Published in MORSKOY GIDROFIZICHESKIY ZHURNAL, Vol. 36, Iss. 2 (2020)

Distribution of ^{137}Cs in the Surface Layer of the Black Sea in Summer, 2017

I. I. Dovhyi[1,*], D. A. Kremenchutskii[1], N. A. Bezhin[1], O. N. Kozlovskaia[1], V. V. Milyutin[2], E. A. Kozlitin[2]

[1]*Marine Hydrophysical Institute of RAS, Sevastopol, Russian Federation*
[2]*Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, Moscow, Russian Federation*
*dovhyi.illarion@yandex.ru

Purpose. The purpose of the study is to investigate distribution of ^{137}Cs in the coastal and deep-water part of the Black Sea. To achieve this goal, the following scientific problems has to be solved: choosing a method for concentrating ^{137}Cs from seawater samples, seawater sampling and ^{137}Cs concentrating, measurements of the obtained samples, discussion of the obtained results and their comparison with the available scientific literature data.
Materials and Results. Distribution of ^{137}Cs activity in the coastal and deep-water part of the Black Sea was studied. The in situ data on spatial-temporal variability of the ^{137}Cs volumetric activity field in the Black Sea surface layer obtained in course of the 95th cruise of the R/V "Professor Vodyanitsky" in June, 14–July 7, 2017 were used. The data on the radionuclide vertical distribution in the sea active layer were obtained at a number of stations. 22 seawater samples were taken and processed at 11 stations. To separate ^{137}Cs from seawater, a ferrocyanide sorbent of the FCC brand was first applied; it was intentionally developed for selective recovery and separation of ^{134}Cs and ^{137}Cs radionuclides from the technological processing solutions and radioactive waste water.
Conclusions. According to the results, the volumetric activity of ^{137}Cs varied spatially in the range 5.7–8.8 Bq/m^3 and amounted on average 6.9 ± 0.2 Bq/m^3. Within the active layer boundaries, vertical distribution of ^{137}Cs was found to be uniform.

Keywords: ^{137}Cs, volumetric activity analysis, Black Sea, active layer, spatial-temporal variability, sorption, selective sorbent.

Acknowledgments: the study was carried out within the framework of the state task No. 0827-2020-0003 “Oceanological processes”, methodological aspects of sorption were studied at the RFBR financial support within the framework of scientific project No. 19-33-60007.

For citation: Dovhyi, I.I., Kremenchutskii, D.A., Bezhin, N.A., Kozlovskaia, O.N., Milyutin, V.V. and Kozlitin, E.A., 2020. Distribution of ^{137}Cs in the Surface Layer of the Black Sea in summer, 2017. *Physical Oceanography*, [e-journal] 27(2), pp. 152-160. doi:10.22449/1573-160X-2020-2-152-160

DOI: 10.22449/1573-160X-2020-2-152-160

Introduction

The distribution of ^{137}Cs after the Chernobyl accident (Chernobyl nuclear power plant) has been studied in many marine expeditions. The main works in this area for 30 years and to date have been carried out at the Institute of Biology of the Southern Seas. The results of these works were published in a number of monographs [1–3] and a large number of scientific papers [4–6]. Significant contribution to the study of the issue was made by American researchers during the expeditions on R/V “K. Piri Reis” (September 1986, May 1987), R/V “Knorr” (June 1988), a number of joint expeditions on R/V “Professor Vodyanitsky” (April

