

# A New Methodological Approach for the Assessment of the $^{238}\text{U}$ Content in Drinking Water

Francesco Caridi <sup>1,\*</sup>, Giuseppe Paladini <sup>1,\*</sup>, Valentina Venuti <sup>1,\*</sup>, Vincenza Crupi <sup>1</sup>,  
Sebastiano Ettore Spoto <sup>1</sup>, Santina Marguccio <sup>2</sup>, Maurizio D'Agostino <sup>2</sup>, Alberto Belvedere <sup>2</sup>  
and Domenico Majolino <sup>1</sup>

<sup>1</sup> Dipartimento di Scienze Matematiche e Informatiche, Scienze Fisiche e Scienze della Terra, Università degli Studi di Messina, Viale Ferdinando Stagno D'Alcontres 31, 98166 Messina, Italy; vcrupi@unime.it (V.C.); sebastianoettore@gmail.com (S.E.S.); dmajolino@unime.it (D.M.)

<sup>2</sup> Agenzia Regionale per la Protezione dell'Ambiente della Calabria (ARPACal)—Dipartimento di Reggio Calabria, Via Troncovito SNC, 89135 Reggio Calabria, Italy; s.marguccio@arpacal.it (S.M.); m.dagostino@arpacal.it (M.D.); a.belvedere@arpacal.it (A.B.)

\* Correspondence: fcaridi@unime.it (F.C.); gpaladini@unime.it (G.P.); vvenuti@unime.it (V.V.)

**Abstract:** The radiological quality of drinking water is directly associated with the health of the population. Indeed, it is well known that the presence of radionuclides in drinking water constitutes a health risk for humans because the consumption of such water increases the likelihood of incurring cancer. For this reason, all the studies aimed at developing new methodologies for the qualitative and quantitative analysis of the radioisotopic composition of drinking water are absolutely desired by the international scientific community, as well as by the institutes that deal with the protection of public health. In this paper, a new methodological approach was developed for the evaluation of the  $^{238}\text{U}$  content in drinking water. A sample coming from Paola, Calabria region, southern Italy, was taken as a case study. The assessment was performed by using High Purity Germanium (HPGe) gamma-ray spectrometry, with the aim of quantifying the specific activity of the  $^{234\text{m}}\text{Pa}$  radioisotope after a preconcentration procedure, and thus to assess the activity concentration of  $^{238}\text{U}$ , in the hypothesis of the secular radioactive equilibrium between it and its daughter. The obtained results were validated through the comparison with the  $^{238}\text{U}$  ( $\mu\text{g}/\text{L}$ ) concentration as measured with Inductively Coupled Plasma-Mass Spectrometry (ICP-MS).

**Keywords:** drinking water; radioactivity; uranium; High Purity Germanium (HPGe) gamma-ray spectrometry; Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)



**Citation:** Caridi, F.; Paladini, G.; Venuti, V.; Crupi, V.; Spoto, S.E.; Marguccio, S.; D'Agostino, M.; Belvedere, A.; Majolino, D. A New Methodological Approach for the Assessment of the  $^{238}\text{U}$  Content in Drinking Water. *Appl. Sci.* **2022**, *12*, 3380. <https://doi.org/10.3390/app12073380>

Academic Editor: Anna Annibaldi

Received: 3 March 2022

Accepted: 25 March 2022

Published: 26 March 2022

**Publisher's Note:** MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



**Copyright:** © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

## 1. Introduction

As is well known, the study of natural radioactivity, due to the presence of primordial radionuclides in the Earth's crust and to cosmogenics [1,2], provides information on the radiological risk for the population and on the variations in background radiation due to nuclear activities, industries, power plants, etc. [3,4]. In this context, environmental monitoring of natural radionuclides and their progeny has received considerable attention around the world [5,6]. Although the environmental aspects of natural radioactivity have been discussed in numerous scientific publications [7–10], the presence of natural radioisotopes in drinking water as a hazard factor for the public has not yet been addressed in sufficient detail [11,12]. It is well known that water is very important for our life, since it constitutes from 50% to 60% of the weight of our body, playing an active role in all its vital processes [13]. For this reason, water must be free from pollutants that could pose a risk to human health [14]. Water quality assurance is therefore one of the most important issues in environmental programs to protect public health [15,16]. The Italian Legislative Decree 28/2016 constitutes the current national legislative reference for the quality of water intended for human consumption as regards radioactivity. It regulates the

modalities of control of radionuclides by means of indicator parameters [17]. Among the natural radioisotopes to be controlled,  $^{238}\text{U}$  is certainly one of the most significant, given the predominant role assumed in the determination of the gross alpha activity concentration, and therefore of the total Indicative Dose (ID) [18].

