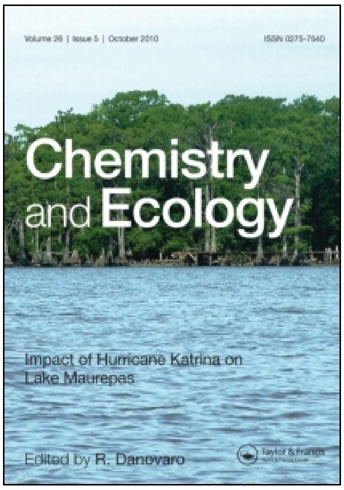

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Retention of ^{137}cesium in acid sulphate soils of South Central Thailand

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RETENTION OF ^{137}CESIUM IN ACID SULPHATE SOILS OF SOUTH CENTRAL THAILAND

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(In final form 5 April 2004)

Adsorption and desorption of ^{137}Cs by acid sulphate soils from the Nakhon Nayok province, South Central Plain of Thailand located near the Ongkarak Nuclear Research Center (ONRC) were investigated using a batch equilibration technique. The influence of added limestone (12 and 18 tons ha^{-1}) on ^{137}Cs adsorption–desorption was studied. Based on Freundlich isotherms, both adsorption and desorption of ^{137}Cs were nonlinear. A large portion (98.26–99.97%) of added ^{137}Cs ($3.7 \times 10^3 - 7.03 \times 10^5$ Bq l^{-1}) was sorbed by the soils with or without added lime. The higher lime treatments, however, favoured stronger adsorption of ^{137}Cs as compared with soil with no lime, which was supported by higher K_{ads} values. The addition of lime, the cation exchange capacity and pH of the soil increased and hence favoured the stronger adsorption of ^{137}Cs. Acid sulphate soils with a high clay content, medium to high organic matter, high CEC, and predominant clay types consisting of a mixture of illite, kaolinite, and montmorillonite were the main soil factors contributing to the high ^{137}Cs adsorption capacity. Competing cations such as NH_4^+, K^+, Na^+, Ca^{2+}, and Mg^{2+} had little influence on ^{137}Cs adsorption as compared with liming, where a significant positive correlation between K_{ads} and soil pH was observed. The ^{137}Cs adsorption–desorption characteristics of the acid sulphate soils studied exhibited a very strong irreversible sorption pattern. Only a small portion (0.09–0.58%) of ^{137}Cs adsorbed at the highest added initial ^{137}Cs concentration was desorbed by four successive soil extractions. Results clearly demonstrated that Nakhon Nayok province acid sulphate soils have a high ^{137}Cs adsorption capacity, which limits the ^{137}Cs bioavailability.

Keywords: Acid sulphate soil; Adsorption; Batch equilibrium technique; Cesium-137; Desorption; Freundlich isoterm; Limed soil

1 INTRODUCTION

There is no natural source of ^{137}Cs in the environment. Its presence in the environment is primarily from nuclear testing or release from nuclear reactors. Atmospheric nuclear testing in the 1950 and 1960s, along with some accidental releases, has led to the contamination of soils with environmental relevant radioactive isotopes including ^{137}Cs (Singh and Gilkes, 1990). The nuclear accident at Chernobyl (26 April 1986) released a considerable

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quantity of ^{137}Cs into the atmosphere. As a result, ^{137}Cs behaviour in soils or sediments has received increasing attention. ^{137}Cs has a physical half-life of 30 years, and its beta decay is accompanied by gamma-ray release of moderate energy. Because of its similarities with potassium, the ^{137}Cs isotope has the potential to be rapidly transferred into the food chain. Because of its environmental concern, ^{137}Cs poses a potential threat to populations inhabiting contaminated environment sites. The limits of ^{137}Cs in drinking water recommended by the World Health Organization (WHO, 1988) and International Atomic Energy Agency (IAEA, 2000) in emergency exposure situations and the exemption level of ^{137}Cs in disposal materials (IAEA, 1996) are listed in Table I. Examples of toxicity of ^{137}Cs to aquatic species are also shown in the same table.

In both terrestrial and aquatic ecosystems, strong binding of ^{137}Cs to soils and sediments reduces its mobility and consequently its assimilation by biota (Singh and Gilkes, 1990). It can be shifted to human populations by root uptake by plants or by drinking of ground water. Cesium in general is strongly adsorbed in most soils. However, certain soil conditions can enhance the mobility and availability of cesium (Evans *et al.*, 1983). Soil characteristics, such as pH, Eh, clay content and organic matter, CEC, and the potassium content determine the capacity for cesium sorption by soils and sediments (Nishita *et al.*, 1956, 1962; Schulz *et al.*, 1959; Frysinger and Thomas, 1960; Fredriksson *et al.*, 1966; Fredriksson, 1970; Pardue *et al.*, 1989; Anderson and Roed, 1994).

Adsorption and desorption processes in soils are important processes controlling the behaviour of trace elements and radionuclides in the terrestrial environment. These processes play an important role in determining the bioavailability, potential mobility, and remobilization of ^{137}Cs and other radionuclides in soils or sediments. Transport and mobility are related to the physical and chemical properties of the radionuclide and the soil material. Sorption studies of radioactive nuclides are important in predicting movement of nuclides from radioactive waste sites to the ground-water environment (Shenber and Eriksson, 1993). Adsorption and desorption of stable cesium and radiocesium in soils or sediments have been documented in previous studies (e.g. Pardue *et al.*, 1989; Singh and Gilkes, 1990; Maguire *et al.*, 1992; Shenber and Eriksson, 1993; Kirikopoulos *et al.*, 1994; Valcke and Cremers, 1994; Wauters *et al.*, 1994; Campbell and Davies, 1995; Ioannides *et al.*, 1996; Stephens *et al.*, 1998; Fuhrmann *et al.*, 2001). Currently, there is a lack of information on radionuclides adsorption and desorption behaviour in acid sulphate soils in Thailand, where there is growing use of radioactive isotopes in many fields, including nuclear reactor facilities.

The aims of this study were: (1) to determine the adsorption and desorption capacity of ^{137}Cs in representative acid sulphate soils in the Nakhon Nayok province, Thailand, located near a proposed nuclear research center; (2) to determine the influence of liming of acid sulphate surface soils on adsorption and desorption of ^{137}Cs; and (3) to identify soil properties governing ^{137}Cs adsorption and desorption.

TABLE I Some standards for ^{137}Cs concentrations allowed in drinking water and disposal materials.

