Radioactive and Chemical Pollution Evaluation in Coastal Sea Sediments

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Abstract: - In this article, coastal sea sediments from three different selected sites of Reggio Calabria and Vibo Valentia districts, Calabria region, Southern Italy, were picked up to quantify natural and anthropogenic radioactivity content and metal concentrations. The aim was to assess any possible radiological health hazard for human beings due to external exposure to gamma rays, as well as the level of pollution due to anthropic radionuclides and metals in the investigated area. To this purpose, High Purity Germanium (HPGe) gamma spectrometry was employed to quantify specific activities of ^{226}Ra, ^{232}Th, ^{40}K, and ^{137}Cs radioisotopes. The absorbed gamma dose rate in air (*D*), the annual effective dose equivalent (*AEDE*) outdoors, the external hazard index (H_{ex}) and the excess lifetime cancer risk (*ELCR*) were also estimated to assess any possible radiological health risk for the population, mainly due to the use of coastal sea sediments for the beach nourishment. Moreover, Inductively Coupled Plasma Mass Spectrometry (ICP-MS) measurements were carried out for the quantitative elemental analysis of the samples, to assess any possible chemical pollution by metals, that could be released into the environment by both natural and anthropogenic sources, through a comparison with the limits set by the Italian Legislation. Finally, the results reported in this paper can be used as a baseline for future investigations concerning a more complete mapping of the radioactivity levels in coastal sea sediments.

Key-Words: - Coastal sea sediments, radioactivity, radiological risk, metals, chemical pollution, High Purity Germanium (HPGe) gamma spectrometry, Inductively Coupled Plasma Mass Spectrometry (ICP-MS).

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1 Introduction

Naturally occurring radioisotopes from the Earth's crust and cosmic radiation, as well as artificially produced radionuclides from nuclear weapons experiments and nuclear facility failures, are a permanent environmental occurrence and constitute notable sources of radiation exposure for human beings, [1], [2], [3], [4], [5]. In particular, natural

radionuclides are uranium (^{238}U and ^{235}U) and thorium (^{232}Th) decay chain products and ^{40}K, primordial and with variable concentrations based on local geological landforms, [6]. Their significance resides in the fact that they account for more than half of the radioactive exposure to which the population is subjected, [7], [8]. Besides these natural radionuclides, man-made ones such as ^{137}Cs, being released into the environment by different anthropogenic practices and being deposited in soils as fallout, also play a significant role in radiation exposure, [9], [10]. Hence, the knowledge of natural and anthropogenic radionuclides-specific activity in environmental matrices is important for establishing background levels of radiation and assessing the effects of radioactive exposure for humans, [11], [12].

In sediments, naturally occurring radioisotopes mainly tend to be accumulated by weathering, erosion, and depositional processes of different geological materials, exhibiting concentrations generally growing as grain size becomes smaller, [13], [14]. The investigation of natural radioactivity in coastal sea sediments may give valuable information on the source and fate of radionuclides in aquatic habitats, helping to establish their distribution and the potential risk to public health from radio contamination of rivers and coastline areas and the use of sea sediments for nourishment of beaches, [15], [16].

Going on, the unregulated urban development surrounding many towns and coastal areas has led to an increasing level of pollutants that have contaminated these aquatic habitats to an alarming degree. Among them, metals are of the greatest concern because of their long-lasting and bio-accumulative character, [17], [18], [19], [20]. They can be delivered to the aquatic environment and accumulated in sediments through the disposal of liquid effluents, chemical leachates, and runoff from residential, manufacturing, and farming activities, and also through atmospheric deposition, [21], [22]. These metals can be leached from sediments to overlying waters through either natural or man-made processes, resulting in a potential hazard to ecosystems, [23].

In this article, coastal sea sediments from three different selected sites of Reggio Calabria and Vibo Valentia districts, Calabria region, Southern Italy, were analyzed to quantify natural (^{226}Ra, ^{232}Th and ^{40}K) and artificial (^{137}Cs) gamma-emitting radionuclides, by using High Purity Germanium (HPGe) gamma spectrometry, to record radioactivity background levels and to check for any possible anthropic radionuclides' pollution, [24]. Moreover, Inductively-Coupled Plasma Mass Spectrometry (ICP-MS) was employed for the quantitative analysis of metals, to evaluate any possible chemical pollution through a comparison with the limits set by the Italian Legislation, [25].