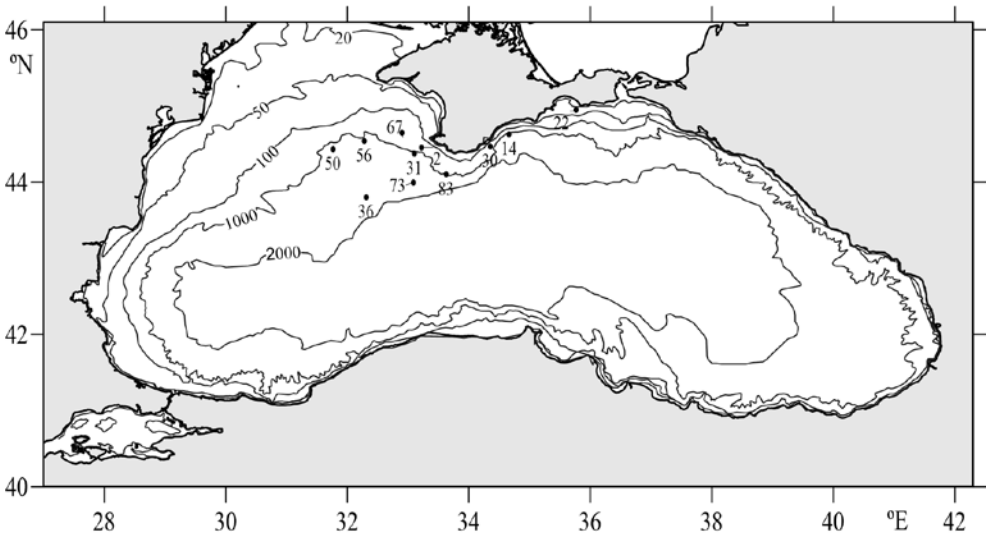
1989, June 1990, August 1992). The main results of these works were published in [7, 8]. A number of works were carried out at Marine Hydrophysical Institute [9].

The result of these studies was the calculation of ^{137}Cs fluxes in the Black Sea [2, 10] and the development of mathematical models of ^{137}Cs transport [11, 12]. In these studies, half-life periods of ^{137}Cs activity, ^{137}Cs activity in the Black Sea before and after the Chernobyl accident and subsequent secondary pollution of the Black Sea were determined.

This study examined the distribution of ^{137}Cs in the coastal and deepwater parts of the Black Sea in the modern period.

Materials and methods

Sampling technique. The arrangement of stations is shown in Fig. 1 The drawings were plotted in *Surfer* (Fig. 1, 3, 4) and *MS Excel* 10 (Fig. 2) application programs).



F i g. 1. Location of the sampling stations in the cruise of R/V ”Professor Vodyanitsky“ (June, 14–July 7, 2017)

Sea water was pumped with a submersible pump into 8 plastic containers (the volume of each was 1m^3) installed on the board of the vessel. From the containers, using the *Unipump JS* 60 on-board pump, the sea water was pumped at 6.7–9.0 l/min volume flow rate through a system of three cartridges connected in series and then dumped overboard. The first cartridge in the direction of water flow was a polypropylene filter with 1 μm pore size (*FCPS1M series, Aquafilter Europe Ltd.*). It served to remove suspended particles from the water. In the second and third cartridges of 700 ml volume, 450 g of ferrocyanide sorbent (of FSS brand) were loaded. On this sorbent the sorption of radiocesium occurred. FSS sorbent is an inorganic sorbent based on nickel-potassium ferrocyanide deposited on the silica gel surface. A pilot batch of sorbent was manufactured at Frumkin Institute of Physical Chemistry and Electrochemistry of the Russian Academy of Sciences (Moscow) according to TU 2641-003-51255813-2007.

In appearance, FSS sorbent has the form of irregular-shaped green granules of 0.25–3.0 mm size. This sorbent is used for processing liquid radioactive waste containing ^{137}Cs; it was first used to concentrate ^{137}Cs from the seawater samples.

After filtration of the water batch, the cartridges with a polypropylene filter and sorbents were dried in air and packed in plastic bags.

Vertical temperature distribution and salinity data were obtained using *Seabird CTD (SBE 911 Plus CTD, Sea-Bird Electronics)*.

Determination of ^{137}Cs activity in samples of sorbents. Measurement of ^{137}Cs activity in sorbent samples was carried out in Marinelli vessels on a low-background gamma spectrometer with a *NaI(Tl)* scintillation detector (diameter – 63 mm, height – 63 mm, the resolution is 7 % based on ^{137}Cs peak, detection efficiency of gamma quantum with an energy of 661.7 keV is 4.5 %). The detector was located in a shield consisting of cast iron and lead rings of 150 and 140 mm thickness, respectively. Registration and processing of spectrometric data was carried out by software on a personal computer. The time of recording the activity of a single sample was on average 16 hours. Calibration of the efficiency of recording ^{137}Cs activity in the samples was performed using a certified soil source with known specific activity *IAEA CU*-2006-03. The error in measuring the activity of each sample (σ) usually did not exceed 5 %.

