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Distribution of radionuclides in ferromanganese concretions and associated sediments from the northern-eastern Gulf of Finland

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Abstract ^{226}Ra displays much higher activities in ferromanganese concretions from the Gulf of Finland than in the associated sediments as a result of the direct adsorption of the ^{226}Ra from seawater onto the surfaces of manganese oxide minerals, the main sorbent of ^{226}Ra, in the concretions. The much higher activity of ^{226}Ra in deep-sea manganese nodules compared to the Gulf of Finland concretions is a function of the much longer period of growth of the deep-sea nodules. The activities of ^{232}Th and ^{40}K in the concretions and in the associated sediments are similar reflecting their association with clastic material. The activity of ^{40}K is higher in all types of ferromanganese crusts compared to the concretions due to the higher amounts of clastic sandy particles (particularly feldspars and micas) incorporated into the crusts during their growth. ^{137}Cs was introduced into the Gulf of Finland as a fall-out from the Chernobyl accident in 1986. The highest activity of ^{137}Cs is recorded in the silty-clayey mud and is the result of the adsorption of Chernobyl ^{137}Cs on these fine-grained sediments. The higher activity of ^{137}Cs in the buckshot concretions compared to the other types of ferromanganese concretions and crusts reflects the relative youth of these concretions. ^{60}Co activities exceeding the detection limit were found in only a few concretions.

Keywords *Ferromanganese concretions, radionuclides, Gulf of Finland.*

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INTRODUCTION

Investigations carried out by the All-Russia Scientific-Research Geological Institute have shown that the formation of ferromanganese concretions in the eastern Gulf of Finland is very rapid involving the deposition of hundreds tonnes of concretions and crusts within a relatively small area annually (Zhamoida et al. 1998, Amantov et al. 2002). Growth rates of the Baltic Sea concretions (0.02-0.30 mm/yr) have previously been estimated by counting microlaminations within the concretions and by comparing the distribution of heavy metals with depth in the concretions and in the associated sediments (Winterhalter & Siivola 1967, Suess & Djafari 1977, Zhamoida et al. 1996, Hlawatsch et al. 2002). In this study, concretions were recovered at 30% of the sampling sites in the investigated area in the eastern part of the Gulf of Finland. The total area of Mn-rich spheroidal concretions within the boundaries of the concretion-rich fields situated in this area (with an average abundance of about 20-30 kg/m^2) was estimated to be about 300 km^2 and a total weight of ore material of about 6 million tonnes (Zhamoida et al. 1996) or even more according to recent data of the mining company “Petrotrans”.

Ferromanganese concretions in the Gulf of Finland may be considered to be important because of their role in actively concentrating heavy metals and phosphorus and their influence on the redox potential of the bottom waters in the gulf (Zhamoida 1996, 1997), because of the interest of commercial firms in mining these deposits (Andreev et al. 2001, Dobretsov et al. 2001) and because the eastern Gulf of Finland was located within the path of the radioactive cloud from the 1986 Chernobyl accident. In this study, we have therefore attempted to establish the main factors controlling the distribution of radionuclides in these concretions. Prior to this study, data on the activity of radionuclides in the Baltic Sea concretions was rather poor (Aksenov et al. 1976, Liebetrau et al. 2002) and completely lacking in concretions from the Gulf of Finland.

Fig. 1 shows the location of the sampling area in the eastern Gulf of Finland. Ferromanganese concretions and crusts are found at water depths of 3 to 100 m. The superficial layer containing the concretions is very variable in thickness and abundance of concretions. Detailed information about the morphology of the concretions, their mineralogy and chemical composition, their mechanisms of growth and age is contained in numerous publications (Varentsov & Blazhchishin 1976, Winterhalter 1980, Zhamoida 1987, 1989, Glasby et al. 1996, Zhamoida et al. 1996, Zhang et al. 2002).

Within most of this area, only occasional concretions were found but, in some places, the abundance of the concretions reaches 50 kg/m^2. Two main types of area containing abundant concretion were distinguished to be relatively "deep" (water depth 35-60 m) and relatively "shallow" (water depth 15-25 m) (Butylin & Zhamoida 1989, Zhamoida et al. 1996).

