Abstract: The Sassi of Matera (Basilicata region, southern Italy) is a peculiar site, but not unique in Italy, from a landscape point of view. Most of the buildings are excavated in rocks of calcarenite origin and used as homes and accommodation facilities. For this reason, the contribution of gamma radiation to the population due to this building material has been investigated for the first time. Even though the type of rock is not mentioned among the construction materials indicated in Italian Legislative Decree 101/2020 to be subjected to radiological characterization, the methodology indicated in the decree was applied, comparing the values with those present in the literature. The content of $^{226}\text{Ra}$, $^{232}\text{Th}$ and $^{40}\text{K}$ was then investigated with gamma spectroscopy, and the gamma index was calculated. The results obtained showed a low level of activity concentration of natural radionuclides in this type of stone, confirming the radiological safety. This result can also support the recovery and restoration initiatives for these buildings to conserve the architectural and landscape heritage of this village.

Keywords: natural stones; building materials; gamma spectroscopy; gamma index; Sassi of Matera

1. Introduction

The Sassi of Matera site constitutes a housing system in the Basilicata region (Southern Italy) erected on the plateau of the Gravina of Matera canyon, which was drilled to create tunnels and architectural sites. The city was built with calcarenite stone, locally called tufo, which is the pivotal element that gave the city its amazing architecture, with its structures both built with and excavated into the stone. In particular, the latter has become the basic constructive cell called lamia or lamione. These two types of buildings coexist in harmony as the excavation work provides the material needed for the lamione [1]. Another example of a similar architecture can be found on Ischia Island, where several buildings were excavated in green tuff, a natural stone which is the result of the volcanic activity of the island dating back to 55000 years ago [2,3]. Since the Sassi site is entirely built with tufo and given that people spend most of their time indoors [4,5], the estimation of the indoor air quality is to be considered fundamental [6]. In fact, tuff (or tufo) is a stone with a granular and very porous structure which, in addition to giving a contribution of gamma radiation, also facilitates the exhalation of radon gas ($^{222}\text{Rn}$).

Tuff is also a very widespread building material (BM) in Italy and in particular in central-southern Italy where it is the most used material for all kinds of construction, such as brick; in some cases, such as those analyzed by us, the building is even excavated in the tuff.

There are different types of tuff: tufts of eruptive pyroclastic origin, such as Ischia, rich in radionuclides of natural origin such as uranium-238 ($^{238}\text{U}$), and tuffs, such as those of Matera, originating from a cement deposit of calcareous waters and consisting mainly of...
calcite or dolomite, which contain radionuclides naturally but in lower concentrations than the first.

Our study focuses on the radiological evaluation of the gamma emitters, which constitute the source of external irradiation, by investigating the content of the main natural gamma-emitter radionuclides. Environmental radioactivity is given by two principal radioactive series: one originating from uranium-238 (\(^{238}\)U) and the other generated by thorium-232 (\(^{232}\)Th). Still, another element plays a fundamental role in gamma radiation exposure, mostly due to its wide distribution in the ecosystem: potassium-40 (\(^{40}\)K). Discernibly, the dose rates depend on the concentration of these elements in soil and stones and on the local geology of each area of interest [2,7,8]. Nevertheless, the analysis of the gamma radiation emitters present in natural stones used as building material (BM) is crucial since natural radiation is responsible for the largest contribution to the external dose of the global population [5]. From the radioprotection and regulatory point of view, the Italian Legislative Decree 101/2020 (Article 29, comma 5) [9], which implemented the Directive 2013/59/EURATOM [10], provided a reference level of activity concentration of natural radionuclides in BM to regulate human exposure and reduce the relative health risks. In particular, the screening tool of the gamma index (\(I_\gamma\)) adopted in the Italian Legislative Decree, firstly proposed in Radiation Protection 112 (RP112) [11] and then reported in Directive 59/2013 EURATOM [10], is employed to gauge the contribution of the gamma exposure from natural stones to the effective dose. The value of \(I\) equal to or greater than 1 is a prudential control tool to identify materials that can lead to exceeding the dose limit. The reference level, applied to external exposure to gamma radiation emitted by BM indoors, in addition to external exposure outdoors, is set at 1 mSv/year. Although the tufa with which the Sassi site is built is not recorded in Annex II of the Decree, which lists all the materials needing the evaluation of the gamma index, in this work we apply the aforementioned methodology to evaluate the concentration of the gamma-emitting radionuclides for this peculiar BM. The obtained results allow understanding if this type of rock could have a radiological impact and, therefore, be part of radioprotection management.

