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SPATIAL DISTRIBUTION OF K,Th AND U ELEMENTAL CONCENTRATION IN SOILS OF THE REPUBLIC OF MACEDONIA

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Abstract

In order to establish a startup database of the natural radioactivity in the Republic of Macedonia (area of 25713 km^2), the elemental concentrations of K, U and Th in the surface soil were determined using high-resolution gamma spectrometry. A total number of 213 soil samples were collected during the period 2008-2009 from the entire territory of the country. The K elemental concentrations were found to be normally distributed with arithmetic mean value of 1.87 %, ranging from 0.26 to 4.44 %. The results for U and Th elemental concentrations were found to be log-normally distributed with geometric mean values 3.08 and 9.29 ppm, and arithmetic means 3.36 (varying from 0.74 to 8.99 ppm) and 10.16 ppm (from 1.6 to 35.77 ppm), respectively. The geometric mean values of the ratios Th/U, K/U and K/Th were found to be: 3.12, 0.61 and 0.20, respectively. The results were compared to the results of the studies from other countries.

Key words: Soil, Potassium, Uranium, Thorium, Gamma spectrometry

Introduction

Radionuclides have been an essential constituent of the Earth since its creation. It has been observed that most of the natural radioactive elements in the soil are primordial radionuclides from the uranium series, thorium series and ^{40}K. The activity concentration of these radionuclides is related to the composition of each lithologically separated area, as well as to the content of the rocks from which the soils originate[1]. However, the differences in the natural radioactivity of soil are closely correlated to their geological origin[2,3]. It has been reported that the higher levels of natural radiation in any area in the world could be associated with volcanic rock, whereas the lower levels to sedimentary rock, with some exceptions [4,5]. On the other hand, the human exposure to natural radiation and the impact of the radiation on the human health are very important issues for any country, since the primordial radionuclides present in soil significantly affect the terrestrial gamma radiation levels. Therefore, measurements of the natural radioactivity in the soil have been performed worldwide, such as the up-to-date investigations in Turkey[6,8], India[7] and Rep. of Srpska[9].

There are no systematic data on this subject available for the Republic of Macedonia. The three previous studies that were found in the open literature were: the first and the second being local studies, pertaining to small parts of the country[10,11], and the third one covering the entire territory, but based on a limited number of samples[12]. In this paper, we present the results of the first systematic study of the K, Th and U elemental concentrations in the surface soil samples taken from all over the country. The study focuses on identification of the differences among the diverse regions. The outcome will be used to establish a baseline map for that area as a reference data to assess any possible changes in

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radioactivity background level due to nuclear, industrial and other human activities in the future.

Study Area

The Republic of Macedonia is a South Eastern European country which is situated in the central Balkan Peninsula on 25713 km^2 area. From geological point of view, the country consists of four geotectonic zones: Western Macedonian zone, Pelagonian massif, Vardar zone and Serbo-Macedonian massif. Between the Vardar zone and the Serbo-Macedonian massif there is a separate area of volcanic rocks, named Kratovsko-Zletovska area [13]. All the aforementioned zones are represented in Fig. 1.