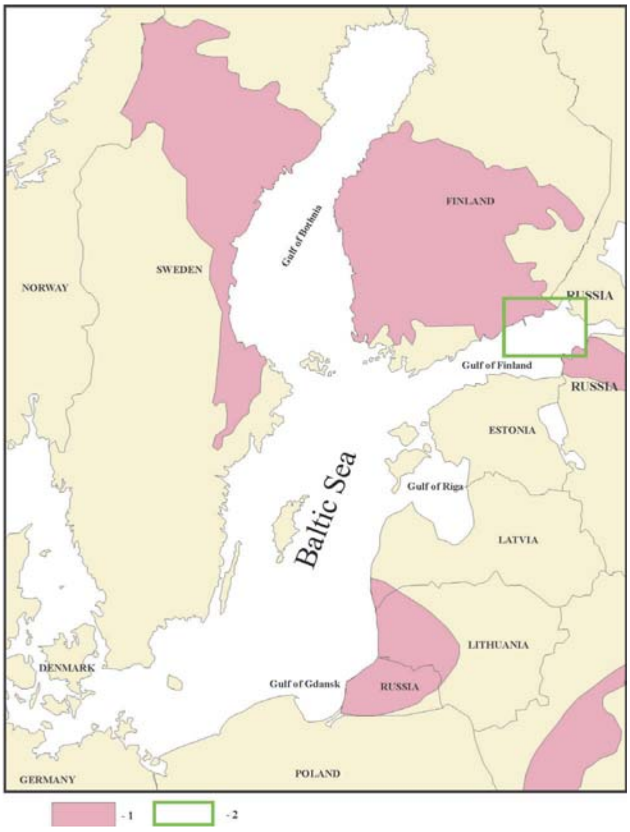

Fig. 1. Schematic map of the Baltic Sea region showing: 1 - areas of radioactive fallout from Chernobyl (>10 kBq/m^2) (after web site publication of Radiation and Nuclear Safety Authority, Finland, 2002); 2 - the location of the sampling area in the eastern Gulf of Finland.

The relatively "shallow" concretion fields are located near the coast or on the shoals. As a rule, these fields are situated within the areas where Upper-Pleistocene glacial lacustrine clay outcrops. Usually, only a thin layer (3-5 cm thick) of unsorted sand covers the clay. The concretions are distributed at the sediment surface or in the sandy layer. The morphology of concretions is variable, but discoidal concretions and concentric rings around erratic nuclei dominate. Detailed descriptions of these morphological types of concretions can be found in Zhamoida (1989) and Glasby et al. (1996).

The relatively "deep" concretion fields are located at the margins of active silty-clay mud deposition. The layer of superficial sediments containing concretions usually covers Lower Holocene lacustrine or Upper Pleistocene glacial lacustrine clay, rarely Upper Holocene (Litorina) marine clay. These fields are typically a few km long and up to 0.5-1.0 km wide, depending mainly on the relief of the sea floor and the extent of the mud. In general, the superficial layer containing the concretions is covered by a thin layer of recent silty-clay mud 10-20 mm thick. However, in some places concretions can be exposed at the surface of the sea floor. The thickness of the layer containing the concretions is usually 5-15 cm, rarely up to 40 cm. A detailed description of the structure of such layers and the morphology of concretions is contained in Zhamoida et al. (1996). Mn-rich spheroidal and buckshot concretions are the main types of concretions of such fields. Locally, spheroidal concretions are replaced by large flat concretions or irregular crusts without erratic nuclei or incorporating large amounts of clastic material. Photographs showing the morphologies of these concretions are shown in Fig. 2.

Ferromanganese concretions of the Gulf of Finland are characterized by a low degree of crystallinity of the ore-forming minerals. The main Mn-minerals present are birnessite, unstable buserite and manganite. Fe-minerals are represented mainly by amorphous or very poorly crystalline iron oxyhydroxide, ferrihydrite and possibly Fe-phosphates. Terrigenous minerals such as quartz, feldspars, hydrated micas and hornblendes are always present.

