

Soil sorption of cesium on calcareous soils of Iran

Rayehe Mirkhani^{A,*}, Mohammad Hassan Roozitalab^B, Saadollah Teimouri^A, Naser Khaleghpanah^A

^AAgricultural, Medical and Industrial Research School, Nuclear Science and Technology Research Institute, Atomic Energy Organization of Iran, P.O. Box 31485-498, Karaj, Iran. Email rmirkhani@nrkam.org

^BICARDA- Office, Tehran, Iran

Abstract

The adsorption behaviour of Cs on two selected calcareous soils (clay and silty clay loam) with contrasting physical and chemical characteristics was studied by means of a batch method. Cs sorption characteristic was determined at 22.5 ± 0.5 °C and in the presence of 0.01M CaCl₂. Freundlich isotherms were found to fit well with experimental data for different levels of adsorbed Cs. Results shown that clayey soil adsorbed more Cs higher than soils having silty clay loam texture.

Key Words

Cs adsorption, Calcareous soils, Freundlich isotherm

Introduction

Cs is an important radionuclide for several reasons: it exhibits almost unlimited solubility; its inventory in radioactive waste is significant (Poinssot *et al.* 1999). One of the radioisotopes of cesium, ¹³⁷Cs, is relatively long-lived and poses considerable radioecological problems (Staunton and Roubaud 1997). The main sources of ¹³⁷Cs contamination of soil are global fallout from the atmosphere as a result of atmospheric nuclear weapons testing, ground surface and underground nuclear explosions, and accidental release from nuclear facilities. Along with these large-scale sources of ¹³⁷Cs contamination of soil, there have been some cases of local contamination that might increase the radiation dose to population in nearby areas (Nabyvanets *et al.* 2000). Furthermore, because of its chemical similarity to K, Cs is readily assimilated by terrestrial and aquatic organisms (Poinssot *et al.* 1999). The study of sorption-desorption phenomena of contaminants by soils is of great interest from an environmental and agricultural point of view. The knowledge of sorption-desorption characteristics by soils is useful in predicting transport in soil water systems and uptake by plants (Smolders *et al.* 1997). It is well known that ion exchange reactions occur dominantly between Cs ions and clay minerals. The bio-availability of Cs⁺ in natural systems depends to a large extent on the adsorption properties of the solid phase (Atun and Kilislioglu 2003).

Cesium uptake by plants depends on adsorption/desorption and fixation/release reactions in the soil as well as root uptake processes controlled by the plant. The aqueous chemistry of Cs⁺ in the environment is controlled by sorption reactions to mineral phases, particularly micaceous clay minerals (Francis and Brinkley 1976). Cs⁺ is strongly and selectively sorbed by the phyllosilicate fraction of soils, sediments, and suspended particulates (Tamura and Jacobs, 1960). Cs⁺ engages in ion-exchange reactions with hydrated cations on planar sites on expansible layer silicates (e.g., Smectites) with selectivity and trend selective fashion to wedge or frayed edge sites (FES) that develop along the weathered periphery of micas (e.g., biotite and muscovite) and their immediate weathering products (hydrous-mica, illite) (Zachara *et al.* 2002). In addition to the dependence of Cs sorption on phyllosilicate minerals, Cs sorption correlates also strongly with the cation exchange capacity (Grutter *et al.* 1990). Also, several factors control Cs sorption to soil such as metal concentration, pH, ionic strength and temperature. The adsorption of cesium depends upon the cationic composition of the exchange complex. This is because the so-called adsorption reaction is in fact an exchange phenomenon. Therefore, the adsorption depends upon the relative affinities of Cs and the charge-compensating cations. The order of decreasing affinity is generally reported to be Cs⁺ > NH₄⁺ > K⁺ > Na⁺ > Ca⁺² (Staunton and Roubaud 1997). Zachara *et al.* (2002) reported that the electrolyte cations have competed with Cs⁺ in micaceous subsurface sediments from the Hanfrod site (USA) for both high and low-affinity sites according to the trend K⁺ >>> Na⁺ ≥ Ca⁺². At high concentration, Cs⁺ adsorption occurred only on high-affinity sites. Na⁺ was an effective competitor for the high-affinity sites at high salt concentrations. The adsorption behavior of Cs ions on a montmorillonite-type clay was investigated in the presence of potassium ions by Atun and Kilislioglu (2003). They used Freundlich isotherm parameters to characterize a site distribution function, which provides information about the affinity ratio of adsorption sites of Cs⁺ and K⁺ ions. The addition of K⁺ to the CsCl solution at different concentrations reduced the amount of Cs⁺ adsorbed on clay.