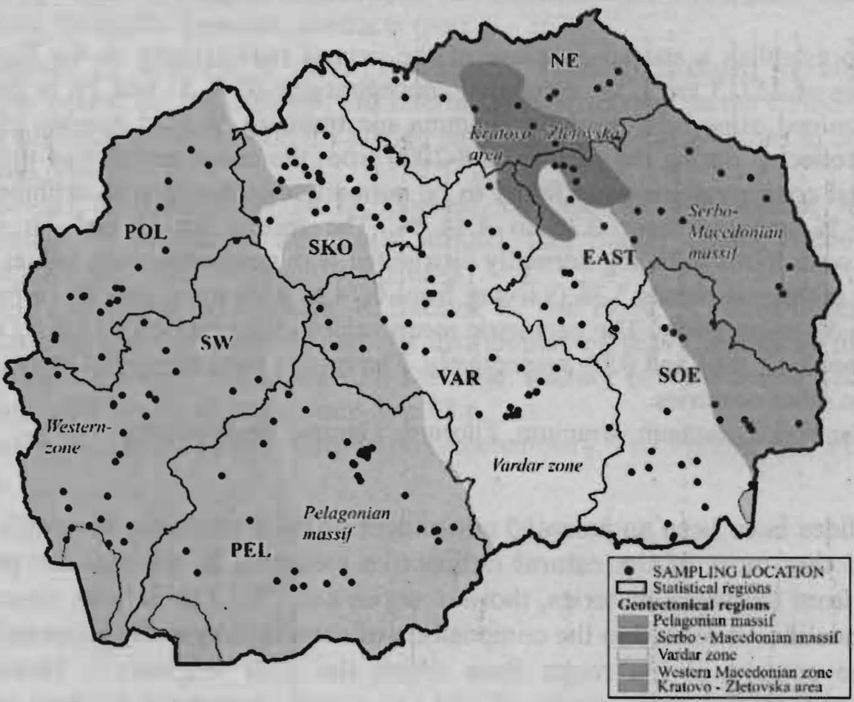

Fig. 1. Map of the sampling spots (dots); 8 Statistical regions (divided by black borderlines); 4 geotectonic zones and one geotectonic area (presented by different shading tones).

The geotectonic zones are characterized by their own geological evolution. The bedrock complexes (magmatic, sedimentary and metamorphic rocks) are different due to the various ages of genesis: from Precambrian to Cenozoic. For the convenience of the data and results presentation, as well as for the needs of future estimation of population exposure and epidemiological studies, a division of the country in 8 statistical regions has been adopted. The statistical regions are: Polog (POL), Southwest (SOW), Pelagonia (PEL), Skopje (SKO), Vardar (VAR), Northeast (NOE), East (EAS) and Southeast (SOE), as presented with black dividing borders in Fig. 1.

Experimental procedure

Sampling and Sample Preparation

A total number of 213 surface soils on 20 cm depth[14] were collected from the sampling locations within the study areas shown in Figure 1, during the period of 2008-2010. The greater part of the impurities, such as stones, pebbles and organic materials was removed from the samples. The samples were than dried, sieved and set in a standard Marinelli beaker of 500 cm^3 to be ready for gamma spectrometry measurements.

Radioactivity Measurements

The gamma spectrometry measurements were carried out with a p-type HPGe detector (Canberra Inc.; 25% relative efficiency, resolution of 1.79 keV at 1.33 MeV, 8192 ch. digital analyser) and software GENIE 2000 for the spectrum evaluation. The efficiency calibration was done with a mixed calibration source (MBSS 2) from the Czech Metrological Institute with same geometry as the one used for the soil samples.

The purpose of the gamma spectrometry measurements was to determine the activity of each of the following radionucleides: ^{40}K, ^{232}Th, ^{238}U. The activity of ^{40}K was determined from the 1460 keV line, whereas the activity of ^{232}Th from the gamma lines of ^{228}Ac (338.32 keV, 911.2 keV, 968.97 keV), ^{208}Tl (583.19 keV) and finally, the activity of ^{238}U was determined from the gamma lines of ^{234}Th (63.28 keV) and ^{234m}Pa (1001.03 keV) [15]. The analysis procedure included subtraction of the background spectrum, correction for interfering lines and correction for self absorption. The verification of the method was performed with two reference materials from the International Atomic Energy Agency, IAEA-385 and PT IAEA-CU-2009-03 proficiency test. The total relative combined uncertainty of each nuclide was: for ^{238}U ($\approx$ 15%) and for ^{232}Th and ^{40}K < 5%, at the 68% confidence level.