The degree of ^{137}Cs (S) recovery from the seawater was calculated according to the equation from [13]:

$$S = \left(1 - \frac{B}{A}\right)100\%,$$

where A, B (Bq) are ^{137}Cs activity in the second and third sorbent cartridges, respectively. A gamma spectrometric analysis of the polypropylene filter contents was not performed.

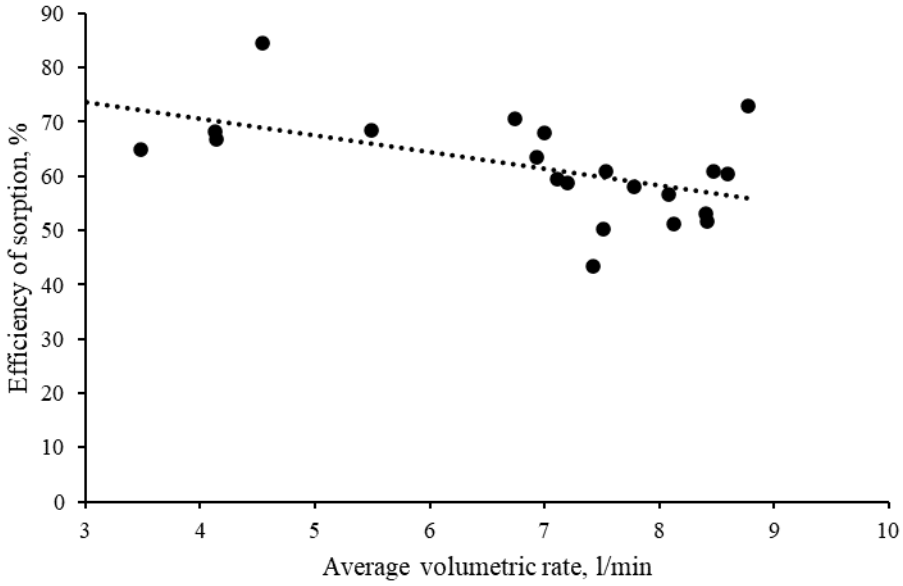
Results and discussion

Sampling technique. A lot of techniques for the radioanalytical determination of ^{137}Cs [14] were proposed. So, for ^{137}Cs concentration a coprecipitation with ammonium phosphormolibdate (APM) is used, as well as sorption on selective sorbents based on APM and insoluble ferrocyanides of various metals.

In order to carry out the sorption concentration of ^{137}Cs, fibrous sorbents obtained by impregnating polymer fibers with transition metal ferrocyanides, for example copper ferrocyanide, are widely used [15]. The disadvantages of this sorbent include the associated recovery of ^{40}K natural radioactive isotope from the seawater. Fibrous sorbents based on mixed potassium-nickel ferrocyanide exhibit greater selectivity with respect to ^{137}Cs and therefore are often used for radioanalytical determination of ^{137}Cs [15]. Thus, a polyacrylate fiber coated with potassium nickel ferrocyanide – KNiFC-PAN – was used to determine ^{137}Cs content in the seawater, and the fibrous sorbent consumption was 5 ml per 20 l of sample [16]. After concentration, the activity of the sorbent solid phase was determined by high-resolution γ-spectrometry using a semiconductor detector from high-purity germanium. The advantage of this method is the use of relatively small volumes of seawater for analysis; the disadvantage is the need to use expensive semiconductor γ-spectrometers. At the same time, in many radiochemical

laboratories, cheaper and more affordable scintillation γ-spectrometers are used to determine the activity of radionuclides.