The content of the main ore-forming components Fe_2O_3+MnO_2+MnO in the concretions lies in the range 45-70% (on a dry-weight basis). The maximum content of MnO_2+MnO in the spheroidal concretions is 51%. The concentrations of most of the minor elements in the concretions are similar to their background concentrations in the superficial sediments. However, the concentrations of Mo, Co, Zn, Pb and Ni are higher than background concentrations, possibly due to anthropogenic influences (Zhamoida et al. 1996, Hlawatsch et al. 2002), and are characterized by a significant level of dispersion. The main factors controlling the variation of the chemical composition of concretions from the Gulf of Finland in relation to the geology, sediment facies, morphology and size of the concretions and other factors have been summarized in the following papers (Winterhalter 1966, Varentsov & Blazhchishin 1976, Butylin et al. 1986, 1989, Butylin & Zhamoida 1989, Glasby et al. 1996, Zhamoida et al. 1996, Zhamoida et al. 2004). Average concentrations of major elements from the different types of concretions in the Gulf of Finland have been presented in Zhamoida et al. (2004).

MATERIALS AND METHODS

Sampling was carried out during geological surveys of the Russian sector of the Gulf of Finland in 1998-2000 from the research vessels *Professor Stockman*, *SChS-2154* and *Meridian*. Samples were collected using an Ocean-0.25 m^2 grab sampler. The concretions and crusts were separated from the associated sediment