Parameters	*Activity of ^{137}Cs*	*Organization*
(1) ^{137}Cs in drinking water (applied for radiation accident or emergency exposure situations).	700 Bq l^{-1} (This is applied for some nuclides including ^{137}Cs based on drinking-water consumption of 700 l per year for adults. The calculated value is based on an effective dose of 5 mSv.)	WHO, 1988
	1000 Bq l^{-1} (The use of this level is for the first year following a nuclear or radiological emergency.)	IAEA, 2000
(2) Exemption level of ^{137}Cs for disposal materials.	10 Bq g^{-1}	IAEA, 1996

2 MATERIAL AND METHODS

2.1 Study Site

The Ongkarak Nuclear Research Center (ONRC) is located in the Ban Sai Mun subdistrict, Ongkarak district, Nakhon Nayok province (latitude 14° 7′ 13.2″ N and longitude 101° 1′ 46.8″ E), in South Central Thailand (Fig. 1). The site is approximately 105 km from Bangkok, and the total area of ONRC is approximately 50,000 m^2. Land uses surrounding the site are primarily agriculture, including paddy rice, shrimp farming, vegetable and fruit production. The center is currently under construction and will be completed in the near future with a 10 MW capacity nuclear reactor. The nuclear facility focus will be on the production of radionuclides for medical uses and research and development applicable to the field of agriculture, industry and environment. Radioactive by-products including ^{137}Cs in waste water released by routine operations or accidents have the potential to contaminate environments such as soil, water and agricultural areas near the nuclear research center.

2.2 Soil Characterization and Sampling

Approximately 1.5 million hectares of acid sulphate soils occur in Thailand. The South Central Plain contains 896,000 ha. The remaining (604,000 ha) are located in various regions near the coast of Thailand (Anurakpongsatorn, 1998). Nakhon Nayok province located in South Central Plain of Thailand contains 103,000 ha of acid sulphate soil (Anurakpongsatorn, 1998).

Three series of acid sulphate soils located within a 5 km radius of the ONRC were sampled. The representative soil groups sampled were Rangsit series, Rangsit very acid series, and Ongkarak series (Fig. 1). Two layers of the soils were used in this study: 0–20 cm of topsoil and 20–40 cm of subsoil. The soils were air-dried and crushed, and

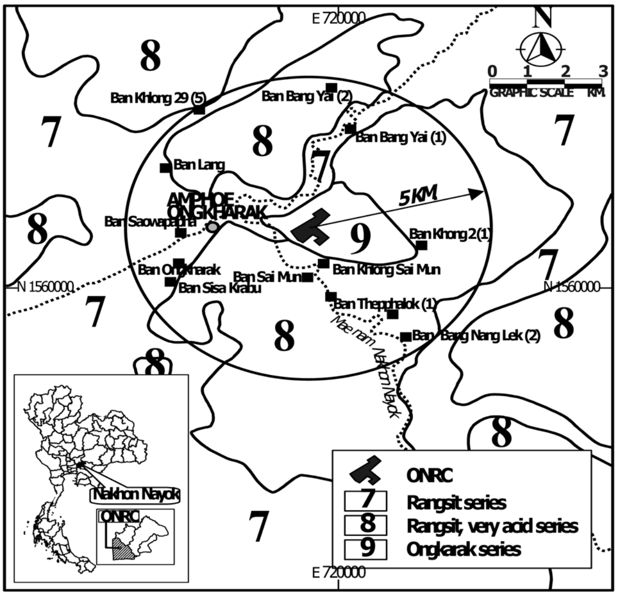

FIGURE 1 Location of study area and sampling boundary of within a radius of 5 km.

any plant debris removed. The dried soils were ground using mortar and screened to pass through a 2 mm sieve. Both physical and chemical properties of the soils were analysed using standard methods. Soil characteristics quantified include: pH in water: soil ratio of 1:1 using a glass electrode pH meter (Klute, 1982); organic matter by the Walkley and Black method; NH_4^+-N by the 1 M KCl method; CEC by the ammonium acetate saturation method (Chapman and Pratt, 1961); exchangeable cations (Ca^{2+}, Mg^{2+}, Na^+, K^+) by leaching with 1 N ammonium acetate and atomic adsorption spectrometer; total Fe and Al by X-ray fluorescence; particle size distribution (percentage sand, silt, and clay) by pipette method; and clay type by X-ray diffraction method. Activity of ^{137}Cs in the soils was determined by neutron activation analysis and gamma-ray spectrometry method, respectively.

2.3 Soil Liming

Because of the low indigenous pH of acid sulphate soils used, farmers generally lime the 0–20 cm topsoil and wait for 1 or 2 months before planting. To duplicate such practice, in this study, the topsoil samples were mixed with limestone (99% $CaCO_3$) at rates of 12 and 18 tons ha^{-1}, the recommended rate for increasing soil pH in these agriculture soils (Attanandana and Vacharotayan, 1984). The adsorption–desorption studies in this experiment began two weeks following lime addition.

2.4 Preparation of ^{137}Cs Solution

Eleven initial concentrations of carrier-free ^{137}Cs aqueous solution were prepared by diluting the standard isotope solution with deionized water. The ^{137}Cs activity ranged from 3.7×10^3 to $7.03 \times 10^{\ 5}$ Bq l^{-1}. The concentrations of ^{137}Cs used in the study were in the range of low-level radioactive waste water classified by IAEA (1970).

2.5 Equilibration Time Study

To determine the time for ^{137}Cs to reach equilibrium in soil solution, a study was conducted using one topsoil and one subsoil of the Ongkarak soil series. The equilibration time studied ranged from 30 min to 24 h (30 min, 1, 5, 10, 15, 20, and 24 h). Only one activity of ^{137}Cs (1.79×10^5 Bq l^{-1}) was used to determine the sorption and equilibrating time.

