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Abstract: In this article, authors report experimental results obtained, with different diagnostics setups, for radon activity concentration measurement in underground water for human use. An overview is given about the performance of different measurement techniques, based on experimental data. The following parameters are compared and discussed: counting efficiency, minimum detectable activity, measurement uncertainty, background, sample volume and treatment. The estimated average value for radon-specific activity in underground water was compared with that one derived from different legislations and directives/guidelines and it was used, with the dose conversion factor for ^{222}Rn, to estimate the annual effective dose, for adult members of public of the investigated region, due to the groundwater radon ingestion.

Subjects: Physics; Applied Physics; Environmental Physics; Experimental Physics

ABOUT THE AUTHOR

Francesco Caridi was born in Reggio Calabria, Italy, on 3 December 1980. In 2003, he earned a Master of Science cum laude degree in Physics at the Messina University, Italy. In 2007, he got his Ph.D. in Physics from Messina University, with excellent final assessment. From July 2007 to December 2008, he served as a research assistant at the Department of Physics of the Messina University. From December 2008 to June 2014, he worked as an expert physicist at the Science Faculty and at the Department of Physics of the Messina University. Currently, he is a Ph.D. researcher at the Agency for Environmental Protection of Calabria, Italy. His research interest includes lasers; laser–matter interaction; plasma production, diagnostics and applications; environmental radioactivity; gamma-spectrometry; liquid scintillation; emanometry; applied physics to cultural heritage, environment, biology and medicine.

Giovanna Belmusto is the director of the Physical Laboratory at the Agency for Environmental Protection of Calabria, Italy. Her research interest includes environmental radioactivity; gamma-spectrometry; liquid scintillation; emanometry.

PUBLIC INTEREST STATEMENT

The main aim of this work is to investigate about experimental results obtained, with different diagnostics setups, for radon activity concentration measurement in underground water for human use. An overview is given about the performance of different measurement techniques, based on experimental data. The following parameters are compared and discussed: counting efficiency, minimum detectable activity, measurement uncertainty, background, sample volume and treatment.

The estimated average value for radon-specific activity in underground water was compared with that one derived from different legislations and directives/guidelines and it was used, with the dose conversion factor for ^{222}Rn, to estimate the annual effective dose, for adult members of public of the investigated region, due to the groundwater radon ingestion.

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Keywords: radon; underground water; liquid scintillation counting (LSC); high resolution gamma-ray spectrometry; emanometry

1. Introduction

Underground waters contain natural radionuclides in various concentrations depending on their origin. Radon is released into waters as a result of natural processes like decay of its parent nuclide ^{226}Ra and predominantly dissolution from the surrounding geological environment (rocks, soils), as reported in literature (Moreno, Bach, Baixeras, & Font, 2014). In water, it may also origin from dissolution of airborne radon into water and other higher radon-bearing water inflows in the catchment area.

Radon solubility in water is relatively low, 0.01 mol kg^{-1} bar^{-1} at 293 K (Lerman, 1979), but, despite it, its activity concentration in waters can be some orders of magnitude higher than that of other natural radionuclides (Calabrese et al., 2006).

The relatively low cost and simplicity of many radon measurement techniques made them common to apply in many laboratories (Caridi, D'Agostino, et al., 2016). Numerous reliable measurement devices are available, with reasonably low detection limits, affordable price and simple operation. Furthermore, sample preparation for the radon analysis in water is usually simple, rapid and does not need extensive chemical manipulations.

In this article, a comprehensive study was conducted at the Physical Laboratory/Calabrian Center for the Ionizing Radiations of the Agency for Environmental Protection of Calabria – Department of Reggio Calabria, Italy, based on a comparison between radon activity concentration measurements in underground waters for human use, performed with high resolution gamma-ray spectrometry, liquid scintillation counting (LSC) and emanometry, to find reliable methods to determine reference values for radon in water samples and to evaluate suitable radon measurements to support work in experimental laboratories. All these approach are considered valid by the World Health Organization without a preferred one (WHO, 2011).