Another important indoor pollutant, already mentioned before, is \(^{222}\)Rn, a radioactive gas whose short-living alpha-emitting daughters (\(^{218}\)Po, \(^{214}\)Pb, \(^{214}\)Bi and \(^{214}\)Po) are responsible for internal exposure to ionizing radiation and can cause serious health damage [12–17]. Due to its natural origin and being a descendant of \(^{238}\)U, radon is also present in natural stones that are used as BM [18,19] and, for this reason, monitoring of the internal environment is often considered necessary [20–27], as structures built in tuff, such as the Sassi site, have the potential to show high levels of radon concentration. In fact, the architectural features can favor the accumulation of radon gas indoors, as in many cases the buildings have only one opening to the outside.

Even if the results of the unique case study about radon activity concentration in the Sasso Barisano complex [28] showed that the radioactivity levels ranged between a minimum value of 25.9 Bq/m\(^3\) and a maximum value of 61.05 Bq/m\(^3\), Sassi of Matera has not been fully investigated. Further investigations are necessary to confirm the results of the previously mentioned study [28], and our research could provide additional information about the radiological characterization of the site.

2. Materials and Methods

2.1. The Sassi Site

The Sassi of Matera site (Figure 1a) is composed of Sasso Barisano and Sasso Caveoso, organized in approximately 80 rupestrian villages, called casali, which were built in a vertical succession [29] (Figure 1b). In addition to this, these structures were organized in housing units that form the vicinato, a public space in which people could work and socialize [30]. Despite the city being considered one of the most peculiar cities in Italy, Matera and the Sassi site were left to decay for many years. In fact, after the Second World War, the site was deemed a “national disgrace”, in conflict with the advance of the modern era [31]. In addition to this, between the 1950s and 1970s, the living conditions of the
populations who inhabited the site were below average: not only did people share living spaces with animals, leading to several endemic diseases, but infant mortality reached high levels [29]. Furthermore, there were also structural instability problems since several buildings and streets were involved in either collapses or soil sinking [32]. Only after being chosen as UNESCO World Heritage Site in 1993 was the Sassi site re-evaluated, and the city was renovated and turned into one of the major art cities of Italy, a transformation that culminated in the nomination, in 2014, for Matera as the European Capital of Culture 2019 [31].

Figure 1. View of the Sassi site (a) and a close-up of the structure built in a vertical succession (b).

2.2. Samples and Preparation

The material used to create the city was the tufa dug out of the calcarenite of the Gravina, which not only can host rupestrian villages in natural and artificial chambers but also can be used as a building material [33]. The tufa, which is found in both the area of interest and the Apulia region [34], is composed of shells and calcareous fossils of different sizes characterized by a yellowish-white color (Figure 2a). It is possible to divide this material into three different categories depending on the size of the grains composing the stone: tenacious, fossilifera and fine grains [35,36]. The basic units of the tufa are grains composed of bioclasts and lithoclasts, the organization of which can vary from poorly to moderately sorted. The dimension of both bioclasts and lithoclasts can fluctuate between 200 and 800 μm, creating a poor micritic matrix [37]. During the years, calcarenites have been used as both building and decorative resources [38], considering their aesthetic, availability, lightness and good workability. Additionally, this material, which is soft and porous, presents low values of conductivity and thermal diffusivity, qualities that enhance its insulation properties [39].
Several stones were gathered in the area to prepare 10 samples, and their preparation was carried out according to UNI EN ISO 18589-2:2015 [40], a protocol that ensures both the homogeneity and uniformity of the sample. To prepare the samples, the stones were reduced to powder by grinding (PM 100 Retech) and sieving and dried in an oven (DIGITRONIC Selecta 2005141) at a temperature of 105 °C for two hours. Lastly, the powder was homogenized in conformity with the measurement techniques [40] (Figure 2b). The resulting material was sealed in a Marinelli beaker for 1 month because $^{226}$Ra and its daughters had to reach the secular equilibrium to ensure a correct measurement. Subsequently, the material was weighed and its density was calculated ($d = 1.5$ kg/L).

