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Technogenic and natural radionuclides in the bottom sediments of the Sea of Azov: regularities of distribution and application to the study of pollutants accumulation chronology

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Abstract. The study of pollutants vertical distribution in seabed sediments is of high interest as they conserve the information on the chronology of pollution level in the past. In the present paper, the results of layer by layer study of Cs-137, Am-241, Pb-210 specific activities as well as concentrations of petroleum components, lead and mercury in 48 sediment cores of the Sea of Azov, the Don River and the Kuban River are examined. In most sediment cores, two peaks of Cs-137 and Am-241 are detected. The upper of them was formed due to the Chernobyl accident in 1986 and the other is related to the global nuclear fallout of 1960s. The specific activity of naturally occurring atmospheric Lead-210 decreases exponentially with the sediment core depth. However, it is influenced by fluvial run-off, coastal erosion, Radium-226 and Radon-222 decay. The data on the radionuclides distribution in the seabed sediments is used to date them. According to the results of dating, most of petroleum components, lead and mercury quantities are concentrated in the upper sediment layer formed in the last 50 to 70 years i.e. in the period of the most important anthropogenic pressure.

1. Introduction

The study of pollutants distribution in the sediment cores is of particular interest as they conserve the information on the chronology of pollution level in the past and so may be considered as the “memory” of aquatic ecosystems. Therefore, the dating of different sediment layers is of high importance. For this purpose, the method of radioactive tracers such as ^{137}Cs and ^{210}Pb is largely applied [1-4].

Cesium-137 and Americium-241 are technogenic radionuclides, their presence in the environment and formation of specific activity peaks in sediment cores are related to the above-ground tests of thermonuclear weapons in 1950s and 1960s and to the accident at the Chernobyl Nuclear Power Plant in 1986. Unlike ^{137}Cs, ^{241}Am is formed directly in bottom sediments due to the decay of ^{241}Pu. So, over time the specific activity of ^{241}Am increases progressively while the specific activity of ^{137}Cs decreases. Lead-210 is a natural radionuclide. It is permanently generated in the atmosphere as a result of decay of radioactive gas Radon-222, and then it precipitates on the earth surface. In the sediment cores, the specific activity of Lead-210 decreases exponentially until the secular equilibrium with the parent radionuclide

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Radium-226. As the half-life of Pb-210 is not very long (22.3 years), this method is suitable only for dating sediments formed during the last century [3, 4].

2. Materials and methods

Earlier in the uppermost layer of bottom sediments of the Sea of Azov and main rivers of its drainage basin the content and composition of technogenic material and the concentrations of different pollutants were determined [5]. The results of this study were very important; however, they are not sufficient for the localization of the sediment layer of anthropogenic impact and analysis of its formation chronology. The present paper considers the results of complex many-years (from 1995 to 2015) studies carried out in the Sea of Azov, the Strait of Kerch, the Don River and the Kuban River and based on the uniform common methodology [6-11]. During the period of this research, five scientific expeditions were carried out in summer and autumn, 48 sediment cores from 20 to 100 cm long were extracted by a 1 m long gravity corer and split longitudinally into 241 samples. The sampling point's locations are depicted in figure 1.

In the samples the concentrations of principal petroleum components (aliphatic, mono- and di-aromatic hydrocarbons (HC), polycyclic aromatic hydrocarbons (PAH) and asphaltic components (AC): resins and asphaltenes) as well as total lead and mercury were determined. The choice of the ingredients was not casual. For the considered region, petroleum components, lead and mercury are the most common and typical contaminants due to the functioning of large industrial centers of Russia and Ukraine, high concentration of population, municipal and transport facilities, port complexes and intense navigation. By now, the volumes of petroleum products and other cargos shipped through the Azov - Don waterway have increased 2 to 3 times compared with the late 1990s. This undoubtedly augments the risk of emergencies related to the oil spills such as the series of ship wreckages in November 2007 during the heavy storm in the Strait of Kerch accompanied by a spill of 1.3 thousand tons of heavy fuel oil. In order to date the studied samples, the specific activities of radionuclides ^{137}Cs, ^{241}Am and ^{210}Pb were measured there. In total, more than thousand determinations of the abovementioned ingredients were made up. The petroleum components were extracted and studied with the use of thin-layer chromatography, infrared and luminescence photometry [8, 9]. The presence of hydrocarbons of contemporary biological origin was also identified. The heavy metals were studied by the atomic absorption spectroscopy [10]. The specific activities of the radionuclides were measured by the method of direct gamma spectrometry [11].

