Assessment of radiological parameters of natural stones in the context of their application as building materials

K.J. Nowak[1], A. Wolska[1]
[1]*Institute of Geological Sciences, University of Wroclaw, pl. M. Borna 9, 50-204 Wroclaw, Poland*

Abstract
Forty three natural stones used as building materials and available on the Polish market have been investigated and assessed with regard to their content of naturally occurring radionuclides. Radionuclides concentrations (K in %, U in ppm, Th in ppm) have been measured by means of the portable gamma spectrometer RS 230 with a BGO detector. Radionuclides concentrations were recalculated into Bq/kg. Average specific activities of ^{40}K, ^{226}Ra and ^{232}Th are 774, 59 and 44 Bq/kg, respectively. These values are similar to typical specific activities in natural building stones in the EU which are 640, 60 and 60 Bq/kg, respectively. However, maximum values equal to 1775, 400 and 125 Bq/kg, respectively are lower than those for building stones in the EU which are 4000, 500 and 310 Bq/kg, respectively. The radilogical hazard due to investigated natural stones has been assessed using activity concentration indices f_1 and f_2 defined in Polish law. For 30% of investigated stones f_1 was equal to or greater than the limit value for building materials used in buildings designed for people and the livestock (f_1=1). The maximum value is 2.1. According to the European Commission this index should not be greater than 1 for materials used in bulk amounts but for materials used superficially the limit value is 6 and none of the investigated stones exceeds this limit. Index defined as f_2 should not exceed the limit value of 200 Bq/kg. In two of forty three cases this limit was exceeded, with the maximum value of 400 Bq/kg.

1. Introduction
Natural stones are commonly used as a material for facades of houses, fireplaces, gravestones and for decorative purposes inside buildings where they cover walls and floor as 3.0 cm thick tiles or slabs. The stones contain naturally occurring radionuclides of terrestrial origin and some of them, such as igneous rocks, may be characterized by elevated radioactivity (UNSCEAR 2000). Typical specific activities of ^{40}K, ^{226}Ra and ^{232}Th in natural building stones in the EU are 640, 60 and 60 Bq/kg, respectively with maximum values equal to 4000, 500 and 310 Bq/kg, respectively (EC 1999).

Radionuclides present in building materials are responsible for both external and internal exposure. The external exposure is caused by gamma rays emitted mainly by radionuclides of uranium ^{238}U and thorium ^{232}Th decay series as well as potassium ^{40}K. The internal exposure is caused by radon (^{222}Rn and ^{220}Rn) and its short-lived decay products. Radon is an alpha emitter that may be easily inhaled and its descendants may be deposited in tissues of the respiratory tract (UNSCEAR 2000).

To predict absorbed gamma dose rate (in nGy/h) inside a building on the basis of radionuclides content in building materials, the mathematical models have been developed. Specific conversion factors have been established (nGy/h per Bq/kg). Values of conversion factors vary depending on the amount of the building material (whether it is used in bulk amounts, e.g. concrete, or it is used as a superficial material), the geometry (whether a building material is used to construct walls, floor and ceiling or walls and floor or maybe to construct only floor, e.g. in wooden houses) as well as thickness and density of building materials. Calculations are performed for a model room of specified dimensions (Markkanen 1995, EC 1999).

In order to assess radiological hazard of building materials, the activity index is commonly used. In the most of countries only one limit value (equal to 1) is determined, not taking into account the manner of application and thickness of building material (OECD/NEA 1979, Lindell 1984, DIH 1986, RM 2007). The European Commission proposed different limit values for building materials used in bulk amounts and for building materials used only for decorative purposes as a superficial material. In the first case the limit value for the activity index is equal to 1 and in the second case is equal to 6 (EC 1999).

The aim of this study was to characterize the variation range of radionuclides content in investigated stones and assess if any of them may pose a radiological hazard on the basis of the analysis of their radiological parameters. What is more, absorbed gamma dose rate inside a building, which all walls are covered by the natural stones used as 3.0 cm thick superficial material, was calculated.