The specific activities of ^{238}U, ^{232}Th and ^{40}K (in Bq kg^{-1}) were converted to potassium, uranium and thorium elemental concentrations, respectively, according to the following equations[16]:

$$\begin{aligned} &1\%\ (K) = 313\ \text{Bq kg}^{-1}\ (^{40}K) \\ &1\text{ppm}\ (U) = 12{,}35\ \text{Bq kg}^{-1}\ (^{238}U),\ \text{and} \\ &1\text{ppm}\ (Th) = 4{,}06\ \text{Bq kg}^{-1}\ (^{232}Th) \end{aligned} \tag{1}$$

The results of U and Th are reported in ppm (parts per million), whereas the activity of potassium is reported in % K because of its presence in the environment along with its stable counterparts.

Results and discussion

Utilizing the specific activity of the gamma spectrometry measurements, the K, U, and Th elemental concentrations were determined using equation (1) for all the 213 soil samples from the study area. The statistics of these results is presented in Table 1, whereas the histograms are shown in Fig.2.

Table 1. Statistical data for elemental concentrations in all 213 analyzed soil samples

Statistical data	K(%)	U(ppm)	Th(ppm)
No. of observations	213	213	213
Minimum concentration	0.26	0.74	1.60
Maximum concentration	4.44	8.99	35.8
Median concentration	1.87	3.18	9.54
Arithmetic mean concentration	1.87	3.36	10.2
Standard deviation	0.61	1.38	4.42
Standard error of the mean	0.04	0.09	0.30
Geometric mean concentration	1.76	3.08	9.29
Geometric standard deviation	1.47	1.53	1.55

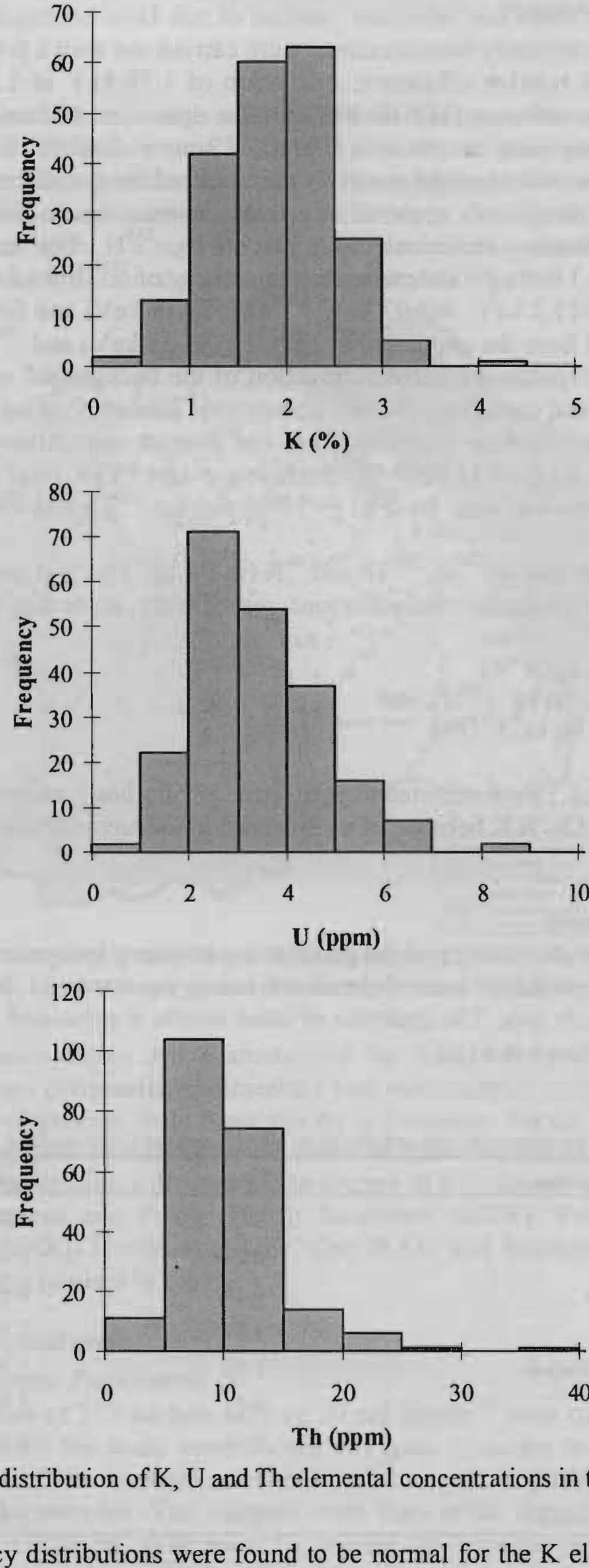

Fig. 2. Frequency distribution of K, U and Th elemental concentrations in the surface soil

