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Measurement of radionuclides and trace metals concentration in surface sediments from the coastal zone of Lavreotiki peninsula

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Abstract This work presents the results of a preliminary study at the coastal zone of the Lavreotiki peninsula, concerning radionuclide and trace metal concentration measurements in sediment samples collected from the seabed of four local gulfs and the corresponding beaches. The radionuclide activity concentrations were determined by means of gamma-ray spectroscopy and the concentration of trace metals by the XRF method. The observed radionuclide levels of both seabed and beach sediment are considered relatively low to medium, in comparison with international values of activity concentration in soil. For most of the trace metals, high concentrations were measured in comparison with guidelines, especially for As, Mn, Pb and Zn.

Keywords sediment, radionuclides, trace metals, Lavreotiki

INTRODUCTION

Lavreotiki, located at the southeast of Attica, Greece, is an area where intense mining and metallurgical activities took place, from ancient until recent times. Past studies have confirmed high trace metal concentrations on the terrestrial zone and on the wider marine area. Yet, until today there are no published data concerning the radionuclide concentrations on the coastal zone of the Lavreotiki peninsula, despite the residential character of the area. This work presents the results of a preliminary study carried out during the spring of 2014, involving radionuclides and trace metal concentration measurements in sediment samples collected from the seabed of four local gulfs and the corresponding beaches.

MATERIALS AND METHODS

Study Area

In total, 7 surface sediments were collected, from 4 different coastal areas (Perdika, Oxygono, Thoricos and Delenia) of the Lavreotiki peninsula, both from the seabed and the corresponding beaches (Figure 1). Due to the morphology of the beach in area 2 (lack of sand sediment) no sample was collected.

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Fig. 1. Sediment sampling positions at the coastal zone of the Lavreotiki peninsula

Methodology

The collected samples were treated at HCMR laboratories through a standardized procedure that included drying, pulverizing and sieving the samples. The samples were placed in plastic containers, which remained sealed for at least 21 days before measurement, in order to achieve secular equilibrium between ^{226}Ra and ^{222}Rn with their progenies. The radioactivity levels were estimated by means of gamma-ray spectroscopy, using a 50% high purity Germanium (HPGe) detector. The detector was surrounded by a lead shield, in order to reduce the contribution of background radiation in the spectrum. Spectrum analysis was performed by using the SPECTRW software package [1].

The energy and efficiency calibration were performed with the use of two reference sources—one of ^{152}Eu with ^{154}Eu impurities and one of ^{40}K . The reference sources were measured in contact geometry with the detector cap, same as the samples. Special attention was given in the accurate calculation of the full-energy peak efficiency of the HPGe detector. Thus, the experimental counts of the calibration sources were subjected to two required corrections. The corrections were made by means of the EFFTRAN code [2, 3] and included: (a) the calculation of true coincidence summing correction factors (TCS) for every gamma-ray energy analysed and (b) corrections, due the different density between the calibration sources and the mean density of the samples, which lead to different self-absorption effects. The two corrections are presented in Figure 2. The final values were fitted according to a literature function [4].

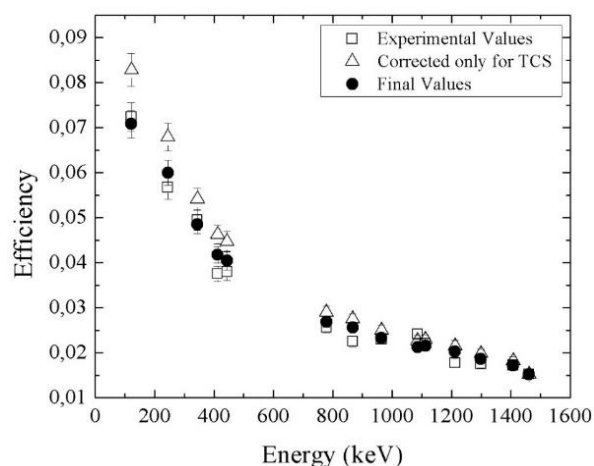


Fig. 2. Full-energy peak corrections for the TCS effect and the different density between the calibration source and the samples

The activity concentration (Bq/kg) for each radionuclide was derived from the analysis of the spectra after the subtraction of the background. Background spectra were recorded regularly between measurements. In order to account for self-absorption effects of the background radiation before the entrance in the detector, the measurement occurred with the use of inert material with similar composition and density with the samples (talc), measured in the same geometry as the samples.

Minimum Detectable Activity (MDA) was calculated from the mean value of the background spectra, for all gamma-ray energies analysed in the sample spectra [5]. The results are presented in Table 1.