2. Material and methods

Forty three natural stones available on the Polish market, both imported and produced in Poland, were investigated. Among them, according to their commercial names, there are granites, basalt, sandstones, dolomites, marbles, schists and travertine. It is important to notice that commercial names do not coincide with petrographic classification. Many of natural stones are named as granites and it is not compatible with the petrographic classification. In such circumstances, the use of commercial names could be confusing and the characteristic of stones in terms of the type of rock would not be reliable. Therefore, the names of natural stones were replaced by codes (NS1 to NS43).

Measurements of uranium U (in ppm), thorium Th (in ppm) and potassium K (in %) contents in stones were performed *in situ* within the product warehouse, using portable gamma spectrometer RS 230 with a BGO detector. *In situ* gamma spectrometric measurements are commonly used to determine radionuclides content in building materials (Chen and Lin 1996, Anjos et al 2011, Solecki et al 2011, Nowak et al 2013). The gamma spectrometer was placed on stacked stone slabs. On each type of stone two to four measurements were conducted. A single measurement lasted 180 s.

The determination of radionuclides content were based on the stripping technique of gamma ray spectrometry. Potassium ^{40}K content was calculated on the basis of its gamma rays at 1461 keV. Uranium ^{238}U content was calculated on the basis of gamma rays at 1765 keV emitted by bismuth ^{214}Bi and thorium ^{232}Th content on the basis of gamma rays at 2615 keV emitted by thallium ^{208}Tl. The calculations were based on the assumption of the existence of equilibrium state between all of the radioisotopes within the decay series. It means that concentrations of following radioisotopes in the decay series, e.g. ^{238}U, ^{226}Ra, ^{214}Bi in uranium series and ^{232}Th, ^{208}Tl in thorium series, are equal. Obtained in this way results of uranium ^{238}U and thorium ^{232}Th contents are referred as equivalent uranium (eU) and equivalent thorium (eTh). U and Th contents in ppm and K contnt in % were recalculated into specific activities of ^{238}U (^{226}Ra),^{232}Th and ^{40}K in Bq/kg using appropriate conversion factors. In the case of the uranium decay series, the results are often reported as ^{226}Ra instead of ^{238}U activity because radionuclides starting from ^{226}Ra are the most important from the radiological point of view (IAEA 2003).

The exposure to external gamma radiation caused by the investigated stones in the center of a model room (5m x 4m area, 2.8 m height) which walls are covered by the stones used as superficial material, was assessed. The indoor absorbed dose rate (in nGy/h) was calculated on the basis of specific dose rates (nGy/h per Bq/kg) established for a superficial material of 3-cm-thick and density 2600 kg/m^3 covering all walls (EC 1999). The indoor absorbed dose rate (in nGy/h) can be expressed as:

$$D = K_1 \cdot S_{Ra} + K_2 \cdot S_{Th} + K_3 \cdot S_K \qquad (1)$$

where S_{Ra}, S_{Th}, S_K are specific activities of ^{226}Ra, ^{232}Th and ^{40}K, respectively in Bq/kg and K_1, K_2, K_3 are specific dose rates of ^{226}Ra, ^{232}Th and ^{40}K equal to 0.12, 0.14 and 0.0096 nGy/h per Bq/kg, respectively.

Radiological hazard of the stones were estimated on the basis of two activity indices, f_1 and f_2, according to the Polish law (RM 2007). The first one, f_1 index, is a dimensionless value and reflects the content of natural radionuclides in a building material, meanwhile f_2 index determines the specific activity of radium ^{226}Ra in Bq/kg. The f_1 index is described by the following formula:

$$f_1 = \frac{S_K}{3000} + \frac{S_{Ra}}{300} + \frac{S_{Th}}{200} \qquad (2)$$

where S_K, S_{Ra}, S_{Th} are specific activities of ^{40}K, ^{226}Ra and ^{232}Th, respectively in Bq/kg.

The limit values for f_1 and f_2 indices in the case of building materials used in buildings designed for people and the livestock are 1 and 200 Bq/kg, respectively. Nevertheless, the excess of 20% of these values is acceptable (RM 2007). According to the European Commission the activity concentration index which corresponds to f_1 index should not be greater than 1 for materials used in bulk amounts but for materials used superficially the limit value is 6 (EC 1999).

