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Radionuclide concentration and radon exhalation in new mix design of bricks produced reusing NORM by-products: The influence of mineralogy and texture

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1 **Radionuclide concentration and radon exhalation in new mix design of bricks produced reusing**  
2 **NORM by-products: the influence of mineralogy and texture.**

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39 **Abstract**

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41 Many industrial by-products contain Naturally Occurring Radioactive Materials (NORM) that  
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43 normally represent a cost in terms of monitoring, risk management and storage. When included in  
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45 new mix designs of bricks, these materials may become a valuable sustainable resource. Before  
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47 marketing, companies involved in development and commercialization of these new building  
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49 materials ensure safety related to radiation, usually by assessing radon-related risk. According to the  
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51 Council Directive 2013/59/Euratom, both raw materials and final products used in building  
52  
53 constructions need to be tested for activity concentration. The present work explores the radionuclide  
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55 concentration and the radon exhalation of bricks obtained recycling different types of potentially  
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57 radioactive wastes: i) trachyte as by-product resulting from quarrying operations, and ii) two different  
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27 types of industrial sludge derived from ceramic tiles industry. Raw materials were studied to foresee  
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28 any potential radioactive risk derived from their use as secondary raw materials, while bricks were  
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529 investigated to assess the influence of mineralogy and texture on their radioactive properties and their  
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730 effective radon-risk. The results obtained here show that, although radon emanation in bricks is  
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1031 primarily determined by radionuclide concentration in the raw materials, textural features  
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1232 significantly affect radon mobility and exhalation.  
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1734 Key words: Bricks; Radioactivity; Radon; Building materials; Industrial by-products.  
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## 2236 **Introduction**

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2437 Building materials produced from rocks and sediments (clay, sand, gravel and soils) contain natural  
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2738 radioactive elements at highly variable concentration levels and can constitute Naturally Occurring  
28  
2939 Radioactive Materials (NORM) [1-11]. Natural radioactivity of building materials contributes to the  
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31  
3240 mean annual radiation dose to population both in terms of external irradiation directly emitted from  
33  
3441 the material and of internal exposure related to the radon exhaled [12-14]. External radiation exposure  
35  
3642 is determined by direct gamma radiation from external sources, and can be assessed from the activity  
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38  
3943 concentrations of radium ( $^{226}\text{Ra}$ ), thorium ( $^{232}\text{Th}$ ), and potassium ( $^{40}\text{K}$ ). Internal radiation exposure  
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4144 by building materials. is caused by inhalation of gaseous radon, released from pores and fractures in  
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4445 the material itself [15-17]. NORM in building materials are mainly associated with the radioactive  
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4646 families of  $^{238}\text{U}$ ,  $^{232}\text{Th}$ , and the primordial  $^{40}\text{K}$ , the radioactivity from the  $^{235}\text{U}$  family being negligible  
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48  
4947 as compared to  $^{238}\text{U}$  on the basis of their relative isotopic abundance. Particular attention should be  
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5148 paid to radon ( $^{222}\text{Rn}$ ), thoron ( $^{220}\text{Rn}$ ), and their daughters, whose inhalation enhances the risk of  
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5449 bronchial and lung cancer [18,19]. NORM include several materials such as bulk rocks used as  
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5650 dimension stones, whose radioactivity is tightly connected with their petrography, or bricks, tiles,  
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5851 cement, concrete and other materials manufactured from mixtures of geological materials such as  
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52 clay, sand, gravel and other components from local or remote sources. Activity concentration of these  
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253 components will contribute to the average radioactivity of the final building material.  
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54 In the last decades, the amounts of waste from human activities and by-products from the industry  
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755 has been constantly increasing, affecting disposal costs and rising dramatic environmental concerns.  
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1056 In addition, our society is facing a progressive shortage of geo-resources as virgin raw materials.  
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1257 Thus, industry searches for alternative secondary raw materials, including the recycling of both  
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1458 wastes and by-products. This trend is partly motivated by an increasing awareness of the need for  
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1759 green strategies [20-28], and partly by the perspective of reducing costs, especially in the production  
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1960 of building material. Although mitigating the impact on the environment by reducing primary geo-  
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2261 resources exploitation, and often even improving their properties, these products are required to  
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2462 undergo health risk assessment and fulfil health standards before being commercialised [14,29,30].  
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2763 When waste and by-products are incorporated into a newly designed building material, the final  
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2964 product will contain all their original chemical components, including radionuclides, yielding a  
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3265 mixture of stable and radioactive components depending on the amounts and composition of the  
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3466 precursor materials employed [31]. Moreover, the texture of the final product may also change during  
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3667 the production process, therefore modifying the permeability of the final product to gases. For  
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3968 example, mineralogy and pore structure of bricks may significantly change during firing, depending  
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4169 on the different raw materials used [32]. Building materials containing secondary raw materials may  
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4470 potentially expose people to radiation: for this reason, it is necessary to investigate radioactivity on  
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4671 both raw materials and final products [33].  
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4972 In Europe, the first attempt to regulate radioactivity of building materials dates back to 1999, when  
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5173 the European Commission released the Radiation Protection 112 [12], a document containing criteria  
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5374 and application rules for dose assessment. In order to estimate exposure from building materials,  
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5675 Radiation Protection 112 introduced the index I, calculated from  $^{226}\text{Ra}$ ,  $^{232}\text{Th}$  and  $^{40}\text{K}$  activity  
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5876 concentrations experimentally determined by high resolution gamma spectrometry. However, it is  
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77 only in 2014 that the European Union enforced the previous documents into the Council Directive  
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278 2013/59/Euratom [34].  
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579 Radiation Protection 112 guidance [12] mandates that “*when industrial by-products are incorporated*  
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780 *in building materials and there is reason to suspect that these contain enhanced levels of natural*  
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1081 *radionuclides, the activity concentrations of these nuclides in the final product should be measured*  
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1282 *or assessed reliably from the activities of all component materials*”. Article 75 of the Council  
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1583 Directive 2013/59/Euratom [34] encompasses different types of building materials, dividing them  
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1784 into natural materials and materials incorporating residues from processing industries. If the activity  
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1985 concentration index (I) of these residues are below the reference levels imposed by the Council  
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2286 Directive 2013/59/Euratom [34], the derived building materials can be used without restriction.  
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2487 In view of a safe re-use in bricks of by-products potentially enriched in natural radioactivity, their  
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2788 physical, chemical, mineralogical, and radiological properties should be considered and accurately  
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2989 characterised. The Council Directive 2013/59/Euratom [34] does not provide guidelines to account  
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3290 for the specific radon exhalation/emanation contribution from the building materials. This specific  
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3491 issue has been recently reviewed in detail by the COST Action Tu1301 NORM4BUILDING, that  
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3692 contributed to collect and organize available information, and set up operational guidelines for the  
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3993 management of all building materials including those containing NORM by-products, and for the  
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4194 formulation of new synthetic ones [14,33]. Radiological aspects in the recycling of by-products in the  
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4495 manufacturing of cement, concrete, ceramics, and other construction materials are discussed in  
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4696 Chapter VII of the COST Action Tu1301 NORM4BUILDING [33]. On the contrary, both traditional  
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4997 bricks and bricks produced using NORM by-products have been poorly studied and most of the  
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5198 standards that regulate radioactivity [12, 34] addressed gamma radiation rather than radon exhalation  
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5399 and the related control of texture and porosity.  
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5600 In this work, we describe the results of an integrated approach aimed at characterizing radioactivity  
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5801 and mineralogy of two series of newly designed bricks obtained from the same base clays, tempered  
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6102 with two different types of ceramic sludge and a by-product of quarrying activity, consisting of finely  
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103 fragmented trachyte waste. Both these types of industrial by-products may potentially increase  
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104 radioactivity of the bricks: sludge from ceramic production could contain radioactive elements  
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105 derived from the additives used for specific treatments (e.g. sintering, hardening, whitening) or added  
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106 to glaze, such as zircon [36]; trachyte is a volcanic rock characterised by relatively high  
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107 concentrations of radionuclides [37].  
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108 The paper is organised as follows:  
11

- 109 - determination of the radioactivity level of bricks as well as of the single raw materials used such as  
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110 base clay and temper from industrial by-products;  
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111 - correlation of radioactivity with mineralogical and physical features, to predict radioactivity in  
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112 newly designed building materials when produced using potentially radioactive by-products;  
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113 - comparison of the radioactivity and the mineralogy of a set of conventional bricks, the mineralogy,  
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114 texture and mechanical properties of which had been already previously determined [27,30,32,35],  
26  
115 with the radioactivity and mineralogy of these new products.  
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## 116 117 **2. Materials**

118 A set of different bricks, and corresponding raw materials, have been analysed. Raw materials include  
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119 four different types of clay, tailings from quarrying activity, two types of sludge from ceramic  
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120 industry, and a dye additive (Table 1). The following clay raw materials provided by the Company  
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121 San Marco-Terreal (Italy) were considered: LG (*Laminato Giallo*, i.e. “Yellow Laminated”), LRS  
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122 (*Laminato Rosa*, “Pink Laminated”), LRSS (*Laminato Rosso*, “Red Laminated”) and LRSSF  
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123 (*Laminato Rosso Forte*, “Intense Red Laminated”). These clays have similar mineralogy but different  
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50 relative abundance of their components, especially carbonates [27]. Two types of industrial by-  
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124 products replacing the traditional temper to produce experimental bricks were characterized: i) two  
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125 types of sludge derived from ceramic industry (samples F and PIR) [35]; ii) a finely fragmented  
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126 trachyte waste produced by quarrying activity (sample TR) at M. Altore, in the Euganean Hills  
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128 Volcanic District (north-eastern Italy) [30]. Furthermore, a Mn-oxide-based dye additive was also  
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3 considered (sample MN), as it is used in one of the commercial bricks here studied (sample N).

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The bricks analysed can be grouped in three different categories (Table 1): i) commercial bricks (produced by San Marco-Terre); ii) experimental bricks obtained by adding the trachyte waste; iii) experimental bricks obtained by adding the two types of sludge from ceramic industry.

The six commercial bricks (samples GP, N, RS, RSS, R6, RCF) are produced by adding 10 wt. % of a quartz-rich sand (sample SS) to the different clayey materials (LG, LRS, LRSS, LRSSF) (Table 1).

The mixtures are fired at different temperatures (Table 1), depending on the specific clay used. In addition, different proportions of a dye (additive MN) were added to sample N, up to 15 wt. %.