The frequency distributions were found to be normal for the K elemental concentrations, though the results for U and Th were found to follow the log-normal distribution (χ^2, Kolmogorov-Smirnov test, $p<0.05$). The statistical analyses for U and Th were performed only for the log transformed values, since the log transformation reduces the influence of extreme values[17].

Taking into account the geological diversity of the area and the fact that the K, U and Th elemental concentrations depend on the composition of each lithologically separated area, as well as from their content in the rocks from which the soils originate, differences between regions were expected to occur. Table 2 shows a summary of the arithmetic mean values and the standard deviation of the K (%), U (ppm), Th (ppm), as well as the geometric mean and geometric standard deviation of the U (ppm), Th (ppm) concentrations for each of the eight statistical regions.

Table 2. K, U and Th elemental concentrations in soils from different statistical regions

		K (%)		U (ppm)				Th (ppm)			
Region	No.	AM	SD	AM	SD	GM	GSD	AM	SD	GM	GSD
SW	34	2.07	0.61	3.78	0.91	3.66	1.30	11.3	2.60	11.0	1.27
SE	20	1.75	0.94	3.22	2.05	2.58	2.04	8.81	5.96	6.69	2.26
VAR	26	1.88	0.57	3.25	1.13	3.09	1.38	11.3	5.19	10.3	1.52
EAST	30	1.94	0.48	3.28	1.11	3.10	1.42	9.62	2.79	9.21	1.36
PEL	38	2.07	0.46	4.43	1.44	4.20	1.40	13.5	5.27	12.8	1.38
POL	19	1.97	0.42	2.84	0.79	2.73	1.35	7.87	2.19	7.58	1.32
NE	14	1.78	0.65	3.14	1.41	2.87	1.54	8.97	3.05	8.52	1.39
SKO	32	1.41	0.44	2.28	0.56	2.20	1.33	7.34	1.77	7.13	1.29

The analysis of variance showed that the differences among the mean values of K, U and Th elemental concentrations for the eight statistical regions are statistically significant (ANOVA, $p = 0.0002$). In addition, the Fisher's LSD-test applied for evaluation of the differences among the mean values, showed that the lowest arithmetic mean value of the K elemental concentration (1.41 %) was found for the Skopje statistical region (LSD, $p < 0.0001$). The later result could be related to the fact that Skopje region belongs to the geotectonic Vardar zone, which is composed of different geological units. But, the area of Skopje is mainly composed of Neogene–Quaternary sediments, mainly by clay and sandstone[18].

On the other hand, the highest arithmetic mean value (4.43ppm) and geometric mean value (4.20 ppm) of U elemental concentration were found for Pelagonija (PEL) statistical region (LSD, $p < 0.0001$). This result was expected, since this region belongs to the Pelagonija Massif which is dominantly composed of granite and metamorphic rocks of the Precambrian period [19].The results of the Fisher's LSD test showed that the lowest U concentration (GM = 2.20 ppm) was found for Skopje region (LSD, $p < 0.0001$). Similar distribution among the statistical regions was found for the Th elemental concentration. The highest average elemental concentration (GM=12.77 ppm) was found for Pelagonija and the lower elemental concentrations: 6.69 ppm, 7.13 ppm and 7.58 ppm were found for Southeast, Skopje and Polog statistical regions, respectively. To visualize the differences among the statistical regions, the interpolated maps of the K, U, Th elemental concentrations were created (Fig. 3). Furthermore, as the K, U and Th elemental concentrations were grouped by geotectonic zones, the differences revealed to be statistically significant (ANOVA, $p<0.0001$).

