Geochemistry International, Vol. 36, No. 11, 1998, pp. 983–990. Translated from Geokhimiya, No. 11, 1998, pp. 1091–1098.

Application of Artificial Radionuclides for the Geochemical Investigations of the Ob and Yenisei Estuaries and Adjacent Regions of the Kara Sea

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Received June 1, 1998

Abstract—The results of a 1997 radiogeochemical investigation are presented for the region of the Ob and Yenisei river estuaries and the adjacent regions of the Kara Sea. The data obtained from water and bottom sediment samples from 59 sites demonstrate that the consideration of natural environmental parameters and the geochemical behavior of various radionuclides is essential for the interpretation of fluctuations in their lateral distribution in the upper layer of bottom sediments. The distribution of radionuclide activity (primarily, ^{137}Cs) over the depth of a drill-core allowed us to recognize probable sources of radioactivity and to estimate the moments of their inflow into the Kara Sea. The distribution of radionuclides in water is largely determined by synoptic conditions in a particular site and hydrologic parameters, especially important in the river–sea mixing zone.

INTRODUCTION

Among the sources of anthropogenic pollution in the Kara Sea are the run-offs of the largest Siberian rivers, the Ob and Yenisei, which could bear the radioactive waste of nuclear plants.

It is well-known that large depositories of active waste are situated east of the Urals. They are transported to Chelyabinsk for reworking. The industrial enterprise Mayak is situated in the southern Urals, where three radiation accidents took place in the radiochemical plant for plutonium separation from 1949 to 1953, 1957, and 1967 [1]. In addition to soil pollution, the contamination involved the hydrologic system connecting the Techa River, where the active waste of the Mayak plant was discharged till 1951, with the rivers flowing into the Kara Sea. Observations of the radioactive pollution levels in these rivers show a consistent increase in the concentrations of radioactive elements relative to background values. Radioelements are carried to the rivers with flood and ground waters. This results in the radioactivity removal through the river system Techa–Iset'–Tobol–Ob into the Kara Sea and further to other seas of the Arctic basin with ocean currents.

The Krasnoyarsk chemical mining plutonium-producing plant is situated 30 km northeast from Krasnoyarsk. The active liquid waste produced in the technologic process comes into underground layers and presents a hazard. The consequences may be unfavorable for both the vicinity of Krasnoyarsk and the Yenisei River. Studies of the radioactive situation in the Yenisei support such alarms: its pollution by water from the plant was observed far from the place of waste discharge [2].

According to the estimate of the State Committee for Hydrometeorology, from 1961 to 1989, the water of the Ob and Yenisei carried into the Kara Sea 110 TBq of ^{137}Cs and 1100 TBq of ^{90}Sr [3].

Radioactive elements are transported by river water into the Kara Sea passing through the zone of river–sea interaction, where the distribution and behavior of the elements might change considerably. The parameters of the environment, such as velocity of water mass movement, salinity, pH, chemical composition, change strongly at the contact of fresh river and saline sea waters. As a result, up to 20–40% of dissolved and 90–95% of suspended material of river run-off could precipitate in this zone [4]. The finest suspensions and colloid particles are the carriers of hydrolyzed radionuclides, such as ^{239}Pu, ^{240}Pu, ^{95}Zr, and others. Particles of clay minerals in suspensions can accumulate considerable amounts of cesium radionuclides owing to the substitution for potassium in the interlayer spaces of crystalline minerals. The radionuclide ^{90}Sr is characterized by the occurrence in a stable water-soluble form, and it is not accumulated in suspensions and bottom deposits [5].

These considerations suggest that investigation of the distribution of artificial radionuclides in the Ob and Yenisei estuaries and adjacent regions of the Kara Sea is especially important for the characterization of radioecological conditions of a natural geochemical barrier, which could be an efficient filter for the retention of chemical elements and their radioisotopes.