2.6 Adsorption–Desorption Studies

Batch equilibrium adsorption experiments using added ^{137}Cs radioisotope were used to generate adsorption relationships. Two grams of soil (dried to a constant weight at 60 °C) were placed into a 50 ml Nalgene centrifuge tube. The adsorption experiments were conducted in duplicate at 27 ± 2°C. Eleven initial concentrations of ^{137}Cs in a form of $^{137}CsCl$ in solution varying from 3.7×10^3 to 7.03×10^5 Bq l^{-1} were prepared as described previously. Twenty milliliters of the $^{137}CsCl$ of various concentrations in aqueous solution was added to the soil samples in the centrifuge tubes, and the tubes were capped. The samples were shaken at 100 rpm over the predetermined equilibrate time, then centrifuged for 10 min at 10,000 rpm. The 24 h shaking time was chosen to ensure equilibrium based on our equilibration time study. After equilibrium was reached, the pH of each sample was measured. Ten milliliters of clear supernatant was withdrawn carefully with a micropipette, taking care not to disperse the very light thin film of soil on top of the soil surface, into the small plastic bottle. The activity of ^{137}Cs in clear supernatant was determined using a gamma-ray spectrometer at 662 keV using a Li (Ge) detector and a multichannel analyser (Pardue *et al.*, 1989). The counting time was sufficient to ensure that the counting error was less than 5%. Two replicate blank samples (1: distilled water with only a soil sample; 2: ^{137}Cs aqueous solution without a soil sample) were also analysed to correct for any activity associated with ^{137}Cs fallout in the soil and ^{137}Cs adsorption by the bottle wall, respectively. The amount of ^{137}Cs sorbed by the soils was calculated by subtracting the initial concentration from the amount remaining in aqueous solution following equilibration. All results were decay-corrected to the date of equilibrating times. The adsorption isoterm using Freundlich equation as described by Sposito (1989) was employed in this study at equilibrium between ^{137}Cs sorbed by soil and left in soil solution as follows:

$$x/m = KC^{1/n}$$

or

$$\log x/m = \log K + 1/n \log C,$$

where x/m is the amount of ^{137}Cs adsorbed per unit of soil (Bq g^{-1}), and C is the equilibrium amount of ^{137}Cs in aqueous solution (Bq l^{-1}). The intercept of the Freundlich equation as indicated by the '*K*' value represents the degree of affinity or adsorption capacity, whereas the adsorption slope ($1/n$) provides an estimate of adsorption intensity or rate of adsorption. The nonlinear regression analysis (power model) was employed to determine the values of K and $1/n$. Although the Freundlich equation is empirical, a theoretical derivation for the equation has been used, assuming that the absolute value of the free enthalpy or the heat of adsorption decreases with increasing surface coverage due to surface heterogeneity or to particle interaction (Harmsen, 1982). It is reasonable to assume that such a mechanism may also apply to the sorption of cesium by soils (Singh and Gilkes, 1990).

The desorption experiments using distilled water were carried out in duplicate using the soil residue from the adsorption experiments. Only the soil treatment with the highest initial activity of ^{137}Cs was chosen for use in the desorption experiment, since there was strong soil adsorption of low ^{137}Cs activity measured. Desorption studies were carried out immediately (without allowing the soils to dry) following the 24 h adsorption experiment. After adsorption was complete, the supernatants were replaced by the same volume of the distilled water containing no carrier-free ^{137}Cs. The centrifuge tubes were agitated to disperse the soils, and the suspensions were shaken for 24 h under the same conditions as those described in the adsorption studies. The desorption process was repeated for four successive 24 h equilibration cycles for each sample. The ^{137}Cs concentrations in the desorption solutions were measured using a gamma-ray spectrometer following each desorption cycle. The activity of ^{137}Cs remaining adsorbed on the soil at each desorption cycle was calculated as the difference between the initial concentration of ^{137}Cs adsorbed and the amount of ^{137}Cs desorbed. Four successive desorption measurements were made in duplicate. Desorption isoterm was constructed using the Freundlich equation in a similar manner to the adsorption isoterm.

2.7 Statistical Analysis

In order to evaluate the relationships between the measured Freundlich adsorption or desorption rate (K_{ads}) and soil parameters, a correlation analysis (Pearson test) was employed. The correlation analysis included an average of two replications for each data point.

3 RESULTS AND DISCUSSION

3.1 Soil Characterization

The physico-chemical properties of the topsoil and subsoils of the studied area are shown in Table II. According to the soil classes defined by the Soil Conservation Services (SCS) and U.S. Environmental Protection Agency (U.S. EPA) (Boulding, 1994), characteristics of soils in the studied area can be classified as follows: extremely acid (pH 3.4–4.0), high CEC (>20 meq 100^{-1} g) and moderately low to high organic matter content (1.8 to $> 4\%$). High percentage of clay content ($>50\%$) was observed for all soils with having clay texture. The clay types in the soils studied are mixture of illite, kaolinite, montmorillonite and vermiculite. Based on chemical analyses these soils contained high plant nutrients level. However, due to very acid condition and high Fe content (2–4.8%) liming the soils are common practice to increasing soil pH to the level necessary for optimizing nutrients release and controlling concentration of cationic micronutrients such as Fe, Mn, and Zn which can be toxic to plants.

3.2 Sorption Equilibration Time

Results for the preliminary kinetic study determining ^{137}Cs equilibrium time is shown in Fig. 2. ^{137}Cs was rapidly absorbed onto soil within the first 30 min and remained constant at 24 h. Accordingly a reaction time of 24 h was used in determining ^{137}Cs equilibration for the soils studied. Similar equilibration time (24 h) for cesium adsorption/desorption studies has been used in previous studies (Balwant and Gilkes, 1990; Shenber and Eriksson, 1993; Campbell and Davies, 1995).

3.3 ^{137}Cs Adsorption

Selected Freundlich isoterm plots for ^{137}Cs adsorption by the three topsoils and subsoils without lime and with added lime (12 and 18 tons ha^{-1}) are displayed in Fig. 3. The adsorption isoterms were plotted using equilibration concentration in aqueous solution (Bq l^{-1}) on the x-axis and the amount sorbed by soil (Bq g^{-1}) on the y-axis. The Freundlich equation (power model) was used in data evolution. The adsorption capacity (K_{ads}) and intensity ($1/n_{\text{ads}}$) parameters obtained from the plots are shown in Table III. Results fitted well with the Freundlich equation, as indicated by the statistically significant coefficient of the determination (R^2) ($P < 0.01$ and $P < 0.05$). It is evident from the fitted lines and the values of the correlation coefficients that the Freundlich equation adequately describes the ^{137}Cs adsorption phenomena in the soil studied.

