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Sequential extraction of Cs and Sr from Ain Oussera soils around Es-Salam research reactor facility

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ABSTRACT

Four types of undisturbed soil in Ain Oussera region around the Es-Salam reactor facility, located in the south of Algiers, Algeria, at about 200 km, were artificially contaminated for one year with stable CsCl and SrCl₂ in order to simulate an accidental release of these elements. This study was performed using sequential extraction procedure based on Shultz method and containing six fractions. The selectivity of the extraction protocol was confirmed by analyzing some elements (Ca, C, Fe, Mn, Si and Al) designed as indicators of the targeted phases. The obtained results showed an acceptable reproducibility, in view of the coefficients of variation that were in most cases less than 15%. The results revealed a clear proportional correlation between the extracted Cs and Sr in fractions for each soil and some of soils physicochemical properties. Organic matter appears to play an important role in the soil retention, particularly for Cs where the extracted percentage exceeds to 30% in whole soils. In contrast, strontium expresses a remarkable affinity for the fraction bound to carbonates. The obtained data also indicate that the availability of Cs in the four soils is less important compared to Sr availability. This is illustrated by the higher value of extracted Sr in the easily extractible phase, including the water-soluble and the exchangeable fraction. © 2015 The Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences.

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Introduction

Pollutants in the soil, usually in trace amounts can be found in chemical forms and in environmental conditions that favor or not their mobility. Mobility and bioavailability of metal contaminants such as radioactive elements like cesium and strontium in the environment depend on the physicochemical forms and soil characteristics. Therefore, it is essential to determine in what form the chemical elements are present and how they are related to the geological matrix. The identification and the determination of the different chemical forms of an element are known as speciation. It is one of the basic criteria for assessing risks of soil pollution posed by

minerals and other radioactive wastes. This characterization is a key factor in understanding and predicting the behavior of trace elements and radionuclides (Schultz et al., 1996). As a natural environment, the soil is a very complex system, and any mechanistic approach requires knowledge of many sorption processes and the main factors governing the partitioning of pollutants between the solid and liquid phases (Desmet et al., 1991).

Chemical modeling remains difficult to implement because of the complex nature of the processes involved and the lack of reliable thermodynamic data: information about the kinetics of environmental processes is unknown, most calculations are done assuming systems at equilibrium. In

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addition, compositions, abundance and properties of many components of natural systems are still poorly understood.

It is therefore necessary to implement indirect approaches to describe the speciation of radionuclides in soil. One of these indirect methods is contacting the soil with a well-known solution and characterizes the resulting leachate. Transfer soil-solution depends on the ability of the soil to fix the radionuclides. This ability depends on the composition of the solid phase (organic, inorganic) and ionic species present in the solution that may compete with polluting elements (Vidal et al., 1995).

Improved understanding of the mechanisms that generate the retention of radionuclides in soils is an essential step in the development of transport models radioactivity, particularly when they are intended for evaluation on large time scales. Included in this context, this study aims to predict the behavior of deliberate or accidental release of radionuclides (^{137}Cs and ^{90}Sr) in Ain Oussera soils near the Es-Salam reactor facility. It also plans to identify the mechanisms responsible of their behavior and to quantify their influence in order to evaluate the soils retention rates and consequently deducing the mobility and the availability of studied elements to prevent possible contamination of groundwater. This can lead to assess the radiological impact on the environment and particularly human health because the groundwater is the unique source of drinking water in this region. To achieve this, an indirect approach based on the sequential extraction method was applied to soils voluntarily contaminated by cesium and strontium. In order to avoid the risk of contamination, we used the cesium-133 (stable) and strontium-88 (stable). The sequential extraction procedure employed in the present work is that proposed by Schultz et al. (1998), but with a slight modification. Originally Schultz method containing 5 fractions and itself is based on that suggested by Tessier et al. (1979). While, the protocol used in this investigation contains six fractions. This choice was made after reviewing the objectivity of the arguments put forward by Schultz et al. (1998) to the major changes introduced in Tessier method. Note that parts of the modifications introduced to Tessier procedure are those recommended by the NIST Speciation Workshop (Schultz et al., 1998).

1. Materials and methods

1.1. Extraction procedure

Selective extraction methods are applied in environmental chemistry trying to simulate the phenomena encountered in nature. Indeed, soils and sediments are subjected to “leaching” by natural electrolyte solutions and/or anthropogenic, i.e., the soil fine particles are often mechanically entrained by the gravity waters from surface to soil deeper layers (Duchaufour, 1997). The main difference between laboratory extractions and natural leaching caused by rainwater is the time factor. Chemical extractions accelerate natural processes by the use of concentrated reagents and/or more aggressive than those usually encountered in a natural environment. Most extraction methods distinguish between five fractions whose names correspond roughly to the phase

targeted by each reagent: exchangeable fraction, adsorbed and/or related to carbonates, bound to organic matter, related to oxyhydroxides more or less crystallized and the residual fraction (Blanco et al., 2004; Fytianos and Lourantou, 2004; Schultz et al., 1998; Tessier et al., 1979). Some authors distinguish between crystallized and amorphous oxides (Larios et al., 2012; Oh et al., 2011; Relić et al., 2005) and another makes the difference between organic matter and humic and fulvic acids (Huang et al., 2012). The main artifacts related to chemical extraction methods are threefold:

1. Solid phases referred are not the only ones attacked. Indeed, highly oxidizing reagent can attack carbonate mineral phases, releasing radionuclides associated with these phases and ultimately lead to an overestimation of the pollutant associated with oxidizable soil components. This is true when organic fraction precedes the carbonate phases.
2. The second potential artifact is the incomplete dissolution of targeted phases where no any reagent can completely dissolve a given phase. This results in an underestimation of the available amount of pollutants.
3. The third problem concerns the readsorption or redistribution of contaminant, which released during the extraction, on particles of the solid phase remaining before separation of aqueous and solid phases.

