DOI: 10.1478/AAPP.1031A1

AAPP | Atti della Accademia Peloritana dei Pericolanti
Classe di Scienze Fisiche, Matematiche e Naturali
ISSN 1825-1242

Vol. 103, No. 1, A1 (2025)

RADIOACTIVITY AND METALS CONTENT OF BEACH SANDS FROM THE SICILY REGION, SOUTHERN ITALY

FRANCESCO CARIDI [a,*], FRANCESCO GREGORIO [a], GIUSEPPE PALADINI [a], STEFANIA LANZA [a], ALBERTO BELVEDERE [b], SANTINA MARGUCCIO [b], MAURIZIO D'AGOSTINO [b], MAURIZIO MESSINA [b], DOMENICO MAJOLINO [a] AND VALENTINA VENUTI [a]

ABSTRACT. This paper reports an investigation aimed at evaluating the radioactivity and metals content of beach sands from the Sicily region, Southern Italy. The specific activity of natural (^{226}Ra, ^{232}Th and ^{40}K) and anthropogenic (^{137}Cs) radionuclides was assessed through High Purity Germanium (HPGe) gamma-ray spectrometry. Radiological hazard indices, *i.e.*, absorbed gamma dose rate (D), annual effective dose equivalent outdoor ($AEDE_{out}$) and excess lifetime cancer risk ($ELCR$), were thus calculated in order to estimate any possible radiological risk for the population that uses to spend summer holidays on this renowned tourist destination. Furthermore, Inductively-Coupled Plasma Mass Spectrometry (ICP-MS) measurements were conducted for the quantitative elemental analysis of the investigated sands, in order to determine any possible chemical pollution by metals. To this aim, different indices such as geo-accumulation index (I_{geo}), contamination factor (CF) and pollution load index (PLI) were calculated with the aim to assess the level of toxicity imposed on the ecosystem by the detected metals. It is noteworthy that the used approach could be applied, in principle, not only for the assessment of the radiological and chemical risk due to the occurrence of potentially harmful elements in a wide range of samples of special environmental interest, but also as guideline for investigations focused on the monitoring of the environmental quality.

1. Introduction

Humans are exposed to ionizing radiation from natural and artificial sources in their life environments (UNSCEAR 2000; Caridi *et al.* 2008; Caridi, Torrisi, and Giuffrida 2010; Torrisi *et al.* 2010; Torrisi, Caridi, and Giuffrida 2011). On one hand, natural radioactivity is a globally common occurrence due to the radioactive decay of primordial radionuclides, *i.e.*, ^{238}U, ^{232}Th and ^{40}K, occurring in the Earth's crust (Ravisankar *et al.* 2012, 2015). Considering that living matter is continuously exposed to natural radiation, the assessment of gamma radiation dose from naturally occurring sources is of great importance for human health care, as it is the largest external dose contributor to the world's population (Fazio *et al.* 2011; Caridi *et al.* 2017b). Accordingly, human exposure to ionizing radiation is among the present scientific topics that is receiving increasing attention. Indeed, there is a growing

awareness of the radiation effects deriving from radioactive elements (Caridi, Messina, and D'Agostino 2017; Shahrokhi *et al.* 2021), whose distribution is not uniform across the Earth's crust. In addition to their own radioisotopes, these elements are commonly found in environmental matrices, particularly in water, rocks, and soils (Fouskas *et al.* 2018; Günoğlu and Seçkiner 2018; Caridi *et al.* 2021). In particular, in this last case, the chemical composition and the natural radioactivity are found to differ significantly according to the geomorphologic and geographic characteristics of the site under investigation (Walencik-Łata and Smolka-Danielowska 2020; Caridi *et al.* 2023). As state of the art, Sicily is one of the most representative examples of geodiversity (Lentini and Carbone 2014), whose large variety of landscapes and natural beauty is the result of the presence of metamorphic (typical of the Peloritani Mountains area), magmatic (Etna, Aeolian Islands, Linosa, Pantelleria, Ustica) and sedimentary rocks. In more detail, beach sand is the result of the combined effects of erosion and weathering on metamorphic and igneous rocks, which contain the highest concentrations of naturally occurring radioisotopes. Consequently, investigations focused on evaluating the activity concentration of natural radionuclides in beach sands facilitate the estimation of the radiological health risk, attributable to external exposure to gamma radiation, for individuals who habitually spend their summer season on these beaches (Rosell, Ortega, and Dies 1991; Papadopoulos *et al.* 2014). Such analysis, in fact, turns out to be a critical task of global concern since, as widely reported in the literature, high exposure to uranium and thorium has various serious health impacts (Jaafar, Podolsky, and Dynan 2013; Kamiya *et al.* 2015; Omar-Nazir *et al.* 2018). Nevertheless, anthropogenic fallout radionuclides, such as ^{137}Cs, are principally attributable to both nuclear tests conducted globally between the mid-1940s and the 1980s, and nuclear accidents. In addition to its ionizing properties, ^{137}Cs has the potential to be poisonous, to bioconcentrate and bioaccumulate in a detrimental manner, and to adversely affect human and ecosystem health (Caridi *et al.* 2017a).