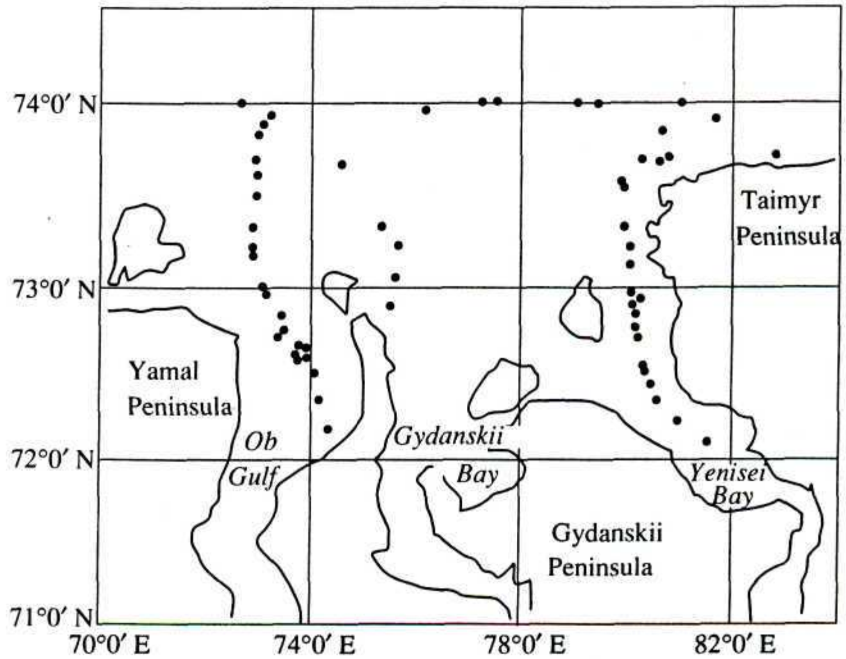

Fig. 1. Location of the study area and sampling sites of Cruise 28 of the R/V *Akademik Boris Petrov.*

The experiments that we carried out in nature in 1995 [6] demonstrated a distinctly spotted character of radioactivity distribution in the bottom deposits and water of Arctic seas, especially in the Kara Sea. The highest concentrations of the radionuclides ^{137}Cs, ^{239}Pu, and ^{240}Pu were found in the southeastern part of the sea. This work was continued and extended in 1997 on aboard the R/V *Akademik Boris Petrov* in the framework of the joint Russia–Germany investigations of the nature of continental run-offs from Siberian rivers and their behavior in the adjacent Arctic basin.

International Cruise 28 was carried out in accordance with the plan of the Russian Academy of Sciences for the study of the ocean (presided by Deputy President of the Russian Academy of Sciences, Academician N.P. Laverov) and in the framework of the agreement between the Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences (GEOKhI RAN, scientific supervisor Academician E.M. Galimov) and the Alfred Wegener Institute of Polar and Marine Research (AWI, scientific supervisor Prof. D. Futererer).

The R/V *Akademik Boris Petrov* of the Russian Academy of Sciences is equipped for studying radioactivity and chemical and organic trace components. A variety of methods and facilities allow for multiparameter investigations in the Ocean, including the observation of a water environment up to a depth of 5000–6000 m, the sampling and analyzing of bottom sediments, and measurements in the near-water atmospheric layer. The R/V has a helicopter platform and a place for the arrangement of a submersible for work at depths of up to 300 m.

The experimental work was carried out in the Ob and Yenisei estuaries, the southern part of the Kara Sea, and the Gydanskii Bay at 59 sites (Fig. 1).

In addition to the study of the distribution and migration of artificial radionuclides in marine environments as markers of geochemical processes, the scientific program of the joint cruise comprised a wide range of problems related to organic and gas geochemistry, the biogeochemical activity of sediments, hydrochemistry of pore water, and behavior of inorganic pollutants.

Researchers from the following institutes took part in the cruise: Vernadsky Institute of Geochemistry and Analytical Chemistry (GEOKhI, Moscow), Shirshov Institute of Oceanology (IO, Moscow), Kurnakov Institute of General and Inorganic Chemistry (IONKh, Moscow), Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry (IGEM, Moscow), Murmansk Institute of Marine Biology (MMBI, Murmansk), Institute of Soil Science and Photosynthesis (Pushkin, Moscow oblast) of the Russia Academy of Sciences and the Institute of Arctic and Antarctic (AANII, St Petersburg), All-Russia Research Institute of Oceanology (VNIIOkeanologiya, St Petersburg), and the Defense Ministry of the Russian Federation.

