Radionuclide Content in Black Sea Sediments from Varna Bay at the Northern Bulgarian Coast

Tz. Nonova[1*], **K. Slavova**[2], **I. Genov**[2], **L. Dobrev**[1], **V. Doncheva**[2], **O. Hristova**[2], **B. Dzhurova**[2]

[1] *Institute for Nuclear Research and Nuclear Energy, Bulgarian Academy of Sciences, Sofia, Bulgaria*

[2] *Institute of Oceanology, Bulgarian Academy of Sciences, Varna, Bulgaria*

[*] *Corresponding author E-mail: nonova@inrne.bas.bg*

Abstract. This work presents data on the accumulation of technogenic ^{137}Cs and natural radionuclides of the ^{238}U and ^{232}Th series (^{238}U, ^{226}Ra, ^{232}Th) and ^{40}K in Black Sea sediments collected from Varna bay at the Northern Bulgarian Black Sea coast. The aim of the study is to be the first step in a future large study of the content of radionuclides in sediments from different geographical areas along the whole Bulgarian coast.

Keywords: radionuclides, coastal sediments, sea water, Black Sea.

1 Introduction

Sustainable management of the ecological condition of the coastal marine environment requires a comprehensive understanding of the processes associated with the entry and migration of various potential pollutants in coastal ecosystems.

Due to the fact that more than 70% of the Earth's surface is ocean, most of the anthropogenic radionuclides are found in the aquatic environment. Their concentrations usually vary from region to region, depending on the location and size of the various sources of contamination [1].

The main sources of anthropogenic marine radioactivity (planned or accidental) are still global deposits of nuclear tests performed in the atmosphere in the 1950s and 1960s and nuclear accidents such as those at Chernobyl and Fukushima.

The Baltic and Black Seas were the seas most affected by the Chernobyl accident. The ^{137}Cs inventory in the Black Sea due to the Chernobyl accident increased to approximately 3 PBq, higher by about a factor of 2 in comparison with the pre-Chernobyl value [2]. The increase in the content of anthropogenic radionuclides in the sea water causes changes in the radiation background and disturbs the ecological balance in the marine environment - in the water, suspended particles, sediment and biota [3–7].

The study of the content of contaminants such as radionuclides and non-radionuclides (nutrients, hydrocarbons, pesticides, heavy metals and other toxic elements) in sediments is of particular importance. The data obtained can be used both to assess the current level of pollution and to collect evidence of past pollution events and a historical overview of pollutant discharges.

The Northern coast of Bulgaria mainly consists of soft sediments, loess, shale, marl, dolomites, limestone or sandstone, overlaid in many areas with beach or wind-blown sand. In the north, suspended material from the Danube delta has settled, carrying a lot of mud. The association of radionuclides with sediments in coastal and estuary areas makes sediments a large reservoir for radionuclides affecting significantly specific marine ecosystems. As the seawater is constantly in contact with organic and inorganic matter from sea shelf, the first necessary step in the estimation of radionuclide migration is the measurement of radionuclide content in sea sediments and setting up a radioecological data base.

However, the current data on the content of radionuclide and non-radionuclide pollutants in sediments from different geographical areas along the Bulgarian Black Sea coast are few. There are a limited number of publications on near-shore sediment samples [8–13]. Data on deep-sea sediments are even scarcer [8].

The present work provides data on the accumulation of nuclides in sediments and water collected in the northern part of the Bulgarian Black Sea coast. The aim of the study is to be the first step in a future large-scale study of the content of radionuclides in sediments from different geographical areas in the Bulgarian Black Sea coast.

2 Sampling

The samples were collected in the autumn of 2018 during a one-day sampling expedition in the Black Sea carried out in the frame of the regional seminar under the TC project RER7009/IAEA on "Improving the management of the Adriatic and Black Sea coasts using nuclear analytical techniques", held in Varna, Bulgaria. The sampling stations are located in the Northern part of the Bulgarian Black Sea coast, in and close to Varna

