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ARTICLE

Determination of radioactive contaminants in sediment and sand samples from the Black Sea by HPGe Gamma-ray spectrometry

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Abstract – The radionuclide activities were measured in sea sediment and coastal sand samples taken from the Black Sea to improve the understanding on coastal pollution as sediments and sand act as a sink for inorganic contaminants from various sources. The core sediments were taken from the Black Sea near to Varna city and sand samples were collected from in the Black Sea Coastal of North Anatolia. Their radionuclide contents were measured using a high resolution gamma-ray spectrometry. The activity results are found to be on the average, $65 \pm 9\,Bq \cdot kg^{-1}$ for ^{210}Pb, $13 \pm 1\,Bq \cdot kg^{-1}$ for ^{137}Cs, $36 \pm 4\,Bq \cdot kg^{-1}$ for ^{226}Ra, $25 \pm 3\,Bq \cdot kg^{-1}$ for ^{232}Th, and $403 \pm 13\,Bq \cdot kg^{-1}$ for ^{40}K in slices from the sediment core. The radionuclide activities in sand samples collected from the Black Sea coastal are measured for ^{7}Be (2.4 ± 0.4 to $5.8 \pm 0.4\,Bq \cdot kg^{-1}$) and for ^{137}Cs (2.0 ± 0.1 to $3.7 \pm 0.2\,Bq \cdot kg^{-1}$). In sand samples, other natural occurring radionuclides ^{226}Ra (6.8 ± 1.1 to $12.5 \pm 1.3\,Bq \cdot kg^{-1}$), ^{232}Th (6.5 ± 0.8 to $16.9 \pm 1.4\,Bq \cdot kg^{-1}$) and ^{40}K(139 ± 8 to $376 \pm 16\,Bq \cdot kg^{-1}$) were also observed, as expected. The present results indicate that there is still noticeable radionuclide contamination in sediments and coastal sands due to mainly the Chernobyl nuclear accident and other conventional industrial wastes.

Keywords: Black Sea / sediment / sand / radionuclide / gamma-ray spectrometry / ^{137}Cs / ^{210}Pb

1 Introduction

Sediment is a natural part of rivers, lakes and sea-marine ecosystems. Thus changes to the sediment balance can cause to variations in these ecosystems. Hence, the study of sediments helps to improve the understanding on coastal pollution as sediments act as a sink for inorganic (such as radionuclides and heavy metals) and organic contaminants from various sources (SedNet, 2018). The Chernobyl accident has resulted in surface contamination especially by radiocesium-137 (^{137}Cs) fission product over vast areas of eastern and northern Europe, and overall the World. This surface contamination has been subject to changes due to physical decay and lateral transport of contaminated soil particles, which has resulted in a still on-going transfer of radionuclides from terrestrial ecosystems to surface water, river bed sediments and flood plains (Van Der Perk *et al.*, 2000; Laptev, 2007). In this context, nuclear analytical techniques are the important tools for providing information on the spatial and temporal trends of radioactive pollutants. They also serve as a dating method for the estimation of their ages. For instance, the use of unsupported ^{210}Pb ($^{210}Pb_{exc}$) is still far off from being a well-established dating tool for recent sediments, up to 20–150 years (Cutshall *et al.*, 1983; Hernandez, 2015). However, the key issue still seems an accurate activity determination of such radionuclides in sediment analysis. Therefore, the effect of self-absorption (F_s), true coincidence summing factors (F_{coi}) and spectral interference (F_{csi}) were taken into account to determine accurate activity of some gamma-emitting radionuclides such as, ^{7}Be, ^{210}Pb, ^{226}Ra, ^{232}Th, ^{137}Cs and ^{40}K in sediment and sand samples when a high resolution gamma-ray spectrometry was used in the measurements. In this study, the radionuclide activities are measured in the sea sediment core taken from Varna and coastal sand samples taken from the Black Sea Region in North Anatolia of Turkey using gamma-ray spectrometry to improve the understanding on coastal pollution as sediments and sand act as a sink for inorganic contaminants from various sources.