During the tests the dependence of ^{137}Cs recovery rate on the volumetric flow rate of seawater transmission through adsorbers with an FCC sorbent was determined (Fig. 2). The results showed that there is a slight decrease in ^{137}Cs recovery rate, on average, from 70 to 60 % with a rate increase from 3 to 9 dm^3/min.



F i g. 2. Dependence of the ^{137}Cs recovery rate on the average volumetric seawater flow rate

The radionuclide recovery rate from seawater depends on many factors: the flow rate of pumping the sample through the sorbent, the final volume of the sample and the radionuclide content. According to the measurement results, ^{137}Cs recovery rate by the FCC sorbent was on average 62 ± 9 %.

The main contribution to the error in the technique used to determine the activity of cesium in sea water is made by the statistical error of the product activity calculation, which did not exceed 7 % for the selected duration of measurement of the obtained activities of sorbents' counted samples and the detector we used.

^{137}Cs distribution and activity profiles. During the period under study, 22 seawater samples were taken and processed at 11 stations. The results are represented in the table.

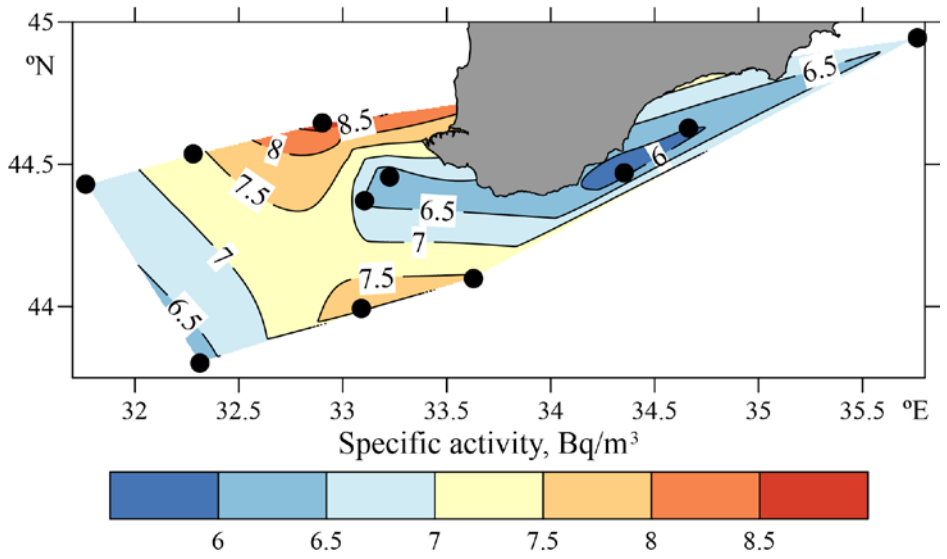
Table

Parameters of samples and stations

Station number	Coordinates of sampling point		Depth, m	Salinity, ‰	Sample volume, m^3	S, %	A_{sp} ^{137}Cs, Bq m^3	Confidence interval
	Northern Latitude	Eastern Longitude						
2	44,456°	33,225°	5	18.28	1.978	72.9	6.01	0.25
			25	18.31	3.096	59.5	6.85	0.25
			65	18.57	2.932	68.1	6.75	0.26
14	44,628°	34,663°	3	18.57	2.013	84.6	6.00	0.35
			20	18.35	3.045	58.0	6.55	0.24
			50	18.52	2.966	53.1	7.29	0.26
22	44,946°	35,764°	3	18.10	2.959	60.9	6.56	0.24
			23	18.29	4.107	60.4	7.17	0.24
30	44,469°	34,353°	3	18.11	2.000	68.4	5.70	0.26
			16	18.14	3.084	43.3	6.99	0.25
			50	18.52	3.083	51.7	6.74	0.24
31	44,372°	33,105°	3	18.25	1.977	66.7	6.44	0.23
			20	18.25	3.056	56.6	6.31	0.23
			60	18.60	3.009	51.1	7.13	0.25
36	43,802°	32,312°	3	18.42	1.984	64.8	6.32	0.27
			20	18.39	3.095	50.3	6.91	0.24
			45	18.63	3.062	70.6	6.95	0.26
50	44,430°	31,764°	3	18.32	8.250	60.8	6.64	0.20
56	44,537°	32,278°	3	18.25	2.000	68.3	7.37	0.30
67	44,646°	32,902°	3	18.30	8.149	58.8	8.76	0.26
73	43,993°	33,088°	3	18.20	8.196	63.6	7.94	0.25
83	44,099°	33,629°	3	17.96	3.717	74.4	7.56	0.34