As a matter of fact, the concentration of uranium in water depends on many factors, including the type of rock of the host aquifer, the presence of oxygen and complexing agents, the chemicals present in the aquifer, the chemical reactions with the ions in solution and the natural contact between uranium ores and water [19]. For example, if the bedrock consists mainly of uranium-rich granitoids and granites and contains soft and slightly alkaline bicarbonate waters, uranium is highly soluble under oxidizing conditions over a wide pH range [20]. Generally, the uranium content of natural water can range from trace levels to 600  $\mu\text{g}/\text{L}$  or more [21].

This article reports a new methodological approach, developed in order to evaluate the  $^{238}\text{U}$  content in a drinking water sample from Paola, Calabria region, southern Italy, taken as a case study. The evaluation was carried out through High Purity Germanium (HPGe) gamma-ray spectrometry measurements, with the aim of quantifying the specific activity of the natural radionuclide  $^{234\text{m}}\text{Pa}$  after preconcentration and therefore of evaluating the activity concentration of  $^{238}\text{U}$ , in secular radioactive equilibrium with its daughter. Generally, such a condition occurs when the half-life of the child radionuclide is much shorter than that of the parent radionuclide. In our case, as the half-life of  $^{234\text{m}}\text{Pa}$  (child) and  $^{238}\text{U}$  (parent) are equal to 69.5 s and  $141 \times 10^{15}$  s, respectively, their secular radioactive equilibrium can be reasonably hypothesized [22,23]. Although the  $^{238}\text{U}$  is a pure alpha-emitter radionuclide, the choice of using HPGe gamma spectrometry with respect to other alpha-based techniques, i.e., alpha spectrometry or liquid scintillation, is due to a more simplified overall analytical activity. The obtained results were then validated by a comparison with the concentration of  $^{238}\text{U}$  ( $\mu\text{g}/\text{L}$ ) determined by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) analysis.

## 2. Materials and Methods

### 2.1. Geological Notes, Sampling and Treatment

A representative sample of drinking water was collected, in three different aliquots, in a water tank at Paola, a selected location of the Calabria region, southern Italy. The GPS coordinates of the sampling point, indicated in the map reported in Figure 1, are 39.351132 (latitude) and 16.038091 (longitude).

The geology of the area around Paola (Figure 2) is mainly composed of heterogeneous crystalline–metamorphic rocks and their related weathering products [24]. Crystalline–metamorphic rocks are indeed affected by weathering processes, which are responsible for their chemical and mechanical transformation when interacting with the atmosphere, the hydrosphere and the biosphere [25].

As reported in the published cartography [24] and several research studies [24,25], marble, phyllarenites, muscovite-biotite gneiss, garnet and epidote micaschists, foliated and laminated granites, conglomerates, arenites and alluvial sediments crop out in the area surrounding the city of Paola. The high uranium concentration in the local drinking water can be explained according to the mineralogical composition of the surrounding area. In particular, with biotite having a relevant role in the sorption of radionuclides in granitic rocks, the high content of biotite can cause uranium enrichment [26]. Moreover, epidote minerals, with their structure composed of endless chains of edge-sharing octahedra that are crosslinked by isolated  $\text{SiO}_4$  tetrahedra and  $\text{Si}_2\text{O}_7$  groups, can incorporate significant amounts of geochemically important trace elements such as uranium [27].



Figure 1. The map of the Calabria region, southern Italy, with the sampling point indicated.

