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Simultaneous determination of ^{222}Rn and ^{220}Rn exhalation rates from building materials used in Central Italy with accumulation chambers and a continuous solid state alpha detector: Influence of particle size, humidity and precursors concentration

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Abstract

A method to determine simultaneously the rates of ^{222}Rn and ^{220}Rn released from building materials quarried in Central Italy is presented. The method makes use of a continuous monitor equipped with a solid state alpha detector, in-line connected to a small accumulation chamber. The effects of chamber leakage and back diffusion on ^{222}Rn free exhalation rate is evaluated. The influence of available exhalation surface, humidity content and precursors concentration on radon and thoron exhalation rates is investigated.

Keywords: Radon; Thoron; Exhalation rates; Building material; Italy

1. Introduction

The strict correlation between indoor radon (^{222}Rn) exposure and potential health hazard to occupants is well known (see for example International Agency Research Cancer (IARC) Monographs, 1988; Steindorf et al., 1995; United States Environmental Protection Agency (USEPA), 1999). The indoor radon concentrations mainly depend on radon exhalation from surrounding soil, but also on exhalation from building materials and radon in domestic water supply. The radon emanating from porous building materials achieves a larger relevance in some areas of the world (the Netherlands, China, Italy), where rocks enriched in radon isotopes precursors, are used as building materials, either as stony materials or in a loose form to prepare cements. Lazio region in Central Italy, and in particular the districts of Viterbo and Colli Albani volcano, belongs to these areas where radon exhaling from building materials adds to high radon emissions from subsoils. In this context the thoron (^{220}Rn) and its decay products dose contribution can exceed the corresponding ^{222}Rn values, as in the indoor environment thoron is considered more likely to originate from exhalation of building material rather than from soils

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due to its short half-life. Under these special circumstances thoron and its daughters cannot be considered of negligible radiological significance, but can represent a significant fraction of the total lung exposure among workers in thoron-related industries and residents in high thoron background areas (Bochicchio et al., 1994; Steinhausler et al., 1994 and references therein). Consequently indoor radon and thoron concentration should be monitored and building materials should be classified on the basis of their radon and thoron exhalation rates to be correlated with their activity concentration index (I, based on the gamma activity of ^{232}Th, ^{226}Ra and ^{40}K). In view of that, a method to measure simultaneously radon and thoron exhalation rates from stony and loose building materials is presented, using accumulation chambers and a continuous radon monitor equipped with a solid state alpha detector, in-line connected with the chamber. The contribution of back diffusion (radon getting back to the building material as radon builds up in the air) and chamber leakage phenomena are evaluated and the role of particle size (in the analyses of loose materials) and humidity on exhalation rates is documented. We aim to create a standardised protocol for the application of measurement criteria. These measurements will supply data/information on radon exhalation from many materials used permanently in buildings. In conclusion a preliminary classification of some building materials used in Lazio region is presented as a starting point of a catalogue of materials to assist construction engineers in making a well-informed and clear decision, having been made fully aware of radon/thoron alert levels in construction materials.

2. General features of Lazio region and selected building materials

The materials analysed in this research are mostly extracted from quarries located in Lazio region (Fig. 1). Their shared characteristic is the frequent use in construction industry.

A large part of these materials belongs to different eruptions of the quaternary volcanic region of Colli Albani (the Alban Hills), located just south of Roma (Fig. 1); this is the case of the "Tufo Lionato" pyroclastic flow, the black pozzolana (a siliceous volcanic ash used to produce hydraulic cement), the "Peperino" pyroclastic flow (from Nemi and Albano areas), a sample of lapilli (fragments of pyroclastic rocks measuring between 4 and 32 mm), a lava flow and another scoriaceous lava containing empty cavities from Nemi area. These materials are often used in construction and their application ranges from the production of grout for pozzolana, to the use as construction stone for tuffs and to the production of paving stones for lavas.

The "Peperino della Via Flaminia" pyroclastic flow originates from an eccentric mouth of the Sabatini volcanic apparatus located just north of Roma and used as cutting stone (Fig. 1).

The "Tufo rosso a scorie nere" pyroclastic flow originates from another volcanic area in Lazio region, known as the Vico volcanic apparatus (Fig. 1). This area, located in the proximity of Viterbo town, north of Roma, is also very important, due to the large amount of erupted materials.