Among the German participants were the Alfred Wegener Institute of Polar and Marine Research (Bremerhaven), Institute of Biochemistry and Marine Chemistry (Hamburg), and GEOMAR Research Center (Kiel).

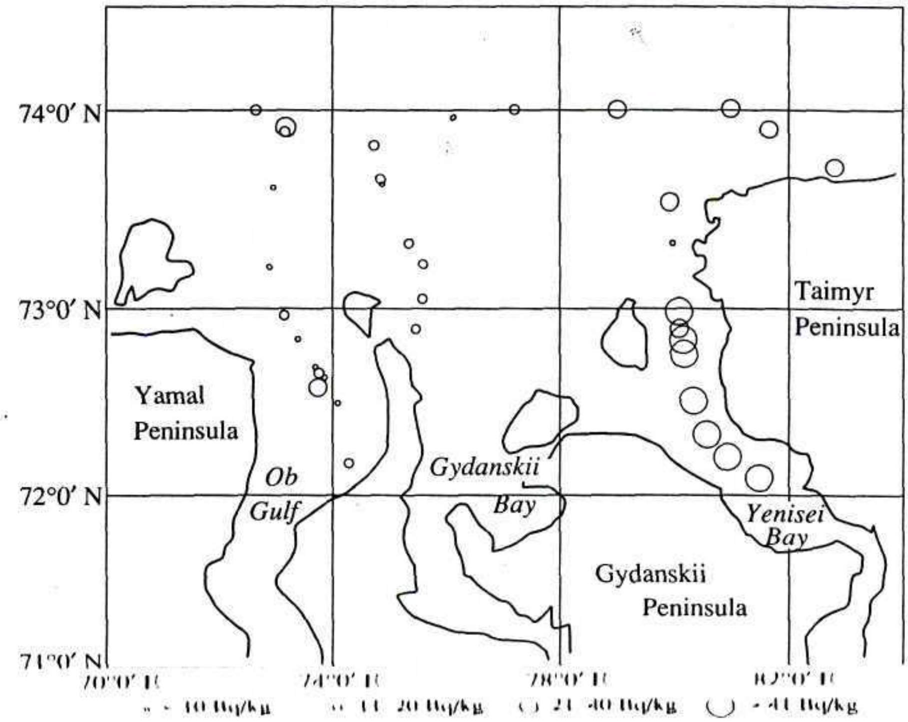

Fig. 2. Distribution of ^{137}Cs in the upper portion (0–2 cm) of bottom sediments.

The program of radiogeochemical work included investigations of the lateral and vertical distribution of cesium, plutonium, and strontium isotopes in water and sediments, and the influence of environmental parameters on the character of their distribution and migration in the regions studied. For the interpretation of the obtained results, additional data were considered on hydrologic water parameters obtained by an STD complex OTS-PROBE Serie-3 and the description of geologic material performed by the geological group of the Alfred Wegener Institute.

SAMPLING AND ANALYTICAL METHODS

Samples of bottom sediments were taken by a box corer (50 × 5 × 50 cm) and a bottom bucket "Okean" with the use of a cylindrical plastic sampling unit provided with a piston and a cylinder, 10 cm i.d. The sample was divided into disks, 1–2 cm thick and dried at 60–80°C.

Water samples were taken by a 200-liter sampler or a pump (without metal parts), and were kept in polyvinyl chloride tanks 150 l in volume. Some of the samples were filtered through a nuclear filter with a pore size of 0.45 μm before analysis.

The analysis of ^{137}Cs in sediments was carried out by direct gamma spectrometry of samples on low-background gamma spectrometers with energy dispersive Ge- and Ge–Li detectors. ^{137}Cs, ^{90}Sr, ^{239}Pu, and ^{240}Pu in water samples and ^{90}Sr, ^{239}Pu, and ^{240}Pu in bottom sediments were analyzed by radiochemical methods.

For the analysis of ^{137}Cs in 100-liter water samples, concentrates were prepared by the sorption method under dynamic conditions and measured by gamma spectrometry. Cobalt ferrocyanide used as a sorbent was mounted in an organic matrix [7]. The matrix consisted of cellulose and polyacrylonitrile copolymer containing thioamide groups. The presence of these groups ensured the strong bonding of ferrocyanide (II) groups with the matrix at a prolonged contact of the sorbent with seawater.