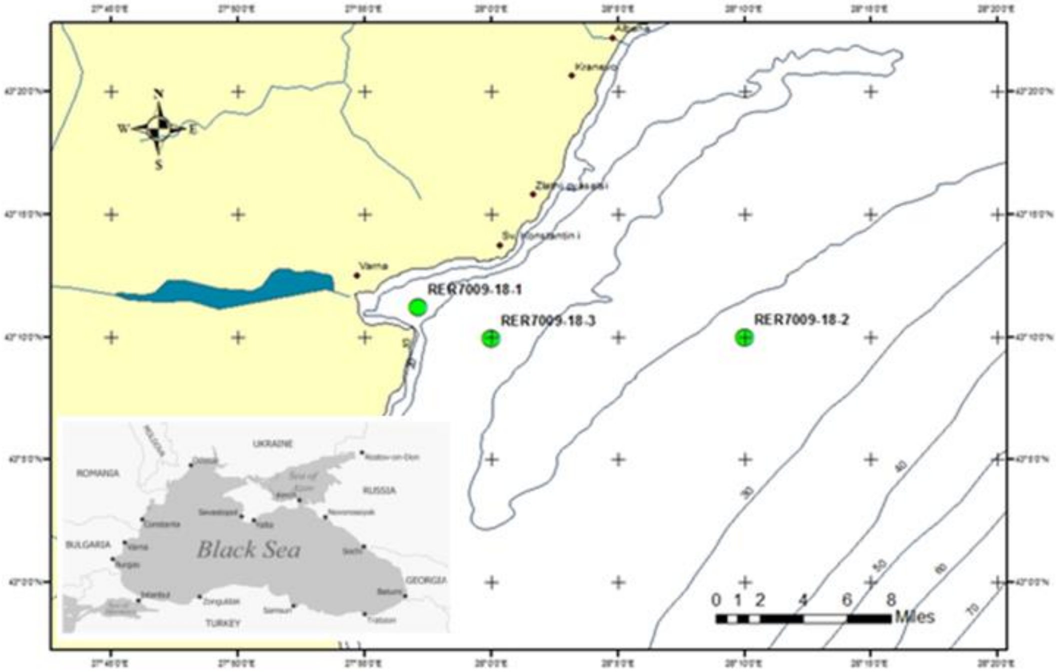

Figure 1. Map of sampling locations.

Bay in front of cape Galata (Figure 1). The Stations RER7009-18-01 and RER7009-18-02 were situated in outer part of Varna Bay and the station RER7009-18-03 was located in front of cape Galata. The stations were selected on the basis of preliminary information on regional geology, bottom morphology and bathymetric maps.

Matrixes with low heterogeneity were chosen for representativeness of the sample results. Deposits where contaminants are likely to accumulate were mainly selected: sandy mud at the three stations (Figure 2).

Sampling at the first station (RER7009-18-01) was performed at about 18 m water depth using the Van Veen grab (Figure 3) under the following meteorological conditions: wind direction – NNE, wind speed – 8 m/s, wave direction – NNE, wave height – 1.5 m, air temperature 12°. The bulk sediments are consisted of dark olive gray (5Y 3/2 color by Munsell soil color chart), very fine sandy mud, very soft with living worms and worms tubes, plant remnants and single mollusks *Chione gallina*.

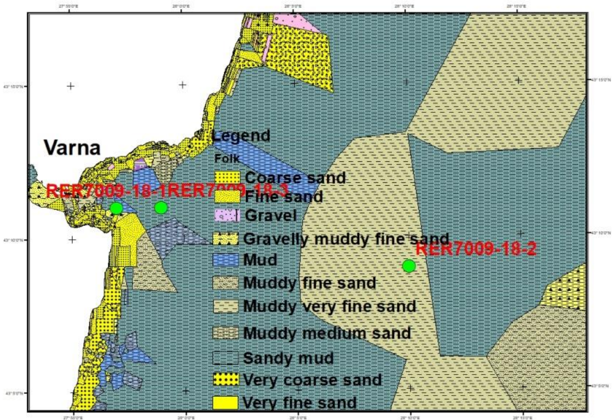

Figure 2. Map of sampling locations.

Figure 3. Sampling with Van Veen grab during the expedition.

Sampling at the stations RER7009-18-02 and RER7009-18-03 was carried out with Multi-Corer equipment at 24.5 m and 22 m water depth, respectively (Figure 4).

Sampling at station RER7009-18-02 was in the following meteorological conditions: wind direction – NNE, wind speed – 13.9 m/s, wave direction – NNE, wave height – 2.5 m, air temperature 17°. Field measurements were per-

Figure 4. Multi-Corer sampling during the expedition.

