Parameters Affecting [137]Cs Migration within Soil Profile

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Several studies have been carried out on the adsorption, distribution and migration of ^{137}Cs within soil profile in the vicinity of the Nuclear Research Center, Atomic Energy Authority, Egypt, in addition to Ismailia Canal areas. The soil physicochemical and mineralogical characteristics were carried out and indicated that the soil samples consist mainly of sand (quartz) and silt fractions. The kinetics of caesium adsorption and its related adsorption isotherms for the tested soils were also studied. The sorption of ^{137}Cs by soil minerals markedly affects its migration rate. The natural background of both locations under study indicated that the ^{137}Cs concentration in the reactor site were found to be 30.82 Bq/kg while that at the canal site was found to be 0.87 Bq/kg. [137]Cs in the reactor site may be originated from the fallout and from the external contamination which affected the background level. The vertical distribution and the migration rate of ^{137}Cs have been studied for the soil profiles in both locations. These rates were found to be 0.056 and 0.031 cm/year for the reactor and canal site respectively.

Introduction

Baseline information of radiation dose and radionuclide distribution in the aquatic and terrestrial environment is essential to understand the human exposure to radiation and calculation of the exposure dose and its damage [1, 2]. As the Egyptian Nuclear Research Centre (NRC) is located in the vicinity of Ismailia Canal (IC), it is considered an important and interesting site of external contamination which affects the migration of radionuclides that may reach the surrounding ecology.

The migration of radionuclides in different types of soil, both vertical and horizontal, is a very important issue in tracing of radioactive contamination of the natural environment. Such studies despite its purely scientific aspect, has also a very practical objective, namely; it allows predicting possible sites of accumulating of radionuclides. This should also help to determine the accessibility of the isotopes to plants and more generally to food chain.[3,4,5]. Other researchers studied the concentration and the distribution of ^{137}Cs in ecosystems and agricultural areas [6, 11]. The mineralogical compositions (sand, silt and clay) affect the behavior of ^{137}Cs absorption kinetics within the soil [2, 3, 4, and 6].

The background activity of ^{137}Cs isotope in most of the Egyptian soils has been found to be less than 1 Bq/kg, which is similar to the natural radioactivity in Ismailia Canal and other locations in Egypt [6, 7].

Concentrations of radioactive ^{137}Cs isotope were measured in particular layers of the profiles selected (near NCR&IC) each sample was separated into fractions and laboratory tests on adsorption kinetics of ^{137}Cs were conducted. The adsorption isotherms were also plotted. A special attention was paid to the effect of the mineral

composition of the soils on the ^{137}Cs migration rate.

Experimental

Sampling procedure

The sampling spots were concentrated in two areas, firstly around the reactor area and spread away around it in circle of about 0.5 km radius, the selected soils from this location had not been farmed for the last 15 years and were scarcely overgrown with short plants. Secondly at Ismailia canal area (active agricultural and industrial area) far from the reactor by about 5km to the west.

Before sampling, the soil surface was cleaned of the over ground plant parts and larger organic pieces. Profiles of the soil were taken from the surface and down to 40 cm depth. The sampling procedure included collecting of soil layers, each of 20x30 cm area. The topmost and the second layers were 2 and 3 cm thick then subsequent 5 cm thick respectively [12]. The samples taken from each profile level were stored in polyethylene bags.

Sample preparation

Samples were dried in an oven at $110^{o}C$ up to constant mass and then screened on a 1 mm sieve to remove stones and larger organic fragments.

Each soil layer was washed on a 0.25 mm sieve onto a 1 dm^3 glass measuring cylinder. Then the cylinder was filled up with water and the contents mixed. The separation of soil into size fractions was carried out following sedimentation method at 25 ^{o}C. Under these conditions, and using stock's equation [13], four size fractions were separated: 0.2-0.1, 0.1-0.05, 0.05-0.02, and less than 0.02mm.

