Accumulation of ^{137}Cs in bottom sediments of the Curonian Lagoon

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Abstract Measurements of activity concentrations and speciation of ^{137}Cs in bottom sediments of the Curonian Lagoon were carried out in samples collected in 1999–2003. In addition, the sorption-desorption processes of caesium in disturbed bottom sediments of fresh and sea water systems were investigated in long-term experiments (up to 375 days) in order to better understand the caesium behaviour during the Baltic Sea water flooding events to the Curonian Lagoon. The modified Tessier method was used to study caesium associations with geochemical phases of bottom sediments. The effect of carbonate coatings of bottom sediments on the Cs sorption-desorption process was observed. The comparative analyses of ^{137}Cs solid phase speciation in bottom sediments after 241 and 375 days of the sorption experiment with that of the ^{137}Cs speciation, determined in the same sediment sample before the sorption experiment, indicated that after 375 days of sorption the equilibrium was not reached, however, the Cs distribution in geochemical phases was found to be close to equilibrium. The desorption experiments evidenced the release of caesium into solution from regular exchange complex and transfer from other phases to the frayed edge sites on the layered clay minerals with its further fixation in the crystal lattice. The remobilization of "fixed" caesium was not observed, on the contrary, the redistribution of caesium with its subsequent fixation in clay minerals was observed, and on a time scale its fixation kinetics was comparable with the sorption experiment. This study showed that flooding events of sea water contaminated with caesium can cause a significant accumulation of caesium in the bottom sediments of the Curonian Lagoon and result in the redistribution of ^{137}Cs activity concentration in the bottom sediments from one area to another.

Key words caesium • sorption • desorption • bottom sediments

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Introduction

The mobility and fate of radionuclides in the environment to a great extent depend on the speciation and on their transformation. Removal processes of portion of water-soluble radionuclides released to the environment are usually related to their sorption onto soil and sediment particles. Natural sediments are usually a sink for various contaminants but they may become a source, for example, under drastically changing environmental conditions in the fresh and saline waters mixing zone.

Caesium is one of the most important anthropogenic radionuclides, which was introduced into the environment through nuclear weapons testing and nuclear accidents at Chernobyl; its inventories in radioactive waste are significant as well. Caesium harmful effects on animate nature are evident taking into account its properties: unlimited solubility, potential mobility and high bioavailability. The sorption-desorption processes of radiocaesium on various minerals have been the subjects of many recent studies [2, 5, 7, 11, 12]. The numerous publications concerning the binding of Cs by clays reflect the importance of this radionuclide relevant to safety assessment, and on the other hand, the search for low-cost barriers for isolation of radioactive wastes

[6, 14, 15]. These studies are mostly dealing with a description of the caesium sorption on homogenous particles of clay minerals. In natural environment, the complex mixtures of minerals are present and for this reason there are difficulties in extrapolation of data obtained in the laboratory sorption experiments to the far-field conditions. In addition, a variety of factors including the water pH, ionic strength, competitive sorption, complexation with inorganic and organic ligands can influence the sorption process and thereby mobility of radionuclides. However, it is now generally recognised that the sorption of ^{137}Cs by soil and sediments is mainly determined by specific sorption onto illite clay minerals, but such parameters as pH and organic matter were found to play less important role in the adsorption of Cs. Three types of ^{137}Cs binding sites to sediment clay components have been identified experimentally. The selective adsorption of Cs by clay minerals has been attributed to the large ionic radius, uncomplexing nature and especially to its low hydration energy. Although cations with similar charge and ionic radii are expected to compete with caesium, the sequence of sorption ability of alkali elements $Na^+ < K^+ < Rb^+ < Cs^+$ is in good agreement with the sequence of effective ionic radii of alkali elements and the sequence of single ion hydration enthalpies of alkali elements [18]. In the clay mineral muscovite, a negative fixed charge arises primarily from isomorphous substitution of Al^{3+} for Si^{4+} in the tetrahedral sheet comprising the siloxane site. In illite mineral, whose composition is very close to that of muscovite, isomorphous substitution of Al^{3+} for Si^{4+} and partly of Fe^{2+} and Mg^{2+} for Al^{3+} enhances the stability of the Cs^+-siloxane surface complex, presumably by promoting the dehydratation of the sorbed Cs cation.

