June, 1986] © *1986 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, *59*, *1863—1868 (1986)*

The Distribution and Characterization of ^{137}Cs in Shallow Water Sediments

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(Received January 22, 1986)

The distribution and characterization of ^{137}Cs in shallow water sediments are investigated. The concentration of ^{137}Cs in surface sediments which have been collected from the 10—20 m depth of Tsukumo Bay, Noto Peninsula, tends to decrease with an increase in the distance from the inner part of the bay to the outer part. Vertically, ^{137}Cs contents gradually decrease to the 10 cm depth and then steeply decrease beyond this depth, until at the 15 cm depth no activity is observed. A sequential extraction technique with several kinds of extractants has been employed to survey the chemical form of the nuclide in the sediments. ^{137}Cs is completely extracted with an ammonium nitrate solution suggesting that the nuclide is strongly adsorbed in the crystal lattice of some clay minerals and is exchangedly desorbed from the sediment phase by ammonium ions in a high concentration. A core sample has been elutriated in five components of different grain sizes, and the contents of sodium, potassium, and ^{137}Cs have been determined. It has been revealed that a unit amount of the finest component contains about three times as much of the nuclide as that of the coarsest one. On the contrary, the potassium contents slightly decrease with the decrease in the particulate size.

The behavior of ^{137}Cs at the seawater/sediment interface, especially in esturine or shallow water, is of very interest because radionuclides of a moderately long half-life have been distributed a world-wide scale as a result of nuclear-weapons testing and reprocessing plants of nuclear power and have thus been introduced into the ecological system in these shallow water regions, closely correlated human activity.

Radiocesium is considered to be present in seawater, principally as a simple Cs^{+} ion like ^{90}Sr, and to be scarcely captured at all by suspended substances such as marine planktons.[1,2] On the other hand, Nagaya et al.[3] have found that up to about 6% of ^{137}Cs exists in coastal seawater, bound to particulate materials. In addition, several investigations have been carried out studying the sorption behavior of the nuclide by means of some clay minerals, rocks, and soil components.[4—8] However, these studies have been concerned with purified soil components, a few synthetic mixtures of clay and soil, or laboratory experiments using natural sediment; little information has appeared in the literature on the distribution of ^{137}Cs in marine sediments. The present paper will describe the distribution and characterization of this nuclide, as correlated with other alkali metals in shallow water sediments which have been elutriated into five components of different grain sizes, the extraction property of ^{137}Cs with several kinds of extractants from the sediment, the sorption and desorption behavior of this nuclide on each elutriated component, and the determination of the sorption capacities of these components for ^{137}Cs.

Experimental

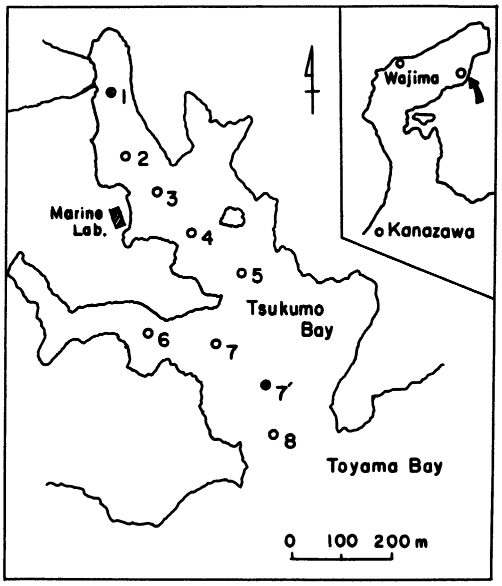

Fig. 1. Sampling Station in Tsukumo Bay.

Apparatus and Reagents. An ORTEC 8501-1523S true coaxial Ge(Li) detector (80 cm^{3}; resolution of ^{60}Co at 1330 keV:1.9 keV; relative efficienty: 15.1%), coupled to an ORTEC Model-6200, 4000-channel pulse height analyzer, was used for the low-level background counting of ^{137}Cs at the Low Level Radioactivity Laboratory, Kanazawa University. A Shimadzu AA-646 atomic absorption/flame-emission spectrophotometer was used for the analyses of sodium and potassium. A Rigaku Denki X-ray powder diffractometer and a Hitachi 20PR refrigerated centrifuge and 500-cm^{3} polyethylene centrifuge bottle were also used.

All the reagents used were of a guaranteed reagent grade.