In this study, we will investigate the sorption behavior of Cesium on calcareous soils and the effect of soil solution composition on adsorption.

Materials and Methods

Thirty one soil samples (8 saline-sodic soils and 22 non-saline soil samples) were collected from Karaj and Eshtehard regions in Iran. Soils were classified in the order of Aridisol. The soil samples were dried at room temperature, and then passed through a 2-mm sieve. Particle sizes determination was made using the hydrometer method. Sand fraction was determined by 0.05mm sieve. Soil EC was measured in saturation extract. Organic matter was determined using the Walkley–Black wet digestion method. Cation exchange capacity (CEC) was measured according to the ammonium acetate (pH=7.0) method. Equivalent calcium carbonate was measured using titration method. Water soluble Na and K were determined in saturation extract by flame photometer. Water soluble Ca and Mg were measured by titration method. X-Ray Diffraction (XRD) was employed to study clay mineralogy of selected soils.

In order to give a range of physical and chemical properties, e.g., clay content and cation concentration, affecting Cs sorption, two surface soil samples on the basis of physical and chemical analysis were selected for cesium sorption isotherm studies. One soil was barren with very high EC and SAR (Haplosalids), and the rest were productive soil under wheat culture with low EC and SAR (Haplocambids).

The soil sorption capacity was investigated in this study by batch method. Sorption experiments were performed in 50 ml screw cap centrifuges tubes containing 5 g of soil. The Cs sorption isotherms were done using eight concentration of CsNO₃ in the range of 2 to 16 mg/l, in the presence of 0.01M CaCl₂ as a background electrolyte with the contact time of 3 hour. The ratio of soil to solution was 1:50 (25 ml of solution was mixed with 500 mg of soil) and shaken for three hours using a reciprocating shaker. The suspensions of soil were centrifuged at 4500 rpm for 15 minutes and the supernatant was filtered through Whatman No.42 filter paper. The solutions from the above treatment were analyzed for Cs using an Atomic Absorption Spectrometer (Sparks *et al.* 1996; Xiangke *et al.* 1999).

Results and Discussion

Chemical and physical properties of selected soils are given in table1. The Soil 1 was a saline-sodic soil with high EC, SAR, and high clay content. Soil 2 was a normal soil with lower EC, SAR, and lower clay content. Fitting the average values of experimental adsorption data to Freundlich (Figure 1) and Langmuir adsorption isotherms have shown that in both soils the Frenudlich isotherm describes the sorption for all data with higher R² and lower standard error. This may be due to more assumptions made in the Langmuir model. The distribution coefficient (K_d) Freundlich isotherm for each data set was determined from intercept of the linear form of equation (Table 2).

Results indicated that Soil 1 (saline-sodic soil) adsorbed Cs higher than that by Soil 2 (normal soil) at same Cs concentration (Figure 2). Comparison of both soils showed that Soil 1 has high clay content, CEC and very low dg, whereas silty clay loam soil has lower clay content, lower CEC and higher dg. Soils with high clay fraction (e.g. Soil 1) have a high affinity for sorption of cesium, and the distribution coefficient value was higher than silty clay loam texture (Soil 2). Giannakopoulou *et al.* (2007) confirmed that particle size fractions and especially clay content plays a predominant role on sorption of Cs.