The layer-type silicates bind Cs either through weak electrostatic interactions or through stronger bonds formed by partial sharing of electrons between Cs and the ligand sites of the clay mineral. Electrostatic associations of hydrated Cs with anionic surfaces within the basal plane or interlayer and dissociated edge hydroxyl groups act as outer-sphere complexes [9, 10]. Electronic bonding at the frayed edge sites, external basalt sites, or within the interlayer leads to inner-sphere complexes, which usually are much more stable than outer-sphere complexes. Caesium sorbed to outer-sphere complexes can be easily desorbed and more mobile in the environment, while inner-sphere sorption complexes can limit the Cs mobility and bioavailability [17]. These inner-sphere adsorption complexes are probably the dominant ones at low concentrations typical of radioactive Cs contamination, and a great amount Cs from contaminated environments is expected to be strongly adsorbed. The complicated behaviour of caesium can be a result of peculiarities of its sorption to various sorption sites of different clay minerals and their mixtures.

The complicated behaviour of caesium in the environment can, in general, be explained by its sorption to various sites of different silicates. In smectites, the isomorphous substitution in both tetrahedral and octahedral layers generates weak negative charges of sheets thus leading to the formation of unstable structure and resulting in wide ranges of cation exchange capacity,

selectivity and swelling properties. Water and cations such as H^+, Na^+, Ca^{2+}, Mg^{2+} can easily penetrate into the smectite interlayer and participate in exchange processes. Mixtures of clay minerals, e.g., illite and smectite present in natural environment cause difficulties in the quantitative estimation of exchangeable and bioavailable caesium, therefore, the semi-empirical methods are used for these purposes [13, 20]. Unlike other heavy metals, Cs does not have affinity to sorb or co-precipitate with Fe-hydroxides. However, organic matter and iron oxides have indirect effect on the ^{137}Cs affinity to the clay minerals. The adsorption of macromolecules on clay minerals influences their affinity to caesium, and clay-humic substance complexes adsorb less caesium than uncoated clay minerals. The coatings of iron oxides block the caesium uptake sites as well. The organic matter and iron oxide coatings on soil and sediment particles can serve as intermediate phases when the exchangeable ^{137}Cs permeates towards the mineral core of clay particles. Moreover, the desorption of exchangeable ^{137}Cs from clay minerals can be inhibited by such coatings [8]. As a result, the value of exchangeable ^{137}Cs measured during the extraction procedures can be reduced. In addition, organic matter enhances sorption and "fixation" of Cs^+ ions in the clay interlayer. The mechanisms of these interactions are poorly understood.

One of the ways to evaluate the associations of radionuclides in the environmental samples is sequential extraction. The obtained results depend on the used procedures such as the ratio between liquid and solid phase, contact time, temperature, mixing conditions, type of separating solid from liquid phase. This method has some disadvantages, such as possible re-adsorption during extraction, insufficient selection of used reagents, influence of conditions, time consumption [1].

Even with the above mentioned disadvantages the sequential extraction method is at present the best tool to analyse associations of radionuclides in the environmental samples because of their low concentration. Knowledge about the radionuclide association with geochemical phases is important from the point of view of the radiation protection since the binding of radionuclides and the stability of geochemical phases provide data on bioavailability and the migration ability of radionuclides.

The objective of this study is to focus on the sorption and desorption behaviour of Cs in the complex heterogeneous system of bottom sediments in order to better understand the caesium behaviour during the Baltic Sea water flooding events to the Curonian Lagoon and transfer of suspended particles from the Curonian Lagoon to the Baltic Sea.