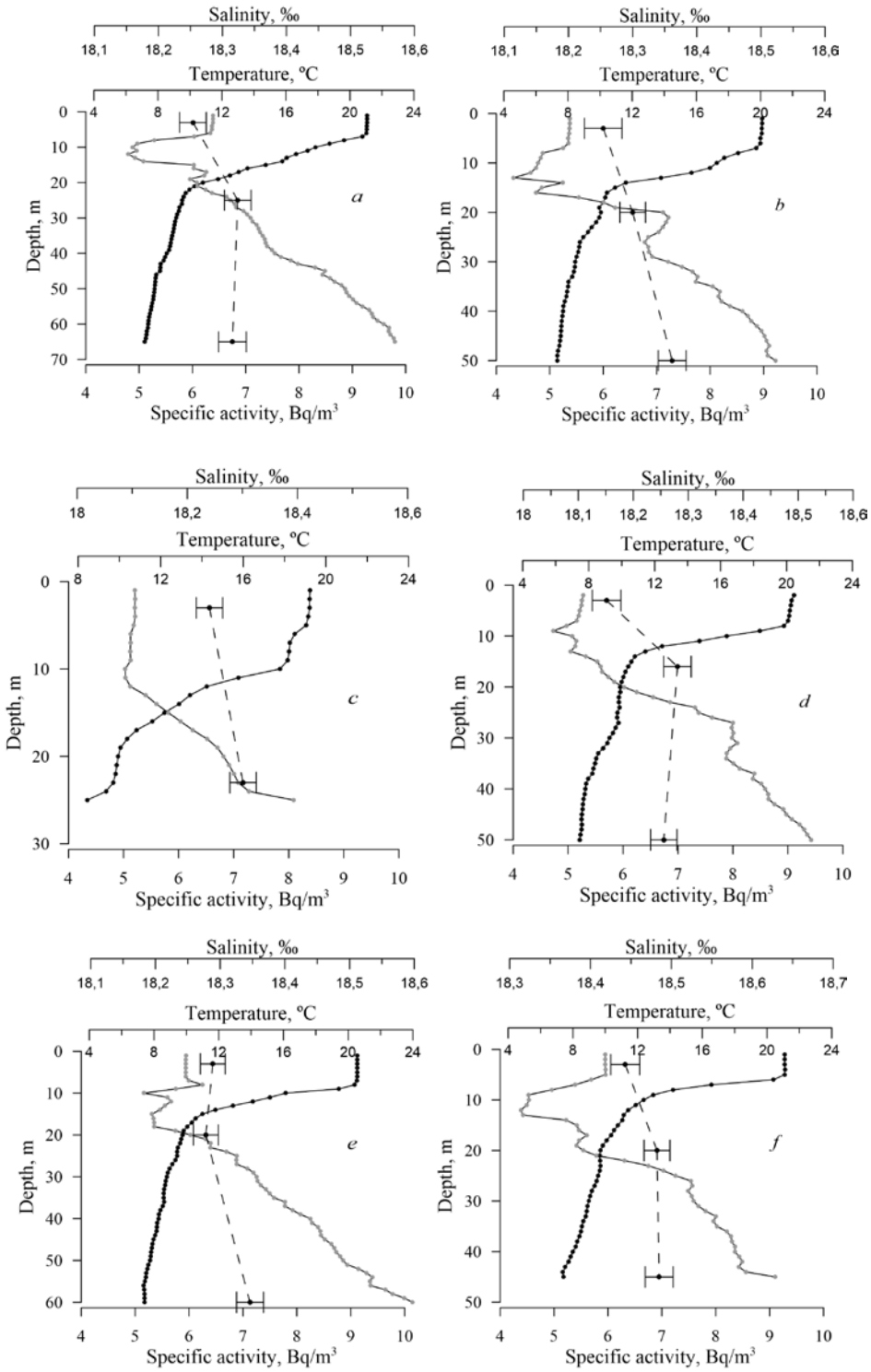
^{137}Cs distribution in the Black Sea surface layer is shown in Fig. 3. ^{137}Cs activity value varied in space within 5.7–8.8 Bq/m^3 range and averaged 6.9 ± 0.2 Bq/m^3. Increased ^{137}Cs activity was observed in the western part of the studied area, lower – in the eastern one. Such spatial variability may be related to the difference in remoteness from the Dnieper mouth [2], which ensures the entry of ^{137}Cs radionuclide, washed out by groundwater from soils, into the Black Sea.