The sedimentation times of these fractions, from a height of 10 cm, were 4.4, 15.5 and 57.1 and more than 57.1 seconds, respectively. The extracted fractions of the sample were rinsed with distilled water and then dried at $100^{o}C$ for further investigations.

Physicochemical analysis

The following physicochemical parameters of the soil profiles were determined such as; exchangeable hydrogen ions concentration (measured as the pH value of suspended soil sample in a 1M KCl solution using a ERH-110 combined electrode and a pH-meter Hi-8417-Hanna instruments). The organic matter content was determined with the use of the roasting method [12]. Exchangeable cations were assayed in a buffered 1N ammonium acetate solution using the conventional batch method, as well as the major cations composition for each profile depth using methods described in previous standard soil analysis studies [12, 14].

Gamma spectrometric measurements

A known mass (1kg) of the homogenized soils samples, taken from each location, was placed in 0.5 dm^3 Marinelli bottle mounted on 1.0 inch CsI(Tl) crystal attached to URSA portable spectrometer connected to 4096-channel pulse height analyze. The detector resolution has a full width at half maximum (FWHM) of 0.9 keV at 0.122 MeV, 1.2 keV at 0.661 MeV and 1.9 keV at 1.33 MeV peaks, and its efficiency is1.8% for ^{137}Cs peak. Caesium activity measurements were calculated using a GAMMA VISION II, ver. 4.11 computer program. Each spectrometric measurement lasted for 24 hours [7].

Sorption experiments

Measurements of caesium sorption were carried out using soil fractions of 0.2-0.1, 0.1-0.05 and 0.05-0.02 mm size for samples collected from the two sites. An amount of 0.5 gm of the soil fractions were added in plastic bottles to 25 cm^3 CsC1 solutions of concentration ranged from $8x10^{-9}$ to $8x10^{-4}$ mol/dm^3, traced with ^{137}Cs at 25 ^{o}C (laboratory temperature). Before the addition of the soil 1.0 cm^3 aliquots of the solutions were taken and their activities measured (A_o). When the soil was added, the suspensions were shacked continuously and after 60 minutes the soil suspensions were centrifuged at 2000 rpm for 15 minutes. Then 1.0 cm^3 aliquots were taken from the supernatants and their radioactivity levels were measured again (A_s). The concentration of caesium sorbed on the soil (C_s) was calculated based on the radioactivity differences before and after the sorption using the following relationship [12]:

$$C_s = \frac{C_o.V_L(1 - \frac{A_L}{A_o})}{m} \qquad (1)$$

Where

C_s = concentration of Cs⁺ adsorbed by the solid, mol/g,

C_o = initial concentration of Cs in solution before adsorption, mol/dm³,

V_L = volume of solution, dm³,

A_L = activity of solution at adsorption equilibrium, Bq,

A_o = initial activity of solution, Bq,

m = mass of soil, g.

The kinetics of caesium adsorption were investigated using the above technique, by withdrawing 1.0 cm³ aliquots for the radioactive assay after 1, 3, 5, 10, 15, 20, 25, 30, 40, 50 and 60 minutes from the moment of the addition of the soil. The initial CsC1 concentration was 8×10^{-6} mol/dm³.

Results and Discussion

Tables (1 and 2) show the results of the physicochemical investigations of the two locations. Table (1) shows the results of the particle size fractions of both selected sites at different depths. It seems that the sand and silt fractions are the more dominant sizes in both sites.

From Table (2) it can be observed that the soils of the same site and from different depths do not differ significantly .In addition, the soil of both sites almost contain similar concentrations of exchangeable cations, only Ca^{2+} and exchangeable hydrogen vary clearly .This leads to differences in the values of the sorption capacities. The largest difference was observed in the C_{org} content in the first two centimetre depth in both sites which in turn results in different permeability of the two layers. Variation in particle size distribution, and in soils chemical composition, results in differences in soil sorption capacities [16].

Samples from both sites were investigated mineralogically by X-ray diffraction method and the results revealed that the sand fraction was mainly quartz and the silt fraction was mainly a smectite mineral.