The order of fractionation plays an important role in the selectivity of the sequential extraction procedures (Miller et al., 1986). It directly affects the choice of reagents and contact time and can lead to other way of result interpretation. According to Shultz, organic matter may oppose the attack of certain phases when it is placed back after those of carbonates and oxyhydroxide phases because solid particles in soils are often coated with a layer of organic matter. For this purpose, Shultz changed the order of Tessier extraction procedure and placed the organic matter early in the procedure, immediately following the exchangeable fraction. This change has had an impact on the choice of reagent used for organic matter oxidation. In fact, the mixture $\text{HNO}_3/\text{H}_2\text{O}_2$, overly aggressive, employed by Tessier cannot be used in this case. It was replaced by sodium hypochlorite NaOCl (5%–6%). Several studies have shown that the use of the NaOCl (5%–6%), for this sequencing, arrives to dissolve organic matter more effectively with a minimum damage to subsequent geochemical phases (Schultz et al., 1998; Shuman, 1983; Anderson, 1963). To avoid artifacts related to incomplete phase dissolutions, Schultz proposed a ratio of 15 mL/g, approximately the double that was used in the Tessier protocol.

It is known that rainwater has an important action on pollutants leaching phenomena from soils and often leading to their availability or bioavailability. Therefore, it seems useful to add a new fraction at the beginning of the Schultz extraction procedure for simulating natural conditions. This consists on dispersing the soil sample in deionized water. It is named: water-soluble fraction, and mainly focused on pollutants associated with soluble salts, weakly bound, e.g., via outer-sphere complex or simply present in the interstitial water. In the literature, there are several protocols including this water-soluble fraction (Larios et al., 2012; Leleyter et al.,

2012; Milačič et al., 2012; Huang et al., 2012; Karak et al., 2011; Al-Masri et al., 2006; Tang et al., 2006; Shi et al., 2005; Sokolik et al., 2001; Vidal et al., 1995) and recommending a contact time from 1 to 24 hr. In the present work, a contact time of 1 hr has been chosen to evaluate the soluble fraction. On the one hand, this time can be enough to extract radionuclides contained in the soluble phase. On the other hand, to minimize any form of ion exchange that can be established between the oxonium ions (H_3O^+ (aq)) and cations retained by soil with increasing contact time. For all extractions, the separation of phases was performed by centrifugation using a centrifuge (Bioblock scientific 2–5, SIGMA) at 3500 rpm then filtered through a 0.2 μm cellulose nitrate filter (Sartorius). At the end, the proposed protocol based on Shultz method and used in the present investigation contains six fractions as presented in Table 1.

1.2. Soil sampling and contamination

Soil sampling was carried out during the period of May to June 2006 at different points around Es-Salam reactor facility. Four undisturbed soils, typical and representative of the studied region, have been chosen. All samples were originating from the surface layer with a depth ranging from 0 to 40 cm and collected at increasing distances (0.8, 10 and 20 km) from the Es-Salam reactor facility. Selected points were appointed: “Site”, “Birine”, “Hade” and “Khachem”. Respectively, the first was named “Site”, as it is close to the reactor site (800 m). The second point is near to the Birine city about 10 km from the reactor to the east. The third is located 20 km southwards. Finally, the last one is situated 20 km northwest. Soil samples were divided into two parts intended respectively for physicochemical analysis and for Cs/Sr contamination. The part destined to the physicochemical analysis was air-dried, sieved through a 2 mm mesh and homogenized with manual stirring before analyses.

Main soil analysis was determined by triplicate in all soil samples. Particle size analysis was made using Robinson’s pipette method (Pansu and Gautheyrou, 2006) and soil pH was measured in 1/5 soil/solution suspension both for pH(H_2O) and pH(KCl) (Yuan et al., 2004). Organic matter and carbonate have been determined using loss-on-ignition (LOI) method and Bernard Calcimeter method (Pansu and Gautheyrou, 2006), respectively. CEC and exchangeable Ca^{2+} , Mg^{2+} , Na^+ and K^+ , were determined using copper ethylenediamine method (Bergaya and Vayer, 1997). All metal analysis was performed by atomic absorption spectrometry (AAAnalyst 400, Perkin Elmer). The oxide amounts were deduced using wavelength dispersive X-ray fluorescence

spectrometry (WDXRF) (MagixPro, Philips). Clay’s analysis were performed by X-ray diffraction using a Philips PW1710 diffractometer with Cu $\text{K}\alpha$ ($\lambda = 1.5406 \text{ \AA}$) radiation.

All chemicals used for the preparation of leaching solutions and for soils analysis were analytically grade reagents. All standards solution used in analysis are PerkinElmer pure atomic spectroscopy standards (ISO 9001 certified).

Soil samples intended for contamination have been cleared of debris, grass and stones, but without being sieved. 300 g of each soil were mixed with 600 mL of solution containing both $^{133}\text{CsCl}$ and $^{88}\text{SrCl}_2$ at the same concentration of 2.5 g/L. The suspension soil/solution was stored at less than 15°C in loosely closed polyethylene bottles for a period of one year in the dark and without agitation, to study the short-term distribution (Shand et al., 1994). After, the contaminated soils were removed and air-dried at room temperature for one week. Subsequently, the soil is divided into small quantities of 10 g each and washed with ethanol three times, then rinsed once with deionized water to remove Cs and Sr free salts. Before being used in extraction experiments, soils were again air-dried for one week then sieved at 2 mm. This contamination technique may accelerate the distribution process of the Cs and Sr in the soils fractions and allows for the study of speciation in a relatively short contamination time.

