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Studying the Radionuclide Composition of Bottom Sediments from St. Petersburg's Rivers

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Abstract—Radiocesium is used to determine the age and rate of sedimentation in three columns of bottom sediments from St. Petersburg's rivers. Pronounced maxima of specific activity are identified in the cross sections of the sediments. Results are used to estimate the average rates of sedimentation for the postwar period.

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INTRODUCTION

The state of bodies of water in large industrial centers is a key factor of urban environmental quality. Discharges of sewage silt areas of water and result in the partial or complete degradation of ecosystems. Technogenic silts accumulated at the bottom of waters are characterised by high toxicity and sedimentation [1], and can contain considerable traces of radionuclides of technogenic origin as well. One of the most complicated problems in studying urban waters is determining the rate of technogenic sedimentation, which normally far exceeds the scale of natural processes. Solving this problem would allow us to optimize measures of water protection, including ways of bottom cleaning. In St. Petersburg, where waters are an important element of the city's historical and architectural image, the goal of maintaining and preserving rivers and canals is of both ecological and aesthetic importance.

Considerable experience has been acquired in determining rates of sedimentation in marine and fresh-water basins using nonequilibrium ^{210}Pb and determining the specific activity of ^{137}Cs [2–8]. Radiocesium allows confident assessment of sedimentation processes of the last 70 years. ^{137}Cs is a chemically active metal that is found in water mainly in the form of Cs^+ cations. It is actively sorbed by clay minerals and accumulated in finely dispersed bottom sediments [8, 9]. There is virtually no vertical migration of chemical elements in deposits. The transport of matter due to molecular diffusion is minimal on our scale of time. Each deposited layer of sediments thus fixes the geochemical environment typical of the moment.

The nuclear tests in the atmosphere in the 1950s and '60s, nuclear power plant accidents, authorized discharges into bodies of water, and emissions into the atmosphere are sources of technogenic radionuclide ^{137}Cs (half-life, 30.08 years). This radionuclide is in the environment because of nuclear weapon tests in the atmosphere in 1949. The greatest atmospheric fallout was recorded in 1963 [8, 9], the year of the Nuclear Test Ban Treaty. In the northern hemisphere, the peak of specific activity associated with the accident at the Chernobyl nuclear power plant in 1986 was recorded in bottom sediments almost everywhere [2, 5, 7, 8]. Radionuclide ^{137}Cs is now one of the main isotopes responsible for the radioactive contamination of the biosphere, and the high level of its specific activity is a real hazard to human health.

The aim of this work was to determine levels of the specific activity of ^{137}Cs in the rivers of St. Petersburg, identify the main sources of this radioisotope, and determine the rate of technogenic sedimentation in urban waters.

EXPERIMENTAL STUDIES OF THE RADIONUCLIDE COMPOSITION OF BOTTOM SEDIMENT SAMPLES

The columns of bottom sediments (deposits) were sampled from three rivers (the Yekateringofka, Karpovka, and Chernaya Rechka) flowing through the historic part of St. Petersburg and subject to intense contamination by industrial plants.

The Yekateringofka River flows from the Neva into Neva Bay. Enterprises of the chemical and food industries, mechanical engineering and shipbuilding, and the production of lead–acid batteries line the waterway. The river is a highway of navigation. A column of bottom sediments 63 cm thick was sampled in the Ol'khovka River estuary. The upper part of the cross section (0–22 cm) consisted of greenish-grey sandy–aleuritic pelites. Below this lie sediments composed of