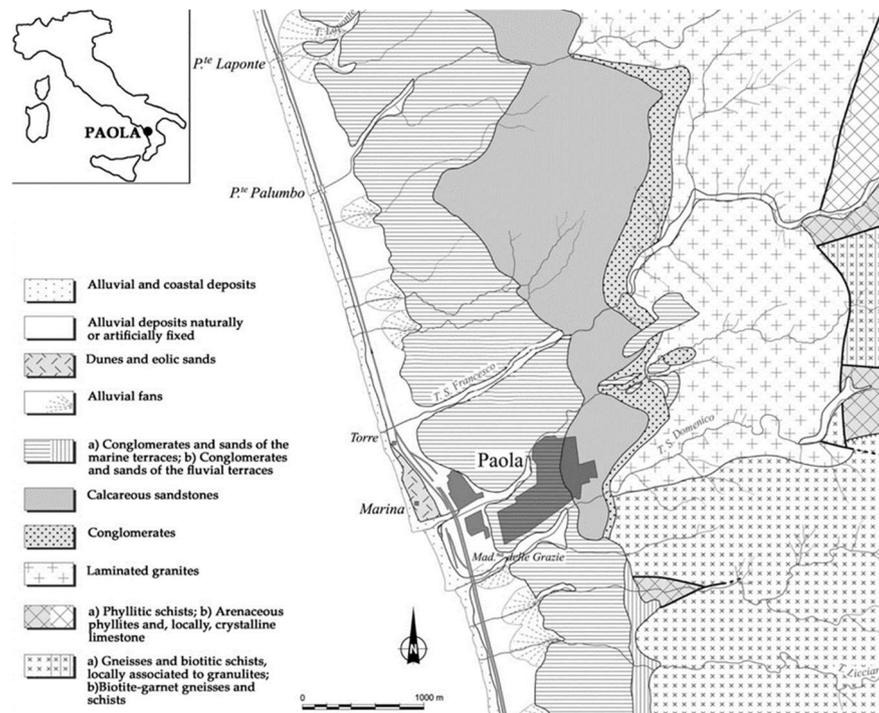


Figure 2. The geological map of the area around Paola, Calabria region, southern Italy.

Each aliquot of drinking water was collected into a 750 mL acidified polyethylene bin, in order to avoid radionuclide precipitation and adsorption on the container walls, and then stored in the laboratory for the sample preparation and analysis. Before use, each beaker was first soaked with diluted nitric acid, then washed, rinsed with distilled water

and finally left to dry in the oven to prevent contamination [28]. In the laboratory, the first aliquot was taken as it was, while the other two were evaporated on a plate in order to reach: (i) a final volume of 250 mL, i.e., factor of preconcentration equal to 3, for the second aliquot and (ii) a final volume of 20 mL, i.e., factor of preconcentration equal to 37.5, for the third aliquot. The volumes of 250 mL and 20 mL correspond to the two sample holder geometries available for the gamma spectrometry analyses [29].

## 2.2. Diagnostics Techniques and Samples Measurements

### 2.2.1. High Purity Germanium (HPGe) Gamma-Ray Spectrometry

For the gamma spectrometry analysis, the first aliquot, as it was, and the second one, preconcentrated, were inserted in a Marinelli container with a volume of 250 mL, while the third one, preconcentrated, was stored in a 20 mL vial. After that, they were counted for 70,000 s and spectra were analyzed in order to obtain the activity concentration of  $^{238}\text{U}$  by means of that of its daughter  $^{234\text{m}}\text{Pa}$ , with which uranium is in secular equilibrium. The 1001.03 keV gamma-ray line was used to determine  $^{234\text{m}}\text{Pa}$  specific activity.

The experimental set-up was composed of a positive biased Ortec HPGe detector (GMX), whose operating parameters are reported in Table 1.

**Table 1.** The HPGe GMX operating parameters.

HPGe GMX Detector	
Parameter	Value
Full Width at Half Maximum	1.94 keV
Peak to Compton ratio	65:1
Relative efficiency	37.5% (at the 1.33 MeV $^{60}\text{Co}$ $\gamma$ -line)
Bias voltage	−4800 V
Energy range	5 keV–2 MeV

It was placed inside lead wells to shield the background radiation environment. It is worth noting that, for the sample holder geometry of 250 mL, efficiency and energy calibrations were performed using a multipeak Marinelli geometry gamma source (BC-4464) of 250 mL capacity, covering the energy range 60–1836 keV, customized to reproduce the exact geometries of samples in a water-equivalent epoxy resin matrix. Moreover, the ANGLE 4 code was employed for the efficiency transfer factors calculations to the 20 mL vial sample holder geometry [30]. The Gamma Vision (Ortec) software was used for data acquisition and analysis [31].

The activity concentration of the investigated radioisotope was calculated using the following formula [32,33]

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

where  $N_E$  indicates the net area of the radioisotope photopeak,  $\varepsilon_E$  and  $\gamma_d$  are the efficiency and yield of the photopeak, respectively,  $V$  is the volume of the sample (L) and  $t$  is the live time (s).

The measurement result uncertainty, coverage factor  $k = 2$ , was calculated taking into account the following components: uncertainty of the counting estimation, of the calibration source, of the efficiency calibration, of the background subtraction and of the  $\gamma$ -branching ratio [34].

The quality of the gamma spectrometry experimental results was certified by the Italian Accreditation Body (ACCREDIA) [35].

