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ORIGINAL PAPER

Natural radioactivity in raw materials used in building industry in Serbia

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Abstract Natural radioactivity is responsible for most of the total radiation dose received by human population. Geological materials used in building industry usually become contaminated with naturally occurring radioactive materials. They are used as mixtures in building industry (kaolin, zircon, frit, feldspar) or mechanically processed and used for covering floors and walls of the rooms (granite). In this paper, activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K in 6 kaolin, 11 zircon, 18 granite, 3 marble, 6 sand, 4 perlite, 4 feldspar, 5 korund and 1 frit samples imported in Serbia were determined by gamma-ray spectrometry. Activity concentration index, dose rate and annual effective dose were calculated for each of the investigated samples. Measurement of an external gamma dose rate by using a commonly available radiation survey meter can give some indication of the need for further investigations. The absorbed dose rate and annual effective doses for workers in the ceramic industry "Keramika Kanjiza Plus" in Serbia working with granite are determined.

Keywords Natural radioactivity · Gamma spectrometry · Activity concentration index · Annual effective dose

Introduction

Humans are daily exposed to radionuclides that occur naturally in the environment. The distribution of naturally occurring radionuclides depends on two factors—the distribution of rocks from which they originate and the processes which result to their removal from the soil and their migration (Joshua et al. 2009). The concentrations of natural radionuclides in rocks have been found to depend on the local geological conditions and as such they vary from one place to another. Higher radiation levels are associated with igneous rocks such as granite, while lower levels are typical for sedimentary rocks. Exceptions have been found, however, in some shales and phosphate rocks with relatively high content of radionuclides determined (Al-Haydari 2011).

Exposure to natural sources of radiation is often influenced or can be influenced by human activities. Building materials, for instance, cause excess external gamma exposure due solely to their influenced exposure geometry when compared with that of the undisturbed earth's crust. Such excess in exposure is commonly excluded from any system of radiological protection. Construction materials can, however, cause substantial radiation exposure if they contain elevated levels of naturally occurring radionuclides (Markkanen Mika 1995). Radiation practices comprise the production, trade in or handling of materials with elevated natural radioactivity causing significant excess exposure of workers or general public.

Since exposure to naturally occurring radiation is responsible for the majority of an average person's yearly received radiation dose, it is not usually considered of any special health or safety significance. However, certain industries handle significant quantities of naturally occurring radioactive material (NORM), which usually ends up in their waste streams. Overtime, as potential NORM hazards had been identified, these industries have increasingly become subject to monitoring and regulation. Building industry is one of these industries known to have

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NORM issues. Natural rocks such as granite, limestone, marble, and so on are widely used in building industry; therefore, it is important to measure the concentration of radionuclides in rocks that are used and those that have the potential of being used as building materials in order to assess the radiological risk to human health (Joshua et al. 2009). In this paper, results of measurements of some imported material (kaolin, zircon, granite, marble, building and construction sands, perlite, feldspar, korund and frit samples) and risk assessment are presented.

Building materials can contain elevated levels of radionuclides including ^{226}Ra, ^{232}Th and ^{40}K. Radioactivity of building materials depends on minerals that are used for their production. The boundaries of radioactive contamination of building materials used in high construction for interior design in Serbia governed by law are as follows: for ^{226}Ra—3 10^2 Bq kg^{-1}; for ^{232}Th-2 10^2 Bq kg^{-1}; and for ^{40}K—3 10^3 Bq kg^{-1} (Official Gazette of Serbia 86/2011). The boundaries of radioactive contamination of building materials used in high building exterior are: for ^{226}Ra—4 10^2 Bq kg^{-1}, for ^{232}Th—3 10^2 Bq kg^{-1}, and for ^{40}K—5 10^3 Bq kg^{-1} (Official Gazette of Serbia 86/2011).

The purpose of issuing safety requirements is to limit the radiation exposure during usage of materials containing elevated levels of natural radionuclides. The goal is to eliminate the most extreme cases of public or occupational exposure.

According to Regulations on the radioactivity control of export, import and transit of the goods (Official Gazette of Serbia 44/2011), all samples of building materials and components for building industry which transit or are imported in Serbia must be tested for level of radioactivity they contain. The radioactivity of building materials, industrial by-products and waste is being investigated by the Nuclear Physics Laboratory, Faculty of Sciences, University of Novi Sad, Serbia, for some 20 years. As a result of these measurements, our laboratory now has a detailed view of Serbians' exposure from these sources of natural radiation. All investigated samples were taken from "Batrovci" border crossing in Serbia during the year 2012 and measured by gamma-ray spectrometry.

Materials and methods

The investigated samples were crushed, homogenized to fine powder and transferred into containers for measurement. A typical sample weight was about 400 g. After homogenization, they were transferred to sample holders (cylindrical containers of 67 mm diameter and 62 mm height) and sealed. In order to ensure radon equilibrium, measurements started at least a month after sealing.

High-resolution gamma-ray spectrometry is widely used for study of natural radioactivity since it is a fast, multi-elemental method of radioactivity measurement (Bikit et al. 2003). The radionuclide content of the samples was measured using the HPGe extended range ORTEC GMX type detector (10 keV–3 MeV) with nominal efficiency of 32 % and resolution of 1.9 keV. The detector is shielded with the cylindrical 12-cm thick lead shield. The five 0.5 m × 0.5 m × 0.05 m plastic veto detectors, produced by SCIONIX, surround the lead shield. The veto plastic scintillators and Ge detector were operated in anticoincidence mode; thus, all events simultaneously detected by any veto and Ge detector were rejected. The active shield reduces the integral background by factor three in the energy range from 50 to 2,800 keV (Bikit et al. 2006). The signals were connected to multichannel analyzer MCA with two analog to digital converters with 8,192 channels through CANBERRA type preamplifiers and amplifiers. MCA was directly connected with PC in which measured spectra were stored and analyzed. The gamma spectra were acquired and analyzed using the Canberra Genie 2,000 software. The program calculates the activity concentration of an isotope from all prominent gamma lines after peaked background subtraction. All measurement uncertainties are presented at 95 % confidence level (Todorovic et al. 2011).

The detector was calibrated by means of a reference radioactive material in cylindrical geometry (NBS Standard Reference Material 4350B). Self-absorption effects due to different densities were taken into account using the ANGLE computer code based on the concept of the effective solid angle (Moens et al. 1981). Such careful calibration was necessary in order to ensure low calibration error (<10 %) in the low-energy region (below 100 keV) where the strongest analytical lines of ^{234}Th (direct ^{238}U descendant) are located.