2. Results and discussion

2.1. Soil analysis

Table 2 lists the basic physicochemical characterization of the four soils used in the present study. According to this analysis, the first fact to note is that the soils have all basic pH. This is mainly due to the low content of Al^{3+} and Fe^{2+} cations and the higher carbonates presence, precisely in “Hade”, “Khachem” and “Birine” soils (Table 2), which can buffer the soils pH to basic values. The small difference between pH(H_2O) and pH(KCl) can be explained by the low presence of kaolinite clay, as indicated in Fig. 1, which generally provides this reserve in protons. With respect to the texture of the samples, there are some differences between the four soils in the particle size distribution. All soils have a relatively high level of sand and silt. Their content of clay or fine fraction varies by more than 24%, case of “Hade”, to about 13%, case of “Site” soil. This size repartition, particularly clay content, can allow each soil its own behavior in terms of metal pollutant retention. Oxide analysis shows, on the one hand, that the silica (SiO_2) content is higher and

Table 1 – Description of the extraction protocol based on Schultz method and adopted in this study.

Fraction	Extractive reagent	Contact time (hr)	pH	Temperature (°C)	Reagent/sample ratio (mL/g)
F1 Soluble	H2O (deionized)	1	Soil/water pH	Room	15/1
F2 Exchangeable	0.4 mol/L MgCl_2	1	5	Room	15/1
F3 Bound to organic matter	NaOCl (5%–6%)	2×0.5	7.5	96	15/1
F4 Bound to carbonates	1 mol/L NaAc in 25% HAc	2×2	4	Room	15/1
F5 Bound to oxyhydroxides	0.04 mol/L $\text{NH}_2\text{OH HCl}$	5	2 (HNO_3)	Room	15/1
F6 residual	$\text{HNO}_3/\text{HCl}/\text{HF}/\text{HClO}_4$	Until complete dissolution		100	

Table 2 – Basic soil properties.

Sampling site	pH (H ₂ O)	pH (KCl)	Al ³⁺ (cmol(+)/kg)	Fe ²⁺ (cmol(+)/kg)	OM (%)	CaCO ₃ (%)	Sand (%)	Silt (%)	Clay (%)	SiO ₂ (%)	Al ₂ O ₃ (%)	MnO (%)	Fe ₂ O ₃ (%)
Khachem	8.42	8.3	0.0088	0.0076	2.14	10.11	53.23	29.87	16.90	52.10	9.67	0.02	2.19
Hade	8.9	8.69	0.0088	0.0112	1.61	19.64	53.01	22.24	24.75	42.70	9.71	0.02	2.50
Birine Site	8.79	8.62	0.0150	0.0038	1.56	8.54	72.42	12.85	14.73	60.31	7.45	0.03	1.37
	8.72	8.33	0.0207	0.0058	0.62	2.16	79.98	7.45	12.57	70.96	12.60	0.03	3.02
Sampling site	CEC (cmol(+)/kg)		CEC of FF ^a devoid of OM (cmol(+)/kg)	CEC of FF with OM (cmol(+)/kg)	Ca ²⁺ (cmol(+)/kg)	Mg ²⁺ (cmol(+)/kg)	K ⁺ (cmol(+)/kg)		Na ⁺ (cmol(+)/kg)				
Khachem	14.22		50.58	70.63	10.07	0.54	0.31		1.56				
Hade	11.62		25.79	49.3	8.14	1.43	0.63		1.01				
Birine Site	14.06		47.42	61.11	9.35	0.47	0.26		0.93				
	8.31		36.58	52.10	6.11	0.38	0.28		0.83				

^a FF: fine fraction (<2 μm) of Ain Oussera soils (with or devoid of organic matter).

varies from one soil to another in accordance with the sand percentage in each soil. On the other hand, low content of MnO and Fe₂O₃ oxides was recorded. This should reflect a poor distribution of the Cs and Sr in the oxyhydroxide fraction. When comparing the values of the cationic exchange capacities, it is obvious that “Khachem” and “Hade” CEC, with 14.22 and 14.06 cmol(+)/kg respectively, should present the highest distribution of Cs and Sr than “Birine” and “Site” soils. The CEC of the fine fraction with organic matter (OM) are higher compared to those without OM, although the OM content is relatively low in the four soils. This may be explained by the presence of humic substances in soils that can form complexes with clay minerals leading to high CEC values. Fig. 1 shows the XRD analysis of the fine fractions (<2 μm) of the four studied soils. According to this analysis,

three clay minerals are mostly found in soil samples: montmorillonite, illite and kaolinite. It is interesting to note that “Hade” soil is characterized by the presence of a particular type of mixed carbonate, dolomite.