Going on, nowadays there is a profoundly concerning prevalence of chemical contaminants in numerous metropolitan areas and coastal regions, attributable to unregulated, accelerated industrialisation and urbanisation processes within such environments (Caridi *et al.* 2009; Mezzasalma *et al.* 2009; Pappa *et al.* 2016; Ali, Khan, and Ilahi 2019; Pappa *et al.* 2019). For this reason, in the present paper the sampling sites were chosen in areas close to the industrial centers of Milazzo, Gela, Melilli and Termini Imerese. The first three sites are in fact considered, from the chemical point of view and according to Italian laws n. 426/1998 and n.266/2005, Sites of National Interest (SIN), *i.e.*, portions of national territory characterized by a high environmental value and subject to various forms of degradation, including environmental contamination; the last site, otherwise, is an industrial area which over the decades has had various uses (mechanical, chemical, etc.). Among pollutants, metals are of great concern due to their long-lasting and bioaccumulative characteristics (Margarone *et al.* 2008; Torrisi *et al.* 2008; Balali-Mood *et al.* 2021). It is imperative to ascertain the provenance of certain metals and comprehend the contamination pathways in systems where concentration levels attain toxic levels, in order to effectively address the extent of the contamination (Liang and Gong 2020). It is worth of note that the pollution of the living habitat by metals is a worldwide concern, taking into account the poisonous effects on biological organisms when allowable concentration levels are overcome (Briffa, Sinagra, and Blundell 2020). Toxic metals can cause individuals' mental, cognitive and

physical decline (Jaishankar *et al.* 2014). In accordance with (Iwuoha, Osuji, and Horsfall 2012; Masindi and Muedi 2018), the presence of metals in soil, water and biota can indicate the existence of natural or man-made sources.

In the light of the above, beach sands sampled in four different selected sites of the Sicily region, Southern Italy, were analyzed in this article through High Purity Germanium (HPGe) gamma-ray spectrometry in order to assess the activity concentration of natural gamma-emitting radionuclides, *i.e.*, ^{226}Ra (in secular equilibrium with ^{238}U), ^{232}Th and ^{40}K, to record radioactivity background levels. In addition, to check any possible artificial radioisotopes contamination (Caridi, Testagrossa, and Acri 2021), the specific activity of ^{137}Cs was also calculated. Subsequently, radiological hazard indices, *i.e.*, absorbed gamma dose rate (D), annual effective dose equivalent outdoor ($AEDE_{out}$) and excess lifetime cancer risk ($ELCR$), were estimated in order to evaluate the potential radiological risk to the population that spend summer holidays in the investigated sampling sites. Finally, a quantitative elemental analysis was conducted using Inductively Coupled Plasma Mass Spectrometry (ICP-MS) as a means of investigating any potential chemical pollution by metals. For this purpose, the assessment of specific indices, such as geo-accumulation index (I_{geo}), contamination factor (CF) and pollution load index (PLI), allowed the possibility to determine the level of toxicity imposed on the ecosystem by the detected metals (Caridi *et al.* 2016b).

It is noteworthy that all the aforementioned investigations on the selected sampling sites have been conducted, for the first time, in the present paper, with the aim of assessing any possible radiological and chemical health risk for the public.

2. Materials and methods

2.1. Samples collection. Table 1 shows the identification (IDs) and GPS coordinates (Datum: WGS84, EPSG:4326) of the four sampling sites, representative of the Tyrrhenian, Ionian, and Southern Sicilian coast.

TABLE 1. The sampling sites, together with their IDs and GPS coordinates

Site ID	Sampling site	GPS position (Datum: WGS84, EPSG:4326)	
		Latitude	Longitude
1	Termini Imerese	37° 58’ 13” N	13° 44’ 54” E
2	Milazzo	38° 12’ 29” N	15° 15’ 43” E
3	Melilli	37° 08’ 19” N	15° 13’ 11” E
4	Gela	37° 02’ 30” N	14° 17’ 17” E

The GPS position was recorded with Topcon HiPer VR GNSS, that uses 542 channels and 7 constellations to obtain an accuracy of 5 mm on the horizontal and 10 mm on the vertical. Four sand samples were collected, one for each site, at an intermediate distance between the shoreline and the end of the beach. Figure 1 shows the map of the sampling area, with the site IDs (1-4) indicated. All sand samples were picked up at a depth of $0 - 15$ cm with a metal sampler and stored in labeled plastic containers before transport to the laboratory.

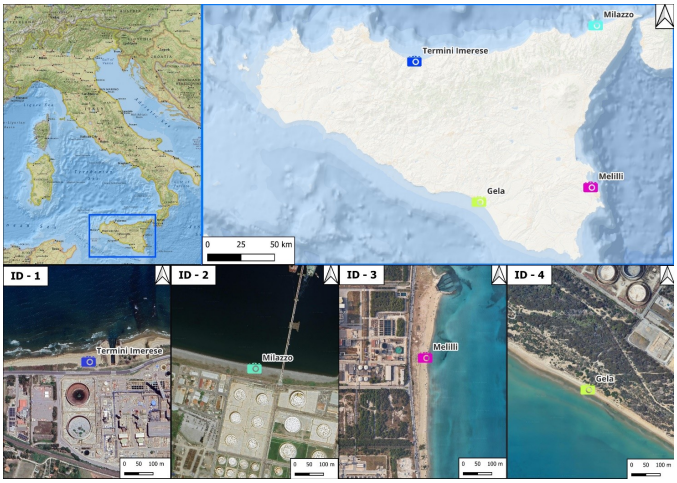

FIGURE 1. The map of the investigated area, with the sampling site IDs (1,. . . , 4) indicated.

2.2. HPGe gamma spectrometry analysis. For HPGe gamma spectrometry analysis, beach sands were dried at 105 °C in an oven for 24 h to completely remove moisture. After drying, each sample was mechanically quartered to reduce its volume while preserving the original distribution of the granules and a fraction was taken. Then, by using a stack of ASTM series sieves with square mesh sizes decreasing from top to bottom, samples were sieved to obtain a particle grain size of less than 2 mm (see Fig. 2) and finally placed in Marinelli sealed containers of 1 L capacity. Later, they were left for 30 days to reach the secular radioactive equilibrium between ^{226}Ra and its daughter products.