3. Results

A summary of the results is placed in Table 1. Specific activities of ^{40}K, ^{226}Ra and ^{232}Th ranged between 121 and 1775, 11 and 400, 8 and 125 Bq/kg, respectively. Average specific activities of ^{40}K, ^{226}Ra and ^{232}Th were 774, 59 and 44 Bq/kg, respectively. These values are similar to typical specific activities in natural building stones in the EU but maximum specific

Table 1. Mean values of specific activities of ^{40}K, ^{226}Ra and ^{232}Th (Bq/kg), absorbed dose rate (nGy/h) as well as activity indices, f_1 and f_2 (Bq/kg) for particular stones

Code	^{40}K (Bq/kg)	$^{226}Ra = f_2$ (Bq/kg)	^{232}Th (Bq/kg)	Dose (nGy/h)	f_1
NS1	1153	75	112	36	1.2
NS2	288	19	14	7	0.2
NS3	758	29	32	15	0.5
NS4	501	30	31	13	0.4
NS5	1198	82	83	33	1.1
NS6	561	153	68	33	1.0
NS7	1775	83	73	37	1.2
NS8	288	38	16	10	0.3
NS9	819	43	49	20	0.7
NS10	379	26	22	10	0.3
NS11	910	35	53	20	0.7
NS12	925	47	41	20	0.7
NS13	804	33	34	16	0.6
NS14	607	25	25	12	0.4
NS15	910	73	88	30	1.0
NS16	1229	27	125	33	1.1
NS17	1244	47	70	27	0.9
NS18	865	40	37	18	0.6
NS19	1411	400	55	69	2.1
NS20	121	15	8	4	0.1
NS21	1471	197	112	53	1.7
NS22	121	21	9	5	0.2
NS23	1563	79	49	31	1.0
NS24	243	17	21	7	0.2
NS25	1047	47	54	23	0.8
NS26	1001	52	72	26	0.9
NS27	152	32	22	8	0.3
NS28	121	11	8	4	0.1
NS29	379	27	24	10	0.3
NS30	137	15	9	4	0.1
NS31	1153	47	55	24	0.8
NS32	774	24	27	14	0.5
NS33	167	16	17	6	0.2
NS34	167	19	16	6	0.2
NS35	182	15	12	5	0.2
NS36	182	14	14	5	0.2
NS37	1244	163	42	37	1.2
NS38	1138	34	61	24	0.8
NS39	1259	50	75	29	1.0
NS40	819	212	12	35	1.0
NS41	152	17	8	5	0.1
NS42	1456	32	43	24	0.8
NS43	1608	74	99	38	1.3
Average	774	59	44	21	0.7