2.3. Gamma Spectroscopy and Gamma Index

The detector employed to analyze the sample was the coaxial high purity germanium (HPGe ORTEC) detector (model GMX-4S4ST), a gamma spectrometry system characterized by a beryllium window with a 48% relative efficiency. The energy resolution, determined in terms of full width at half maximum (FWHM), resulted equal to 2.16 keV for 1.33 MeV. Due to the presence of the beryllium window, the system presents good sensitivity even at energies lower than 100 keV. The spectrum, obtained using the Ortec DSPEC-LF unit and the MCA Emulator Software, was examined with the GammaVision Spectrum Analysis Software. To reduce the external background, a 10 cm lead circular wall was placed around the detector. In addition to this, background gamma spectra were collected to estimate the gamma radiation in the laboratory where the sample was analyzed. The counting time necessary to obtain a good statistic was equal to 20 hours for both the samples and the background. The transition energies of $^{238}$U, $^{232}$Th and $^{40}$K were taken into account to study the gamma-ray spectrum of the sample. In particular, the full energy peaks were 63.2 and 92.5 keV for $^{234}$Th ($^{238}$U), 186 keV for $^{226}$Ra, 46.5 keV for $^{210}$Pb ($^{238}$U), 911.1 and 968.9 keV for $^{228}$Ac ($^{232}$Th) and 1461 keV for $^{40}$K. The interference between gamma lines of 186 keV for $^{226}$Ra and 186 keV for $^{235}$U was solved by sharing the areas of the respective peaks in the function of each relative branching ratio with an appropriate peak fit program. Energy calibration and efficiency for γ-ray spectrometry were obtained using as standard a mixed nuclide source (Eckert & Ziegler Nuclitec GmbH),
density 1 g/cm$^3$, activity 49 kBq, range of use 60–1836 keV, resolution 3% and a Marinelli geometry 1 L, similar to that used for samples.

The standard uncertainty was calculated according to what is reported in ISO 18589-3:2015 [40]. The combined uncertainty in the final specific activity, resulting from the analysis of the spectrum and the application of the various corrective factors, has the following equation (1):

$$\sigma_t = \sqrt{\sigma_{\text{count}}^2 + \sigma_{\text{nor}}^2 + \sigma_{\text{eff}}^2 + \sigma_{\text{sum}}^2 + \sigma_{\text{abs}}^2 + \sigma_{\text{nucl}}^2 + \frac{\sigma_{\text{geo}}^2}{3} + \sigma_{\text{adl}}^2 + \sigma_s^2}$$

(1)

where the various contributions to the total uncertainty $\sigma_t$ are as follows:

- $\sigma_{\text{count}}$ = counting uncertainty estimate;
- $\sigma_{\text{nor}}$ = additional normally distributed uncertainty estimate;
- $\sigma_{\text{sum}}$ = random summing uncertainty estimate;
- $\sigma_{\text{abs}}$ = absorption uncertainty estimate;
- $\sigma_{\text{nucl}}$ = nuclide uncertainty estimate;
- $\sigma_{\text{eff}}$ = efficiency uncertainty estimate;
- $\sigma_{\text{geo}}$ = geometry uncertainty estimate;
- $\sigma_{\text{sys}}$ = systematic (uniformly distributed) uncertainty estimate;
- $\sigma_{\text{adl}}$ = additional user-defined uncertainty factor;
- $\sigma_s$ = sample size uncertainty.

The minimum detectable activity (MDA) of the system was estimated with 95% confidence level [41]. The factors that influence the MDA are the calibration geometry, the backgrounds (induced by the system and the source), the resolution of the detector and the particular nuclide. For our measurements, we applied the traditional ORTEC method [42].

The gamma index was calculated using the equation (2) adopted by both the European Commission and the Legislative Decree 101/2020 [9]:

$$I_\gamma = \frac{C_{\text{Ra}}}{300 \text{ Bq/kg}} + \frac{C_{\text{Th}}}{200 \text{ Bq/kg}} + \frac{C_{\text{K}}}{3000 \text{ Bq/kg}}$$

(2)

where $C_{\text{Ra}}$, $C_{\text{Th}}$ and $C_{\text{K}}$ correspond to $^{226}$Ra, $^{232}$Th and $^{40}$K activity concentrations in the building material, respectively.

3. Results

The activity concentrations of the radionuclides for 10 samples and MDA values are reported in Table 1.

Table 1. Values of activity concentration of 10 samples.

| Sample | $^{226}$Ra (Bq/kg) | err | $^{232}$Th (Bq/kg) | err | $^{40}$K (Bq/kg) | err |
|--------|------------------|-----|------------------|-----|----------------|-----|
| #1     | 3.52             | 0.74 | 5.85             | 1.93 | 4.02           | 0.80 |
| #2     | 3.48             | 0.73 | 5.73             | 1.89 | 4.78           | 0.96 |
| #3     | 2.98             | 0.63 | 4.98             | 1.64 | 4.92           | 0.98 |
| #4     | 4.25             | 0.89 | 6.2              | 2.04 | 5.37           | 1.07 |
| #5     | 2.54             | 0.53 | 5.23             | 1.72 | 4.47           | 0.89 |
| #6     | 3.15             | 0.66 | 4.96             | 1.64 | 4.59           | 0.92 |
| #7     | 4.75             | 1.00 | 5.35             | 1.77 | 5.04           | 1.01 |
| #8     | 3.35             | 0.70 | 5.12             | 1.69 | 4.33           | 0.87 |
| #9     | 2.76             | 0.58 | 5.62             | 1.85 | 4.12           | 0.82 |
| #10    | 3.12             | 0.66 | 5.58             | 1.84 | 4.28           | 0.86 |
| MDA    | 1.04             | 0.7  | 1.3              |      |                |      |