Going on, in order to reduce the statistical uncertainty, a total acquisition time of 70000 s was used, and spectra were analyzed in order to quantify the activity concentration of ^{226}Ra, ^{232}Th, ^{40}K and ^{137}Cs. In particular, i) the 351.92 keV ^{214}Pb and 1120.29 keV ^{214}Bi gamma-ray lines were used to quantify the ^{226}Ra activity concentration; ii) the 911.21 keV 228Ac gamma-ray line was employed to assess the ^{232}Th specific activity; iii) the 1460.8 keV and 661.66 keV gamma-ray lines were used to evaluate the activity concentration of ^{40}K and ^{137}Cs, respectively.

Gamma spectrometry measurements were carried out through an electrically-cooled ORTEC HPGe detector (GMX) placed inside lead wells for shielding the background radioactivity (Caridi *et al.* 2016a). In detail, it is a reverse biased semiconductor having a 1.94 keV FWHM resolution, a 37.5% relative efficiency at the reference peak (^{60}Co at 1.33 MeV) and a 65:1 peak to Compton ratio (Caridi *et al.* 2019). Moreover, for the energy and efficiency calibrations, a multi-peak Marinelli geometry gamma source (BC-4464) of 250 mL capacity, covering the energy range 60 keV–1836 keV and customized to reproduce the exact geometries of samples in a water-equivalent epoxy resin matrix, was employed (Eckert-Ziegler 2020). For each identified radionuclide, the specific activity was calculated

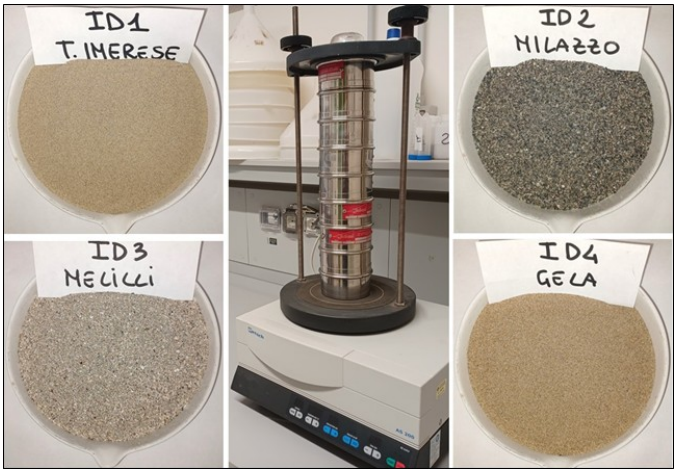

FIGURE 2. The four samples with grain size lower than 2 mm, together with the employed stack of sieves (center).

as:[1]

$$C(Bq\ kg^{-1}\text{dry weight, d. w.}) = \frac{N_E}{\varepsilon_E t \gamma_d M} \tag{1}$$

where N_E, ε_E and γ_d account for the net area, the efficiency and yield of a photopeak at energy E, respectively; M is the dry mass of the sample (kg) and t is the acquisition time (s). The measurement uncertainty is a combined standard at the coverage factor k = 2, taking into account counting statistics, nuclear data library, calibration efficiency, sample quantity, and self-absorption correction. Finally, the quality of the gamma spectrometry experimental results was certified by the Italian Accreditation Body (ACCREDIA 2021).

2.3. Assessment of the radiological health risk.

2.3.1. *Absorbed γ-dose rate (D).* To evaluate the radiological risk for human beings, the assessment of the absorbed γ dose rate (D) evaluation is the first step (UNSCEAR 2000). It was estimated as follows:

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

where C_{Ra}, C_{Th}, and C_K are the specific activities (Bq kg^{-1} d.w.) of ^{226}Ra, ^{232}Th, and ^{40}K in the analyzed beach sands, respectively.

2.3.2. *Annual Effective Dose Equivalent outdoor ($AEDE_{out}$).* The Annual Effective Dose Equivalent outdoor ($AEDE_{out}$) for an individual spending three months (during the summer period) in the investigated sampling sites was calculated as reported in (UNSCEAR 2000):

$$AEDE_{out}(\mu Sv\ y^{-1}) = D(nGy\ h^{-1}) \times 2160\ h \times 0.7\ Sv\ Gy^{-1} \times 0.2 \times 10^{-3} \tag{3}$$

[1]ORTEC: Gamma Vision Software User Manual (2020)

where the conversion coefficient to effective dose of 0.7 Sv Gy^{-1} and the outdoor occupancy factor of 0.2 were used.

2.3.3. *Excess lifetime cancer risk (ELCR).* The excess lifetime cancer risk (*ELCR*) index gives the lifetime probability of having developed cancer at a given level of exposure and, in particular, it accounts for the number of extra cancers expected in a certain population as a result of the exposure to a carcinogen at a given dose (Avwiri and Egieya 2013):

$$ELCR = AEDE_{out} \times D_L \times R_F \tag{4}$$

where D_L is the average duration of life (estimated to be 70 years) and R_F is the risk factor (Sv^{-1}), *i.e.*, fatal cancer risk per Sievert, equal to 0.05 for the public, as established by the International Commission on Radiological Protection (ICRP) for stochastic effects (ICRP 2012).

2.4. Inductively Coupled Plasma Mass Spectrometry (ICP-MS) measurements. For the ICP-MS analysis, approximately 0.5–1.0 g of sample, together with 3 mL of ultrapure (for trace analysis) HNO_3 (67–69%) and 9 mL of ultrapure (for trace analysis) HCl (32–35%) (aqua regia), were directly introduced into a 100 mL TFM vessel, according to (U.S. EPA. 2007). For the measurements a Thermo Scientific (Waltham, MA, USA) iCAP Qc ICP-MS was employed (U.S. EPA. 2014). 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.e.*, removable quartz injector. The instrument was operated in a single collision cell mode, with kinetic energy discrimination (KED), using pure Helium as the collision gas. All samples were presented for analysis using a Cetac ASX-520 (Teledyne Cetac Technologies, Omaha, NE, USA) and for each one, data were recorded in duplicate. Noteworthy, the quality of the ICP-MS experimental results was certified by ACCREDIA (2021).