Nine experimental bricks were obtained by tempering the most siliceous clayey material (LRSSF) with 5, 10 and 15 wt. % (samples with prefix B5, B10 and B15, respectively) of sand-sized fragments of trachyte, and firing each mixture at three different temperatures: 900, 1000, 1100 °C (suffix 9, 10 and 11, respectively).

Two additional experimental bricks (samples MF and B\_PIR) were obtained tempering the most carbonate-rich clay (LGP) with 10 wt. % of the two different types of sludge (F and PIR); both mixtures were then fired at 1050 °C (same firing temperature as commercial bricks GP and N obtained from the same base clay). Types of material and experimental conditions are summarized in Table 1.

### 3. Methods

The chemical composition of the samples was determined by X-ray fluorescence (XRF) on an S4 Pioneer (Bruker AXS) spectrometer, with an estimated detection limit of 0.01 wt. % for major elements; trace elements, expressed in ppm, have the following analytical detection limits: Zr = 15 ppm, Rb = 18 ppm; Sr = 20 ppm; Cr 11 = ppm; Zn = 15 ppm; Ni = 1 ppm; Pb = 17 ppm. ZAF method was employed for quantitative analysis [38], while the NCS DC 74301 (GSMS-1) standard was used for calibration [39].



153 X-ray powder diffraction (XRPD) was applied to identify the mineral phases of raw materials and  
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154 fired products. Diffraction data were acquired using a PANalytical X'Pert PRO diffractometer,  
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155 operating in Bragg-Brentano reflection geometry with CoK $\alpha$  radiation, 40 kV of voltage and 40 mA  
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156 of filament current, equipped with an X'Celerator detector. Qualitative analysis of diffraction data  
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157 was carried out with X'Pert HighScore Plus<sup>®</sup> software (PANalytical) and the PDF-2 database. The  
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158 petrographic and textural characteristics of thin sections were examined under a polarized light optical  
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159 microscope (Olympus DX-50, equipped with a Nikon D7000 digital microphotography system).  
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160 Texture and reaction microstructures were examined by Scanning Electron Microscopy (SEM) with  
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161 a CamScan MX-2500 microscope, coupled with an EDAX Sapphire Si(Li) detector (LEAP+Si(Li)  
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162 crystal), equipped with a LaB<sub>6</sub> cathode operating at 20 kV and 160 nA.  
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163 The distribution of pore-access size (radius range: 0.001-100  $\mu\text{m}$ ) was determined by Mercury  
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164 Intrusion Porosimetry (MIP) on a Model 9410 Micromeritics Autopore apparatus, which can generate  
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165 a pressure of 414 MPa. Freshly cut samples of approximately 2 cm<sup>3</sup> were oven-dried for 24 hours at  
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166 110 °C and then analyses.  
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167 Nitrogen adsorption was used to determine brick porosity in the range (in diameter) between 0.0002  
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168 and 0.3  $\mu\text{m}$ . Sorption isotherms were obtained at 77 K, on a Micromeritics Tristar 3000 in continuous  
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169 adsorption conditions. Prior to measurement, samples were heated at 130 °C for 24 h and outgassed  
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170 to 10<sup>-3</sup> Torr on a Micromeritics Flowprep. Specific surface area of pores was determined by  
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171 Brunauer–Emmett–Teller (BET) theory based on the physical adsorption of gas onto the surface of a  
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172 solid.  
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173 Activity levels of raw material and finite products were evaluated both measuring concentrations of  
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174 K, U, Th and descendants by XRF, and high-resolution  $\gamma$ -ray spectroscopy. Samples were analysed  
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175 with two p-type coaxial Hyper Pure Germanium crystal detectors (HPGe), a PROFILE (Ortec-  
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176 Ametek Inc.) with an extended energy range (20–2000 keV) and a conventional GEM model (Ortec-  
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177 Ametek Inc.) with an energy range 80-2000 keV. These detectors have relative efficiency of 20% and  
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178 38%, and resolution (FWHM) at 1332.5 keV of 1.9 keV and 1.8 keV, respectively. Both systems

179 were calibrated for energy and efficiency using a liquid standard source (Eckert & Ziegler  
 180 Multinuclide standard solution 7501) in a jar geometry (diameter = 56 mm; thickness = 10 mm).  
 181 Spectra were acquired for 1 day to optimize peak analysis. Spectra were subsequently processed and  
 182 analysed with the Gamma Vision-32 software (version 6.07, Ortec-Ametek Inc.) [40]. <sup>226</sup>Ra was  
 183 determined at 186 KeV correcting the peak area by the <sup>235</sup>U interference according to the method  
 184 proposed by Gilmore (2008) [41], under the hypotheses of secular equilibrium between <sup>226</sup>Ra-<sup>238</sup>U  
 185 and natural <sup>235</sup>U/<sup>238</sup>U isotopic ratio. <sup>238</sup>U and <sup>232</sup>Th were then determined using the emissions of their  
 186 radioactive daughters <sup>226</sup>Ra and <sup>228</sup>Ac.

187 The minimum detectable activity (CR<sub>MDA</sub>) was calculated according the so-called Traditional  
 188 ORTEC method available in GammaVision according to the expression:

$$189 \quad CR_{MDA} = \frac{\frac{100}{SENS} \cdot \left( \sqrt{2 \cdot B_1 + \frac{2500}{SENS^2}} + \frac{50}{SENS} \right)}{LT}$$

190 where SENS is the Peak Cutoff value (%) on the Analysis tab (40% in this work), B1 is the Peak  
 191 background, and LT is the Live Time (sec).

192 Conversion from activity concentration (Bq/kg) to bulk elemental weight fraction was obtained  
 193 through the following conversion factors [42]:

194 1% K = 309.7 Bq/kg

195 1 ppm U = 12.35 Bq/kg

196 1 ppm Th = 4.072 Bq/kg

197 Council Directive 2013/59/Euratom [34] defines the Activity Concentration Index (I) in order to  
 198 quantify and regulate the exposure to gamma radiation originating from radionuclides in building  
 199 materials:

$$200 \quad I = C_{Ra226} / 300 \text{ Bq/kg} + C_{Th232} / 200 \text{ Bq/kg} + C_{K40} / 3000 \text{ Bq/kg}$$

201 where C<sub>Ra</sub>, C<sub>Th</sub> and C<sub>K</sub> are the specific activities of <sup>226</sup>Ra, <sup>232</sup>Th and <sup>40</sup>K, respectively, expressed in  
 202 Bq/kg. The activity concentration index value of 1 can be used as a conservative screening tool for  
 203 identifying materials that may cause the reference level (1 mSv per year) to be exceeded [34].

204 The alpha-index ( $I\alpha$ ) may be used to regulate the exposure to radon originating from radionuclides in  
1 building materials [43,44]:

$$206 I\alpha = C_{Ra}/200 \text{ Bq/kg}$$

207 The reference levels of  $I\alpha$  and  $I$  are 0.5 and 1, respectively [12,34,43].

208 To assess the radiation hazard of the bricks, the radium equivalent activity ( $Ra_{eq}$ ) was calculated  
10 according to the method introduced by Beretka and Methew (1985) [45] with the following equation:

$$210 Ra_{eq} = C_{Ra} + 1.43 C_{Th} + 0.07 C_K \leq 370 \text{ Bq/kg.}$$

211 Radon emanation and exhalation from a porous material in indoor air should be regarded as a  
18 combination of different processes and factors. Firstly, the radon emanation derives from the solid-  
19 phase lithology and its characteristic naturally occurring radioactivity. Secondly, since radon atoms  
20 recoil and migrate into the pore space, texture and physical features can sensibly affect exhalation.

215 Radon exhalation from the investigated materials was measured by electrets. To this scope, brick  
26 samples were cut into cubes (edge = 5 cm) to obtain a measurable external surface. Each sample was  
27 introduced in suitable airtight bottles (volume = 0.00372 m<sup>3</sup>) containing two electrets in SST  
30 configuration [Kotrappa]; prior to analysis, radon blank was checked in the closed bottle in the  
31 absence of sample. For each sample a parallel measurement with an empty bottle was carried out for  
32 background radon subtraction under the same environmental conditions. After tightly sealing the  
33 bottles, radon exhalation was allowed over a suitable time (5-7 days); eventually the bottles were  
34 opened and electrets retrieved and read, and the experiment repeated. The final exhalation value was  
35 taken as the average of two subsequent readings. The radon exhalation rate ( $Q_A$ ) was then evaluated  
36 as follows:

$$225 Q_A \left[ \frac{Bq}{d} \right] = \frac{V\lambda}{1 - \frac{1 - e^{-\lambda T}}{\lambda T}} [\langle C \rangle_{sample} - \langle C \rangle_{blank}]$$

226 where  $\lambda$  is the decay constant of <sup>222</sup>Rn (0.18145 d<sup>-1</sup>),  $T$  the measurement time in days,  $V$  the free  
57 volume inside the bottle,  $C$  the radon concentration in Bq/m<sup>3</sup> and the angular brackets indicate  
58 average over time ( $T$ ).  
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229 Finally, specific surface exhalation rate ( $Ea$ ) is calculated dividing  $Q_A$  by the sample surface  $S$  in  
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230 square meters:

$$231 \quad Ea \left[ \frac{Bq}{d \ m^2} \right] = \frac{Q_A}{S}.$$

232 The radon release per unit mass of the material, specific mass exhalation rate ( $Em$ ), can be calculated  
9  
233 dividing  $Q_A$  by the mass  $m$  in kilograms of the sample:

$$234 \quad Em \left[ \frac{Bq}{d \ kg} \right] = \frac{Q_A}{m}.$$

235 According to Stoulos et al. (2003) [13] and Righi and Bruzzi (2006) [44], the radon emanation  
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236 coefficient ( $\eta$ ), representing the percentage of radon produced from grains and free in porous system,  
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237 can be also defined as follows:

$$238 \quad \eta = Q_A / C_{Ra} \ m \ \lambda_{Rn}$$

239 where  $Q_A$  is the measured radon exhalation rate (Bq/d),  $C_{Ra}$  the  $^{226}\text{Ra}$  content (Bq/kg),  $\lambda_{Rn}$  the  $^{222}\text{Rn}$   
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240 decay constant (1/d), and  $m$  is the mass of the sample (kg).