Table1. Chemical and physical properties of selected soils

	Clay (%)	Silt (%)	Sand (%)	Texture	dg	δg	Na ⁺ (mg/L)	K ⁺ (mg/L)	Ca ⁺⁺ (mg/L)	Mg ⁺⁺ (mg/L)
Soil 1	58.85	38.19	2.19	Clay	0.0043	6.27	17627.9	70.05	1372.67	436.27
Soil 2	28.75	51.87	19.37	Silty Clay Loam	0.0208	10.69	79.3	19.92	90.18	37.67

	CEC (meq/100g)	CaCO ₃ (%)	OC (%)	EC (dS/m)	SAR (mmol/L) ^{0.5}	Soil type
Soil 1	17.65	21.15	0.51	60.1	106.13	Saline-Sodic
Soil 2	11.69	22.03	0.97	1.003	1.77	Nonsaline

The particle size and clay mineralogical analyses indicated that the Soil 1 had higher amounts of clay content and vermiculite and illite type clay minerals than Soil 2, which means that there was more surface area to retain more Cs in Soil 1. The affinity of illites and vermiculites for Cs is generally assumed to be due to the presence of frayed edges sites and wedge zones. The results illustrated that the Cs sorption in two selected soils is high; the saline-sodic soil had higher affinity to Cs and higher K_d value, due to its higher clay content and the presence of more vermiculite.

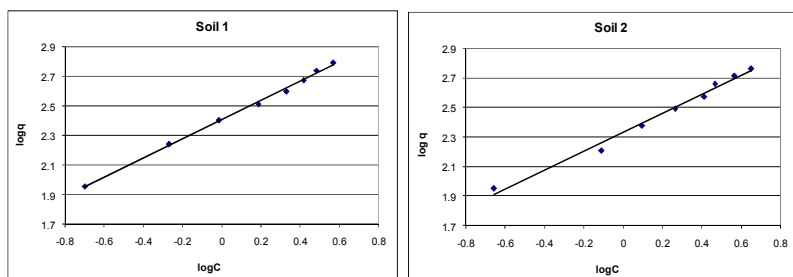


Figure1. Freundlich isotherm (linear curves) of cesium in the Soil 1 and Soil 2.

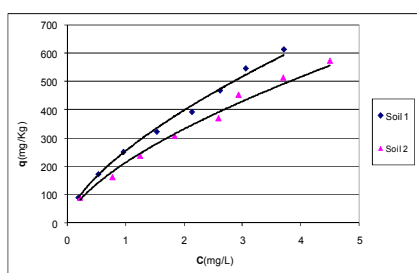


Figure2. Comparison of Freundlich isotherms of cesium in two soils.

Table2. Freundlich isotherm parameters for sorption of Cs on the studied soils.

	K_d	$1/n$	SE	R^2
Soil 1	253.98	0.6468	0.016	0.9972
Soil 2	213.3	0.637	0.033	0.9870

Slope ($1/n$) of fitted lines is less than one and this indicates that the sorption of Cs on these soils is concentration dependent. Table (1) shows that the concentrations of Na, Ca, Mg and K in the saline-sodic soil are respectively 212, 15, 11 and 3.5 times more than that in Soil 2. Bangash (1991) reported that the ability of some cations to depress the adsorption of cesium followed the order of $K^+ > Ca^{+2} > Mg^{+2} > Na^+$. However, saline-sodic soil studied has high cation concentrations, but adsorbed more Cs in different Cs concentrations than that of Soil 2. At initial Cs concentrations, the difference between two soils was relatively low (Figure 2) but in the higher concentrations of Cs, the differences became larger. Decreases in K_d with increasing salt concentration have been observed for various exchange systems (Staunton and Roubaud 1997). One effect of ionic strength that may account for some of the observed change in selectivity is the increase in tactoid size with increasing ionic strength (Van Bladel and Laudelout, 1967). Tactoids are smaller in the presence of monovalent cations such as K and Cs and when the electrolyte concentration is low (Verburg and Baveye 1994). On the other hand, cations specially K ion strongly constrains the Cs adsorption because the cations with similar radius and hydration energy compete more effectively against each other on the Illite and Vermiculite surfaces. Furthermore, evidence shows that because of its lower hydration energy, Cs is adsorbed stronger than K.