Handling, storage or any other operations involving materials containing elevated levels of natural nuclides always cause some excess exposure to the workers. The extent of exposure varies considerably in different operations depending on the exposure geometries, occupation times, dusting conditions, etc. Exposure assessment therefore cannot be based solely on known activity concentrations of the material. For practical purposes, it is useful to have an estimate for the levels of activity concentrations above which it is possible to exceed some predefined level of exposure. These levels of radioactivity in materials can be evaluated by assuming the presence of some extreme exposure conditions. Such conditions occur when the worker is continuously exposed to external gamma radiation from a semi-infinite source of that material while the air that is being inhaled contains dust originating from that material simultaneously. Measurement of an external gamma dose rate by using a commonly available radiation survey meter can give some indication of the need for further investigations (Markkanen Mika 1995). Annual effective doses for workers in the ceramic industry "Keramika Kanjiza Plus" in Serbia who have been working with granite are determined. Measurements were performed by the calibrated "Inspector" radiation monitor made by S.E.INTERNATIONAL, Inc., USA (operating range 0.01–1,000 mSv h^{-1}; accuracy: +10 %).

Activity concentration index, or gamma index I, takes into account typical ways and amounts in which the material is used in a building (EC 1999) and its derivation indicates whether the annual dose due to the excess external gamma radiation in a building might exceed 1 mSv. Gamma index is given as:

$$I = \frac{C_{Ra}}{300} + \frac{C_{Th}}{200} + \frac{C_{K}}{3000} \quad (1)$$

where C_{Ra}, C_{Th} and C_K are activity concentrations for ^{226}Ra, ^{232}Th and ^{40}K in Bq kg^{-1}, respectively.

The limit value that activity concentration index should not exceed depends on the dose criterion (EC 1999), the way and the amount the material is used in buildings (Krstic et al. 2007). For building materials, investigation levels can be derived for practical monitoring purposes (Ademola and Ayeni 2010). For materials used in bulk amounts, the exemption dose criterion (0.3 mSv y^{-1}) corresponds to an activity concentration index $I \leq 0.5$, while the dose criterion of 1 mSv y^{-1} is met for $I \leq 1$. For superficial and other building materials with restricted fractional mass usage, the exemption dose criterion (0.3 mSv y^{-1}) corresponds to an activity concentration index $I \leq 2$, while the dose criterion of 1 mSv y^{-1} is met for $I \leq 6$ (EC 1999). According to UNSCEAR 2000, the average worldwide exposure is 2.4 mSv y^{-1} due to natural sources.

According to EC 1999, the absorbed dose rate in a room air can be calculated by using the specific dose rates given in Krstic et al. 2007. The specific dose rates (in units nGy h^{-1} per Bq kg^{-1}) for ^{226}Ra, ^{232}Th and ^{40}K are given for different materials. Dose rate indoors are calculated according to EC 1999 for:

1. Gypsum and bricks as

$$D = 0.92 \cdot C_{Ra} + 1.1 \cdot C_{Th} + 0.08 \cdot C_K \quad (2)$$

2. Marble, ceramics, granite and roofing tile as

$$D = 0.12 \cdot C_{Ra} + 0.14 \cdot C_{Th} + 0.0096 \cdot C_K \quad (3)$$

The results are shown in Figs. 1, 2, 3, 4, 5, 6, 7, 8, 9 and these values were used to calculate annual effective doses (EC 1999). The annual effective dose, D_e, due to gamma radiation from building materials was calculated as:

$$D_e = 0.7\ \text{SvGy}^{-1} \cdot 7000\ \text{h} \cdot D \quad (4)$$

where D must be taken in μGy h^{-1}; 0.7 SvGy^{-1} is effective absorbed dose conversion factor and 7,000 h is annual exposure time (Krstic et al. 2007). The values for annual effective dose D_e is overestimated for the professional exposure; however, it can be applied in extreme cases.

Results and discussion

Activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K in controlled samples of imported building materials are presented in Figs. 1-9. Artificial isotope ^{137}Cs is negligible in examined samples.

Figure 1a presents the activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K, gamma index, dose rate and annual effective dose for 6 kaolin samples. Kaolin is a group of fine clay minerals with the chemical composition of $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$ which means that two-layer crystals (silicon–oxygen tetrahedral layer joined to alumina octahedral layer) exist alternately. Clay minerals include kaolinite, nacrite, dickite, montmorillonite, illite, chlorite, attapulgite and anauxite. Kaolin is the most important among the industrial clays in terms of both its consumption and value. Its properties like fine particle size, platy shape, inertness, non-toxicity, high brightness and whiteness make it most versatile mineral, with applications in a wide variety of industries. Kaolin is used extensively in the ceramic industry, where its high fusion temperature and white burning characteristics make it particularly suitable for the manufacture of white ware (china), porcelain and refractories (Mokobia 2011; Turhan 2009; Walley El-Dine et al. 2004).

^{226}Ra in kaolin samples was in the range from 121(11) Bq kg^{-1} (sample No. 5 from Spain) to 178(15) Bq kg^{-1} (sample No. 1, kaolin clay from United Kingdom), Table 1, Fig. 1a. The highest activity concentration (143(8) Bq kg^{-1}) of ^{232}Th was found in kaolin obtained from Spain (Sample No. 4, kaolin A-521), and the lowest (86(6) Bq kg^{-1}) activity was in raw kaolin sample No. 2 from Bosnia and Herzegovina, Fig. 1a. The kaolin sample No. 6 from Bosnia and Herzegovina contained the largest concentration (1,189(60) Bq kg^{-1}) of ^{40}K, while the smallest concentration was measured in the sample No. 5 from Spain (140(50) Bq kg^{-1}), Table 1, Fig. 1a. Obtained values of gamma index I ranged from 1.08(0.13) to 1.29(0.05) for kaolin samples, so it was concluded that they did not exceed the exemption dose criterion (0.3 mSv y^{-1}) (EC