Materials. Sediment samples were collected from a depth of about 10—20 m in Tsukumo Bay, Noto Peninsula, with a Smith-Mackintire sampler and a Phleger gravity corer. The sampling sites are illustrated in Fig. 1. After sampling, core samples were immediately collected, by using a polyacrylic resin cylinder (i.d. 50 mm), from the sample collected by means of the Smith-Mackintire sampler. The core was cut into three layers, each 30 mm long. Each layer of the core was immediately centrifuged at 7000 G for 30 min at 5 °C to remove any interstitial water. The centrifuged samples were then submitted to elutriation as follows: About 30 g of the sample was placed in a polycarbonate resin beaker, stirred with 800 cm^3 of distilled water, and then allowed to stand for 3 min. After thus standing, the suspension was transferred into another polycarbonate resin beaker. The residual sediment in the first beaker was treated as has been described above, using fresh distilled water, until the supernatant became almost clear. The suspensions were collected in the second beaker. The deposited fraction was named 3MP. The contents of the second beaker were stirred vigorously and then allowed to stand for 10 min. The suspensions obtained by the same procedure were collected in the third beaker. The deposited sediment fraction was named 10MP. Then, the suspension was sequentially elutriated into the fractions deposited after standing 1 h and 5 h and suspended after standing 5 h, these fractions being named 1HP, 5HP, and 5HS respectively. At the same time, in a small portion of the first suspension the chloride concentration was determined by Mohr's method in order to evaluate the contribution of seawater to the determination of sodium and potassium in the sediment.

Determination of ^{137}Cs. About 0.7—10 g of a dry sample was used for the γ-counting of ^{137}Cs. The samples available in amounts larger than 3 g were made into a disc 20 or 50 mm diameter by pressing, while the others were shielded in a small polyethylene pouch; then γ-counting was performed. In the sequential extraction procedure, about 30 g of the dry sample was used.

Determination of Sodium and Potassium. About 0.2 g of the sample was decomposed with an acid mixture (0.5 cm^3 of 60% perchloric acid+3 cm^3 of concd nitric acid+ 5 cm^3 of 47% hydrofluoric acid) in a PTFE beaker by heating on a hot plate at ca. 120 °C. This treatment was repeated 3—4 times. The residue was then dissolved in 5 cm^3 of 6 mol dm^{-3} hydrochloric acid and filtered through Toyo No. 5B filter paper. The filtrate was made up to 25 cm^3 with pure water. After appropriate dilution, sodium and potassium were analyzed by means of flame photometry at the wavelengths of 589.3 and 766.2 nm respectively.

Sequential Extraction of ^{137}Cs from the Sediment. About 30 g of a dry surface sediment sample containing 0.30$\pm$ 0.014 pCi ^{137}Cs g^{-1} was put into a 100 cm^3 stoppered polyethylene centrifuge tube and shaken with 50 cm^3 of a methanol–acetone mixture (1:1 v/v) for 30 min. After centrifugation at 3000 rpm for 20 min, the supernatant was separated, evaporated to a small volume in a PTFE beaker, and then transferred into a shallow plastic dish 50 mm in diameter in order to dry it up. Finally, the contents of the dish were submitted to γ-counting. Next, to the sample remaining in the centrifuge tube 50 cm^3 of a 0.5 mol dm^{-3} magnesium chloride solution was added; the contents were then shaken and centrifuged as has been described above. The γ-counting of the magnesium chloride extract was also carried out. Then, the residual sediment was treated successively with a 0.5 mol dm^{-3} sodium hydroxide solution, 1 mol dm^{-3} hydrochloric acid, and a 50% ammonium nitrate solution. Finally, the residual sediment, which had been reduced to 23.6 g during the extraction procedure, was dried and pressed into a disc 50 mm in diameter for γ-counting.

Sorption Experiments of ^{137}Cs Using the Sediments. Filtered seawater which had been collected from the surface of Tsukumo Bay was spiked with ^{137}Cs (nitrate form) so as to make its concentration about 20000 cpm cm^{-3} and then allowed to stand for 1 d in order to attain equilibrium. An air-dried elutriated sample was pulverized to under 400 mesh with an agate mortar and placed (1.0 g) in a polycarbonate resin beaker. Then about 400 cm^3 of the ^{137}Cs-spiked sea water was added to it, after which the contents were vigorously stirred and allowed to stand with a loose cover. After one day, 3 cm^3 of supernatant was pipetted out and filtered through a small piece of dry filter paper. One cm^3 of the filtrate was pipetted out into a polyethylene test tube, and the radioactivity was measured by means of a NaI(Tl) scintillation counter. The contents of the beaker were then stirred and allowed to stand for one more day. The measurement of the radioactivity of the supernatant was carried out as has been described above until an equilibrium was attained.