The determination of ^{90}Sr in water samples included the preliminary precipitation of strontium carbonate and subsequent extraction chromatographic refinement. The analysis of specimens was carried out on a low-background beta analyzer with a gas flow counter, which registered the energy of ^{90}Sr or daughter ^{90}Y after the attainment of equilibrium. The samples of bottom sediments were leached with acids before analysis. The analysis was carried out using the scheme described by Kremlyakova [8].

The analysis of plutonium in water samples included preliminary coprecipitation and concentration of plutonium with iron hydroxide (from 100-liter samples) with subsequent ion-exchange refinement and plutonium separation on lanthanum fluoride [9]. The precipitate was separated by a membrane filter, and its activity was measured on an alpha spectrometer. To

Table 1. Equilibrium partition coefficient (K_d) of ^{137}Cs for various types of bottom sediments

Group no.	Type of bottom sediments	K_d	Sorption effect
1	Coarse-grained sediments with a low fraction of pelitic particles of organic–mineral composition of shallow bottom areas with intense exchange at media interface	10–20	Weak
2	Pelitic sediments of organic-mineral composition with high content of sand–silt fraction of shallow and moderately deep floor regions with an intense exchange of disperse phases at media interface	40–70	Medium
3	Pelitic sediments consisting mainly of organic-mineral colloids with intense exchange of disperse phases at media interface	>100	Strong

determine plutonium in bottom sediments, samples were boiled initially with $KBrO_3$ in 7 M HNO_3 and treated then by the same procedures of refinement and plutonium separation that were used for the analysis of water samples.

RESULTS AND DISCUSSION

Figure 2 shows the lateral distribution of ^{137}Cs in the upper layer of bottom sediments. These results confirm our previous inferences on the considerable influence of the lithology of the upper sedimentary layer on the ^{137}Cs activity level [6]. For instance, reduced sediments represented by mud material with sand grains are poor sorbents for cesium, whereas sediments with high content of clay material show a high sorption capacity with respect to ^{137}Cs. To support this conclusion, experiments were carried out on board on the sorption of ^{137}Cs (after ^{134}Cs) by various types of sediments. The experiments were carried out in the following way.

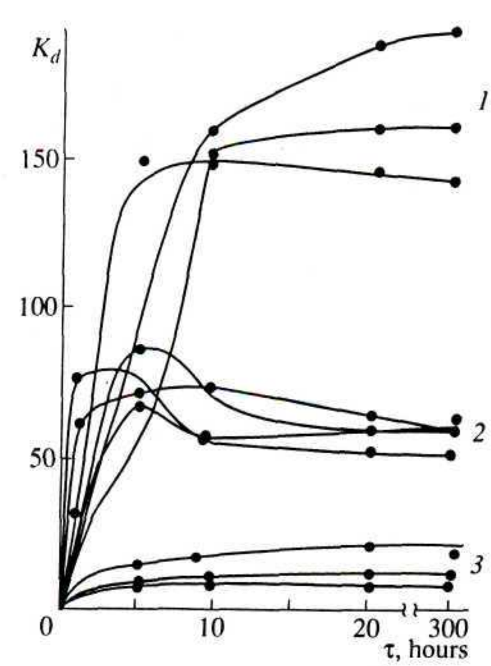

Fig. 3. Dynamics of radiogenic cesium sorption (for cesium-134) by various types of bottom sediments.

^{134}Cs was introduced into a 100-ml water sample, the sample was kept for several hours in order to attain isotopic equilibrium, and the bottom sediment charge was then added ($v/m = 20$). In specific time intervals, the activity of the water aliquotes was measured and the partition coefficient was calculated by the equation $K_d = (S/1 - S)V/m$. The data presented in Fig. 3 and Table 1 suggest that the bottom sediments may be divided into several major groups with respect to the degree of ^{137}Cs fixation differing in composition and proportions of clay and sand materials.

