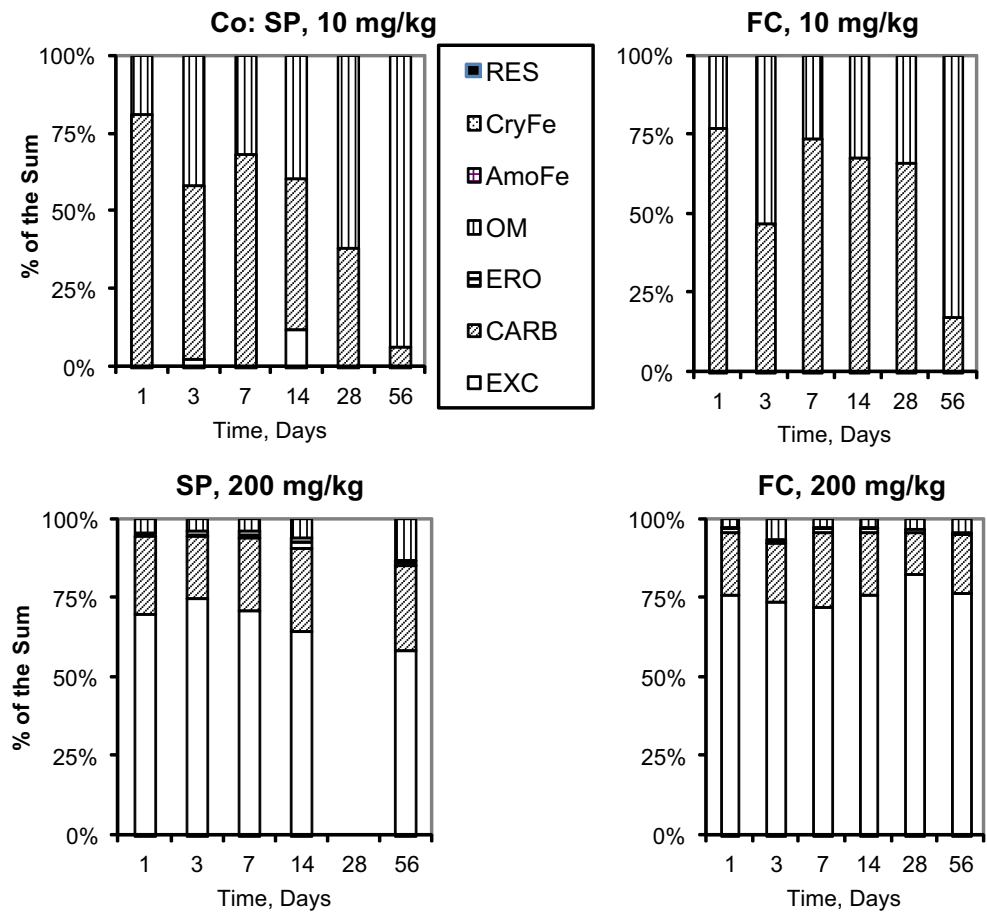


Fig. 3 Distribution of Co among solid-phase components in soils treated with CoCl_2 at 10 and 200 mg/kg levels under saturated paste (SP) and field capacity (FC) moisture regimes (Co data in Day 28 at 200 mg/kg treatment level under the SP moisture was not available)