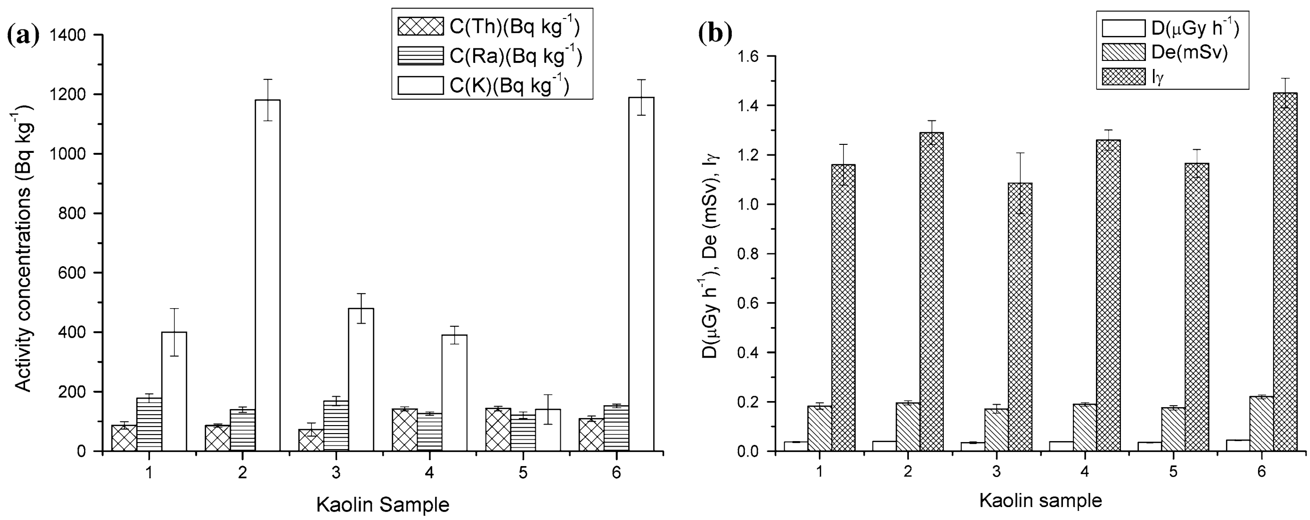

Fig. 1 **a** Activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K in kaolin samples, **b** gamma index, dose rate and annual effective dose for kaolin samples

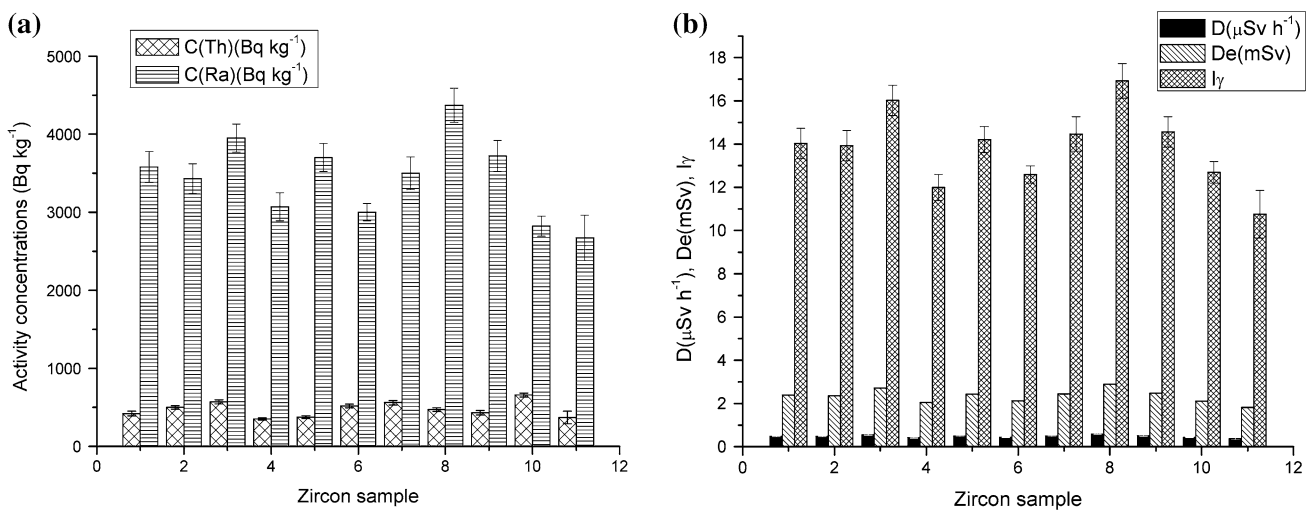

Fig. 2 **a** Activity concentrations of ^{226}Ra and ^{232}Th in zircon samples, **b** gamma index, dose rate and annual effective dose for zircon samples

1999). The indoor dose rate ranged from 35(4) to 44.9(1.9) nGy h^{-1}, Fig. 1b.

The results of measurements of the activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K, gamma index, dose rate and annual effective dose in 11 zircon samples are presented in Fig. 2a. Zirconium silicate ($ZrSiO_4$) is one of the most important compounds obtained from zircon sands; baddeleyite is a natural form of zirconium (ZrO_2). Zircon sands can be found as natural raw materials as well as a by-product of heavy-mineral sand mining and processing (as cassiterite, rutile and ilmenite) (Bruzzi et al. 2000).

Australia, South Africa, the USA, Ukraine, India, China, Brazil and Sri Lanka are the largest exporters of zirconium minerals at present. The most important uses of zircon sands are as refractories, foundry sands and ceramic opacifiers. In the ceramic commercial products, it important to draw the attention on the role played by porcelain stoneware, producing tiles containing appreciable amount of zircon sand, responsible of an increase in radioactivity.

The zircon mineral within its mineral structure contains trace amounts of uranium and thorium. Typical activities of uranium and thorium in Australian zircons are in the range 1,000–4,000 Bq kg^{-1} (Cooper 2005). Radioactive equilibrium will exist between the radionuclides within their respective decay series. Because zircon is used directly in the manufacture of refractory materials and glazes, these products will contain similar amounts of radioactivity. Higher concentrations, however, may be found in zirconia (Cooper 2005).

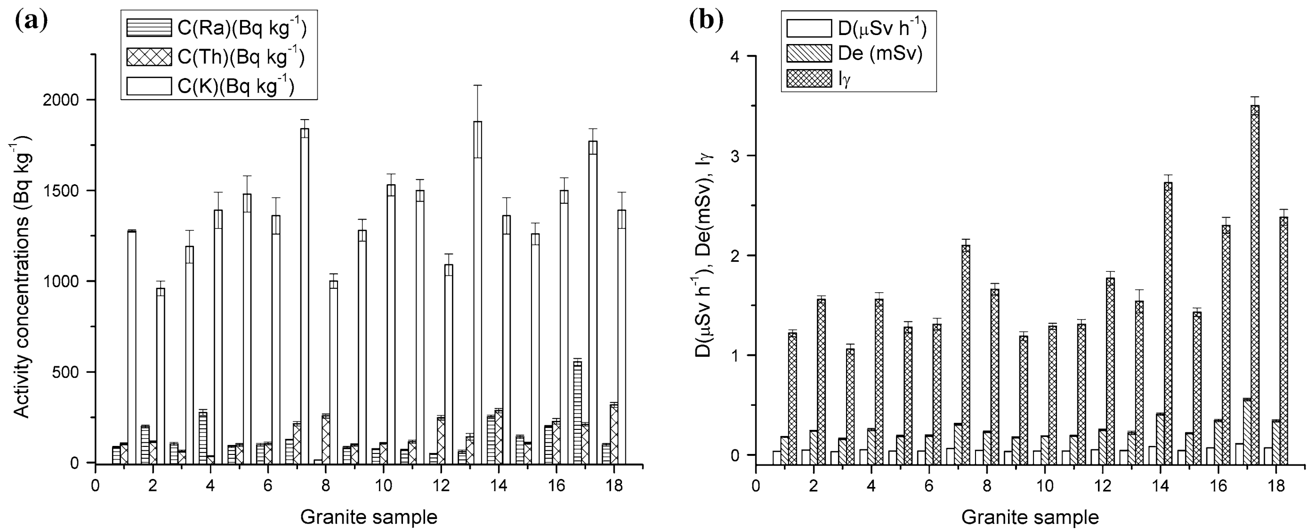

Fig. 3 **a** Activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K in granite samples, **b** gamma index, dose rate and annual effective dose for granite samples