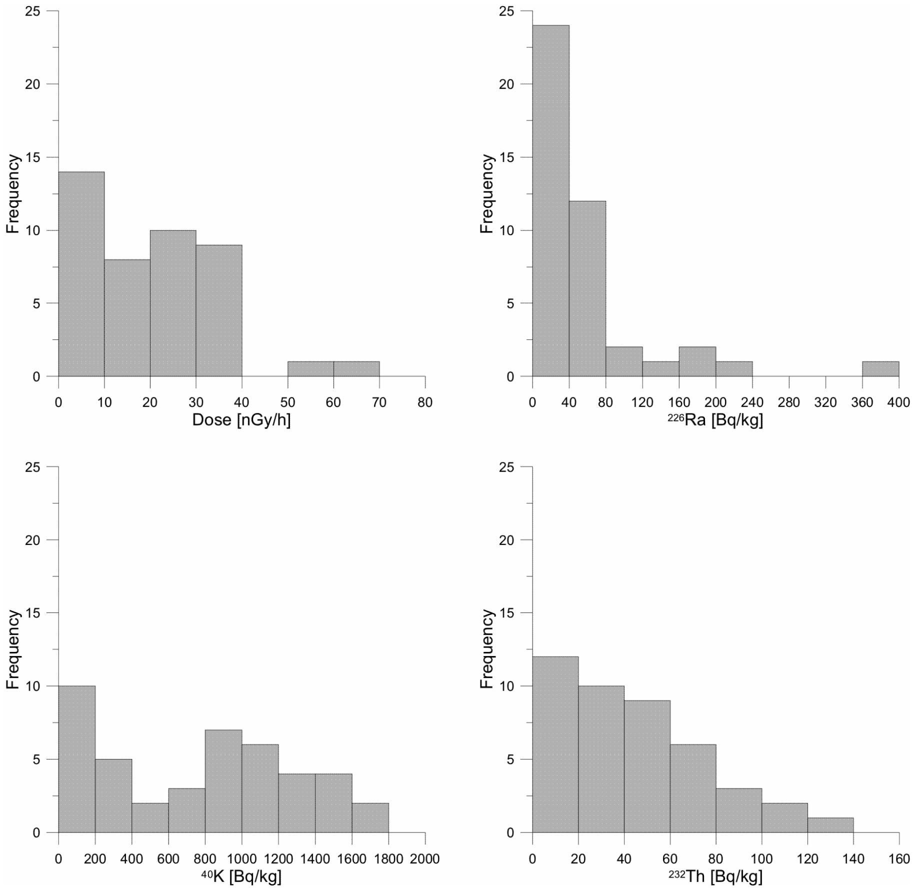


Figure 1. Frequency distribution for absorbed dose rate (nGy/h) and specific activities of ^{226}Ra, ^{40}K and ^{232}Th (Bq/kg)