### 2.2.2. Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)

The concentration of  $^{238}\text{U}$  was obtained through ICP-MS analysis with a Thermo Scientific iCAP Qc ICP-MS. 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 operated in a single collision cell mode, with kinetic energy discrimination (KED), using pure He as collision gas. All samples were presented for analysis using a Cetac ASX-520. The iCAP Qc ICP-MS operated in a single KED mode using the parameters reported in Table 2 [36]. For the “direct analysis” of analytes in drinking water where sample turbidity is <1 NTU, the sample was prepared by the appropriate addition of nitric acid (1%).

**Table 2.** The iCAP Qc ICP-MS operating parameters.

iCAP Qc Detector	
Parameter	Value
Nebulizer gas	0.98 L/min
Auxiliary gas	0.8 L/min
Collision cell gas He	4.5 mL/min
Point per peak	One
Forward power	1550 W
Cool gas flow	14.0 L/min
Optimized dwell time for analyte	0.01 s
Repeat per sample	Three
Sample uptake/wash time	45 s each

Sample material in solution was introduced by pneumatic nebulization into a radiofrequency plasma where energy transfer processes cause desolvation, atomization and ionization. Ions were extracted from the plasma through a differentially pumped vacuum interface and separated on the basis of their mass-to-charge ratio by a quadrupole mass spectrometer having a minimum resolution capability of 1 amu peak width at 5% peak height. Ions transmitted through the quadrupole were detected by an electron multiplier or Faraday detector and the ion information processed by a data handling system. Interferences relating to the technique had to be identified and corrected. Such corrections included compensation for isobaric elemental interferences and interferences from polyatomic ions derived from the plasma gas, reagents or sample matrix. Instrumental drift as well as suppressions or enhancements of instrument response caused by the sample matrix were corrected for using internal standards [36].

The quality of the ICP-MS results was certified by the Italian Accreditation Body (ACCREDIA) [35].

The massic elemental concentrations in µg/L for uranium was converted in  $^{238}\text{U}$  activity concentration, according to the following formula [37]

$$C = \frac{\lambda N_A f}{MK} F \quad (2)$$

where  $C$  is the measured specific activity (Bq/L) of the radionuclide under consideration,  $\lambda$  the decay constant of the measured isotope of element ( $\text{s}^{-1}$ ),  $N_A$  the Avogadro's number,  $f$  the fractional atomic abundance in nature,  $M$  the atomic mass (kg/mol),  $K$  a constant with value of  $10^6$  for U and  $F$  the fraction of element in the sample.

### 2.3. Accuracy Assessment

In order to assess the accuracy of the experimental  $^{238}\text{U}$  specific activity obtained by the new methodological approach here proposed, a comparison between HPGe gamma spectrometry and ICP-MS results was performed through the z-score calculation, according to [38]

$$z = \frac{x - X}{\sqrt{u_x^2 + U_x^2}} \quad (3)$$

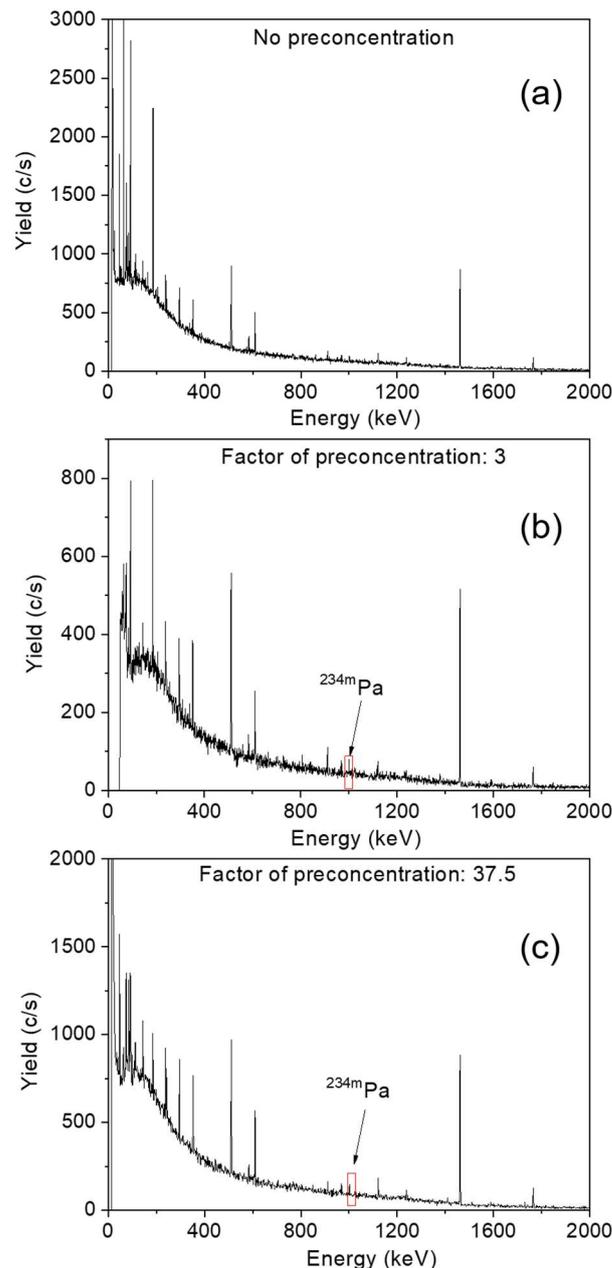
where  $x$  is the  $^{238}\text{U}$  activity concentration obtained by HPGe gamma spectrometry,  $X$  the  $^{238}\text{U}$  concentration (in µg/L) obtained by ICP-MS and then converted into specific activity