2.2. Selectivity of extraction

In order to examine the selectivity of the extraction protocol used in the present study, some elements designed as indicators of the targeted phases were analyzed by atomic absorption spectrometry after each fractionation. Calcium was selected to indicate both exchangeable and carbonate fraction. Carbon was chosen to indicate oxidizable fraction or bound to organic matter. Extracted Mn and Fe were designed to indicate the reducible fraction. However, Al and Si can be

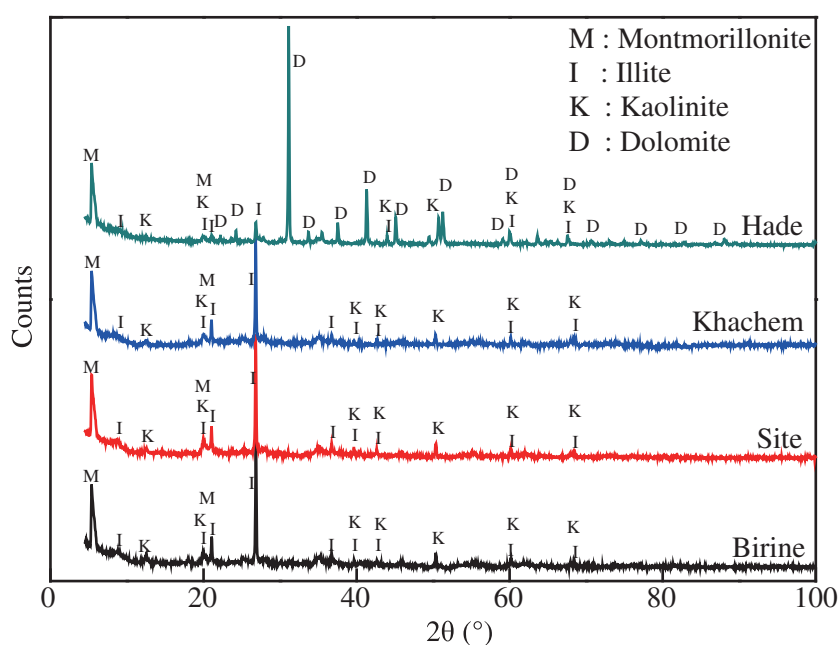


Fig. 1 – XRD spectra of the fine fraction (<2 μm) of Ain Oussera soils (devoid of organic matter).

found in both highly insoluble mineral phase, such as SiO₂ and Al₂O₃ as well as in aluminosilicate minerals or clays, although results presented here indicate the latter.

As shown in Fig. 2 the exchangeable Ca extracted during the second fraction F2, was equal to 6.41, 8.07, 3.72 and 20.98 mg/g for “Birine”, “Khachem”, “Site” and “Hade” soils respectively. When expressed in cmol(+)/kg these results were approximately in the same order than those obtained during the exchangeable Ca determination in the soil analysis section (Table 2). This indicates that the reagent (MgCl₂) employed in the extraction method to remove exchangeable Cs and Sr is efficiency and selective. On the other hand, extracted Ca from the fraction bound to carbonates (F4) seems to be also selective. Indeed, the extracted Ca was: 79.48 (76.56%), 101.32 (81.83%), 4.72 (49.17%) and 160.79 mg g⁻¹ (80.61%) for “Birine”, “Khachem”, “Site” and “Hade” soils respectively. The values shown in parentheses correspond to the percentage of Ca, in this fraction (F4), calculated from the total calcium content in each soil. It is also worth mentioning that during the organic matter attack by the NaOCl reagent, there is no significant release of calcium in F3 which is a good selectivity sign. Concerning the second indicator element (carbon), it should be noted that after each fractionation carbon was determined using Walkley–Black wet digestion method (Nelson and Sommers, 1982). The results shown in Fig. 2 indicate that before OM attack, approximately the same quantity of carbon was observed in both soluble and exchangeable fraction for each soil. Immediately after OM attack by NaOCl, the amount of C drops dramatically and

reaching 0.6, 0.8, 0.5, and 0.7 mg/g for “Birine”, “Khachem”, “Site” and “Hade” soils respectively, then disappears in the succeeding fractions (F4, F5 and F6). Firstly, this proves the advantage of placing the fraction bound to organic matter just after the exchangeable fraction and secondly, this shows the selectivity of the reagent used in the protocol. Concerning the oxide fraction unfortunately, our results in soil analysis section (Table 2) indicate that the amounts of Mn and Fe Oxides in each soil were very weak leading to small leachable quantities of Fe and Mn in the reducible fraction as indicated in Fig. 2. In such conditions, it is difficult to assess the selectivity of the reagent used to dissolve this fraction. However, the concentration of iron in the residual fraction may be attributed to the fact that it is incorporated into the phyllosilicate structure or as goethite or hematite which have resisted to the NH₂OH-HCl attack. For aluminum and silicon, as shown in Fig. 2, there were almost concentrated in the residual fraction F6 of aluminosilicate, indicating that these elements were associated with relatively insoluble mineral phases (clays).

2.3. Sequential extraction of Cs and Sr in studied soils

The concentration with standard deviation of the two elements Cs and Sr observed in each fraction of the four soils as well as the coefficients of variation are grouped in Table 3. Fig. 3 shows also, in terms of percentage, the distribution of the two elements in the four studied soils. Specify that in the present study, eight replicates of 2 g of