In [10], it was noted that according to observations carried out in 2007, ^{137}Cs activity in the Black Sea surface layer was 20 Bq/m^3. Thus, for the 11-year period 2007–2017 a decrease in ^{137}Cs activity average value to 7–8 Bq/m^3 is observed. The obtained data are consistent with the literature. According to [2], the half-life of ^{137}Cs is 8.6 years for 1987–2011. The decrease in ^{137}Cs activity in the Black Sea surface layer is associated with its radioactive decay and penetration into the lower layers [2]. The results of numerical experiments aimed at studying the evolution of ^{137}Cs concentration field in the Black and Mediterranean Seas obtained using the *POSEIDON-R* model are presented in [12]. For the modeling area No. 69, according to the mentioned work, the activity of ~ 8 Bq/m^3 refers to 2017.



F i g. 3. Activity of ^{137}Cs in the surface layer (up to 3 m) in the Black Sea nearby the Crimea Peninsula

^{137}Cs activity profiles were obtained at 6 stations (Fig. 4). In all cases, the variation of ^{137}Cs activity with depth did not exceed the error in determining this parameter. The obtained data are consistent with the literature [10], according to which no changes in ^{137}Cs activity were detected up to 50 m depth compared to the surface activity.



F i g. 4. Activity of ^{137}Cs in the upper mixed layer of the Black Sea at stations *2* (*a*), *14* (*b*), *22* (*c*), *30* (*d*), *31* (*e*), *36* (*f*)

Conclusion

For the first time, ferrocyanide sorbent of FCC brand based on potassium-nickel ferrocyanide and silica gel was used for the separation of ^{137}Cs from the seawater samples. High recovery rates (over 60 %) of ^{137}Cs by this sorbent are shown.

^{137}Cs activity values obtained for the studied region vary within the range of 5.7–8.8 Bq/m^3 and, on average, were equal to 6.9 ± 0.2 Bq/m^3. Increased values of ^{137}Cs activity are observed in the western part of the studied region, lower ones – in the eastern part. According to observational data, ^{137}Cs activity in the depth range of 3–65 m varies within the error range of the method. ^{137}Cs activity values obtained in the work are consistent with the results of numerical experiments that were carried out using the *POSEIDON-R* model.