2 Materials and methods

2.1 Study area

The beach sand samples were collected from different locations (Düzce, Bartın, Sinop and Trabzon cities) in North of Anatolia Black Sea Coastal Region, as shown in Figure 1. Three sand samples were taken from each location. For sediment sampling, one-day sampling expedition under IAEA RER 7009 project was conducted in the Black Sea on 26th

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Fig. 1. Map of sampling locations in the Black Sea for sediment and sand samples.

September 2018, on-board of R/V *Akademik ship* in collection of sediment samples (surface and cores) using Van Veen grab and multicorer equipment, core slicing was performed with the aid of extruder that was used by the professional experts, and then made preservation and transportation of sample bags (IAEA, 2018). In the course of sediment sampling in the Black Sea, one of the sediment cores from Varna, Bulgaria was coded as RER7009-18-02-04 (Location: 43 11. 000 N, 027 59.000 E, 24.5 m depth at 12.00 AM-12.30 PM, Multi-corer, 4 cores)

2.2 The radioactivity measurement method

In sand sample preparation procedure, all wet sand samples were dried at 105 °C in an oven for overnight (~ 14 h) to remove moisture. The sand samples (its density) were sieved to remove gravels in larger sizes (> 0.8 mm) and then were filled in a 450 ml Marinelli beaker. These beakers were sealed tightly, using silicon glue. The sediment core were cut into on-board during expedition, packed in nylon locked-bags and transferred to the laboratory. They were dried, grinded and sieved at room conditions. Then, the parts of powdered sediment samples were filled in plastic tubes (1.5 cm diameter × 3.5 cm filling height) at about 5–6 g in weights to measure in the well of a HPGe detector.

A p-type, well (φ16 mm × 40 mm depth) geometry HPGe detector with a 44.8% relative efficiency (Canberra GCW 4023) and a n-type HPGe detector with a 78.5% relative efficiency (Ortec GMX70P4S Model) were used in the measurements. Each detector was shielded in a 10 cm thick-Pb lined with 1 mm Sn and 1.6 mm Cu to reduce substantially background. The spectrometers were calibrated using multi-nuclide standard sources in a Marinelli beaker geometry. The samples were counted on the periods between ~ 2 to 4 days. From each measured peak area, the net counts of the peak were determined by peaked-background method, based on blank-background measurement of ~ 7 days.

For two different gamma spectrometer systems used, the detection efficiencies were first determined experimentally using standard multi-nuclide sources based on sand and epoxy matrices (purchased from Eckert Ziegler Inc. and Czech Metrology Institute). Then these measured efficiencies were validated with those of calculated ones by using GESPECOR (Ver 4.2) software and MEFFTRAN based on Monte Carlo simulation model of a Marinelli beaker geometry. In the well-type Ge detector, the certified reference Irish sediment material coded as IAEA-385 containing natural (^{210}Pb,^{226}Ra, ^{232}Th, ^{238}U,^{40}K) and artificial (^{137}Cs, ^{241}Am, etc.) radionuclides. The reference IAEA-385 sample filled in small tube was counted to compare with the results from the sediment core samples taken from the Black Sea.

2.3 Results and discussion

In low level gamma-ray spectrometry, the required correction factor such as spectral interference, self-absorption and true coincidence summing effects have crucial importance when one aims to obtain high accurate and precise results. In this work, the spectral peak interference correction methodology was employed for particular peaks, as described in our previous study (Yücel *et al.*, 2009). The spectral interference factors F_{csi} were calculated for the analytical peaks, such as 46.5 keV (^{210}Pb), 63.3 keV (^{234}Th), 186.2 keV (^{226}Ra) and 609.3 keV (^{214}Bi), 583 keV (^{208}Tl) and 1460.8 keV (^{40}K) due to potentially interferences from ^{235}U, ^{238}U and ^{232}Th decay products occurring naturally in samples. As given in Table 1, it is worth noting that higher spectral interference F_{csi} factor of 0.425 was estimated for the correction of 186.2 keV (^{226}Ra) peak area due to 185.7 keV of ^{235}U itself, naturally existing in uranium and also a factor $F_{csi} = 0.0921$ was applied to the 1460.8 keV (^{40}K) peak areas due to 911 keV of ^{228}Ac (^{232}Th) contribution.