2.5. Evaluation of the level of metals contamination. The level of metals contamination in the analyzed samples was evaluated by calculating some pollution indices, *i.e.*, geo-accumulation index (I_{geo}), contamination factor (CF) and pollution load index (PLI), as reported in the following.

2.5.1. *Geo-accumulation index.* The accumulation index is given as:

$$I_{geo} = Log_2[C_n/kB_n] \tag{5}$$

where C_n is the concentration of the potentially hazardous trace element in the sample, Bn is the geochemical background value in average shale (Turekian and Wedepohl 1961) of the element n and k = 1.5 is the background matrix correction factor, that was introduced to account for possible deviations in the background readings due to lithogenic effects. As reported by Naji and Ismail (2011), $I_{geo} \leq 0$ means no contamination; $0 < I_{geo} \leq 1$ no/moderate contamination; $1 < I_{geo} \leq 2$ moderate contamination; $2 < I_{geo} \leq 3$ moderate/strong contamination; $3 < I_{geo} \leq 4$ strong contamination; $4 < I_{geo} \leq 5$ strong/extreme contamination and $I_{geo} > 5$ extreme contamination.

2.5.2. *Contamination factor.* The contamination factor is expressed as reported below:

$$CF = C_{metal}/C_{background} \tag{6}$$

where C_{metal} and $C_{background}$ are the concentration and the background values for each metal, respectively (Håkanson 1980). According to Yuan *et al.* (2012), $CF \leq 1$ indicates no contamination, $1 < CF \leq 3$ low or moderate contamination, $3 < CF \leq 6$ high contamination, $CF > 6$ very high contamination.

2.5.3. *Pollution load index.* The pollution load index is the n-th root of the product of contamination factor (CF) of metals:

$$PLI = (CF_1 \times CF_2 \times CF_3 \times ... \times CF_n)^{1/n} \tag{7}$$

where n is the number of metals (Chandrasekaran *et al.* 2015). As reported by Selvaraj, Ram Mohan, and Szefer (2004), $PLI > 1$ means pollution presence, whereas $PLI < 1$ indicates no pollution.

3. Results and discussion

3.1. Radioactivity analysis. Table 2 reports the mean activity concentrations C_{Ra}, C_{Th}, C_K and C_{Cs} of ^{226}Ra, ^{232}Th, ^{40}K and ^{137}Cs, respectively, in the analyzed beach sands, for all the sampling sites.

TABLE 2. The mean activity concentrations C_{Ra}, C_{Th}, C_K and C_{Cs} in the analyzed beach sands, for all the sampling sites.

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	5.1 ± 0.7	3.8 ± 0.7	46.2 ± 6.7	< 0.09
2	14.1 ± 2.2	19.1 ± 3.1	435 ± 64	< 0.18
3	9.8 ± 1.3	2.8 ± 0.6	30.1 ± 5.3	< 0.11
4	37.2 ± 5.6	18.4 ± 2.9	75.7 ± 11.7	< 0.14

It is worth of note that, in the case of radiocaesium, C_{Cs} was found to be lower than the minimum detectable activity in all cases, thus reasonably excluding any possible man-made radioactive contamination of analyzed samples. From the results, it can be noticed that C_{Ra} ranges between (5.1 ± 0.7) Bq kg^{-1} d.w. (ID1) and (37.2 ± 5.6) Bq kg^{-1} d.w. (ID4); C_{Th} varies from (2.8 ± 0.6) Bq kg^{-1} d.w. (ID3) to (19.1 ± 3.1) Bq kg^{-1} d.w. (ID2); C_K ranges between (30.1 ± 5.3) Bq kg^{-1} d.w. (ID3) and (435 ± 64) Bq kg^{-1} d.w. (ID2).

A comparison between the measured activity concentrations of natural radioisotopes investigated in this study, for each sampling site, and the world average specific activity values for soil, considered as the environmental reference matrix (UNSCEAR 2000), revealed that C_{Ra} is lower than the world average value (*i.e.*, 35 Bq kg^{-1} d.w.) in all cases except for the sampling site ID4; C_{Th} is lower than the world average value, *i.e.*, 30 Bq kg^{-1} d.w., in all cases; C_K is lower than the 420 Bq kg^{-1} d.w. average world concentration for

all the analyzed samples except for those from the sampling site ID2. As widely reported in literature, the different values of C_{Ra}, C_{Th}, and C_K strongly depend on the chemical composition and mineralogical features of the analyzed samples (Suresh *et al.* 2011; Morelli *et al.* 2012; Caridi *et al.* 2023). In detail, the highest values of C_{Ra}, C_{Th}, and C_K, could be due to the presence of ilmenites, almandine-rich garnets and K-feldspar, respectively, as main radioisotope-bearing minerals present in the analyzed samples (Caridi *et al.* 2022). Anyway, further investigations about the chemical and mineralogical composition of the investigated beach sands through analytical techniques such as X-Ray Fluorescence (XRF) spectroscopy, Micro-Raman Scattering (MRS) and X-ray Diffraction (XRD) will be carried out in the next future.

3.2. Evaluation of radiological hazard effects. The calculated values of the radiological hazard indices are reported in Table 3.

TABLE 3. Calculated values of D, $AEDE_{out}$ and $ELCR$ for the analyzed beach sands, for all the sampling sites.