The K_{ads} values for both topsoils and subsoils without lime ranged from 3.15 to 8.04, whereas the $1/n_{\text{ads}}$ values ranged from 0.8464 to 0.9956. The K_{ads} values for all topsoils limed at 12 tons ha^{-1} ranged from 15.07 to 18.61 and from 24.77 to 29.59 at 18 tons ha^{-1}, whereas the $1/n_{\text{ads}}$ values of all topsoils limed at a rate of 12 tons ha^{-1} ranged from 0.8133 to 0.8614 and from 0.7449 to 0.8569 at 18 tons ha^{-1}. The variation in the K_{ads} and $1/n_{\text{ads}}$ values indicated that the soils varied in both capacity and intensity (rate) to adsorb ^{137}Cs. The sequences of the K_{ads} values for the three series of the soils with lime and no added lime were RT-L2 > RT-L1 > RT > RS, RVT-L2 > RVT-L1 > RVT > RVS, and OT-L2 > OT-L1 > OS > OT. The $1/n_{\text{ads}}$ values can be arranged in the following order: RS > RT-L1 > RT-L2 > RT, RVT > RVS > RVT-L1 > RVT-L2, and OT > OS > OT-L1 > OT-L2. The measured K_{ads} values clearly demonstrated that the capacity of ^{137}Cs sorbed into the topsoils with no added lime was lower than the topsoils

TABLE II Physical and chemical characteristics of the studied soils.

	*Soil code**					
Parameters analysed	*RT*	*RS*	*RVT*	*RVS*	*OT*	*OS*
Soil depth (cm)	0–20	20–40	0–20	20–40	0–20	20–40
Stable Cs (mg kg^{-1})	6.0	6.4	5.9	6.3	5.9	6.2
pH	4.0	3.7	3.7	3.5	3.4	3.5
OM (%)	4.43	1.80	2.89	2.90	2.24	2.89
NH_4^+ –N (mg kg^{-1})	14.4	9.8	24.0	15.0	11.6	12.0
Total Fe (%)	2.24	3.83	3.76	3.46	4.79	3.92
Total Al (%)	0.46	0.54	0.56	0.55	0.57	0.55
CEC (meq 100 g^{-1})	28.33	24.97	29.71	27.58	24.15	24.74
Exchangeable cations (meq 100 g^{-1})						
Ca^{2+}	1.00	1.17	1.77	1.25	1.16	2.18
Mg^{2+}	1.98	3.25	2.36	2.78	2.07	2.36
Na^+	0.76	1.19	0.42	0.93	0.67	0.89
K^+	0.29	0.21	0.42	0.28	0.37	0.23
Particle size distribution						
Sand (%)	8.6	7.8	2.8	1.2	3.1	3.1
Silt (%)	33.5	31.1	37.1	36.0	36.1	38.7
Clay (%)	61.1	60.1	62.8	60.8	57.9	58.2
Texture class	Clay	Clay	Clay	Clay	Clay	Clay
Clay type						
Kaolinite	Small	Small	Small	Small	Small	Small
Illite	Small	Small	Small	Small	Small	Small
Montmorillonite	Trace	Trace	Trace	Trace	Trace	Trace
Vermiculite	Trace	Trace	Trace	Trace	Trace	Trace
Quartz	Trace	Trace	Trace	Trace	Trace	Trace
Goethite	Trace	Trace	Trace	Trace	Trace	Trace
Interstratified 10 and 14 Å	Trace	Trace	Trace	Trace	Trace	Trace
Feldspar	Trace	–	–	–	–	–

*RT: Rangsit topsoil; RS: Rangsit subsoil; RVT: Rangsit very acid topsoil; RVS: Rangsit very acid subsoil; OT: Ongkarak topsoil; OS: Ongkarak subsoil.

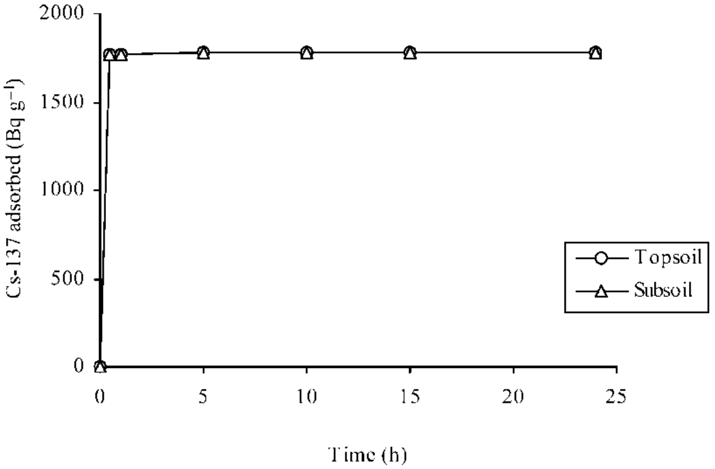

FIGURE 2 Equilibrating time required for ^{137}Cs adsorbed by Ongkarak soils.