REFERENCES

1. Polikarpov, G.G., Egorov, V.N., Gulin, S.B., Stokozov, N.A., Lazorenko, G.E., Mirzoeva, N.Yu., Tereshchenko, N.N., Tsytsugina, V.G., Kulebakina, L.G., Popovichev, V.N., Korotkov, A.A., Evtushenko, D.B., Zherko, N.V. and Malakhova, L.V., 2008. *Radioecological Response of the Black Sea to the Chernobyl Accident*. Sevastopol: ECOSI-Hydrophysics, 666 p. (in Russian).
2. Gulin, S.B. and Egorov, V.N., 2016. Radioactive Tracers in the Black Sea: A Tool for Environmental Assessment and Ecological Regulation. In: V. Korogodina, C. Mothersill, S. Inge-Vechtomov and C. Seymour, eds., 2016. *Genetics, Evolution and Radiation.* Cham: Springer, pp. 303-313. doi:10.1007/978-3-319-48838-7_25
3. Mirzoeva, N.Yu., Gulin, S.B. and Miroshnichenko, O.N., 2018. Strontium and Cesium Radionuclides. In: A.P. Lisitsin, ed., 2018. *The Black Sea System.* Moscow: Scientific World, pp. 605-624. doi:10.29006/978-5-91522-473-4.2018 (in Russian).
4. Egorov, V.N., Povinec, P.P., Polikarpov, G.G., Stokozov, N.A., Gulin, S.B., Kulebakina, L.G. and Osvath, I., 1999. ^{90}Sr and ^{137}Cs in the Black Sea after the Chernobyl NPP Accident: Inventories, Balance and Tracer Applications. *Journal of Environmental Radioactivity*, 43(2), pp. 137-155. doi:10.1016/S0265-931X(98)00088-5
5. Gulin, S.B., Egorov, V.N., Duka, M.S., Sidorov, I.G., Proskurnin, V.Yu., Mirzoyeva, N.Yu., Bey, O.N. and Gulina, L.V., 2015. Deep-Water Profiling of ^{137}Cs and ^{90}Sr in the Black Sea: A Further Insight into Dynamics of the Post-Chernobyl Radioactive Contamination. *Journal of Radioanalytical and Nuclear Chemistry*, 304(2), pp. 779-783. doi:10.1007/s10967-014-3848-9
6. Gulin, S.B., Mirzoyeva, N.Yu., Egorov, V.N., Polikarpov, G.G., Sidorov, I.G. and Proskurnin, V.Yu., 2013. Secondary Radioactive Contamination of the Black Sea after Chernobyl Accident: Recent Levels, Pathways and Trends. *Journal of Environmental Radioactivity*, 124, pp. 50-56. doi:10.1016/j.jenvrad.2013.04.001
7. Buesseler, K.O., Casso, S.A., Hartman, M.C. and Livingston, H.D., 1990. Determination of Fission-Products and Actinides in the Black Sea Following the Chernobyl Accident. *Journal of Radioanalytical and Nuclear Chemistry*, 138(1), pp. 33-47. doi:10.1007/BF02049345
8. Buesseler, K.O. and Livingston, H.D., 1997. Time-Series Profiles of ^{134}Cs, ^{137}Cs and ^{90}Sr in the Black Sea. In: E. Özsoy and A. Mikaelyan, eds., 1997. *Sensitivity to Change: Black Sea, Baltic Sea and North Sea. NATO ASI Series (Series 2: Environment), vol. 27.* Dordrecht: Springer, pp. 239-251. https://doi.org/10.1007/978-94-011-5758-2_19
9. Eremeev, V.N., Chudinovskikh, T.V., Batrakov, G.F. and Ivanova, T.M., 1991. Radioactive Isotopes of Caesium in the Waters and Near-Water Atmospheric Layer of the Black Sea. *Soviet Journal of Physical Oceanography*, 2(1), pp. 57-64. doi:10.1007/BF02197418
10. Delfanti, R., Özsoy, E., Kaberi, H., Schirone, A., Salvi, S., Conte, F., Tsabaris, C. and Papucci, C., 2014. Evolution and Fluxes of ^{137}Cs in the Black Sea/Turkish Straits System/North Aegean Sea. *Journal of Marine Systems*, 135, pp. 117-123. doi:10.1016/j.jmarsys.2013.01.006