Table 1. Detailed information on the collected samples

Station	**Latitude**	**Longitude**	**Samples**	**Lithology**	**Color** (by Munsell soil color chart)	**Other**
RER7009-18-01 (17.9 m water depth)	43°11.0 N	27°57.0 E	S-1-18-01	very fine sandy mud, very soft	5Y 3/2 dark olive gray	living worms and worms tubes, plant remnants and single mollusks Chione gallina
RER7009-18-02 (24.5 m water depth)	43°09.0 N	28°10.0 E	S-2-18-02-01	very fine sandy mud (or silt)	5G/4/1 dark greenish gray 5Y/4/2 olive gray	
			S-3-18-02-02		5G/4/1 dark greenish gray	
			S-4-18-02-03		5G/4/1 dark greenish gray 5Y/4/2 olive gray	remnants of shells (fine to small fragments)
			S-5-18-02-04			abundance of small to big shells fragments, whole shells *Paphia, Chione*
			Water-18-02			
RER7009-18-03 (22 m water depth)	43°09.6 N	28°00.0 E	S-6-18-03-01	soft silty clay (very fine sandy clay)	5Y 4/2 olive gray	whole disarticulated mollusk *Cardium papilosum*
			S-7-18-03-02			
			S-8-18-03-03			remnants of shells
			S-9-18-03-04			remnants of shells (whole and fragments)
			Water-18-03			

formed on: water temperature 20.5°, dissolved oxygen – 7.85 mg/L, pH – 8.30 and salinity $18.2\,^{0}/_{00}$. The sampling of the third station 7009-18-03 was performed under meteorological conditions: wind direction – NNE, wind speed – 13.9 m/s, wave direction – NNE, wave height – 2.5 m, air temperature 14°. The following field measurements were performed: water temperature 20.6°, dissolved oxygen – 7.57 mg/L, pH – 8.34 and salinity $17.6\,^{0}/_{00}$.

Sediment samples were placed in double plastic bags and after labeling and frozen saved for further laboratory testing. The water samples were taken in special bottles and transported to the laboratory for analysis. Detailed information on the collected samples is shown in Table 1.

3 Sample Preparation and Analyses

The present analyzes are initial tests and their purpose is to optimize the sampling technique, the preliminary preparation and the conditions of measurement, as well as adaptation of the methodology for testing of small amounts of sediment and water samples. Therefore, only the first fraction (0–1 cm) of each core was examined.

As a first step in the study of sediments and water, all samples were analyzed to determine the content of gamma radionuclides using low-level gamma spectrometry. For this purpose, the sediment samples were dried at about 90-100°C and all large particles and debris (residues of shells, live worms and tubes of worms, plant residues and single mollusks) were mechanically removed. After homogenization the samples were placed in special hermetic containers for a period of at least four weeks before measurements. This procedure is applied to ensure the equilibrium within the Uranium decay series for estimation of the natural radioisotopes. The aqueous phase taken with the sediments was also enclosed in plastic containers for measurement.

The gamma spectrometry measurements were carried out by means of HPGe – GMX 50P4 detector Ortec type with 54.9% counting efficiency and energy resolution 2.3 KeV at 1332 KeV (^{60}Co). The obtained spectra were processed with the computer code WINNER. The spectrometric systems were calibrated by energy and by efficiency with certified calibration sources with wide energy range. The time for measurement was selected during the working process according to capabilities of the equipment (24 h for sediments and 72 h for water).

The ^{137}Cs and ^{40}K specific activities were measured by their main gamma-lines of 661.6 keV and 1460.7 keV. The ^{238}U content was determined from the ^{234}Th line at 63.3 keV, assuming equilibrium. The ^{238}U content was controlled by ^{235}U line at 186 keV (corrected by subtraction of radium) using the known ratio ^{238}U/^{235}U. The ^{226}Ra content in the samples was determined indirectly from the lines of the ^{226}Ra daughters ^{214}Bi and ^{214}Pb. In the ^{232}Th series we determined ^{228}Ra by each of the its daughter lines – ^{228}Ac, ^{224}Ra, ^{212}Pb, ^{208}Tl and calculated the mean to obtain the ^{228}Ra content. The obtained values can be ascribed to the parent ^{232}Th, assuming equilibrium with its daughter ^{228}Ra.