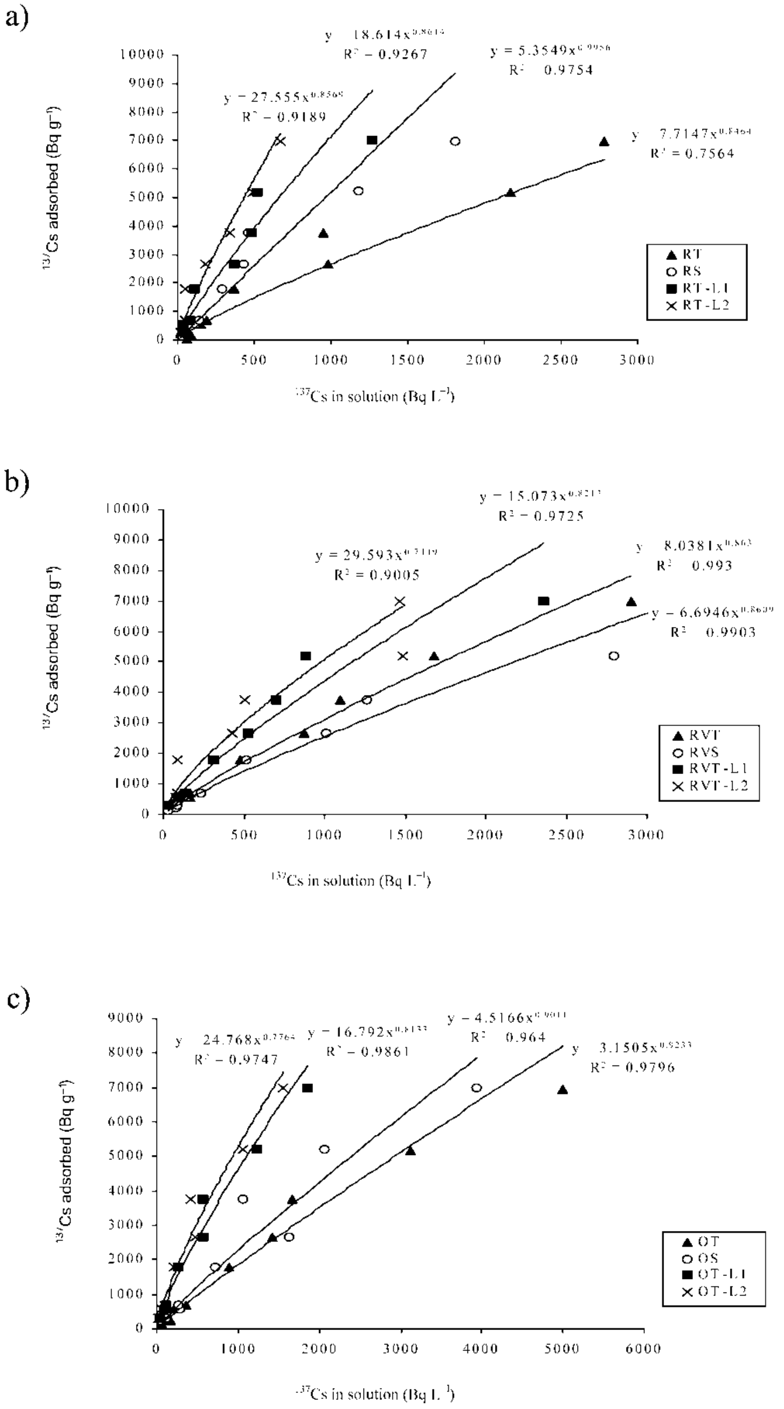

FIGURE 3 Freundlich adsorption isoterms of ^{137}Cs from studied soils. (a) RT: Rangsit topsoil; RS: Rangsit subsoil; RT-L1: Rangsit topsoil with liming 12 tons ha^{-1}; RT-L2: Rangsit topsoil with liming 18 tons ha^{-1}; (b) RVT: Rangsit highly acidic topsoil; RVS: Rangsit highly acidic subsoil; RVT-L1: Rangsit highly acidic topsoil with liming 12 tons ha^{-1}; RVT-L2: Rangsit highly acidic topsoil with liming 18 tons ha^{-1}; (c) OT: Ongkarak topsoil; OS: Ongkarak subsoil; OT-L1: Ongkarak topsoil with liming 12 tons ha^{-1}; OT-L2: Ongkarak topsoil with liming 18 tons ha^{-1}.

TABLE III Freundlich adsorption parameters for ^{137}Cs from studied soils and some relating parameters.

Soil series	*Treatment by limestone*	*Soil code*[†]	*Depth (cm)*	*Soil pH*	K_{ads}	$1/n_{ads}$	R^2	*Percentage adsorption*[‡]
Rangsit	No	RT	0–20	4.0	7.71	0.8464	0.7564*	98.26–99.93
	No	RS	20–40	3.7	5.35	0.9956	0.9754**	99.74–99.88
	12 tons ha^{-1}	RT-L1	0–20	4.71	18.61	0.8614	0.9267**	99.82–99.94
	18 tons ha^{-1}	RT-L2	0–20	5.22	27.56	0.8569	0.9189**	99.91–99.97
Rangsit very acid	No	RVT	0–20	3.7	8.04	0.8630	0.9930**	99.59–99.81
	No	RVS	20–40	3.5	6.69	0.8609	0.9903**	99.47–99.77
	12 tons ha^{-1}	RVT-L1	0–20	4.25	15.07	0.8213	0.9725**	99.66–99.89
	18 tons ha^{-1}	RVT-L2	0–20	4.90	29.59	0.7449	0.9005**	99.72–99.95
Ongkarak	No	OT	0–20	3.4	3.15	0.9233	0.9796**	99.29–99.62
	No	OS	20–40	3.5	4.52	0.9011	0.9640**	99.23–99.72
	12 tons ha^{-1}	OT-L1	0–20	4.27	16.79	0.8133	0.9861**	99.74–99.89
	18 tons ha^{-1}	OT-L2	0–20	4.61	24.77	0.7764	0.9747**	99.78–99.93

[†] RT: Rangsit topsoil; RS: Rangsit subsoil; RT-L1: Rangsit topsoil with liming 12 tons ha^{-1}; RT-L2: Rangsit topsoil with liming 18 tons ha^{-1}; RVT: Rangsit very acid topsoil; RVS: Rangsit highly acidic subsoil; RVT-L1: Rangsit highly acidic topsoil with liming 12 tons ha^{-1}; RVT-L2: Rangsit highly acidic topsoil with liming 18 tons ha^{-1}; OT: Ongkarak topsoil; OS: Ongkarak subsoil; OT-L1: Ongkarak topsoil with liming 12 tons ha^{-1}; OT-L2: Ongkarak topsoil with liming 18 tons ha^{-1}.

[‡] Percentage of initial ^{137}Cs added ranging from 3.7×10^3 to 7.03×10^5 Bq l^{-1}.

*, **Significant at $P < 0.05$ and $P < 0.01$, respectively.

treated with 12 and 18 tons ha^{-1} of limestone. Results showed that by raising the pH of soils, ^{137}Cs adsorption was increased. Wild (1995) reported that the capacity of soils to hold exchangeable cations depends on the pH. It has been reported that soils with a lower pH are less favourable for cesium sorption (Campbell and Davies, 1995). However, the high percentages (98.26–99.97%) of ^{137}Cs adsorbed in the soils in this study (even in non-limed soils with low pH (3.4–4.0)) suggest that the clay texture, high CEC, and high organic matter of these acid sulphate soils are the dominant variables controlling ^{137}Cs adsorption. Generally, CEC is related to soil clay content, type of clay, and organic matter (Shenber and Eriksson, 1993; Tan, 1994).

Increases in liming rates in soils result in higher values for the K_{ads} and lower values for $1/n_{ads}$. The higher K_{ads} values of the soils corresponded to a lower concentration of ^{137}Cs in the soil solution. These results support increases in the potential to retain ^{137}Cs in soil, thus reducing the bioavailability and mobility. A mobility study by Schimmack and Bunzl (1989) showed that cesium mobility decreased in limed soils. The higher K_{ads} and lower $1/n_{ads}$ values of the limed soils with a higher pH would be expected with a higher CEC. This rate of lime application increases the adsorption of ^{137}Cs in the acid sulphate topsoils. The increase in adsorption of ^{137}Cs in soils is associated with the increase in CEC of the soils by raising the pH (Adriano *et al.*, 1984; IAEA, 1994). This is a result of the dissociation of some of the functional groups, particularly those of the organic matter, which increases with increasing pH, thus providing more negatively charged sites for cation exchange (IAEA, 1994).