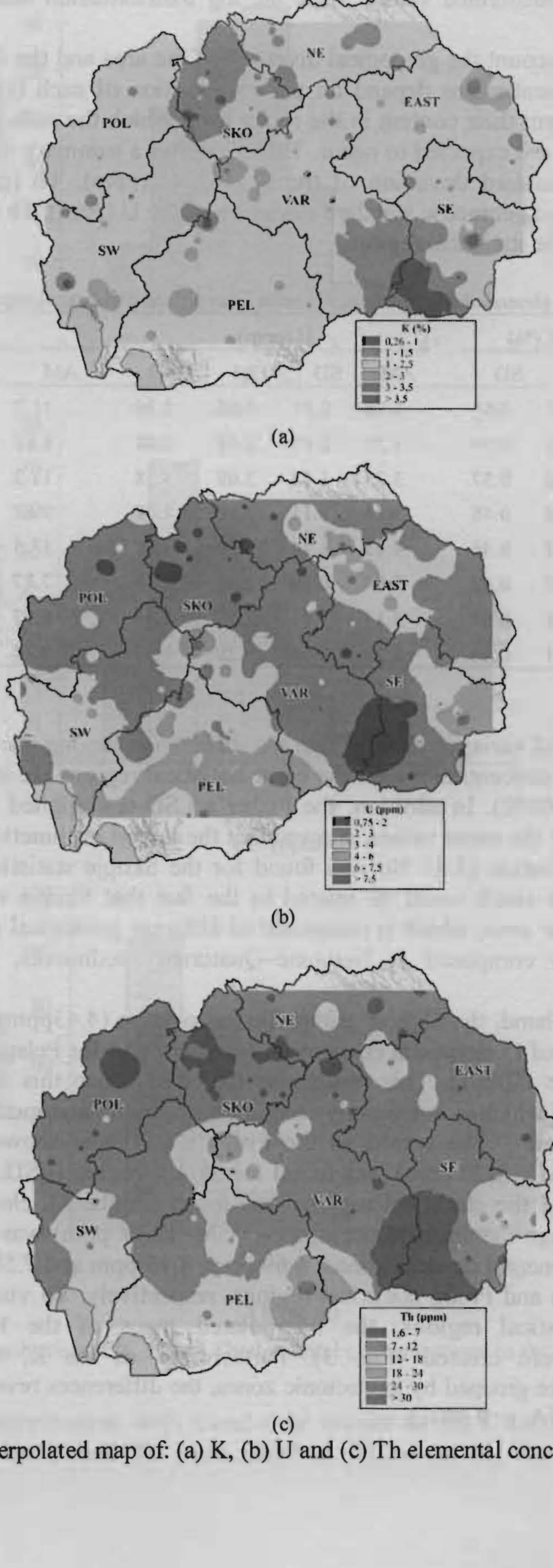

Fig. 3. Interpolated map of: (a) K, (b) U and (c) Th elemental concentration.

Hence, the lowest K elemental concentration was found for the Vardar zone (LSD, $p<0.0001$), whilst the values for the other zones comprised one single group. The results showed that the U and Th elemental concentrations in the Pelagonija massif and the Kratovsko-Zletovska area are significantly higher in comparison to other geotectonic zones (LSD, $p<0.0001$). The results of the arithmetic mean values of U and Th elemental concentrations in the soils from Kratovsko-Zletovska area (4.65ppm and 13.06ppm, respectively) turned to be very similar to those of the Pelagonija Massif (4.45ppm and 14.63ppm, respectively) but significantly higher than those of other geotectonic zones.