Table 1. Contents of Potassium and ^{137}Cs in Surface Sediments (Tsukumo Bay, 1983-9-19)

Station	Depth	K	^{137}Cs	^{137}Cs/K
	m	%	pCi/g dry	pCi/meq
1	10	1.19	0.45$\pm$0.02	1.4_8
2	16	1.14	0.35$\pm$0.03	1.1_9
3	21	1.23	0.35$\pm$0.02	1.1_1
4	23	1.40	0.24$\pm$0.03	0.6_7
5	24	1.34	0.26$\pm$0.02	0.7_6
6	20	1.56	0.20$\pm$0.03	0.5_0
7	21	1.30	0.27$\pm$0.03	0.8_1
8	22	1.11	0.17$\pm$0.03	0.5_9

Measurement of Distribution Coefficient, K_d. Each sediment sample which adsorbed ^{137}Cs in the above experiment was separated from the supernatant by decantation, followed by centrifugation using a 50 cm^3 polyethylene bottle. The sediment in the bottle was washed with a small portion of seawater, and the washing was rejected by centrifugation. This procedure was repeated several times. Finally, 40 cm^3 of filtered seawater was put into the bottle, and the bottle was shaken for 24 h. After centrifugation, the radioactivity of the supernatant was measured as above.

Measurement of Sorption Capacity for ^{137}Cs. Cesium chloride (3.75 g) was dissolved in 200 cm^3 of the ^{137}Cs-spiked seawater. About 0.5 g of the powdered elutriated sample was then added to 25 cm^3 of the above seawater containing 1.39 meq of cesium (about three times the contents of sodium and potassium), and the contents were shaken for 20 h. After centrifugation, 1 cm^3 of the supernatant was submitted to γ-counting and the sorption capacity was calculated.

X-Ray Powder-Diffraction Measurement. In order to estimate the mineral composition of each elutriated sample, X-ray powder diffractometry was carried out. In particular, in order to distinguish the peaks of the clay minerals, measurements were performed after treating the sample with several kinds of reagents, e.g., ethylene glycol for montmorillonite and haloisite, ammonium nitrate for magnesium vermicurite, hydrochloric acid for kaolinite, vermicurite and chlorite, and potassium acetate for kaolinite minerals. The parameters used were Cu K_α (15 mA, 35 kV), a Ni filter, and a slit system (1°—0.3 mm—1°).

Results and Discussion

Distribution of ^{137}Cs in the Sediments. The ^{137}Cs contents of surface sediments of Tsukumo Bay are given in Table 1. The ^{137}Cs contents tend to decrease

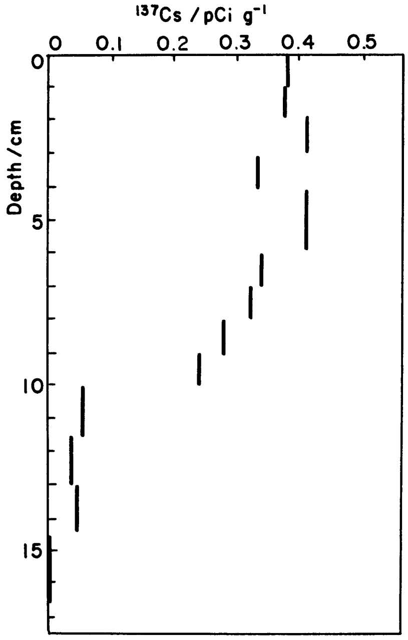

Fig. 2. Vertical distribution of ^{137}Cs in a sediment core.