through Equation (2),  $u_x$  the total uncertainty of the HPGe gamma spectrometry results (at a coverage factor  $k = 1$ ) and  $U_x$  the uncertainty of the ICP-MS results (for  $k = 1$ ).

For environmental radioactivity measurements the criterion of acceptability of  $z \leq 2$  was used [39].

### 3. Results and Discussion

Figure 3 reports the HPGe gamma spectra acquired, for the investigated drinking water sample, with no preconcentration (a), factor of preconcentration equal to 3 (b) and to 37.5 (c).



**Figure 3.** The HPGe gamma spectra acquired, for the investigated drinking water sample, with no preconcentration (a), factor of preconcentration equal to 3 (b) and 37.5 (c).

The 1001.03 keV gamma-ray line of  $^{234m}\text{Pa}$  appears more and more evident in the spectra, as the preconcentration of the analyzed sample increases. According to Equation (1), the activity concentration of  $^{238}\text{U}$ , in the hypothesis of the secular radioactive equilibrium

between it and its daughter, was found to be not quantifiable without preconcentration, and equal to  $(0.76 \pm 0.22)$  Bq/L and  $(0.31 \pm 0.13)$  Bq/L for factors of preconcentration 3 and 37.5, respectively.

Moreover, these results were then compared with the concentration of  $^{238}\text{U}$  obtained through ICP-MS measurement. The massic elemental concentration for uranium turned out to be  $(5.6 \pm 1.1)$   $\mu\text{g/L}$  and, according to Equation (2), it was converted in  $^{238}\text{U}$  activity concentration, giving rise to a specific activity of  $(69 \pm 14)$  mBq/L. The comparison was therefore performed by calculating the z-score parameter, as reported in Equation (3). It was found to be not quantifiable without preconcentration, and equal to 3.13 and 1.85 for factors of preconcentration 3 and 37.5, respectively.

On the basis of the obtained results, we can therefore affirm that the preconcentration of a drinking water sample with a factor equal to 37.5, followed by a gamma spectrometry analysis of the preconcentrated aliquot, allows us to quantify, with a high degree of accuracy ( $z\text{-score} < 2$ ), the specific activity of  $^{238}\text{U}$ .

As a matter of fact, it is widely reported in the literature that  $^{238}\text{U}$  in drinking water is usually quantified by means of a gamma spectrometry, under the hypothesis of secular equilibrium with its daughter  $^{234}\text{Th}$ , using the percolation through a mixed bed ion exchange resin as a preconcentration technique, with the reduction to a final volume of 1 L starting from 80 L (preconcentration factor 80), or 2 L starting from 300 L (preconcentration factor 150) [40,41]. In the light of this, it must be emphasized how the methodological approach reported in this article is characterized by a relatively simple preconcentration process that does not require the use of chemical procedures. In addition, it can be of great utility in commonly performed drinking water monitoring activities, in which aliquots with volumes of the order of a few liters are sampled.

Finally, from the point of view of the radiological health risk assessment, it is important to point out that the activity concentration of  $^{238}\text{U}$  in the analyzed drinking water sample taken as a case study is much lower than the reference value of 3 Bq/L, corresponding to an Indicative Dose of 0.1 mSv/year [42]. This last parameter, calculated in the precautionary hypothesis that the water sample contains only the radioisotope in question, that the age class considered is only the one corresponding to adults, and that the water consumption is equal to 730 L/year [43], is set as a threshold by the regulatory limit [42]. Therefore, it is possible to exclude any radiological health risk for the population of the studied area, with reference to the drinking water consumption.