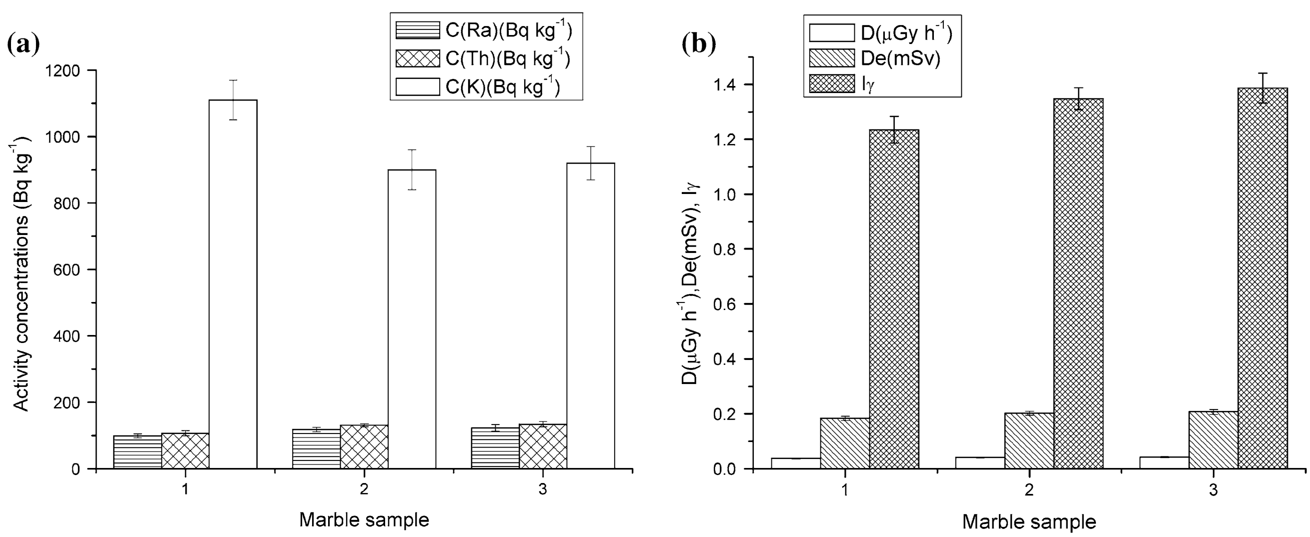

Fig. 4 **a** Activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K in marble samples, **b** gamma index, dose rate and annual effective dose for marble samples

The largest value of all measured ^{226}Ra activity concentrations (4,370(220) Bq kg^{-1}) was found in zircosil sample No. 8 from the UK. ^{232}Th activity ranged from 351(15) Bq kg^{-1} (sample No. 4, zircobit, Italy) to 658(24) Bq kg^{-1} (sample No. 10, zircosil 5, Italy), Table 1, Fig. 2a. In all examined samples, ^{40}K activities were below detection limit. Obtained values of gamma index I ranged from 10.7(1.1) to 17.0(0.8), which exceeds the dose limit of 1 mSv y^{-1} (EC 1999). The indoor dose rate ranged from 372(37) to 590(26) nGy h^{-1}. Only in four samples (No. 4, 6, 10 and 11), the values of annual effective dose, D_e, do not exceed the average worldwide exposure of 2.4 mSv y^{-1} (UNSCEAR 2000), Table 1, Fig. 2b.

Results of activity concentration measurements, gamma index, dose rate and annual effective dose for 18 granite samples are presented in Fig. 3. Granite is widely distributed throughout the continental crust and presents the most abundant plutonic rock present in mountain belts. Because of the large quantities of granite that occur in nature, geologists believe that most granites had been formed either by melting, partial melting or metamorphosis of deeply buried shale and sandstone (Alnour 2012). Some granite has been reported to have higher radioactivity, thereby raising some concerns about their safety. Granite has been extensively used as a dimension stone and as flooring tiles in public and commercial buildings and

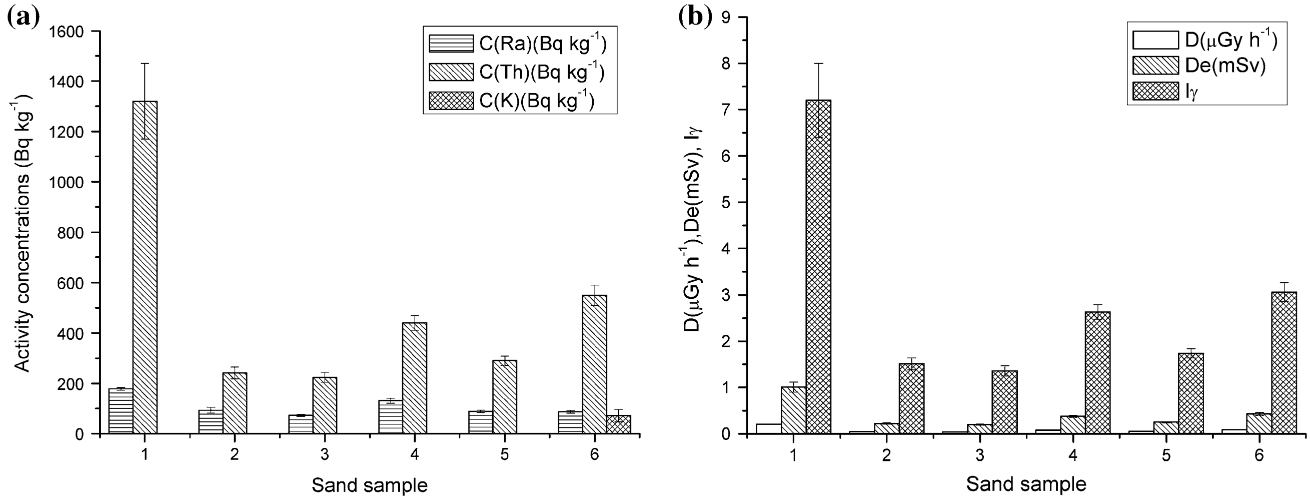

Fig. 5 **a** Activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K in sand samples, **b** gamma index, dose rate and annual effective dose for sand samples