In order to evaluate the relationships between the measured Freundlich adsorption rate (K_{ads}) and soil parameters, a correlation analysis (Pearson test) was employed. The *r*-values obtained are presented in Table IV. A highly significant positive correlation was obtained between the K_{ads} value and the soil pH ($r = 0.957^{**}$, $P < 0.01$) indicated that the adsorption capacity of the soils for ^{137}Cs increased with increasing soil pH (3.40–5.22). In addition, the significant positive correlation between the K_{ads} and CEC value ($r = 0.958^{**}$, $P < 0.01$) measured indicated that the adsorption capacity of the soils for ^{137}Cs increased with increasing CEC of the soils (24.15–29.71 meq 100 g^{-1}). This would suggest that the pH and CEC of the soils strongly influence the adsorption capacity for ^{137}Cs.

TABLE IV Correlation coefficients between Freundlich adsorption parameters and soil characteristics ($n = 12$).

Soil characteristics	K_{ads}
Stable Cs (mg kg^{-1})	−0.100 n.s.
PH	0.957**
% OM	0.609 n.s.
NH_4–N	0.716 n.s.
CEC	0.958**
Total Fe	0.427 n.s.
Total Al	−0.619 n.s.
Exchangeable Ca^{2+}	−0.080 n.s.
Exchangeable Mg^{2+}	−0.011 n.s.
Exchangeable Na^{+}	−0.306 n.s.
Exchangeable K^{+}	0.228 n.s.
% Sand	0.180 n.s.
% Silt	−0.134 n.s.
% Clay	0.948**

*Correlation is significant at $P < 0.05$.
**Correlation is significant at $P < 0.01$.
n.s.: not significant ($P > 0.05$).

A significant positive correlation between the Freundlich adsorption rate and clay content was measured in this study ($r = 0.948^{**}$, $P < 0.01$). A high percentage of adsorption was observed in the soils with high clay contents (57.9–62.8%). This is consistent with the observation that some inorganic components of soil, particularly clays, have a large capacity of adsorbing and retaining cesium (Anderson and Roed, 1994). The clay minerals found in acid sulphate soils in this study are dominated by illite, kaolinite, and montmorillonite. The influence of clay types on the adsorption of ^{137}Cs in these soils is explained by the relative uniform distribution of the three clay soil groups.

There was no significant correlation between the K_{ads} value and organic matter content (1.8–4.43%). However, in general, a higher percentage of adsorption was measured for soils with a medium to high organic matter content. This phenomenon may be attributed to the fact that ^{137}Cs sorption is largely dependent on the mineral phase, even in soils with a high organic matter content (Shand *et al.*, 1994; Rigol *et al.*, 1999).

There was also no significant correlation between Freundlich adsorption parameters and total Fe (2.24–4.79%) and total Al (0.46–0.57%) in the soils used in this study. This is consistent with the study by Campbell and Davies (1995), which found that the cesium, unlike other heavy metals, does not have an affinity to sorb onto, or coprecipitate with, Fe oxide.

To evaluate the potential risk of ^{137}Cs to human in the vicinity of ONRC by direct ingestion of ground-water from the contaminated soils, the measured ^{137}Cs retention capacity of the studied soils (using the measured Freundlich adsorption isotherms) (Fig. 3) and the reported limits of ^{137}Cs concentrations in drinking water recommended by WHO (700 Bq l^{-1}) and IAEA (1000 Bq l^{-1}) (Table I) were compared. Based on the regulatory limits for ^{137}Cs in drinking water (700 l year^{-1} consumption) and the measured ^{137}Cs retention capacities of acid sulphate soils of 1300, 3100, and 3900 Bq g^{-1}, respectively, for non-limed and limed presence at 12 and 18 tons ha^{-1}, ^{137}Cs activity in soil solution would be below the reported limits for ^{137}Cs in drinking water.

3.4 ^{137}Cs Desorption

The desorption isoterms of ^{137}Cs of the soil are shown in Fig. 4. The desorption parameters illustrated by K_{des} and $1/n_{\mathrm{des}}$ are listed in Table V. The desorption data were statistically fitted with the Freundlich equation ($P < 0.01$ and $P < 0.05$). It was found that the Freundlich desorption constant (K_{des}) for ^{137}Cs was much larger than the respective adsorption constant (K_{ads}), and the $1/n_{\mathrm{des}}$ values, an index of the intensity or rate of desorption, were much smaller than the $1/n_{\mathrm{ads}}$ values for all soils (with and without liming). Such results indicate that the activation energies for ^{137}Cs desorption were much larger than those for adsorption ($K_{\mathrm{des}} > K_{\mathrm{ads}}$), and the rates of desorption were much slower than the rates of adsorption ($1/n_{\mathrm{des}} > 1/n_{\mathrm{ads}}$). These results show that ^{137}Cs is strongly retained by adsorption mechanism for both limed and non-limed soils.

The K_{des} values of the topsoils and subsoils receiving no lime ranged from 6449 to 6840, whereas the $1/n_{\mathrm{des}}$ values ranged from 0.0022 to 0.0105. The K_{des} values of the topsoils limed at a rate of 12 and 18 tons ha^{-1} ranged from 6864 to 6966 and from 6883 to 6968, respectively, whereas the $1/n_{\mathrm{des}}$ values ranged from 0.0007 to 0.0026 and from 0.0004 to 0.0023, respectively. The difference in the desorption capacity in the soils with lime and non-lime presence may be related to the difference in strengths of ^{137}Cs retention attributed to differences in soil characteristics as mentioned earlier in the adsorption studies. The sequences of the K_{des} values for the soils with lime and non-lime presence were RT-L2 > RT-L1 > RS > RT, RVT-L2 > RVT-L1 > RVT > RVS, and OT-L2 > OT-L1 > OT > OS, whereas the $1/n_{\mathrm{des}}$ values can be arranged in the following order: RS > RT-L1 > RT-L2 > RT, RVT > RVS > RVT-L1 > RVT-L2, and OT > OS > OT-L1 >