Other materials, widely used within the construction industry and easily available in Lazio region, but with a different origin and nature, have been also included in the present study. This is the case of:

- the renowned "travertino", a cutting stone coming from the quarries located east of Rome, and used for the building decoration and for pavements (Fig. 1), since the Roman Age. Many famous monuments in Rome were decorated with this stone, like the Coliseum,
- the "Rosso Veronese", a calcareous-marly rock extracted from quarries located in the area of Verona City (Veneto region),
- the "Tufo giallo napoletano" pyroclastic flow originated from a freatomagmatic eruption in the area of the Campi Flegrei near Napoli (Campania region), also known as "Ignimbrite Campana",
- siliceous sands from Maputo (Mozambique) used for preparing cement have been made available in the frame of a cooperation program between "Roma Tre" University and the Mozambique government,
- a brick produced by furnaces in Pesaro town (Marche Region), but widely sold in Central Italy.

3. Analytical methods

Several different methods to measure radon and thoron exhalation rates from soil or building materials make use of accumulation chambers associated with alpha particle detectors, like scintillation cell or "Lucas cells" (Talbot et al., 1998; Cosma et al., 2001; van der Pal et al., 2001; Fujiyoshi et al., 2002), ionisation chambers (Ferry et al., 2002) and solid state alpha detectors (Chao et al., 1997; De Martino et al., 1998; Keller et al., 2001). In this paper a new method based on small accumulation chambers connected to a continuous Radon Gas Monitor, model RAD7, produced by Durridge Company, 7 Railroad Avenue D, Bedford, MA 01730, equipped with a solid state alpha detector is presented. The method allows the simultaneous measurements of radon and thoron using only the ^{218}Po peak for ^{222}Rn and ^{216}Po peak for ^{220}Rn, obtaining a rapid equilibrium between polonium and radon nuclei. The radon and thoron progenitor activities

Fig. 1. Lazio Region (Italy) with its main volcanic districts and location of towns cited in the text. In the inset, Italy with location of Lazio, Campania, Marche and Veneto regions is shown.

(^{226}Ra and ^{232}Th) along with that of ^{40}K have been determined using γ-spectroscopy with a 0.19 cm^3 High-Purity Germanium (HPGE) coaxial detector, model GMX-30190-P, produced by EG&G ORTEC, 100 Midland Road, Oak Ridge, TN 37831-0895, USA.

3.1. Preparation of samples

Samples have been prepared according to simple procedure of crushing and/or sieving to separate particles of different size in order to evaluate the influence of grain size on radon and thoron exhalation rates. The analysed materials have been either heated to 110 °C or left to equilibrate with ambient air to study the role of humidity on radon release rates. Finally samples have been weighed (from 500 to 1000 g) and placed in the accumulation chamber or in the Marinelli beakers (for γ-spectroscopy). Stony materials have been also cut and shaped into approximately $12 \times 9 \times 4$ cm slabs using a diamond saw and their surface exhalation rates have been calculated.

3.2. Experimental set-up

The experimental set-up (Fig. 2) makes use of small vessels (volume = 4.3 L) made of polyvinyl chloride (PVC) as radon and thoron accumulation chambers. As studies on packaging and storing of radioactive waste demonstrates (see for example Tomasella et al., 1995), PVC can be considered a radon-tight material, unless exposed to high levels of gamma radiations that may have effects on the radon permeation. The chamber is connected via vinyl tubing to a gas-drying unit filled with a desiccant ($CaSO_4$ with 3% $CoCl_2$, as indicator) and to the RAD7 radon monitor. The chamber can be isolated through stopcocks fixed at opposite sides of the container.

The sample is placed at the bottom of the accumulation chamber which is sealed with silicon and the system is purged by nitrogen gas for more than 20 min to reduce the initial radon concentration down to zero. The chamber is then connected in a closed loop configuration and the stopcocks are opened. The instrument draws air from the accumulation chamber, through the desiccant and an inlet filter, into the measurement chamber. The air is then returned to the enclosure from the RAD7 outlet. The filtered air decays inside the chamber, producing detectable alpha emitting progeny, particularly the polonium isotopes. A high voltage of 2500 V is applied to the chamber walls. The solid state detector converts alpha radiation directly to an electrical signal using an alpha technique which is able to discriminate the electrical pulses generated by α-particles from the four radioisotopes of polonium (^{218}Po, ^{216}Po, ^{214}Po, ^{212}Po) with energies of 6.0, 6.7, 7.7 and 8.8 MeV, respectively. In this way, it is possible to use only the ^{218}Po peak for ^{222}Rn and ^{216}Po for ^{220}Rn, obtaining a rapid equilibrium between polonium and radon nuclei, because the equilibrium between ^{218}Po and ^{222}Rn is achieved in about 15 min (about five times the half-life of ^{218}Po), and between ^{216}Po and ^{220}Rn in a few seconds. Using this approach it is possible to measure radon specific activity and to study the variations of ^{222}Rn over a period of 15 min. The radon growth curve to equilibrium is monitored with cycle times of 2 h for about 20 days. The experiments were performed under dry conditions (relative humidity was controlled at under 10%) and room temperature from 18 to 26 °C.