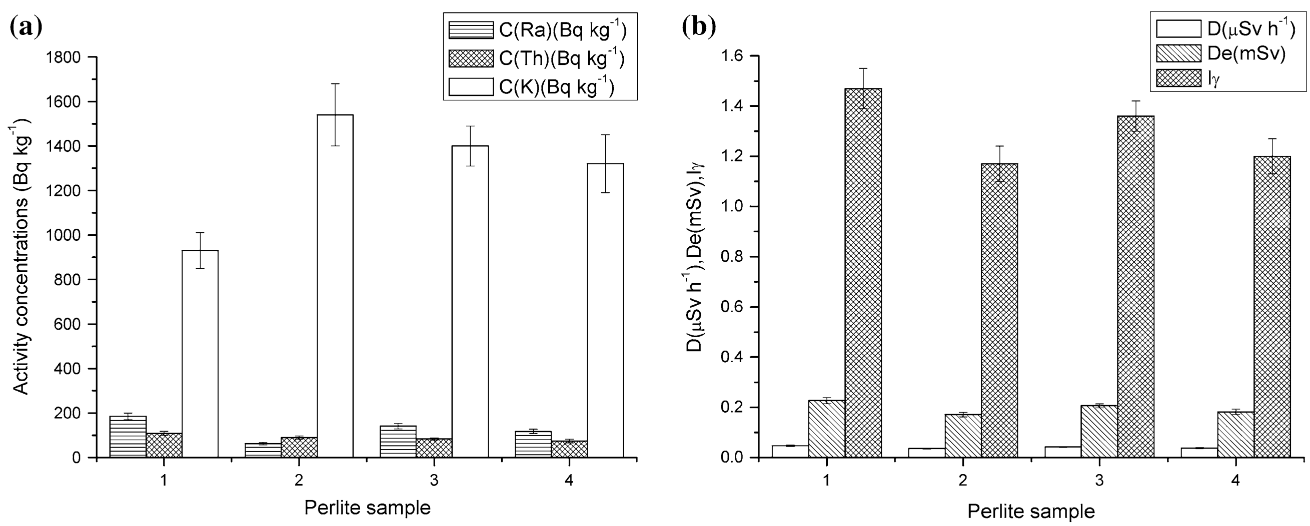

Fig. 6 **a** Activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K in perlite samples, **b** gamma index, dose rate and annual effective dose for perlite samples

monuments. Polished granite is also a popular choice for kitchen countertops due to its high durability and aesthetic qualities. These stones can contain admixtures of ^{40}K and the decay series of U-nat and ^{232}Th (which can include a number of progeny radioisotopes that emit gamma rays with characteristic intensities and energies ranging from some tens of keV to several MeV). The use of such decorative granites as building materials in home can result in the long-term whole-body exposure of the occupants to this radiation (Llope 2011). The granite samples were collected from importer at "Batrovci" border crossing in Serbia. Importers of granite are generally stonecutters, so the samples are mainly in the form of already processed blocks. Although it is known that many granites (certainly those with exotic color patterns) vary in chemical composition with rather large variations in the activity concentrations that can occur by taking samples from different locations on the same stone block, samples were taken in the way to less damage the granite blocks.

Dose rate calculation and dose estimates given in Fig. 3b assume uniform distribution of radioisotope concentrations throughout the volume of the stone. This assumption can fail for some granites, which might have "hot spots" within an overall less radioactive bulk volume. The use of such dose calculations following the spectroscopic measurements of small samples that happen to include such localized hot spots would thus lead to significant overestimates of the dose (Llope 2011). Measured activity concentrations of ^{40}K had relatively uniform distribution across all samples with values of 1–2 kBq kg^{-1},

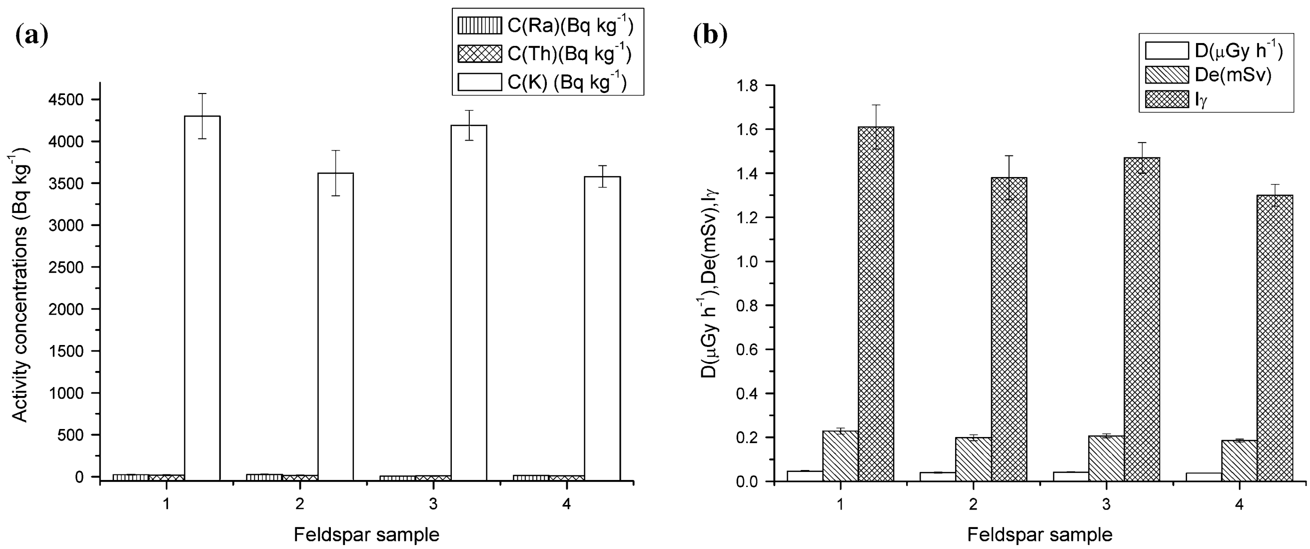

Fig. 7 **a** Activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K in feldspar samples, **b** gamma index, dose rate and annual effective dose for feldspar samples