Methods

A sample of bottom sediments collected in the Curonian Lagoon was used for sorption experiments. The sampling locations are presented in Fig. 1. Total carbon (TC) and total organic carbon (TOC) were determined using a LECO CS-125 analyser. The grain size distribution was determined by the gravimetric
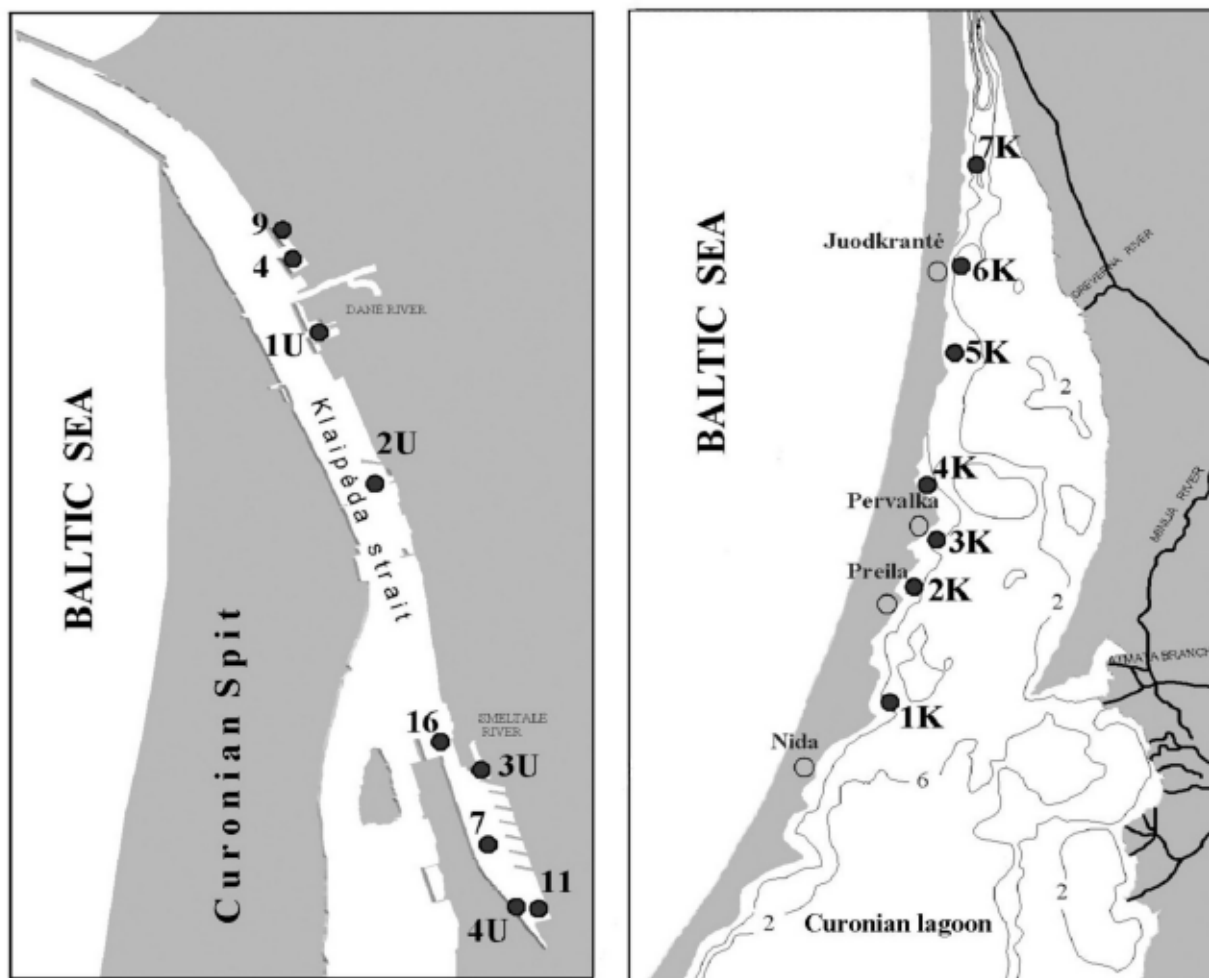
Fig. 1. Sampling locations.

pipette method. The stable Cs concentration was determined using ICP-MS, and clay minerals were identified by X-ray diffraction. The sample was passed through a 1-mm mesh sieve and homogenized. Then it was divided into equal portions, placed into plastic vessels and 40 ml of filtered sea water of 7.0‰ salinity labelled with ^{134}Cs was mixed with 4 g of sediments and sealed by Parafilm TM. The total concentration of Cs in solution was 0.04 ppb. The contents of vessels were mixed 5 min/day using a magnetic stirrer. Samples were stored in the dark at 4°C at different contact times between solution and sediments. Another sorption experiment was performed in the dark and samples were stored in a room where the temperature in wintertime was about 5–7°C and in summertime about 20°C. The experiment was started in November and the amount of ^{134}Cs activity added to the samples was reduced by a factor of two as compared to the first experiment. The solids were separated by centrifugation at 4000 rpm for 15 min. The sample was carefully mixed and split into two equal parts. One of those was used for sequential extraction analyses and the other one for the desorption experiment. Details of the experiment are described in publication [16].