From the analysis of the counts in each photopeak, with the SPECTRW software, the activity concentration (Bq/kg) for each radionuclide was calculated from the following expression:

$$Activity = \frac{counts \cdot TCS_{cor}}{eff \cdot I_{\gamma} \cdot time \cdot m}$$

where, *counts* are the experimental counts, TCS_{cor} is the correction factor for the true coincidence summing effect for each gamma-ray energy, calculated with the EFFTRAN code, *eff* is the full-energy peak efficiency, calculated from the fitted function, I_{γ} is the emission probability of the gamma-ray, *time* is the time measurement of the sample (24 hours) and *m* is the net mass of the sample (kg).

The following table includes the analysed gamma-rays for each radionuclide, the radioactivity series in which they belong, the intensity of the gamma-ray analysed, the efficiency of the detector for that energy, the correction factor for the TCS effect, calculated with the EFFTRAN code and the Minimum Detectable Activity (MDA) for each energy.

Table 1. The gamma-ray analysed for each radionuclide with the corresponding intensity, the radioactive series in which they belong, the absolute efficiency of the detector in each energy, the correction factor for the true coincidence summing effect for each gamma-ray and the Minimum Detectable Activity for all gamma-rays analysed.

Radionuclide	Energy (keV)	I_{γ} (%)	Radionuclide Series	Absolute Efficiency	Correction Factor TCS	MDA (Bq/kg)
⁴⁰ K	1460.8	10.67	-	0.017	1	23.2
¹³⁷ Cs	661.7	85.2	-	0.030	1	0.7
²¹⁴ Pb	351.9	37.1	²³⁸ U	0.048	1.0011	1.7
²¹⁴ Bi	609.3	46.1	²³⁸ U	0.032	1.1381	1.7
²¹² Pb	238.6	43.5	²³² Th	0.060	1.0001	1.3
²⁰⁸ Tl	583.2	30.36	²³² Th	0.033	1.1687	2.0
²²⁸ Ac	911.2	26.6	²³² Th	0.024	1.0317	2.8
²²⁸ Ac	969.0	16.23	²³² Th	0.023	1.0317	4.3
²²⁶ Ra	186.2	3.51	²³⁸ U	0.062	1.0002	-
²³⁵ U	185.7	57.2	²³⁵ U	0.062	1.0337	1.1

For every sample analysed

- The activity concentration of ⁴⁰K and ¹³⁷Cs was determined from the analysis of the 1460.8 keV and 661.7 keV photopeaks, respectively.

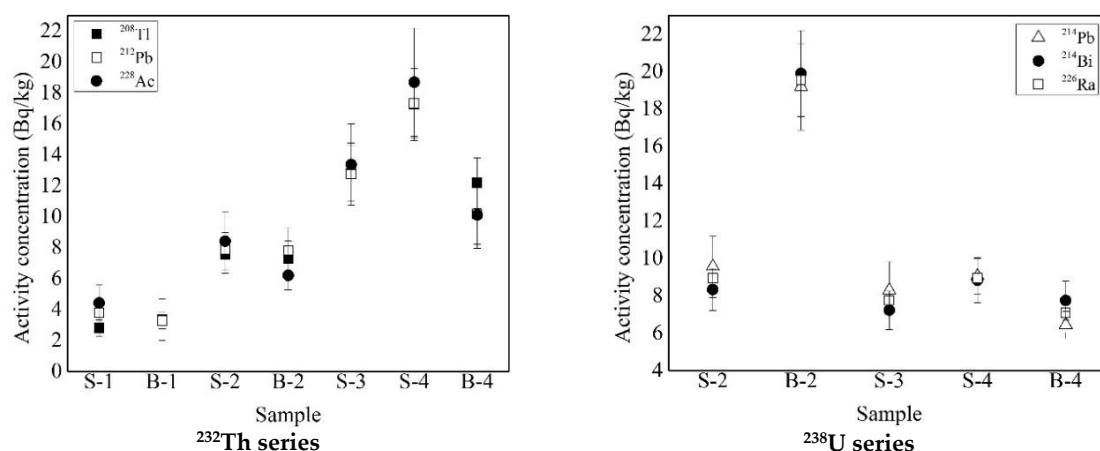
- The activity concentration of ^{214}Pb , ^{214}Bi and ^{208}Tl was calculated from the counts of the photopeaks 351.9 keV, 609.3 keV and 583.2 keV, respectively.
- The activity concentration of ^{212}Pb was calculated directly from the analysis of the triplet at ~240 keV into two components. The first component was the desired peak of ^{212}Pb (238.6 keV) and the other component the doublet of ^{214}Pb (241.9 keV) and ^{224}Ra (241.0 keV).
- The activity concentration of ^{226}Ra was estimated indirectly from the mean activity concentration of ^{214}Pb and ^{214}Bi , assuming secular equilibrium between the three isotopes.
- The activity concentration of ^{235}U was estimated indirectly by analysing the doublet at ~186keV, as one peak. The known activity concentration of ^{226}Ra was turned in counts, through equation (1). The counts due to ^{226}Ra present in the double peak were subtracted from the total counts of the peak. The difference was attributed to the ^{235}U counts, present in the peak.
- The activity concentration of ^{228}Ac was derived from the weighted mean of the two photopeaks analysed (991.2 keV and 969.0 keV).
- The concentration of trace metals was estimated by the XRF method [6].