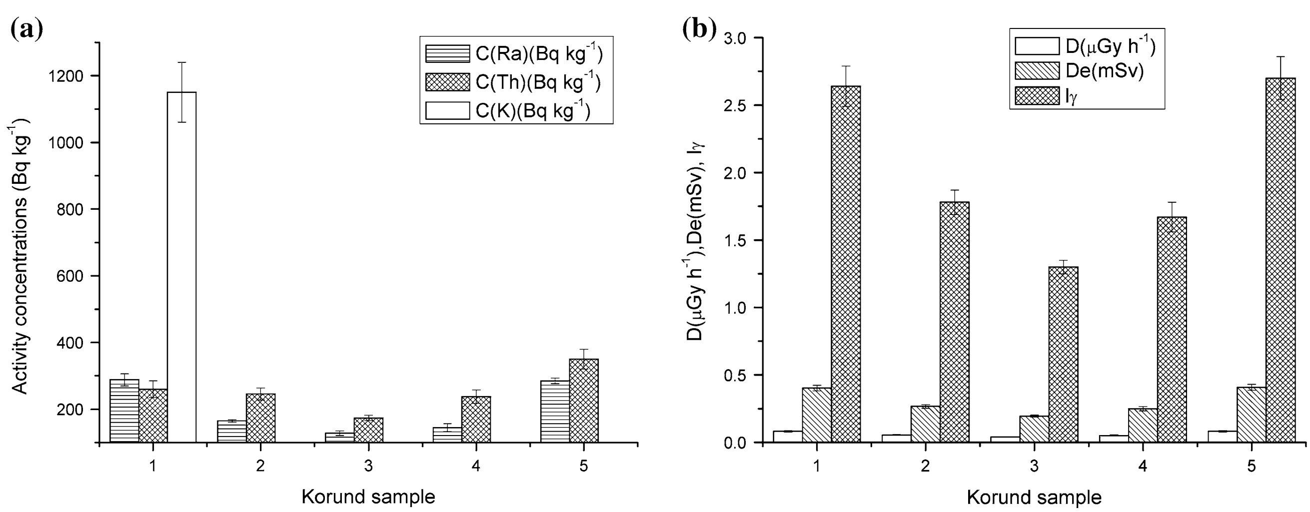

Fig. 8 **a** Activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K in korund samples, **b** gamma index, dose rate and annual effective dose for korund samples

while the ^{226}Ra and ^{232}Th activity concentrations showed more variation, Fig. 3a. These values are comparable with results of activity concentrations from decorative granites for usage as building materials (Najam et al. 2013, Llope 2011).

The values of activity concentration index of the samples varied between 1.06 (0.05) (sample No. 3, granite in slabs, Italy) to 3.50(0.09) (sample No. 17, Granite block Kashmir White, Italy), Table 1, Fig. 3b. In terms of the use of granites in building construction, none of the samples exceeded the recommended upper limit or recommended exemption level for exposure to external gamma radiation (EC 1999). The indoor dose rate ranged from 32.7(1.6) to 83.5(2.3) nGy h^{-1}, Table 1, Fig. 3b. The obtained values for annual effective dose did not exceed limits defined in EC 1999 and UNSCEAR 2000.

Activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K in marble samples, as well as gamma index, dose rate and annual effective dose in marble samples, are presented in Fig. 4. Construction marble is a stone composed of calcite, dolomite or serpentine which is capable of taking a very high polish. The lowest values of activity concentrations of ^{226}Ra (99(6) Bq kg^{-1}) and ^{232}Th (107(8) Bq kg^{-1}) and highest value for ^{40}K (1,110(60)) have been found in sample No. 1 (marble stone from Germany), Table 1, Fig. 4a. It can be noticed that activity concentrations of

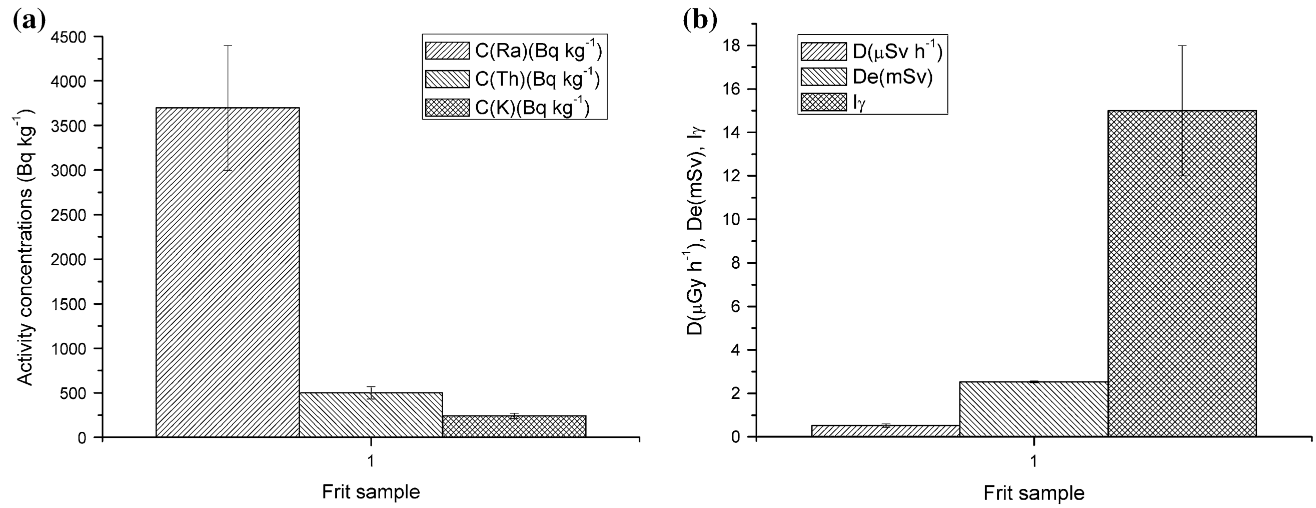

Fig. 9 **a** Activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K in frit samples, **b** gamma index, dose rate and annual effective dose for frit samples

^{226}Ra, ^{232}Th and ^{40}K obtained in our measurements were higher in comparison with published results (Walley El-Dine 2001). Values of gamma index I ranged from 1.23(0.05) to 1.39(0.06). The indoor dose rate ranged from 37.5(1.5) to 42.4(1.7) nGy h^{-1}, while values for annual effective dose did not exceed limit of 0.3 mSv y^{-1} (EC 1999), Table 1, Fig. 4b.

Activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K in building and abrasive sand samples, gamma index, dose rate and annual effective dose for 6 sand samples are shown in Fig. 5. The lowest values of activity concentrations of ^{226}Ra (72(4) Bq kg^{-1}) and ^{232}Th (224(20) Bq kg^{-1}) were found in sample No. 3 (abrasive sand from Australia), Table 1, Fig. 5a. ^{40}K activity (71(25) Bq kg^{-1}) was found only in sample No. 6 (abrasive sand from India). Values of gamma index I ranged from 1.36(0.11) (sample No. 3) to 7.2(0.8) (sample No. 1), Table 1, Fig. 5b. The indoor dose rate ranged from 40(3) to 206(21) nGy h^{-1}, and values for annual effective dose exceeded limit of 0.3 mSv y^{-1} (EC 1999) for sample No. 4 (abrasive sand from Australia). For sample No. 1 (sand from Switzerland), annual effective dose was beyond limit of 1 mSv y^{-1} as well. Comparing our results with Cevik et al. 2009, it can be concluded that activity concentrations of ^{226}Ra and ^{232}Th were comparable with Cevik et al. 2009, except for sample No. 1 (sand from Switzerland), which exceeded all values reported for ^{226}Ra and ^{232}Th activity concentrations for sand from other countries in the world (Cevik et al. 2009). ^{40}K activity concentrations in all samples were below detection limit, except for sample No. 6 (abrasive sand from India), Table 1, Fig. 5a.

Figure 6 presents the results of gamma spectrometric measurements for 4 perlite samples with values obtained for gamma index, dose rate and annual effective dose. Perlite is an amorphous volcanic glass with relatively high water content, which is typically formed by the hydration of obsidian. It occurs naturally and has the unusual property of great volume expansion when heated sufficiently. It is an industrial mineral and very useful commercial product with small weight after processing. Many commercial applications for perlite have been developed particularly because of its low density and relatively low price. In the construction and manufacturing fields, it is used in lightweight plasters and mortars, insulation and ceiling tiles (Rehspringer et al. 2007). Activity concentrations of investigated samples for ^{226}Ra ranged from 63(6) Bq kg^{-1} (sample No. 2, raw perlite "FF–EXTRA" from Hungary) to 185(15) Bq kg^{-1} (sample No. 1, perlite from Italy). ^{232}Th activity concentrations ranged from 75(8) to 109(9) Bq kg^{-1}, and ^{40}K activity concentrations ranged from 930(80) to 1,320(130) Bq kg^{-1}, Table 1, Fig. 6a. For all measured samples, gamma index was determined to be I $\leq$ 2. The indoor dose rate ranged from 37.2(2.1) to 42.1(1.9) nGy h^{-1}, and values for annual effective dose did not exceed limit of 0.3 mSv y^{-1} (EC 1999), Table 1, Fig. 6b.

The results of gamma spectrometric measurements of feldspar samples and values obtained for gamma index, dose rate and annual effective dose are given in Fig. 7. Feldspars crystallize from magma in both intrusive and extrusive igneous rocks as veins and are also present in many types of metamorphic rock. Feldspar is a common raw material used in glassmaking, ceramics, and to some extent as a filler and extender in paint, plastics, and rubber. Alumina from feldspar improves hardness, durability and resistance to chemical corrosion of a product in glassmaking. In ceramics, on the other hand, the alkalis in feldspar (calcium oxide, potassium oxide and sodium

Table 1 List of samples

Sample	Sample number	Sample name	Origin of the sample
Kaolin	1	Kaolin clay	United Kingdom
	2	Raw kaolin	Bosnia and Herzegovina
	3	Kaolin	United Kingdom
	4	Kaolin A-521	Spain
	5	Kaolin	Spain
	6	Kaolin	Bosnia and Herzegovina
Zircon	1	Zircobit MO	Italy
	2	Zirconium	Italy
	3	Zircosil	Italy
	4	Zircobit	Italy
	5	Zircosil 300 M	Spain
	6	Zirconium ores	France
	7	Zircobit MO	Spain
	8	Zircosil	United Kingdom
	9	Zeta zircon superfine	Holland
	10	Zircosil 5	Italy
	11	Zirconia powder	Italy
Granite	1	Granite block	South Africa
	2	Granite	Holland
	3	Granite in slabs	Italy
	4	Granite block	Italy
	5	Granite block African red II CH	South Africa
	6	Granite block African red II CH	Panamma
	7	Granite	Finland
	8	Granite MRIND	India
	9	Granite block	Spain
	10	Granite block Rosa Porrino	South Africa
	11	Granite block Rosso Africa Dark	South Africa
	12	Granite block Tropical Green	Italy
	13	Granite block Porkala Red	Italy
	14	Granite block Vanga Red	Italy
	15	Granite block Kashmir White	Italy
	16	Granite block	China
	17	Granite block Kashmir White	Italy
	18	Granite Celina Grey	Italy
Marble	1	Marble stone	Germany
	2	Marble slab	USA
	3	Marble slab	USA

Table 1 continued

Sample	Sample number	Sample name	Origin of the sample
Sand	1	Sand	Switzerland
	2	Sand	Australia
	3	abrasive sand	Australia
	4	abrasive sand	Australia
	5	abrasive sand	Belgium
	6	abrasive sand	India
Perlite	1	Perlite	Italy
	2	Raw perlite "FF-EXTRA"	Hungary
	3	Raw perlite "FF-EXTRA"	Hungary
	4	Perlite	Slovenia
Feldspar	1	Feldspar	Germany
	2	Feldspar	Germany
	3	Feldspar	Czech Republic
	4	Feldspar	Czech Republic
Korund	1	Korund	Germany
	2	Korund	Germany
	3	Korund	Slovenia
	4	Korund	Czech Republic
	5	Korund	Czech Republic
Frit	1	Frit (FROE-5001)	Spain

oxide) act as a flux, lowering the melting temperature of a mixture (Zhang et al. 2011). The observed activity concentration of our samples for ^{226}Ra ranged from 7.3(2.8) to 28(5) Bq kg^{-1}, for ^{232}Th from 9(3) to 18(5) Bq kg^{-1} and for ^{40}K from 3,580(130) to 4,300(270) Bq kg^{-1}, Table 1, Fig. 7a. For all measured feldspar samples, gamma index was determined to be $I \leq 2$. The indoor dose rate ranged from 37.8(1.3) to 47(3) nGy h^{-1} and values for annual effective dose did not exceed limit of 0.3 mSv y^{-1} (EC 1999), Table 1, Fig. 7b. The obtained results are comparable with those given in Walley El-Dine et al. 2011.