Site ID	D (nGy h^{-1})	$AEDE_{out}$ (μSv y^{-1})	ELCR ($\times 10^{-3}$)
1	6.6	8.1	0.03
2	36.2	44.4	0.16
3	7.5	9.2	0.03
4	31.5	38.6	0.14

In particular, D varies in the range between 6.6 nGy h^{-1} (ID1) and 36.2 nGy h^{-1} (ID2). Such differences can be ascribed to the diverse content of natural radionuclides in the mineral phases of which the analyzed beach sands are made of (Morelli *et al.* 2012). Going on, values of $AEDE_{out}$ are in the 8.1 μSv y^{-1} (ID1) $-$ 44.4 μSv y^{-1} (ID2) range, lower than the world average value of 70 μSv y^{-1} set for soil (UNSCEAR 2000) in all cases, and much lower than the threshold level provided by the Italian legislation (Legislation 2020) for the public (0.3 mSv y^{-1}), thus confirming no hazard effects for the local population from the radiological point of view. Finally, $ELCR$ values are 0.03×10^{-3}, 0.16×10^{-3}, 0.03×10^{-3} and 0.14×10^{-3} for site IDs 1, 2, 3 and 4, respectively. It is important to underline that the assessment of the radiological hazards for the public, only on the basis of $ELCR$, is not possible, since reliable and standardized mortality and morbidity statistics are not accessible.

3.3. Metals analysis and assessment of the level of metals contamination. Table 4 reports the metals content (μg g^{-1} d.w.) in the analyzed beach sands, for all the sampling sites.

Noteworthy, in the case of Cd, Hg and Tl, a concentration lower than the minimum detectable one in all samples was found, while the measured concentrations of all the remaining detected metals turned out to be lower than the contamination thresholds values (Legislation 2006) in all cases. Going on, Table 5 reports I_{geo}, CF and PLI values, as calculated through Eqs. (5-7) that are lower than 0, 1 and 1, respectively, in all cases.

TABLE 4. Metals content (μg g^{-1} d.w.) in the analyzed beach sands, as obtained through ICP-MS analysis.

ICP-MS Analysis

	Site ID				
	1	2	3	4	Threshold limit
Cd (μg g^{-1}d.w.)	< 0.1	< 0.1	< 0.1	< 0.1	2
Co (μg g^{-1}d.w.)	2.7	4.3	0.6	9.8	20
Hg (μg g^{-1}d.w.)	< 0.05	< 0.05	< 0.05	< 0.05	1
Ni (μg g^{-1}d.w.)	5.4	13.1	2.2	21.4	120
Pb (μg g^{-1}d.w.)	3.7	4.4	2.4	10.6	100
Cu (μg g^{-1}d.w.)	2.6	10.2	2.5	10.8	120
Tl (μg g^{-1}d.w.)	< 0.1	< 0.1	< 0.1	< 0.1	1
V (μg g^{-1}d.w.)	11.1	28.9	7.8	32.9	90
Zn (μg g^{-1}d.w.)	18.5	32.6	9.5	45.5	150

Thus, in the light of the above reported results, all recorded metals cannot be considered as pollutants for the investigated samples, and, for this reason, they do not constitute a risk to human health.

4. Conclusions

The natural and anthropogenic radioactivity and metals content of beach sands from the Sicily region, Southern Italy, were investigated through High Purity Germanium (HPGe) gamma-ray spectrometry and Inductively Coupled Plasma Mass Spectrometry (ICP-MS). The assessment of the absorbed gamma dose rate (D), annual effective dose equivalent outdoor ($AEDE_{out}$) and excess lifetime cancer risk ($ELCR$), was accomplished with the aim to evaluate any possible radiological health risk for tourists or inhabitant population. Moreover, the ecological risk imposed on the ecosystems by detected metals was assessed through different pollution indices, *i.e.*, geo-accumulation index (I_{geo}), contamination factor (CF) and pollution load index (PLI).

TABLE 5. Calculated values of I_{geo}, CF and PLI for the analyzed beach sands, for all the sampling sites.

Site ID	Metal	Index of contamination		
		I_{geo}	CF	PLI
1	Co	−3.40	0.14	0.07
	Ni	−4.24	0.08	
	Pb	−3.02	0.19	
	Cu	−4.70	0.06	
	V	−4.13	0.09	
	Zn	−2.95	0.19	
2	Co	−2.73	0.23	0.18
	Ni	−2.96	0.19	
	Pb	−2.77	0.22	
	Cu	−2.73	0.23	
	V	−2.75	0.22	
	Zn	−2.13	0.34	
3	Co	−5.57	0.03	0.03
	Ni	−5.53	0.03	
	Pb	−3.64	0.12	
	Cu	−4.75	0.06	
	V	−4.64	0.06	
	Zn	−3.91	0.10	
4	Co	−1.54	0.52	0.30
	Ni	−2.25	0.31	
	Pb	−1.50	0.53	
	Cu	−2.64	0.24	
	V	−2.57	0.25	
	Zn	−1.65	0.48	

As conclusions, i) $AEDE_{out}$ was found to be lower than the threshold level provided by the Italian legislation for the public, therefore reasonably excluding radiological hazard effects; ii) I_{geo}, CF and PLI values indicated that no contamination due to the investigated metals is present in the analysed samples.

It is worth of note that the used approach could be used, in principle, for the assessment of the chemical risk due to the occurrence of potentially harmful elements in a wide variety of environmental specimens. This would provide a guideline for further investigations specifically focused on the monitoring of the environmental quality. Finally, this study has some limitations associated with the limited number of sampling points and tested heavy metals. To overcome such limitations, in the forthcoming period, the present paper will consider the establishment of an augmented number of sampling sites, with the objective of achieving a more comprehensive and representative network across the entire region. Furthermore, the inclusion of a greater number of metals will also be contemplated.

References

ACCREDIA (2021). URL: https://www.accredia.it/.

Ali, H., Khan, E., and Ilahi, I. (2019). "Environmental Chemistry and Ecotoxicology of Hazardous Heavy Metals: Environmental Persistence, Toxicity, and Bioaccumulation". *Journal of Chemistry* **2019**, 6730305. DOI: 10.1155/2019/6730305.