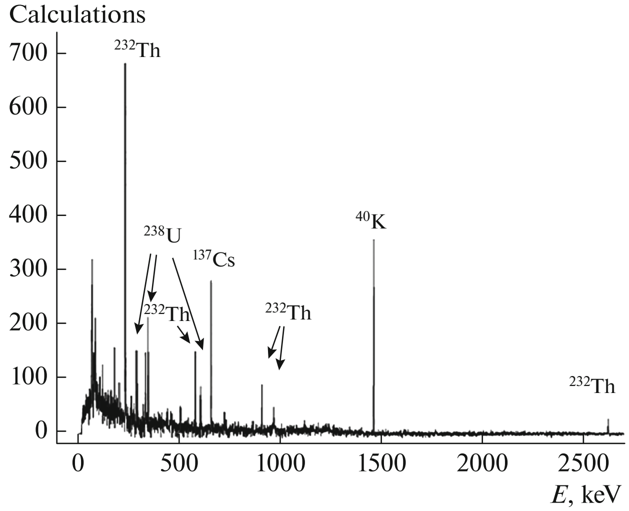

Fig. 1. Radionuclide spectrum for a sample of bottom sediments taken from the Yekateringofka River at a depth of 31–34 cm.

black aleuritic pelites with numerous petroleum hydrocarbons and inclusions of wood and sand particles.

The Karpovka River is one of the arms of the Neva River separating Petrogradsky and Aptekarsky Islands. The Karpovka is 3 km long, 20 m wide, and as much as 2.6 m deep. Plants manufacturing tools and batteries were in operation at the sampling site. In its middle and upper reaches, the river flows through a residential area. A column of sediment 38 cm thick was collected in its lower reaches. The sediments of its upper part (0–9 cm) were aleuritic–pelite sands, below which were dark grey sandy pelites.

Chernaya Rechka is located in the northwestern part of the city and flows into the Bol'shaya Nevka. It is lined by active and abandoned plants for the production of paint and abrasive materials, metalworking, tool-making, and radioelectronics. Its column of sediments is 47 cm thick. The sediments consist of sand–aleuritic pelite, but a layer 33–39 cm thick is dominated by aleuritic–pelitic sand. The deposits are black and highly contaminated by petroleum hydrocarbons. They also contain a large volume of remains from vegetation.

To measure the activity of radionuclides in the samples, we used spectrometric complexes based on a hyper-pure Ge detector and a Ge–Li detector. The Ge detector had GEM10P4 energy resolution no worse than 620 eV with respect to the peak of radionuclide ^{57}Co with an energy of 122 keV. Its energy resolution with respect to the peak of radionuclide ^{60}Co with an energy of 1332 keV was no worse than 1.7 keV at a relative efficiency of detection of 10% for this energy. The Ge–Li detector had an energy resolution of no worse than 2.2 keV with respect to the peak of radionuclide ^{60}Co with an energy of 1332 keV at a relative efficiency of detection of 10% for this energy. The gamma spectrometers' energies and efficiency of detection were calibrated using three radionuclides: ^{60}Co, ^{152}Eu, and ^{137}Cs [10]. Since the columns of bottom sediments were separated into segments with samples 1.5–3 cm thick, preliminary estimates showed the concentration of the studied radionuclides would be negligible. They were affected by the low concentration of ^{137}Cs in the bottom sediments, along with the processes of lateral migration in the sediments associated with the fairly high mobility of this radionuclide [11]. The expected specific activity therefore might not have exceeded 10 Bq/kg in some samples, so a special procedure was developed for precisely calibrating our spectrometric systems' efficiency of detection. The geometric and structural parameters (length, height, homogeneity) of the studied samples were considered, and the relevant measurements of the spectrometers' efficiency of detection were made using radionuclide sources for calibration. The relative error in determining the spectrometers' efficiency of detection was 1.5%, so the main sources of error in determining the specific activity of ^{137}Cs were statistical errors associated with the systems' detection of gamma quanta and ones that emerged during the subsequent analysis of the obtained spectrometric information. This procedure thus allowed reliable identification of radionuclide ^{137}Cs in the samples of bottom sediments and calculations of their specific activities up to 1 Bq/kg, with a relative error of no more than 19%.

The procedure for measuring the specific activities of samples consisted of two stages. At the first stage, the spectrometers measured the background conditions for 24 h. An empty plastic container of a certain geometric size and mass was placed into a spectrometer with no samples. The container was then loaded with dried and specially prepared samples. At the second stage, the spectrum of radionuclides from each sample was measured. The period of exposure was also 24 h. Finally, the background spectrum was subtracted from the measured spectrum of each sample.

