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University of Zagreb, R. Croatia and Croatian UNESCO-IGCP
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2nd *INTERNATIONAL WORKSHOP ON THE PROJECT*

ANTHROPOGENIC EFFECTS ON THE HUMAN ENVIRONMENT IN THE NEOGENE BASINS IN THE SE EUROPE

PROCEEDINGS

Edited by
Bermanec & Serafimovski

Zagreb, 6-7 October 2011

MONITORING DEPOSITION OF ANTHROPOGENIC INTRODUCED ELEMENTS IN AIR. CASE STUDY: COPPER MINE ENVIRON

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Abstract

The total deposited dust was used as sampling media for monitoring the distribution of heavy metals in an area with intensively exploited copper minerals (Bučim copper mine, R. Macedonia). The content of Cu and Pb was determinate using atomic emission spectrometry with inductively coupled plasma (ICP-AES). Within the study area, three sampling spots (settlements) were selected: villages Bučim and Topolnica and the town of Radoviš. In the copper mine environ, there are some values above the national maximum permitted value for deposited dust (300 mg m^{-2} d^{-1}). Larger amounts of dust are deposited in the villages Bučim and Topolnica (annual average values of 489 mg m^{-2} d^{-1}, and 309 mg m^{-2} d^{-1} respectively) with a maximum value (815 mg m^{-2} d^{-1}) obtained in the Bučim village. Higher contents of Cu and Pb were obtained from deposited dust samples collected from Topolnica village (max. value 1183 mg kg^{-1} and 184 mg kg^{-1}, respectively).). In the town of Radoviš deposited dust was not above the maximum permitted amount for deposited dust, but higher content of Cu and Pb contents were found (max. values 1171 mg kg^{-1} and 189 mg kg^{-1} respectively).

Keywords: Total deposited dust, monitoring, heavy metals, copper mine, Republic of Macedonia

Introduction

Heavy metals in the atmosphere originated mainly from dust dispersion from metal refining, fossil fuel combustion, vehicle exhausts, and other human activities and stay in the atmosphere until they are removed by a variety of cleansing processes (Vallero, 2008; Agarval, 2009). Particular emphasis is given on ore deposits, mining, processing and flotation plants as significant anthropogenic sources of dust. Copper mine with open ore pit type present a potentially emission source of heavy metals in air. Main processes that allow it are: minerals blasting, drilling and crushing, their loading and transportation to processing and flotation plants. From other hand, large amounts of ore waste and flotation tailings are deposited at open, continuously exposited to air flow and winds caring-out. People are directly exposed to the effects of heavy metals through inhalation of airborne micro particles from atmospheric dust (Jarup, 2003; Godish, 2004).

Atmospheric total deposition (deposited dust) is very useful mechanism for monitoring the fate of anthropogenic elements introduced into the atmosphere (Čačković et al., 2009). Fine powder with a high content of heavy metals is generated as a result of emissions from the processing of ores and metallurgical process and is distributed as a result of wearing the wind. Many investigations have focused on the chemical composition and the content of toxic substances in deposited dust (Morselli et al., 2003; Avila and Rodrigo, 2004; Polkowska et al., 2005; Vike, 2005, Stafilov et al., 2011).

In order to determine the amount of fine dust contained in the air, samples of total deposited matter (deposited dust) were collected at three locations in the area of Bučim copper mine, R. Macedonia.

Study area

The study area occupies the "Bučim" mine environ, located in the eastern Republic of Macedonia part (Fig. 1). The mine and the ore processing plant have been functioning since 1979 and it is assumed that the mine has about 40 million tons of ore reserves. Ore tailings are dropped out at open site near the mine, occupies a surface of 0.80 km^2. The ore tailings deposit has about 130 million tons of ore tailings. Exposure of this great mass of ore tailings to constant air flow and wind leads to the distribution of fine dust in the air.

Geological description. The Bučim-Damjan-Borov Dol area is divided into two tectonic blocks. The Bučim tectonic block and the southern tectonic block Damjan are a part of the Vardar zone. The blocks are divided by a fault of first order in the SE direction. Despite the disposition in two different tectonic blocks, the metallogenic area is unified based on the similarities of Tertiary magmatism and the analogous ore mineralisations. The Bučim copper-porphyry deposit with additional gold mineralisation is found in the northern block (Stefanova et al., 2004).