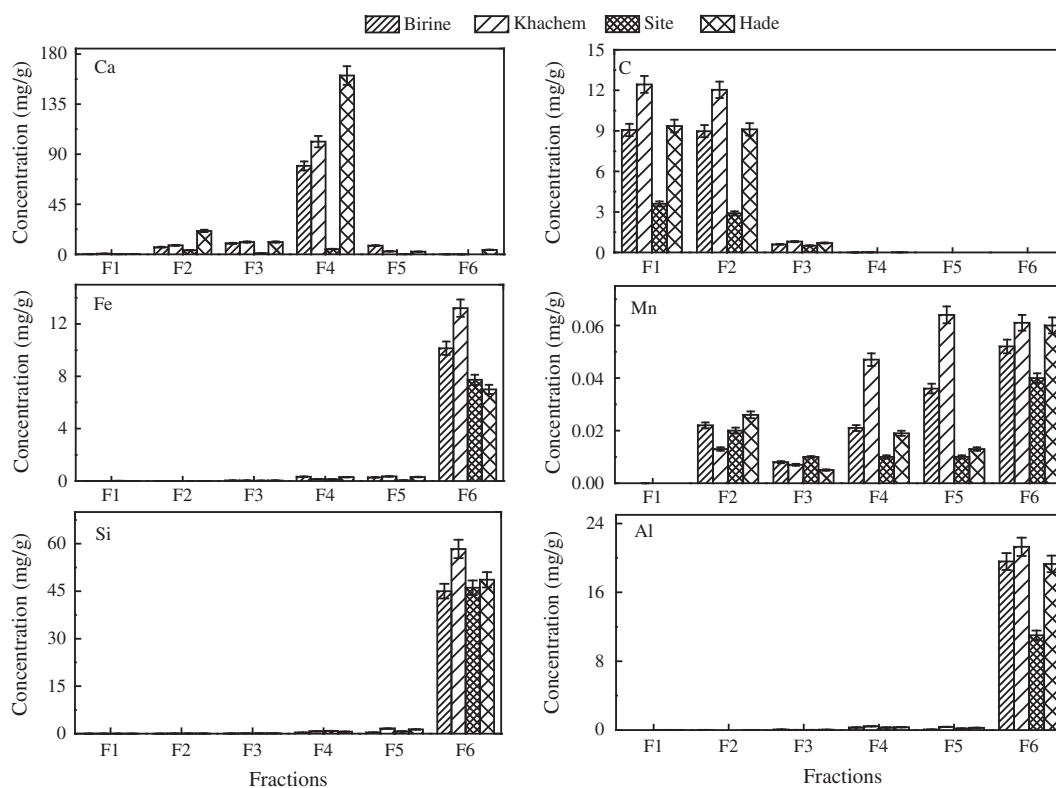


Fig. 2 – Analysis of the stable elements indicators of the targeted phases (Ca, C, Fe, Mn, Al and Si). F1: soluble; F2: exchangeable; F3: Organic matter; F4: carbonates; F5: oxides; F6: residual.

Table 3 – Amounts of Cs and Sr in each extracted fraction for different soils.

Fraction	“Birine”		“Khachem”		“Site”		“Hade”	
	Cs (mg/g)	Sr (mg/g)	Cs (mg/g)	Sr (mg/g)	Cs (mg/g)	Sr (mg/g)	Cs (mg/g)	Sr (mg/g)
Soluble (F1)	0.154 ± 0.036 (23.43%)	0.058 ± 0.003 (5.92%)	0.376 ± 0.016 (4.35%)	0.302 ± 0.005 (1.82%)	0.306 ± 0.053 (17.24%)	0.216 ± 0.016 (7.55%)	0.176 ± 0.015 (8.26%)	0.205 ± 0.011 (5.55%)
Exchangeable (F2)	1.984 ± 0.006 (0.28%)	1.547 ± 0.039 (2.53%)	1.827 ± 0.086 (4.70%)	1.849 ± 0.041 (2.24%)	1.273 ± 0.049 (3.88%)	0.896 ± 0.021 (2.33%)	1.428 ± 0.090 (6.28%)	1.514 ± 0.120 (7.94%)
Organic matter (F3)	1.288 ± 0.040 (3.13%)	0.469 ± 0.035 (7.55%)	1.752 ± 0.126 (7.20%)	1.347 ± 0.148 (10.98%)	1.819 ± 0.200 (10.98%)	0.128 ± 0.009 (6.84%)	1.411 ± 0.113 (8.03%)	0.317 ± 0.033 (10.34%)
Carbonates (F4)	0.237 ± 0.038 (15.91%)	0.413 ± 0.038 (9.13%)	0.328 ± 0.049 (14.96%)	0.897 ± 0.149 (16.65%)	0.067 ± 0.007 (11.02%)	0.056 ± 0.008 (14.22%)	0.218 ± 0.039 (17.90%)	0.178 ± 0.018 (10.11%)
Oxides (F5)	0.011 ± 0.001 (5.71%)	0.027 ± 0.001 (5.32%)	0.121 ± 0.011 (8.74%)	0.129 ± 0.008 (5.99%)	0.030 ± 0.005 (16.27%)	0.003 ± 0.001 (38.50%)	0.040 ± 0.005 (13.43%)	0.004 ± 0.0003 (6.26%)
Residual (F6)	0.241 ± 0.019 (7.69%)	0.009 ± 0.001 (11.88%)	0.324 ± 0.084 (25.96%)	0.014 ± 0.002 (11.41%)	0.131 ± 0.008 (5.92%)	0.007 ± 0.001 (15.31%)	0.388 ± 0.006 (1.51%)	0.033 ± 0.001 (3.00%)
Total (mg/g)	3.91	2.52	4.73	4.54	3.63	1.31	3.66	2.25

Coefficient of variation is shown in parentheses.

each homogenized soil samples were used for every sequential extraction. The coefficients of variation indicated a great homogeneity; they were in most cases less than 15%, except for the fraction corresponding to oxides (F5) for Sr in “Site” soil which presents a reproducibility of above 38% (Table 3). This higher value may be due to the low level of Sr concentration found in this fraction (0.003 ± 0.001 mg/g). As a general, sources of errors are multiples; they may be due to sample loss during sequential extractions, lack of representativity of the soil samples or the measurement uncertainty. Overall, results are satisfactory in terms of reproducibility, in view of the coefficients of variation shown in parentheses in Table 3.