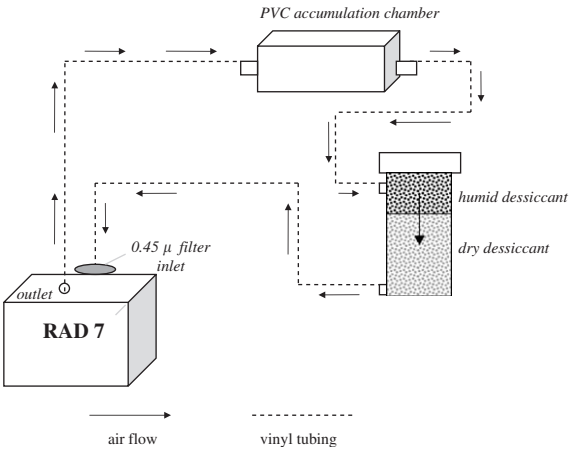

Fig. 2. Experimental set-up to measure radon and thoron exhalation rates

The specific activity of ^{222}Rn and ^{220}Rn is obtained from a calibration factor determined from the radon chambers run by the US EPA and the US Department of Energy (Durridge Company Inc., 2000). Its value is 0.006 count min^{-1} Bq^{-1} m^3 for both isotopes.

3.3. Measure of the Rn growth curve in the accumulation chamber and estimates of leakage and back-diffusion rates

The concentration of radon and thoron exhaled from the samples in the accumulation chamber increases exponentially and tends to an equilibrium value between exhaled and decayed nuclide. At this time the activity in the chamber equals that in the pores. Taking this equilibrium value into consideration and having reduced the initial radon concentration of the chamber down to zero, due to purging with nitrogen gas, it is possible to calculate the radon and thoron free exhalation rates (E_0, Bq s^{-1}) using the following equation (Petropolous et al., 1999):

$$E_0 = \frac{C \times \lambda V}{1 - e^{-\lambda t}}, \quad (1)$$

where C is the equilibrium concentration [Bq m^{-3}], λ is the decay constant [s^{-1}], V is the effective volume of the test apparatus (the chamber, the vinyl tubings and the measurement chamber of the radon monitor) [m^{-3}] and t is time [s]. This equation is valid if there is no leakage of radon and thoron out of the container and if the activity concentration in the container air is low compared to the activity concentration in the pore air of sample (no back-diffusion effects). In general, if the container free volume is at least 10 times larger than the sample pore volume, the back-diffusion effects should be avoided (Petropolous et al., 1999).

If leakage and back-diffusion phenomena occur, the growth of radon and thoron in the chamber follows an exponential trend, where the effective time constant (λ_{eff}, s^{-1}) is not the decay constant, but is equal to:

$$\lambda_{eff} = \lambda + \lambda_{leak} + \lambda_{back}, \quad (2)$$

where λ_{leak} (s^{-1}) and λ_{back} (s^{-1}) depend on leakage and back diffusion, respectively. In this case, the free exhalation rate (E_0) can be calculated using the following equation:

$$E_0 = \frac{C \times \lambda_{eff} V}{1 - e^{-\lambda_{eff} t}}. \quad (3)$$

The values of λ_{leak} and λ_{back} can be determined using the equation proposed by Chao et al. (1997), for the leakage rate (q, $m^3 s^{-1}$) and the back-diffusion rate (D, s^{-1}), where $\lambda_{leak} = q/V$ and $\lambda_{back} = D$.

The value of λ_{leak}, which presumably is not affected by radon loss due to permeation through the PVC chamber (Tomasella et al., 1995), is determined by measuring for a period of 24 h the decay of Rn gas which is still contained in the accumulation chamber when the sample is removed. If this operation is carried out without opening too much the lid closing the container, a large part of the gas previously accumulated in the chamber is not lost. It must be outlined that the value of starting radon concentration is not important in this leakage experiment, being necessary only that some radon is present in the chamber.

$$\lambda_{leak} = \left(\frac{M_f - M_l}{C_b - C_0}\right), \quad (4)$$

where M_f is the initial slope of the radon decay curve without leakage [Bq $m^{-3} s^{-1}$], M_l represents the slope of the experimental curve [Bq $m^{-3} s^{-1}$], C_b is the initial radon concentration in the chamber during the leakage experiment [Bq m^{-3}] and C_0 is the background mean radon concentration in the laboratory [Bq m^{-3}].