The mean values of activity concentration calculated for 10 different samples and the mean gamma index are reported in Table 2.
Table 2. Mean values of activity concentration of the analyzed radionuclides and $I_\gamma$.

| Scheme          | $^{226}$Ra (Bq/kg) | $^{232}$Th (Bq/kg) | $^{40}$K (Bq/kg) | $I_\gamma$ |
|-----------------|--------------------|--------------------|------------------|-----------|
| Sassi of Matera | 3.0 ± 0.7          | 5 ± 2              | 5.0 ± 0.1        | 0.04 ± 0.01 |

The results were subsequently compared with those listed in the ISTISAN report 17/36 [43], a database containing the activity concentration measurements of natural radionuclides in European BM. ISTISAN report 17/36 presents data from approximately 23,000 samples of bulk materials (bricks and concrete), their constituents (concrete, NORM residues, etc.) and superficial materials employed in most European countries. In particular, the activity concentration values measured in our Sassi of Matera stones were compared with those relative to materials of a similar nature, such as the limestone, as reported in Table 3.

Table 3. Activity concentration of the radionuclides measured in the limestone listed in the ISTISAN report 17/36.

| Building Material  | Number of Samples | $^{226}$Ra (Bq/kg) | $^{232}$Th (Bq/kg) | $^{40}$K (Bq/kg) | Ref. |
|--------------------|-------------------|--------------------|--------------------|------------------|-----|
| Limestone_1        | 27                | Mean: 11, Max: 30, Min: 0.4 | Mean: 2, Max: 22 | Mean: 46, Max: 47 | [44] |
| Limestone_2        | 1                 | Mean: 65, Max: 6, Min: 6 | |
| Limestone_3        | 1                 | Mean: 76, Max: 8 | |

4. Discussion

The comparison between the data reported in Table 3 and the results in Table 2 shows that the radioactive content in the tufo employed to build the Sassi of Matera site is extremely low, confirming the data acquired in the case study in which radon concentration measurements were conducted [28]. In fact, the values found in both analyses verify the low levels of radioactivity in this building material. In addition, it is possible to observe that only the activity concentration of $^{232}$Th presents a value comparable to the ones of the limestones recorded in the ISTISAN report [43]. Contrarily, the other two elements ($^{226}$Ra and $^{40}$K) differ from the reference level. This is probably because, although they are calcarenites, these limestones have different origins (Sicily [44] and northern Italy [18]) and therefore differ from the stone of the Gravina of Matera canyon. Thus, the analyzed tufo is characterized by lower levels of radioactivity than other similar building materials, such as the tuff that can be found on Ischia Island. In fact, a previous study [2] revealed that the measured activity concentration values were higher than those relative to the Sassi site, although they did not exceed the reference level indicated by the European Commission in the Directive 2013/59/EURATOM [10] and the Italian Legislative Decree 101/2020 [9]. The dissimilarities between the results found in these studies can be explained considering the different origins of the two building materials. In fact, from the mineralogical point of view, the tuff can be calcareous of sedimentary origin, like the tufo of Sassi of Matera, or of eruptive pyroclastic origin, such as green tuff of Ischia Island.

5. Conclusions

The concentration of natural radionuclides in building materials is considered of great importance from the point of view of radiation protection, as indicated both in the RP and in the European Directive, implemented in Italy by Legislative Decree 101/2020. The tufo of Sassi of Matera is not listed in Annex II of the decree; therefore, its analysis is not considered mandatory, as it belongs to the class of calcarenites. However, we decided to examine the samples collected to obtain more data on this fascinating site and on its base construction unit. This study analyzed the activity concentration of $^{226}$Ra, $^{232}$Th and $^{40}$K, and the gamma index ($I_\gamma$) was also calculated.
Our preliminary results show that the $I_\gamma$ value is much lower than both the reference level and the average values of similar stones, such as limestone, reported in the literature.

Although our results do not raise any concerns for the inhabitants’ radiological safety, gamma characterization can provide useful information when planning renovation and remediation works in accordance with legislative requirements. It would be desirable to conduct a more detailed study on the activity concentration of radionuclides in this BM. In addition, a more thorough analysis of the radon concentration could offer a better radiological characterization of the tufo, since it represents a typical stone found throughout the Basilicata region.

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