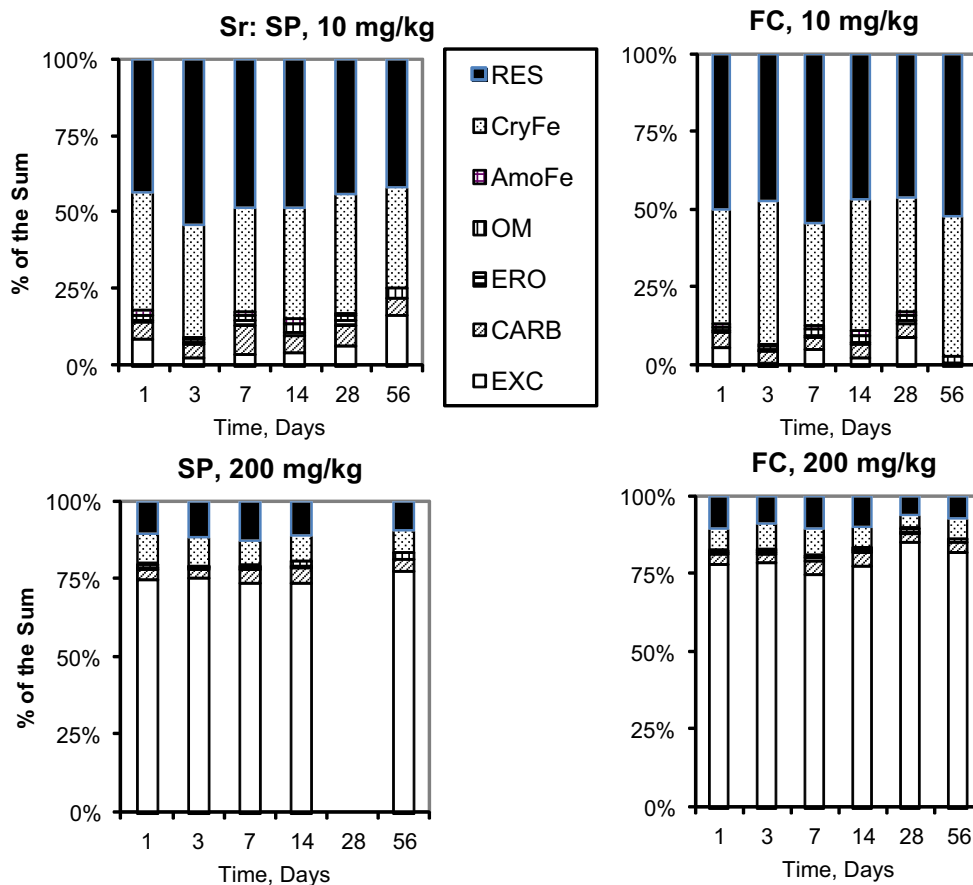


and the CARB fraction. With time, more Co was redistributed into the OM fraction. The geochemical cycle of cobalt is similar to those of iron and manganese and is likely to be associated with many minerals of these metals. When cobalt is in soil, its behavior is reliant on the Mn oxide phase formation. Tani et al. (2003) showed that cobalt had a high capacity to be absorbed by Mn oxides. Cobalt reacts easily with any metals that are geochemically or biochemically with iron. These interactions have a vital role in the fate of cobalt in soils and its absorption by plants (Wasserman et al. 2008). In the aging and submerged-dried cycling studies, Co was found to be associated with Mn oxide fraction (23 to 100 % of total Co) and Fe oxide fractions (0 to 77 % of total Co) of the soils as either Co (II) species or a mixed Co (II) and Co (III) species (Beak et al., 2011). The surface speciation of Co in the Mn/Fe oxide fraction suggests an inner sphere complex was present. However, the present study indicates that the current coastal soil contained a low amount of Mn and Mn oxide (<0.0002 %) and frequent oxidation/reduction of coastal soils may have leached out most of its Mn oxides, leading to an insignificant portion presence of Co binding in the Mn oxides (as extracted as easily reducible oxide-ERO fraction). Mico et al. (2008) pointed that soil effective cation exchange capacity (CEC) and exchangeable calcium were the most consistent single

predictors of the EC50 values based on added Co. This indicates that exchangeable form of added Co was significant bioavailable sources for plants. Wasserman et al. (2008) reported the spiked ⁶⁰Co was mostly present in the oxidizable (organic matter) fraction in the histosol and was dominated in the acidic and easily reducible fractions in tropic acidic ferralsol. They also found addition of organic matter increased Co and decreased the transfer factor of ⁶⁰Co and ¹³⁷Cs in radish.