The modified Tessier [19] sequential extraction method was used to study association of Cs in sediments. The following extracting agents were used and sub-

sequent characterizations are:

1 M $MgCl_2$, pH 7.0 (exchangeable),
1 M NH_4Cl, pH 7.0 (exchangeable),
1 M $NH_4C_2H_3O_2$, pH 5.0 (carbonate bound),
0.1 M $Na_2P_2O_7$ (organically bound),
0.04 M $NH_2OH \cdot HCl$ (oxide bound),

residue was measured directly by gamma spectrometry.

Fractions were separated using centrifugation and filtration through a membrane filter 0.2 μm.

Desorption experiments were performed using natural river water. Samples were poured with 20 milliliters of a solution mixed 5 min/day by a magnetic stirrer left to stand overnight, mixed again 5 min and centrifuged at 4000 rpm and the procedure was repeated during 10 days.

^{137}Cs and ^{134}Cs activities were measured on an intrinsic germanium detector (resolution (1.9 keV/1.33 MeV) and efficiency (42%). An efficiency calibration of the system was performed using calibration sources of different densities and geometry that were close to real measured samples. For the source preparation, a reference solution from AMERSHAM, UK Solution No. FD 998 was used. The measurement accuracy was tested in intercomparison runs, organized by the Risø National Laboratory, Denmark. The precision of ^{134}Cs measurements by gamma spectrometry was < 3% at ± 1σ.

Results and discussion

Data on measurements of ^{137}Cs activities concentrations in sediments from the Curonian Lagoon are presented in Table 1. Activity concentration of ^{137}Cs measured in surface sediments (0–2, 0–3 cm) varied from 8 Bq/kg to 207 Bq/kg. Variations in activity concentrations of ^{137}Cs can be attributed to the different mineralogical composition of sediments, peculiarities of sedimentation processes and different contact time with marine water during the flooding events. Investigations of the association of ^{137}Cs in the bottom sediments collected in the Curonian Lagoon indicated that only 1% of ^{137}Cs could be extracted using 1 M $MgCl_2$ and about 10% – using 1 M NH_4Cl. Thus 1% of ^{137}Cs sorbed on regular exchange complex can be easily desorbed under normal conditions and about 10% under anoxic ones.

Studies of fraction distribution performed on bottom sediments show that in the Curonian Lagoon (Fig. 2) ^{137}Cs is strongly associated with sediment particles. About 70% of ^{137}Cs were found in acid-soluble and residual fractions. Usually, clay minerals are responsible for strong binding of caesium in soils and sediments.

Obtained data are in good agreement with studies performed on sorption and release of caesium from particulate matter of the Baltic coastal zone indicated that effective sorption of [137]Cs (up to 80%) by bottom sediments, and illite was identified as a dominant clay mineral [11]. In order to better understand the caesium behaviour during the Baltic Sea water flooding events to the Curonian Lagoon and to investigate peculiarities of its sorption-desorption and fixation kinetics in the complex heterogeneous system of bottom sediments were examined.

Data from two sorption experiments of radiocaesium from sea water labelled with [134]Cs showed that

Table 1. [137]Cs activities in bottom sediments in the Curonian Lagoon.