The total ¹³⁷Cs activity in the profiles collected from the reactor site area amounted to 30.82 Bq/kg, while in the canal area was 0.87 Bq/kg and this value is markedly lower than the average natural radioactive background in the Egyptian soil. As it can be seen from Table (1), the canal site

soil is composed mainly of fine mineral particles of a size below 0.1 mm which are subject to washing away together with caesium adsorbed on their surfaces.

Figure (1) shows the kinetics of caesium sorption on size fractions that were separated from the Ismailia Canal site. Fig. (2) Presents the sorption kinetics of ¹³⁷Cs on smectite (smallest particle size fraction) and sand (largest particle size fraction) from the reactor site. It can be concluded from the two figures that the adsorption equilibrium was reached within several minutes after contacting the soil with the CsC1 solution. It is evident that the equilibrium was achieved most rapidly on sand from the reactor soil and on the large size fraction from the canal site soil with the particle size ranging from 0.2 to 0.1mm. In the light of the laboratory tests, the retention of Cs⁺ on the surface layers of the reactor site soil seems to be caused by efficient sorption of Cs⁺ on smectite portion.

It was found that the caesium uptake follows the Freundlich isotherm equation [16] $S = kC_{eq}^{(1/n)}$ Where S=Concentration of caesium on solid phase. C_{eq}=Concentration of caesium in solution at equilibrium.
K and n=are constants.

It can be observed from the adsorption isotherms, (Fig. 3) that semctite particles exhibit the largest caesium sorption capacity. It can also be seen from the isotherms that sand, when present in soil, can sorb caesium only in small quantities.

The migration of Cs, bonded with fine mineral grains and soil colloids, together with infiltrating water is a consequence of the strongest sorption of Cs on the fine fractions. Fine solid particles are also more tractable to migration in soil due to the biological activity of growing plant roots as well as of small organisms and animals living in soil [17]. As a result of the above processes, caesium can migrate carried by soil particles. Also, the very fine caesium-carrying particles can be easily blown around by winds and washed away by percolating water. It is very likely that such processes are involved in the migration of caesium in the reactor site soil.

Soil minerals, especially quartz and smectite exhibit a stratified structure [15]. Caesium,

introduced onto soil surface initially is bonded reversibly on the surface of the minerals, but in the course of time, caesium becomes irreversibly bonded due to slow diffusion and ion exchange with, e.g., K^+, Ca^{+2} and mg^{+2} ions, in the interlayer spaces inside those stratified minerals [15]. Thus, the irreversibly bonded caesium is immobilized on the mineral surfaces and its migration in soil will occur only when there are favourable conditions to the co-migration of the soil particles on which Cs is strongly sorbed.

The above discussions presented differences in possible migration pathways of caesium and the varying physicochemical properties of the two tested soils result in different average vertical migration rates of Cs^+ in these soils [18, 19]. The vertical migration rates were obtained from the following formula:

$$V_{av.} = \frac{d_{1/2}}{t} \qquad (2)$$

where $d_{1/2}$ is the thickness of a soil layer containing half of the total caesium activity in a tested profile (cm), and t is the migration time (years). It was assumed that the migration time was 18 years counting from the period of the first sample collected in 1990. The vertical migration rates were found to be 0.056 and 0.03 cm/year for the reactor site soil and the canal site respectively. Such low values of the average migration rate cause ^{137}Cs to remain in the upper layers of the soils up to a depth of a few centimetres. This indicates that ^{137}Cs, to a large extent, is permanently bonded with soil minerals through the chemical interaction rather than a physical one.

The results confirm the assumption that the migration rate of Cs^+ in the soil is affected primarily by the mineral composition of soil since the mineral fraction determines the way caesium is bonded[17,18]. When minerals contain a stratified structure is present in soil the migration rate of Cs decreases with time. As a result it is frequently observed that the migration of the newly contaminated caesium is faster than the migration of Cs originating from the global fallout because the process of caesium immobilization takes many years. Blocking of the active sites by caesium liberated from fallout can be one of the factors that differentiate the migration rates of caesium from new contamination sources and from the fallout in the 1990's. Subsequently, the new contamination

caesium can migrate faster to deeper layers of soil where it can finally adsorb on free adsorption sites. However, even in case of fast and strong adsorption on soil minerals caesium is able to migrate constantly, in very small quantities deeper into soil. This is a result of natural processes such as precipitation or biological activity of living organisms. The migration rate depends not only on the sorption properties of the soil, but also, on the size of the soil particles [19].