The influence of the geochemical parameters of the upper sedimentary layer on the activity distribution patterns is recorded to a certain extent in the lateral distribution of ^{90}Sr (Table 2). No such regularity was observed for the distribution of ^{239}Pu and ^{240}Pu (Fig. 4). This could be explained primarily by the insufficient number of analyzed samples in the estuary region despite the fact that analytical results for samples collected in 1995 were also used in this work.[1]

During the investigation of the vertical distribution of ^{137}Cs, many of the samples displayed significantly higher counts of this radionuclide in some core layers (Fig. 5). Noteworthy are the high ^{137}Cs concentrations at a depth of 6–7 cm in the samples from the Yenisei and Ob Gulfs. Similar results were obtained also by us in 1995 during Cruise 22 of the R/V *Akademik Boris Petrov* (Fig. 6). The comparison of these data with the description of the vertical structure of sediments (Figs. 7, 8) suggests that the significant vertical ^{137}Cs variations are not related to the structural heterogeneity in the vertical section. These changes in counts are linked more likely with varying rates of radioactivity supplied into the marine environment. In this case, this process should record the modern stage of sedimentation in the upper layer of bottom sediments depending upon the particular conditions of precipitation in a given region. It is conceivable that the high radioactivity at a depth of 6 cm is related to the Chernobyl accident and may be dated at 1986. This inference seems to be reasonable and is supported by published data on the presence of Chernobyl radionuclides in the Kara Sea

[1] Samples were processed in the Radiochemical Laboratory, GEOKhI RAN.

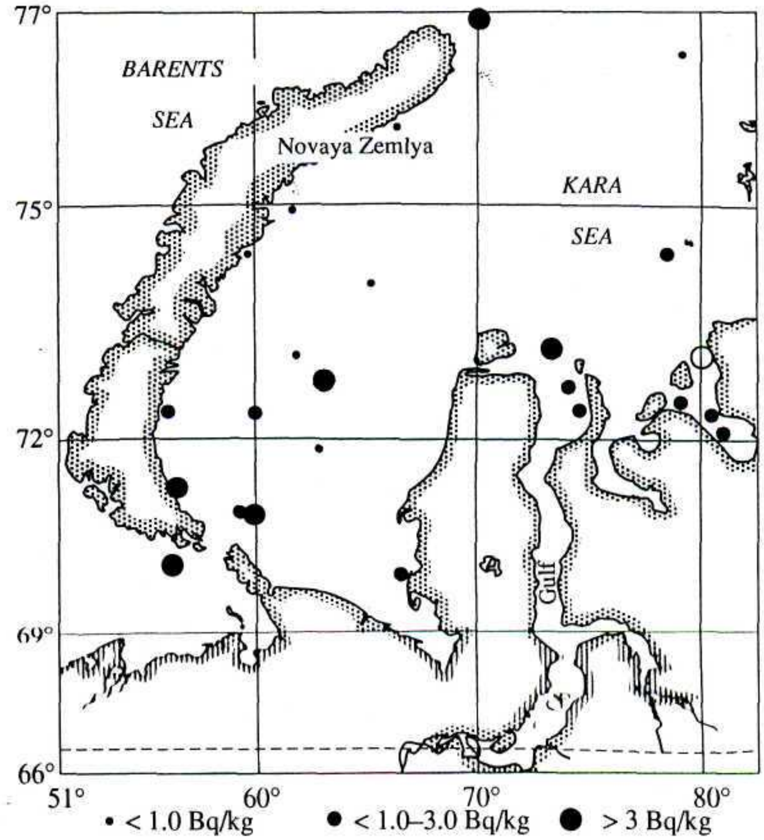

Fig. 4. Distribution of ^{239}Pu and ^{240}Pu in the upper portion (0–2 cm) of bottom sediments.

and in the bottom sediments of the upper reaches of the Ob River [10, 11]. If our hypothesis is correct, the younger sediment layers with lower radioactivity allow inferences on the real supply of radioactivity into the bottom sediments of this region at certain time intervals. Using the data on ^{137}Cs vertical distribution in 1995 and 1997 and assuming that the ^{137}Cs activity maximum in samples from both the Ob and Yenisei Gulfs is due to the Chernobyl accident of 1986, we estimated the probable sedimentation rate as ~0.5 cm/y.

The investigation of the vertical distribution of strontium radioisotope provides additional evidence supporting our conjectures (Fig. 9). Although ^{90}Sr variations with the depth of the core are not so spectacular, there is a correlation with the vertical ^{137}Cs distribution at a correlation coefficient of +0.5.