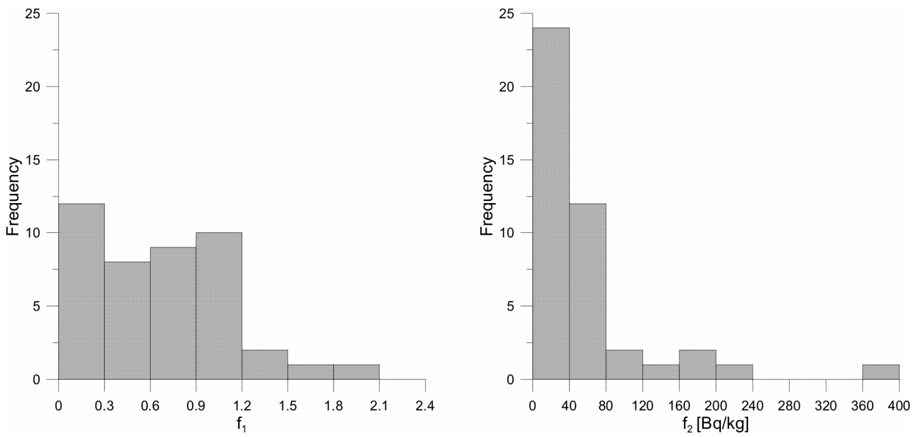
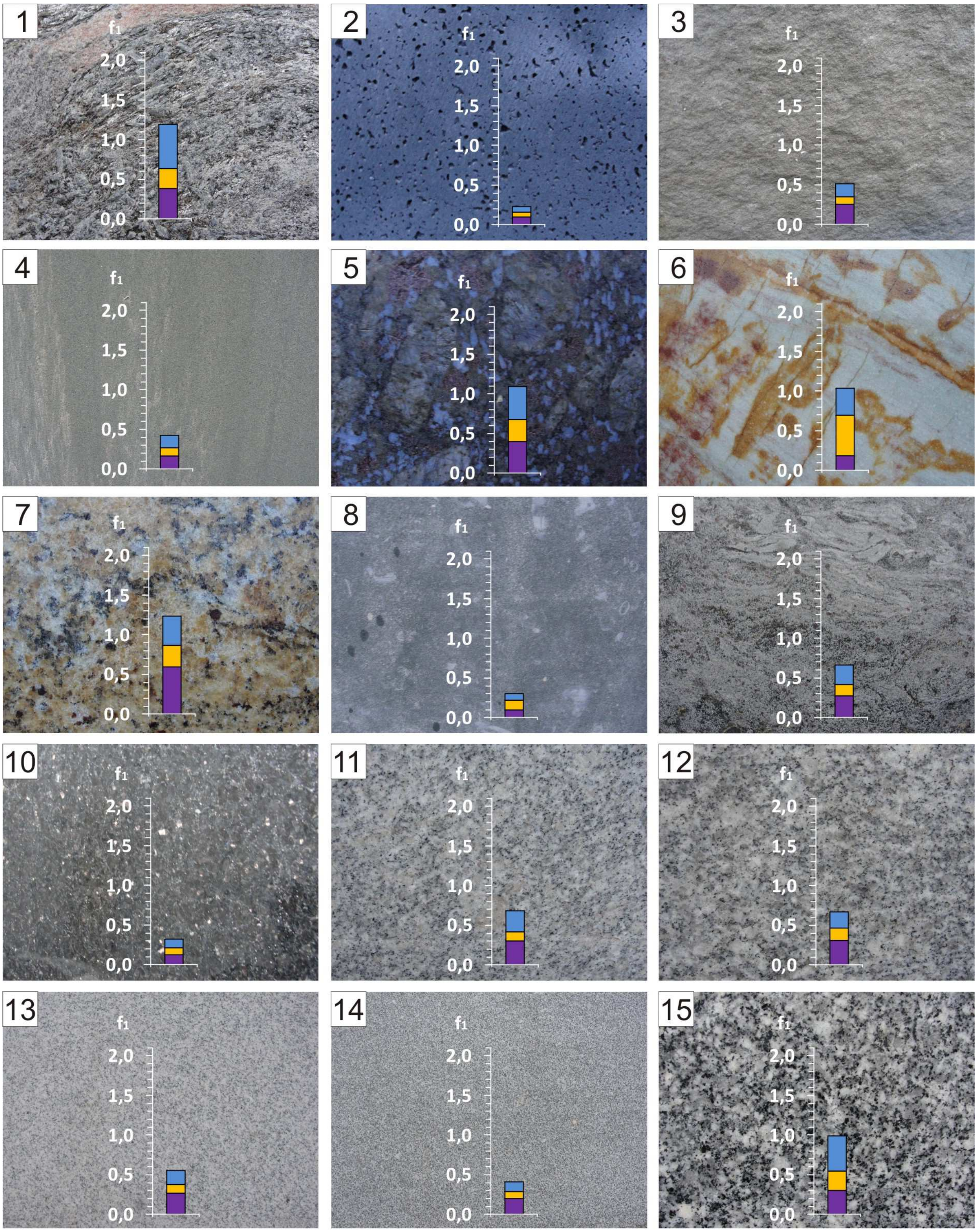