11. Staneva, J.V., Buesseler, K.O., Stanev, E.V. and Livingston, H.D., 1999. The Application of Radiotracers to a Study of Black Sea Circulation: Validation of Numerical Simulations against Observed Weapons Testing and Chernobyl ^{137}Cs Data. *Journal of Geophysical Research*, 104(C5), pp. 11099-11114. doi:10.1029/1998JC900121
12. Bezhenar, R., Maderich, V., Schirone, A., Conte, F. and Martazinova, V., 2019. Transport and Fate of ^{137}Cs in the Mediterranean and Black Seas System during 1945–2020 period: A Modelling Study. *Journal of Environmental Radioactivity*, 208-209, 106023. doi:10.1016/j.jenvrad.2019.106023
13. Mann, D.R. and Casso, S.A., 1984. In Situ Chemisorption of Radiocesium from Seawater. *Marine Chemistry*, 14(4), pp. 307-318. doi:10.1016/0304-4203(84)90027-6
14. Lehto, J. and Hou, X., 2011. *Chemistry and Analysis of Radionuclides: Laboratory Techniques and Methodology*. Weinheim: Wiley-VCH, 406 p.
15. Šebesta, F., 1997. Composite Sorbents of Inorganic Ion-Exchangers and Polyacrylonitrile Binding Matrix. *Journal of Radioanalytical and Nuclear Chemistry*, 220(1), pp. 77-88. doi:10.1007/BF02035352
16. Breier, C.F., Pike, S.M., Šebesta, F., Tradd, K., Breier, J.A. and Buesseler, K.O., 2016. New Applications of KNiFC-PAN Resin for Broad Scale Monitoring of Radiocesium Following the Fukushima Dai-ichi Nuclear Distaster. *Journal of Radioanalytical and Nuclear Chemistry*, 307(3), pp. 2193-2200. doi:10.1007/s10967-015-4421-x

About the authors:

Illarion I. Dovhyi, Senior Research Associate, Marine Hydrophysical Institute of RAS (2 Kapitanskaya St., Sevastopol, 299011, Russian Federation), Ph. D. (Chem.), **ORCID ID: 0000-0001-8706-3810**, dovhyi.illarion@yandex.ru

Dmitrii A. Kremenchutskii, Junior Research Associate, Marine Hydrophysical Institute of RAS (2 Kapitanskaya St., Sevastopol, 299011, Russian Federation), **ORCID ID: 0000-0002-8747-6612**, d.kremenchutsky@gmail.com

Nikolay A. Bezhin, Senior Research Associate, Marine Hydrophysical Institute of RAS (2 Kapitanskaya St., Sevastopol, 299011, Russian Federation), Ph. D. (Tech.), **ORCID ID: 0000-0002-1670-4251**, nickbezhin@yandex.ru

Ol'ga N. Kozlovskaya, Junior Research Associate, Marine Hydrophysical Institute of RAS (2 Kapitanskaya St., Sevastopol, 299011, Russian Federation), **SPIN-code: 5386-4791**, o.n.kozlovska@gmail.com

Vitaly V. Milyutin, Chief of Laboratory of Chromatography of Radioactive Elements, Frumkin Institute of Physical Chemistry and Electrochemistry of RAS (31, bldg. 4, Leninsky Prospekt, Moscow, 119071, Russian Federation), Dr. Sci. (Chem.), **SPIN-code: 3106-6795**, vmilyutin@mail.ru

Evgeny A. Kozlitin, Senior Research Associate, Laboratory of Chromatography of Radioactive Elements, Frumkin Institute of Physical Chemistry and Electrochemistry of RAS (31, bldg. 4, Leninsky Prospekt, Moscow, 119071, Russian Federation), Ph. D. (Chem.), **ORCID ID: 0000-0002-0381-8786**, evgeny_kozlitin@mail.ru

Contribution of the co-authors:

Illarion I. Dovhyi – sampling during the 95th cruise of R\V "Professor Vodyanitsky", discussion of the obtained results

Dmitrii A. Kremenchutskii – sampling during the 95th cruise of R\V "Professor Vodyanitsky", discussion of the obtained results

Nikolay A. Bezhin – methodological aspects of ^{137}Cs sorbtion, discussion of the obtained results

Ol'ga N. Kozlovskaya – measuring of the samples, discussion of the obtained results

Vitaly V. Milyutin – obtaining a sorbent for ^{137}Cs concentration, discussion of the obtained results

Evgeny A. Kozlitin – obtaining a sorbent for ^{137}Cs concentration, discussion of the obtained results

The authors have read and approved the final manuscript.

The authors declare that they have no conflict of interest.