On the other hand, figure 4 presents the ^{137}Cs activities in the particular layers of the soil profiles. It can be clearly shown that the ^{137}Cs activity distribution differs substantially between the tested profiles. In case of the canal site soil, the distribution is rather uniform up to a depth of 30 cm except 0-2 and 2-5 cm layers. In these two, topmost layers, the caesium activity level were twice as high as in the remaining samples. These Cs^+ migration rates are in accordance with those reported in a work conducted by other investigator on Ismailia canal site [2].The activity in the 0-2 cm layer constitutes 14% of the total caesium activity in the profile. The phenomenon of caesium retention in the topmost layer of soil is even more clearly seen in reactor site soil profile where the activity of ^{137}Cs in the 0-2 cm layer amounted to 58% of the total caesium activity in this profile. In order to determine the percentage of the content of ^{137}Cs originating from any recent change above the fallout, a sample from a reactor area collected at 1990 (about 18 years ago) was subjected also to radio analysis for [137]Cs.

Two samples were collected from the same location at the reactor, sample one was taken in year 2008, while sample two was collected in 1990 and kept in clean hermetically sealed plastic bottle. Gamma spectrometry was performed on the two samples in 2008 .For sample 1, the ^{137}Cs concentration was found to be 10.25 Bq/kg .By using the decay equation and half-life concept it can be shown that this activity tend to be 15.23 Bq/kg in year 1990 .As for sample 2 ,the results showed that the ^{137}Cs concentration in 2008 was equal to 6.08 Bq/kg .similarly, using the decay equation and the half life time concept ,this value tend to be 9.22 Bq/kg , which assumed to be due to the natural fallout only. The difference in the activity between the two samples if they were collected and counted at the same time in 1990 is

5.81 Bq/Kg .This difference may arise from some external source of contamination. This difference reaches by natural decay to 3.83 Bq/Kg in 2008. This value is confirmed by the difference between the measured values of the two reactor samples counted in year 2008 which was found to be3.87 Bq/Kg as summarized in Table (3). The sample collected from the canal at the same time contained ^{137}Cs amounted to 0.87 Bq/Kg. Taking into consideration that the canal area is far from the reactor site and hardly subjected to any external contamination and in the same time it is a cultivated area, this value present the most acceptable back ground level for those areas [6, 7].

Table (1): Soil fraction composition of the tested soil sites

PROFILE DEPTH cm	REACTOR SITE YIELD OF SIZE FRACTIONS %				PROFILE DEPTH cm	CANAL SITE YIELD OF SIZE FRACTIONS %			
	0.2-0.1 mm	0.1-0.05 mm	0.05-0.02 mm	<0.002 mm		0.2-0.1 mm	0.1-0.05 mm	0.05-0.02 mm	<0.002 mm
0-2	22	48	30	8	0-2	5	65	30	10
2-5	19	40	41	14	2-3	11	58	31	12
5-10	19	40	41	16	3-5	7	60	33	13
10-15	19	39	42	14	5-10	5	65	30	15
15-20	20	39	41	13	10-15	6	63	31	13
20-25	25	34	41	14	15-20	7	62	31	13
25-30	23	34	43	16	20-25	5	63	32	19
30-35	23	31	46	18	25-30	4	63	33	18
35-40	23	30	47	22	30-35	5	65	30	17
40-45	23	23	54	33	35-40	6	63	31	15