Measurements detected the presence of radionuclide ^{137}Cs in the samples of bottom sediments found at different depths. Figure 1 presents the spectrum of one such sample taken from a depth of 31–34 cm. Almost all radionuclides of natural origin and the dominant Th series radionuclides are seen in the spectrum. Technogenic radionuclide ^{137}Cs also shows a fairly clear peak.

Considering the amount of ^{137}Cs put into the environment in the past, we might expect to see peak values of the specific activity of this radionuclide in the columns of bottom sediments. This would allow estimates of the average rates of sedimentation at parts of the considered waters, assuming a linear dependence between the peaks in depth. The average rates of sedimentation after 1963 (SR_1) and 1986 (SR_2) were calculated using the formulas in [7]: $SR_1 = d_1/(t_0\ 1963)$ and

Table 1. Specific activity of ^{137}Cs in bottom sediments and estimated rates of sedimentation in marine and freshwater bodies of Eurasia

Body of water	Maximum values, Bq/kg	Rate, cm/yr	Source
Lake Qattinah, Syria	10.2	0.80–1.0	[2]
Beibu Gulf, South China Sea	2.03	0.46	[3]
Gulf of Corinth, Greece	28.5	0.56	[5]
Litochoro Coast, Greece	42.0	0.54	[5]
Lake Uluabat, Greece	22.5	0.41	[5]
Adriatic Sea	12.3	0.18–0.4	[6]
San Simeon Bay, Spain	11.2	0.25–0.62	[8]
Gulf of Salonika, Greece	87.8	0.18–0.22	[12]
Sukhoe More Bay, White Sea	5.1	–	[13]
Baltic Sea	261	0.27–0.57	[14]
Gulf of Bothnia	1614	0.16–0.18	[14]
Kattegat	11.2	–	[14]
Daya Bay, South China Sea	0.64	–	[15]
Lakes of Siberian South	Up to 100	0.35	[16]
Lakes of Siberian North	Up to 40	0.25–0.3	[16]
Gulf of Ob	11.7	0.4–0.75	[17]
Yenisei Bay	42.6	0.5	[17]
Vostochno-Novozemel'skii Trench	6.8	0.11–0.5	[17]
Sedov Bay	4.8	0.10	[17]

$SR_2 = d_2/(t_0\ 1986)$, where t_0 is the year of sampling, and d_1 and d_2 are the depths of the peaks corresponding to the recorded events (in cm).

RESULTS AND DISCUSSION

Our analysis of the literature results from studying the specific activity of ^{137}Cs showed that its values in bottom sediments of marine, lacustrine, and river areas of Europe and Asia were usually 10–20 Bq/kg at the peak of nuclear weapon testing (1963) and during the accident at the Chernobyl nuclear power plant (1986) (Table 1). The values in the eastern part of Eurasia (South China Sea) are even notably lower (<2 Bq/kg) [3, 15]. However, some waters do not fit this pattern. In the Gulf of Bothnia and the northern part of the Baltic Sea that were affected by the Chernobyl trace, the activity in the corresponding horizon of sediments has values exceeding the detected background by 1–2 orders of magnitude [14]. In addition, some territories now have active sources of ^{137}Cs, raising the content of the radionuclide in the upper layers of bottom sediments [12, 16, 17].

The specific activities of ^{137}Cs in the bottom sediments of St. Petersburg's rivers do not exceed 14.90 ± 1.22 Bq/kg (Fig. 2), suggesting they conform to the modern background value. The content of ^{137}Cs in the studied sediments was primarily associated with the atmospheric fallout of residual amounts of the radionuclide. This is also indicated by the low dispersion of the values obtained in the different waters of the city. We may therefore be fairly confident that St. Petersburg has no major industrial sources of ^{137}Cs put into the environment.