2.3.1. Water-soluble fraction

The results of the soluble fraction (F1) obtained during the application of the modified Schultz protocol for the four soils

are presented in Fig. 3 and Table 3. Recall that this fraction intends to extract water-soluble cesium and strontium weakly bound, *e.g.*, to soluble salts or simply present in the interstitial water. According to the results (Fig. 3), it appeared that cesium is more mobile in “Khachem” (7.95%) and “Site” (8.44%) soils than in “Hade” (4.18%) and “Birine” (3.94%) soils. Dissolution of cesium bearing phases or solid phases into solution with a cation exchanging with Cs in “Site” and “Khachem” soils are plausible explanations. Knowing also that the dissociation reaction of water is natural and spontaneous; water in its molecular form is always associated with oxonium ions ($H_3O^+_{aq}$) and hydroxide (OH^-_{aq}), thus it can also perform cation exchange and extract exchangeable cesium, weakly bound to soil by outer-sphere complex. As in the case of cesium, strontium is also more mobile in the “Site” (16.52%) and to a lesser degree in “Hade” (9.09%) and

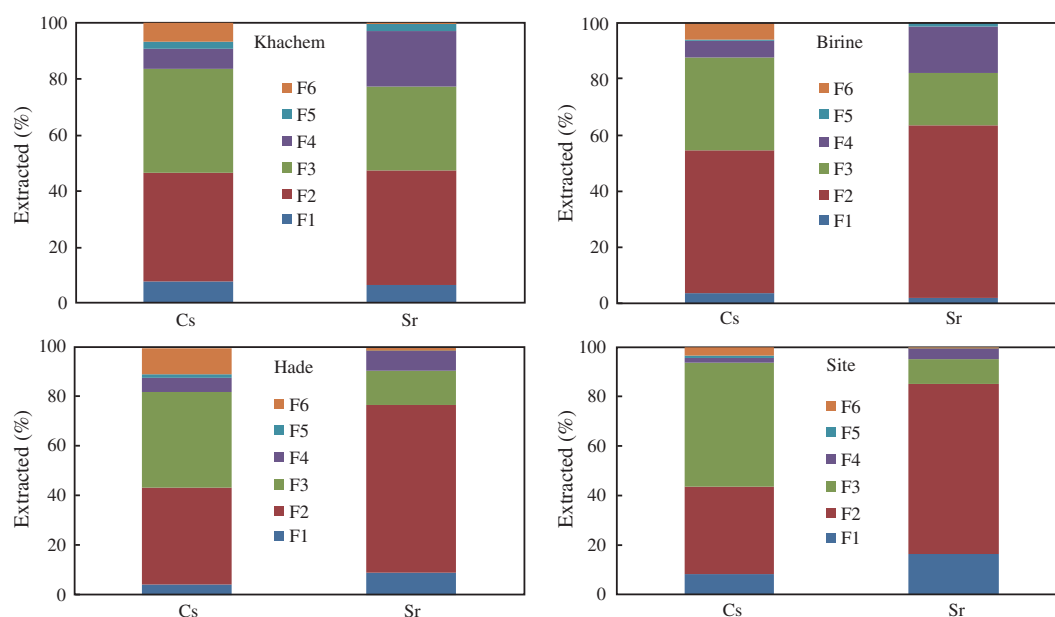


Fig. 3 – Distribution percentages in the six fractions for Cs and Sr using sequential extraction procedure. F1: soluble; F2: exchangeable; F3: Organic matter; F4: carbonates; F5: oxides; F6: residual.

“Khachem” (6.65%). “Birine” with only (3.94%) of water-soluble Sr, like in the case of cesium, remains as the most resistant to the element release in this soluble phase. However, it is foreseeable that the strontium is more mobile than cesium. Hence, Sr under the effect of rainfall should be more available for plant uptake and further migration in all soils, same conclusion was deduced by Forsberg et al. (2001).

2.3.2. Exchangeable fraction

Cesium is generally considered to be less mobile in most geological formations. In soils containing a few percent of organic matter, the partition soil-Cs solution is controlled mainly by an ion exchange mechanism on non-specific sites (Poinssot et al., 1999). This mechanism relates, in particular, to illite and montmorillonite, where appear along frayed edge sites that play an important role in the selective adsorption of Cs (Cornell, 1993). The results (Fig. 3) show a large mobility of cesium in the four soils which resulted in relatively high extraction percentage (“Birine” 50.67%, “Khachem” 38.64%, “Site” 35.10% and “Hade” 39.02%). This may be due to the relatively short period of contamination (one year). It is also important to note that there are some correlations between soil properties and the quantities of extracted cesium (Table 3). For example, “Khachem” (1.827 ± 0.086 mg/g) and “Birine” (1.984 ± 0.006 mg/g) which present higher extracted amount of Cs, their CEC values are higher than those of “Hade” and “Site” (Table 2).

Geochemical behavior of strontium is characterized by a strong mobilization in exchangeable phase (Forsberg et al., 2001). The sorption mechanisms of this element on soils and its mobility in the environment have been widely studied, particularly because of the environmental issues caused by strontium migration. Many authors have found that the strontium interaction with soils, sediments and rocks during transport is mainly governed by cation exchange when the pH is less than 9 (Lefèvre et al., 1993; Jackson and Inch, 1983; Torstenfelt et al., 1982). These findings are quite in agreement with the results obtained in the exchangeable fraction F2 (Fig. 3). Indeed, the rates of extracted strontium are high for all soils, ranging from 40.74% (“Khachem”) to 68.62% (“Site”). In terms of mass concentration, expressed in mg/g (Table 3), the amounts of extracted strontium in decreasing order were: “Khachem” (1.849 ± 0.041) > “Birine” (1.547 ± 0.039) > “Hade” (1.514 ± 0.120) > “Site” (0.896 ± 0.021), it's in agreement with the decreasing order of their CEC in cmol(+)/kg “Khachem” (14.22) > “Birine” (14.06) > “Hade” (11.62) > “Site” (8.31).