The obtained values agree with the data on sedimentation rates in the same region determined from ^{210}Pb measurements [11].

It should be also noted that some of the samples from the Ob Gulf show a second significant increase in ^{137}Cs count at a depth of 15 cm (Fig. 5). This may suggest a considerable supply of this radionuclide in 1967, when one of the greatest accidents took place on the Mayak plant.

Table 2. ^{90}Sr content in the upper layer (0–2 cm) of bottom sediments

Site no.	Site location	^{90}Sr content, Bq/kg
12	Ob Gulf	7.7
18	Kara Sea	4.0
21	Kara Sea	2.8
33	Yenisei Bay	7.2
34	Yenisei Bay	11.6

Table 3. ^{90}Sr Content in the surface water layer

Site no.	Site location	^{90}Sr content, Bq/m^3
1	Kara Sea	4.8
12	Ob Gulf	12.2
19	Kara Sea	2.9
24	Kara Sea	6.0
32	Yenisei Bay	8.2
34	Yenisei Bay	11.6
42	Kara Sea	1.2
55	Gydanskii Bay	2.9
65	Barents Sea	2.0

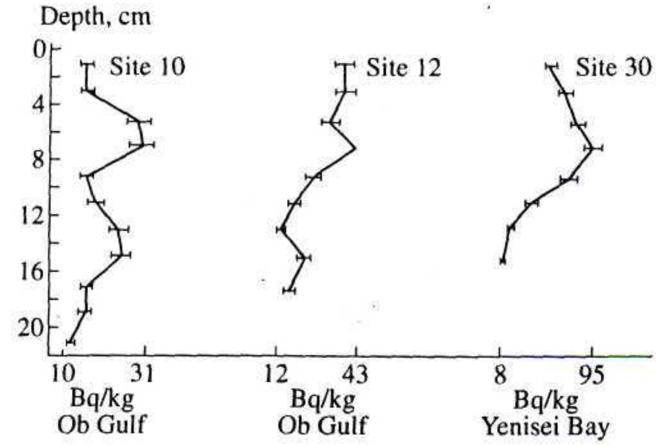

Fig. 5. Distribution of ^{137}Cs specific activity over the core depth. Cruise 28 of the R/V *Akademik Boris Petrov*, 1997.

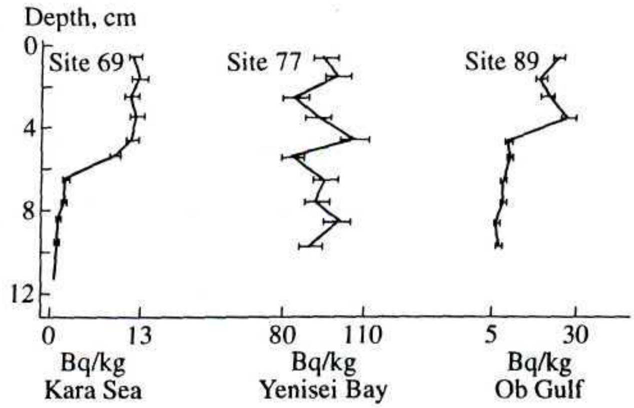

Fig. 6. Distribution of ^{137}Cs specific activity over the core depth. Cruise 22 of the R/V *Akademik Boris Petrov*, 1995.

To estimate more accurately the sedimentation rates, experiments are now in progress on the determination of ^{210}Pb in the samples of bottom sediments by the radiochemical method with the radiometry of end specimens with respect to ^{210}Pb or daughter ^{210}Bi.

Research in this direction should be continued both in the accumulation of statistical material on the concentration of various radionuclides upstream in the Ob and Yenisei and in expanding studies on the development of express methods for the separation and refinement of the radionuclides ^{210}Pb and ^{210}Bi.