#### 4. Conclusions

In the present article, a new methodological approach to evaluate the  $^{238}\text{U}$  content in drinking water was reported. A sample from Paola, a selected location of the Calabria region, southern Italy, was taken as a case study.

HPGe gamma-ray spectrometry was employed, with the aim of quantifying the specific activity of the  $^{234\text{m}}\text{Pa}$  radioisotope after a preconcentration procedure and thus to assess the activity concentration of  $^{238}\text{U}$ , under the hypothesis of the secular radioactive equilibrium between it and its daughter. The accuracy of the obtained results was then evaluated through the calculation of the z-score parameter, taking into account the  $^{238}\text{U}$  ( $\mu\text{g/L}$ ) concentration, as measured with ICP-MS as reference value.

From the results, i.e., z-score equal to 1.85 for a factor of preconcentration equal to 37.5, the validity of the proposed methodological approach is assessed.

Moreover, with reference to the radiological health risk evaluation, the specific activity of  $^{238}\text{U}$  in the analyzed drinking water sample was much lower than the reference value of 3 Bq/L, set as a threshold by the regulatory limit. This result thus indicates that the ingestion of drinking water might not pose any significant radiological health hazards for the population of the studied area.

**Author Contributions:** Conceptualization, F.C. and V.V.; methodology, F.C. and V.C.; validation, D.M.; formal analysis, A.B., S.M. and M.D.; investigation, F.C., S.E.S., G.P. and V.V.; resources, F.C.,

V.C. and D.M.; data curation, F.C.; writing-original draft preparation, F.C.; supervision, D.M. and V.V. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research received no external funding.