241 Data obtained from the previously described analytical methods, were statistically treated according  
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342 to multivariate approaches, consisting in the cluster analysis (CA) and principal component analysis  
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343 (PCA), using Statgraphics® Centurion XVI software package. CA represents an optimal approach  
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344 for the management of chemical data, since it can describe the natural structure of the dataset and  
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445 homogeneous subsets of samples (defined as clusters), which differ from the others to some extent,  
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446 expressed by the dissimilarity level. PCA is a multivariate approach which converts a dataset  
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447 originally described by numerous variables, possibly correlated, into a dataset expressed new  
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448 variables (called principal components), which emphasises the maximum variability among the  
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449 samples. PCA was performed on the chemical data to evaluate the elements mainly affecting the  
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450 differences between bricks, and it was also applied considering the physical parameters (density,  
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451 porosity, surface area) as well as the those related to the radiation activity ( $I$ ,  $I\alpha$ ,  $Ea$ ,  $Em$ ,  $C_{Ra}$ ) in order  
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57  
452 to define which of these variables mainly contribute to describe the differences among the bricks, and  
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453 to identify possible correlations between various parameters. These statistical approaches, therefore,  
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254 were used to better interpret the possible relationships between the physical, compositional and  
1 structural parameters of the bricks with a special attention to the radon-related effects.  
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256

## 257 **4. Results**

### 258 **4.1 Raw materials**

#### 259 **4.1.1 Chemical and mineralogical characterization**

260 Chemical composition of clayey materials shows significant differences in CaO and MgO suggesting  
14 variable content in carbonates (see Table 2). In particular, samples LRS and LG have both higher  
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261 concentrations of these oxides and Loss on Ignition (LOI) than LRSS and LRSSF. This agrees with  
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262 the mineralogical composition (Table 3) which indicates that they are illite-chlorite carbonate-rich  
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21  
263 clays, with significant amounts of calcite and dolomite.  
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265 Trachyte (sample TR) is rich in Na<sub>2</sub>O and K<sub>2</sub>O (Table 2; Na<sub>2</sub>O + K<sub>2</sub>O ~ 10 wt. %), consistently with  
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27  
266 the abundance of anorthoclase (an alkali feldspar) and plagioclase, associated with minor amounts of  
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29  
30  
267 biotite and quartz (Table 3) (see Coletti et al., 2018 [30], and also data referring to M. Altore trachyte  
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33  
268 in Germinario et al., 2018 [46]); zircon and magnetite occur as accessory minerals as recognised  
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269 under optical microscope, and account for the Zr (559 ppm) and Fe<sub>2</sub>O<sub>3</sub> (3.26%) contents (Table 2).  
37

38  
39  
270 Sludge materials F and PIR are rich in silica and alumina (Table 2). Quartz and feldspar dominate  
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41  
271 their mineralogy (Table 3). Sludge F is characterized by mullite and amorphous phase (Table 3) [35],  
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43  
272 suggesting an origin from ceramic production in which the firing process reached temperatures above  
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45  
273 900 °C, when mullite starts to form from illite-muscovite and/or kaolinite breakdown [47] and  
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47  
274 sintering occurs. Sludge PIR contains higher amounts of feldspars (both alkali-feldspar and  
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275 plagioclase), illite and minor amounts of carbonates, as evidenced by the content in CaO and from  
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276 LOI (2.19 and 4.35 wt. %, respectively; Table 2), and by the presence of calcite reflections in the  
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54  
277 diffraction pattern (Fig. 1S). This sample also contains relatively high amounts of Zn, Cr and Sr  
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278 (4915, 2201 and 567 ppm, respectively). These elements are diagnostic of ceramic manufacturing  
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279 applied to confer specific physical and aesthetical characteristics to the final material body and  
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280 surface: in particular, ZnO is generally used in ceramics as a fluxing agent, Cr to obtain a wide variety  
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281 of different hues, while Sr produces matte glazes [48]. The high amount of Zr both in sludge F and  
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282 PIR (1583 and 7157 ppm, respectively) is probably related to the wide use of this element in the  
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283 ceramic industry both for tile enamel whitening and as a structural component; however, its use has  
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284 been strongly reduced in recent times, to avoid its excessive concentration in NORM [48]. PIR  
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1285 presents also moderate amounts of Pb (77 ppm). In the past, Pb has been used as melting agent;  
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286 nowadays it is mainly used in the production of glaze.  
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16  
1287 Sample MN is a Mn-oxide ( $Mn_2O_3$ ; hausmannite) and is used as a dye (added to the raw materials in  
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288 ~15 wt. %) to obtain dark-grey coloured bricks [27].  
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#### 290 **4.1.2 Natural radioactivity**

291 Table 4 reports the activity concentration of  $^{226}Ra$ ,  $^{232}Th$  and  $^{40}K$  in the raw materials. The measured  
292 values on clay span over a range between 29 Bq/kg and 50 Bq/kg for  $^{226}Ra$ , between 34 Bq/kg and 59  
293 Bq/kg for  $^{232}Th$ , and between 29 Bq/kg and 50 Bq/kg for  $^{40}K$ . These values are consequently reflected  
294 in the correlated I value (Table 4), providing a minimum of 0.47 for clay LG and a maximum of 0.70  
295 for clay LRSS, in both cases below the recommended value of 1 [34].  
296

297 Also,  $\alpha$ -indexes of clayey materials have all values below the recommended value ( $I\alpha \leq 0.5$ , Table 4)  
298 [12], with the maximum value registered for clay LRSS ( $I\alpha = 0.25$ ).  
299

300 Among the industrial by-products, F shows very low  $^{226}Ra$  activity concentration with values below  
301 the minimum detectable activity of the instrument, while TR and PIR have the highest measured  
302 values. TR has 52 Bq/kg of  $^{226}Ra$  and shows a very high value of  $^{40}K$  (1210 Bq/kg), approximately  
303 twice as much as the other samples, owing to the abundance of alkali feldspars in trachyte (Table 3),  
304 which is naturally characterised by a relatively high radioactivity [37].  
305

306 Sludge PIR has the highest activity concentration value of  $^{226}Ra$  (120 Bq/kg, Table 4), responsible  
307 for the high  $I\alpha$  value (0.60, Table 4), probably connected to the high content in Zr, and supposedly in  
308 other high-field-strength elements (HFSE) such as U and Th [49]. Dye additive MN has very low  
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306 values of activity concentration (Table 4), below minimum detectable activity for all the analysed  
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307 elements. The highest  $Ra_{eq}$  have been detected for samples TR and PIR (216 Bq/kg and 219 Bq/kg,  
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4  
308 respectively), much higher than those of the clayey materials, quartz-rich sand, and of the other by-  
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309 products, with values between 30 Bq/kg and 189 Bq/kg (Table 4). This is in agreement with activity  
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310 concentration of the critical radionuclides in the different raw materials, determining slightly higher  
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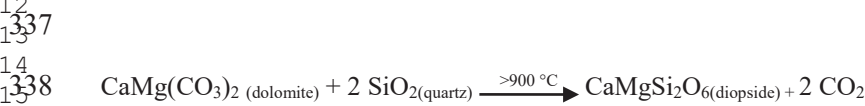
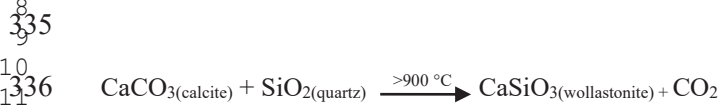
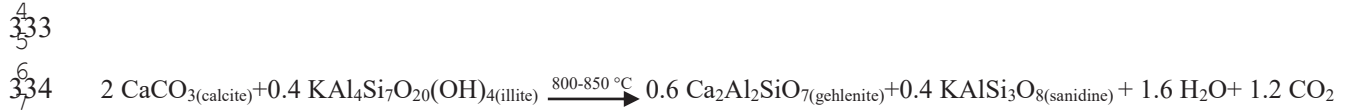
## 4.2 Bricks

### 4.2.1 Chemical composition and mineralogy

The chemical composition of the investigated bricks (Table 2) is consistent with that of the clay materials used and the temper added (Table 1). The dendrogram of figure 1a reports the hierarchical cluster analysis of the chemical composition performed on XRF data (Table 2). It shows that bricks GP and FM produced using a carbonate-rich clay (LG) are clustered together (cluster 1) and separated from the two bricks N and B\_PIR produced using the same clay, but obtained by adding the by-products MN and PIR, respectively, which appear as isolated outliers (Fig. 1a) for the higher MnO, Zr and Zn contents, respectively (score and loading plot in Fig. 1b, Table 2). Bricks obtained using low-Ca clays (LRSS and LRS) form a distinct cluster (cluster 2) (Fig. 1a), whereas those produced using clay LRSSF group all together in cluster 3 (Fig. 1a). These latter were obtained adding to the base clay a quartz or trachyte sand, respectively; despite the different chemical composition of the added temper, these bricks group together and are separated from all the others for the higher content in  $SiO_2$ ,  $Na_2O$ ,  $Fe_2O_3$ ,  $P_2O_5$  as well as of Ni.

From a mineralogical point of view, the commercial bricks can be distinguished on the basis of the used clayey materials, temper/additive and firing temperature (Table 3). The new minerals formed at temperature above 800 °C are the result of carbonates (calcite and dolomite) and illite decomposition and their sub-solidus reactions with quartz and feldspar grains. These phases form reaction rims and

331 often display non-stoichiometric compositions. Nonetheless, the main reactions taking place at the  
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332 grain boundaries can be described as follows [22,23,50]:



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340 Brick N contains bustamite  $\text{CaMnSi}_2\text{O}_6$ , a member of the wollastonite group, isomorphic with  
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341 wollastonite, which developed from the sub-solidus reaction between hausmannite, calcite and quartz  
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342 [35]:



344 Brick R6, instead, shows a completely different mineralogy, characterised by persistence of clay-  
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345 forming minerals such as illite, chlorite, and still showing carbonates (calcite and dolomite) because  
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346 fired at 600 °C, thus below their breakdown temperature [27,47,51] (Table 3).

347 Bricks obtained from the addition of the two types of sludge (F and B\_PIR) are very similar under a  
37  
348 mineralogical viewpoint to the commercial brick GP, also manufactured using the same carbonate-  
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349 rich clay LG (Table 3), being all enriched in wollastonite and diopside.

