Comparison of Radioactivity and Metal Pollution Concentrations in Marine Sediment Samples Obtained from the Aegean Sea (Turkey) and the Calabria Region (Italy)

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Abstract: - Marine sediments are the basic reservoir for radionuclide and metal hold because of their diverse composition. These sediments accumulate naturally occurring radionuclides such as ^{226}Ra, ^{232}Th, and ^{40}K as a result of scavenging and settling processes in the water column. The knowledge of the levels and distributions of the radionuclides such as U, Th, and Ra and heavy metals have common environmental concerns along with the health hazards to human beings, animals as well as the marine environment.

This study was to assess the concentrations of some heavy metals (Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Zn) and three main natural radionuclides (^{226}Ra, ^{232}Th, and ^{40}K) within the surface sediments collected from Turkey (Aegean Sea) and Italy (Calabria region). Activity concentrations of natural radionuclides were measured by High Purity Germanium (HPGe) gamma spectrometry. Heavy metal levels were determined by inductively coupled plasma mass spectrometry (ICP-MS) in Italy and inductively coupled plasma optic emission spectrometry (ICP-OES) in Türkiye. The activity concentrations ^{226}Ra, ^{232}Th, and ^{40}K at Aegean Sea region (Türkiye) ranged from 9 ± 1 Bq kg^{-1} dry weight (d.w.) to 60 ± 2 Bq kg^{-1} (d.w.) for ^{226}Ra; from 6 ± 0.3 Bq kg^{-1}(d.w.) to 64 ± 1 Bq kg^{-1} (d.w.) for ^{232}Th; for ^{40}K, 250 ± 13 Bq kg^{-1}(d.w.) to 978 ± 6 Bq kg^{-1} (d.w.) and at Calabria region (Italy) ranged from 14 ± 1 Bq kg^{-1} dry weight (d.w.) to 54 ± 9 Bq kg^{-1} (d.w.) for ^{226}Ra; from 12 ± 1 Bq kg^{-1}(d.w.) to 83 ± 8 Bq kg^{-1} (d.w.) for ^{232}Th; for ^{40}K, 470 ± 20 Bq kg^{-1}(d.w.) to 1000 ± 70 Bq kg^{-1} (d.w.). The mean concentrations of Mn, Fe, Ni, Cu, Zn, Cr, Cd, and Pb were 197.6; 8139.3; 6.3; 6.0; 24.9; 10.5; 0.05 and 6.8 mg kg^{-1} (d.w.) in Italy and 187.0; 6993.5; 10.0; 14.3; 29.9; 21.7; 0.02 and 7.1 mg kg^{-1} (d.w.) in Turkey, respectively. From the measured specific activities, radium equivalent activity, the absorbed dose rate, annual effective dose equivalent, and external hazard index due to the natural radionuclides were calculated to assess the health risk. Radium equivalent activity was lower than the world average for both Turkey and Italy. And also, the external hazard indices were found to be below the hazard limit of unity.

Key-Words: - Gamma spectrometer, metal, radionuclide, sediment

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1 Introduction

The natural radiation level in a region varies with cosmic radiation as well as with the presence of naturally occurring radionuclides in the Earth's crust, atmosphere, and water bodies, [1]. These exist in various geological formations such as the earth's crust, rocks, soils, plants, water, sediments, and air. Humans are exposed to ionizing radiation from natural radionuclides from the environment. The main natural contributors to external exposure from gamma rays are ^{226}Ra, ^{232}Th, and ^{40}K, [2], [3].

Heavy metals are one of the main pollutants in our environment and their high levels may indicate the presence of anthropogenic pollutant sources, [4]. Heavy metal contamination in marine environments is generally monitored by measuring concentration in biota and sediment.

Determinations of the concentration of radionuclides and metals in various objects of the environment are now actively used to assess the ecological state of regions. In the environment such monitoring and assessment work is being actively carried out for soil, seawater, sands, and sediments, [5], [6]. Sediment in lakes, rivers, and the sea can be a source of contamination of aquatic organisms. For example, contaminated sedimentary materials used as fertiliser can increase radioactivity levels in the soil, which can reach humans through the food chain. As sediments are one of the basic carriers of heavy metals and radionuclides into the marine ecosystem, it has a major role in monitoring heavy metal and radionuclide pollution in the aquatic environment, [7]. Many investigations have been conducted worldwide to assess the activity concentrations of NORMs in sediment. It is of great importance for the assessment of the dose to the population, which plays a vital role in the investigation of health risks from radioactivity in sediment and soil and will provide a baseline for changes in environmental radioactivity due to human activities.