2 Materials and Methods

2.1 Samples Collection and Preparation

Five samples of coastal sea sediments, around 1 kg everyone, were collected for each of the three selected locations (Figure 1), at a depth of 8-10 m.
In detail, the GPS coordinates of the sampling points are 38°28'28.3" N and 15°54'32.7" E for ID1, 38°30'27.3" N and 15°55'04.73" E for ID2, 38°32'25.9" N and 15°55'50.4" E for ID3, respectively. Sampling was performed according to the following process: the sampler was cocked and depressed at a steady speed to enable it to contact the seabed in the proper position. Upon contact with the seabed, the operator scored the GPS coordinates and recovered the sampling instrument. As soon as the sampler touched the surface, it was rapidly retrieved to prevent any stresses that would alter its content, externally rinsed to ensure no contamination, and its content was drained into a tank and stored in well-sealed and labeled 1 L acidified polyethylene containers to prevent radionuclide precipitation and absorption on the container sides.

In the laboratory, all sediments were oven-dried at 105° C, sieved to a particle size of less than 2 mm, and placed into 1 L capacity Marinelli airtight containers. After 40 days, secular radioactive equilibrium was reached between ^{226}Ra and its daughter products, and sediments were ready to be analyzed by High Purity Germanium (HPGe) gamma spectrometry, [26].

Fig. 1: Location of the sampling sites, in Reggio Calabria (ID1 and ID2) and Vibo Valentia (ID3) districts

2.2 HPGe Gamma Spectrometry Measurements

For the HPGe gamma spectrometry analysis, coastal sea sediments were counted for 70000 seconds, to reduce the statistical uncertainty, and spectra were analyzed to obtain the activity concentrations of ^{226}Ra (by using the 295.21 keV and 351.92 keV ^{214}Pb and 1120.29 keV ^{214}Bi gamma-ray lines), ^{232}Th (by using the 911.21 keV and 968.97 keV ^{228}Ac γ-ray lines), ^{40}K (through its gamma-line at 1460.8 keV) and ^{137}Cs (through its gamma-line at 661.66 keV), [27].

The experimental set-up was a positively biased detector (GEM), with FWHM of 1.85 keV, peak-to-Compton ratio of 64:1, and relative efficiency of 40 % at 1.33 MeV (^{60}Co), placed inside lead wells to shield the background radiation environment. It is worth noting that, for the sample holder geometry of 1 L, efficiency and energy calibrations were carried out with a multipeak Marinelli geometry gamma source (AK-5901) of 1 L capacity, covering the energy range 60-1836 keV, customized to reproduce the exact geometries of samples in a water-equivalent epoxy resin matrix. The Gamma Vision software was used for data acquisition and analysis, [28].

The specific activity (Bq kg^{-1} dry weight, d.w.) of the detected radionuclides was given by, [29]:

$$C = \frac{N_E}{\varepsilon_E t \gamma_d M} \quad (1)$$

where N_E indicates the net area of a peak at energy E, ε_E and γ_d is the efficiency and yield of the photopeak at energy E, respectively, M is the mass of the sample (kg) and t is the live time (s), [30].
The quality of the gamma spectrometry experimental results was certified by the Italian Accreditation Body (ACCREDIA), [31].

2.3 ICP-MS Measurements

The concentration of As, Cd, Cu, Hg, Ni, Pb, Sb, Tl, Zn, and Cr_{tot} was obtained through ICP-MS analysis using a Thermo Scientific iCAP Qc ICP-MS. Particles with a size smaller than 2 mm, previously served, were further minced at a size of about 100 μm through an agate ball mill. After, a quantity of 0.5 g of this sample, together with 9 mL of ultrapure (67-69%) HNO_3 and 3 mL of ultrapure (32-35%) HCl were directly introduced into a 100 mL TFM vessel. Acid digestion was performed using a CEM microwave unit system, Mars 6 touch control, in one step, at 1000 W and 175 ºC, with a maintenance time of 4 minutes and 30 seconds, followed by a 20-minute cooling, [32]. After cooling, vessel contents were filtered and filled up to 50 mL with distilled H_2O. The final sample was then diluted at a concentration of one order of magnitude lower than the initial value.

The sample introduction system consisted of a Peltier cooled (3 ˚C), baffled cyclonic spray chamber, PFA nebulizer, and quartz torch with a 2.5 mm i.d. removable quartz injector. The instrument was operated in a single collision cell mode, with kinetic energy discrimination (KED), using pure He as the collision gas. All samples were presented for analysis using a Cetac ASX-520. The iCAP Qc ICP-MS was operated in a single KED mode using the following parameters: 1550 W forward power; 0.98 L/min nebulizer gas; 0.8 L/min auxiliary gas; 14.0 L/min cool gas flow; 4.5 mL/min collision cell gas He; 45 s each for sample uptake/wash time; optimized dwell times per analyte (0.1 s, except 0.5 s for As, Hg, Cr and Se); one point per peak and three repeats per sample.