350 All the experimental bricks obtained by adding trachyte waste to the LRSSF clay display similar  
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351 mineralogical composition, with the occurrence of newly formed silicate phases. Diopside is present  
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352 in small amounts, being the raw clay (LRSSF) very poor in dolomite, while gehlenite is abundant and  
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353 its amount increases as a function of increasing firing temperatures (Table 3). Although firing  
51  
354 temperatures always exceed typical dolomite and calcite decarbonation temperatures (750 and 850  
54  
355 °C, respectively), small amounts of calcite survived decomposition as shown in the diffraction  
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356 patterns of the bricks fired at 900 and 1000 °C, while dolomite completely disappeared. Moreover,  
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357 the small amount of illite observed in bricks fired at 1000 °C indicates that amorphisation was not



358 complete at this temperature. This may also be connected to inhomogeneity in the temperature  
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359 distribution within the kiln, which could have determined the survival of structural domains of  
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360 minerals generally destructured at slightly lower temperatures than firing temperature [30] or as  
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361 consequence of non-total amorphisation of illite. Furthermore, biotite in these bricks derives from the  
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362 trachyte waste; its abundance gradually decreases with increasing firing temperature (Table 3).

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#### 364 **4.2.2 Radionuclides activity concentration**

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365 The radioactivity levels measured in the studied bricks are comparable with those reported in the  
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366 literature [5,7,13,52,53,54]. The lowest  $^{226}\text{Ra}$  value was measured in brick N, equal to 29 Bq/kg  
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367 (Table 4). This value is lower than that measured in the clay GP used to produce this brick (45 Bq/kg).

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368 This can be explained assuming a dilution effect due to the addition of the dye additive MN, which  
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369 presents the lowest concentration of natural nuclide among the studied materials (Table 4). The same  
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370 effect can be invoked when the sludge F (Table 4) is added to the same clayey material LG.

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371 Radionuclide concentration in the brick FM results to be lower (40 Bq/kg) than that of the brick  
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372 obtained using the same clay but tempered with standard quartz-rich sand SS (brick GP, 45 Bq/kg).

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373 Conversely, the brick B\_PIR, obtained from the same clay LG with the addition of the sludge PIR,  
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374 characterised by a high radioactive concentration (120 Bq/kg), displays higher  $^{226}\text{Ra}$  concentration  
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375 (55 Bq/kg) than brick GP (Table 4). The same considerations apply to  $^{232}\text{Th}$  and  $^{40}\text{K}$  concentrations.

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43  
376 Bricks tempered with the trachyte waste TR present generally higher radioactive concentration than  
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377 the corresponding commercial bricks obtained using the same clay tempered with a quartz-rich sand  
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378 (brick RCF, 43 Bq/kg). Bricks tempered with trachyte waste have values of  $^{226}\text{Ra}$  concentration  
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379 between 46 and 55 Bq/kg, while  $^{232}\text{Th}$  concentration ranges between 43 and 56 Bq/kg, except for  
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53  
380 bricks B5.9 and B15.11, in which it is 66 Bq/kg.  $^{40}\text{K}$  concentration for this set of bricks is comprised  
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381 between ~ 600 and 1016 Bq/kg, and the maximum values have been measured for bricks B5.9 (1016  
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382 Bq/kg), B5.11 and B15.11 (1000 Bq/kg).

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383 The activity indexes (Table 4) range between 0.53 and 0.82 for I and 0.15 and 0.27 for I $\alpha$ ,  
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384 respectively. None of the two parameters exceeds the reference levels reported in the Council  
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385 Directive 2013/59/Euratom [34] and RP112 [12]. The radium equivalent activity (Ra<sub>eq</sub>) is always  
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386 < 370 Bq/kg.

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#### 388 **4.2.3 Radon exhalation rate**

389 In order to determine the contribution of the by-products to the internal radiation dose, which accounts  
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390 for the largest fraction of radiation dose from building materials, <sup>222</sup>Rn emission of the investigated  
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391 bricks was measured. Table 5 lists the radon exhalation rates and emanation fraction. Among the  
20  
392 commercial bricks analysed, the lowest radon exhalation rate has been recorded for brick RCF (Table  
23  
393 5), produced using the clay material (LRSSF) with the lowest carbonate content (see CaO wt. % in  
25  
394 Table 2). The bricks produced with clays richer in carbonates show wide variability. All the bricks  
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395 produced with the clay LG, enriched in carbonates, and tempered with different materials (bricks GP,  
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396 N, FM and B\_PIR) show considerable differences in their exhalation rate. This is undoubtedly  
33  
397 partially determined by differences in the chemical composition of the temper (e.g. bricks FM and  
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398 B\_PIR made using the two different types of ceramic sludge), partially by the textural features,  
37  
399 especially porosity, which develops during firing upon CO<sub>2</sub> release from calcinated carbonates, and  
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400 depending on the different reactions taking place at increasing temperature and on the specific temper  
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401 used. This is particularly evident when considering the two bricks RSS and R6, both based on clay  
45  
402 LRSS and the same quartz-rich temper but displaying significantly different <sup>222</sup>Rn exhalation rate  
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403 (0.017 Bq/d and 0.084 Bq/d, respectively). In these two materials, the different firing temperatures  
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50  
404 (950 °C for RSS vs. 600 °C for R6) determined the development of significantly different textures,  
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53  
405 in terms of both pore-size distribution and pore fraction [35]. Since <sup>226</sup>Ra, the precursor of <sup>222</sup>Rn, has  
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406 the same concentration in both bricks (Table 4), the high radon exhalation rate observed in brick R6  
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407 (Table 5), is reasonably determined by the different pore structure. The same stands for the lower

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408 surface exhalation rate of brick RSS ( $2.84 \text{ Bq/d}\cdot\text{m}^2$ ) as compared to brick R6 ( $8.58 \text{ Bq/d}\cdot\text{m}^2$ ) (Table  
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409 5).

410 Bricks obtained using trachyte waste as a temper have generally higher exhalation rate when fired at  
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411 lower temperature (e.g.  $900 \text{ }^\circ\text{C}$ ). Moreover, radon exhalation rate decreases increasing the amount of  
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412 trachyte waste added (Table 5). This is apparently a contradiction, considering that trachyte has  
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413 significantly higher NORM level than clay (Table 4). However, this could be attributed to the  
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414 influence of trachyte acting as a flux agent capable to modify the matrix texture [30] and promote  
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415 sintering at lower firing temperature than other types of temper. These textural changes thus reduce  
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416 radon exhalation rate despite the higher precursor activity concentration levels [55].

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417 Bricks produced with addition of sludge (FM and B\_PIR) have intermediate values of surface  
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418 exhalation rate ( $2.84 \text{ Bq/d}\cdot\text{m}^2$  and  $2.23 \text{ Bq/d}\cdot\text{m}^2$ , respectively).

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#### 420 **4.2.4 Density and porosity**

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421 Bricks (GP, N, FM, B\_PIR and RS) obtained using a carbonate-rich clay (LG and LRS) yielded the  
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33  
422 highest values of open porosity  $\varepsilon$  (%), ranging between 42 and 50% (Table 6). Among the bricks  
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36  
423 produced using sludge (F and PIR), B\_PIR is the one showing the lowest  $\varepsilon$  value: sludge PIR caused  
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38  
424 a decrease in total porosity of about 6% with respect to the commercial brick GP (produced using the  
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425 same clay, and tempered with quartz-rich sand). It is also interesting to observe the effect of this  
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43  
426 sludge on brick microstructure. Bricks display higher average pore size, as shown by comparing the  
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427 percentage of pores larger than  $1 \mu\text{m}$  in commercial bricks and in those produced with sludge (Table  
47  
48  
428 6). Brick FM, produced using sludge F, has a higher open porosity (50%), mainly constituted by pores  
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429 smaller than  $1 \mu\text{m}$  ( $\varepsilon_{<1\mu\text{m}} = 47\%$ ). Nonetheless, brick FM presents the highest density ( $1600 \text{ kg/m}^3$ ,  
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53  
430 Table 6) among the bricks produced with the carbonate-rich clay LG. This could be determined by  
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431 the specific properties of sludge F (Table 3) rich in amorphous phase, as revealed from the XRPD  
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432 data and for the highest melting phase reached during firing, capable to seal pores.

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433 Commercial bricks (RSS, R6 and RCF) produced using carbonate-poor clays (LRSS and LRSSF)  
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434 display lower open porosity (between 34% and 39%, Table 6), with brick R6 showing the lowest  
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435 value, being fired at low temperature (600 °C). This brick has an apparent density ( $\rho_a = 1700 \text{ kg/m}^3$ )  
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436 considerably different from the actual density ( $\rho_r = 2580 \text{ kg/m}^3$ ), suggesting a high fraction of closed  
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437 pores. Nevertheless, small size open pores remain predominant, as confirmed by the high value of  
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438 adsorbed nitrogen leading to a specific area of  $10.24 \text{ m}^2/\text{g}$  according to the BET method, i.e. the  
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439 highest micro-porosity value among all the other samples (Table 6).

440 Open porosity in bricks obtained by adding trachyte waste is quite variable but shows a general trend:  
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441 it increases in bricks fired at 1000 °C and decreases in those fired at 1100 °C, while bulk density ( $\rho_r$ )  
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442 increases with the firing temperature. Evaluating the pore range  $< 0.1 \mu\text{m}$ , small pores prevail in  
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443 bricks fired at 900 °C; their fraction gradually decreases with increasing firing temperature and with  
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444 increasing trachyte waste content, also when compared with brick RCF obtained using the same clay,  
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445 but different temper. Thus, the addition of trachyte tailings in the experimental bricks is likely  
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446 responsible of changes in the microstructure, enhancing bulk density and pore size, leading to the  
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447 formation of a more compact material [30]. Changes in the pore system are also well demonstrated  
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448 by the decrease of the specific surface area at increasing firing temperature, as confirmed by the BET  
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449 experiment (Table 6).

## 451 5. Discussion

452 The obtained emanation coefficients range between 0.002 and 0.109 (Table 5) in agreement with  
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453 those reported by Stoulos et al. (2003) [13] and Righi and Bruzzi (2006) [44]. Most of the bricks have  
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454  $\eta$  value below 0.04, with the exception of brick R6 reaching 0.109; this result is related to the material  
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455 texture and porosity [4,56,57,58], despite the radionuclide concentration being similar to that  
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55  
456 observed for the other bricks (Table 4).