The objective of this work however is to determine the heavy metals (Fe, Mn, Zn, Cu, Ni, Pb, Cr, Cd) and radioactivity levels of ^{226}Ra, ^{232}Th, and ^{40}K in marine sediments from coastal areas of Aegean Sea (Turkey) and Calabrian region (Italy) and to evaluate the probable health risks associated with them. The data will be useful as baseline data to be used in subsequent studies for the areas studied and also in carrying out any environmental health surveillance.

2 Materials and Method

2.1 Sample Collection and Preparation

In Italy, marine sediment samples of about 1 kg were collected in selected Ionian and Tyrrhenian Calabrian locations, indicated in Figure 1(a).

In Turkey, marine sediment samples were collected from the sites of Bodrum, Didim, Urla, and Aliağa (Aegean Sea, Turkey) as shown in Figure 1(b).

The same procedure for the sample preparation was adopted. All of the samples were oven dried at a temperature of 105ºC and sieved through a 2 mm. Then, the samples were put in a container and completely stored for at least 4 weeks to achieve the radiative balance of natural radionuclides and their progenies.

2.2 Gamma Spectrometric Analysis

Specific activities of radionuclides in sediments were measured using a coaxial HPGe detector in multilayer shielding. Determination of counting efficiency and calibration was done by using the soid mixed source (containing radionuclides in the energy range 80 to 2500 keV) provided by the Isotope Product Laboratories. To acquire and elaborate data, the Gamma Vision (Ortec) software was employed.

The specific activity C (Bq kg^{-1} d.w.) of each investigated radionuclide was assessed with the following equation:

$$C = \frac{N_E}{\varepsilon . t . \gamma . M} \quad (1)$$

where N_E, ε, γ, M (kg), and t (s.) are the net area of a photopeak at energy E, its efficiency, its yield, the mass sample, and the lifetime, respectively.

2.3 Metal Analysis

The sediment sample (approximately, 1 g) was dissolved with mixed acid (5 mL H_2SO_4, 3 mL HNO_3, 5 mL HF, 0.5 mL $HClO_4$) in a Teflon beaker, [8]. After that, the dissolved sample was to 100 mL with 2 % HNO_3, and the concentrations of heavy metal (Cd, Cr, Ni, Pb, Cu, Zn, Mn, and Fe) were determined by ICP-OES at Türkiye.

The sediment sample (approximately, 0.5-0.7 g) was dissolved in mixed acid (3 mL of ultrapure (67–69%) HNO_3 and 9 mL of ultrapure (32–35%) HCl) were directly introduced into the TFM vessel. Acid digestion was performed using a Milestone microwave unit system, Ethos touch control, in three steps: 15 minutes at 1000W and 200 ºC; 10 minutes at 700W and 200 ºC; 10 minutes cooling,

[9]. After cooling, vessel contents were filtered and filled up to 50mL with distilled H_2O. The final sample was then diluted at a concentration of one order of magnitude lower than the initial value.

The concentrations of heavy metals (Cd, Cr, Ni, Pb, Cu, Zn, Mn, and Fe) were determined by a Thermo Scientific iCAP Qc ICP-MS in Italy, [10].

Fig. 1: Location of the sampling site: (a) Italy and (b) Turkey

2.4 Radiological Hazards

Following the measurement of the radionuclide concentrations in the samples, the radium equivalent activity (Ra_{eq}), the absorbed dose rate (D), the annual effective dose equivalent (AEDE), and the external hazard index (H_{ex}) were used as radiological indicators to estimate the radiological implications of the use of the marine sediment samples.

Ra_{eq} was calculated as the Eq. (2), [11], [12]:

$$Ra_{eq} = C_{Ra} + 1.43\, C_{Th} + 0.077\, C_K \quad (2)$$

where C_{Ra}, C_{Th}, and C_K are the activity concentrations of ^{226}Ra, ^{232}Th, and ^{40}K, respectively.