3. Results and discussion

According to the results of the study, in the uppermost sediment layer the maximum specific activity of Cesium-137 (103.3 Bq·kg^{-1} of dry weight (d.w.)) was detected in the southern part of the Sea of Azov adjacent to the Strait of Kerch. This fact may be accounted for the isotope sorption by silty sediments from the near-bottom higher salinity waters entering from the Black Sea. The minimum values occurred in the mouth areas of the Don River and the Kuban River. In general, the sediment cores extracted in central and southeastern parts of the Sea of Azov were characterized by higher specific activities of Cesium-137 and Americium-241 than ones taken in the Golf of Taganrog. A well-defined upper peak of ^{137}Cs specific activity related to the Chernobyl accident was found in all the studied sediment cores. In the deeper parts of the Sea of Azov and of the Gulf of Taganrog, in the hydrodynamic conditions favorable for the sediment precipitation and accumulation, this peak was detected at 5-10 cm sediment core depths (51-116 Bq·kg^{-1}). In the shallow eastern part of the Gulf of Taganrog the maximum ^{137}Cs specific activity was fixed in the superficial layer (35-79 Bq·kg^{-1}). In the delta and in the near-delta part of the Don River the peak is located at 20-40 cm depth (14–43 Bq·kg^{-1}) suggesting higher sedimentation rates. In most sediment cores the second peak of ^{137}Cs activity was also found in deeper layers. It may be associated with global fallout from aboveground testing of thermonuclear weapons in 1950s and 1960s. This peak is not as distinct as the first one due to radioactive decay and probably lateral and vertical migration.