The self-absorption (F_s) and true coincidence summing correction factors (F_c) should be taken into account carefully in low level gamma-ray spectrometry. Therefore, they were calculated using Monte Carlo based GESPECOR program for a tube geometry in the well of a p-type Ge detector and a Marinelli Beaker geometry on the endcap of an n-type Ge detector. The sand samples contain 97–98% SiO_2 and 2–3% Fe and Zr determined by EDXRF with a 25 mm^2 active surface area silicon drift detector (FWHM = 132 eV at 5.89 keV) associated with 50 kVp Ag-anode X-ray tube (Amptek, 2019). The results given in Table 1 indicate that the magnitude of F_s factors ranged from 1.40–1.66 for 46.5 keV (^{210}Pb), and 1.25–1.43 for 63. keV peak (^{234}Th) are relatively larger in Black Sea coastal sands for the case of Marinelli beaker geometry. However, the F_s factors are only on the order of 1.25–1.38 for 46.5 keV (^{210}Pb) energy for sea sediments when the sediment samples in the small tube were counted in the well of HPGe detector. The true coincidence summing F_c factors varied from 18–20% for 583.2 keV (^{208}Tl), 15–16% for 609.3 keV (^{214}Bi), 17–18% for 1120 keV (^{214}Bi) analytical peaks due to their decay schemes and close counting conditions, respectively. These results indicate that F_c factors also cannot be neglected in the accurate activity measurements for the present counting geometries because this is a case of a close counting geometry, *i.e.* the sample is

Table 1. Correction factors for the case of sand matrix in a Marinelli beaker with a 78.5% efficient HPGe detector.

Nuclide	Energy (keV)	Self-absorption F_s	True coincidence summing F_c	Spectral interference F_{csi}
^{210}Pb	46.54	1.66	1.00	Negligible
^{234}Th (^{238}U)	63.3	1.43	1.00	~%7.5 due to Th contribution
^{226}Ra	186.21	1.24	1.00	A multiplying factor of 0.428 due to185.7 keV of ^{235}U
^{214}Pb	295.22	1.21	1.00	Negligible
^{228}Ac	338	1.19	1.04	Negligible
^{214}Pb	351.93	1.19	1.00	Negligible
^{8}Be	477.6	1.17	1.00	No interference
^{208}Tl	583.2	1.15	1.20	Negligible
^{214}Bi	609.32	1.15	1.16	Negligible
^{137}Cs	661.66	1.15	1.00	No interference
^{228}Ac	911	1.13	1.03	Negligible
^{234m}Pa (^{238}U)	1001.03	1.12	1.00	~0.5% due to Th contribution
^{226}Ra	1120.09	1.11	1.18	Negligible
^{40}K	1460.82	1.10	1.00	~9.2% due to Th contribution

Table 2. The activity values measured in beach sand samples in Black Sea coastal region.

	Location(s)			
Nuclide	Trabzon (41°00' 08,4" N 39°45' 35,4" E)	Sinop (41°56' 49,2" N 34°20' 45,0" E)	Bartın (41°44' 51, 16" N 32°23' 15,73" E)	Düzce (41°05' 39, 6" N 31°08' 30,2" E)
	Activity concentration ($Bq \cdot kg^{-1}$)			
^{7}Be	2.4 ± 0.4	2.5 ± 0.5	4.2 ± 0.4	5.8 ± 0.4
^{137}Cs	3.7 ± 0.2	3.2 ± 0.2	3.6 ± 0.3	2.0 ± 0.1
^{226}Ra	12.5 ± 1.3	8.9 ± 1.3	6.8 ± 1.1	11.9 ± 1.2
^{232}Th	16.9 ± 1.4	8.9 ± 1.0	6.5 ± 0.8	14.2 ± 1.1
^{40}K	376 ± 16	172 ± 9	139 ± 8	251 ± 11

counted either on the endcap of an n-type Ge detector or in the well of a p-type Ge detector.