The data on the distribution of radionuclides in water suggest that the concentrations of water-soluble cesium species increase with increasing salinity (Fig. 10). The distribution of ^{90}Sr in surface samples shows considerable scatter (Table 3). We believe that this is

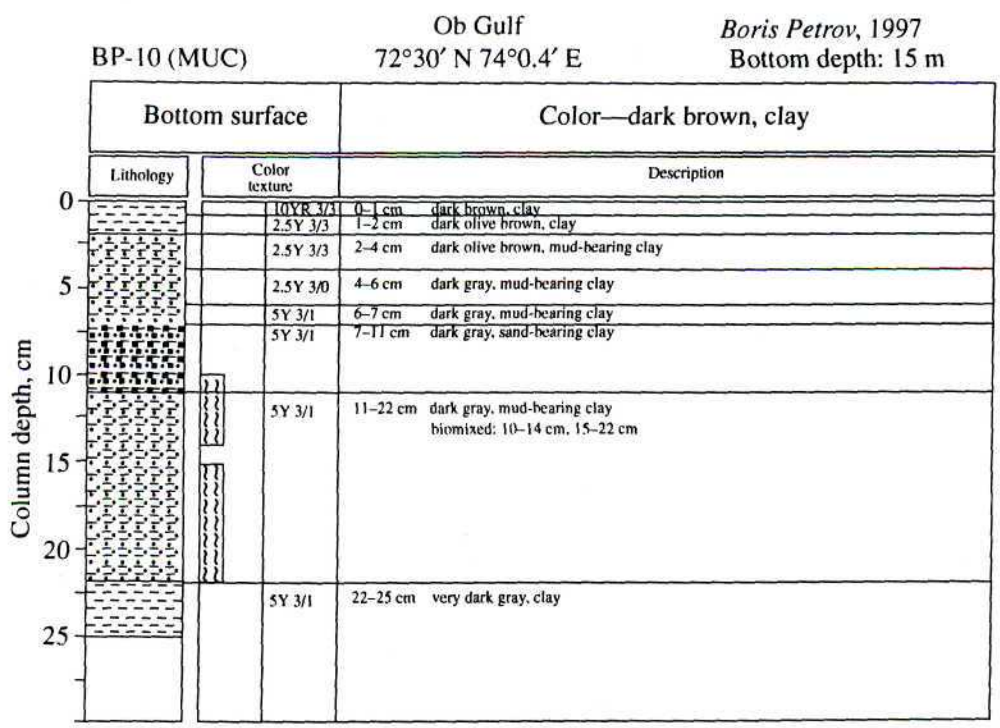

Fig. 7. Characteristics of geologic material from a typical sampling site in the Ob Gulf.

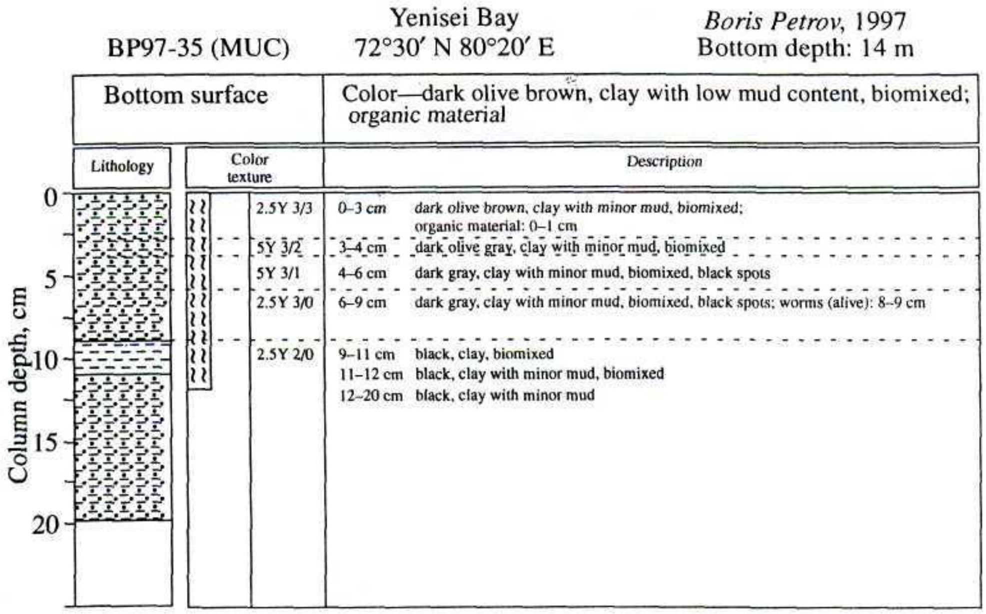

Fig. 8. Characteristics of geologic material from a typical sampling site in the Yenisei Bay.