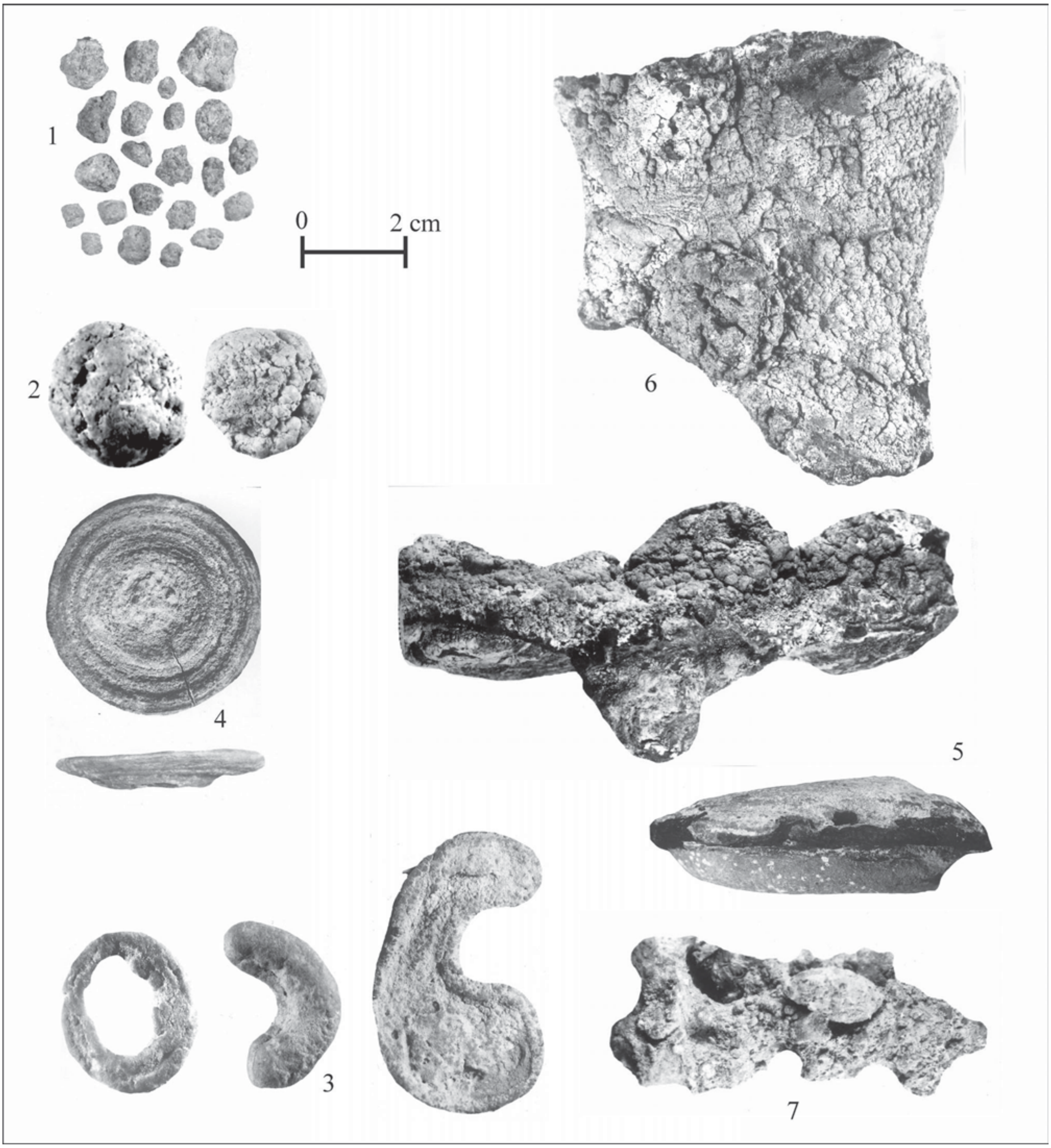

Fig. 2. Photographs of typical ferromanganese concretions from the eastern Gulf of Finland: 1 - buckshot concretions; 2 - spheroidal concretions; 3 - irregular concretions; 4 - discoidal concretions; 5 - concentric rings around erratic nuclei; 6 - large flat concretions or crusts without erratic nuclei; 7 - irregular crusts incorporating large amounts of clastic material.

Table 1. Median and standard deviation of activity of gamma-emitting radioisotopes (Bq/kg) in the main types of ferromanganese concretions and crusts in the Gulf of Finland. A_b is the back-ground median value, σ is the standard deviation, N is the number of samples.

Type of concretion	N	Isotope							
		^{226}Ra		^{232}Th		^{40}K		^{137}Cs	
		A_b	σ	A_b	σ	A_b	σ	A_b	σ
Buckshot concretions	17	310	87	51	20	416	85	122	93
Spheroidal concretions	37	417	329	45	16	352	129	65	32
Concretions of irregular forms	8	275	104	38	10	437	125	36	8
Discoidal concretions	19	231	94	45	16	354	187	44	19
Concentric rings around erratic nuclei	14	265	66	76	34	719	42	47	32
Large flat concretions or crusts without erratic nuclei	7	283	96	45	27	667	71	84	63
Irregular crusts incorporating large amounts of clastic material	5	300	120	61	5	725	231	92	42

onboard and divided into six types of concretions and one type of crust (Table 1). The samples were then dried at 105-110°C and ground prior to analysis. 107 samples of concretions displaying different morphologies were analyzed.

The major elements were analyzed by classical chemical methods and X-ray fluorescence spectroscopy at the VSEGEI laboratories. The minor elements were determined by atomic emission and atomic absorption spectrometry.

The natural (^{226}Ra, ^{232}Th, ^{40}K) and anthropogenic (^{137}Cs) radionuclides in the concretions and crusts were determined using a RADEK gamma-ray scintillation spectrometer. The scintillation detector contained an 80x80 mm NaI(Tl) crystal. The resolution of the detector was better than 8-10% on the ^{137}Cs line at 661.7 keV. Minimum measuring activity for ^{40}K –37 Bq, ^{137}Cs – 2.8 Bq, ^{226}Ra –8.2 Bq, ^{232}Th – 5.6 Bq, ^{60}Co –3.8 Bq.