The value of λ_{back} can be calculated using the following equation (Chao et al., 1997):

$$\lambda_{back} = \frac{M_e}{C} - (\lambda + \lambda_{leak}), \quad (5)$$

where M_e is the initial slope of the radon build up curve inside the accumulation chamber [Bq $m^{-3} s^{-1}$] and C is the equilibrium concentration [Bq m^{-3}].

The value of λ_{eff} can be also calculated from the following equation:

$$\lambda_{eff} = M_e/C. \quad (6)$$

Another approach, followed for example by De Martino et al. (1998), is to apply a non-linear curve fit to experimental data C versus t, in the form $y = a(1 - e^{-bx})$, where $a = E_0/\lambda_{eff} \times V$ and $b = \lambda_{eff}$.

3.4. Gamma spectrometry

The γ-spectroscopy measurements were made using a hyperpure germanium detector with a resolution of 1.84 keV at 1.33 MeV, properly shielded from background radiation. The activity of ^{226}Ra [Bq kg^{-1}] has been measured using the ^{214}Bi peak at 609.3 keV. The ^{228}Ac peak at 911.2 keV and ^{40}K peak at 1461 keV have been used for the measurement of ^{232}Th and ^{40}K activities [Bq kg^{-1}], respectively. The measurement were carried out 20 days after the sample was sealed in the Marinelli beaker having a diameter equal to that of detector and a volume of 700 mL. The counts rate recorded for samples was then transformed in activity concentration using standard materials with known activity of investigated isotopes. On the basis of the obtained specific activities, an activity concentration index [I, Bq kg^{-1}], introduced by the European Commission as a screening tool for identifying building materials which might be of concern, has been obtained using the following equation (EC-Radiation protection, 1999):

$$I = \frac{^{232}\mathrm{Th}}{200} + \frac{^{226}\mathrm{Ra}}{300} + \frac{^{40}\mathrm{K}}{3000}. \quad (7)$$

4. Discussion

4.1. Equilibrium and exhalation rates

Samples have been enclosed in the radon chamber and the radon concentration growth inside the container has been followed from zero to an equilibrium value. The radon equilibrium has been achieved earlier than 20 days (about five times the half-life of ^{222}Rn), due to the phenomena, other than decay, that produce a decrease of radon concentration in the chamber air. De Martino et al. (1998) reported a similar phenomenon of anticipated equilibrium and hypothesised that this could be due to diffusion and back-scattering occurring in the chamber. In this paper leakage and back-diffusion effects are investigated as possible causes of an early equilibrium. The phenomena have been studied and quantified using radon data, because the half-life of thoron (56 s^{-1}) is too short to allow the observation of them. Consequently, time constants due to leakage (λ_{leak}) and back diffusion (λ_{back}) have been evaluated by application of Eqs. (4) and (5), respectively. The values of λ_{leak} range from (1.2 to 8.7) $\times 10^{-3} s^{-1}$ (with associated uncertainties of 7–15%) and those of λ_{back} from (1.3 to 3.5) $\times 10^{-3} s^{-1}$ (with average uncertainties of 10%), resulting in λ_{eff} equal to 1.0–1.2 $\times 10^{-3} s^{-1}$ (with average uncertainties of 10–12%), which is the same order of magnitude of λ. All the uncertainties cited in the text and reported in the tables are expressed as 1σ. This demonstrates that leakage and back-diffusion phenomena occur during the experiments and cannot be neglected. An example of an experimental radon growth curve obtained for a slab of Tufo Giallo Napoletano is reported in Fig. 3 and compared with the theoretical curve described by Eq. (3) and with other two curves corrected for leakage and/or back diffusion. The theoretical curve (curve 1), where both chamber leakage and back diffusion were considered, fits very well with the experimental data, indicating the validity of the approach used in this study to estimate free radon exhalation rates of building materials. The other two curves, where the radon loss due to back diffusion alone (curve 2) and the loss due to leakage and back diffusion

(curve 3) were not evaluated, reach equilibrium values which are coherently higher than the experimental data. They were obtained from a modified versions of Eq. (3) where λ_{eff} is replaced by $\lambda+\lambda_{back}$ (curve 2) and from Eq. (1) (curve 3). The radon free exhalation rates of all materials have been calculated using Eq. (3) and are reported in Table 1. They are about 30% higher than the values that would have been obtained if the chamber leakage and the back-diffusion phenomena had not been quantified.

