

UDC: 504

**DETERMINATION OF RADIONUCLIDES IN BOTTOM SEDIMENT SAMPLES
TAKEN FROM THE CENTRAL PART OF AZERBAIJAN SECTOR
OF THE CASPIAN SEA**

F.Y. Humbatov

Institute of Radiation Problems of ANAS

hfamil@mail.ru

Abstract: In this study concentrations of radionuclides in sediment samples taken from the central part of the Azerbaijan sector of the Caspian Sea were investigated to obtain information about the radioactivity and radiological hazards. Sediment samples were analyzed for ^{226}Ra , ^{228}Ra , and other radionuclides (^{40}K , ^{60}Co , ^{134}Cs , and ^{137}Cs) via gamma-spectrometry using a Canberra intrinsic germanium detector placed in lead shield thickness 11 cm. Received results for radionuclides in sediment samples were evaluated by applying a table with characteristics value of natural radionuclides.

Keywords: Caspian Sea, sediment, radionuclides, Gamma spectroscopy

1. Introduction

The Caspian is the largest inland body of water in the world, containing some 44% of the globe's inland waters. The Caspian Sea occupies a deep depression on the boundary between Asia and Europe with a water level at present 27 m below sea level. It is approximately 1200 km long with a maximum width of 466 km. It contains 79,000 km³ of water and has a total coastline of more than 7000 km. The Caspian is fed by five major rivers or river groups: in the north the Volga (80% of total inflow) and the Ural (5%); in the west the Terek, Sulak, and Samur (4-5%) and the Kura (7-8%); and, in the south, the short mountain rivers from the Iranian Alborz range (4-5%). Azerbaijan has more than 800 km of coastline along the Caspian Sea and almost the entire country is part of the Sea's catchment area. Environmental problems of the Caspian Sea are multiple and various in their origin. On one hand, they are caused by the commercial use of the sea; on the other hand, human activity impacts coastal areas, including input from rivers in the Caspian. As the Caspian is an inland water body, anthropogenic impacts on catchment area (about 3.5 million km²) accumulate here. Anthropogenic impact on the Caspian ecosystem occurs concurrently with various natural endogenous and exogenous processes. It is primarily sea level changes, periodical seismic activity, surges and retreats, mud volcanoes, and neo-tectonics. Special features of the Caspian include constant alterations of its area, volume, and configuration of the coastline and water column structure. Anthropogenic activity, as well as a natural impact, can have a chronic (long term) or acute (short term) effect. The sources of pollution are industrial, agricultural, and accidental discharges and sewage. The main sources of pollution to the Caspian Sea have generally been considered to be offshore oil production and land-based sources, notably the Volga River [1]. In this study concentrations of radionuclides in sediment samples from the central part of the Azerbaijan sector of the Caspian Sea were investigated to obtain information about the sources, degree of contaminations, and radiological hazards.

2. Materials and methods

Sediment samples from the 14 stations selected in the central part of the Azerbaijan sector of the Caspian Sea were collected by Van Veen Grab. From each station for measurement radionuclides, approximately 1 kg sample was taken from the surface oxic layer of sediment and stored in a container that was frozen on returning to the laboratory. Sediment samples were analyzed for ^{226}Ra , ^{228}Ra , and other radionuclides (^{40}K , ^{60}Co , ^{134}Cs , and ^{137}Cs) via gamma-spectrometry using a Canberra intrinsic germanium detector placed in lead shield thickness 11 cm.