Sr was distributed among solid-phase components rapidly and changed a little during the rest of the 2-month period (Fig. 4). At the low level (10 mg/kg), Sr was rapidly distributed among all solid-phase components with a strong tendency into the more stable CryFe and RES fractions. At the high loading level (200 mg/kg), Sr was dominantly present in the EXC fraction (75 % of the added) and to some extent the CryFe and RES fractions. This indicates that Sr at the high loading levels might have a high mobility and bioavailability in the ecosystem. Since Sr is the major radionuclides with nuclear power plant accident, the extensive research on Sr form and fates in soils have been investigated (Amano et al. 1999; Arapis et al. 1997; Kagan and Kadatsky 1996; Pavlotskaya et al. 1976 etc.). The mobility of strontium radionuclides in soil profiles was strongly dependent on soil

Fig. 4 Distribution of Sr among solid-phase components in soils treated with SrCl₂ at 10 and 200 mg/kg levels under saturated paste (SP) and field capacity (FC) moisture regimes. (Sr data in Day 28 at 200 mg/kg treatment level under the SP moisture was not available)



properties, e.g., the kind and content of the soil organic matter. Kagan and Kadatsky (1996) reported that ⁹⁰Sr occurred in easily exchangeable forms with high mobility. Migration of ⁹⁰Sr seemed to be high in soils. Arapis et al. (1997) studied the migration of ⁹⁰Sr and found that the migration of ⁹⁰Sr was between 0.7 and 1.5 cm per year, but a large portion of the residual ⁹⁰Sr was still in the upper 10 cm of the soil layer. Another study by Pavlotskaya et al. (1976) revealed that ⁹⁰Sr was easily co-precipitated by hydrous Fe oxides, which lead to an accumulation of ⁹⁰Sr in Fe-rich soils. The present study indicated that high amount of Sr (30–50 %) was bound to the crystalline iron oxides (CryFe) at the low loading level (10 mg/kg) and more than 75 % was in the EXC fraction in the high level (200 mg/kg). Amano et al. (1999) reported speciation of radioactive Cs and Sr in undisturbed surface soil along the river in the exclusion zone (30-km zone) near the Chernobyl nuclear power plant. They found that Sr-90 in the soil was presented mainly in the water soluble and exchangeable fractions, which were easily accessible to river water as a dissolved fraction.

Among these three metals, Cs showed the highest percentages in the soluble and exchangeable form (EXC), followed by Sr and Co at both low and high loading level (10 and 200 mg/kg) under both moisture regimes. At the high level, the overall bioavailability of these metals followed

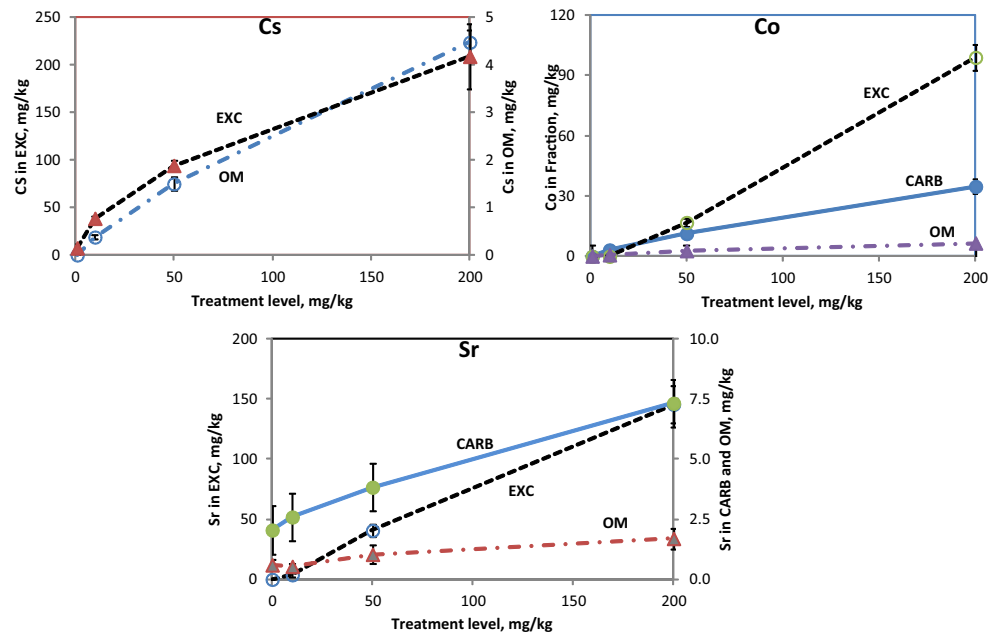
Cs>Sr≥Co assuming the decreasing order of the bioavailability of metals bound in the solid-phase components (Han et al. 2002).