According to the UNSCEAR 2000 report[4]., the world mean value of U and Th elemental concentrations in soils ranges from 1.3 to 8.9ppm and from 2.7 to 15.8ppm, with average global value of 2.8 ppm and 7.4 ppm, respectively. If we compare the FYR of Macedonia's average values of U (3.36ppm) and Th (10.16ppm) elemental concentrations to the average world values, one would conclude that the values are somewhat higher than the world mean, but at the same time, they are in the reported range of values. The same document reports that the global average K elemental concentration is 1.3%, which is lower than the average value obtained in this study (1.87%). Additionally, the idea was to compare the obtained results with the results of studies of some other countries. For example, from the investigations made in Cyprus, for 115 soil samples taken from the different lithological units, the arithmetic mean values of K, U and Th elemental concentrations are found to be: 0.4%, 0.6 ppm and 1.2 ppm respectively[1]. For Provincia dell Aquila (Central Italy), the corresponding values are: 0.88%, 1.97ppm and 10.1ppm for K, U and Th respectively[20]. There is a great similarity between the results of this study and the results from the Republic of Serbia, where the K, U and Th elemental concentrations were reported to be: 1.98 (0.88-2.99) %, 2.76 (1.2-6.24) ppm and 10.4 (4.45-21) ppm, respectively [21]. The comparison of the results is presented in Table 3.

Table 3 Comparison of the results of K, U and Th elemental concentrations in soils of R of Macedonia with results of some other countries

Region/country	K(%)	U(ppm)	Th(ppm)	Reference
FYR of Macedonia	1.87 (0.26-4.44)	3.08 (0.74-8.99)	9.29 (1.6-35.8)	Present study
Provincia dell Aquila (Central Italy),	0.88 (0.047-1.86)	1.97(0.41-5.7)	10.1 (0.36-58)	[20]
Sebia and Montenegro	1.98 (0.88-2.99)	2.76(1.2-6.24)	10.4 (1.45-21.0)	[21]
Cyprus	0.4 (0.0001-1.9)	0.6 (0.0008-3.2)	1.2 (0.003-9.8)	[1]
World average	1.34 (0.45-2.72)	2.80 (1.30 -8.91)	7.39 (2.71-15.8)	[4]

In order to identify the relative depletion or enrichment of the investigated radionuclides in the surface soil, the correlations between K, U and Th elemental concentrations were studied by means of Pearson correlation coefficient as a measure of the linear dependence. The highest correlation, $R = 0.78$, was found between the Th and U elemental concentrations. Lower correlations appeared for K versus U ($R = 0.56$) and for K versus Th ($R = 0.59$). Furthermore, the following ratios between the concentrations: Th/U, K/U, K/Th in the surface soil were determined. The results for the ratios in this study were distributed within a wide interval of values which followed the log normal distribution (χ^2 and Kolmogorov-Smirnov test, $p < 0.05$).

The geometric mean value of the ratio Th/U was 3.01 (with geometric standard deviation of 1.30), with individual values distributed in the interval from 1.38 to 7.75. Hence, the obtained mean value is matching the theoretical value for normal continental soils (3.0)[1]. This ratio is comparable to the values of 2.93 and 2.88 reported for Jordan, obtained for soil of sediment and volcanic origin, respectively [21] and 3.89 reported for Serbia and Montenegro[21]. For the ratios K/U and K/Th elemental concentrations it was derived: 0.57 (0.16–1.44) and

0.19 (0.05–0.59), respectively. The values for the aforementioned ratios for Serbia were 0.76 and 0.50, respectively[21].

For further elucidation, the ratios Th/U, K/U and K/Th, grouped in 4 different geotectonic zones, were analyzed and compared. The ANOVA test indicated that Th/U ratio was not significantly different among the zones (p = 0.115) (Fig. 4a).