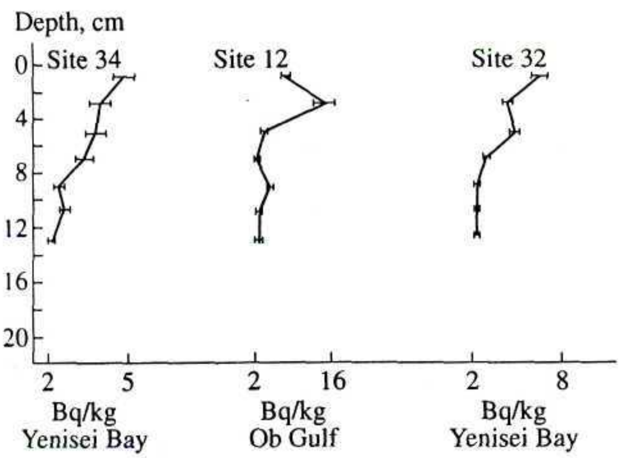

Fig. 9. Distribution of ^{90}Sr specific activity over the core depth, Cruise 28 of the R/V *Akademik Boris Petrov.*

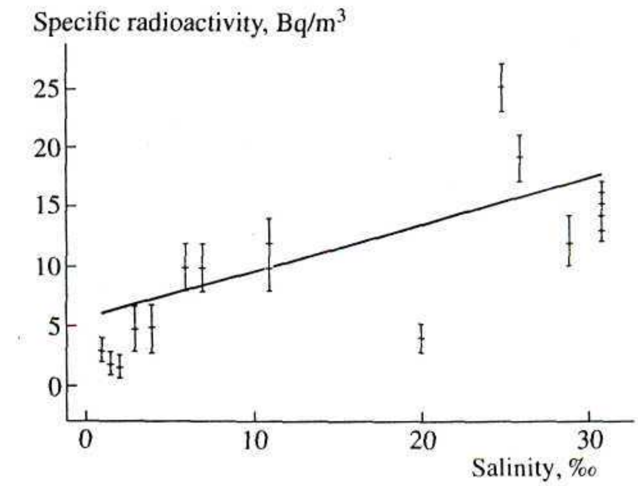

Fig. 10. Concentration of dissolved ^{137}Cs in water samples as a function of salinity.

mainly due to the influence of various sources, which, owing to frequent changes in synoptic and hydrological parameters, could result in a spotted character of radionuclide distribution.

Thus, our studies yielded the rather objective characteristics of radioecological conditions in the estuaries of the Siberian rivers, the Ob and Yenisei, and the adjacent regions of the Kara Sea. Consideration of natural parameters and of the geochemical behavior of radionuclides helps in explaining fluctuations in their lateral and vertical distribution. Our data on the vertical distribution of radionuclides (especially, ^{137}Cs) in the Ob and Yenisei sediments allowed us to recognize potential sources of radioactivity and moments of their supply into the Kara Sea. Since Siberian rivers are characterized by large drainage areas, it is important to distinguish contributions from flood water and possible pollution by industrial plants in the total radioactivity of river water discharged into the Kara Sea. Of course, now there is no ground to claim a high pollution level in the Kara Sea due to Ob and Yenisei run-off, because the concentration of particular radionuclides in the southern Kara Sea is not higher than their specific activity in the marine environments of other basins, for example, in the North or Baltic seas [6]. Nevertheless, taking into account the potential sources of radioactivity which may influence the pollution level of Siberian rivers, we believe that the monitoring studies of radio-

ecological conditions in the Ob and Yenisei rivers and the adjacent areas of the Kara Sea are important and should involve geochemical data on the environments of these regions.

ACKNOWLEDGMENTS

The authors thank T.A. Goryachenkova for help in the analytical work and discussion of the results on the distribution of ^{239}Pu and ^{240}Pu and G.Yu. Solov'eva and A.N. Ligaev for their help in ^{137}Cs and ^{90}Sr analysis. The work was financially supported in 1998 by the Vernadsky Nongovernmental Ecological Foundation.

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