As far as thoron exhalation rates are regarded, the effects of leakage and back diffusion were not observed and evaluated because of the short half-life of thoron. Consequently thoron exhalation rates, (calculated from Eq. (1) and reported in Table 1) do not represent free exhalation rates, even if the phenomena of leakage and back diffusion should presumably affect thoron in the same proportion of radon. In this case, the values of thoron exhalation rates reported in Table 1, should be about 30% lower than the corresponding free exhalation rates, as inferred from radon data. In any case the thoron exhalation rates calculated for several building materials used in Lazio region are relevant, even if affected by large uncertainties, and cannot be neglected when calculating the total lung exposure among residents in similar high thoron background areas where thorium-enriched materials are often used in buildings.

4.2. Influence of particle size and humidity on exhalation rates

In order to evaluate the influence of particle size on radon and thoron exhalation rates, a sample of lapilli from Colli Albani volcano district has been heated to 110 °C and then sieved at the following grain size: >4, 4–2, 2–1, 1–0.5, 0.5–0.25, <0.25 mm. About 1 kg of each granulometric fraction, as well as 1 kg of the whole-rock sample, has been prepared, placed in the accumulation chamber and counted. Results are reported in Table 2 and expressed as surface exhalation rates (mBq $m^{-2} s^{-1}$). An inverse correlation between grain size and exhalation rates can be observed and interpreted in terms of larger surface/volume ratio, and in turn larger exhalation surface, of small particles compared with larger ones. The whole-rock sample, consisting mainly of larger grains (about 60% of grains ranging from 4 to 1 mm), achieved values of radon exhalation rates (0.67 ± 0.02 mBq $m^{-2} s^{-1}$) in the range of the most abundant