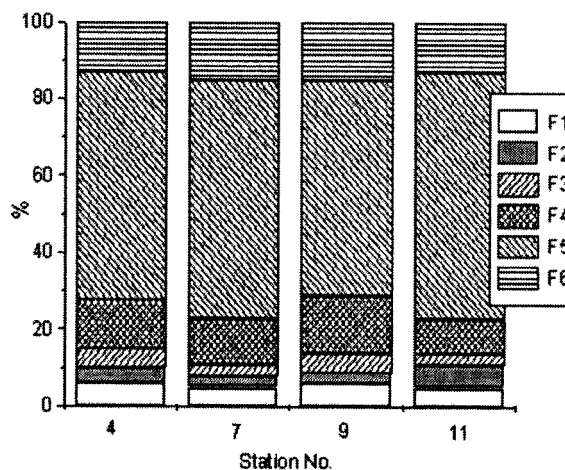| Sample number	Location	Specific activity in bottom sediments (Bq/kg)
A-3	Curonian Lagoon	13 ± 1
C-3		41 ± 4
H-2		129 ± 21
I-5		127 ± 13
U-13		154 ± 9
Y-10		98 ± 12
1K		13 ± 1
2K		121 ± 11
3K		16 ± 1
4K		12 ± 1
5K		29 ± 3
6K		86 ± 11
7K		114 ± 11
1U	Klaipeda strait	89 ± 9
2U		8 ± 1
3U		133 ± 13
4U		104 ± 12
5U		55 ± 20
4		140 ± 3
7		140 ± 3
9		207 ± 3
11		189 ± 3

Fig. 2. Speciation of ^{137}Cs in bottom sediment of Curonian Lagoon samples (F1 – exchangeable; F2 – carbonates; F3 – oxides; F4 – organic; F5 – acid-soluble; F6 – residue).

results obtained from two experiments with different concentrations of caesium differ insignificantly. Results of sorption of [134]Cs in the sediments after different contact time indicated that more than 70% of [134]Cs tracer was sorbed during the first three days. Visible decrease in exchangeable fraction occurs only after 11 days of contact time. Similar results were obtained during the second experiment, when the amount of [134]Cs activity added to the samples was reduced by a factor of two as compared to the first experiment.

The decrease of about 15% in activity in contacting solution was observed during the whole experiment. The exchangeable fraction extracted with $MgCl_2$ solution reveals insignificant variations. The most interesting sorption process was found for the caesium distribution between exchangeable (NH_4Cl), carbonate and residual fractions. The observed distribution in exchangeable fraction to a great extent deals with sorption process on the illite mineral, when Cs is isolated from the surrounding solution by fixating it in the clay lattice. This process is responsible for a rather quick sorption rate determined in the first stage of the sorption experiment. The decrease in the caesium amount in the exchangeable fraction desorbed by NH_4^+ possibly corresponds to the decrease in the number of frayed edge sites available for Cs sorption. The decrease in the sorption rate accompanied by an increase in association of [134]Cs with carbonate fraction can be attributed to the effect of coatings that is normally observed in natural heterogeneous sediments. Particles of different sizes are usually present in the sediments, the mineralogy of particles is different, moreover their surfaces could be covered fully and/or partly with the coating of different origin, e.g., iron compounds and organic substances. There are some publications considering the role of surface coatings in which this effect was studied by removing iron or organic substances from sediments and later used for sorption experiments [4]. These studies confirmed that surface coatings have a marked effect on the ability of clay to sorb Cs.

In the sediment sample used for the sorption experiment, a high content of carbonate was determined (up to 30%). This sample was collected in the Curonian

Lagoon where the precipitation of $CaCO_3$ was observed and attributed to high concentrations of Ca in the Nemunas river water. The deposition of $CaCO_3$ on sediment particles and the formation of carbonate coating are possible during the intrusions of saline water to the Curonian Lagoon, as a result of interaction of clay particles originated from the fresh water environment of the low ionic strength and high concentration of Ca^{2+} and HCO_3^- with high ionic strength and NaCl containing marine water. Thus, the increase in percentage of caesium associated with the carbonate fraction can be interpreted as an effect of carbonate coatings on Cs^+ sorption in the carbonate-rich sediments. It is well known that Cs^+ forms soluble carbonates, like Na and other alkali elements, and that the ionic radius of Cs^+ greatly exceeds that of Ca^{2+}. Therefore, there can be no doubt that co-precipitation of Cs^+ with calcite should be insignificant. The maximum partition coefficient determined for K^+ ($K_d = 10^{-3}$) can be used for upper limit in estimation of Cs^+ incorporation into calcite [3]. Thus, a negligible amount of Cs usually observed in carbonate fraction after the sequential extraction can be considered as traces of Cs^+ incorporated in calcite during co-precipitation and/or Cs^+ sorbed on regular exchange complex sites under carbonate coatings. It should be noted that from the point of view of availability it is not so important whether Cs^+ is incorporated in the carbonate or sorbed on regular exchange complex sites under carbonate coatings, caesium would be released into environment in the case of dissolution of carbonate (e.g., under low pH). This is important for understanding the sorption process and for the evaluation of discrepancies in data obtained from experiments with pure minerals and natural soil and sediments.