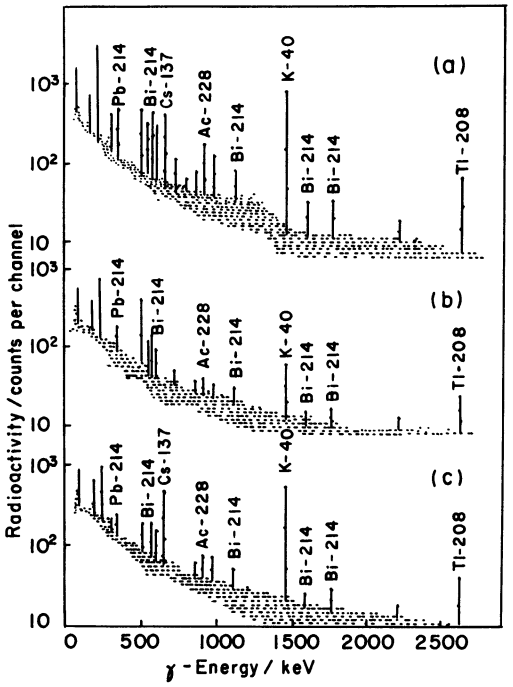

Fig. 3. Gamma-spectra of the raw sediment and extracts. (a) raw sediment, (b) extract with 1 mol dm^{-3} HCl, (c) extract with 50% NH_4NO_3.

with an increase in the distance from the inner part of the bay to the outer part. This fact suggests that, after ^{137}Cs has been transferred into the bay in several ways, e.g., through the river water and precipitation, and from the surroundings, this nuclide should sink down rather quickly and be captured by bottom sediments.

A core sample collected at St. 7' with the Phleger gravity corer was cut in 10 mm sections, and the γ-activity was measured. The vertical profile of the ^{137}Cs contents thus obtained is illustrated in Fig. 2. At 7—8 cm from the surface, the ^{137}Cs contents decrease to about one half-of that at the surface; beyond a depth of 10 cm the radioactivity of ^{137}Cs steeply decreases, until no activity is observed at the depth of 15 cm.

At the same time, the age of each section was determined by means of the ^{210}Pb method. The depth vs. time curve showed a straight line between depths of 30 mm and 110 mm, corresponding to about 44 years. As can be seen from Fig. 2 and the results of the age determination, ^{137}Cs can only slowly migrate downward through the sediment layers after deposition.

Extraction of ^{137}Cs from the Sediment Phase. Figure 3 (a)—(c) show the γ-spectra of the raw sediment, the extracts with 1 mol dm^{-3} hydrochloric acid, and 50% ammonium nitrate solutions. No measurable peak for ^{137}Cs is found in the spectra of the extracts with the methanol–acetone mixture, magnesium chloride, and sodium hydroxide solutions, as in the final residual sediment as hydrochloric acid extract (b). On the other hand, the extract with the ammonium nitrate solution gave a sharp peak of the nuclide, and the radioactivity of ^{137}Cs in the extract indicates that an almost complete extraction has been attained. Thus, scarcely ^{137}Cs seems to be present bound to any organic substances such as a humic substance, weakly or electostatically adsorbed on sediment surfaces, or in acid-soluble form. Miettinen et al.[9] have also reported that only 5% of the ^{134}Cs was eluted with 0.1 mol dm^{-3} hydrochloric acid from a ^{134}Cs-labelled sediment which had been collected from the Gulf of Finland. In the present experiments, however, about 15% of the initial amount of ^{137}Cs in the raw sediment was lost during the sequential extraction; this could not be measured in each extract. Therefore, an unmeasurable amount of the nuclide might be extracted in every extraction step according to the sorption-desorption equilibrium. On the other hand, the fact that almost all the ^{137}Cs was extracted in the 50% ammonium nitrate solution indicates that the nuclide in the sediments is contained in the phase of clay minerals and is exchangedly desorbed from the sediment by ammonium ions in a high concentration, because the effective ionic radii of ammonium ions and cesium ions resemble each other,[10] so the former ion can intrude into the crystal lattice of clay minerals and replace the latter ion.

Distribution of ^{137}Cs in the Components of Different Grain Sizes of the Sediments. Two samples collected from St. 1 and 7' were investigated for the distribution of ^{137}Cs, depending on the difference in the grain sizes of the components of the sediments.