Table (2): Chemical properties of the tested soils

PROFILE DEPTH cm	pH (KCl)	$C_{org.}$	REACTOR SITE Exchangeable cations meq/ 100g of soil					Sum of basic cations	Sorption capacity meq/100g
			Ca^{+2}	Mg^{+2}	K^+	Na^+	Hh*		
0-2	4.7	1.92	4.15	0.88	0.79	0.05	3.30	5.87	9.17
2-5	4.3	0.87	3.84	0.73	0.44	0.04	3.30	5.05	8.35
5-10	4.3	0.66	3.76	0.68	0.35	0.04	3.15	4.83	7.98
10-15	4.2	0.54	4.27	0.76	0.25	0.07	3.15	5.35	8.50
15-20	4.3	0.69	3.69	0.71	0.27	0.06	3.15	5.00	8.15
20-25	4.3	0.66	3.84	0.67	0.30	0.05	3.15	4.86	8.01
25-30	4.3	0.27	5.12	0.98	0.26	0.05	2.55	6.41	8.96
30-35	4.5	0.21	5.34	1.00	0.29	0.09	2.10	6.72	8.82
35-40	4.6	0.12	5.17	0.97	0.27	0.06	1.65	6.47	8.12
40-45	4.8	0.09	4.98	0.95	0.21	0.06	1.35	6.20	7.55
CANAL SITE									
0-2	5.0	5.10	6.41	1.02	0.78	0.07	7.20	8. 28	15.48
2-3	3.5	2.34	4.49	0.50	0.43	0.08	8.85	5.50	14.35
3-5	3.5	1.50	3.97	0.41	0.33	0.08	8.85	4.79	13.64
5-10	3.5	1.35	3.62	0.31	0.22	0.10	8.85	4.25	13.10
10-15	3.4	0.84	2.94	0.20	0.13	0.12	7.50	3.39	10.89
15-20	3.4	0.72	2.84	0.17	0.14	0.11	7.95	3.26	11.21
20-25	3.4	0.60	2.83	0.14	0.14	0.11	7.95	3.22	11.17
25-30	3.5	0.54	3.97	0.20	0.17	0.15	8.25	4.49	12.74
30-35	3.3	0.78	5.59	0.26	0.24	0.20	9.30	6.29	15.59
35-40	3.4	0.72	6.74	0.41	0.41	0.35	9.00	7.91	16.91

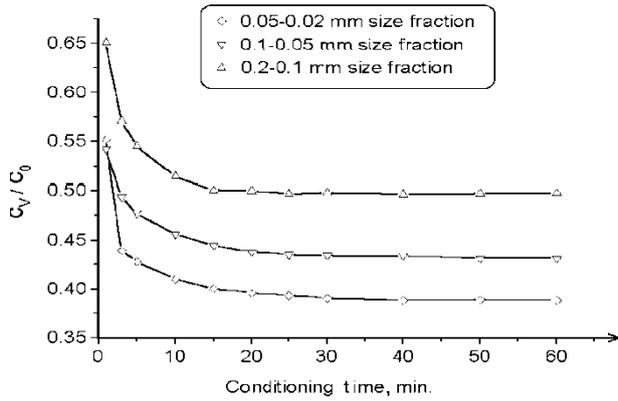* Exchangeable hydrogen ion concentration

Fig. (1): Adsorption kinetics of Cs $^+$ on different size fractions (0.20- 0-0.1 mm, 0.1- 0.05 mm, 0.05-0.02 mm) extracted from the canal site. Initial concentration of CsC1 solution: C_o =8.0x10^{-6} mol/dm^3
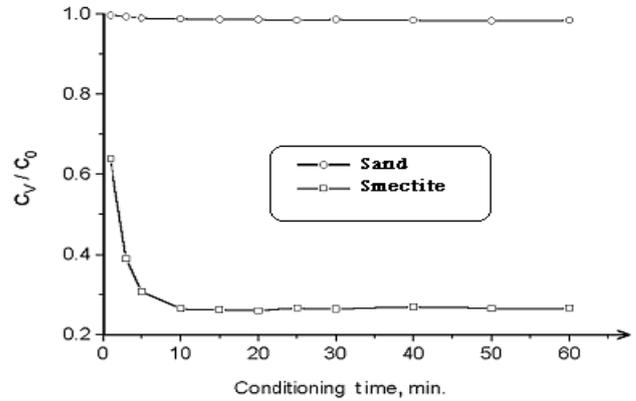