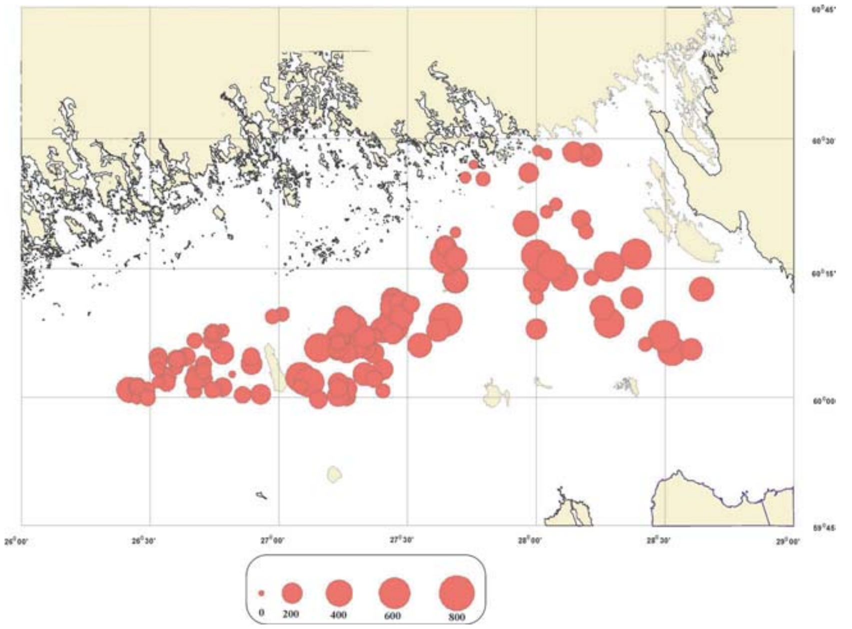

Fig. 4. Schematic map showing the position of the sampling sites and activity of ^{137}Cs (Bq/kg) in ferromanganese concretions and crusts in the Gulf of Finland.

RADIOELEMENT DISTRIBUTION IN CONCRETIONS

The median activities and their standard deviations for each radionuclide in each type of concretion are shown in Table 1. Figs 3 and 4 show the locations of the sampling sites and the activities of ^{226}Ra and ^{137}Cs in ferromanganese concretions and crusts in the Gulf of Finland.

The data show that the levels of ^{226}Ra in the concretions and crusts are much higher than in all types of bottom sediments irrespective of the

Table 2. Median and standard deviation of activity of gamma-emitting radioisotopes (Bq/kg) in bottom sediments from the Gulf of Finland. A_b is the back-ground median value, σ is the standard deviation, N is the number of samples, (I) – area of Chernobyl fall-out zone; (II) – area outside Chernobyl fall-out zone.

Type of sediments	Isotope								N
	^{226}Ra		^{232}Th		^{40}K		^{137}Cs		
	A_b	σ	A_b	σ	A_b	σ	A_b	σ	
Silty-clayey mud	52	31	75	34	805	303	560 (I) 84 (II)	458 (I) 57 (II)	221
Silty sands, sandy silts, sandy clays	49	35	30	14	678	203	61	39	34
Sands	27	15	33	14	968	210	27	17	89
Coarse-grained sands with gravel and pebbles	28	22	35	5	1005	289	21	22	19

morphology of the concretions (Tables 1, 2). This is confirmed by the results of profiling with an underwater-towed spectrometer, which showed that the concretion field is characterized by an intense radium anomaly (Fig. 5). The concretions and crusts are therefore significant concentrators of ^{226}Ra. By contrast, the levels of ^{232}Th are lower on average in the concretions than in the silty-clayey sediments and the levels of ^{40}K are significantly higher in the sediments than in the concretions.

The distribution of ^{137}Cs shows a different trend. The levels of ^{137}Cs in the concretions and crusts are similar to or somewhat higher than those in the bottom sediments with the exception of recent silty-clayey mud which is characterized by ^{137}Cs levels several times higher than the concretions (Tables 1, 2). This is confirmed by the results of underwater profiling that show that the concretion field is marked by minimal ^{137}Cs activity compared to the muds (Fig. 5). These observations demonstrate that the ^{137}Cs activity of the recent silty-clayey mud is much higher than background in accordance with the fact that the Gulf of Finland was located along the trajectory of the fall out from Chernobyl in 1986 (Fig. 1) (Kankaanpää et al. 1997, Anokhin et al. 1999, Grigoriev 2003, Grigoriev & Marchenko 2003). By contrast, the concretions accumulate ^{137}Cs to a much lesser extent.