Avwiri, G. O. and Egieya, J. M. (2013). "Radiometric assay of hazard indices and excess lifetime cancer risk due to natural radioactivity in soil profile in Ogba/Egbema/Ndoni local government area of Rivers state, Nigeria". *Academic Research International* **4**, 54–65.

Balali-Mood, M., Naseri, K., Tahergorabi, Z., Khazdair, M. R., and Sadeghi, M. (2021). "Toxic Mechanisms of Five Heavy Metals: Mercury, Lead, Chromium, Cadmium, and Arsenic". *Frontiers in Pharmacology* **12**, 227. DOI: 10.3389/fphar.2021.643972.

Briffa, J., Sinagra, E., and Blundell, R. (2020). "Heavy metal pollution in the environment and their toxicological effects on humans". *Heliyon* **6**, e04691. DOI: 10.1016/j.heliyon.2020.e04691.

Caridi, F., D'Agostino, M., Belvedere, A., Marguccio, S., Belmusto, G., and Gatto, M. F. (2016a). "Diagnostics techniques and dosimetric evaluations for environmental radioactivity investigations". *Journal of Instrumentation* **11**. DOI: 10.1088/1748-0221/11/10/C10012.

Caridi, F., D'Agostino, M., Messina, M., Marcianò, G., Grioli, L., Belvedere, A., Marguccio, S., and Belmusto, G. (2017a). "Lichens as environmental risk detectors". *The European Physical Journal Plus* **132**. DOI: 10.1140/epjp/i2017-11459-y.

Caridi, F., Di Bella, M., Sabatino, G., Belmusto, G., Fede, M. R., Romano, D., Italiano, F., and Mottese, A. (2021). "Assessment of natural radioactivity and radiological risks in river sediments from Calabria (Southern Italy)". *Applied Sciences* **11**, 1–14. DOI: 10.3390/app11041729.

Caridi, F., Marguccio, S., D'Agostino, M., Belvedere, A., and Belmusto, G. (2016b). "Natural radioactivity and metal contamination of river sediments in the Calabria region, south of Italy". *The European Physical Journal Plus* **131**, 1–10. DOI: 10.1140/epjp/i2016-16155-x.

Caridi, F., Marguccio, S., Durante, G., Trozzo, R., Fullone, F., Belvedere, A., D'Agostino, M., and Belmusto, G. (2017b). "Natural radioactivity measurements and dosimetric evaluations in soil samples with a high content of NORM". *The European Physical Journal Plus* **132**, 56. DOI: 10.1140/epjp/i2017-11343-x.

Caridi, F., Messina, M., Belvedere, A., D'Agostino, M., Marguccio, S., Settineri, L., and Belmusto, G. (2019). "Food salt characterization in terms of radioactivity and metals contamination". *Applied Sciences* **14**, 2882. DOI: 10.3390/app9142882.

Caridi, F., Messina, M., and D'Agostino, M. (2017). "An investigation about natural radioactivity, hydrochemistry, and metal pollution in groundwater from Calabrian selected areas, southern Italy". *Environmental Earth Sciences* **76**, 668. DOI: 10.1007/s12665-017-7031-9.

Caridi, F., Paladini, G., Marguccio, S., Belvedere, A., D'Agostino, M., Messina, M., Crupi, V., Venuti, V., and Majolino, D. (2023). "Evaluation of Radioactivity and Heavy Metals Content in a Basalt Aggregate for Concrete from Sicily, Southern Italy: A Case Study". *Applied Sciences* **13**, 4804. DOI: 10.3390/app13084804.

Caridi, F., Spoto, S. E., Paladini, G., Venuti, V., Crupi, V., Ricca, M., and Majolino, D. (2022). "Natural radioactivity content and mineralogical composition of beach sands from the Gulf of Squillace, Southern Italy: a case study". *Atti della Accademia Peloritana dei Pericolanti. Classe di Scienze Fisiche, Matematiche e Naturali* **100**(2), A11 [13 pages]. DOI: 10.1478/AAPP.1002A11.

Caridi, F., Testagrossa, B., and Acri, G. (2021). "Elemental composition and natural radioactivity of refractory materials". *Environmental Earth Sciences* **80**, 170. DOI: 10.1007/s12665-021-09430-y.

Caridi, F., Torrisi, L., and Giuffrida, L. (2010). "Time-of-flight and UV spectroscopy characterization of laser-generated plasma". *Nuclear Instruments and Methods in Physics Research Section B* **268**(5), 499–505. DOI: 10.1016/j.nimb.2009.11.018.

Caridi, F., Torrisi, L., Margarone, D., and Borrielli, A. (2008). "Investigations on low temperature laser-generated plasmas". *Laser and Particle Beams* **26**(2), 265–271. DOI: 10.1017/S0263034608000311.

Caridi, F., Torrisi, L., Mezzasalma, A. M., Mondio, G., and Borrielli, A. (2009). "Al_2O_3 plasma production during pulsed laser deposition". *The European Physical Journal D* **54**(2), 467–472. DOI: 10.1140/epjd/e2009-00052-6.

Chandrasekaran, A., Ravisankar, R., Harikrishnan, N., Satapathy, K. K., Prasad, M. V. R., and Kanagasabapathy, K. V. (2015). "Multivariate statistical analysis of heavy metal concentration in soils of Yelagiri Hills, Tamilnadu, India – Spectroscopical approach". *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* **137**, 589–600. DOI: 10.1016/j.saa.2014.08.093.

Eckert-Ziegler (2020). *Calibration Sources*. URL: https://www.ezag.com/products/isotope-products/.

Fazio, E., Mezzasalma, A. M., Mondio, G., Serafino, T., Barreca, F., and Caridi, F. (2011). "Optical and structural properties of pulsed laser ablation deposited ZnO thin film". *Applied Surface Science* **257**(6), 2298–2302. DOI: 10.1016/j.apsusc.2010.09.092.