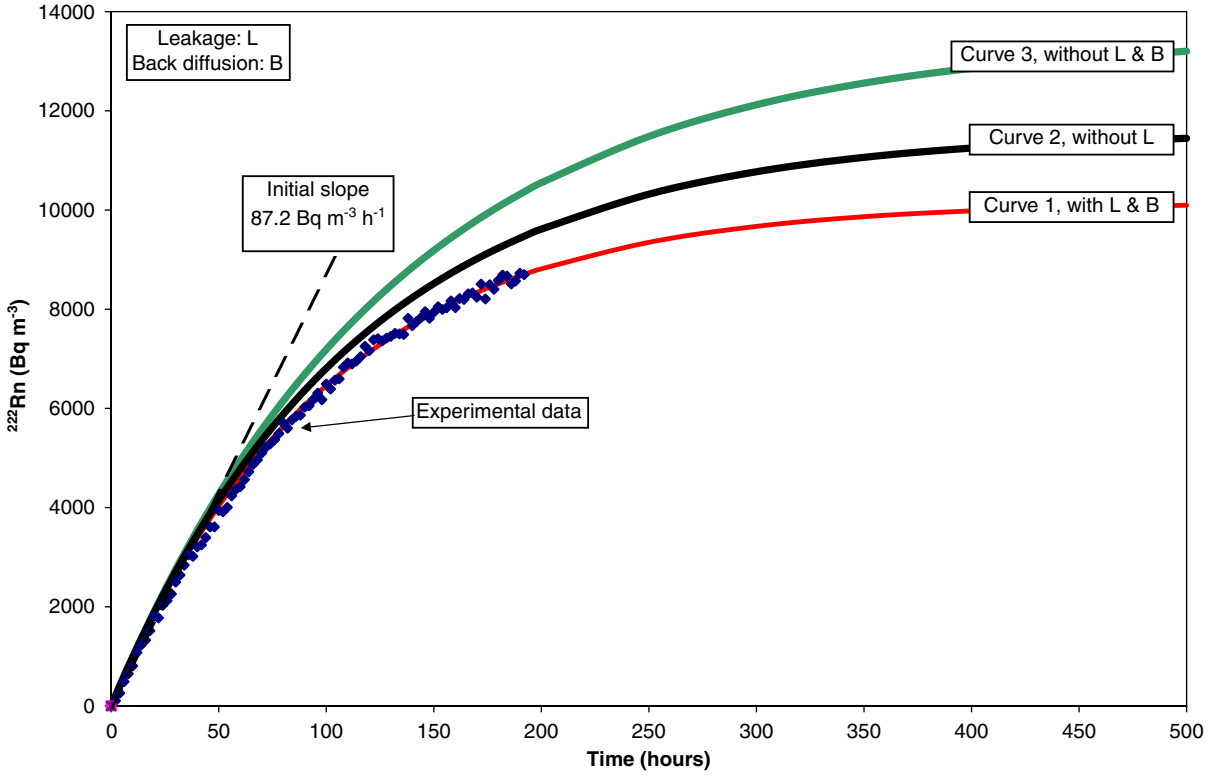

Fig. 3. Experimental radon growth curve of a slab of "Tufo Giallo Napoletano" pyroclastic flow compared with a theoretical curve described by Eq. (3) (curve 1) and other two curves corrected for leakage (curve 2) and leakage and back diffusion (curve 3). Error bars ranging from 10–15% (for radon concentration lower than 1000 Bq m^{-3}) to 3–4% (for radon values from 1000 to about 9000 Bq m^{-3}) have not been reported.

Table 1
Radon and thoron exhalation rates of studied samples

Sample	Provenance	^{222}Rn E_0 (mBq m^{-2} s^{-1})	^{220}Rn E (mBq m^{-2} s^{-1})
Black pozzolana	Colli Albani district	10.3 ± 0.7	6290 ± 726
"Tufo Lionato" [a,b]	Colli Albani district	0.24 ± 0.03	270 ± 197
Scoriaceous lava from Nemi[c]	Colli Albani district	0.69 ± 0.08	1210 ± 473
"Peperino" from Marino[a]	Colli Albani district	0.37 ± 0.02	249 ± 179
"Peperino" from Marino[c]	Colli Albani district	0.95 ± 0.11	1000 ± 450
"Peperino" from Albano[a]	Colli Albani district	0.43 ± 0.05	108 ± 82
Lapilli[b]	Colli Albani district	0.67 ± 0.02	875 ± 170
Lava from Nemi[a]	Colli Albani district	0.62 ± 0.06	81 ± 75
"Tufo rosso a scorie nere" [a]	Vico district	1.52 ± 0.09	709 ± 251
"Peperino della Via Flaminia" [a,b]	Sabatini district	0.16 ± 0.03	427 ± 103
"Peperino della Via Flaminia" [b,c]	Sabatini district	0.29 ± 0.07	873 ± 64
"Rosso Veronese" [a]	Veneto Region	0.010 ± 0.005	53 ± 36
"Travertino from Tivoli"[a,b]	Tivoli, Lazio Region	0.015 ± 0.08	Not detected
"Travertino from Tivoli"[b,c]	Tivoli, Lazio Region	0.018 ± 0.009	34 ± 30
"Tufo giallo napoletano"[a,b]	Campania Region	0.74 ± 0.12	162 ± 102
Brick[a]	Sold in Lazio Region	0.05 ± 0.01	69 ± 48
Siliceous sands	Mozambique	0.04 ± 0.02	69 ± 32

Errors are quoted as 1σ.
[a]Slab of material.
[b]Dried at 110 °C.
[c]Crushed and sieved (grain size <0.25 mm).

fractions (0.52–0.98 mBq m^{-2} s^{-1}). Three more sample, ("Tufo Lionato", "Tufo Giallo Napoletano" and "Tufo Rosso a Scorie Nere" pyroclastic flows) were crushed, sieved at the following size (>2, 2–0.5, <0.5 mm) and heated at 110 °C in order to further investigate the inverse dependence of exhalation rates on grain size. The values of their radon and thoron exhalation rates (Table 2) reflect also in these experiments their inverse covariance with grain size. The effect of available exhalation surface on exhalation rates has been finally investigated on another set of samples ("Tufo Giallo Napoletano", "Peperino" from Marino area, "Peperino della Via Flaminia" pyroclastic flows and "Travertino" from Tivoli quarries) cut and shaped into approximately 12 × 9 × 4 cm slabs. The same materials have been also crushed, sieved (grain size <0.25 mm) and measured. A comparative view of radon and thoron exhalation rates obtained for the stony and the crushed subsamples is reported in Table 2. The results strengthen the point that the slabs, averagely characterised by exhalation surfaces smaller than those available for crushed materials (the finer ones, in particular), show lower exhalation rates.