When comparing the extracted percentage of cesium and strontium in this fraction (Fig. 3), it shows that strontium is more mobile than cesium; this observation has been already highlighted by several authors (Takeda et al., 2008; Choi et al., 2008; Murali and Mathur, 2002; Sokolik et al., 2001; Dai and Tao, 1999).

2.3.3. Oxidizable fraction

Cesium is known to be relatively mobile in organic soils, particularly when organic matter content is in the order of several tens of percent (Staunton et al., 2002; Wang et al., 2000). The relationship between the sorption of cesium and organic matter is complex, since the presence of a small amount of clay in soil is sufficient to make the sorption

governed mainly by clay specific sites (Rigol et al., 2002). The results of extracted cesium for this fraction are shown in Table 3 and Fig. 3. They indicate, on the one hand, that about half of the cesium content in soils is retained only by the organic phase. On the other hand, the classification of soils according to the decreasing order of Cs extracted quantities (Table 3) (“Khachem” 1.752 ± 0.126 mg/g > “Hade” 1.411 ± 0.113 mg/g > “Birine” 1.288 ± 0.040 mg/g) is in agreement with their organic matter content (Table 2) (“Khachem” 2.14% > “Birine” 1.61% > “Hade” 1.56%) excepting the “Site” soil where the extract was 1.819 ± 0.200 mg/g while the OM value was 0.62%.

In soil, strontium and cesium cations can be adsorbed by the clay-humus complex which reduces their mobility and delay their migration. However, due to its constant competition with calcium often present at levels significantly higher, strontium cannot always form complexes with organic ligands such as humic or fulvic acids (Stevenson and Fitch, 1986). In view of the content of exchangeable calcium in the four soils relatively higher, the results of extracted strontium from this fraction, shown in Fig. 3, were significantly lesser than those of cesium. It should be noted that some of soil properties are also consistent with the amounts of extracted strontium. Indeed, the CEC, the organic matter content and the CEC of the fine fraction with OM (Table 2) vary from one soil to another according to the same order of variation of the extracted quantities of Sr (“Khachem” 1.347 ± 0.148 mg/g > “Birine” 0.469 ± 0.035 mg/g > “Hade” 0.317 ± 0.033 mg/g > “Site” 0.128 ± 0.009 mg/g), organic matter (“Khachem” 2.14% > “Hade” 1.61% > “Birine” 1.56% > “Site” 0.62%) and CEC of the fine fraction with OM (“Khachem” 70.63 cmol(+)/kg > “Birine” 61.11 cmol(+)/kg > “Site” 52.10 cmol(+)/kg > “Hade” 49.3 cmol(+)/kg).

Organic matter, although it is present in small quantities in the four soils, is remarkably involved in the retention of both elements. Indeed, the maximum rates extracted during the oxidizable fraction is more than 50% (“Site”) for Cs and around 30% for Sr (“Khachem”). This is certainly due to the contribution of organo-mineral complexes that humic substances form together with clays.

2.3.4. Carbonates fraction

The elements of this fraction were precipitated or co-precipitated with carbonates (Yong et al., 1993). Several studies have confirmed the adsorption of metals on the carbonates surface in the soil, particularly on the calcite (Zachara et al., 1991). So, there are two mechanisms of metal retention in this fraction (adsorption and precipitation). According to the results shown in Fig. 3, extracts percentages of cesium are low and do not reflect the carbonates content in soils (Table 2) (“Khachem” 10.11%, “Birine” 8.54% and “Hade” with 19.64%). Except the “Site” soil where effectively does not contain much carbonate (2.16%). Even in case of cesium carbonate formation, it is known that most of cesium compounds are soluble including carbonates and hydroxides (Bouzidi et al., 2010), then can be extracted early in the soluble fraction. However, the extracted cesium (“Khachem” 0.328 ± 0.049 mg/g > “Birine” 0.237 ± 0.038 mg/g > “Site” 0.067 ± 0.007 mg/g) varies as function of carbonates content in soil (“Khachem” 10.11% > “Birine” 8.54% > “Site” 2.16%). It is important to note that “Hade” does not followed the previous order

indeed the extracted amount of Cs (0.218 ± 0.039 mg/g) was lesser than “Khachem” and “Birine”, while its content in carbonate was higher (19.64%).

Due to its chemical similarity to calcium, strontium can replace it in the structure of several minerals. Studies have shown that approximately 10% of strontium retained cannot be remobilized (Ohnuki and Kozai, 1994), due to its partial substitution to calcium in mineral species such as calcite or anhydrite. It is known that the celestite (SrSO_4) and strontianite (SrCO_3) are the main two strontium ores. In certain conditions, strontium can form insoluble minerals and replenish its origin ores (celestite and strontianite). In acidic medium, the celestite may precipitate and control the concentration of dissolved Sr^{2+} . While in basic medium, as is the case of our soils, the precipitation of strontianite is capable to control the Sr^{2+} concentration. As shown in Fig. 3, the distribution of strontium in the carbonate phase is relatively higher. This is consistent with what was already mentioned indicating that strontium precipitates as strontianite, co-precipitated in calcite or simply adsorbed in carbonates. As in the case of cesium, the classification of the extracted strontium in decreasing order (“Khachem” 0.897 ± 0.149 mg/g > “Birine” 0.413 ± 0.038 mg/g > “Site” 0.056 ± 0.008 mg/g) is consistent with the carbonates percentage in soils. Except the “Hade” soil, as in the case of Cs, the higher carbonate content ($\approx 20\%$) does not imply significant strontium retention (0.178 ± 0.018 mg g^{-1}). Recall that the carbonates in this soil are as dolomite, a type of mixed carbonate of calcium and magnesium. Few studies refer to this mineral compound especially in the field of cations speciation in soils. Therefore, our interpretation will be based solely on the results obtained in this study, which show that strontium and cesium are much retained by carbonates such as calcite than carbonates such as dolomite.