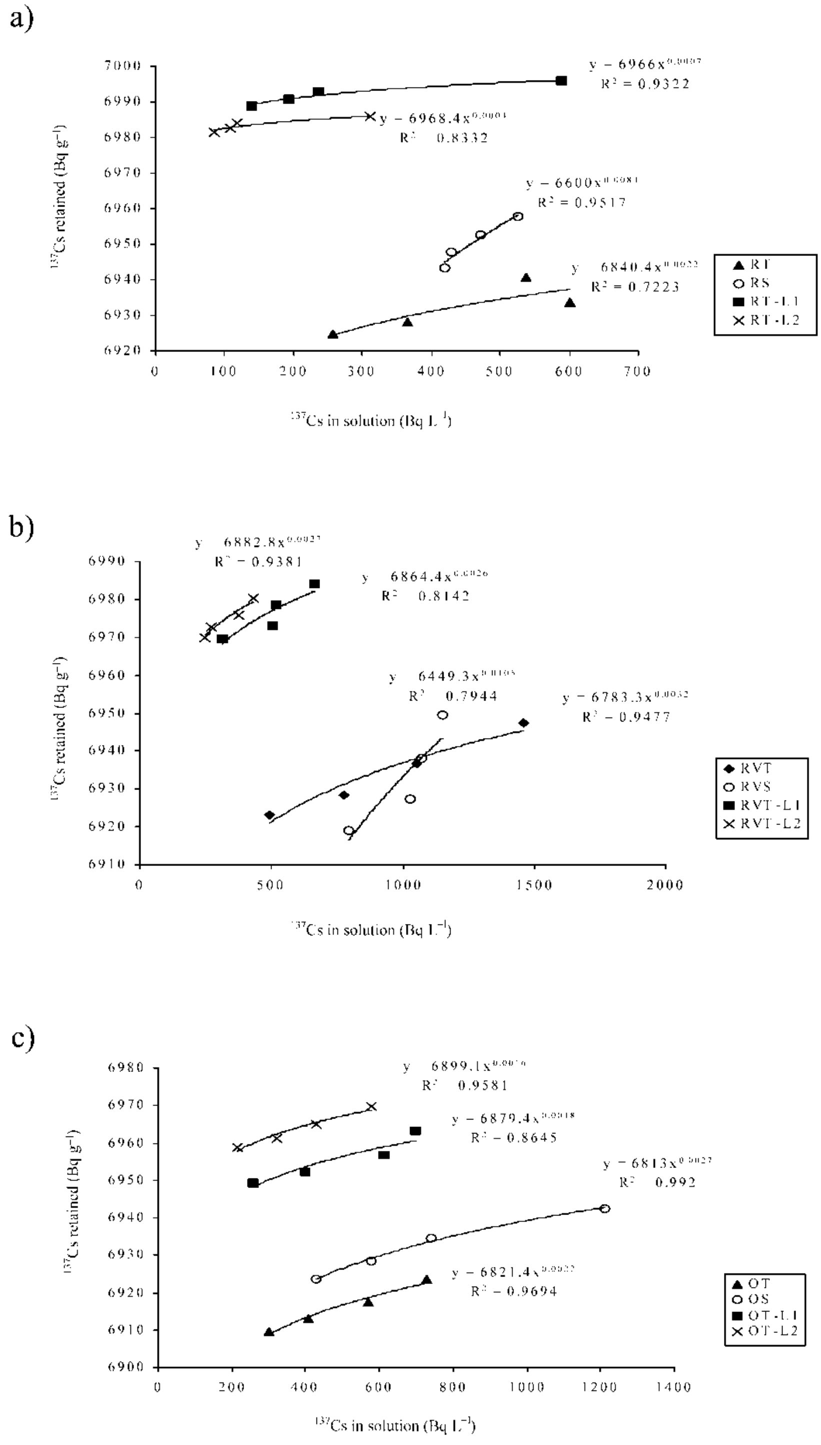

FIGURE 4 Freundlich desorption isoterms of ^{137}Cs from studied soils (a) RT: Rangsit topsoil; RS: Rangsit subsoil; RT-L1: Rangsit topsoil with liming 12 tons ha^{-1}; RT-L2: Rangsit topsoil with liming 18 tons ha^{-1}; (b) RVT: Rangsit highly acidic topsoil; RVS: Rangsit highly acidic subsoil; RVT-L1: Rangsit highly acidic topsoil with liming 12 tons ha^{-1}; RVT-L2: Rangsit highly acidic topsoil with liming 18 tons ha^{-1}; (c) OT: Ongkarak topsoil; OS: Ongkarak subsoil; OT-L1: Ongkarak topsoil with liming 12 tons ha^{-1}; OT-L2: Ongkarak topsoil with liming 18 tons ha^{-1}.

TABLE V Freundlich desorption parameters for ^{137}Cs and total amount of ^{137}Cs desorbed from studied soils.

Soil series	*Soil code*†	*Initial amount adsorbed (Bq g^{-1})*	K_{des}	$1/n_{des}$	R^2	*Total amount*	*Desorbed*
Rangsit	RT	6970	6840	0.0022	0.7223*	25.80	0.37
	RS	6981	6600	0.0084	0.9517**	18.46	0.27
	RT-L1	7004	6966	0.0007	0.9322**	11.60	0.17
	RT-L2	6991	6968	0.0004	0.8332*	6.22	0.09
Rangsit highly acidic	RVT	6981	6783	0.0032	0.9477**	37.75	0.54
	RVS	6980	6449	0.0105	0.7944*	40.45	0.58
	RVT-L1	6993	6864	0.0026	0.8142*	19.99	0.29
	RVT-L2	6986	6883	0.0023	0.9381**	13.19	0.19
Ongkarak	OT	6948	6821	0.0022	0.9694**	20.01	0.29
	OS	6972	6813	0.0027	0.9920**	29.57	0.43
	OT-L1	6972	6879	0.0018	0.8645*	19.59	0.28
	OT-L2	6977	6899	0.0016	0.09581**	15.42	0.22

†RT: Rangsit topsoil; RS: Rangsit subsoil; RT-L1: Rangsit topsoil with liming 12 tons ha^{-1}; RT-L2: Rangsit topsoil with liming 18 tons ha^{-1}; RVT: Rangsit highly acidic topsoil; RVS: Rangsit highly acidic subsoil; RVT-L1: Rangsit highly acidic topsoil with liming 12 tons ha^{-1}; RVT-L2: Rangsit highly acidic topsoil with liming 18 tons ha^{-1}; OT: Ongkarak topsoil; OS: Ongkarak subsoil; OT-L1: Ongkarak topsoil with liming 12 tons ha^{-1}; OT-L2: Ongkarak topsoil with liming 18 tons ha^{-1}.

*, **Significant at $P < 0.05$ and $P < 0.01$, respectively.