RESULTS AND DISCUSSION

The results of the analysis are presented in Figure 3.

The radionuclides activity concentrations ranged between 68 and 340 Bq/kg for ^{40}K , while for ^{137}Cs and ^{235}U , the concentrations were lower than 1.5 Bq/kg and 2.5 Bq/kg, respectively, in all study areas. As for the activity concentrations of the radionuclides belonging to the radioactive series of ^{232}Th (namely ^{208}Tl , ^{212}Pb and ^{228}Ac) and ^{238}U (namely ^{214}Bi , ^{214}Pb and ^{226}Ra), the values ranged between 3 and 17 Bq/kg and below 1.8 and 20 Bq/kg, respectively. Additionally, the concentration of trace metals from the analysis of the seabed and beach sediments were found to range as follows: As (34 - 3382 ppm), Ba (140 – 1071 ppm), Cr (52 – 140 ppm), Cu (8 – 121 ppm), Mn (333 – 7162 ppm), Ni (19 – 60 ppm), Pb (122 – 5986 ppm), Sr (224 – 1068 ppm), V (35 – 152 ppm), Zn (97 – 8077 ppm) and Zr (5 – 79 ppm).

The observed radionuclide levels of both seabed and beach sediment are considered relatively low to medium, in comparison with international values of activity concentration in soil [7]. For most of the trace metals, high concentrations were measured in comparison with guidelines [8], especially for As, Mn, Pb and Zn.



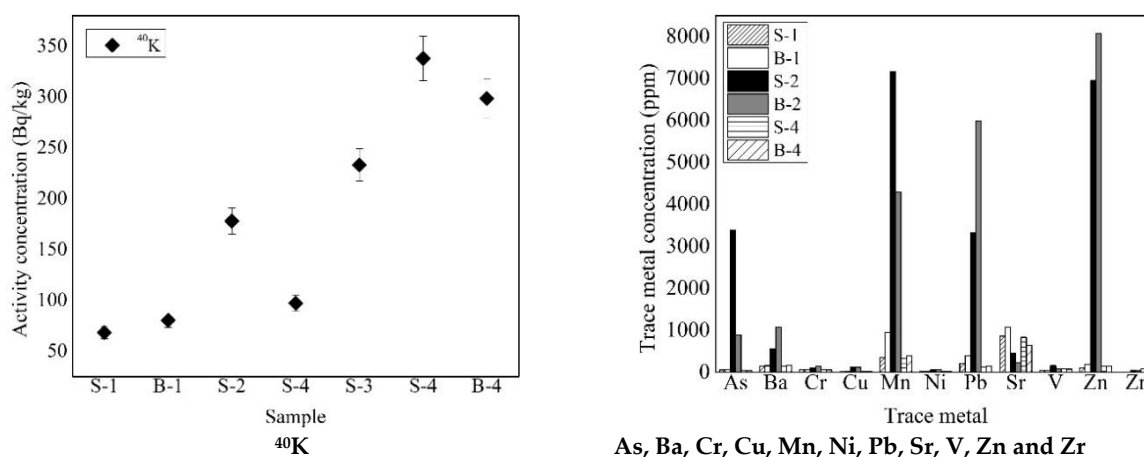


Fig. 3. The activity and trace metals concentration for all samples analysed.

CONSLUSIONS

This study provides information for the radionuclides and trace metal concentrations in the coastal zone of the Lavreotiki peninsula. The levels of the radionuclides measured were low in all study areas, while those of trace metals, were above the sediment quality guidelines in most areas, and especially high in area 2. The results of this preliminary study highlight the necessity for systematic monitoring, of the Lavreotiki peninsula (both terrestrial and sea zone), aiming to an extensive and detailed mapping of radionuclides and trace metal for site characterization purposes.

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