Finally, the measured radioactivity of ^{7}Be, ^{137}Cs, ^{226}Ra, ^{232}Th, and ^{40}K contained in coastal sand dune samples collected from different cities in North of Anatolia are given in Table 2. The measured activities in sand samples are varied from 2.4 ± 0.4 to 5.8 ± 0.4 $Bq \cdot kg^{-1}$ for ^{7}Be as a cosmogenic radionuclide and 2.0 ± 0.1 to 3.7 ± 0.2 $Bq \cdot kg^{-1}$ for ^{137}Cs as a fission product, and also other natural radionuclides such as ^{226}Ra, ^{232}Th and ^{40}K were also observed. The results indicate that the radionuclide contamination in coastal sands mainly due to the Chernobyl nuclear accident and to other industrial activities conducted at those locations near to the Black Sea coastal region of North Anatolia is still noticeable.

The radioactivity results for some sediment samples prepared from RER7009-18-02-04 core collected from Black Sea, Varna are given in Table 3. The highest activity concentration of ^{137}Cs in the samples sliced from this sediment core was found to be 12.5 ± 0.7 $Bq \cdot kg^{-1}$ (min: 8.2 ± 0.5 $Bq \cdot kg^{-1}$ to max: 18.2 ± 0. $Bq \cdot kg^{-1}$), on the average, because of global fallout of radionuclides after nuclear weapon tests and the Chernobyl accident, and other industrial wastes coming from the Danube river and its branches located closely to that location. As natural radionuclides, ^{226}Ra (mean: 36 ± 4; min: 33 ± 3 to max: 40 ± 4 $Bq \cdot kg^{-1}$), ^{232}Th (mean: 25 ± 3; min: 23 ± 3 to max: 29 ± 4 $Bq \cdot kg^{-1}$) and ^{40}K (mean: 36 ± 4; min: 33 ± 3 to max: 40 ± 4 $Bq \cdot kg^{-1}$) activity concentrations in single sediment core layers (each slice is 1 cm thickness, total 27 slices) did not show much variability. The measured activities of ^{210}Pb, ^{226}Ra and ^{232}Th and ^{137}Cs decrease with increasing sediment depth. For instance, the activity concentration distribution of ^{210}Pb with increasing depth (x) is in the form of $C(x) = 84.61 \cdot e^{-0.021}x$ with the regression coefficient $R^2 = 0.71$. In other words, it can be said that the decreasing trend in the measured activity results behaves exponentially rather than linear with increasing the depth from top (0–1 cm) to bottom (26–27 cm) in each 1 cm thick slice.

3 Conclusions

When one aims to obtain high quality radioactivity measurement results using gamma ray spectrometry, it should be made some crucial corrections for the measured quantities. First, the magnitudes of F_s factors are remarkable higher for 46.5 keV (^{210}Pb) and 63.3 keV (^{234}Th), especially in sand samples because of containing heavy element contents such as Fe, Zr in coastal sand dune samples. The second correction is

Table 3. The radionuclide activity distribution for RER7009/18 02-04 multicorer sediment slices with increasing depth.