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457 The main parameters describing radon release from a solid are the radon surface exhalation rate  $Ea$   
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458 ( $\text{Bq/d}\cdot\text{m}^2$ ), and the radon mass exhalation rate  $Em$  ( $\text{Bq/d}\cdot\text{kg}$ ). These values can be either obtained  
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459 from direct measurements [56] or estimated when other parameters of the materials are known  
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 460 [58,59], i.e. the  $^{226}\text{Ra}$  activity concentration ( $C_{\text{Ra}}$ , Bq/kg), the coefficient of emanation ( $\eta$ ), the  
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 461 porosity ( $\varepsilon$ , %) and the density ( $\rho$ , kg/m<sup>3</sup>). Nonetheless, there are limitations in both these approaches.  
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 462 Previous works describe porosity as a key factor controlling emanation power of building materials  
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 463 [13,56], but without quantifying its actual effect. Indeed, porosity plays an important role in physical-  
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 464 mechanical properties and in the decay behaviour of building materials [27,60,61,62], and so it does  
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 465 for radon migration [63,64]. Moreover, chemical and mineralogical composition and texture of bricks  
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 466 may change considerably, depending on the starting raw materials, their relative abundance and grain-  
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 467 size, and firing conditions [27,35]. Therefore, they represent ideal model materials wherein to  
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 468 investigate the influence of porosity on radon exhalation. In general, assessment of radon emanation  
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 469 power requires better understanding on the influence of porosity and pore-size distribution, and on  
 25  
 470 the influence of radionuclides concentration in relation to texture, which determines the emanation  
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 471 pathways ultimately determining the effective amount of radon emitted.  
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 472 Semkow and Parekh (1990) [65] described the importance of grain-size, which controls radon  
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 473 diffusion through porosity and surface area [66].

474 Mass emanation ( $Em$ ) normalised to porosity ( $Em_\varepsilon$ ) can be obtained by the following equation:

$$475 \quad Em_\varepsilon = 1 - Em (\varepsilon - C_{\text{Ra}}) / C_{\text{Ra}}$$

476 and mass emanation normalised to  $^{226}\text{Ra}$  concentration ( $Em_{C_{\text{Ra}}}$ ) as:

$$477 \quad Em_{C_{\text{Ra}}} = 1 - Em (C_{\text{Ra}} - \varepsilon) / \varepsilon,$$

478 where  $Em$  is the measured mass exhalation rate (Bq/d kg),  $C_{\text{Ra}}$  the  $^{226}\text{Ra}$  activity concentration  
 47  
 479 (Bq/kg), and  $\varepsilon$  the porosity (%).

50  
 5480 The binary plot of radon exhalation rate vs. normalised mass emanation clearly shows a better  
 52  
 5481 correlation when data are normalised to porosity ( $Em_\varepsilon$ ;  $R^2 = 0.96$ ; Fig. 2a) than to  $^{226}\text{Ra}$  concentration  
 54  
 5482 ( $Em_{C_{\text{Ra}}}$ ;  $R^2 = 0.86$ ; Fig. 2b). This suggests that texture, and especially open porosity, affects radon  
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 5483 exhalation more than  $^{226}\text{Ra}$  concentration.  
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484 According to Semkow and Parekh (1990) [65], radon emanation power is sensitive to pores with size  
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485 between  $5 \cdot 10^{-40}$   $\mu\text{m}$  and  $0.1 \mu\text{m}$ , although the latter are a key for radon transport inside the material.

486 This is confirmed by the data collected on bricks in the present study. The correlation between  
487 emanation mass ( $Em$ ) measured by E-PERM and total porosity as measured by MIP (Fig. 3a) is very  
488 poor ( $R^2 = 0.03$ ), while the one with the fraction of pores  $< 0.1 \mu\text{m}$  (Fig. 3b) is considerably better  
489 ( $R^2 = 0.59$ ). This suggests that the fraction of smaller pores is the most reactive to radon emission.

490 The same behaviour is observed considering the specific surface areas,  $S_0$ . The specific surface area  
491 can be calculated from the average pore radius  $r$  (assuming all pores are cylindrical) [35,67], and the  
492 total pore intrusion volume  $dV/V$  (measured by MIP) as follows:

$$493 S_0 = 2\pi r h$$

494 where the average height ( $h$ ) is calculate as:

$$495 h = \frac{dV^2}{V} / \pi r$$

496 The correlation between radon emanation mass and specific surface area ( $\text{m}^2/\text{g}$ ) is much higher ( $R^2 =$   
497  $0.60$ ; Fig. 3c) than considering the total porosity (Fig. 3a). This is related to a linear relationship  
498 between emanation power and the specific surface area [68]. This observation is supported also by  
499 the data obtained from BET, wherein pores with diameter below  $0.3 \mu\text{m}$  are analysed, although radon  
500 mass emanation and BET surface areas correlation is not so straightforward ( $R^2 = 0.48$ ; Fig. 3d).

501 A similar result was obtained comparing radon emanation mass with the specific surface area  $S_0$   
502 assuming the average pore size equal to  $0.005 \mu\text{m}$  and determining  $h$  by partial  $dV/V$  calculated in  
503 the range of pores less than  $0.005 \mu\text{m}$ :  $R^2$  value obtained in such condition ( $0.39$ , Fig. 3e), is similar  
504 to what obtained by BET ( $0.48$ , Fig. 3d). Thus, despite different analytical methods for the  
505 determination of the pores system are considered, the specific surface area is in such case related to  
506 a range of pores size overlapping in MIP and BET. According to Semkow and Parekh (1990) [65],  
507 the emanation power is less sensitive to larger pores. This is also observed for the studied bricks;  
508 when the specific surface area is calculated over the total porosity using an average pore size of  $0.5$   
509  $\mu\text{m}$  (Fig. 3f), the parameters are not correlated ( $R^2 = 0.04$ ).

Principal Component Analysis (PCA) (Fig. 4a) applied to the main physical properties and chemical components of the bricks further indicates the correlations among textural features, chemistry and radioactivity. The purpose of this analysis is to determine which of these variables is mostly affecting radon emanation of the bricks. The score and loading plot of the first three components (Fig. 4a), shows that PC1 is positively correlated with MnO, CaO and MgO that are grouped with BET surface area ( $S_{aBET}$ ), while it is negatively correlated with variables associated with natural radionuclides activity concentration, bulk density and Fe-oxides. PC2 is positively correlated with variables related to radon exhalation ( $Ea$  and  $Em$ ), LOI, and fine-size porosity (BET surface area  $S_{aBET}$  and  $\epsilon_{MIP<0.1\mu m}$ ). In order to enlighten differences among the various bricks, the binary plot of PC1 and PC2 was also considered (Fig. 4b). In this case bricks are distributed according to their specific mix design. Thus, bricks obtained from the most siliceous clay (LRSSF) with the addition of trachyte waste are all clustered together as a result of the highest radioactive content, expressed by the values of  $I$ ,  $I\alpha$  and  $C_{Ra}$ , the highest bulk density and content of  $Al_2O_3$ ,  $Na_2O$ ,  $TiO_2$ ,  $P_2O_3$ ,  $Ni$ , and  $Rb$ . On the other hand, bricks obtained from the carbonate-rich clay (LG) are grouped in correspondence to CaO and MgO. Therefore, PCA summarizes the influence of different mineralogical, chemical and physical variables in relation with radon emanation and transport.

## 6. Conclusions

Radioactivity and radon exhalation rate of bricks produced using NORM by-products have been determined and compared with those of similar commercial bricks. All investigated samples provided values below the reference levels indicated in the Council Directive 2013/59/Euratom concerning basic safety standards for protection against exposure to ionising radiations.

While radon emanation in bricks is primarily determined by the concentration of the parent radionuclides from the uranium-238 series in the samples resulting from the composition of the mixture of natural and waste materials, radon exhalation also depends on the pore system, which controls radon mobility. Because the characteristics of the pore system are influenced by the initial

536 mineral composition and by the transformations taking place during firing process, firing conditions  
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537 also contribute to determine net radon exhalation rate. Starting from the same clayey material as  
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538 commercial brick RCF and adding increasing proportions of trachyte waste, we may expect a  
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539 progressive increase of radon exhalation. Instead, although all the samples produced adding the  
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540 trachyte waste present higher exhalation rate compared to brick RCF, our data show that radon  
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541 exhalation rate decreases by increasing the amount of trachyte. This can be explained by considering  
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542 that the alkali feldspar present in the trachyte waste acts as a flux, thus promoting sintering  
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543 proportional with trachyte waste content and firing temperature. Total open porosity initially  
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544 increases from 900 °C to 1000 °C due to proceeding of sheet silicates decomposition, and then  
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545 decreases from 1000 °C to 1100 °C, due to further sintering, while open porosity < 0.1 μm and surface  
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546 area (both BET and MIP) continuously decrease with increasing temperature. A similar observation  
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547 arises considering samples RSS and R6. These two samples have the same composition, but they  
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548 have been fired at different temperatures (950 °C and 600 °C, respectively). For this reason they have  
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549 similar <sup>226</sup>Ra, <sup>232</sup>Th and <sup>40</sup>K radioactivity concentration, but significantly different radon exhalation  
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550 rate, which is four times lower in the sample RSS fired at higher temperature. In this sample,  
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551 carbonate decomposition and consequent fluxing effect of the released CaO determined an increase  
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552 in total open porosity, but a significant reduction of open porosity < 0.1 μm and surface area (both  
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553 BET and MIP), similarly to what observed in samples containing trachyte waste.  
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554 This indicates that texture evolution during firing determines significant changes in porosity and pore  
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555 size distribution, eventually determining changes in gas transport pathways through the pore system  
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556 and modifying radon exhalation rate.  
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### 33 **Table headings**