Table 2. Radionuclide concentration (Bq/kg ± SE) in studied sediment samples

Stations	Samples	^{137}Cs Bq/kg ± SE	^{40}K Bq/kg ± SE	^{238}U Bq/kg ± SE	^{226}Ra Bq/kg ± SE	^{232}Th Bq/kg ± SE
RER7009/18-01	S-1-18-01	1.18 ± 0.09	611 ± 49	12.4 ± 1.2	12.8 ± 0.9	13.6 ± 0.9
RER7009/18-02	S-2-18-02-01	0.82 ± 0.06	518 ± 41	10.5 ± 0.9	9.8 ± 0.7	12.4 ± 0.8
	S-3-18-02-02	0.79 ± 0.05	556 ± 44	11.2 ± 0.9	10.2 ± 0.8	11.8 ± 0.8
	S-4-18-02-03	0.73 ± 0.06	553 ± 45	10.8 ± 0.9	9.7 ± 0.7	12.2 ± 0.9
	S-5-18-02-04	0.76 ± 0.06	529 ± 42	10.4 ± 0.8	9.8 ± 0.8	12.6 ± 0.8
RER7009/18-03	S-6-18-03-01	0.64 ± 0.05	727 ± 52	11.4 ± 0.9	10.7 ± 0.9	11.7 ± 0.7
	S-7-18-03-02	0.68 ± 0.05	715 ± 57	11.2 ± 0.8	10.2 ± 0.8	12.4 ± 0.8
	S-8-18-03-03	0.72 ± 0.06	732 ± 58	10.8 ± 0.7	9.8 ± 0.7	12.6 ± 0.9
	S-9-18-03-04	0.65 ± 0.05	733 ± 55	11.5 ± 0.8	10.3 ± 0.8	12.3 ± 0.8

4 Results and Discussion

The obtained results for technogenic ^{137}Cs and natural radionuclides of the ^{238}U and ^{232}Th series (^{238}U, ^{226}Ra, ^{232}Th) and ^{40}K in sediments are presented in Table 2.

Table 3 shows the total mean values for each radionuclide concentration obtained for the three stations.

The analysis of the obtained results shows that the measured values for each radionuclide except ^{40}K in the samples from first station (RER7009-18-01) are slightly higher. The data for the other two stations (RER7009-18-02 and RER7009-18-03) are comparable.

Table 3. Mean radionuclide content (Bq.kg^{-1}±SD) obtained for the studied stations

Nuclide	RER7009-18-01 (17.9 m)	RER7009-18-02 (24.5 m)	RER7009-18-03 (22 m)
^{137}Cs	1.18 ± 0.05	0.78 ± 0.04	0.67 ± 0.03
^{40}K	611 ± 28	539 ± 18	726 ± 8
^{238}U	12.4 ± 0.7	10.4 ± 0.4	11.2 ± 0.3
^{226}Ra	12.8 ± 0.4	9.9 ± 0.2	10.3 ± 0.4
^{232}Th	13.6 ± 0.5	12.6 ± 0.3	12.3 ± 0.4

The data from the present study of sediments were compared with our data from previous studies obtained for sediments collected from geographically close stations at a depth of 50–60 meters 20 years ago. The results obtained are higher than those measured in the present study – 5.2 Bq/kg for ^{137}Cs, 12.5 Bq/kg for ^{238}U, 55.5 Bq/kg for ^{226}Ra, 15 Bq/kg for ^{232}Th [9, 10].

The obtained data were also compared with data obtained by us for the content of radionuclides in near-shore sediments collected at about 10–20 meters depth along the entire Northern Bulgarian coast over the past 20 years. The calculated mean values for near-shore sediments are significantly higher than those measured in the present study – 16.4 Bq/kg for ^{137}Cs, 29 Bq/kg for ^{238}U, 27 Bq/kg for ^{226}Ra, 19.6 Bq/kg for ^{232}Th [9–12].

The ^{232}Th/^{238}U activity ratios calculated for the sediment samples showed values of 1.09 for the sediments from station RER7009-18-01, 1.21 and 1.10 for the RER7009-18-02 and RER7009-18-03 stations, respectively. This indicates that in the sediment from station RER7009-18-01 ^{238}U is less abundant than ^{232}Th in the all studied sediments. Opposite dependence has been found in studies of near-shore sediments.The calculated ^{232}Th/^{238}U activity ratios values vary in the range 0.75–1.0, independently of the sediment type showing that ^{232}Th is less abundant than ^{238}U. Our data show that the 238U and 226Ra values are close at all stations – 226Ra/238U activity ratio (mean value) for all sediments is in the range 0.95–1.03 and are close to the equilibrium.

The data obtained for water samples are below the minimum detectable activity (MDA) of the method used. To obtain reliable results, additional studies are needed to optimize the conditions of sample preparation and measurement parameters.

5 Conclusions

The present work provides data on the accumulation of nuclides in the sediments and waters collected in and close to Varna Bay in front of cape Galata in the Northern Bulgarian Black Sea coast. The study is the first step in a future large-scale study of the content of radionuclides in the sediments from different geographical areas in the Bulgarian Black Sea coast.