Sediment slice	Core sample code RER7009/18 02-04[a]	The measured activity concentrations ($Bq \cdot kg^{-1}$)				
No.	Slice thickness (from top to bottom)	^{210}Pb	^{226}Ra	^{232}Th	^{137}Cs	^{40}K
1	0–1 cm	65 ± 10	38 ± 4	26.7 ± 3.2	12.3 ± 0.7	409 ± 14
2	1–2 cm	81 ± 12	34 ± 5	24.8 ± 3.6	12.4 ± 0.8	424 ± 16
3	2–3 cm	92 ± 11	37 ± 3	24.3 ± 2.3	18.2 ± 0.7	444 ± 13
4	3–4 cm	82 ± 12	40 ± 4	28.0 ± 3.6	15.4 ± 0.9	426 ± 15
5	4–5 cm	62 ± 8	37 ± 3	26.3 ± 2.6	13.4 ± 0.6	410 ± 12
6	5–6 cm	79 ± 13	37 ± 5	29.4 ± 3.8	12.5 ± 0.8	411 ± 15
7	6–7 cm	73 ± 10	36 ± 4	26.0 ± 3.3	15.0 ± 0.8	412 ± 14
8	7–8 cm	74 ± 10	34 ± 4	27.9 ± 2.8	13.9 ± 0.7	422 ± 13
9	8–9 cm	58 ± 10	38 ± 5	24.6 ± 3.4	13.5 ± 0.8	396 ± 15
10	9–10 cm	73 ± 10	39 ± 4	24.5 ± 2.6	13.8 ± 0.7	399 ± 12
11	10–11 cm	76 ± 11	37 ± 4	26.4 ± 3.3	15.3 ± 0.8	423 ± 14
12	11–12 cm	89 ± 13	33 ± 5	24.6 ± 3.7	14.9 ± 0.9	445 ± 17
13	12–13 cm	70 ± 9	37 ± 4	25.7 ± 2.7	14.8 ± 0.7	396 ± 12
14	13–14 cm	61 ± 9	36 ± 4	25.7 ± 2.9	13.7 ± 0.7	404 ± 13
15	14–15 cm	66 ± 10	33 ± 5	25.5 ± 3.6	12.8 ± 0.8	392 ± 15
16	15–16 cm	61 ± 8	33 ± 3	25.7 ± 2.5	11.6 ± 0.5	403 ± 12
17	16–17 cm	62 ± 9	37 ± 4	25.2 ± 3.2	12.3 ± 0.7	440 ± 15
18	17–18 cm	53 ± 10	37 ± 4	23.1 ± 3.1	9.5 ± 0.7	393 ± 14
19	18–19 cm	56 ± 8	36 ± 3	23.0 ± 2.4	10.5 ± 0.5	379 ± 12
20	19–20 cm	48 ± 8	37 ± 4	26.4 ± 3.0	10.6 ± 0.6	380 ± 13
21	20–21 cm	59 ± 9	35 ± 4	23.8 ± 3.2	11.6 ± 0.7	386 ± 14
22	21–22 cm	50 ± 7	35 ± 4	24.5 ± 2.6	12.3 ± 0.6	396 ± 12
23	22–23 cm	59 ± 8	35 ± 3	24.0 ± 2.4	10.6 ± 0.5	387 ± 11
24	23–24 cm	52 ± 7	34 ± 3	24.5 ± 2.3	9.6 ± 0.5	372 ± 9
25	24–25 cm	51 ± 7	35 ± 3	24.4 ± 2.5	9.0 ± 0.5	366 ± 9
26	25–26 cm	46 ± 6	37 ± 3	25.4 ± 2.6	8.2 ± 0.5	391 ± 10
27	26–27 cm	47 ± 6	35 ± 3	25.7 ± 2.4	10.2 ± 0.5	389 ± 9
	Average	65 ± 9	36 ± 4	25.4 ± 3.0	12.5 ± 0.7	403 ± 13

[a] Location: 43 11. 000N Latitude, 027 59. 000E Longitude; water depth: 24.5 m; time: 12:00–12:30; Varna (Bulgaria); Black Sea Sediment; sampling date: 26 Sept. 2018; equipment: Multicorer.

required for true coincidence summing effects for particular peaks and for the case of close counting geometry. The third correction should be made for the spectrally interference peaks for the more accurate analysis.

Under the IAEA RER 7009 project, the present results were obtained using a well-established gamma-ray spectrometric method with a p-type, well-HPGe detector. The obtained results can be used to compare and/or integrate into a larger scale regional interpretation with those results provided by many partners or scientists obtained by using different methodologies since field studies on sediment quality of the Black Sea coastal areas are scarce and the results are not easily accessible.

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