2.4 Evaluation of Radiological Hazard Effects

Radiological parameters, such as the absorbed gamma dose rate in the air (*D*), the annual effective dose equivalent (*AEDE*) outdoors, the external hazard index (H_{ex}) and the excess lifetime cancer risk (*ELCR*), were estimated to assess any potential radiological health risk to humans, [33], [34].

In particular, the absorbed dose rate calculation is the first major step to evaluating the health risk, [35]:

$$D\ (\text{nGy h}^{-1}) = 0.462C_{Ra} + 0.604C_{Th} + 0.0417C_K \quad (2)$$

where C_{Ra}, C_{Th}, and C_K are the specific activities, in Bq kg^{-1} d.w., of ^{226}Ra, ^{232}Th, and ^{40}K, respectively.
Going on, the annual effective dose equivalent, received by an individual, is given by, [36]:

$$AEDE_{out}\ (\text{mSv y}^{-1}) = D\ (\text{nGy h}^{-1}) \cdot 8760\ \text{h} \cdot 0.7\ \text{Sv Gy}^{-1} \cdot 0.2 \cdot 10^{-6} \quad (3)$$

where 0.2 is an outdoor occupancy factor and 0.7 Sv Gy^{-1} is the conversion coefficient from the absorbed dose to the effective dose received, [37].

Moreover, the external radiation hazard index, to set the radiation dose to a value lower than 1 mSv y^{-1} was defined, [38]:

$$H_{ex} = (C_{Ra}/370 + C_{Th}/259 + C_K/4810) \leq 1 \quad (4)$$

Finally, the excess lifetime cancer risk index gives the probability of cancer development during a lifetime at a certain amount of exposure. It accounts for the number of extra cancers that are expected in a defined population as a result of exposure to a carcinogen at a particular dose, [38]:

$$ELCR = AEDE_{out} \cdot D_L \cdot R_F \quad (5)$$

where D_L is the mean human life duration (estimated to be 70 years) and R_F the risk factor (Sv^{-1}), i.e. fatal cancer risk per Sievert, equal to 0.05 for the public according to the International Commission on Radiological Protection (ICRP) recommendation, [39].

3 Results and Discussion

3.1 Radioactivity Analysis and Radiological Hazard Effects Assessment

The average activity concentrations of detected radionuclides, ^{226}Ra, ^{232}Th, ^{40}K, and ^{137}Cs, in the investigated samples, are reported in Table 1 for each sampling site.

Table 1. The average activity concentrations C_{Ra}, C_{Th}, $C_{K,}$ and C_{Cs} (average value ± standard deviation) of, respectively, ^{226}Ra, ^{232}Th, ^{40}K, and ^{137}Cs, were evaluated for each sampling site.

ID	C_{Ra} (Bq kg^{-1} d.w.)	C_{Th} (Bq kg^{-1} d.w.)	C_K (Bq kg^{-1} d.w.)	C_{Cs} (Bq kg^{-1} d.w.)
1	(19.6 ± 2.7)	(32.3 ± 4.9)	(800 ± 112)	< 0.2
2	(13.5 ± 2.2)	(23.4 ± 2.9)	(543 ± 81)	< 0.1
3	(13.2 ± 2.1)	(24.3 ± 3.1)	(825 ± 91)	< 0.1

The observed variability, location by location, can be due to the large changes in chemical and mineralogical properties and rare-earth elements of the marine backdrop, [40].

As far as natural radionuclides are concerned, the ^{40}K specific activity is more than one order of magnitude greater than that of ^{226}Ra and ^{232}Th radionuclides, as usually occurs in soil samples. In detail, the specific activities range from (13.2 ± 2.1) Bq kg^{-1} d.w. to (19.6 ± 2.7) Bq kg^{-1} d.w., from (23.4 ± 2.9) Bq kg^{-1} d.w. to (32.3 ± 4.9) Bq kg^{-1} d.w. and from (543 ± 81) Bq kg^{-1} d.w. to (825 ± 91) Bq kg^{-1} d.w. for ^{226}Ra, ^{232}Th, ^{40}K, respectively. It is worth noting that the highest specific activity of ^{226}Ra and ^{232}Th were found in site ID1, while ^{40}K was in site ID3.

Furthermore, taking into account that worldwide average concentrations of ^{226}Ra, ^{232}Th, and ^{40}K in soils, as reported by [31], are 35 Bq kg^{-1} d.w., 30 Bq kg^{-1} d.w. and 400 Bq kg^{-1} d.w., respectively, we can notice that, in our case, the specific activity concentration is lower than the average world value in all cases for ^{226}Ra. Moreover, it is higher than the mean worldwide value only for site ID1 for ^{232}Th, while it is higher than the worldwide one in all cases for ^{40}K. These results are strictly related to the mineralogical composition of the coastal sea sediments themselves, as widely reported in the literature, [41], [42], [43], [44].