2. Materials and methods

2.1. Samples collection and treatment

A representative sample of groundwater was collected, in three different aliquots, at Mammola, a selected location of Calabria, south of Italy, as indicated in Figure 1.

The first aliquot was collected into 2 L of acidified polyethylene bin, to avoid radionuclide precipitation and adsorption on walls of the container. The bin was filled to the brim to prevent radon loses, tightly sealed and labeled, and then stored in the laboratory for the preparation into a 1-L Marinelli beaker before analysis. Before use, the beaker was first soaked with diluted nitric acid, washed, rinsed with distilled water and left dry in the oven to prevent contamination. After 3 h, the secular radioactive equilibrium between ^{222}Rn and its daughter products was attained and the sample was ready for gamma spectrometry counting.

The second aliquot (10 ml) was mixed with 10 ml of scintillation cocktail (PerkinElmer Opti-Fluor O) and stored, tightly sealed and labeled, in a 20-ml plastic vial before the liquid scintillation analysis.

The third aliquot was needed to determine the ^{222}Rn activity concentration with the emanometry setup. Sampling technique, or lack of it, is generally the major source of error in measuring the radon content of water. The water sampled had to be representative of the water being tested and it had never been in contact with air. For this reason, a tube was attached to the faucet

Figure 1. The map with the underground water sampling point, Mammola, put in evidence.
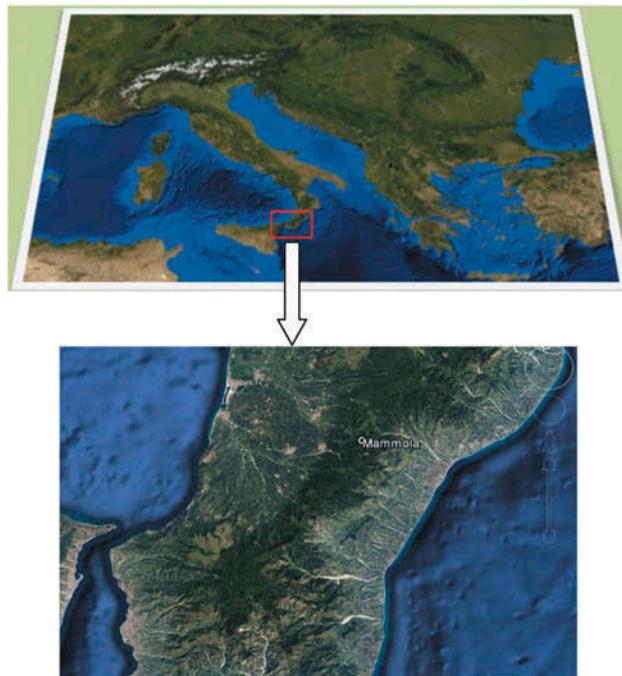
feeding water to the interior of a 250-ml vial at the bottom of the bowl; in this way, water can overflow freely from the bowl. After the sampling, a label stating the date, time and source of the water was applied.

The time between sampling and analysis reporting was less than 48 h in all cases, to make the correction for ^{226}Ra not necessary (Papastefanou, 2002).

2.2. Diagnostics techniques and sample measurements

For the gamma spectrometry measurement, the groundwater sample was counted for 70,000 s and analyzed to obtain the activity concentration of ^{222}Rn through the 295.21 keV and 351.92 keV ^{214}Pb and 1120.29 keV ^{214}Bi gamma-ray lines. The experimental setup is composed by an Ortec HPGe negative biased detector (GMX), with Full Width at Half Maximum (FWHM) of 1.94 keV, Peak-to-Compton ratio of 65:1 and relative efficiency of 37.5% at 1.33 MeV (^{60}Co). It is placed inside a lead well to shield the background radiation environment. Efficiency and energy calibrations were performed using a multi-peak Marinelli geometry gamma source (SV 277) of 1 L capacity, covering the energy range 59.54—1,836 keV, customized to reproduce the exact geometries of the sample in a water-equivalent epoxy resin matrix. The Gamma Vision 8.0 (Ortec) software was used for data acquisition and analysis (Ortec, 2010).