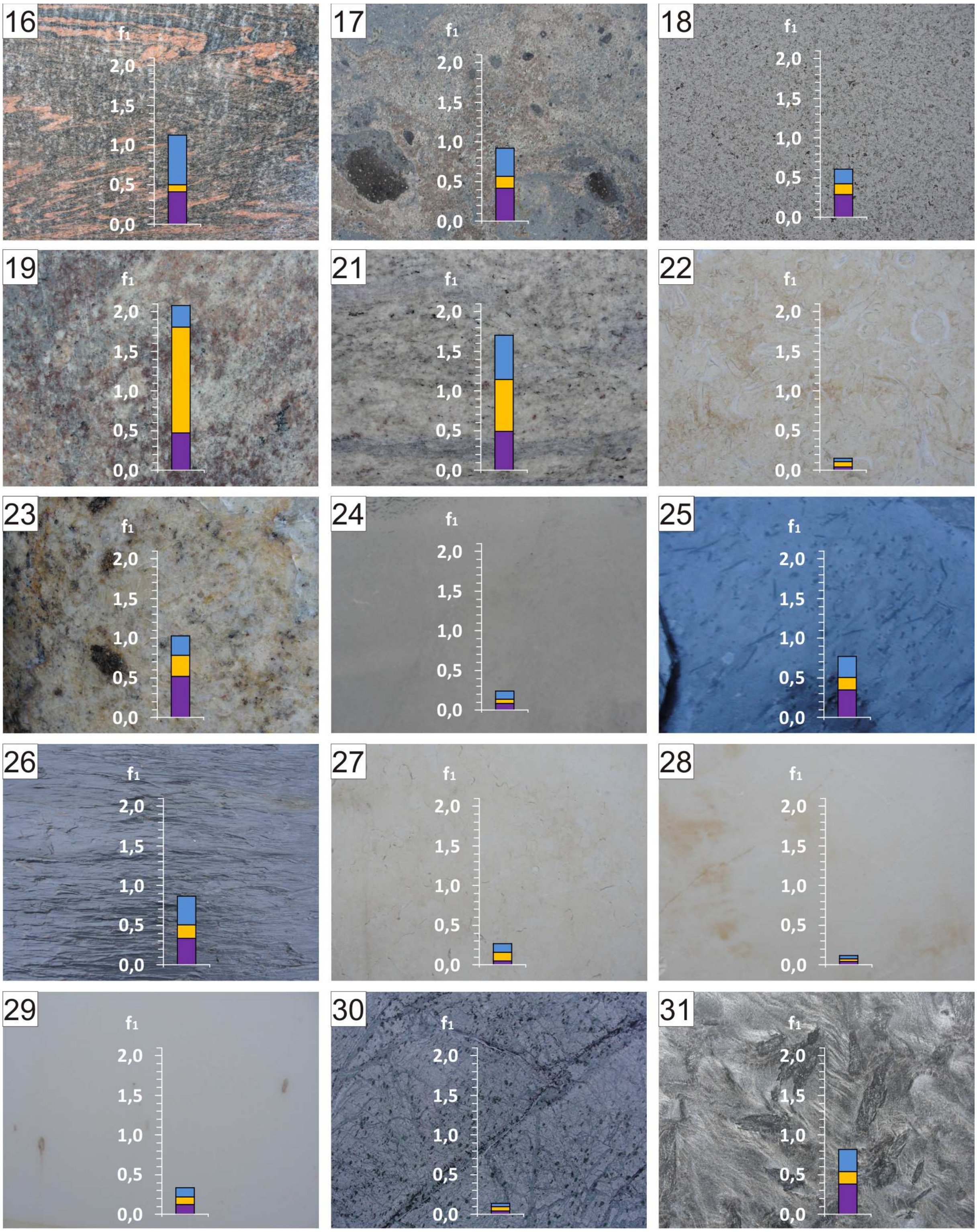