3.3 Effects of loading levels on binding and distribution of Cs, Co, and Sr

Increases in the loading levels of these elements significantly increased their presence in the most bioavailable and labile form—soluble and exchangeable (EXC). Cs, Co, and Sr in the EXC fraction linearly increased with the additional levels (Fig. 5). In addition, Cs in the OM fraction significantly increased with the loading level as well. Co and Sr in the OM fraction slowly increased with the loading levels. Similarly, Co and Sr in the CARB fraction had a liner relationship with the loading levels.

Han and Banin (2001) proposed fractional isotherm methods to indicate the sensitivity of each solid-phase components to host and bind added soluble metals into soil. Those fractions sensitive to adding levels are more bioavailable than the most stable solid-phases such as Fe oxides and clay mineral binding fractions which are relatively not sensitive to added amount of metals. This study indicates that Co, Sr, and Cs in the soluble and exchangeable fraction may be the most bioavailable, while the carbonate bound and organic

Fig. 5 Changes of distribution of Cs, Co, and Sr in solid-phase components (mg/kg) with the loading levels (mg/kg) in soils after the first day under saturated paste (*SP*) moisture regime



matter bound fractions may be to some extent labile and still bioavailable to microbes and plants.

3.4 Effects of time on redistribution of Cs, Co, and Sr in the soil

With the time, all these three metals were slowly redistributed from the more labile, soluble, and bioavailable fractions into the more stable and less soluble fractions (Figs. 2, 3, and 4). In general, more transformation occurred for Cs and Co than for Sr among solid-phase components. Cs was slowly transferred from the soluble and exchangeable form (EXC) into the RES (clay minerals) and other solid-phase components (CARB, ERO, AmoFe, and CryFe). Cs was less bound to organic matter and more affiliated with clay minerals and Fe/Mn oxides (Fig. 2). Tsukada et al. (2008) reported that Cs was strongly absorbed by clay fractions, clay minerals, and organic matter. Fe and Mn sesquioxides also retard the migration of cesium in soil (Arapis et al. 1997; Grin et al. 1999).

Clearly, Co was transferred from the CARB fraction into the OM fraction with time. It seems that organic matter became the more important sinks for Co (Fig. 3). During the 2-month period of incubation, the role of Mn oxide was not observed as indicated in the literature. This is due to low concentrations of Mn and Mn oxides in the present coastal soil (Table 1). Han et al. (2002) reported that native Co in arid soils was strongly correlated with changes of Mn/Fe oxides and was transferred from Mn oxide (ERO) fraction into the carbonate (CARB) and EXC fractions in soil under saturated paste regime. The current study implies that added Co in the coastal soil behaved differently from native Co in upland soils.

