Sorption behavior of cesium on various soils under different pH levels

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Abstract

In the present study we investigated the sorption behavior of Cs in four different soils (sandyloam, loam, clayloam and clay) by using batch experiment. Cs sorption characteristics of the studied soils were examined at $4 \, mg \, L^{-1}$ Cs concentration, at various pH levels, at room temperature and with $0.01 \, M \, CaCl_2$ as a background electrolyte. Among different soils the decrease of k_d (distribution coefficient) of cesium, at all pH levels, followed the sequence sandyloam > loam > clayloam > clay, indicating that the particle size fractions and especially the clay content plays predominant role on sorption of Cs. The effect of pH on cesium sorption displays a similar pattern for all soils, depending on soil type. At acid pH levels less cesium was sorbed, due to a greater competition with other cations for available sorption sites. The maximum sorption of Cs was observed at pH 8, where the negative charge density on the surface of the absorbents was the highest. For all soils was observed significantly lower Cs sorption at pH 10.
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1. Introduction

Radiocesium, as a contaminant, has been dispersed into the environment by nuclear weapons testing, nuclear wastes and accidents such as that at Chernobyl in 1986. The interactions of radioactive isotopes of Cs with soils are of concern in environmental studies, due to the high transferability, wide distribution, high solubility, long half-life and the easily assimilation by living organism. As a result of these properties, Cs radionuclides are considered among the most hazardous products of nuclear fission, capable to reach the top of food chain and thus to become a risk factor for human health.

It is assumed that the fate of radionuclides in the environment follows the behavior of stable elements. According to many authors [1,2] the soil-to-plant transfer factor of radioactive Cs is well correlated with that of stable Cs, indicating that the properties of stable Cs in different ecosystems may be regarded as a useful tool in predicting the behavior of [137,134]Cs. Therefore, to facilitate experimental studies on radiocesium sorption and mobility in the environment, the utilization of stable Cs was applied.

Sorption reactions at soil–water interfaces are one of the most important phenomena, which determine the fate, bioavailability, and transport of Cs in aquatic/soil environments and biota. A key factor for Cs sorption is the content of clay and especially the type of clay minerals present in soils [3]. Cesium has very small hydration energy, thus the electrostatic attraction of Cs ions by clay particles is large and therefore are preferentially sorbed [4]. In addition to the dependence of Cs sorption on phyllosilicate minerals, Cs sorption correlates also strongly with the cation exchange capacity [5].

Several factors control Cs sorption to soil such as metal concentration [6], pH [7], ionic strength [8] and temperature [9]. However, the publications on the role of pH on Cs availability are only few and refer mostly to synthetic materials. According to Wang et al. [7] the concentration of surface species (uncharged surface group, positively charged surface group, negatively charged surface group) can be obtained as a function of pH, influencing the Cs sorption. Possible mechanisms of the effect of pH on Cs sorption include the increase of variable negative charge, the modification of metal speciation, the displacement of the equilibrium of surface complexation reaction and the competition of H_3O^+ for negative sites.

The aim of the present work was to investigate the sorption behavior of Cs in four different soils, with different physico-chemical properties and on various pH levels by using the batch

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method. Correct determination of Cs sorption mechanics on soil colloids is important for understanding the fate of this pollutant in environment and will facilitate successful environmental remediation procedures.

2. Materials and methods

2.1. Soil analysis

Four surface soil samples from Northern Greece were chosen in order to give a range of physical properties, e.g., clay content affecting Cs sorption. The soils were air-dried, passed through a 2 mm sieve and stored before analysis.

Particle size analyses were made using the hydrometer method with a 2 h reading for clay content [10]. Soil pH was measured in a 1:1 soil/distilled water (w/v) suspension [11]. Organic matter was determined using the Walkley–Black wet digestion method [12]. Cation exchange capacity and exchangeable K were measured according to the ammonium acetate (pH 7.0) method [13,14]. The soil samples were treated in triplicate and the means reported.

2.2. Sorption experiments

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 each soil. One concentration, 4 mg L^{-1} of CsCl, was prepared in the presence of 0.01 M $CaCl_2$ as a background electrolyte, at room temperature. In order to adjust the desirable pH 30 ml of buffer solution at pH 5, 7, 8 and 10 was added. The ratio of mass of soil to volume of solution was 1:10. After shaking for 16 h the solution was immediately separated from suspensions by centrifuging [15]. The solutions from the above treatment were analyzed for Cs using a Varian SpectrAA-300 atomic absorption spectrometer [16]. In all cases, standards (stock standard solution of 1.000 $\mu g\, ml^{-1}$ concentration) and blank were always treated in the same way as the samples to minimize matrix interferences during the analysis.