The amount of each component obtained by elutriation, the contents of ^{137}Cs, sodium and potassium,

Table 2. Analytical Data of the Components Obtained by Elutriation of Sediment Core

Layer	Component[a)]	Weight %	Na %	K %	^{137}Cs pCi/g dry	^{137}Cs/K pCi/meq
Station 1						
Upper	3MP	62.6	1.10	1.28	0.26±0.03	0.7_8
	10MP	8.7	0.53	1.09	0.39±0.16	1.3_9
	1HP	9.2	0.41	1.09	0.43±0.14	1.5_9
	5HP	6.3	0.25	1.06	1.57±0.33	5.2_3
	5HS	13.0	0.11	0.31	0.76±0.16	4.4_7
Middle	3MP	63.6	1.17	1.23	0.31±0.04	1.0_0
	10MP	9.1	0.66	1.14	0.38±0.09	1.2_3
	1HP	8.9	0.43	1.13	0.59±0.14	2.0_3
	5HP	5.4	0.21	0.98	0.63±0.19	2.6_3
	5HS	12.9	0.09	0.48	1.01±0.13	6.7_3
Lower	3MP	66.6	1.24	1.33	0.31±0.03	0.9_7
	10MP	8.0	0.68	1.16	0.65±0.06	2.2_4
	1HP	8.9	0.62	1.17	0.62±0.08	2.2_1
	5HP	5.4	0.19	1.01	0.82±0.15	3.2_8
	5HS	11.7	0.11	0.51	1.05±0.04	6.1_8
Station 7′						
Upper	3MP	43.2	1.38	1.54	0.09±0.03	0.2_3
	10MP	12.1	1.06	1.31	0.19±0.08	0.5_7
	1HP	14.5	0.71	1.18	0.43±0.13	1.4_8
	5HP	13.6	0.32	0.89	0.57±0.08	2.4_8
	5HS	16.5	0.15	0.87	0.58±0.08	2.6_4
Middle	3MP	42.3	1.39	1.56	0.12±0.03	0.2_7
	10MP	10.0	1.05	1.31	0.46±0.09	1.3_9
	1HP	16.3	0.77	1.20	0.36±0.07	1.1_4
	5HP	13.5	0.30	0.89	0.51±0.09	2.1_7
	5HS	17.8	0.14	0.89	0.66±0.07	3.0_0
Lower	3MP	45.4	1.43	1.52	0.05±0.02	0.1_3
	10MP	12.1	1.05	1.39	0.32±0.15	0.8_9
	1HP	16.2	0.60	1.18	0.22±0.07	0.7_6
	5HP	12.4	0.32	0.95	0.67±0.07	2.7_9
	5HS	13.9	0.17	0.90	0.64±0.14	2.7_8

a) Grain sizes of the components are; 3MP: 31—16 µm, 10MP: 16—7.8 µm, 1HP: 7.8—3.9 µm, 5HP: 3.9—1.9 µm, 5HS: <1.9 µm.

and the ^{137}Cs/K ratios (pCi/meq) in these components are shown in Table 2. The weight percentages of the coarsest component most abundant in both sediments are above 62 and 42% respectively in St. 1 and 7'. The next most abundant component consists of the finest particulates in both sediments; their weight percentages are above 12 and 14% for St. 1 and 7' respectively. This tendency is observed in every three layer of the sediment core. The concentration of ^{137}Cs in the unit amount of each component of the elutrilated sediment sample shows a more marked tendency, that is, the finer the grain size of the component, the higher the concentration of ^{137}Cs. The finest component contains about three times the quantity of the nuclide as the coarsest ones. On the contrary, the potassium contents slightly decrease with the decrease in grain size. Subsequently, the ^{137}Cs/K ratios show a remarkable increase with the decrease in the grain size of the components. In St. 1 and 7', the ratios for the finest components amount to more than 6 and 10 times, respectively, those of the coarsest ones. These facts indicate that the nuclide tends to concentrate in the fine components of the sediment, in spite of its lower sodium and potassium contents. As a result of the X-ray powder diffraction measurements, it was observed that the peak height of potassium feldspar was highest for the coarsest component, while that of cristobalite was dominant in the finest component, except for calcite in St. 7'. However, because, unfortunately, no detailed information has been obtained on clay minerals in the present study, it is still obscure to what kinds of clay minerals the highest concentration of ^{137}Cs in the finest componet of the sediments should be attributed. In any event, it can be thought that the fine components contain a large number of exchangeable sites for cesium and that they probably exist in some clay minerals such as montmorillonite and kaolinite, as has been reported many authors.[4—8]