Figure 2. Frequency distribution for f_1 and f_2 index (Bq/kg)


1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
f_1
2,0
1,5
1,0
0,5
0,0


16
f1
2,0
1,5
1,0
0,5
0,0
17
18
19
21
22
23
24
25
26
27
28
29
30
31

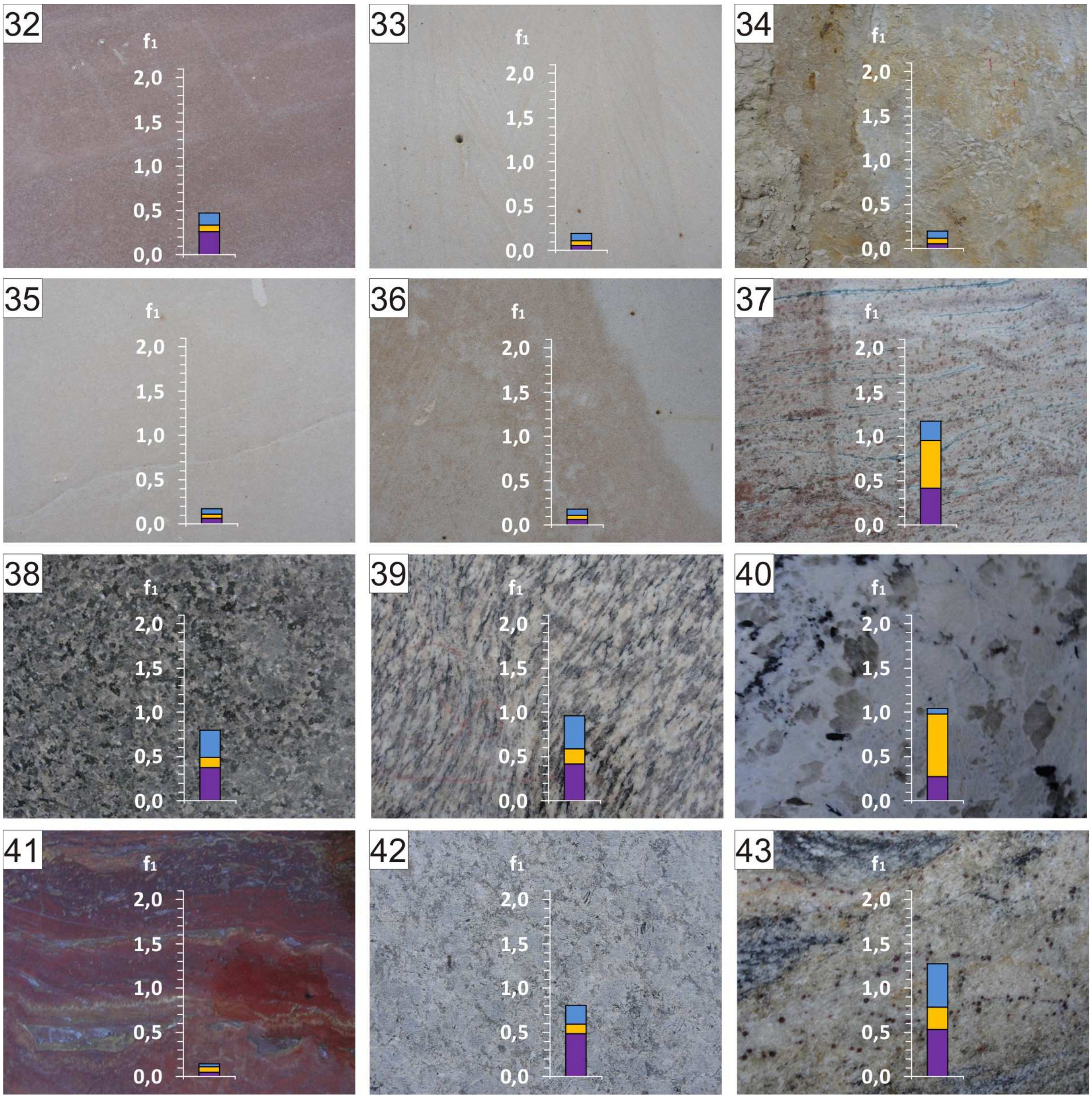


Figure 3. Contribution of ^{232}Th – blue, ^{238}U (^{226}Ra) – yellow, ^{40}K – violet in forming f_1 index

activities of ^{40}K, ^{226}Ra and ^{232}Th are lower than those for building stones in the EU. Modal interval for ^{40}K, ^{226}Ra and ^{232}Th is 0-200, 0-40 and 0-20 Bq/kg, respectively (Fig.1).

Calculated absorbed dose rate ranged from 4 to 69 nGy/h with the maximum value for NS 19 stone which is characterized by the greatest specific activity of ^{226}Ra among all of the investigated stones (Table 1). Modal interval for dose rate is 0-10 nGy/h (Fig.1).

The value of f_1 index ranged from 0.1 to 2.1 with the maximum value for NS 19 stone. Modal interval for f_1 index is 0-0.3 (Fig.2). The contribution of ^{40}K, ^{226}Ra and ^{232}Th in forming f_1

index ranged between 20 and 60%, 10 and 70%, 10 and 60%, respectively (Fig.3). For 30% of investigated stones f_1 was equal to or greater than the limit value for building materials used in buildings designed for people and the livestock (f_1=1) according to the Polish law (Fig.4). Taking into account that the limit value for superficial materials, suggested by the European Commission, is equal to 6, none of the investigated stones exceeded this limit.

Index defined as f_2 ranged between 11 and 400 Bq/kg (Table 1). Modal interval for f_2 is 0-40 Bq/kg (Fig.2). According to the Polish law f_2 index should not exceed the limit value equal to 200 Bq/kg. In two of forty three cases this limit was exceeded, with the maximum value of 400 Bq/kg.