Absorbed cesium concentrations in the solid phase were determined from the difference between the initial Cs concentration and the equilibrium concentration. The background electrolyte solution was used to simulate natural soil conditions where there is often a large excess of Ca ions. This background electrolyte was intended to minimize the nonspecific sorption of Cs so that specific sorption will predominate. The sorption experiments were conducted in duplicate and the means reported.

The equilibrium distribution coefficient (k_d) was used to characterize Cs sorption:

$$k_d = \frac{C_s}{C_l}$$

where C_s is the amount of sorbate sorbed per unit mass of absorbent (mg g^{-1}) and C_l is the equilibrium solution concentration (mg ml^{-1}).

Table 1
Physicochemical properties of the selected soils ($n = 3$)

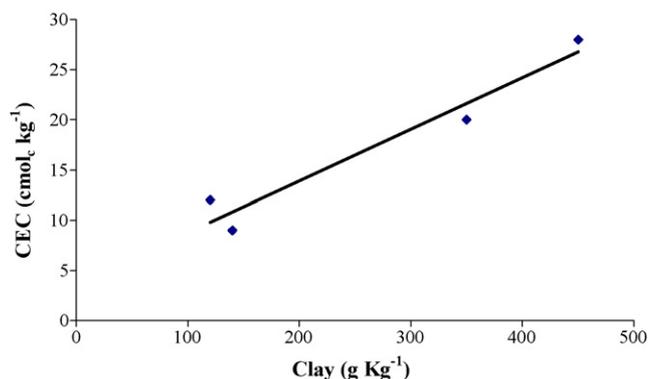|	Soil 1	Soil 2	Soil 3	Soil 4
Particle size analysis (g kg^{-1})				
Clay	140	350	450	120
Silt	240	310	200	400
Sand	620	340	350	480
Texture	SL	CL	C	L
pH (1:1) (s/w)	5.6	6.5	7.2	7.8
Organic Matter (%)	1.14	3.97	2.32	1.61
C.E.C. (cmol$_c$ kg^{-1})	9	20	28	12
Exchangeable K^+ (cmol$_c$ kg^{-1})	0.19	0.59	0.54	0.19

Fig. 1. Correlation between clay content and CEC of the studied soils.

3. Results and discussion

Selected physicochemical properties of the studied soils are presented in Table 1. The soils were either slightly acidic or alkaline (pH > 5.5) and contained various amounts of organic matter. Exchangeable K, as an index of soil available K for plant uptake in all cases was low, although the soils 2 and 3 contained three times more potassium than soils 1 and 4. Sand content ranged between 340 and 620 g kg^{-1} and clay contents between 120 and 450 g kg^{-1}. The cation exchange capacity (CEC) was highly correlated to clay content ($r = 0.97^{***}$, $p < 0.05$; Fig. 1).

The effect of soil type on Cs sorption was highly significant, at all pH levels. The k_d values indicate that the clay soil (soil 3) exhibit the higher sorption of Cs, followed by the clayloam (soil 2) and the loam soil (soil 4) (Table 2). The minimum sorption of Cs was displayed by sandyloam soil (soil 1), with the lowest CEC (Table 1). In order to evaluate the relationships between the k_d and soil parameters, correlation analysis was employed. The results showed that the particle size distribution plays an important role on sorption of Cs and that the distribution coefficient

Table 2
Distribution coefficient k_d (ml g^{-1}) of Cs on studied soils under different pH levels

pH	Soil 1	Soil 2	Soil 3	Soil 4
5	11.73	20.56	89.50	20.21
7	11.06	21.90	23.20	16.04
8	49.35	135.50	209.80	75.47
10	10.57	24.45	54.10	15.72

Table 3
Correlation coefficient between k_d of Cs under the different pH levels and clay content of studied soils

pH	Clay content
5	0.79
7	0.90[*]
8	0.96[**]
10	0.90[*]

[*] $p < 0,1$.
[**] $p < 0,05$.

exhibited a certain correlation with clay content in all pH values (Table 3). This supports the hypothesis that the clay fraction of soils, which consists by sheet silicate minerals, has a high affinity for sorption of Cs [15]. The 2:1 layer silica minerals in soils and sediments and especially illite is considered to be a major factor in Cs selectivity and sorption [17]. X-ray diffraction data have shown that the mineralogical composition of soil 3 dominated by the presence of 2:1 phyllosilicate clay minerals (illite and vermiculite), interpreting the high sorption capacity of this soil (unpublished data).