The comparative analyses of ^{134}Cs fraction distribution after 241 and 375 days of the sorption experiment with that of the ^{137}Cs distribution, determined in the same sediment sample before the sorption experiment, indicated that after 375 days of sorption the equilibrium was not fully reached, but distribution was found to be close to equilibrium (Fig. 3). In addition, the decrease
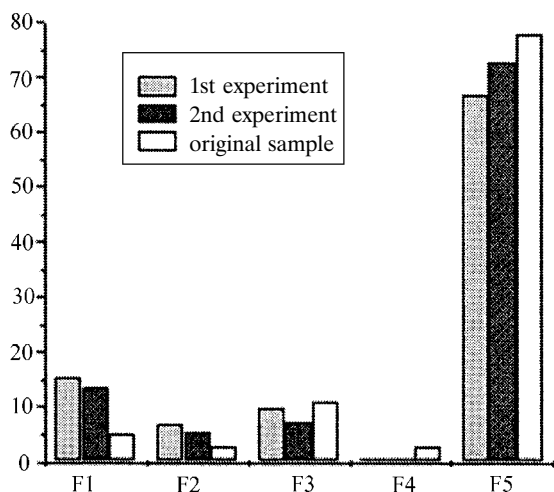
Fig. 4. Comparison of fraction distribution before and after desorption: a – 1st experiment, b – 2nd experiment) (F1 – contact solution; F2 – exchangeable ($MgCl_2$); F3 – exchangeable (NH_4Cl); F4 – carbonates; F5 – organic; F6 – oxides; F7 – residue).

in association of ^{134}Cs with carbonate fraction was found on the 241st and the 375th day of sorption that indicated the reduction of the coatings effect when equilibrium was reached.

Results of desorption experiments presented in Fig. 4 reveal an insignificant amount of Cs desorbed from the regular exchange sites, from which Mg^{2+} can easily displace Cs^+. However, a higher content of caesium tracer held in the residual fraction after desorption experiments clearly demonstrates the redistribution of ^{134}Cs between geochemical fractions during the desorption procedure. One possible explanation is the quick exchange reactions, but another – probably deals with the coatings inhibiting desorption. The redistribution found in samples evidenced the caesium transfer to the frayed edge sites on the layered clay minerals with its further fixation in the crystal lattice. Thus, the short-term desorption experiments indicated an insignificant release of Cs^+ from the regular exchange complex. The remobilization of "fixed" caesium was not observed, on the contrary, the redistribution of caesium