OT-L2. The lower desorption constant (K_{des}) and the higher rate of desorption ($1/n_{des}$) of the soils correspond to a high concentration of ^{137}Cs in the soil solution. The results showed that the higher liming rate, the higher the desorption constant (K_{des}) and the lower the rate of desorption ($1/n_{des}$). The percentages of cumulative desorption of all soils with lime and non-lime presence were very low in all cases (0.09–0.58%). This suggested that the adsorption of ^{137}Cs was not totally reversible under these experimental conditions. In addition, the amount of ^{137}Cs released from the non-lime soils and limed soils from application of the equivalent of 12 and 18 tons ha^{-1} from the first to the fourth cycle extractions was 471–1020, 290–491, and 155–386 Bq l^{-1}, respectively. The highest concentration (1020 Bq l^{-1}) of ^{137}Cs released from non-limed soils is slightly higher than the IAEA standard (Table I) for drinking water (1000 Bq l^{-1}, respectively). For the two lime treatments (12 and 18 tons ha^{-1}), the amount of ^{137}Cs released is lower than the standards for drinking water (WHO and IAEA). Higher lime-application rates lead to less ^{137}Cs release. These results indicate that it would be safe for people to ingest water directly from acid sulphate soils (limed and non-limed presence) contaminated with ^{137}Cs. The large amount of ^{137}Cs adsorbed (6972–7004 Bq g^{-1}) would result in little ^{137}Cs in soil solution (Table V).

Figure 5 shows the cumulative amount of ^{137}Cs desorbed from the experimental soils with lime and no added lime. In those graphs, the cumulative amount of ^{137}Cs desorbed from the different soils (Bq g^{-1}) is plotted against the cycle of extractions (four extractions). The patterns of desorption of all experiment soils suggested that the amounts of ^{137}Cs desorbed gradually decreased, reaching a steady state after four cycles (96 h) of extractions especially for the limed topsoils with two liming rates. The ^{137}Cs found in the first extract would certainly correspond to the readily exchangeable form found on the non-specific ion exchange surface sites, which can be released by desorption. Also, it is reasonable to assume that ^{137}Cs released by further extraction is much more difficult, perhaps existing in non-exchangeable or the selective binding site, or that it can be released only by breakdown of the clay structure. However, the mechanism of desorption is not clear due to the clay types of acid sulphate soils with the mixed illite, kaolinite, and montmorillonite.

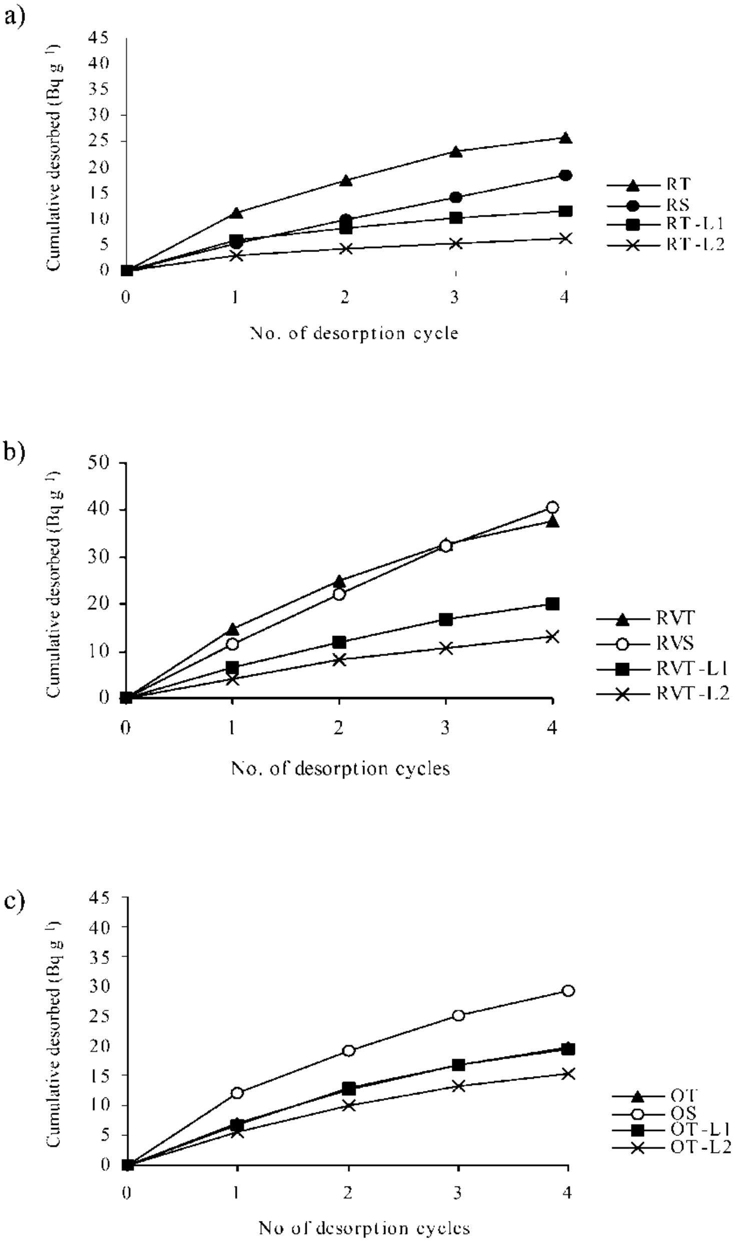

FIGURE 5 Cumulative desorbed amounts of ^{137}Cs from studied soils (a) RT: Rangsit topsoil; RS: Rangsit subsoil; RT-L1: Rangsit topsoil with liming 12 tons ha^{-1}; RT-L2: Rangsit topsoil with liming 18 tons ha^{-1}; (b) RVT: Rangsit highly acidic topsoil; RVS: Rangsit very acid subsoil; RVT-L1: Rangsit highly acidic topsoil with liming 12 tons ha^{-1}; RVT-L2: Rangsit highly acidic topsoil with liming 18 tons ha^{-1}; (c) OT: Ongkarak topsoil; OS: Ongkarak subsoil; OT-L1: Ongkarak topsoil with liming 12 tons ha^{-1}; OT-L2: Ongkarak topsoil with liming 18 tons ha^{-1}.

4 CONCLUSIONS

The results from this study show that ^{137}Cs is strongly adsorbed (98.26–99.97%) by acid sulphate soils in both limed and non-limed soils. Liming, however, did increase the amount of ^{137}Cs adsorption. Because of the high clay content, high CEC, and medium to high organic matter, these acid sulphate soils have a high affinity to adsorb ^{137}Cs. Desorption of ^{137}Cs from these soils was extremely slow (0.09–0.58%). The strong adsorption capacity of these acid sulphate soils would reduce the potential contamination of ^{137}Cs in both surface water and groundwater, should a release from the nuclear research center (ONRC) occur.

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