The affinity of illite for Cs is generally assumed to be due to the presence of frayed edge sites (FES). Their strong affinity for Cs is due to the small hydration energy of the cation, inducing total or partial collapse of clay layers [18].

Several authors have also found that Cs sorption related to soil physicochemical characteristics, such as CEC, clay content, pH and potassium availability [19,20].

The pH of aqueous solution in batch experiments is an important factor for the sorption of metals by geochemical materials. The pH dependence of Cs sorption on four studied soils, at an initial Cs concentration $4 \, mg \, L^{-1}$, is showed by a k_d versus pH plot (Fig. 2). The effect of the pH on Cs sorption displays a similar pattern for all studied soils, depending on soil type.

The k_d is relative low at acid pH and this may be attributed to H^+ competition for available Cs^+ sorption sites. According to Tamura and Jacobs [21], H^+ ions are effective in removing Cs^+ ions that are fixed at the lattice edges of clay minerals. In addition at the acid pH levels there is a greater dissolution of clay minerals with a destruction of some of the sites responsible for fixing Cs^+ resulting to lower cesium sorption. Heinrich [22], suggests that the acidic nature of soils increase the bioavailability of Cs. As illustrated by Fig. 2, at pH 7 very little sorption occurs. Under
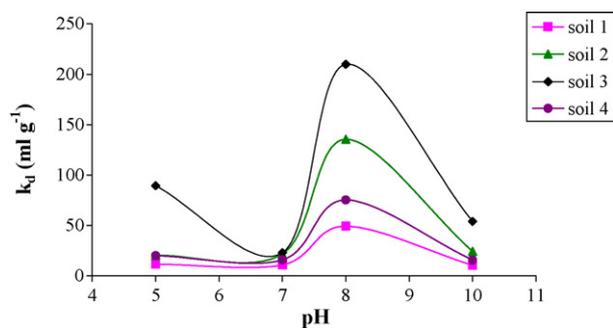
these specific experimental conditions, it can be also supported that the four soils exhibit a similar behavior when the pH is neutral.

The results of the present work showed that the maximum sorption of Cs was observed at pH 8. The high sorption levels of Cs indicate a high fixation capacity of the studied soils for cesium ions in this pH region. According to the values of k_d, it seems that the clay soil (soil 3) was influenced greatly from the changes of the pH. The k_d of clay soil at pH 8 was higher by a factor of 4 compared with the respective k_d of the sandyloam soil (soil 1).

The increase in k_d for pH 8 is ascribed to the significant high negative charge density of the clay minerals. As pH increasing, the number of protons on the soil surface decreasing and more electrostatically attractive surface to the cations occur, allowing more Cs^+ to be sorbed. Wang et al. [23] found that at high pH, Cs sorption on bentonite may be dominated by surface complexation and thus the distribution coefficient of Cs is higher at high pH values than those at low pH. According to Oscarson et al. [24] less Cs is sorbed at pH 5 than at pH 8.5.

Significantly less Cs sorbed by the studied soils at pH 10. A possible formation of carbonate or hydroxide species at this high pH level is likely to caused complexation of Cs^+ ions resulting to lower Cs amount of available for sorption [25].

4. Conclusions

Based on our results, the increase of pH affects the mechanisms of Cs sorption by clay fraction, thus controlling the fate and the mobility of Cs. At low pH values the sorption is relative low for all soils. This is of great concern, since the acidification of soils (use of fertilizers, acid rain etc.) can cause the Cs in soils to desorb and thus become more bioavailable in the environment.

Acknowledgements

Fig. 2. The k_d values of Cs as a function of pH of four studied soils.

References

[1] H. Tsukada, H. Hasegava, S. Hisamatsu, S. Yamasaki, Transfer of Cs and stable Cs from paddy soil to polished rice in Aomori, Japan, J. Environ. Radioact. 59 (2002) 351–363.
[2] S. Yoshida, Y. Muramatsu, M. Dvornik, A. Zhuchenko, I. Linkov, Equilibrium of radiocaesium with stable caesium within biological cycle of contaminated forest ecosystems, J. Environ. Radioact. 75 (2004) 301–313.
[3] M.A. Shenber, A. Eriksson, Sorption behaviour of caesium in various soils, J. Environ. Radioact. 19 (1993) 41–51.
[4] N.L. Hakem, I.Al. Mahamid, J.A. Apps, G.J. Moridis, Sorption of cesium and strontium on Hanford soil, J. Radioanal. Nucl. Chem. 246 (2000) 275–278.
[5] A. Grütter, R.H. Von Gunten, M. Kohle, E. Rössler, Sorption, desorption and exchange of cesium on glaciofluvial deposits, Radiochim. Acta 50 (1990) 177–184.
[6] S.A. Adeleye, P.G. Clay, M.O.A. Oladipo, Sorption of caesium, strontium and europium ions on clay minerals, J. Mater. Sci. 29 (1994) 954–958.