The activity concentration (Bq/L) of each identified radionuclide was calculated using the following equation:

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

where N_E indicates the net area of a peak at energy E; ε_E and γ_d are the counting efficiency and yield of the photopeak at energy E, respectively; t is the live time (s) and V is the sample volume (L). The measurement uncertainty is a combined standard one at coverage factor $k = 2$, taking into account the following components: counting statistics, counting efficiency, activity of the calibration source, sample volume and uncertainty on ^{222}Rn half-life. The minimum detectable activity concentration is calculated according to the literature (Caridi, Marguccio, et al., 2016):

$$MDC = \frac{4.65\sqrt{B}}{\varepsilon_E t V} \qquad (2)$$

where B indicates background counts, ε_E is the counting efficiency of the photopeak at energy E, t is the live time (s) and V is the sample volume (L). The ^{222}Rn measurement in the analyzed water sample was performed following the operative procedure MET-13 of the Italian Institute for the Environmental Protection and Research (ISPRA, 2015).

A photo of the experimental setup is shown in Figure 2a.

For the LSC, the sample stored in the vial, mixed with the scintillation cocktail, was counted for 60 min. The scintillator is a PerkinElmer Tricarb 4910 TR, with an energy range of 0–2 MeV (beta particles) and 0–10 MeV (alpha particles). For ^{222}Rn detection, its counting efficiency takes into account both alpha and beta decay modes and is of 420%; its background is of 31.59 cpm and the scintillator works in Normal Count Mode (Perkin-Elmer, 2009). To prepare calibration sources, ^{226}Ra or ^{222}Rn standard solution can be used. Only ^{222}Rn is extracted into the organic scintillator but ^{226}Ra stays in the aqueous phase. Therefore, it doesn't influence the counting efficiency calibration. As water and other dissolved materials are not transferred into the scintillation cocktail (only ^{222}Rn), quenching correction is not needed. The measurement uncertainty is a combined standard one at coverage factor k = 2, and it takes into account the following components: counting statistics, counting efficiency, activity of the calibration source, uncertainty on ^{222}Rn half-life, total efficiency and weighing (sample, standard solution). The minimum detectable activity concentration is calculated according to Equation (2). The ^{222}Rn measurement in the analyzed water

Figure 2. A photo of the experimental HPGe gamma-spectrometry (a), LSC (b) and emanometry (c) setups.

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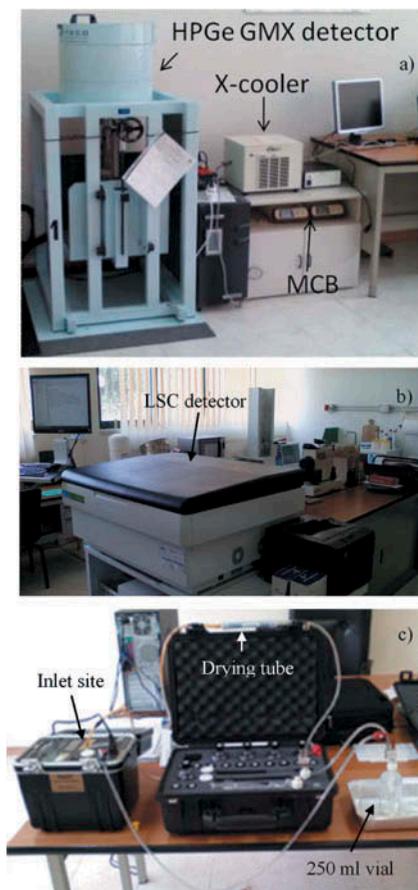
sample was performed following the international standard ISO 13164-4:2015: Water quality Radon-222 – Part 4 (ISO 13164-4, 2015). A photo of the experimental setup is shown in Figure 2b.