**Institutional Review Board Statement:** Not applicable.

**Informed Consent Statement:** Not applicable.

**Conflicts of Interest:** The authors declare no conflict of interest.

## References

1. Caridi, F.; D'Agostino, M.; Messina, M.; Marciànò, G.; Grioli, L.; Belvedere, A.; Marguccio, S.; Belmusto, G. Lichens as environmental risk detectors. *Eur. Phys. J. Plus* **2017**, *132*, 189. [[CrossRef](#)]
2. Omar-Nazir, L.; Shi, X.; Moller, A.; Mousseau, T.; Byun, S.; Hancock, S.; Seymour, C.; Mothersill, C. Long-term effects of ionizing radiation after the Chernobyl accident: Possible contribution of historic dose. *Environ. Res.* **2018**, *165*, 55–62. [[CrossRef](#)] [[PubMed](#)]
3. Alzubaidi, G.; Hamid, F.B.S.; Abdul Rahman, I. Assessment of Natural Radioactivity Levels and Radiation Hazards in Agricultural and Virgin Soil in the State of Kedah, North of Malaysia. *Sci. World J.* **2016**, *2016*, 6178103. [[CrossRef](#)]
4. Günoğlu, K.; Seçkiner, S. Evaluation of dose parameters and radiological hazards in gravel samples of Konyaaltı Beach, Antalya. *Arab. J. Geosci.* **2018**, *11*, 457. [[CrossRef](#)]
5. Ravisankar, R.; Chandramohan, J.; Chandrasekaran, A.; Prince Prakash Jebakumar, J.; Vijayalakshmi, I.; Vijayagopal, P.; Venkatraman, B. Assessments of radioactivity concentration of natural radionuclides and radiological hazard indices in sediment samples from the East coast of Tamilnadu, India with statistical approach. *Mar. Pollut. Bull.* **2015**, *97*, 419–430. [[CrossRef](#)]
6. Caridi, F.; D'Agostino, M.; Belvedere, A.; Marguccio, S.; Belmusto, G. Radon radioactivity in groundwater from the Calabria region, south of Italy. *J. Instrum.* **2016**, *11*, P05012. [[CrossRef](#)]
7. Ramasamy, V.; Suresh, G.; Meenakshisundaram, V.; Ponnusamy, V. Horizontal and vertical characterization of radionuclides and minerals in river sediments. *Appl. Radiat. Isot.* **2011**, *69*, 184–195. [[CrossRef](#)]
8. Caridi, F.; D'Agostino, M.; Belvedere, A.; Marguccio, S.; Belmusto, G.; Gatto, M.F. Diagnostics techniques and dosimetric evaluations for environmental radioactivity investigations. *J. Instrum.* **2016**, *11*, C10012. [[CrossRef](#)]
9. Laraia, M. Radioactive contamination and other environmental impacts of waste from nuclear and conventional power plants, medical and other industrial sources. In *Environmental Remediation and Restoration of Contaminated Nuclear and Norm Sites*; Woodhead Publishing Series in Energy; Elsevier: Amsterdam, The Netherlands, 2015; pp. 35–56. [[CrossRef](#)]
10. Khaled, A.; Hessein, A.; Abdel-Halim, A.M.; Morsy, F.M. Distribution of heavy metals in seaweeds collected along marsa-matrouh beaches, Egyptian mediterranean sea. *Egypt. J. Aquat. Res.* **2014**, *40*, 363–371. [[CrossRef](#)]
11. Caridi, F.; Belmusto, G. Assessment of the public effective dose due to the <sup>222</sup>Rn radioactivity in drinking water: Results from the Calabria region, southern Italy. *J. Instrum.* **2021**, *16*, P02033. [[CrossRef](#)]
12. Håkanson, L. An Ecological Risk Index for Aquatic Pollution Control—A Sedimentological Approach. *Water Res.* **1980**, *14*, 975–1001. [[CrossRef](#)]
13. Eckerman, K.; Harrison, J.; Menzel, H.G.; Clement, C.H. ICRP publication 119: Compendium of dose coefficients based on ICRP publication 60. *Ann. ICRP* **2012**, *41*, 1–130. [[CrossRef](#)] [[PubMed](#)]
14. Caridi, F.; Messina, M.; D'Agostino, M. An investigation about natural radioactivity, hydrochemistry, and metal pollution in groundwater from Calabrian selected areas, southern Italy. *Environ. Earth Sci.* **2017**, *76*, 668. [[CrossRef](#)]
15. Briffa, J.; Sinagra, E.; Blundell, R. Heavy metal pollution in the environment and their toxicological effects on humans. *Heliyon* **2020**, *6*, e04691. [[CrossRef](#)]
16. Zheng, L.-G.; Liu, G.-J.; Kang, Y.; Yang, R.-K. Some potential hazardous trace elements contamination and their ecological risk in sediments of western Chaohu Lake, China. *Environ. Monit. Assess.* **2010**, *166*, 379–386. [[CrossRef](#)]
17. Caridi, F.; Belmusto, G. Overview of the technologies for assessment of natural radioactivity in drinking water. *J. Instrum.* **2019**, *14*, T02002. [[CrossRef](#)]
18. Caridi, F.; Belmusto, G. Gross Alpha and Beta Radioactivity Evaluation in Drinking Water: Results from the Calabria Region, Southern Italy. *Int. J. Environ. Res.* **2021**, *15*, 695–700. [[CrossRef](#)]
19. Andò, S. Gravimetric separation of heavy minerals in sediments and rocks. *Minerals* **2020**, *10*, 273. [[CrossRef](#)]
20. Hassan, N.M.; Rasmussen, P.E.; Dabek-Zlotorzynska, E.; Celo, V.; Chen, H. Analysis of Environmental Samples Using Microwave-Assisted Acid Digestion and Inductively Coupled Plasma Mass Spectrometry: Maximizing Total Element Recoveries. *Water Air Soil Pollut.* **2007**, *178*, 323–334. [[CrossRef](#)]
21. Turekian, K.K.; Wedepohl, K.H. Distribution of the elements in some major units of the earth's crust. *Geol. Soc. Am. Bull.* **1961**, *72*, 175–192. [[CrossRef](#)]
22. Kraemer, T.F.; Genereux, D.P. Chapter 20—Applications of Uranium- and Thorium-Series Radionuclides in Catchment Hydrology Studies. In *Isotope Tracers in Catchment Hydrology*; Kendall, C., McDonnell, J., Eds.; Elsevier: Amsterdam, The Netherlands, 1998; pp. 679–722. ISBN 978-0-444-81546-0.
23. Northern Agency Tronox Mines, Appendix D, Uranium Equilibrium Report. Response, Assessment, and Evaluation Services (RAES). In *Tetra Tech, Ed.*; Tetra Tech: Pasadena, CA, USA, 2019.