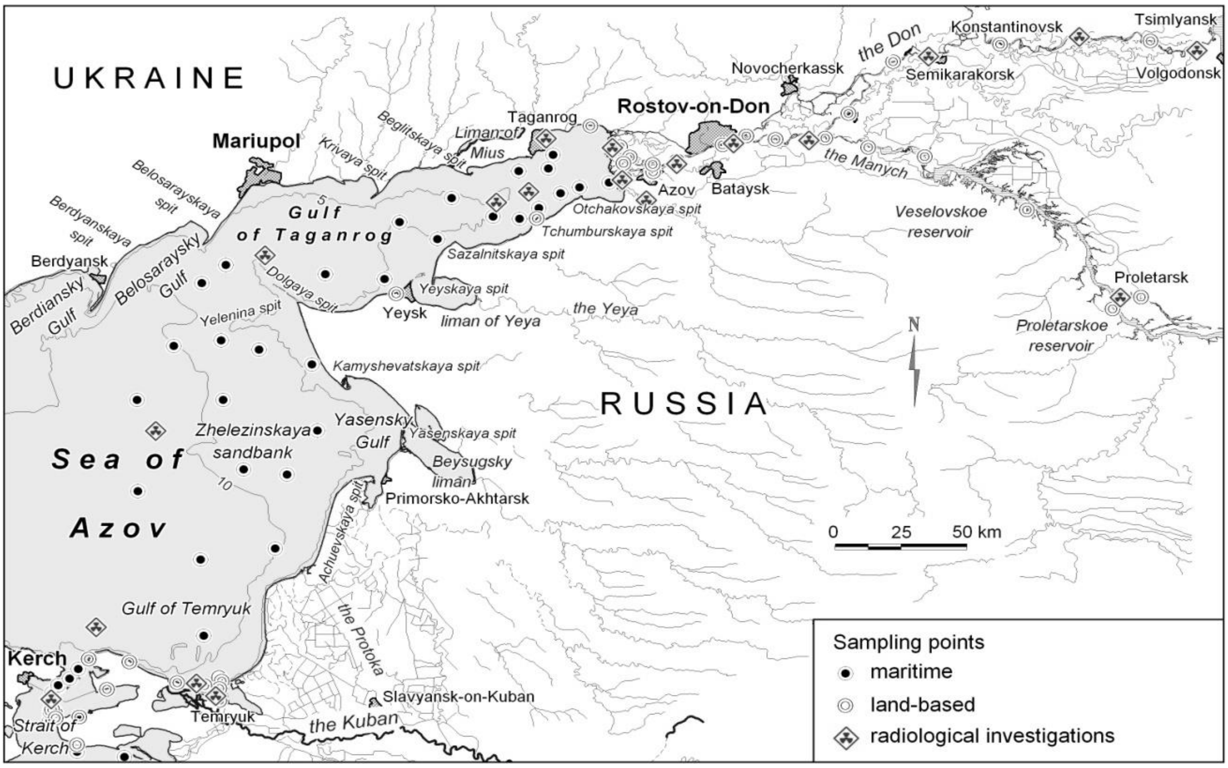

Figure 1. Sampling points in the Sea of Azov and in the Lower Don River basin.

The maximum specific activity of Americium-241 (18.0 Bq·kg^{-1}) was detected in the deeper part of the Sea of Azov. Significant activities of Am-241 are detected in most sediment cores. In some of them two peaks are found. Obviously, the upper peak corresponds to the Chernobyl fallout and the other located in a deeper sediment core layer corresponds to the global radioactive fallout of 1960s. Am-241 is a decay product of Pu-241 (half-life is about 14 years). It accumulates over time since the fallout of plutonium isotopes, as its half-life is 30 times longer than the half-life of Pu-241. The level of ^{241}Am pollution of bottom sediments is relatively high due to ^{241}Pu significant contribution to the global fallout and its almost total decay into ^{241}Am. Vertical distribution of Am-241 specific activity in the sediment cores is similar to that one of Cs-137. Conversely, its deeper peak corresponding to the period of global radioactive fallout of 1960-s is much more distinct and often even more important than the peak corresponding to the accident in Chernobyl.

The specific activity of Lead-210 decreases with the sediment core depth from 240–727 Bq·kg^{-1}in the superficial layer to 179–288 Bq·kg^{-1}at 50 cm depth. However, regular stirring-up of shallow sea sediments and multitude of terrigenous sources of Lead-210 complicate the use of this data for the dating purposes. Exponential character of decrease of the ^{210}Pb specific activity is not often evident because of distorting influence of the isotope import with the fluvial run-off, coastal erosion material, and in consequence of the ^{226}Ra and ^{222}Rn decay. In order to eliminate the influence of these factors, the method of multiple regression analysis was applied to the balance equation (1) that includes all the above-mentioned sources of ^{210}Pb isotope [9].

$$A(^{210}Pb) = A(^{210}Pb_a)e^{-\frac{\lambda x}{s}} + A(^{210}Pb_t)e^{-\frac{\lambda x}{s}} + \frac{A(^{226}Ra)}{\lambda}(1-e^{-\frac{\lambda x}{s}}) + \frac{A(^{222}Rn)}{\lambda}(1-e^{-\frac{\lambda x}{s}}) \quad (1)$$

- $A(^{210}Pb)$: Total specific activity of ^{210}Pb in each sediment layer
- $A(^{210}Pb_a)$: Specific activity of atmospheric ^{210}Pb
- $A(^{210}Pb_t)$: Specific activity of terrigenous ^{210}Pb
- $A(^{226}Ra)$: Secular equilibrium activity of ^{226}Ra
- $A(^{222}Rn)$: Secular equilibrium activity of ^{222}Rn
- $\frac{A(^{226}Ra)}{\lambda}(1-e^{-\frac{\lambda x}{s}})$: Specific activity of ^{210}Pb generated in bottom sediments in consequence of ^{226}Ra decay
- $\frac{A(^{222}Rn)}{\lambda}(1-e^{-\frac{\lambda x}{s}})$: Specific activity of ^{210}Pb generated in bottom sediments in consequence of ^{222}Rn decay

In this equation, λ is the Pb-210 decay constant (0.0311 $year^{-1}$); x is the depth of considered layers in the sediment cores (cm); s is the average sedimentation rate ($cm \cdot year^{-1}$).