The sampling techniques applied require special equipment and qualified personnel. The methods used for preliminary and laboratory sample preparation, as well as the measurement methods are suitable for sediment samples. In order to obtain accurate and reproducible results for very small amounts of water samples, additional analyzes are needed to optimize the pre-sample preparation procedures as well as the measurement conditions.

Acknowledgements

This study has been carried out under the frame of the TC Project RER7015/IAEA "Enhancing Coastal Management in the Mediterranean, the Black Sea, the Caspian Sea and the Aral Sea by Using Nuclear Analytical Techniques" and the National Science Programme "Environmental Protection and Reduction of Risks of Adverse Events and Natural Disasters", approved by the Resolution of the Council of Ministers No 577/17.08.2018 and supported by the Ministry of Education and Science (MES) of Bulgaria (Agreement No D01-363/17.12.2020).

References

[1] Livingston H.D., Povinec P.P. (2000) Anthropogenic marine radioactivity, *Ocean and Coastal Management* **43** 689-712.

[2] Egorov V.N., Povinec P.P., Polikarpov G.G., Stokozov N.A., Gulin S.B., Kulebakina L.G., Osvath I. (1999) ^{90}Sr and ^{137}Cs in the Black Sea after the Chernobyl NPP accident: inventories, balance and tracer applications. *J. Env. Radioact.* **43** 137-155.

[3] Livingston H.D., Buesseler K.O., Izdar E., Konik T. (1986) Characteristics of Chernobyl Fallout in the Southern Black Sea. EML-460. US Department of Energy, Environmental Measurement Laboratory, New York, 214-223.

[4] Buesseler K.O., Livingston H.D., Hohjo S., Hay B.J., Manganini S.J., Degens E., Ittekot V., Izdar E., Konuk T. (1987) Chernobyl radionuclides in a Black Sea sediment trap. *Nature* **329** 825-828.

[5] Nikitin A.I., Medinets W.I., Tchumishew W., Katrich I., Wakulowskij S.M., Kozlow A.I., Lepeshkin W.I. (1988) Radioaktiwnoe zagryazenie Chernogo morya wsledstwie awarii na Chernobilskoj AEC po sostoyaniu na oktyabr 1986. *Atomnaya Energiya* **6** 134-136.

[6] Kulebakina L., Polikarpov G. (1989) Radiological investigation of Black Sea ecosystems after the Chernobyl accident. In: *Proceedings of the Conference on Radioecology High Tatras*, Czechoslovakia, pp. 131-155.

[7] Gulin S.B., Polikarpov G.G., Egorov V.N., Martin J.M., Korotkov A.A., Stokozov N.A. (2002) Radioactive contamination of the north-western Black Sea sediments. *Estuarine, Coastal and Shelf Science* **54** 541-549.

[8] Kolarova et al. (1980). Gamma Spectrometric Investigations of Marine Sediments, Water and Algae at the Black Sea Side. https://inis.iaea.org/collection/NCLCollectionStore/_Public/13/712/13712621.pdf.

[9] Strezov A., Nonova Tz., Ayranov M., Stoilova T., Mitev K. (2001) Assessment of Radionuclide and Heavy Metal Pollution in Black Sea Sediments and Algae. In: *Proc. 3rd Black Sea Int. Conf. "Environmental protection technologies for Coastal Areas",* Varna, Bulgaria, June 2001, pp. 44-55.

[10] Strezov A., Nonova Tz., Stoilova T., Petkov P. (2002). Radionuclide and Heavy Metal Content in Marine Ecosystems at the Bulgarian Black Sea Coast, *CIEMS Series*, ISSN 1563-2727, pp. 97-99.

[11] Strezov A., Nonova Tz. (2004) Monitoring of radionuclide and heavy metals in sediments and macrophytes from Black Sea ecosystems. In: *Book of Extended Synopses: International Conference on Izotopes in Environmental Studies – Aquatic Forum-2004*, Monaco, France, 25-29 October 2004, IAEA-CN-118, pp. 552-553.

[12] Strezov A., Nonova Tz. (2006) Anthropogenic Contamination in Marine Ecosystems at Northern Bulgarian Black Sea Sector. *Ovid. Univ. Ann. Chem*. **17** 13-16.

[13] Peycheva K, Stancheva M, Georgieva S, Makedosnki L (2016) Heavy metals in water, sediments and marine fishes from Bulgarian Black Sea. https://www.emecs.or.jp/en/wp-content/uploads/2019/09/mona-dinkova-stancheva-2.pdf.