The results of gamma spectrometric measurements of korund samples together with measured values for gamma index, dose rate and annual effective dose are given in Fig. 8. Korund consists of high-quality acryl substance, originally developed composition of catalysts and fixers, ceramic ultra thin microspheres with rarefied air. Special supplements are added to the basic composition of the material which excludes the appearance of corrosion on the metal surfaces as well as mold forming on concrete surfaces at conditions with increased humidity medium. Described combination makes this material light, flexible and elastic, while possessing excellent adhesion to the covered surface (Carter and Norton 2007). The highest value for ^{226}Ra and ^{40}K was found in sample No. 1 (korund

Table 2 The results of dose rate measurements in the ceramic industry "Keramika Kanjiza Plus" in Serbia

Location	Description	Ionizing radiation dose rate (μSv h^{-1})
Raw material storage	Granite—contact geometry	0.50
Raw material storage	On 1 m distance from granite storage	0.34–0.43
Indoor storage	Granite—contact geometry	0.257
Indoor storage	On 1 m distance from granite storage	0.137
Conveyor belt—place of glazing	Vessel with glaze	0.173

from Germany), Table 1, Fig. 8a. Activity concentrations for ^{232}Th in korund samples ranged from 174(8) to 350 (30) Bq kg^{-1}. Gamma index I for sample No. 1 and sample No. 5 was in the range $2 \leq I \leq 6$ whereby values for annual effective dose for these samples did not exceed limit of 1 mSv y^{-1} (EC 1999). For other measured samples, we got $I \leq 2$ whereby values for annual effective dose for these samples did not exceed limit of 0.3 mSv y^{-1} (EC 1999). The indoor dose rate ranged from 39.7(1.4) to 83(5) nGy h^{-1}, Table 1, Fig. 8b.

In Fig. 9, the results of gamma spectrometric measurements for frit sample with value for gamma index, dose rate and annual effective dose can be seen. Frits are indispensable constituents of most industrial ceramic glazes which mature at temperatures below 1,150 °C (Carter and Norton 2007). Frits are typically intermediates in the production of raw glass, as opposed to pigments and shaped objects. Glazed tiles could be radioactive because they contain little amount of the frit. ^{226}Ra activity concentration in frit sample was determined to be 3,700(700) Bq kg^{-1}, ^{232}Th concentration was 500(70) Bq kg^{-1} and for ^{40}K was measured 240(30) Bq kg^{-1}. Gamma index I was 15(3) which clearly exceeded dose limit of 1 mSv y^{-1}. The indoor dose rate was 516 (85) nGy h^{-1}, and value for annual effective dose due to gamma radiation from investigated frit sample was found to be 2.53(0.04) mSv, Fig. 9b.

The results of dose rate measurements for workers in the ceramic industry "Keramika Kanjiza Plus" in Serbia working with granite are presented in Table 2.

The results of dose rate measurements are up to 5 times higher in relation to the background (0.10 mSv h^{-1}), Table 2. The workers who have been working in raw material storage with granite could have received an annual effective dose of 1 mSv (for 2,000 working hours per year), which is comparable with the maximum recommended annual effective dose for professionals of 20 mSv based on the Law on Protection Against Ionizing Radiation and Nuclear safety of Serbia (Official Gazette of Serbia 36/2009).

Conclusion

In the paper, the activity concentrations of the natural radionuclides (^{226}Ra, ^{232}Th and ^{40}K) were measured in 6 kaolin, 11 zircon, 18 granite, 3 marble, 6 sand, 4 perlit, 4 feldspar, 5 korund and 1 frit samples by gamma-ray spectrometry. All measured samples (Table 1) contain considerable concentrations of ^{226}Ra, ^{232}Th or ^{40}K. Comparing our values of measured activity concentrations of ^{226}Ra, ^{232}Th or ^{40}K with values of activity concentrations of materials which can, in extreme conditions, cause an annual dose of 1 or 5 mSv for workers given in Markkanen Mika 1995, it can be concluded than all measured values are lower than those given in Markkanen Mika 1995. The results presented in the paper should mainly refer to professional exposure.

The results of gamma spectrometric measurements are useful for the assessment of radiation doses due to the naturally radioactive element content in investigated samples. Obtained values are as follows: Gamma index I ranged from 1.08(0.13) to 1.29(0.05) for kaolin samples, which does not exceed the exemption dose criterion (0.3 mSv y^{-1}) (EC 1999). Obtained values of gamma index I for zircon samples ranged from 10.7(1.1) to 17.0(0.8), which exceeds dose limit of 1 mSv y^{-1} (EC 1999). The values of annual effective dose D_e do not exceed the average worldwide exposure of 2.4 mSv y^{-1} (UNSCEAR 2000) only in four zircon samples (zircobit from Italy, zirconium ores from France, zircosil 5 from Italy and zirconia powder from Italy). The values of activity concentration index of the granite samples varied between 1.06(0.05) (granite in slabs, Italy) and 3.50(0.09) (Granite block Kashmir White, Italy). In view of the use of granites in building construction, none of the samples exceeds the recommended upper limit or recommended exemption level for exposure to external gamma radiation (EC, 1999). For marble samples, the indoor dose rate ranged from 37.5(1.5) to 42.4(1.7) nGy h^{-1}, and values for annual effective dose do not exceed limit of 0.3 mSv y^{-1} (EC 1999). Values of gamma index I for sand samples ranged from 1.36(0.11) to 7.2(0.8). The indoor dose rate ranged from 40(3) to 206(21) nGy h^{-1}, and values for annual effective dose exceed limit of 0.3 mSv y^{-1} (EC 1999) for abrasive sand from Australia (sand sample No. 4, Table 1). For sand from Switzerland (sand sample No. 1, Table 1), annual effective dose exceeds limits of 1 mSv y^{-1}. For all measured perlite and feldspar samples, gamma index was determined to be $I \leq 2$, and values for annual effective dose do not exceed limits of 0.3 mSv y^{-1} (EC 1999). Gamma index I for korund sample from Germany (korund sample No. 1, Table 1) and korund sample from Czech Republic (korund sample No. 5) was in the range $2 \leq I \leq 6$, and values for annual effective dose for these samples did not exceed limits of 1 mSv y^{-1} (EC 1999). For other measured korund samples, values for $I \leq 2$ and values for annual effective dose also do not exceed limit of 0.3 mSv y^{-1} (EC 1999). Gamma index I for frit sample was 15(3), which clearly exceeds dose limit of 1 mSv y^{-1}.

Annual effective doses for workers in the ceramic industry "Keramika Kanjiza Plus" in Serbia who have been working with granite were determined. The results of dose rate measurements are up to five times higher in relation to the background (0.10 mSv h^{-1}).

The radioactivity of building materials depends on the minerals that are used for their production. Some materials used in construction have high concentrations of ^{226}Ra, ^{232}Th and ^{40}K. They are used as mixtures in the building industry (kaolin, zircon, frit and feldspar) or mechanically processed and used for covering floors and walls of the rooms (tiles and granite). Some commercial materials (such porcelain stoneware and glazed tiles) are more radioactive because they contain appreciable amount of zircon sands or frit. However, having in mind the amount of these materials in standard construction cannot be concluded that they are the largest source of radioactive pollution in flats (Todorovic et al. 2013).

Measurements presented in this work confirm that radiation exposure and attributed risk should be reduced by careful choice of building material during construction.

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