Fig. (2): Adsorption kinetics of Cs$^+$ on semctite and sand, extracted from the reactor Site soil. Initial CsCl solution concentration: C_o = 8x10^{-6} mol/dm^3
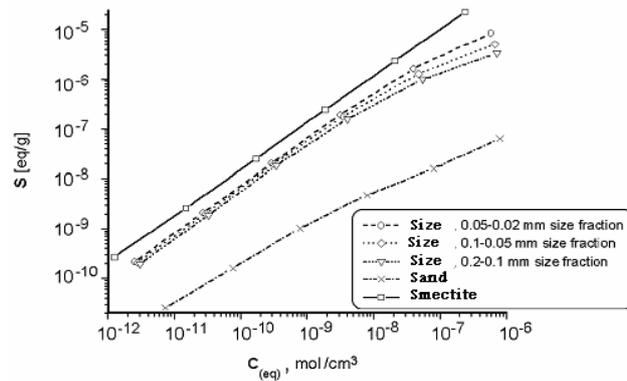

Fig. (3): Adsorption isotherm of Cs$^+$ on minerals fractions separated from the tested soils
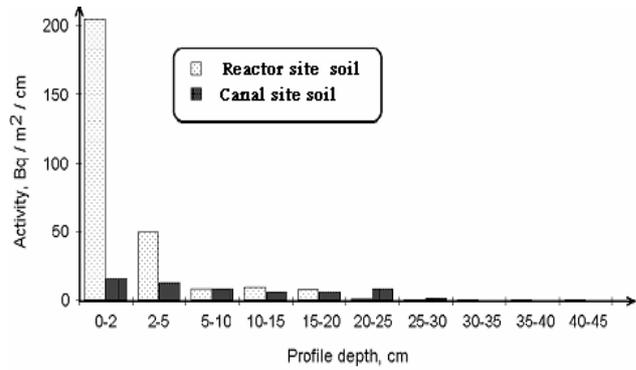

Fig. (4): Distribution of ^{137}Cs activity at different depths in the two tested soil profiles

Table (3):Cs^{137} activity in reactor samples collected in years 1990 and 2008, and from Canal site collected in year 2008

Year of sampling and locations	Cs^{137} Activity in 2008* (Bq/kg)	Cs^{137} Activity in 1990** (Bq/kg)
Reactor site 2008	10.25	15.23
Reactor site 1990	6.08	9.22
Difference in Cs^{137} Activity (Bq/m^2/cm)	5.81	3.83
Canal site 2008	0.87	--

* Natural Cs137 activity counted in 2008
**Calculated natural Cs137 activity in 1990 based on the measured activity in 2008 .and decay equation

Conclusions

In conclusion, it should be highlighted that the vertical migration of caesium in soil is a very slow process. The migration rates ranged from a fraction of millimetres to few millimetres per year and consequently Cs remains retained in the upper layers of soil, in a zone reaching plant roots. Because of the strong adsorption of the soil minerals, caesium does not occur in soil in the ionic form. For this reason, only a very small amount of Cs can be absorbed by plants and then transferred to further links of the food chains. Model measurements confirmed that the retention of Cs in the soil is affected primarily by soil minerals. Semctite separated from the reactor soil exhibited the strongest sorption ability among the tested minerals. The strong retention of Cs on semctite is most likely responsible for a larger accumulation of the isotope in the reactor soil compared with the canal site .It was found that in the reactor soil, there was 58% of the total activity of Cs in its 0-2 cm profile layer while in the canal site soil profile, in the topmost layer; there was only about 14% of the total caesium activity. Also the study showed that 39% of the Cs present in the reactor site is due to man-made contamination, but the total activity is still within the acceptable limits [5].

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