The absorbed gamma dose rate in the air was calculated using Eq. (3), [13], [14]:

$$D\ (nGy\ h^{-1}) = 0.462\ C_{Ra} + 0.604\ C_{Th} + 0.0417\ C_K \quad (3)$$

Where, C_{Ra}, C_{Th}, and C_K are the radioactivity concentration in Bq kg^{-1}.

The annual effective dose equivalent due to natural radioactivity was calculated using Eq. (4).

$$AEDE\ (mSv\ y^{-1}) = D\ (nGy\ h^{-1}) \times 8760 \times 0.7\ (Sv\ Gy^{-1}) \times 0.2 \times 10^{-6} \quad (4)$$

Where 0.7 Sv Gy^{-1} is the conversion coefficient for an absorbed dose in the air to an effective dose in the human body and 0.2 is an outdoor occupancy factor.

The external exposure to gamma rays in the study region is called the external hazard index, or Hex. This index is given by the following Eq. (5):

$$H_{ex} = \frac{C_{Ra}}{370} + \frac{C_{Th}}{259} + \frac{C_K}{4810} \leq 1 \quad (5)$$

where C_{Ra}, C_{Th}, and C_K are the radioactivity concentration of ^{226}Ra, ^{232}Th, and ^{40}K in Bq kg^{-1}, respectively.

3 Result and Discussion

The activity concentrations of ^{226}Ra, ^{232}Th, and ^{40}K in marine sediment samples from the Aegean Sea (Turkey) and the Calabria region (Italy) are reported in Table 1.

In the Aegean Sea, the mean activity concentrations were found to be 21.50, 23.13, and 541.88 Bq kg^{-1}, respectively. The concentrations of the radionuclides in the Aegean Sea were higher in Aliağa locations (A7 and A8) compared to the other locations, [15]. In the Calabrian region, the mean activity concentrations were found to be 26.63, 37.63, and 793.75 Bq kg^{-1}, respectively and the highest specific activity of ^{226}Ra, ^{232}Th, and ^{40}K is found at site I6 for all of them.

Table 1. Gamma spectrometry results for the analyzed samples

Sampling Station Code		^{226}Ra Bq kg^{-1} (d.w.)	^{232}Th Bq kg^{-1} (d.w.)	^{40}K Bq kg^{-1} (d.w.)
Aegean Sea (Turkey)	A1	12±1	15±1	350±14
	A2	10±1	15±1	290±14
	A3	10±1	7±1	624±35
	A4	9±1	6±0.3	576±26
	A5	11±1	14±1	378±14
	A6	15±1	16±1	250±13
	A7	45±8	48±7	889±32
	A8	60±2	64±1	978±6
Calabria region (Italy)	I1	14±1	25±3	940±70
	I2	22±3	12±1	470±20
	I3	22±2	26±2	610±30
	I4	15±2	18±2	690±50
	I5	26±5	40±4	870±60
	I6	54±9	83±8	1000±70
	I7	42±4	70±6	850±60
	I8	18±1	27±2	920±30

The worldwide average concentrations of the radionuclides ^{226}Ra, ^{232}Th, and ^{40}K reported by UNSCEAR are 35, 30, and 400 Bq kg^{-1}, respectively. The results show that the mean activity of ^{226}Ra, ^{232}Th, and ^{40}K in sediments of Aliağa (Aegean Sea) is higher than the world average. Aliağa, polluted by heavy domestic and industrial pollution, is located in the eastern Aegean Sea. The economy of Aliağa is mainly based on oil refineries such as Tüpraş (Turkey's second-largest oil refinery) and Petkim (petrochemical plant). In addition, there are iron and steel mills, two thermal power plants (natural gas-based), fertiliser and paper mills, and many other industrial facilities in the gulf, [15].

In Italy, the specific activity of ^{226}Ra in sediment samples is lower than the average world value in all cases, except for sites I6 and I7. The activity concentration of ^{232}Th is higher than the worldwide one only for sites I5, I6, and I7. The activity concentration of ^{40}K is higher than the average world value for all investigated samples, [10].

The levels of heavy metals (Fe, Mn, Zn, Cu, Ni, Pb, Cr, and Cd) analyzed in samples collected from Turkey (Aegean Sea) and Italy (Calabria region) are summarized in Table 2.

In this study, all the metals analyzed and the average values obtained at the sampling sites are listed as follows: Fe > Mn > Zn > Cr > Cu > Ni > Pb > Cd.