DATA PROCESSING

In order to understand the factors controlling the uptake of radionuclides in the concretions and the influence of the morphology of the concretions on this process, statistical analysis of the median values and dispersion of each radioisotope in each of the concretions and crusts was undertaken using the Student t-test and Fisher criteria (Table 1). From this, the following observations could be made.

Spheroidal concretions are characterized by higher levels of ^{226}Ra and a greater dispersion in its distribution than the other types of relatively "deep" field concretions such as buckshot concretions and large flat concretions and crusts. Irregular crusts formed by the cementation of superficial deposits are more or less similar to spheroidal concretions in the main parameters of ^{226}Ra distribution. By contrast, discoidal concretions and concentric rings of ferromanganese oxides around erratic nuclei located within the shallow-water areas are characterized by somewhat lower levels of ^{226}Ra. The morphology of

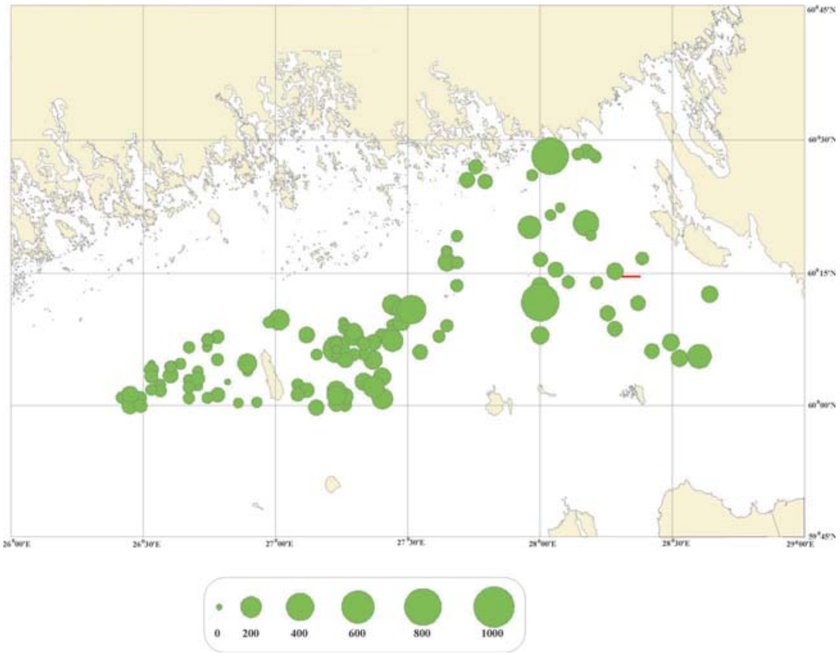

Fig. 3. Schematic map showing the position of the sampling sites and activity of ^{226}Ra (Bq/kg) in ferromanganese concretions and crusts in the Gulf of Finland. * Red line – location of the underwater gamma-spectrometric profile across the field of ferromanganese concretions (see Fig.5).