When estimating rates of sedimentation, we must specify the distinctive nature of these processes in the waters of St. Petersburg. The authors of [1, 18] showed that technogenic sediments began to form at the bottom of the rivers in the first half of the 1950s, the postwar period of industrial development. The approximate rates of sedimentation calculated by lithostratigraphic means were 0.5–1.0 cm/yr; however, they could vary strongly, depending on the sampling site. The accumulative process in the rivers was complicated by the erosion of sediments in periods of strong floods (1955 and 1975), especially in the Yekateringofka River, and by local bottom-cleaning efforts (the Karpovka River). The redistribution of bottom sediments as a result of erosion, reclamation, and underwater landslides was also recorded by other authors [5, 15, 17]. Our analysis of the rates of sedimentation in the urban waters was therefore conducted with respect to the above factors.

The fullest cross section of the sediments was obtained from the Yekateringofka river (the Ol'khovka River estuary); its bottom (57–63 cm) was not found to contain any ^{137}Cs. It is likely that the bottom layer of sediments formed before 1949 (Fig. 2a). The average

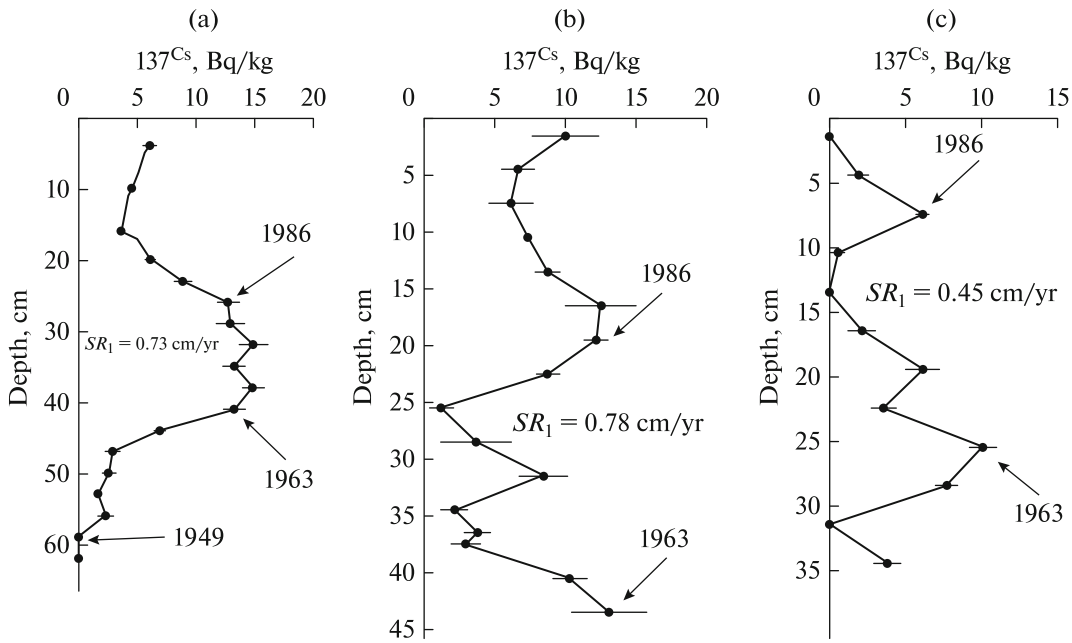

Fig. 2. Vertical profiles of the specific activity of radionuclide ^{137}Cs in the bottom sediments of the (a) Yekateringofka, (b) Chernaya Rechka, and (c) Karpovka rivers.

rates of sedimentation in the post-war period would then be 0.79 cm/yr. Higher in the cross section, a horizon of sediments with increased specific activity of ^{137}Cs (12.78 to 14.90 Bq/kg) was found in the interval of 24–42 cm. Based on the common trend of the change in activity, we suggest the lower layer of this horizon formed in 1963, and the upper layer (above which specific activity drops suddenly) formed in 1986. Calculations of the rates of sedimentation according to these markers yield 0.73 cm/yr from 1963 to now, 0.75 cm/yr from 1986 to now, and 0.70 cm/yr from 1963 to 1986. All rates of sedimentation testify to the stable dynamics of the process throughout the considered period.