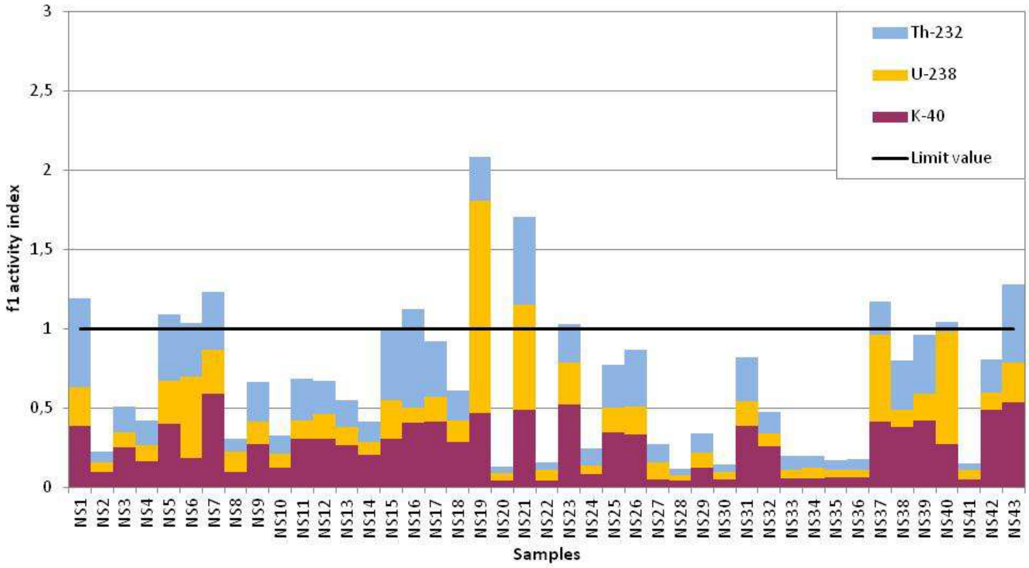


Figure 4. Contribution of ^{232}Th – blue, ^{238}U (^{226}Ra) – yellow, ^{40}K – violet in forming f_1 index with marked limit value equal to 1

4. Conclusions

According to the Polish law, 13 out of 43 investigated natural stones should be considered as materials which may pose a radiological hazard to living beings. Nevertheless, there is only one limit value for f_1 activity index established not taking into account that building materials may be used in bulk amounts or superficially. Considering that investigated stone slabs will be used as a superficial material, the limit value of 6 for activity concentration index, proposed by the European Commission, seems to be more reasonable. In this case, none of the stones are hazardous in radiological point of view and may be safely used in buildings designed for people and the livestock.

ACKNOWLEDGEMENTS
This work was co-financed by the European Union as a part of the European Social Fund.

REFERENCES

Anjos, R.M., Ayub, J.J., Cid, A.S., Cardoso, R., Lacerda, T. 2011. External gamma-ray dose rate and radon concentration in indoor environments covered with Brazilian granites. J. Environ. Radioact. 102: 1055-1061.

Ching-Jiang Chen, Yu-Ming Lin. 1996: Assessment of building materials for compliance with regulations of ROC. Environment International, Vol. 22, Suppl. 1: S221-S226.

DIH (Department of Industrial Hygiene). 1986. Radiological health protection standards for building materials. BG6566-86. Beijing.

IAEA, 2003. Guidelines for radioelement mapping using gamma ray spectrometry data. IAEA-TECDOC-1363.

Lindell, B. 1984. A radon control programme in theory and practice. Radiat. Prot. Dosim. 7: 417-425.

Markkanen, M. 1995. Radiation Dose Assessments for Materials with Elevated Natural Radioactivity. Report STUK-B-STO 32. Finnish Centre for Radiation and Nuclear Safety, Helsinki.

Nowak, K., Solecki, A., Śliwiński, W., Tchorz-Trzeciakiewicz, D. 2013. Assessment of radiological parameters of natural stones by means of in situ gamma spectrometry. Górnictwo Odkrywkowe 5-6: 181-185.

OECD/NEA, 1979: Exposure to radiation from the natural radioactivity in building materials. Report by an NEA Group of Experts. Paris OECD-NEA.

Radiological protection principles concerning the natural radioactivity of building materials – Radiation Protection 112. European Commission 1999.

Rozporządzenie Rady Ministrów z dnia 2 stycznia 2007 r. w sprawie wymagań dotyczących zawartości naturalnych izotopów promieniotwórczych potasu K-40, radu Ra-226 i toru Th-228 w surowcach i materiałach stosowanych w budynkach przeznaczonych na pobyt ludzi i inwentarza żywego, a także w odpadach przemysłowych stosowanych w budownictwie; Dz. U. z 2007 r., nr 4, poz. 29 [in Polish].

Solecki, A., Nowak, K., Śliwiński, W., Tchorz-Trzeciakiewicz, D. 2011. In situ gamma spectrometry as a tool of building material radiation safety assessment? 14th International Congress of Radiation Research. Warszawa: p. 219.

UNSCEAR 2000. Sources and effects of ionazing radiation. Report to the General Assembly with scientific annexes. United Nations, New York.