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 3650 **Table 1:** Raw materials (clayey materials, temper and additives) and bricks production recipe (with  
 37  
 38 relative firing temperature).  
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 43  
 4453 **Table 2:** Chemical composition of raw materials and bricks, expressed in wt. % of oxides for the  
 45  
 46 major and minor elements and Loss On Ignition (LOI), and trace elements expressed in ppm. < DL:  
 47  
 48 below the detection limit. \*: not measured.  
 49  
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 5357 **Table 3:** Mineralogical composition of clayey materials, temper, additive and bricks determined by  
 54  
 55 XRPD. Mineral abbreviations after Whitney and Evans (2010) [69]: Qz = quartz; Pl = plagioclase;  
 5658 Afs = alkali-feldspar; Cal = calcite; Dol = dolomite; Ill = illite; Chl = chlorite; Bt = Biotite; Hem  
 57  
 58 = hematite; Hsm = hausmannite; Crs = Cristobalite; Mul = mullite; Di = diopside; Gh = gehlenite;  
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761 Wo = wollastonite; Bst = bustamite; Kln = kaolinite; Crd = cordierite; AM = amorphous. Estimated  
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762 relative abundance: \*\*\*\*\* = very abundant; \*\*\* = abundant; \*\* = medium; \* = scarce; + = rare; - =  
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763 absent.  
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765 **Table 4:** Natural radioactivity in raw materials and bricks including activity concentrations of  $^{226}\text{Ra}$ ,  
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11  $^{232}\text{Th}$ , and  $^{40}\text{K}$  (Bq/kg), concentration of elemental U, Th, and K (ppm) and  $I_{\alpha}$  and  $I$  indexes and  
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13  $Ra_{eq}$  (Bq/kg). Experimental data below the Minimum Detectable Activity (MDA) are reported as  
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15 <MDA as determined from spectrum processing.  
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22 **Table 5:** E-PERM results:  $Q_A$ , exhalation rate (Bq/d);  $E_a$ , surface exhalation rate (Bq/d·m<sup>2</sup>);  $E_m$ ,  
23  
24 mass exhalation rate (Bq/d·kg);  $\eta$ , emanation coefficient.  
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29 **Table 6:** Physical parameters. MIP results:  $\epsilon_{tot}$ , total open porosity (%);  $\rho_r$ , bulk/real density (kg/m);  
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31  $\rho_a$ , apparent density (kg/m);  $\epsilon_{<0.1\mu m}$ , open porosity < 0.1  $\mu\text{m}$  (%);  $\epsilon_{<1\mu m}$ , open porosity < 1  $\mu\text{m}$  (%);  
32  
33  $\epsilon_{>1\mu m}$ , open porosity > 1  $\mu\text{m}$  (%);  $\epsilon_{0.1-1\mu m}$ , open porosity between 0.1 and 1  $\mu\text{m}$  (%). N<sub>2</sub> adsorption:  
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35  $S_{aBET}$ , BET surface area (m<sup>2</sup>/g). MIP:  $S_{aMIP}$ , MIP surface area (m<sup>2</sup>/g);  $S_{aMIP<0.05\mu m}$ , surface area for  
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37 pores < 0.05  $\mu\text{m}$  (m<sup>2</sup>/g);  $S_{aMIP<0.5\mu m}$ , surface area for pores < 0.5  $\mu\text{m}$  (m<sup>2</sup>/g).  
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## 41 42 43 **List of Figures** 44

45  
46 **Figure 1:** a) Dendrogram of cluster analysis according to average linkage method and square  
47  
48 Euclidean distance; b) score and loading plot of the principal component analysis performed on the  
49  
50 XRF chemical data of the studied bricks. PC1, PC2 and PC3 cover 41.3%, 30.8% and 12.2% (total  
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52 84.3%) of the total variance, respectively.  
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785 **Figure 2:** Correlation between radon mass exhalation rate ( $Em$ ) versus: a) mass emission ( $Em_\epsilon$ )  
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786 normalised for total porosity considering all the studied bricks; b) mass emission ( $Em_{CRa}$ ) normalised  
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787 for  $^{226}\text{Ra}$  concentration considering all the studied bricks.  
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789 **Figure 3:** a) correlation between measured radon mass exhalation rate  $Em$  (Bq/d·kg) and total  
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11 porosity  $\epsilon$  (%); b) correlation between measured radon mass exhalation rate  $Em$  (Bq/d·kg) and open  
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13 porosity  $\epsilon_{<0.1\mu\text{m}}$  (%); c) correlation between measured radon mass exhalation rate  $Em$   
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15 (Bq/d·kg) and surface area  $S_{aMIP}$ , determined by MIP measurements, ( $\text{m}^2/\text{g}$ ); d) correlation between  
16  
17 measured radon mass exhalation rate  $Em$  (Bq/d·kg) and surface area  $S_{aBET}$ , determined by BET  
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19 measurements ( $\text{m}^2/\text{g}$ ); e) correlation between measured radon mass exhalation rate  $Em$  (Bq/d·kg) and  
20  
21 surface area for pores  $< 0.05 \mu\text{m}$   $S_{aMIP<0.05\mu\text{m}}$ , determined by MIP measurements, ( $\text{m}^2/\text{g}$ ); f) correlation  
22  
23 between measured radon mass exhalation rate  $Em$  (Bq/d·kg) and surface area for pores  $< 0.5 \mu\text{m}$   
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25  $S_{aMIP<0.5\mu\text{m}}$ , determined by MIP measurements ( $\text{m}^2/\text{g}$ ).  
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34 **Figure 4:** Scores and loading plots of PCA performed on the following variables:  $I\alpha$  index; I index;  
35  
36 the major elements  $\text{SiO}_2$ ,  $\text{TiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{CaO}$ ,  $\text{MgO}$ ,  $\text{MnO}$ ,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$  and  $\text{P}_2\text{O}_5$  (expressed as  
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38 wt. %); the trace elements Zr, Rb, Sr, Pb, Cr, Ni and Zn (expressed as ppm); LOI (Lost On Ignition,  
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40 wt. %);  $\epsilon_{\text{tot}}$ , total open porosity (%);  $\rho_r$ , real density ( $\text{kg}/\text{m}^3$ );  $\epsilon_{<0.1\mu\text{m}}$ , open porosity  $< 0.1\mu\text{m}$  (%);  $S_{aBET}$ ,  
41  
42 BET surface area ( $\text{m}^2/\text{g}$ );  $S_{aMIP}$ , MIP surface area ( $\text{m}^2/\text{g}$ );  $Em$ , radon mass exhalation rate (Bq/d·kg);  
43  
44  $Ea$ , radon surface exhalation rate (Bq/ d· $\text{m}^2$ );  $C_{\text{Ra}}$ , activities of  $^{226}\text{Ra}$  (Bq/kg) PC1, PC2 and PC3  
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46 representing 34.7%, 26.9% and 16.4% of total variance, respectively.  
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53 **Supplementary material:**  
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56 **Figure 1S:** XRPD pattern of sample PIR. Mineral abbreviations as in Table 3.  
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	sample	type	
	LG	Clay	
	LRS	Clay	
	LRSS	Clay	
	LRSSF	Clay	
raw materials	SS	Standard temper (quartz-rich sand)	
	TR	Temper (waste 1 = trachyte by-product from quarry)	
	F	Temper (waste 2 = sludge from ceramic industry)	
	PIR	Temper (waste 3 = sludge from ceramic industry)	
	MN	Dye additive (Mn <sub>2</sub> O <sub>3</sub> , hausmannite)	
	brick	mix design	firing T (°C)
commercial bricks	GP	Clay LG + siliceous temper (10 wt. %)	1050
	N	Clay LG + siliceous temper (10 wt. %) + MN (15 wt. %)	1050
	RSS	Clay LRSS + siliceous temper (10 wt. %)	950
	R6	Clay LRSS + siliceous temper (10 wt. %)	600
	RS	Clay LRS + siliceous temper (10 wt. %)	980
	RCF	Clay LRSSF + siliceous temper (10 wt. %)	1050
bricks made with trachyte waste	B5.9	Clay LRSSF + temper TR (5 wt. %)	900
	B5.10	Clay LRSSF + temper TR (5 wt. %)	1000
	B5.11	Clay LRSSF + temper TR (5 wt. %)	1100
	B10.9	Clay LRSSF + temper TR (10 wt. %)	900
	B10.10	Clay LRSSF + temper TR (10 wt. %)	1000
	B10.11	Clay LRSSF + temper TR (10 wt. %)	1100
	B15.9	Clay LRSSF + temper TR (15 wt. %)	900
	B15.10	Clay LRSSF + temper TR (15 wt. %)	1000
	B15.11	Clay LRSSF + temper TR (15 wt. %)	1100
bricks made with ceramic sludge	FM	Clay LG + temper F (10 wt. %)	1050
	B_PIR	Clay LG + temper PIR (10 wt. %)	1050

		SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MnO	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	TiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	LOI	Zr	Rb	Sr	Pb	Cr	Ni	Zn
raw materials	LG	39.81	10.63	3.87	0.08	4.75	17.76	0.54	2.37	0.43	0.11	19.65	116	81	157	17	74	46	69
	LRS	51.50	12.72	4.43	0.09	3.41	10.45	0.70	2.74	0.54	0.12	13.29	147	98	116	22	89	42	77
	LRSS	57.77	14.14	4.85	0.10	2.68	6.16	1.09	2.99	0.63	0.13	9.47	167	106	86	27	89	36	85
	LRSSF	63.57	13.62	5.06	0.11	2.29	3.85	0.96	2.61	0.84	0.13	6.94	186	96	87	24	115	45	80
	TR	65.27	16.59	3.26	0.07	0.61	1.74	5.06	5.06	0.65	0.18	0.92	674	114	239	18	<DL	1	83
	F	72.52	18.36	1.20	0.01	0.51	1.00	3.11	2.31	0.71	0.11	0.16	1583	*	*	*	*	*	*
	PIR	65.68	17.83	2.07	0.03	0.65	2.19	3.37	1.85	0.60	0.16	4.35	7157	211	567	77	2201	37	4915
commercial bricks	GP	50.17	13.19	4.80	0.09	5.61	20.39	0.72	2.84	0.49	0.13	1.56	128	100	187	20	83	58	80
	N	42.42	11.67	4.93	12.86	4.93	17.63	0.60	2.66	0.52	0.15	1.63	127	90	162	48	76	56	193
	RSS	63.79	15.28	5.16	0.11	2.87	7.01	0.99	3.20	0.66	0.13	0.78	164	118	105	28	90	41	91
	R6	60.32	14.35	4.85	0.11	2.69	6.22	0.93	3.03	0.64	0.13	6.74	149	105	94	25	93	40	81
	RS	59.46	14.53	4.94	0.09	3.69	11.06	0.89	2.99	0.59	0.13	1.62	143	109	135	25	93	51	87
	RCF	65.29	13.81	5.41	0.10	3.06	6.52	1.52	2.41	0.72	0.15	1.01	201	124	181	38	18	78	117
bricks made with trachyte waste	B5.9	64.06	13.92	5.44	0.12	3.06	6.74	1.86	2.39	0.68	0.17	1.56	258	121	218	36	174	108	108
	B5.10	64.23	14.12	5.50	0.12	3.16	6.73	1.88	2.41	0.69	0.18	0.99	234	121	222	34	256	131	102
	B5.11	64.99	14.05	5.48	0.12	3.13	6.76	1.92	2.42	0.68	0.17	0.28	233	122	215	38	160	110	104
	B10.9	63.89	14.24	5.45	0.11	2.98	6.21	2.07	2.58	0.69	0.18	1.60	265	124	224	32	162	108	289
	B10.10	64.34	14.35	5.43	0.10	2.97	6.27	2.09	2.58	0.69	0.18	0.99	259	125	219	35	165	103	104
	B10.11	64.82	14.47	5.52	0.12	3.03	6.29	2.09	2.62	0.71	0.18	0.15	257	126	223	38	170	110	102
	B15.9	64.55	14.40	5.35	0.12	2.81	5.96	2.27	2.71	0.70	0.18	0.93	282	125	227	34	155	93	104
	B15.10	64.41	14.58	5.35	0.11	2.84	5.99	2.31	2.75	0.72	0.18	0.75	285	125	230	30	157	95	105
	B15.11	65.04	14.55	5.42	0.11	2.89	5.94	2.30	2.72	0.72	0.19	0.13	272	125	223	37	143	95	105
bricks made with ceramic sludge	FM	53.88	13.40	4.18	0.08	5.06	17.85	1.43	2.58	0.53	0.12	0.89	323	122	235	33	111	56	360
	B_PIR	54.64	14.11	3.79	0.26	4.53	16.67	1.79	2.40	0.53	0.13	1.14	2032	132	335	131	462	41	1192