24. Lanzafame, G.; Zuffa, G.G. Geologia e petrografia del Foglio Bisignano (Bacino del Crati, Calabria). *Geol. Rom.* **1976**, *15*, 223–270.
25. Calcaterra, D.; Parise, M. Weathering in the crystalline rocks of Calabria, Italy, and relationships to landslides. In *Weathering as a Predisposing Factor to Slope Movements*; Geological Society, London, Engineering Geology Special Publications: London, UK, 2010; pp. 105–130. [[CrossRef](#)]
26. Idemitsu, K.; Obata, K.; Furuya, H.; Inagaki, Y. Sorption Behavior of Uranium(VI) on a Biotite Mineral. *MRS Online Proc. Libr.* **1994**, *353*, 981–988. [[CrossRef](#)]
27. Frei, D.; Liebscher, A.; Franz, G.; Dulsk, P. Trace Element Geochemistry of Epidote Minerals. *Rev. Mineral. Geochem.* **2004**, *56*, 553–606. [[CrossRef](#)]
28. Caridi, F.; D'Agostino, M. Evaluation of drinking water radioactivity content and radiological risk assessment: A new methodological approach. *J. Instrum.* **2020**, *15*, P10016. [[CrossRef](#)]
29. Babu, S.H.; Kumar, K.S.; Suvardhan, K.; Kiran, K.; Rekha, D.; Krishnaiah, L.; Janardhanam, K.; Chiranjeevi, P. Preconcentration technique for the determination of trace elements in natural water samples by ICP-AES. *Environ. Monit. Assess.* **2007**, *128*, 241–249. [[CrossRef](#)]
30. Ortec Angle 4 Software User Manual. 2016. Available online: <https://www.ortec-online.com/-/media/ametekortec/manuals/a/angle-mnl.pdf?la=en&revision=a81e1418-e874-4693-be48-0c2b47f38166> (accessed on 3 March 2022).
31. Caridi, F.; Di Bella, M.; Sabatino, G.; Belmusto, G.; Fede, M.R.; Romano, D.; Italiano, F.; Mottese, A. Assessment of natural radioactivity and radiological risks in river sediments from Calabria (Southern Italy). *Appl. Sci.* **2021**, *11*, 1729. [[CrossRef](#)]
32. Caridi, F.; Acri, G.; Belvedere, A.; Crupi, V.; D'Agostino, M.; Marguccio, S.; Messina, M.; Paladini, G.; Venuti, V.; Majolino, D. Evaluation of the radiological and chemical risk for public health from flour sample investigation. *Appl. Sci.* **2021**, *11*, 3646. [[CrossRef](#)]
33. Huang, Y.; Lu, X.; Ding, X.; Feng, T. Natural radioactivity level in beach sand along the coast of Xiamen Island, China. *Mar. Pollut. Bull.* **2015**, *91*, 357–361. [[CrossRef](#)]
34. Caridi, F.; Paladini, G.; Venuti, V.; Crupi, V.; Procopio, S.; Belvedere, A.; D'agostino, M.; Faggio, G.; Grillo, R.; Marguccio, S.; et al. Radioactivity, metals pollution and mineralogy assessment of a beach stretch from the Ionian coast of Calabria (Southern Italy). *Int. J. Environ. Res. Public Health* **2021**, *18*, 12147. [[CrossRef](#)]
35. ACCREDIA. Available online: <https://www.accredia.it/> (accessed on 17 January 2022).
36. *Thermo Fisher iCAP Q Operating Manual*; Thermo Fisher: Waltham, MA, USA, 2012.
37. Dragović, S.; Janković, L.; Onjia, A.; Bačić, G. Distribution of primordial radionuclides in surface soils from Serbia and Montenegro. *Radiat. Meas.* **2006**, *41*, 611–616. [[CrossRef](#)]
38. Berengolts, A.; Lindenbaum, M. On the distribution of z-score. *Iran. J. Sci. Technol. Trans. A Sci.* **2008**, *32*, A1. [[CrossRef](#)]
39. *UNI CEI EN ISO/IEC 17025*; General Requirements for the Competence of Testing and Calibration Laboratories. UNI: Milan, Italy, 2018.
40. Forte, M.; Bertolo, A.; D'Alberti, F.; De Felice, P.; Desideri, D.; Esposito, M.; Fresca Fantoni, R.; Lorenzelli, R.; Luciani, A.; Magnoni, M.; et al. Standardized methods for measuring radionuclides in drinking water. *J. Radioanal. Nucl. Chem.* **2006**, *269*, 397–401. [[CrossRef](#)]
41. Forte, M.; Rusconi, R.; Cazzaniga, M.; Sgorbati, G. The measurement of radioactivity in drinking water. *Microchem. J.* **2007**, *105*, 98–102. [[CrossRef](#)]
42. *Italian Legislation D. Lgs. n. 28/2016*; FAO, FAOLEX: Rome, Italy, 2016; pp. 1–4.
43. Kamiya, K.; Ozasa, K.; Akiba, S.; Niwa, O.; Kodama, K.; Takamura, N.; Zaharieva, E.K.; Kimura, Y.; Wakeford, R. Long-term effects of radiation exposure on health. *Lancet* **2015**, *386*, 469–478. [[CrossRef](#)]