According to the results of radiological analysis, the highest sedimentation rates are in the delta and near-delta part of the Don River (5 to 14 mm of wet matter per year). The lowest rates are in the shallow eastern part of the Gulf of Taganrog (1 to 2 mm of wet matter per year) in spite of considerable sediment runoff of the Don River. That is because of low depths (2 to 5 m) and high hydrodynamic activity of water column favoring regular stirring-up and carrying out of sediments. In the deeper central and southern parts of the Sea of Azov, the sedimentation rates rise up to 4 mm per year. The results of the sediment precipitation rates determination by the method of sediment traps prove these estimates for the eastern and northeastern parts of the Sea of Azov (2 to 3 mm of wet matter per year). However, in the shallow Gulf of Taganrog the rates of observed sediment precipitation are much higher than the sedimentation rates determined by the radiological methods. This may be accounted for the regular remobilization of sediments under storm conditions.

Now let us consider vertical distribution of common pollutants in the studied sediment cores. The total concentrations of petroleum components in the uppermost sediment layer vary from 0.05 to 1.21 mg g^{-1} d w. The highest values are detected in the Don River and the Kuban River deltas (on average 0.51 and 0.47 $mg \cdot g^{-1}$ d w respectively), in the southeastern and central parts of the Sea of Azov (on average 0.33 and 0.22 mg g^{-1} d w respectively).

Most of the petroleum components quantity is concentrated in the upper sediment layers formed in the last 50 to 70 years, i.e. in the period of high anthropogenic pressure. In the Gulf of Taganrog, the thickness of this layer is about 10 to 15 cm, in the dipper sectors of the sea it raises up to 20 cm and even reaches 30 to 50 cm in the lower parts and deltas of the Don River and the Kuban River. These differences are accounted not only for the pollution chronology but also and mostly for the different sedimentation rates. In the Don River and the Kuban River sediments, the resins and asphaltenes being the conservative indicators of chronic oil pollution prevail over hydrocarbons. On the contrary, in the Gulf of Taganrog and in the principal part of the Sea of Azov, except for the impact zones surrounding industrial centers and port terminals, the hydrocarbons dominate. A huge part of them consists of contemporary metabolic products of aquatic organisms. In most sediment, cores taken in the Gulf of Taganrog and the Gulf of Temryuk the highest concentrations of oil components are detected at 5 to 10 cm sediment core depths. This sediment layer is located under the peak of ^{137}Cs specific activity related to the Chernobyl accident and may be dated back to the period from 1955 to 1985. In the Don River sediments, such layer is also found, but in the reason of higher sedimentation rates its thickness rises up to 30 cm. In the central part of the Sea of Azov, the highest concentrations are detected in the uppermost sediment layer that has been formed during the last 15 years.

The concentrations of lead in the sediment cores vary from 12 to 43 μg g^{-1} d w, on average 18 μg g^{-1}. It is found out that in the Gulf of Taganrog, lead reacts actively with organic matter while in the principal part of the Sea of Azov their concentrations do not correlate. The highest concentrations of lead are detected in the upper sediment layers up to 20 cm sediment core depth. In the deeper layers, they usually droppe rapidly. A direct correlation (with coefficients ranging from 0.30 to 0.94) is found between the radioactive Lead-210 specific activity and the total lead concentration. This means that the decay of ^{222}Rn isn't the only source of ^{210}Pb precipitating from the atmosphere. Lead-210 is also present in the coal dust and coal ash transported with air masses and surface run-off.

The concentrations of mercury in the sediment cores varies from 0.025 to 0.28 μg·g^{-1} d w, on average 0.067 μg g^{-1}. In most cases, they decrease with sediment core depth. However, in some sediment cores, as it is also found out for the petroleum components, the maximum values were fixed in the deeper sediment layers formed between 1955 and 1985. In all the sediment cores, the content of mercury closely correlates with the content of organic carbon.

4. Conclusion

Therefore, the comparative analysis of the data on the vertical distribution of petroleum components, heavy metals, technogenic radionuclides Cs-137 and Am-241 and natural radionuclide Pb-210 in the sediment cores of the Sea of Azov, the Don River and the Kuban River allowed locating the layer of high anthropogenic impact and dating it. This superficial sediment layer contains the most of petroleum components, lead and mercury quantities. Its thickness varies from 15 to 50 cm. According to the results of radiological dating, these sediments were formed in the last 50 to 70 years, i.e. in the period of high anthropogenic pressure. Moreover, the most polluted sediment layers were formed in 1970s and 1980s.

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