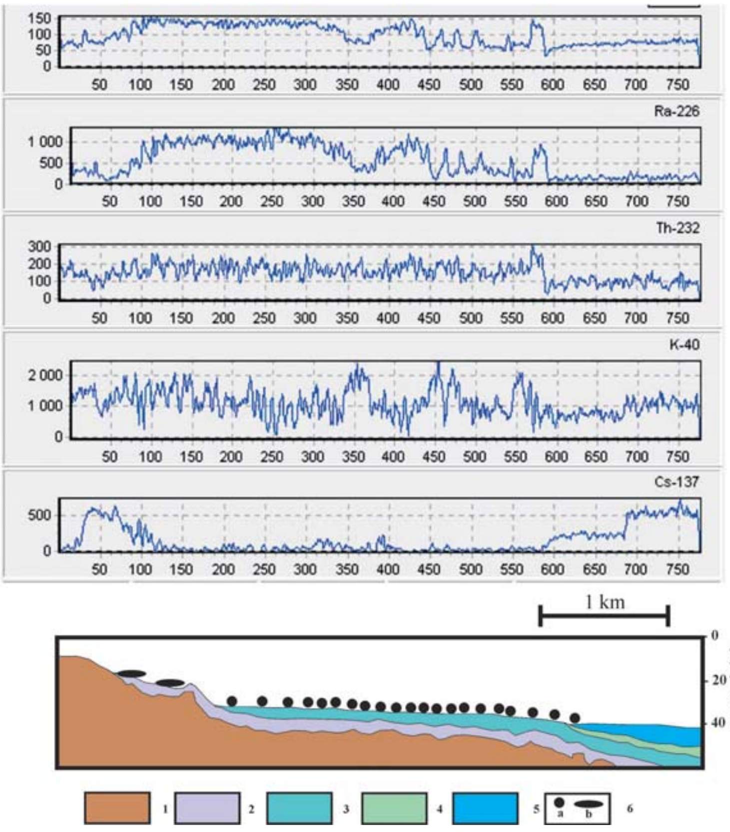

Fig. 5. Profile of the dose of the general gamma-ray (upper profile) and the activity of gamma – ray emitting nuclides (all in standard relative units) across the field of ferromanganese concretions. Data obtained by underwater gamma-spectrometric profiling. (Location of the profile is shown at the Fig.3). 1-3 – Upper-Pleistocene sediments: 1 – glacial till, 2 – varved clays, 3 – glacial lacustrine clays of the Baltic Ice Lake; 4-5 – Holocene sediments: 4 – lacustrine clays, 5 – marine silty-clayey mud; 6 – Fe-Mn concretions: a – spheroidal concretions, b – discoidal concretions.

the concretions therefore appears to have only a slight influence to the uptake of ^{226}Ra in the concretions. However, this influence is not statistically significant because of the generally high level of ^{226}Ra content in all types of concretions and crusts and its markedly heterogeneous distribution.

Statistical processing of the ^{232}Th data does not reveal any regularity in the distribution of ^{232}Th in different types of concretions. Relatively high concentration of ^{232}Th was determined in concentric rings around erratic nuclei and irregular crusts incorporating large amounts of clastic material. These findings are in accord with the conclusions of Blazhchishin et al. (1982) that ferromanganese concretions do not adsorb ^{232}Th from seawater and that its content is dependent on the amount of clastic material incorporated into the concretions.

By contrast, statistical processing of the data for ^{40}K divides the concretions and crusts into two groups. The first group includes buckshot, spheroidal, discoidal and irregular concretions, which do not significantly differ in their mean values and dispersions of low ^{40}K concentrations. The second group includes all types of the Fe-Mn crusts and is characterized by higher levels of ^{40}K on average. It may be assumed that the higher levels of ^{40}K in the crusts reflect higher contents of clastic sandy particles (particularly feldspars and micas) in the crusts (Zhamoida & Grigoriev 2002). The high concentrations of ^{40}K in the concentric ring around erratic clastic nuclei may be explained by the incorporation of part of the nuclei into the analyzed samples during grinding.

The concretions and crusts may be also divided into two groups in the case of ^{137}Cs. The first group includes buckshot concretions, large flat concretions or crusts without erratic nuclei and irregular crusts incorporating large amounts of clastic material. These concretions are characterized by somewhat higher levels of ^{137}Cs and do not significantly differ in mean values or dispersion. The spheroidal concretions also gravitate towards this group, although they are characterized by lower levels of ^{137}Cs. This can be explained by the fact that the majority of the ^{137}Cs were transported into the Gulf of Finland after the Chernobyl accident in 1986. Since the growth rate of the spheroidal concretions is very rapid (0.02-0.30 mm yr^{-1}) (Zhamoida 1987, Zhamoida et al. 1996), it is clear that ^{137}Cs can be only incorporated into the outer layers of the concretions. The total ^{137}Cs in the spheroidal concretions must therefore be lower than that in the modern buckshot concretions. As previously shown (Zhamoida 1987, Zhamoida & Grigoriev 2002), large flat concretions and crusts without erratic nuclei, as well as irregular crusts incorporating clastic material, are formed in local areas within the relatively "deep" concretion fields characterized by very high rates of growth. The second group including shallow-water discoidal concretions and concentric rings around erratic nuclei is characterized by lower levels of ^{137}Cs. It therefore appears that the level of ^{137}Cs accumulation in the concretions is mainly dependent on the nature of the concretions. Higher levels of ^{137}Cs occur in concretions from the relatively "deep" concretion fields and lower levels in concretions from the shallow-water fields.