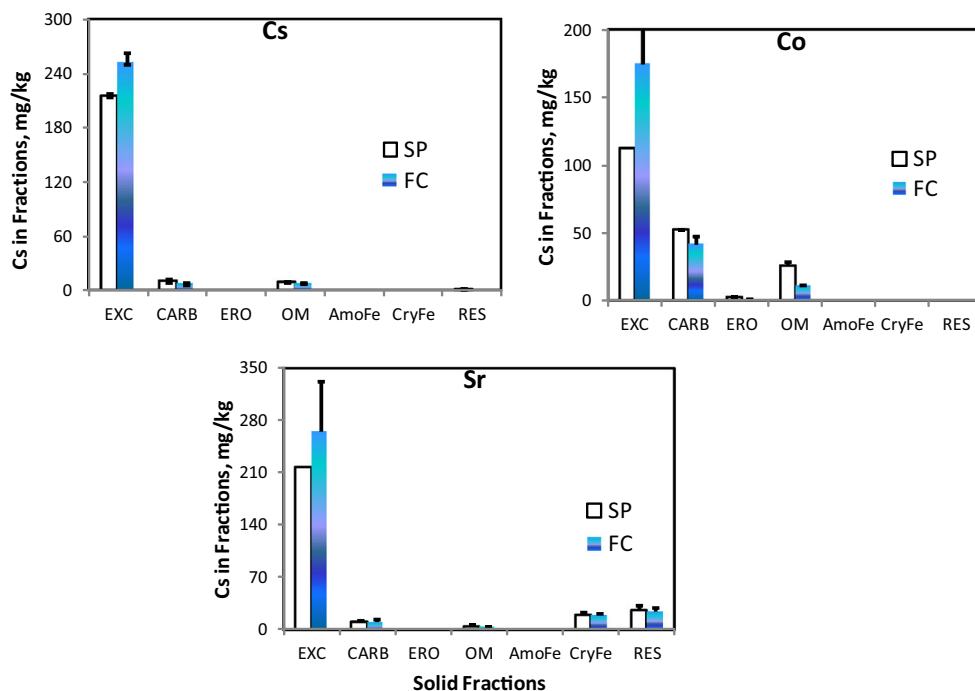
Sr changed little among solid-phase components with time in the coastal soil (Fig. 4).

3.5 Effects of moisture regimes on redistribution of Cs, Co, and Sr in the soil

Moisture regime is an important environmental factor controlling the speciation of metals and their fates in the coastal ecosystems. In general, saturation moisture (SP) resulted in the significant lowering concentrations of Cs, Co, and Sr in the soluble and exchangeable form (EXC) than field capacity moisture regime (FC) (Fig. 6). Biogeochemical reduction of both Fe/Mn oxides occurred, and formation of carbonate minerals are the dominant factors responsible for effectiveness in lowering solubility of these metals in soils. This is an important mechanism for coastal soils to effectively mobilizing/redistributing these elements from more bioavailable and soluble forms into less soluble and more stable form with time.

Under saturated regime, redox potential rapidly decreased while the pH slightly increased, resulting in the significant decrease in the overall pH+pE. pE+pH reached the lowest point after 1 week saturation then stabilized with the time (Fig. 7). With decrease in pE+pH, iron was reduced from iron oxides such as AmoFe fraction into soluble and exchangeable (EXC) fraction and formation of carbonate (CARB) in the SP moisture regime, compared to less changes in Fe among solid-phase components at the field capacity moisture regime. At reducing conditions, Fe/Mn oxide reduction serve as a major driving force for redistributing added trace elements in soils. Han and Banin (1996) reported that with decreases in pE+pH, Fe/Mn were transferred from Mn oxide (ERO), iron oxide (AmoFe and CryFe) into the more soluble and exchangeable

Fig. 6 Comparisons of distributions of Cs, Co, and Sr in each individual fractions (mg/kg) of soils at 200 mg/kg treatment after 56 days of incubation under two moisture regimes (*SP* saturated paste, *FC* field capacity) (The difference in the EXC fraction between *SP* and *FC* was at 5 % significant level)



form (EXC), and formation of new carbonate (CARB). With formation of Fe/Mn carbonates, more Co was formed initially in the soil, but with time Co in the CARB continued to be transferred into the OM fraction. Grybos et al. (2007) reported reducing conditions in coastal wetlands lead to the release of