Below are main the steps of sample procedures:

1. The sieved fraction was homogenized and dried in a drier at 110 deg C for 48 h
2. Sample aliquots were sieved through a 2 mm mesh size.
3. Dried sample aliquot is weighed and transferred to Marinelli or analogical beakers with known geometrical efficiency
4. After sealing of beaker, the sample is stored for more than 3-week to ensure that secular equilibrium between the nuclear chain members had been attained

Before determining the radioactivity by gamma spectrometer, an empty beaker with identical geometry was counted for 4 h to measure the background spectrum. This spectrum is necessary to establish a high confident background level to be used for the determination of the specific activities of the analyzed samples. Sample applied for conservation in the beaker is placed on the HPGe detector and counted for the same counting time (4 h). After this was calculated of geometrical efficiency for each of samples. The activities of the radionuclides were calculated using the net area of the peak, accumulation time, absolute peak efficiency at close geometry, absolute γ -ray emission probability, and the sample volume. All gamma spectrometric analyses were performed in silicone sealed Marinelli beakers after aging for one month to allow for ingrowth of ^{222}Rn and daughters. The photopeaks from the radon daughters ^{214}Pb and ^{214}Bi at 295, 352, and 609 keV were used to quantify ^{226}Ra , and the ^{228}Ac peaks at 338 and 911 keV were used for ^{228}Ra [2-4].

3. Results and discussion

Radionuclide concentrations in 14 sediment samples from the central part of the Azerbaijan sector of the Caspian Sea were investigated for determining the radioactivity by gamma spectrometer. Below are tests results for radionuclide contents and radioactivity of sediment samples (Table 1).

Table 1

Radionuclide Concentrations in sediment samples from the central part of Azerbaijan sector of the Caspian Sea

Station	^{226}Ra Bq/kgdm	^{232}Th Bq/kgdm	^{40}K Bq/kgdm	^{60}Co Bq/kgdm	^{134}Cs Bq/kgdm	^{137}Cs Bq/kgdm
St.1	57	11	138	<1.2	<1.2	3.1
St.2	48	24	406	<1.2	<1.2	<1.3
St.3	42	7.8	140	<1.2	<1.2	2.6
St.4	72	17	242	<1.2	<1.2	3.7
St.5	72	10	151	<1.2	<1.2	<1.3
St.6	36	17	230	<1.2	<1.2	3.4
St.7	66	8.2	101	<1.2	<1.2	<1.3
St.8	88	14	148	<1.2	<1.2	<1.3

St.9	76	12	173	<1.2	<1.2	3.1
St.10	59	16	293	<1.2	<1.2	<1.3
St.11	61	12	126	<1.2	<1.2	<1.3
St.12	48	13	268	<1.2	<1.2	<1.3
St.13	50	8.7	130	<1.2	<1.2	4.8
St.14	71	12	139	<1.2	<1.2	4.4
Min	36	8	101	<MDA	<MDA	2.6
Max	88	24	406	<MDA	<MDA	4.8
Med	60	12	150	<MDA	<MDA	3.4
Mean	60	13	192	<MDA	<MDA	3.6
St Dev	15	4	85			0.8
CV	24	34	45			22
MDA- Minimal Detectable Activity Bq/kgdm- Becquerel per kilogram of dried sample						

^{238}U , ^{232}Th , and ^{40}K are 3 main natural radioactive elements that continue to be on Earth from the creation of our solar system. The reason is the very high half-life period of these isotopes. Below table is collected of main data about our concern isotopes and their related contents on Earth crust minerals [5].

Nuclide	Symbol	Half-life	Natural Activity of rocks
Uranium 238	^{238}U	4.47×10^9 yr	99.2745% of all natural uranium; 0.5 to 4.7 ppm total uranium in the common rock types
Thorium 232	^{232}Th	1.41×10^{10} yr	1.6 to 20 ppm in the common rock types with a crustal average of 10.7 ppm
Radium 226	^{226}Ra	1.60×10^3 yr	0.42 pCi/g (16 Bq/kg) in limestone and 1.3 pCi/g (48 Bq/kg) in igneous rock
Potassium 40	^{40}K	1.28×10^9 yr	soil - 1-30 pCi/g (37-1100 Bq/kg)

Natural activities of ^{226}Ra and ^{228}Ra in sediment samples can change in a broad range. Below are the given of monitoring results for Central European (Czech republic) river/lake sediment samples [6].