The calculated radium equivalent activities vary from 53.8 (A2) to 226.8 (A8) Bq kg^{-1} with an average of 105.1 Bq kg^{-1} for Turkey (Aegean Sea) and from 75.4 (I2) to 249.7 (I6) Bq kg^{-1} with an average of 145.7 Bq kg^{-1} for Italy (Calabria region). Thus, the values of Ra_{eq} of ^{226}Ra, ^{232}Th, and ^{40}K found in sediment samples were lower than the upper limit of Ra_{eq} is 370 Bq kg^{-1}.

Table 2. The concentrations of heavy metals in marine sediment for all sites (mg kg^{-1} dw)

Parameters		Fe	Mn	Zn	Cu	Ni	Pb	Cr	Cd
Aegean Sea (Turkey)	Min	2175	40	3	3	3	1	9	0.01
	Max	18470	545	84	36	33	16	65	0.05
	Mean	6995	187	30	14	10	7	22	0.02
Calabria region (Italy)	Min	2689	51	8	2	2	2	3	0.01
	Max	16834	263	43	13	16	20	28	0.09
	Mean	8140	198	25	6	6	7	11	0.05

In this study, the absorbed dose rate due to ^{226}Ra, ^{232}Th, and ^{40}K in sediment varied from 25.77 to 107.16 nGyh^{-1} with an average of 50.49 nGyh^{-1} for Türkiye and that for Italy varied from 37.01 to 116.78 with an average value of 69.88 nGyh^{-1}. In Italy, the absorbed dose rate is lower than the world average value (59 nGyh^{-1}) only for sites I2, I3, and I4. In Türkiye, the absorbed dose rate is higher than the world average value (59 nGyh^{-1}) only for sites A7 and A8. The values obtained are generally comparable with the world average of 59 nGyh^{-1}.

The outdoor AEDE values for Italy marine sediment samples in sites I5, I6, and I7 and Türkiye marine sediment samples in sites A7 and A8 exceed the world average value of 85 μSv y^{-1}.

The H_{ex} index is lower than unity for all investigated samples, thus reasonably avoiding any possible radiological health risks for humans, [16]. The H_{ex} index is less than unity for all samples examined, therefore radiological health risks for humans are not considered to be a risk for both Turkey and Italy.

4 Conclusion

Heavy metal pollutants and natural radioactivity concentrations in the marine environment are one of the most severe pollution concerns. These elements, indeed, attach to particles in marine ambiance and then accumulated in sediments.

The sources of these elements in the marine environment can be either naturally coming from the Earth's crust or anthropogenic such as industrial activity and mining. However, alteration in their concentration in natural ecosystems has led to an understanding of the adverse effects over the past decades since they can enter the food chain through the ingestion of marine foods. So, high concentrations of heavy metals and radionuclides in the sediments have a great effect on the food chain and can cause a major hazard to the aquatic environment and human health.

The activity concentration of natural radionuclides, ^{226}Ra, ^{232}Th, and ^{40}K was quantified by using HPGe gamma spectrometry for marine sediments collected from the Calabria region (Italy) and Aegean Sea (Türkiye). Heavy metals such as Mn, Fe, Ni, Cu, Zn, Cr, Cd, and Pb in sediment samples were measured using ICP-OES and ICP-MS.

The activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K determined in this study are comparable with other studies in the Mediterranean area performed in the area of Cyprus, [17], Greece, [18], where anthropogenic activities in the nearby affecting the area were no detected. In particular, the mean activity concentrations of ^{226}Ra, and ^{232}Th were lower than the value of the world averages where ^{40}K was greater than that. In the present study, the calculated H_{ex} values for all sediment samples are less than unity, which does not cause any harm to the population in all regions.

Heavy metal results showed that Fe is the most abundant metal in the sediment samples analysed in this study due to the abundance of iron in the structure of the earth's crust, [7]. Also, on average, the heavy metal concentrations in the Aegean Sea sediments are similar to those in the sediments of the Calabria region.

Evidence is provided for the evaluation of coastal sediment metal toxicity and radionuclide contamination by comparing two different countries (Turkey and Italy), sea (Aegean Sea and Mediterranean Sea), and coastal areas.

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Conflict of Interest

The authors have no conflict of interest to declare.