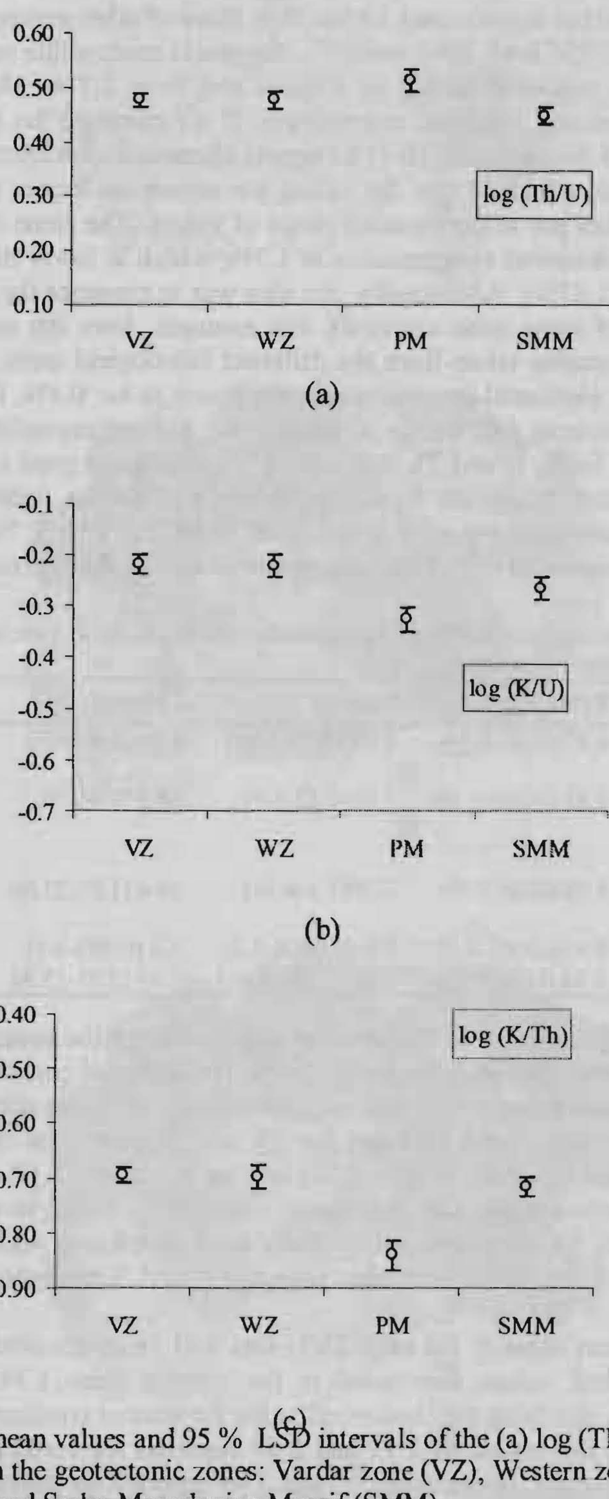

Fig. 4. Arithmetic mean values and 95 % LSD intervals of the (a) log (Th/U), (b) log (K/U) (c) log (K/Th) within the geotectonic zones: Vardar zone (VZ), Western zone (WZ), Pelagonian massif (PM) and Serbo-Macedonian Massif (SMM).

However it indicated significant differences for the K/U and K/Th ratios ($p < 0.05$). The K/U and K/Th ratios in the Pelagonian Massif (PM) were significantly lower in comparison to those of the other three geological groups (LSD, $p = 0.006$ and $p < 0.0001$, respectively), which is presented in Fig. 4b and 4c. For comparison, lower K/U and K/Th ratios in soils from volcanic origin have also been reported for soils in Jordan[22].

Conclusion

The K, U and Th elemental concentrations were determined for 213 samples of surface soil taken from the entire area, subject to this research (Republic of Macedonia). After the statistical processing of the results, the arithmetic mean values (± standard deviation) of the elemental concentrations for all samples were found to be (1.87 ± 0.61) % for K, (3.4 ± 1.4) ppm for U and (10.2 ± 4.4) ppm for Th. Taking into account the log-normal distribution of the U and Th results, the corresponding geometric mean values were found to be 3.1 ppm and 9.3 ppm, respectively.

From the statistical analysis, significant differences among the values for different regions and geotectonic zones were found. The higher values for U and Th elemental concentrations were related to soils of volcanic origin, whereas the lower values were associated to soils of sedimentary origin. From the analysis of the Th/U, K/U and K/Th ratios, it was evident that only the values for K/U and K/Th are correlated to the geology, whereas their statistically significant lower values were related to the soils of volcanic origin.

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