		Qz	Itt	Chl	Afs	Pl	Cal	Dol	Hem	Crs	Hsm	Mul	Kln	Bt	AM	
raw materials	LG	****	**	**	*	*	****	***	+		-	-	-	-	-	
	LRS	****	**	**	*	**	**	**	+		-	-	-	-	-	
	LRSS	****	**	**	**	**	*	*	+		-	-	-	-	-	
	LRSSF	****	**	**	**	**	+	+	+		-	-	-	-	-	
	TR	**	-	-	***	***	-	-	-		-	-	-	*		
	F	****	-	-	-	***	-	-	-	+	-	**	-	-	-	**
	PIR	****	*	-	**	***	*	-	-		-	-	*	-	-	-
	MN	-	-	-	-	-	-	-	-		****	-	-	-	-	-
		Qz	Itt	Chl	Afs	Pl	Cal	Dol	Hem	Wo	Di	Gh	Bst	Crđ	Bt	AM
commercial bricks	GP	****	-	-	**	*	-	-	*	**	***	***	-	-	-	**
	N	****	-	-	**	*	-	-	*	**	***	***	***	-	-	***
	RSS	****	-	-	*	**	-	-	*	*	+	+	-	-	-	-
	R6	****	**	**	*	***	**	**	*	-	-	-	-	-	-	-
	RS	****	-	-	*	**	-	-	*	*	*	*	-	-	-	-
	RCF	****	-	-	*	**	-	-	*	*	*	**	-	-	-	-
bricks made with trachyte waste	B5.09	****	*	-	**	**	+	-	*	-	*	*	-	+	+	**
	B5.10	****	+	-	**	**	+	-	*	-	*	**	-	-	+	**
	B5.11	****	-	-	**	**	-	-	*	-	*	***	-	-	+	***
	B10.09	****	+	-	**	**	+	-	*	-	*	*	-	+	+	*
	B10.10	****	+	-	**	**	+	-	*	-	*	**	-	-	+	*
	B10.11	****	-	-	**	**	-	-	*	-	*	***	-	-	+	***
	B15.09	****	*	-	***	***	+	-	*	-	*	*	-	+	++	*
	B15.10	****	+	-	***	***	+	-	*	-	*	**	-	-	++	*
	B15.11	****	-	-	***	***	-	-	*	-	*	***	-	-	++	**
bricks made with ceramic sludge	FM	****	-	-	**	**	-	-	-	*	**	**	-	-	-	****
	B_PIR	****	-	-	*	***	-	-	+	*	***	***	-	-	-	**

		<sup>226</sup> Ra (Bq/kg)	σ%	<sup>232</sup> Th (Bq/kg)	σ%	<sup>40</sup> K (Bq/kg)	σ%	U (ppm)	σ	Th (ppm)	σ	K (wt.%)	σ	I	I <sub>α</sub>	Ra_eq (Bq/kg)
raw materials	LG	31	11	37	7	526	3	3	-	9	-	2	-	0.47	0.16	125
	LRS	29	17	34	10	633	6	2	-	8	-	2	-	0.48	0.14	126
	LRSS	50	12	59	10	716	6	4	-	14	1	2	-	0.70	0.25	189
	LRSSF	34	21	44	7	491	4	3	1	11	-	2	-	0.50	0.17	135
	SS	-	-	-	13	279	6	-	-	1	-	1	-	-	-	30
	TR	52	6	50	3	1210	2	4	-	12	-	4	-	0.82	0.26	216
	F	-	-	<8	-	<58	-	-	-	-	-	-	-	-	-	-
	PIR	120	6	41	6	511	6	10	1	10	1	2	-	0.78	0.60	219
	MN	-	-	<7	-	<47	-	-	-	-	-	-	-	-	-	-
commercial bricks	GP	45	14	47	9	700	3	4	1	11	1	2	-	0.62	0.22	161
	N	29	17	43	7	654	6	2	-	11	1	2	-	0.53	0.15	137
	RSS	41	14	52	7	757	3	3	-	13	1	2	-	0.65	0.21	168
	R6	41	13	50	6	719	3	3	-	12	1	2	-	0.62	0.20	162
	RS	36	17	44	6	755	2	3	1	11	1	2	-	0.60	0.18	151
	RCF	43	13	46	7	666	3	3	-	11	1	2	-	0.60	0.21	156
bricks made with trachyte waste	B5.9	55	12	56	8	1016	6	4	1	14	1	3	-	0.80	0.27	206
	B5.10	50	11	43	7	614	3	4	-	11	1	2	-	0.59	0.23	155
	B5.11	47	17	66	8	1000	6	3	1	16	1	3	-	0.82	0.24	212
	B10.9	46	7	45	4	663	2	4	-	11	1	2	-	0.60	0.23	157
	B10.10	51	12	44	8	693	3	4	-	11	1	2	-	0.62	0.25	163
	B10.11	47	16	44	9	843	6	4	1	11	1	3	-	0.66	0.23	169
	B15.9	46	10	43	6	689	3	4	-	11	1	2	-	0.59	0.23	155
	B15.10	46	1	53	9	761	6	4	-	13	1	2	-	0.67	0.23	175
	B15.11	47	17	66	8	1000	6	4	-	10	1	2	-	0.61	0.26	160
bricks made with ceramic sludge	FM	40	12	54	8	696	3	3	0.40	13	1	2	-	0.64	0.20	167
	B_PIR	55	9	46	12	599	6	4	0.41	11	1	2	-	0.61	0.28	163

		Exhalation rate $Q_A$ (Bq/d)	Surface exhalation rate $E_a$ (Bq/d·m <sup>2</sup> )	Mass exhalation rate $E_m$ (Bq/d·kg)	Emanation coefficient $\eta$
commercial bricks	GP	0.014	1.28	0.133	0.016
	N	0.019	1.87	0.179	0.034
	RSS	0.017	2.84	0.176	0.023
	R6	0.084	8.58	0.803	0.109
	RS	0.016	1.65	0.153	0.024
	RCF	0.000	0.00	0.000	0.000
bricks made with trachyte waste	B5.9	0.040	3.64	0.321	0.032
	B5.10	0.015	0.96	0.143	0.016
	B5.11	0.003	0.26	0.024	0.003
	B10.9	0.029	2.96	0.275	0.033
	B10.10	0.034	3.35	0.310	0.034
	B10.11	0.024	2.80	0.266	0.031
	B15.9	0.030	2.89	0.250	0.030
	B15.10	0.013	1.52	0.113	0.014
B15.11	0.023	2.31	0.206	0.022	
bricks made with ceramic sludge	FM	0.028	2.84	0.282	0.039
	B_PIR	0.022	2.23	0.222	0.022

		$\epsilon_{\text{tot}}$ (%)	$\rho_a$ (kg/m <sup>3</sup> )	$\rho_r$ (kg/m <sup>3</sup> )	$\epsilon_{<0.1\mu\text{m}}$ (%)	$\epsilon_{<1\mu\text{m}}$ (%)	$\epsilon_{>1\mu\text{m}}$ (%)	$\epsilon_{0.1-1\mu\text{m}}$ (%)	$S_{\text{aBET}}$	$S_{\text{aMIP}}$	$S_{\text{aMIP}<0.05\mu\text{m}}$	$S_{\text{aMIP}<0.5\mu\text{m}}$
commercial bricks	GP	47.45	1400	2680	0.62	46.31	1.14	45.69	2.54	2.04	0.03	0.11
	N	46.87	1500	2870	0.83	46.02	0.86	45.18	4.33	2.57	0.04	0.10
	RSS	38.83	1540	2550	2.24	33.45	5.39	31.21	3.58	1.73	0.06	0.04
	R6	34.20	1700	2580	8.55	31.06	3.21	22.51	10.24	7.05	0.14	0.03
	RS	42.25	1540	2660	2.86	39.90	2.35	37.04	5.32	2.37	0.08	0.06
	RCF	35.85	1700	2580	1.13	24.05	11.80	22.92	1.56	1.20	0.02	0.26
Bricks made with trachyte waste	B5.9	25.22	1560	2090	3.16	20.37	4.86	17.21	2.11	2.94	0.12	0.02
	B5.10	38.10	1590	2570	1.30	22.24	15.93	20.94	2.21	1.63	0.06	0.02
	B5.11	34.40	1650	2520	0.93	16.80	17.67	15.87	0.63	0.90	0.05	0.02
	B10.9	27.50	1570	2170	5.11	20.53	7.03	15.42	1.93	3.26	0.12	0.01
	B10.10	38.39	1580	2560	1.73	23.39	15.00	21.66	0.98	1.57	0.07	0.02
	B10.11	19.40	1610	2000	0.00	11.36	8.04	11.36	0.58	0.27	0.01	0.01
	B15.9	23.22	1640	2140	4.10	19.17	4.05	15.07	1.48	3.44	0.13	0.01
	B15.10	36.97	1600	2550	2.57	23.07	13.89	20.50	0.95	2.44	0.08	0.02
	B15.11	27.58	1670	2310	0.53	14.68	12.90	14.15	0.50	0.60	0.03	0.01
bricks made with ceramic sludge	FM	49.57	1600	3100	2.61	47.21	2.36	44.60	1.99	1.07	0.08	0.32
	B_PIR	41.98	1460	2520	0.54	24.02	17.96	23.48	2.31	1.81	0.04	0.24