For the emanometry measurement, the Durridge RAD7 + RAD H$_2$O setup was employed to measure radon in water over a concentration range of from less than 10 pCi/L to greater than 400,000 pCi/L (Durridge Radon Instrumentation, 2015). The equipment is portable and battery operated, and the measurement is fast. This experimental setup gives results after a 30-min analysis with a high sensitivity. The method is simple and straightforward, with no harmful chemicals to use. In particular, a vial containing the water sample was set up in a closed air loop with the RAD7. Its pump operated automatically for 5 min to aerate the sample, distributing the radon that was in the water throughout the loop. The RAD7 waited a further 5 min, while the ^{218}Po count rate approached equilibrium and then it counted for four 5-min cycles. The radon concentration in the water was directly calculated (Durridge Radon Instrumentation, 2015), according to the operative procedure MET-37 of the ISPRA (2015). The alpha counting efficiency can be determined by using radon in air calibration chambers with accurately established ^{222}Rn activity concentration (Cothern & Rebers, 1990). The background is of 0.10 cpm. The measurement uncertainty is a combined standard one at coverage factor k = 2, taking into account the following components: counting statistics, counting efficiency, radon transfer, activity of the calibration source, calibration factor, counting cell volume, sample volume, radon concentration in the ionization chamber before sample injection and uncertainty on ^{222}Rn half-life. A photo of the experimental setup is shown in Figure 2c.

A comparison of the various diagnostics techniques used for the determination of radon in underground water is shown in Table 1, together with a summary of their main features.

2.3. Radiation dose estimation

In order to control radiation exposure to the public, estimation of the total annual effective dose due to ingestion of ^{222}Rn in water samples was done on the basis of the experimental activity concentration and dose conversion factor of the selected radionuclide:

$$H_{\text{ing}}\left(\frac{\mu\text{Sv}}{\text{year}}\right) = \text{DCF}_{\text{ing}} \times C_{Rn-222} \times I_{\text{w}} \times 365 \qquad (3)$$

where DCF$_{\text{ing}}$ is the dose conversion factor by ingestion of ^{222}Rn in water samples by adults (3.5 × 10^{-9} Sv/Bq) and I_{w} is the average daily water consumption rate (about 2 L/day) (WHO, 2004).

Table 1. A comparison of the various diagnostics techniques used for the determination of radon in underground water for human use

Diagnostics techniques	Counting efficiency (%)	Lowest detection limit (Bq/L)	Measurement uncertainty (k = 2) (%)	Background (cpm)	Sample volume (L)	Sample treatment
HPGe gamma-spectrometry	0.83[a]	0.10	4.98	0.01	1	No
LSC	420[b]	1.36	1.81	31.59	0.010	Yes
Emanometry	90[c]	0.37	3.97	0.10	0.250	No

[a]At 1.33 MeV peak (^{60}Co).
[b]Including ^{222}Rn, ^{218}Po, ^{214}Pb, ^{214}Bi and ^{214}Po.
[c]Including ^{218}Po.

3. Results and discussion

3.1. Radioactivity analysis

Table 2 shows the location (with GPS coordinates) of the groundwater sampling point, together with the activity concentration of ^{222}Rn as measured through HPGe gamma-spectrometry, LSC and emanometry. Experimental results referred to the ^{222}Rn-specific activity, as obtained with these three diagnostics techniques taking into account the decay correction, are in very good agreement between them and with reference levels for the investigated area, as reported in the database of the ISPRA (2016), confirming that the performance of each of the discussed analytical setups is adequate for radon activity measurements in underground waters for human use. In particular, we obtained a value of 144.75 ± 7.22 Bq/L with the HPGe gamma-spectrometer (147.16 ± 2.85 Bq/L) with the liquid scintillator and (147.25 ± 5.85 Bq/L) with the emanometer. These values depend on the ^{222}Rn content in rocks or solid aquifers in the area where groundwater is located and the residence time of waters/rocks–soils in contact as well. The investigated sampling point is located in an area where the geological setting is the "Calabrian-Peloritan arc" (Atzori, Ferla, Paglionico, Piccarreta, & Rottura, 1984). Its rocks are acidic intrusive igneous, characterized by the highest natural radioactivity, with a high uranium content. ^{222}Rn radioactivity values here obtained are slightly higher than the parameter value reported by the Italian Legislation (2016) (100 Bq/L), but, as written there, in addition to the parameter value for the concentration of radon activity, a reference level lower than 1,000 Bq/L was established, beyond which the adoption of corrective and cautionary measures is justified on radiological protection reasons, without the need of further considerations.