Regarding anthropogenic radioactivity content, we notice that the activity concentration of ^{137}Cs is lower than the minimum detectable activity value in all cases, excluding radioactive contamination of anthropic origin for the investigated samples.

Going on, radiological hazard indices are reported in Table 2 for all the investigated sampling sites.

Table 2. Radiological hazard indices for all the investigated sampling sites.

ID	D (nGy h^{-1})	$AEDE_{out}$ (μSv y^{-1})	H_{ex}	$ELCR$ ($x10^{-3}$)
1	61.9	75.9	0.34	0.27
2	43.0	52.8	0.24	0.18
3	55.2	67.7	0.30	0.24

In detail, the absorbed dose rate, as evaluated by using equation (2), is higher than the world average value (57 nGy h^{-1}), [37], only for site ID1. The annual effective dose equivalent, received by an individual and obtained through equation (3), never exceeds 1 mSv y^{-1}, which is set as the maximum limit by, [45]. Moreover, the external radiation hazard index, as resulting from equation (4), is lower than unity for all investigated samples. Thus, in light of the aforementioned results, radiological health risks for the population due to external exposure to gamma rays, mainly due to the use of coastal sea sediments for beach nourishment, can be considered negligible. Finally, excess lifetime cancer risk values, as obtained by using equation (5) the $AEDE_{out}$ values calculated by equation (3), are in very good agreement with the literature, [46], [47], [48]. It is worth noting that the assessment of the radiological health hazards for the population only based on the calculated *ELCR* is not possible, because trustworthy and standardized mortality and morbidity statistics are not affordable.

3.2 Metals Analysis

Table 3. Average contents (mg kg^{-1} d.w.) of metals detected in the investigated samples by ICP-MS analysis, were evaluated for each sampling site. In the last column, the threshold limit set by the Italian legislation is reported for comparison.

	Site ID			
	1	2	3	*Threshold limit*
C_{As}	1.07	1.49	1.21	12
C_{Cd}	< 0.1	< 0.1	< 0.1	0.3
C_{Cu}	1.83	2.61	1.93	19
C_{Hg}	< 0.05	< 0.05	< 0.05	0.3
C_{Ni}	1.69	2.54	1.33	30
C_{Pb}	2.85	3.01	1.87	30
C_{Sb}	0.09	0.06	0.05	2
C_{Tl}	< 0.1	< 0.1	< 0.1	0.3
C_{Zn}	6.93	25.5	33.1	124
$C_{Cr\text{-}tot}$	2.61	4.64	2.42	50

Table 3 reports the average contents (mg kg^{-1} d.w.) of metals detected in the investigated samples by ICP-MS analysis, evaluated for each sampling site.

It can be noticed that in all cases the experimental values remain below the contamination thresholds set by, [49], [50]. Consequently, these metals cannot be treated as pollutants, they do not cause unpleasant effects neither compromise the well-being of the environment nor pose a risk to human health, [51].

4 Conclusion

The specific activity of natural and anthropic radioisotopes, i.e., ^{226}Ra, ^{232}Th, ^{40}K, and ^{137}Cs, was quantified through HPGe gamma spectrometry for coastal sea sediments picked up from different sampling points of Reggio Calabria and Vibo Valentia districts, Calabria region, Southern Italy. Moreover, to assess any possible radiological health risk for the population, mainly due to the use of coastal sea sediments for beach nourishment, the absorbed gamma dose rate in air, the annual effective dose equivalent outdoors, the external hazard index, and the excess lifetime cancer risk were calculated. Obtained results put into evidence low levels of radioactivity, thus discarding any significant radiological health risk for the population.

Going on, the presence of potentially hazardous elements (such as As, Cd, Cu, Hg, Ni, Pb, Sb, Tl, Zn, and Cr_{tot}) was assessed through ICP-MS measurements. To estimate the degree of pollution by these metals, their concentrations were compared with threshold limits set by the Italian Legislation. Obtained results indicate that metal concentrations are much lower than the contamination reference values, thereby ruling out pollution.

Noteworthy, as a direction for future research, this study can be used as a baseline for investigations about radioactivity background levels in coastal sea sediments of the investigated area. Furthermore, it should be remarked that the approach stated in this article might be applied, in principle, for the assessment of any potential radiological hazard for human beings due to the presence of radioactive elements in sediments, by constituting a guideline for investigations focused on the monitoring of the radiological and chemical quality of these samples, with a strong impact on the real life. No Artificial Intelligence methods can be applied to this study.

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