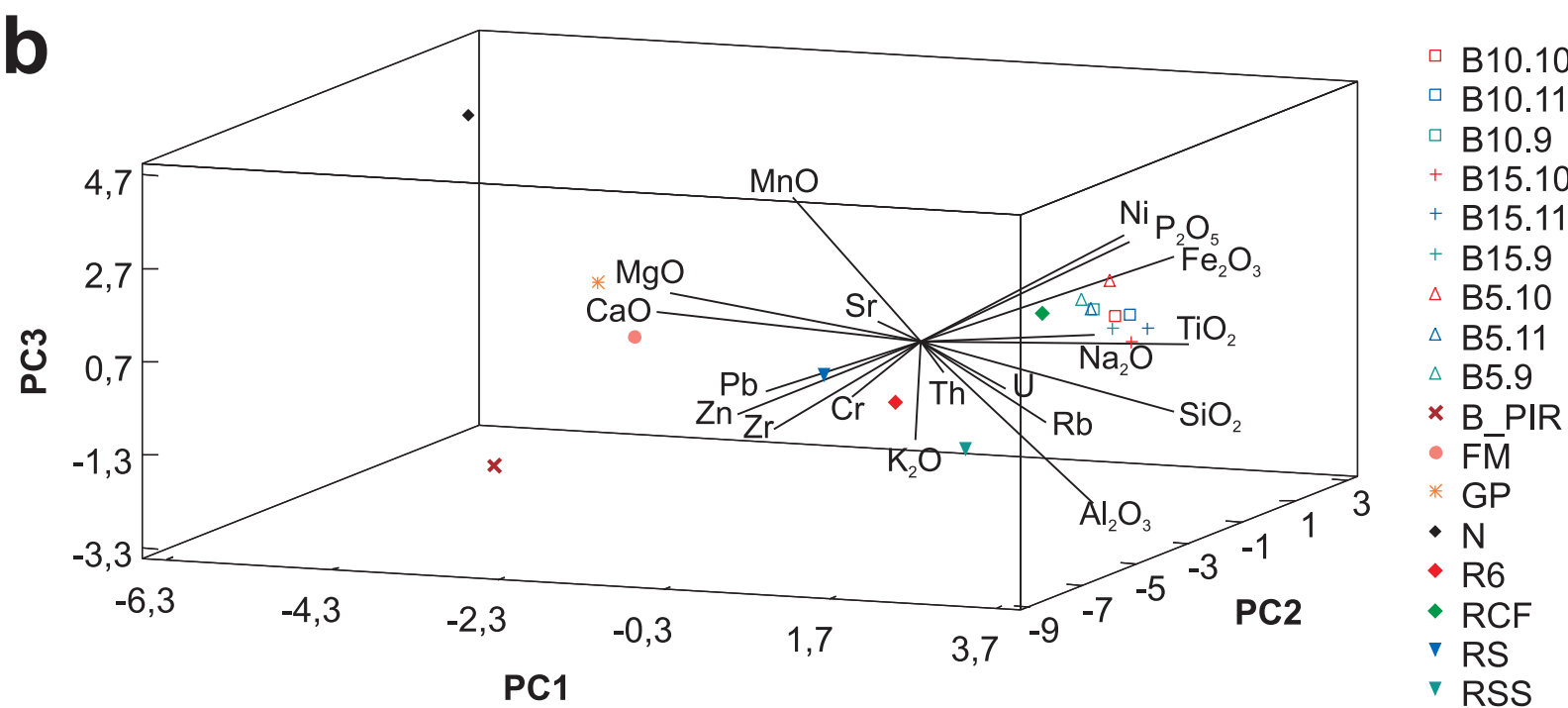
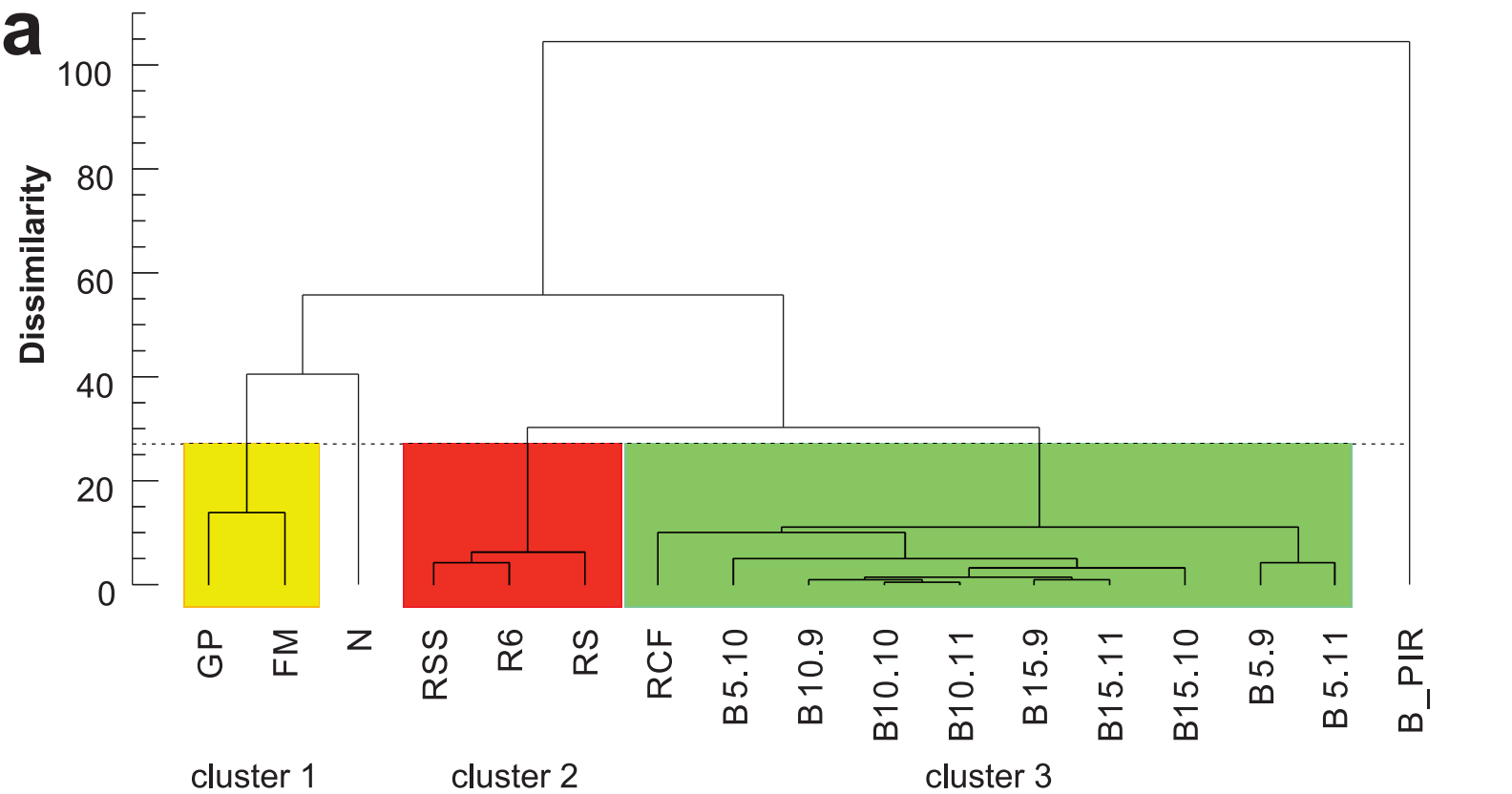


Figure 2

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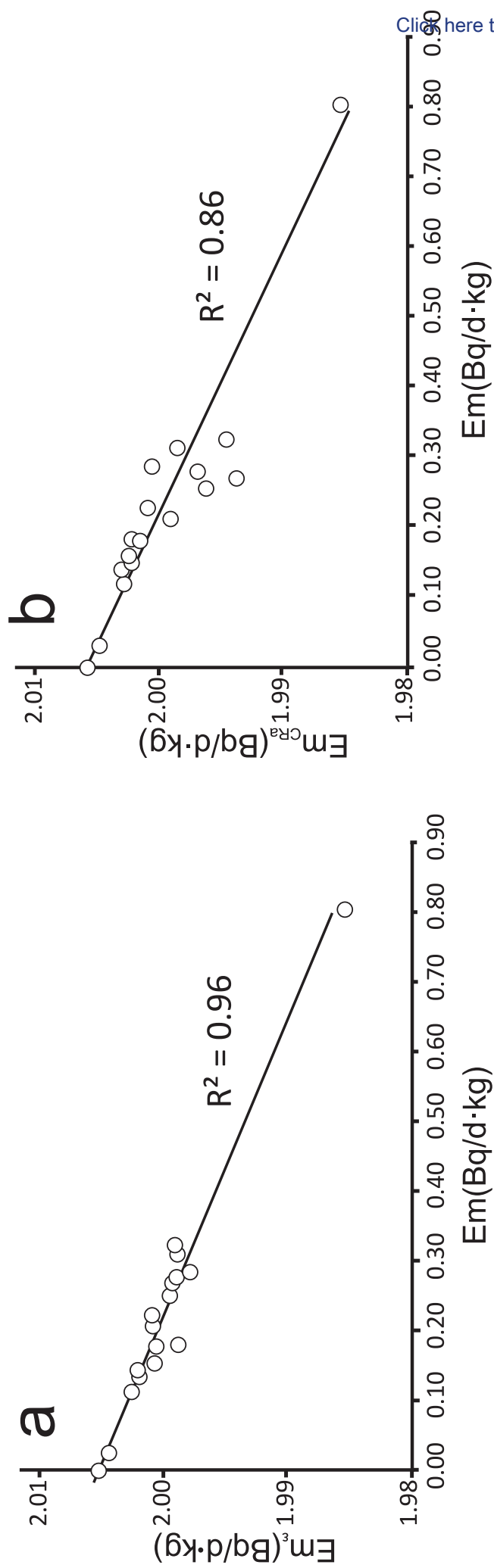


Figure 3

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