The rate of sedimentation was determined earlier for the Ol'khovka River estuary by means of nonequilibrium ^{210}Pb, which could not be used here because of possible erosion and the mixing of sediments, along with the anomalously high content of bulk Pb, especially in the lower part of the cross section (up to 5.54% on a dry matter basis), where the specific activity of ^{210}Pb displayed sudden growth [19]. We used the model of constant initial concentration to determine the estuary's age, but only within those intervals of the sediment cross section that were characterized by a nearly equal content of bulk Pb. Geochemical indicators were also used as markers of certain stages of sedimentation. The average rate of sedimentation estimated for the post-war period was 0.67 cm/yr, reflecting the good consistency of results (0.78 cm/yr according to ^{137}Cs) obtained under conditions of high variability of the lithofacies of bottom sediments.

The specific activities of ^{137}Cs measured in the sediments of the Chernaya Rechka River showed that the bottom layer of our column formed after 1950, since it was characterized by relatively high specific activity of the radionuclide (Fig. 2b). Two pronounced peaks of ^{137}Cs content were recorded along the sediment cross section, in the intervals of 43–46 cm (13.09 ± 2.68) and 18–21 cm (12.24 ± 0.86). The first maximum was attributed to that of radionuclide fallout in 1963; the second, with the accident in 1986. The average rates of sedimentation at the sampling site were therefore 0.78 cm/yr from 1963 to now, 0.59 cm/yr from 1986, and 1.04 cm/yr from 1963 to 1986. The revealed differences in the rate of technogenic sediment accumulation thus fit within the history of water discharges into the Chernaya Rechka River during the peak industrial activity in the 1960s and '70s.

The most complicated distribution pattern of ^{137}Cs specific activity was observed in the sediment section of the Karpovka River, where bottom-cleaning efforts have been made in some places. This explains the low content of radionuclide ^{137}Cs (below the threshold of the sensitivity of our spectrometric device) at certain depths along the section of bottom sediments. However, the vertical distribution of specific activity and its absolute value suggest that sediments within the interval of 24–27 cm formed during the peak atmospheric cesium fallout in 1963, while the Chernobyl maximum can be attributed to the layer of 6–9 cm (Fig. 2c). The average rate of sedimentation was 0.45 cm/yr from 1963 until 1986, after which it fell to 0.22 cm/yr. It could be as high as 0.78 cm/yr in the interval between the two years. This profile of the rates is generally explained by the growth of industrial production peaking in the 1960–1970s, while almost all enterprises along the Karpovka River shut down in the early 21st century, reducing the technogenic load considerably.

The measured average values of specific activity of ^{137}Cs in the studied rivers fell in the order Yekateringofka River (7.99 ± 2.42) > Chernaya Rechka River (7.40 ± 1.99) > Karpovka River (4.67 ± 1.55). The most likely explanation for these differences is the grain-size composition of their bottom sediments. In the Karpovka River, they differ by having the largest sand fraction with low adsorption potential. The measured values of specific activity of ^{137}Cs in the bottom sediments of the rivers pose no hazard to the health of St. Petersburg's citizens, since the permissible specific activity of ^{137}Cs in solid materials is 100 Bq/kg, in accordance with [20],

CONCLUSIONS

Our studies confirm it is hard to obtain results when using radionuclides to estimate the rate of sedimentation in the waters of urbanized territories. The main reasons for this are the inconsistency of accumulation resulting from interference by natural and anthropogenic factors, and the high levels of chemical contamination. The distribution of the specific activities along the sediment cross section nevertheless correlates quite well with the history of technogenic development of the studied territory over the last 70 years. The estimated average rates of sedimentation in the studied waters indicate considerable transformation of the lithodynamic regime typical of rivers flowing under natural or weakly disturbed conditions.

Our findings confirm there were no industrial sources of ^{137}Cs in the environment of the city center either in the past or recently. They show the safe health levels of specific activity of the radionuclide that characterize deposits of the city's waters.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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