Fouskas, F., Godelitsas, A., Argyraki, A., Pappa, F. K., and Tsabaris, C. (2018). "Metal concentrations and radioactivity in sediments at the northern coastal zone of Ikaria Island, eastern Mediterranean, Greece". *Journal of Radioanalytical and Nuclear Chemistry* **317**, 55–68. DOI: 10.1007/s10967-018-5843-z.

Günoğlu, K. and Seçkiner, S. (2018). "Evaluation of dose parameters and radiological hazards in gravel samples of Konyaaltı Beach, Antalya". *Arabian Journal of Geosciences* **11**, 417. DOI: 10.1007/s12517-018-3801-2.

Håkanson, L. (1980). "An Ecological Risk Index for Aquatic Pollution Control – A Sedimentological Approach". *Water Research* **14**, 975–1001. DOI: 10.1016/0043-1354(80)90143-8.

ICRP (2012). "Compendium of Dose Coefficients based on ICRP Publication 60". *Annals of the ICRP* **41** (Supplement 1). ICRP Publication 119. URL: https://www.icrp.org/publication.asp?id=ICRP%20Publication%20119.

Iwuoha, G. N., Osuji, L., and Horsfall, M. J. (2012). "Index model analysis approach to heavy metal pollution assessment in sediments of Nworie and Otamiri Rivers in Imo State of Nigeria". *Research Journal of Chemical Sciences* **2**(8), 1–8. URL: https://www.isca.me/rjcs/Archives/v2/i8/1.ISCA-RJCS-2011-182.php.

Jaafar, L., Podolsky, R. H., and Dynan, W. S. (2013). "Long-Term Effects of Ionizing Radiation on Gene Expression in a Zebrafish Model". *PLoS One* **8**(7), e69445, 1–10. DOI: 10.1371/journal.pone.0069445.

Jaishankar, M., Tseten, T., Anbalagan, N., Mathew, B. B., and Beeregowda, K. N. (2014). "Toxicity, mechanism and health effects of some heavy metals". *Interdisciplinary Toxicology* **7**(2), 60–72. DOI: 10.2478/intox-2014-0009.

Kamiya, K., Ozasa, K., Akiba, S., Niwa, O., Kodama, K., Takamura, N., Zaharieva, E., Kimura, Y., and Wakeford, R. (2015). "Long-term effects of radiation exposure on health". *The Lancet* **386** (9992), 469–478. DOI: 10.1016/S0140-6736(15)61167-9.

Legislation (2006). *Italian D. Lgs. 152/2006*.

Legislation (2020). *Italian D. Lgs. 101/20*.

Lentini, F. and Carbone, S. (2014). *Geologia della Sicilia*. Mem. Descr. Carta Geol. d'It., XCV, figg. 533, tavv. 5, tabb. 5, 1 Carta Geologica f.t. ISPRA, pp. 7–414.

Liang, L. and Gong, P. (2020). "Urban and air pollution: a multi-city study of long-term effects of urban landscape patterns on air quality trends". *Scientific Reports* **10**, 18618. DOI: 10.1038/s41598-020-74524-9.

Margarone, D., Torrisi, L., Borrielli, A., and Caridi, F. (2008). "Silver plasma by pulsed laser ablation". *Plasma Sources Science and Technology* **17**(3), 035019. DOI: 10.1088/0963-0252/17/3/035019.

Masindi, V. and Muedi, K. (2018). "Environmental Contamination by Heavy Metals". In: *Heavy Metals*. Ed. by H. Saleh and R. Aglan. IntechOpen. Chap. 7, pp. 115–133. DOI: 10.5772/intechopen.76082.

Mezzasalma, A. M., Mondio, G., Serafino, T., Caridi, F., and Torrisi, L. (2009). "Electronic properties of thin films of laser-ablated Al_2O_3". *Applied Surface Science* **255**(7), 4123–4128. DOI: 10.1016/j.apsusc.2008.10.116.

Morelli, D., Immé, G., Cammisa, S., Catalano, R., Mangano, G., La Delfa, S., and Patanè, G. (2012). "Radioactivity measurements in volcano-tectonic area for geodynamic process study". *EPJ Web of Conferences*. Environmental Physics **24**, 05009: *Environmental Radioactivity 2010*. DOI: 10.1051/epjconf/20122405009.

Naji, A. and Ismail, A. (2011). "Assessment of Metals Contamination in Klang River Surface Sediments by using Different Indexes". *EnvironmentAsia* **4**, 30–38. DOI: 10.14456/ea.2011.5.

Omar-Nazir, L., Shi, X., Moller, A., Mousseau, T., Byun, S., Hancock, S., Seymour, C., and Mothersill, C. (2018). "Long-term effects of ionizing radiation after the Chernobyl accident: Possible contribution of historic dose". *Environmental Research* **165**, 55–62. DOI: 10.1016/j.envres.2018.04.005.

Papadopoulos, A., Christofides, G., Koroneos, A., and Stoulos, S. (2014). "Natural radioactivity distribution and gamma radiation exposure of beach sands from Sithonia Peninsula". *Central European Journal of Geosciences* **6**, 229–242. DOI: 10.2478/s13533-012-0157-0.

Pappa, F. K., Tsabaris, C., Ioannidou, A., Patiris, D. L., Kaberi, H., Pashalidis, I., Eleftheriou, G. E., Androulakaki, E. G., and Vlastou, R. (2016). "Radioactivity and metal concentrations in marine sediments associated with mining activities in Ierissos Gulf, North Aegean Sea, Greece". *Applied Radiation and Isotopes* **116**, 22–33. DOI: 10.1016/j.apradiso.2016.07.006.