^{226}Ra (Bq/kg)	1999	2000	2001	2002	2003
Minimum	24	20	16	21	18
Average	69	78	71	66	68
Maximum	381	1375	5855	4275	292

$^{228}\text{Ra} = ^{228}\text{Th} = ^{232}\text{Th}$ (Bq/kg)	1999	2000	2001	2002	2003
Minimum	19	20	16	20	18
Average	53	44	50	53	54
Maximum	211	115	127	133	127

For evaluation of investigation results and estimation of radioactivity levels in sediment samples were applied table with characteristics value of natural radionuclides.

	Geological Min, Bq/kg	Geological Max Bq/kg	Sediment Min Bq/kg	Sediment Max Bq/kg
Ra ²²⁶	16	48	16	5855
Th ²³²			16	211
K ⁴⁰	37	1100		

Isotopes Co⁶⁰, Cs¹³⁴, and Cs¹³⁷ are artificial radionuclides that are registered in all area of Earth as the results of global sedimentation after atmospheric tests of nuclear bombs in the last century. Between then ¹³⁷Cs is the most distributed artificial radionuclide which content can reach up to 200 Bq/kg depend on geographical area. There are limited data in open publish about ¹³⁷Cs in Caspian Sea sediment samples. In article [7] authors find that in the Iranian sector of the Caspian Sea ¹³⁷Cs are in the range from 0.3 Bq/kg to 63 Bq/kg with a mean value of 11 Bq/kg.

Our report include radioactivity results for isotopes Ra²²⁶, Th²³², K⁴⁰, Co⁶⁰, Cs¹³⁴, and Cs¹³⁷ which are the main radionuclides responsible for the formation radiation background in investigated samples. In Table 2 shown radioactivity ranges registered in sediment samples from the central part of the Azerbaijan sector of the Caspian Sea and reference data from the previous section.

Table 2

Radioactivity ranges registered in sediment samples

Station	²²⁶ Ra Bq/kgdm	²³² Th Bq/kgdm	⁴⁰ K Bq/kgdm	⁶⁰ Co Bq/kgdm	¹³⁴ Cs Bq/kgdm	¹³⁷ Cs Bq/kgdm
Min	36	8	101	<MDA	<MDA	2.6
Mean	60	13	192	<MDA	<MDA	3.6
Max	88	24	406	<MDA	<MDA	4.8
Geological, Min	16		37			
Geological, Max	48		1100			
Sediment ref Min	16	16				
Sediment ref Max	5855	211				63

4. Conclusions

Although ²²⁶Ra average and maximum values are above Earth Crust geological maximum value, they are much less of ²²⁶Ra activity in Central European sediment samples. Registered ²³²Th activities in investigated sediment samples are in the range of minimal value of Central European sediment samples.

⁴⁰K activities registered in sediment samples are in range geological mineral ranges for ⁴⁰K. For artificial radionuclides, ⁶⁰Co, and ¹³⁴Cs radioactivity level were below of minimum detectable activity levels for all studied samples. Observed levels of ¹³⁷Cs were less than the reference level of ¹³⁷Cs in regional sediment samples.

Registered ²²⁶Ra, ²³²Th, and ⁴⁰K radioactivity are considered as sourced by Natural ²³⁸U, ²³²Th and ⁴⁰K radionuclides as results of natural geochemical originated processes. ¹³⁷Cs registered in investigated sediment samples are considered as results of global sedimentation of ¹³⁷Cs from the atmosphere.