Conclusion

The Freundlich isotherm adequately describes the Cs sorption for all experiments, but the Langmuir model is not applicable to describe the adsorption. Cesium sorption on soil minerals depends upon the concentration of Cs in solution, the nature of the mineral surface, ionic strength, and presence of competing ions in the solution phase. The higher CEC and higher amounts of Vermiculite- type clay minerals compensated the negative competitive effects of K on Cs affinity by a saline sodic soil.

References

- Atun G, Kilislioglu A (2003) Adsorption behavior of cesium on montmorillonite-type clay in the presence of potassium ions. *Journal of Radioanalytical and Nuclear Chemistry* **258**(3), 605-611.
- Bangash MA, (1991) Adsorption of fission products and other radionuclides on inorganic exchangers. A thesis of PHD in chemistry, University of the Punjab, Lahore.
- Francis CW, Brinkley FS (1976) Preferential adsorption of ^{137}Cs to micaceous minerals in contaminated freshwater sediment. *Nature* **260**, 511-513.
- Giannakopoulou F, Haidouti C, Chronopoulou A, Gasparatos D (2007) Sorption behavior of cesium on various soils under different pH levels. *Journal of Hazardous Materials* **149**, 553-556.
- Grutter A, von Gunten HR, Kohler M, Rossler E (1990) Sorption, desorption and exchange of cesium on glaciofluvial deposits. *Radiochimica Acta* **50**, 177-184.
- Nabyvanets BY, Gesell TF, Jen MH, Chang WP (2000) Distribution of ^{137}Cs in soil along Ta-han river valley in Tau-Yuan County in Taiwan. *Journal of Environmental Radioactivity* **54**, 391-400.
- Poinssot C, Baeyens B, Bradbury MH (1999) Experimental and modeling studies of cesium sorption on illite. *Geochimica et cosmochimica Acta* **63**, 3217-3227.
- Smolders E, Brande KVD, Merckx R (1997) Concentration of ^{137}Cs and K in soils solution predict the plant availability of ^{137}Cs in soils. *Environmental Science & Technology* **31**, 3432-3438.
- Sparks DL, Page AL, Helmke PA, Leoppert RH, Soltanpour PN, Tabatabai MA, Johnston GT, Sumner ME (1996) Methods of soil analysis, Soil Science Society of American, Madison, Wisconsin, USA.
- Staunton S, Roubaud M (1997) Adsorption of ^{137}Cs on montmorillonite and illite: effect of charge compensating cation, ionic strength, concentration of Cs, K and fulvic acid. *Clay and Clay minerals* **45**(2), 251-260.
- Tamura T, Jacobs DG (1960) Structural implications in cesium sorption. *Health Phys* 2: 391-398.
- Van Bladel R, Laudelout h (1967) Apparent irreversibility of ion-exchange reactions clay suspensions. *Soil Science* **104**, 134-137.
- Verburg K, Baveye p (1994) Hysteresis in the binary exchange of cations on 2:1 clay minerals: A critical review. *Clay and Clay Minerals* **42**, 207-220
- Xiangke W, Wenming D, Jinzhou D, Zuyi T (1999) Sorption and desorption of radiocesium on calcareous soil: Results from batch and column investigations. *Journal of Radioanalytical and Nuclear Chemistry* 783-787.
- Zachara JM, Smith SC, Liu C, McKinley JP, Serne RJ, Gassman PL (2002) Sorption of Cs^+ to micaceous subsurfaces sediments from Hanford site USA. *Geochimica et cosmochimica Acta* **66**(2), 193-211.