Co and other trace elements into soil solution by 25–20 factors which was concomitant with reductive dissolution of soil Fe-oxyhydroxide reduction as well as with strong dissolved organic matter release. Han and Banin (2000) also observed that saturated incubation of arid soils released

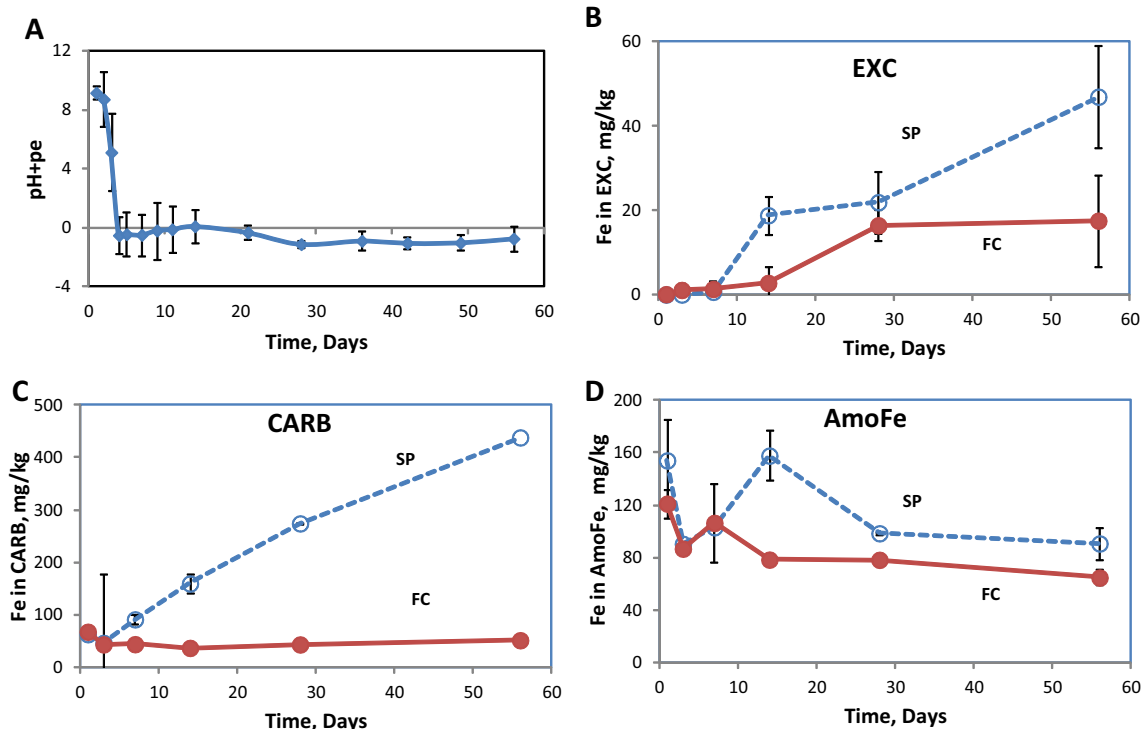


Fig. 7 Changes of pH+pe (a) in soils under saturated paste (*SP*) and Fe distribution among solid-phase components (mg/kg) with time (days) in soils under *SP* and field capacity (*FC*) moisture regimes

significant soil native Co and other trace elements into the soluble and exchangeable form.

4 Conclusions

This study shows that when cesium, cobalt, and strontium entered a US coastal soil from the northern Gulf of Mexico, they were dominantly presented in the soluble and exchangeable form ($Cs > Co$ and Sr), possessing high potential bioavailability, mobility, and ecotoxicity. The current results provided the fundamental information for designing the remediation and control strategy targeting this specific bioavailable and labile form of these three elements. The cost-effective remediation technology to remediate these metals would include those technologies quickly removing the soluble and exchangeable forms, such as ion exchangeable resin, nano adsorbents and minerals, and bio/phytoremediation.

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