Fig. 3. Comparison of fraction distribution in samples from 1st and 2nd experiments and original sample (F1 – exchangeable; F2 – carbonates; F3 – organic; F4 – oxides; F5 – residue).
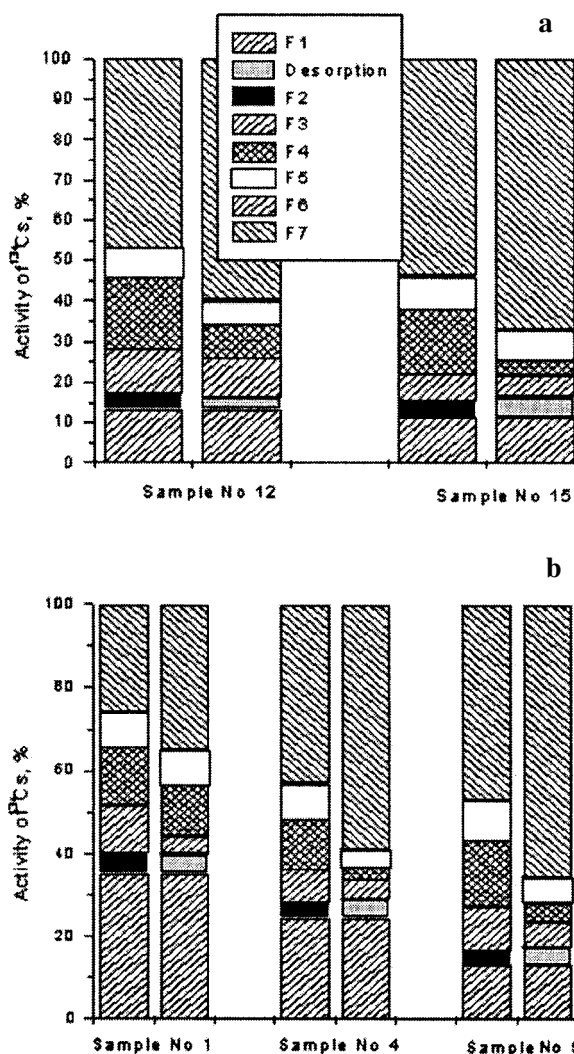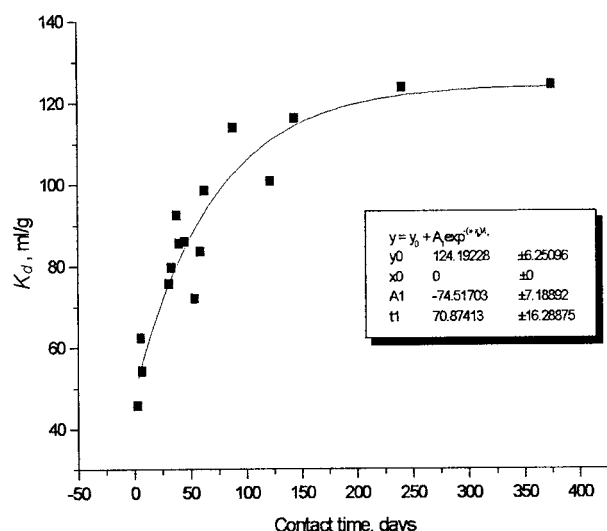
Fig. 5. K_d for [134]Cs as a function of contact time for sediment (sediment/sea water ratio 1:10) (1st experiment).

towards its fixation in clay minerals was observed, and on a time scale its fixation kinetics was comparable with the sorption experiment. Experiments have shown the double effect of coatings on sorption of Cs on bottom sediments: at primary stage of sorption coatings inhibit sorption of Cs, however, later they can inhibit the release of Cs to the surrounding solution.

Data obtained from these experiments were used to calculate the K_d coefficients both for total bottom sediments and different geochemical sediments phases (Figs. 5 and 6). It can be seen that residual fraction, which reflects the Cs sorption on clay minerals, is the most important in Cs incorporating to bottom sediments, while the role of other geochemical phases is relevant only during two months of sorption experiment.

This study indicated that flooding events of sea water contaminated with caesium can cause a significant accumulation of caesium in the bottom sediments of the Curonian Lagoon and result in the redistribution of ^{137}Cs activity concentration in the bottom sediments from one area to another.
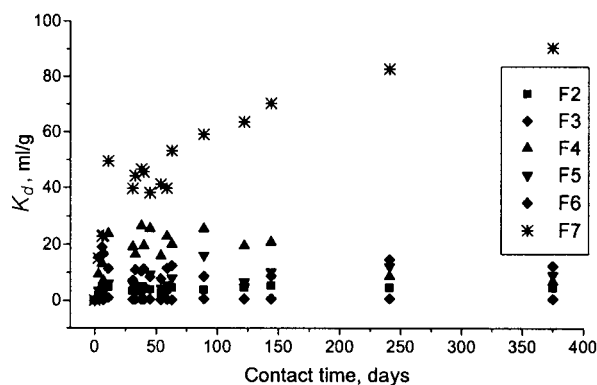

Fig. 6. K_d for [134]Cs in different fractions as a function of contact time for sediment (sediment/sea water ratio 1:10) (1st experiment) (F2 – exchangeable (MgCl$_2$); F3 – exchangeable (NH$_4$Cl); F4 – carbonates; F5 – organic; F6 – oxides; F7 – residue).

Conclusions

The equilibrium of Cs distribution between geochemical phases of bottom sediments was not reached even after 375 days of the sorption experiment.

The desorption experiment indicated an insignificant release of Cs$^+$ from regular exchange complex and transfer of Cs$^+$ from all studied phases to the fixed sites of the interlayer of clay minerals.

The predominant association of Cs with clay minerals controls the sorption process of this nuclide.

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