The influence of humidity on radon exhalation rates has been studied on two slab samples ("Tufo Giallo Napoletano" and "Tufo Litoide" pyroclastic flows) consisting of subsamples dried at 110 °C for 24 h and subsamples left to equilibrate with ambient humidity (about 40–60%). The results (Table 3) show that humid materials have always higher exhalation rates than dried samples and an explanation of this can be found in the lower recoil distance of radionuclides in water-filled pores than in air-filled pores (Wiegand, 2001). This results in a higher probability of the recoiled radon atoms to stay into water-filled pores and not being reabsorbed by other grains, and in turn determines larger exhalation rates from humid samples.

4.3. *Influence of radon and thoron precursors concentration on exhalation rates and evaluation of the activity concentration index*

In order to evaluate how radon and thoron exhalation rates are influenced by the activity concentration of their precursors (^{226}Ra and ^{232}Th, respectively), gamma spectrometry analyses have been carried out on several building materials. The specific activity [Bq kg^{-1}] of ^{226}Ra, ^{232}Th and ^{40}K, along with the activity concentration index calculated using Eq. (7), are reported in Table 4.

Two groups of samples, one characterised by high specific activities of ^{226}Ra and ^{232}Th (always much larger than 10 Bq kg^{-1} and up to 350–400 Bq kg^{-1}) and another with specific activity low values ($\leqslant$10 Bq kg^{-1}) can be distinguished, with the exception of the brick with values of 30–40 Bq kg^{-1}.

Table 2
Radon and thoron exhalation rates as a function of sample grain size, that is of available exhalation surface

Sample	Provenance	Grain size (mm)	Radon exhalation rate ($mBq\,m^{-2}\,s^{-1}$)	Thoron exhalation rate ($mBq\,m^{-2}\,s^{-1}$)
Lapilli	Colli Albani district	Whole rock	0.67 ± 0.02	875 ± 170
Lapilli	Colli Albani district	>4	0.52 ± 0.05	596 ± 89
Lapilli	Colli Albani district	4–2	0.52 ± 0.05	516 ± 77
Lapilli	Colli Albani district	2–1	0.98 ± 0.10	725 ± 109
Lapilli	Colli Albani district	1–0.5	0.98 ± 0.10	1060 ± 159
Lapilli	Colli Albani district	0.5–0.25	1.12 ± 0.08	1140 ± 171
Lapilli	Colli Albani district	<0.25	1.14 ± 0.08	2000 ± 300
"Tufo Lionato"	Colli Albani district	Slab	0.24 ± 0.03	270 ± 197
"Tufo Lionato"	Colli Albani district	>2	0.31 ± 0.06	2030 ± 635
"Tufo Lionato"	Colli Albani district	2–0.5	0.35 ± 0.07	977 ± 457
"Tufo Lionato"	Colli Albani district	<0.5	0.39 ± 0.09	953 ± 301
"Tufo Giallo Napoletano"	Campania region	Slab	0.74 ± 0.12	162 ± 102
"Tufo Giallo Napoletano"	Campania region	>2	2.87 ± 0.25	498 ± 368
"Tufo Giallo Napoletano"	Campania region	2–0.5	2.18 ± 0.18	815 ± 308
"Tufo Giallo Napoletano"	Campania region	<0.5	2.69 ± 0.47	1060 ± 410
"Tufo Rosso a Scorie Nere"	Vico district	Slab	1.52 ± 0.09	709 ± 251
"Tufo Rosso a Scorie Nere"	Vico district	>2	3.87 ± 0.37	1081 ± 506
"Tufo Rosso a Scorie Nere"	Vico district	2–0.5	4.30 ± 0.26	1460 ± 364
"Tufo Rosso a Scorie Nere"	Vico district	<0.5	4.74 ± 0.25	3020 ± 553

Errors are quoted as 1σ.

Table 3
Effects of humidity on radon exhalation rates

Sample	Humidity content	Provenance	^{222}Rn E_0 ($mBq\,m^{-2}\,s^{-1}$)
Slab of "Tufo Giallo Napoletano"	Dried at 110 °C	Colli Albani district	0.74 ± 0.12
Slab of "Tufo Giallo Napoletano"	Left to equilibrate with ambient humidity	Colli Albani district	1.76 ± 0.02
Slab of "Tufo Lionato"	Dried at 110 °C	Colli Albani district	0.24 ± 0.03
Slab of "Tufo Lionato"	Left to equilibrate with ambient humidity	Colli Albani district	0.36 ± 0.01

Errors are quoted as 1σ .