Pappa, F. K., Tsabaris, C., Patiris, D. L., Eleftheriou, G. E., Ioannidou, A., Androulakaki, E. G., Kokkoris, M., and Vlastou, R. (2019). "Temporal investigation of radionuclides and heavy metals in a coastal mining area at Ierissos Gulf, Greece". *Environmental Science and Pollution Research* **26**, 27457–27469. DOI: 10.1007/s11356-019-05921-5.

Ravisankar, R., Chandramohan, J., Chandrasekaran, A., Prince Prakash Jebakumar, J., Vijayalakshmi, I., Vijayagopal, P., and Venkatraman, B. (2015). "Assessments of radioactivity concentration of natural radionuclides and radiological hazard indices in sediment samples from the East coast of Tamilnadu, India with statistical approach". *Marine Pollution Bulletin* **97**, 419–430. DOI: 10.1016/j.marpolbul.2015.05.058.

Ravisankar, R., Chandrasekaran, A., Vijayagopal, P., Venkatraman, B., Senthilkumar, G., Eswaran, P., and Rajalakshmi, A. (2012). "Natural radioactivity in soil samples of Yelagiri Hills, Tamil Nadu, India and the associated radiation hazards". *Radiation Physics and Chemistry* **81**, 1789–1795. DOI: 10.1016/j.radphyschem.2012.07.003.

Rosell, J. R., Ortega, X., and Dies, X. (1991). "Natural and artificial radionuclides on the northeast coast of Spain". *Health Physics* **60**, 709–712. DOI: 10.1097/00004032-199105000-00010.

Selvaraj, K., Ram Mohan, V., and Szefer, P. (2004). "Evaluation of metal contamination in coastal sediments of the Bay of Bengal, India: geochemical and statistical approaches". *Marine Pollution Bulletin* **49**, 174–185. DOI: 10.1016/j.marpolbul.2004.02.006.

Shahrokhi, A., Adelikhah, M., Chalupnik, S., and Kovács, T. (2021). "Multivariate statistical approach on distribution of natural and anthropogenic radionuclides and associated radiation indices along the north-western coastline of Aegean Sea, Greece". *Marine Pollution Bulletin* **163**, 112009. DOI: 10.1016/j.marpolbul.2021.112009.

Suresh, G., Ramasamy, V., Meenakshisundaram, V., Venkatachalapathy, R., and Ponnusamy, V. (2011). "Influence of mineralogical and heavy metal composition on natural radionuclide concentrations in the river sediments". *Applied Radiation and Isotopes* **69**(10), 1466–1474. DOI: 10.1016/j.apradiso.2011.05.020.

Torrisi, L., Caridi, F., and Giuffrida, L. (2011). "Protons and ion acceleration from thick targets at 10^{10} W/cm^2 laser pulse intensity". *Laser and Particle Beams* **29**(1), 29–37. DOI: 10.1017/S0263034610000728.

Torrisi, L., Margarone, D., Borrielli, A., and Caridi, F. (2008). "Ion and photon emission from laser-generated titanium-plasma". *Applied Surface Science* **254**(13), 4007–4012. DOI: 10.1016/j.apsusc.2007.12.031.

Torrisi, L., Visco, A. M., Campo, N., and Caridi, F. (2010). "Pulsed laser treatments of polyethylene films". *Nuclear Instruments and Methods in Physics Research Section B* **268**(19), 3117–3121. DOI: 10.1016/j.nimb.2010.05.067.

Turekian, K. K. and Wedepohl, K. H. (1961). "Distribution of the Elements in Some Major Units of the Earth's Crust". *GSA Bulletin* **72**(2), 175–192. DOI: 10.1130/0016-7606(1961)72[175:DOTEIS]2.0.CO;2.

U.S. EPA. (2007). *Method 3051A (SW-846): Microwave Assisted Acid Digestion of Sediments, Sludges, and Oils (Revision 1)*. Washington, D.C. URL: https://www.epa.gov/esam/us-epa-method-3051a-microwave-assisted-acid-digestion-sediments-sludges-and-oils.

U.S. EPA. (2014). *Method 6020B (SW-846): Inductively Coupled Plasma-Mass Spectrometry (Revision 2)*. Washington, D.C. URL: https://www.epa.gov/esam/epa-method-6020b-sw-846-inductively-coupled-plasma-mass-spectrometry.

United Nations Scientific Committee on the Effects of Atomic Radiation (2000). *Sources and Effects of Ionizing Radiation*. URL: https://www.unscear.org/docs/publications/2000/UNSCEAR_2000_Report_Vol.I.pdf.

Walencik-Łata, A. and Smolka-Danielowska, D. (2020). "^{234}U, ^{238}U, ^{226}Ra, ^{228}Ra and ^{40}K concentrations in feed coal and its combustion products during technological processes in the Upper Silesian Industrial Region, Poland". *Environmental Pollution* **267**, 115462. DOI: 10.1016/j.envpol.2020.115462.

Yuan, H., Song, J., Li, X., Li, N., and Duan, L. (2012). "Distribution and contamination of heavy metals in surface sediments of the South Yellow Sea". *Marine Pollution Bulletin* **64**, 2151–2159. DOI: https://doi.org/10.1016/j.marpolbul.2012.07.040.

---

[a] Università degli Studi di Messina,
Dipartimento di Scienze Matematiche e Informatiche, Scienze Fisiche e Scienze della Terra,
Viale F. Stagno d'Alcontres 31, 98166 Messina, Italy

[b] Agenzia Regionale per la Protezione dell'Ambiente della Calabria (ARPACal),
Dipartimento di Reggio Calabria,
Via Troncovito SNC, 89135 Reggio Calabria, Italy

* To whom correspondence should be addressed | email: fcaridi@unime.it

Communicated 6 May 2024; manuscript received 14 June 2024; published online 10 February 2025