For the purpose of comparison, the activity concentration of ^{222}Rn has been obtained from literature for groundwaters from other parts of the world and is presented in Table 3. The average value of ^{222}Rn experimentally obtained in this article (146.41 ± 5.31 Bq/L) is only higher than that one referred to the UK, Northern Ireland (Sherwood Sandstone Aquifer), but lower than all others here reported (Spain – La Garrotxa region, Poland – the Sudety Mountains, Finland, Germany – east

Table 2. The location (with GPS coordinates) of the groundwater sampling point, together with the activity concentration of ^{222}Rn as measured through HPGe gamma-spectrometry, LSC and emanometry

Sampling point	GPS coordinates	^{222}Rn activity concentration (Bq/L)		
		HPGe gamma-spectrometry	LSC	Emanometry
Mammola (Borehole)	38°21'02.8" N 16°10'34.7" E	144.75 ± 7.22	147.16 ± 2.85	147.25 ± 5.85

Table 3. The activity concentration of ^{222}Rn obtained from literature for groundwaters from other parts of the world

^{222}Rn activity concentration (Bq/L)	Country, region	Geology
1–1,000	Spain, La Garrotxa region	Volcanic
3,043	Poland, the Sudety Mountains	Volcanic (e.g., crystalline rocks)
3,800	Finland	Soil (no detail)
1,220	Germany, east Bavaria	Granite, gneiss
17–3,856	Portugal, Nisa	Granites, sediments
5.8–36.6	UK, Northern Ireland	Sherwood Sandstone Aquifer

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Bavaria, Portugal – Nisa) (Pereira, Pereira, Neves, Azevedo, & Campos, 2015; Przylibski et al., 2014; Salonen, 1988; Trautmannsheime, Schindlmeier, & Hübel, 2002).

3.2. Evaluation of radiological hazard effects

The estimated value of the annual effective dose H_{ing} due to ingestion of ^{222}Rn in water received by adults living in the investigated region was calculated with Equation (3), by using the ^{222}Rn average activity concentration experimentally measured (146.41 ± 5.31 Bq/L).

It resulted about 0.37 mSv/year. Epidemiological studies have shown that the risk associated with the ingestion of water containing this level of radon radioactivity is rather limited (United Nations Scientific Committee on the Effects of Atomic Radiation [UNSCEAR], 2000). The limitation of the radon content in underground water for human use finds its justification not so much in the limitation of the dose from ingestion (as seen it is rather limited), but rather in the fact that water with high levels of radon can contribute to the enhancement of the radon concentration indoor (Calabrese et al., 2006). In this regard, however, it is useful to remember that when the sampling is not directly made in homes, but rather in sites upstream of them (as the case reported in this article), results are an overestimation of the real radon concentration in the water that flows from household taps.

4. Conclusions

An overview was given on the most common water radon measurement techniques: high resolution gamma-ray spectrometry, LSC and emanometry. ^{222}Rn-specific activity experimental results, as obtained with these three diagnostics techniques, are in very good agreement between them and with the literature. For this reason, it is possible to conclude that the performance of each of the discussed methods is adequate for radon activity measurements in underground waters for human use. Methods are straightforward and capable of providing prompt measurement information about radon levels in water samples.

In order to estimate the radiological hazard effects due to intake of radon through water, the annual effective dose received by adult members of the public living in the investigated region was estimated. The recorded average value was of about 0.37 mSv/year, lower than that one recommended by Italian legislation, D.Lgs. 28/2016 (2.55 mSv/year), that establishes the requirements for the protection of the population health in relation to radioactive substances present in water intended for human consumption. This result thus indicates that ingestion of groundwater from the investigated area might not pose any significant radiological health hazards, from the radon radioactivity point of view.

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