The first group of samples, consisting of volcanic materials from Central Italy, is highly enriched in ^{226}Ra (97–294 $Bq\,kg^{-1}$) and even more in ^{232}Th (183–470 $Bq\,kg^{-1}$), while the second one, consisting of limestone, travertine or siliceous sands, is poorly radioactive. If a comparison of radon and thoron exhalation rates, with the specific activities of ^{226}Ra and ^{232}Th, respectively, is made, without taking into account other factors like for example the grain size and the humidity of the sample, a rough positive correlation between exhalation rates and specific activity of precursors can be recognised, but this is not always true. For example, among the investigated samples, the pozzolana is characterised by the highest radon and thoron exhalation rates, but not by the highest specific activity of ^{226}Ra (in particular) and ^{232}Th. If the pozzolana sample is then compared with a material ("Tufo Lionato" pyroclastic flows) with similar ^{226}Ra specific activity

Table 4
Specific activity of ^{226}Ra, ^{232}Th and ^{40}K of several building materials used in central Italy, along with their activity concentration index (I)

Sample	Grain size (mm)	Provenance	^{226}Ra (Bq kg^{-1})	^{232}Th (Bq kg^{-1})	^{40}K (Bq kg^{-1})	I (Bq kg^{-1})
Black pozzolana	Whole rock	Colli Albani district	142	341	85	2.2
"Tufo lionato"	4–2	Colli Albani district	158	398	187	2.6
"Tufo lionato"	<0.125	Colli Albani district	150	470	181	2.9
"Peperino" from Marino	<0.25	Colli Albani district	97	195	128	1.3
Lapilli	Whole rock	Colli Albani district	220	379	251	2.7
Lapilli	4–2	Colli Albani district	228	376	264	2.7
"Tufo rosso a scorie nere"	Just crushed	Vico district	254	389	157	2.8
"Peperino della via Flaminia"	Just crushed	Sabatini district	124	183	149	1.4
"Rosso Veronese"	Just crushed	Veneto Region	1.8	5.5	5.1	0.03
"Travertino" from Tivoli"	Just crushed	Tivoli, Latium Region	2.9	8.3	2.4	0.05
"Tufo giallo napoletano"	4–2	Campania Region	229	273	169	2.2
"Tufo giallo napoletano"	<0.125	Campania Region	294	380	161	2.9
Brick	Just crushed	sold in Latium	32	44	67	0.3
Sands	Whole rock	Mozambique	7.4	9.8	10.2	0.08

Associated uncertainties, expressed as 1σ, are of the order of 2–3%.

(140–150 Bq kg^{-1}), the pozzolana radon exhalation rate results 20 times larger than that of "Tufo Lionato". Several other examples could be made indicating that the values of specific activity of radon and thoron precursors (as well as of activity concentration index) cannot be used to proportionally estimate the radon and thoron exhaled from a building material and then accumulating in the indoor environment. Factors like available exhaling surface, sample humidity, as well as air temperature and pressure, strongly influence the process of radon and thoron release and should be considered with extreme attention.

5. Conclusions

The main conclusion of this research can be summarised as follows:

(1) Building materials should be classified on the basis of their radon and thoron exhalation rates, simultaneously determined using a simple protocol, not expensive and easy to reproduce, rather than only on the basis of their activity concentration index. This approach and policy has been already adopted by the Netherlands which have developed a "radiation performance index" (van der Graaf et al., 2001), calculated on the basis of the dose contributions from both gamma radiation and radon exhalation of building materials.
(2) The exhalation rates measurements should allow the evaluation of leakage and back-diffusion phenomena which could take place during the experiments in order to calculate the free exhalation rates of building materials. The experiments presented in this paper have shown that the evaluation of chamber leakage and back diffusion lead to a correction of radon exhalation rates of about 30%.
(3) Experimental conditions should be properly fixed and strictly respected because the values of exhalation rates are strongly variable and dependent on factors like grain size, sample humidity and air temperature.
(4) The thoron contribution to the total lung exposure among residents in buildings where materials with high thoron exhalation rates are used should not be neglected. This is particularly important for Lazio region in central Italy, but applies to other high thoron background areas where thorium-enriched materials are used in buildings.
(5) Catalogues of building materials classified on the basis of their attitude to release radon and thoron should be consulted by construction engineers. The materials should be tested taking into account their specific use for building or decoration. The experimental protocol should approach the ambient conditions occurring in indoor environments, even if it is very difficult to effectively reproduce them because of the extreme variability of meteorological/climatic conditions, different habits of occupants and different type and size of buildings.

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