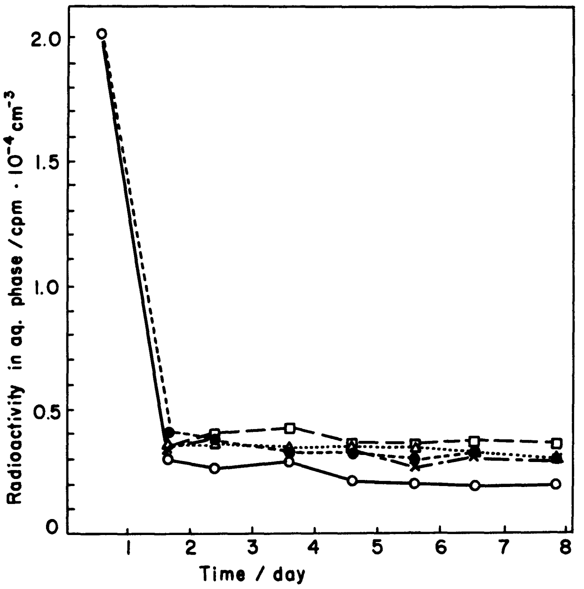

Fig. 4. Radioactivity change in aqueous phase according to sorption of ^{137}Cs on the elutriated components: 3MP —□—, 10MP —*—, 1HP, ····△····, 5HP —●—, and 5HS —○—.

Table 3. Distribution Coefficients, K_d, for the Sorption of ^{137}Cs on the Components Obtained by Elutriation of Sediment Core (Upper Layer)

Component	amount used	K_d	K_d
		Sorption from 400 cm^3 of sea water	Desorption by 40 cm^3 of sea water
	g dry		
3MP	1.039	2050	2160
10MP	1.023	2630	—
1HP	1.029	2460	2610
5HP	1.030	2560	2990
5HS	1.105	3650	3850

Table 4. Sorption Capacity for Cesium and Exchange Balance between the Correlated Elements

Sample	Sorption capacity for Cs	Na contents	K contents	Cs sorbed/(Na+K) ratio
	meq g^{-1}	meq g^{-1}	meq g^{-1}	
3MP	0.32	0.61	0.39	0.32
10MP	0.15	0.46	0.34	0.19
1HP	0.20	0.30	0.31	0.33
5HP	0.23	0.13	0.23	0.64
5HS	0.29_7	0.06_5	0.23	1.01

In the present investigation, laboratory experiments using ^{137}Cs tracer have been performed to clarify the above postulation.

Sorption of ^{137}Cs on the Sediments. The results obtained by sorption experiments on the ^{137}Cs on the elutriated components of sediments are shown in Fig. 4. A blank experiment no sorption of the nuclide on the walls of the beakers used was observed. During 24 h standing, the sorption equilibrium seems almost to be attained, since the decrease in the radioactivity in the aqueous phase becomes significantly slow after one-day standing. After seven days, the sorption equilibrium is completely attained, when about 81.2% of ^{137}Cs has been adsorbed by the coarsest component, while by the finest component about 90% of the initial activity is captured from seawater in a volume 400 as much as the sediment phase. Furthermore, it was observed that the latter component adsorbed ^{137}Cs more quickly than the former one.

The distribution coefficients of ^{137}Cs between the sediments and seawater are shown in Table 3. (The 10MP sample was mistested because the sorption behavior very closely resembled the 5HP component.) The results show that the K_d values increase with the decrease in the grain size of the sediment components. In the present study, the components of different grain sizes were pulverized to under 400 mesh; therefore, the surface areas are thought to be not so very different and to have no effect on the K_d value or the sorption capacity. Thus, the K_d value for the finest component is about 1.8—1.9 times that for the coarsest ones. As can be seen from Table 3, a fairly good agreement is observed between the K_d values which were obtained by the two opposing experiments: the sorption of ^{137}Cs by the sediment component from 400 cm^3 of seawater and the desorption of nuclide adsorbed on the sample with 40 cm^3 of seawater.

In Table 4, the sorption capacities of the components for cesium are shown, together with the concentrations of sodium and potassium, and the ratio of cesium to sodium plus potassium. From the results given in the table, it can be seen that only 20—30% of the alkali metals are replaced by cesium for the coarsest components, while in the case of the finest component almost all the alkali metals are exhanged with cesium. Another experiment using seawater containing one half the amount of cesium and the tracer gave very similar capacity values. These results may indicate that the fine component of the elutriated sediments has a larger number of exchangeable sites for ^{137}Cs than the coarse ones; this is probably the reason for the higher ^{137}Cs contents in the finest component of the sediment in spite of the rather lower contents of sodium and potassium.

The present work was partially supported by a Grant-in-Aid for Scientific Research (No. 58380021) from the Ministry of Education, Science, and Culture.

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