COMPARISON WITH DEEP-SEA MANGANESE NODULES

It is possible to compare the levels of ^{226}Ra and ^{232}Th activities in ferromanganese concretions from the Gulf of Finland and deep-sea nodules from the Pacific Ocean. For example, according to Moore (1984), the average activity of ^{226}Ra in deep-sea nodules from the Clarion and Clipperton zone in the Pacific Ocean recalculated from dpm/g to Bq/kg is 4230 Bq/kg; for ^{232}Th – 87 Bq/kg. According to Huh and Ku (1984, 1990) the outer layers (0-0.31 mm) of ferromanganese nodules from the northern Pacific Ocean are characterized by the following average activities recalculated to Bq/kg: for ^{226}Ra – 3835 Bq/kg and for ^{232}Th – 1093 Bq/kg. According to Kuznetsov (1993) the average recalculated activity of ^{232}Th for different morphological types of nodules in the Pacific Ocean lies in the range 213-324 Bq/kg. The levels of ^{226}Ra in deep-sea manganese nodules are therefore much higher then those in ferromanganese concretions from the Gulf of Finland in contradiction to the findings of Staric et al. (1962). The much higher ^{226}Ra content in deep-sea nodules can possibly be explained by the much longer period of sorption of the radioisotope onto the surface of these nodules compared to that in the young concretions from the Gulf of Finland. The activities of ^{232}Th in deep-sea manganese nodules are also higher than in the concretions from the Gulf of Finland. However, there is also considerable dispersion of the average activities of ^{232}Th from 87 Bq/kg to 1093 Bq/kg in deep-sea nodules based on the results of different authors. This is probably related to the amount and type of clastic and biogenic material incorporated into the nodules.

CONCLUSIONS

Our data show that ferromanganese concretions are the principal concentrator of ^{226}Ra in the Gulf of Finland. The activity of ^{226}Ra in the concretions exceeds that in the bottom sediments several fold. The level of ^{226}Ra in concretions and crusts from the "deep" concretion fields situated at the edge of areas of silty-clay sedimentation is not much higher than in concretions of the shallow-water fields where silty-clay is absent. This supports the idea that most of the ^{226}Ra is taken up in concretions directly from the water column and is not involved in prior sorption on clay particles. The small increase in the ^{226}Ra content in the concretions from the "deep" fields can be explained by the higher contents of manganese oxides, the main sorbent of ^{226}Ra, in these concretions.

By contrast, the levels of ^{232}Th in the concretions depend, to some extent, on the type of concretion and are similar to those in the bottom sediments. The levels of ^{40}K in the concretions are on average higher in the sediments than in the concretions. This is a function of the amount of silty and sandy K-bearing terrigenous minerals incorporated into the growing concretions and crusts from the sediment.

The process of accumulation of ^{137}Cs in the concretions differs markedly from that of ^{226}Ra. Theoretically, ferromanganese concretions should be characterized by a high sorption capacity for ^{137}Cs, which is a monovalent element with a large ionic radius. However, ^{137}Cs is only slightly enriched in the concretions. Most of the ^{137}Cs in the Gulf of Finland are adsorbed on clay particles with only a small part introduced directly from the water column. All the concretions occur within the areas of low or possibly net sedimentation. The amount of clay minerals directly incorporated into the concretions is therefore low with the result that the levels of ^{137}Cs in the concretions and crusts are also low.

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