References

1. M.M. Ahmadov, F.Y. Humbatov, Determination of Radionuclides and Metals Concentration in Caspian Sea Sediments, Journal of Radiation Researches, vol.5, №2, 2018, Baku, p.442-448.
2. Famil Yusif Humbatov, Bahruz Allahverdi Suleymanov, Majid Mirza Ahmedov, Valeh Saleh Balayev., Radium Isotopes in an Oil-Field Produced Lake near Baku, Azerbaijan., Journal of Environmental Protection, 2016, 7, 1149-1156
3. Burnett, W.C., et al. (2002) Assessing Methodologies for Measuring Groundwater Discharge to the Ocean. EOS, 83, 117-123. <http://dx.doi.org/10.1029/2002EO000069>
4. Landsberger, S., Brabeca, C., Caniona, B., Hashema, J., Lua, C., Millsapa, D. and Georgeb, G. (2013) Determination of ^{226}Ra , ^{228}Ra and ^{210}Pb in NORM Products from Oil and Gas Exploration: Problems in Activity Underestimation Due to the Presence of Metals and SelfAbsorption of Photons. Journal of Environmental Radioactivity, 125, 23-26. <http://dx.doi.org/10.1016/j.jenvrad.2013.02.012>
5. www.umich.edu/~radinfo/introduction/natural.htm
6. Limnologica - Ecology and Management of Inland Waters, Volume 35, Issue 3, 15 September 2005, p. 177-184 www.sciencedirect.com/science/article/pii/S0075951105000423
7. Darabi Golestan F, Hezarkhani A, Zare MR (2013) Interpretation of the Sources of Radioactive Elements and Relationship between them by Using Multivariate Analyses in Anzali Wetland Area. Geoinfor Geostat: An Overview 1:4. doi:10.4172/2327-4581.1000114

ОПРЕДЕЛЕНИЕ РАДИОНУКЛИДОВ В ПРОБАХ ДОННЫХ ОТЛОЖЕНИЙ ВЗЯТЫХ ИЗ ЦЕНТРАЛЬНОЙ ЧАСТИ АЗЕРБАЙДЖАНСКОГО СЕКТОРА КАСПИЙСКОГО МОРЯ

Ф. Ю. Гумбатов

Резюме: В данном исследовании изучались концентрации радионуклидов в пробах донных отложений, взятых в центральной части Азербайджанского сектора Каспийского моря, для получения информации о радиоактивности и радиологической опасности. Образцы отложений были проанализированы на ^{226}Ra , ^{228}Ra и другие радионуклиды (^{40}K , ^{60}Co , ^{134}Cs и ^{137}Cs) с помощью гамма-спектрометрии с использованием германиевого детектора фирмы Canberra, помещенного в свинцовый домик толщиной 11 см. Полученные результаты для радионуклидов в пробах донных отложений оценивали с помощью таблицы с характеристик значениями природных радионуклидов.

Ключевые слова: Каспийское море, донные отложения, радионуклиды, гамма-спектроскопия.

XƏZƏR DƏNİZİNİN AZƏRBAYCAN SEKTORUNUN MƏRKƏZİ HİSSƏSİNDƏN GÖTÜRÜLMÜŞ DİB ÇÖKÜNTÜSÜ NÜMUNƏLƏRİNDƏ RADİONUKLİDLƏRİN TƏYİNİ

F.Y. Hümbətov

Xülasə: Bu tədqiqat işində, Xəzər dənizinin Azərbaycan sektorunun mərkəzi hissəsindən götürülmüş dib çöküntüsü nümunələrində radioaktivlik və radioloji təhlükələr barədə məlumat əldə etmək üçün radionuklidlərin konsentrasiyası tədqiq edilmişdir. Dib çöküntüsü nümunələri ^{226}Ra , ^{228}Ra və digər radionuklidlərə (^{40}K , ^{60}Co , ^{134}Cs və ^{137}Cs) görə, Canberra firmasının istehsalı olan, 11 sm qalınlıqlı qurğusun

evcikdə yerləşdirilmiş germanium detektorlu qamma-spektrometrlə analiz edilmişdir. Dib çöküntüsü nümunələrindəki radionuklidlər üçün alınan nəticələr təbii radionuklidlərin xüsusiyyətlərinə görə tərtib edilmiş cədvəl tətbiq edilərək qiymətləndirilmişdir.

Açar sözlər: Xəzər dənizi, dib çöküntüsü, radionuklidlər, Gamma spektroskopiya