[7] X. Wang, T. Rabung, H. Geckeis, Effect of pH and humic acid on the adsorption of cesium onto g-Al$_2$O$_3$, J. Radioanal. Nucl. Chem. 258 (2003) 83–87.

[8] M. Frury, S. Czigany, G. Chen, J.B. Harsh, Cesium migration in saturated silica sand and Hanford sediments as impacted by ionic strength, J. Contam. Hydrol. 71 (2004) 111–126.

[9] C. Liu, J.M. Zachara, O.Q. Qafoku, S.C. Smith, Effect of temperature on ^{137}Cs sorption and desorption in subsurface at the Hanford Site, U.S.A., Environ. Sci. Technol. 37 (2003) 2640–2645.

[10] G.W. Gee, J.W. Bauder, Particle-size analysis, in: A. Klute (Ed.), Methods of Soil Analysis. Part 1, 2nd ed., ASA, SSSA, Madison, WI, 1986, pp. 383–411, Agron. Monogr. 9.

[11] E.O. McLean, Soil pH and Lime Requirement, in: A.L. Page, et al. (Eds.), Methods of Soil Analysis, Part 2, ASA, SSSA, Madison, WI, 1982, pp. 199–223, Agron. Monogr. 9.

[12] D.W. Nelson, L.E. Sommers, Total Carbon, Organic Cardon and Organic Matter, in: A.L. Page, et al. (Eds.), Methods of Soil Analysis. Part 2, ASA, SSSA, Madison, WI, 1982, pp. 539–577.

[13] J.D. Rhoades, Cation exchange capacity, in: A.L. Page, et al. (Eds.), Methods of Soil Analysis. Part 2, ASA, SSSA, Madison, WI, 1982, pp. 149–157, Agron. Monogr. 9.

[14] G.W. Thomas, Exchange cations, in: A.L. Page, et al. (Eds.), Methods of Soil Analysis. Part 2, ASA, SSSA, Madison, WI, 1982, pp. 159–164, Agron. Monogr. 9.

[15] L.S. Campbell, B.E. Davies, Soil sorption of cesium modelled by the Langmuir and Freundlich isotherm equation, Appl. Geochem. 10 (1995) 715–723.

[16] D.S. Veresoglou, J.T. Tsialtas, N. Barbayiannis, G.C. Zalidis, Caesium and strontium uptake by two pasture plant species grown in organic and inorganic soils, Agr. Ecosyst. Environ. 56 (1995) 37–42.

[17] C.W. Francis, F.S. Brinkley, Preferential adsorption of ^{137}Cs to micaceous minerals in contaminated freshwater sediments, Nature 260 (1976) 511–513.

[18] B.L. Sawhney, Selective sorption and fixation of cations by clay minerals: a review, Clay Miner. 20 (1972) 93–100.

[19] P. Schuller, J. Handl, R.E. Trumper, Dependence of ^{137}Cs soil to plant transfer factor on soil parameters, Health Phys. 55 (1988) 575–577.

[20] K.E. Bergeijk, H. Van Noordijk, J. Lembrechts, M.J. Frissel, Influence of pH, soil type and soil organic matter on soil to plant transfer of radiocaesium and strontium as analyzed by a non parametric method, J. Environ. Radioact. 15 (1992) 275–286.

[21] T. Tamura, D.G. Jacobs, Structural implications in cesium sorption, Health Phys. 2 (1960) 391–398.

[22] G. Heinrich, Uptake and transfer factor of ^{137}Cs by mushrooms, Radiat. Environ. Bioph. 31 (1992) 39–49.

[23] X. Wang, X. Tan, C. Chen, L. Chen, The concentration and pH dependent diffusion of ^{137}Cs in compacted betonite by using capillary method, J. Nucl. Mater. 345 (2005) 184–191.

[24] D.W. Oscarson, R.L. Watson, H.G. Miller, The interaction of trace levels of cesium with montmorillonitic and illitic clays, Appl. Clay Sci. 2 (1987) 29–39.

[25] M. Gutierrez, H.R. Fuentes, A mechanistic modeling of montomorillonite contamination by cesium sorption, Appl. Clay Sci. 11 (1996) 11–24.