When comparing Cs and Sr mobility in the carbonate fraction, it's clear that strontium is less mobile than Cs since it is chemically similar to calcium.

2.3.5. Reducible fraction

The reducible material of a soil is mainly composed of iron and manganese oxides, in particular known to fix the metals in trace amounts (Jenne, 1968). Such as clays, metal oxyhydroxides are secondary minerals resulting from weathering processes, slightly soluble in the pH range of soils. They are divided into three size classes: in the form of “coatings”, “bridges” between the various components of the soil or “concretions” as isolated particles (Sposito, 1989).

The results of the present study show that a low quantity of cesium is associated with iron and manganese oxides (“Khachem” 0.121 ± 0.011 mg/g > “Hade” 0.040 ± 0.005 mg/g > “Site” 0.030 ± 0.005 mg/g > “Birine” 0.011 ± 0.001 mg/g). This is probably due to the small amounts of iron and manganese oxides in the four soils (Table 2). Same remarks for strontium, the results show that the desorbed amount during this fraction is extremely low reflecting the low levels of Fe and Mn oxides (“Khachem” 0.129 ± 0.008 mg/g > “Hade” 0.004 ± 0.0003 mg/g > “Site” 0.003 ± 0.001 mg/g > “Birine” 0.027 ± 0.001 mg/g). In conclusion, the amounts of Cs and Sr associated with the reducible fraction are low (Fig. 3) and the consequences of this availability will be minimal.

2.3.6. Residual fraction

The elements in the residual fraction (F6), strongly fixed to soil constituents are considered as unavailable under natural conditions. Cesium is fixed especially inside illite layers on specific sorption sites with an irreversibly reaction.

Amounts of extracted cesium in this fraction (Table 3) (“Hade” 0.388 ± 0.006 mg/g > “Khachem” 0.324 ± 0.084 mg/g > “Birine” 0.241 ± 0.019 mg/g > “Site” 0.131 ± 0.008 mg/g) are relatively low. However, given the contamination time fairly short (1 year) and in view of the extremely slow fixing kinetic of the cesium in specific sites within the interlayer spaces of clays, it may be admitted that these quantities are reasonable. Also note that the desorption percentage of cesium in decreasing order are consistent with the variation of the fine fraction (clay) in the same decreasing order (Table 2) (“Hade” 24.75% > “Khachem” 16.90% > “Birine” 14.73% > “Site” 12.57%).

As regards the kinetic sorption of strontium, most authors distinguish at least two phases in the process:

- (1) Short-term phase (1 hr to 1 day) during which the concentration of sorbed Sr increases rapidly (Torstenfelt et al., 1982)
- (2) Long-term phase (several months to several years) where there is a very slow increase of the sorbed Sr (Torstenfelt et al., 1982).

These two phases correspond to different sorption mechanisms. The rapid sorption phase is generally attributed to ion exchange sites easily accessible on the surface of minerals (Torstenfelt et al., 1982). The second phase generally indicates a slow step of diffusion inside the matrix minerals to more specific sites (Torstenfelt et al., 1982). The contact time between the soil and the Sr solution is therefore an essential data in the characterization of strontium sorption properties in a soil, particularly to evaluate the residual fraction contribution.

Extraction results after one year of contact (“Hade” 0.033 ± 0.001 mg/g > “Khachem” 0.014 ± 0.002 mg/g > “Birine” 0.009 ± 0.001 mg/g > “Site” 0.007 ± 0.001 mg/g) do not appear to reflect widespread diffusion of strontium in aluminosilicates minerals. This can be explained by the slow binding kinetics of strontium as indicated above in long-term phase. In contrast, the decreasing amounts of desorbed Sr in the four soils, as in the case of cesium, translate perfectly their fine fraction content.

3. Conclusions

A sequential extraction procedure, based on Shultz method, for the determination of the geochemical fractionation of Cs and Sr, has been applied to four undisturbed soils, in Ain Oussera region, around the Es-Salam reactor facility, previously contaminated. The selectivity of the extraction protocol was investigated by analyzing some elements (Ca, C, Fe, Mn, Si and Al) indicators of the targeted phases and appeared to be satisfactory. The method produced acceptable results in reproducibility terms, in view of the coefficients of variation that were in most cases less than 15%. The applied sequential extraction procedure revealed that clear proportional correlation was evident between the extracted

amount of Cs and Sr in fractions for each soil and some of their physicochemical properties. The obtained results revealed also that the organic matter, complexed with clay minerals, plays a significant role in the retention of Cs and Sr and constitutes their important pool in the soils.

The extraction data suggest that the availability of Cs for plant uptake and further migration in all soils is less important compared to Sr availability. Indeed, the easily extractible phase including the water-soluble and the exchangeable fraction was: 54.61%, 46.59%, 43.54% and 43.20% for “Birine”, “Khachem”, “Site” and “Hade” respectively. While for strontium is: 63.63%, 47.39%, 85.14% and 76.35% for “Birine”, “Khachem”, “Site” and “Hade” respectively.

Given the relatively short time of contamination (one year) and the low annual rainfall in Ain Oussera region (100–400 mm), it is quite reasonable to expect that the intentionally or accidentally release of Cs and Sr, will be significantly retained by the studied soils. This finding allows concluding that the threat of groundwater contamination by these elements is considerably reduced in long-term and consequently the radiological impact on the environment and human health in the region is insignificant.

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