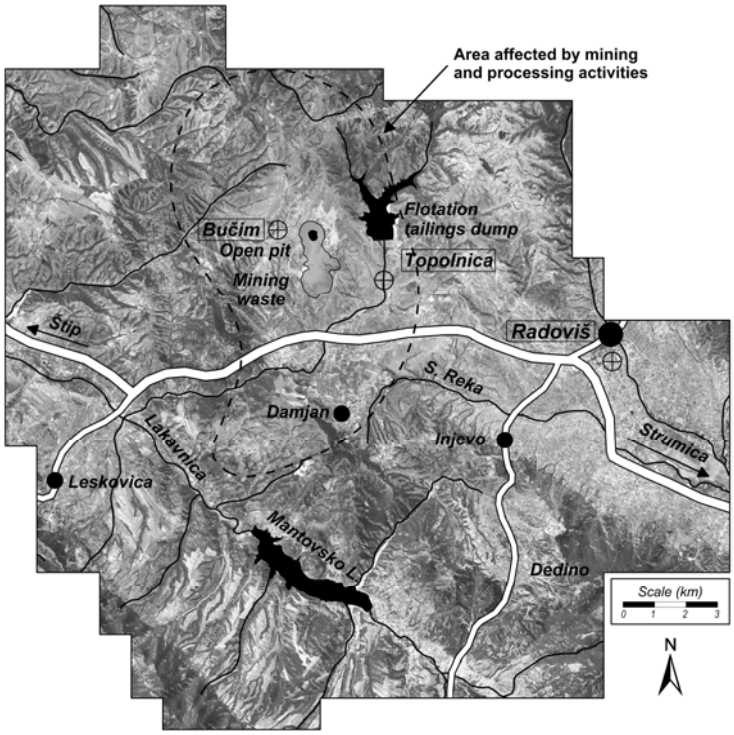

Fig. 1. Location of study area and sampling points for deposited dust

Experimental

Monthly samples of deposited dust were collected at three monitoring sites in copper mine environ: the town of Radoviš and the villages Bučim and Topolnica during 2009 (Fig. 1). Samples were collected using the dust deposition gauges. The obtained results were expressed in mg m^{-2} d^{-1} (i.e. the mass of dust deposited per m^2 per day). A deposit gauge, which comprises a 28±1 cm diameter funnel inserted into a plastic container (at least 5-10

liters in size) through a rubber stopper. Stand approximately 2 m tall and a canister which holds the plastic container to protect it from sunlight. After 30±2 days, any deposited matter in the funnel was washed into the plastic container using distilled water.

The collected rainwater of each sample was evaporated near dryness and then 3-5 mL of nitric acid, *p.a.* (MERCK, Germany) was added and transfers in to the 25 mL volumetric flasks. The content of Cu and Pb in digested samples was determined using ICP-AES (Varian 715-ES). The optimal instrumental parameters for this technique were previously given (Stafilov et al., 2011).

Results and discussion

The obtained values for the contents of the investigated elements were statistically processed using basic descriptive statistics. From the results obtained in this investigation it is evident that a large amounts of deposited dust were recorded in the close vicinity of the mine (villages Bučim and Topolnica) in some periods of the year the values are above the maximum permitted amount of dust powder (300 mg m^{-2} d^{-1}). Maximum value for the total deposited dust (815 mg m^{-2} d^{-1}) was obtained in August in the Bučim village. The annual average for the total deposited dust in the vicinity of the Bučim village is 489 mg m^{-2} d^{-1}, for Topolnica the 309 mg m^{-2} d^{-1} and accounted for Radoviš is 97 mg m^{-2} d^{-1} (Fig. 2).

As it can be seen from the data presented in Table 1, the median values for Cu in samples of deposited dust taken from the Radoviš area is 396 mg kg^{-1} and the ranges (from 94.8 to 1171 mg kg^{-1}, with high variation in monthly values) for the Topolnica village the median values in samples of deposited dust is 150 mg kg^{-1} with ranges (from 52.5 to 1183 mg kg^{-1}) and for the Bučim village the median values in deposited dust samples is 145 mg kg^{-1} and the ranges from 85.3 to 317 mg kg^{-1}. From these results can be seen that the maximum value for the content of Cu was obtained from Topolnica village (settlement near by the flotation tailings landfill) as presented in Fig. 3.

Table 1. Statistical parameters for annual values for the content of copper and lead in samples of deposited dust (in mg kg^{-1})

Element	N	Sampling site					
		Vill. Bučim		Vill. Topolnica		Radoviš	
		Median	Range	Median	Range	Median	Range
Cu	12	145	85.3-317	150	52.5-1183	396	94.8-1171
Pb	12	25.7	12.1-56.6	26.8	7.20-184	69.5	20.1-189

Similar results were obtained for the content of Pb. Previously investigations separated Cu and Pb as anthropogenic introduced elements in the study area (Balabanova et al., 2009; 2010; 2011; Stafilov et al, 2010). Maximum value for Pb was obtained from the town of Radoviš (189 mg kg^{-1}). Variability in monthly values for lead contents is due to the fact that higher contents of this anthropogenic element are continuously introduced in air with traffic and industry characteristic for the town. Despite the large amounts of total deposited dust from Bučim village, high values for the Pb content were not found (Fig. 4).

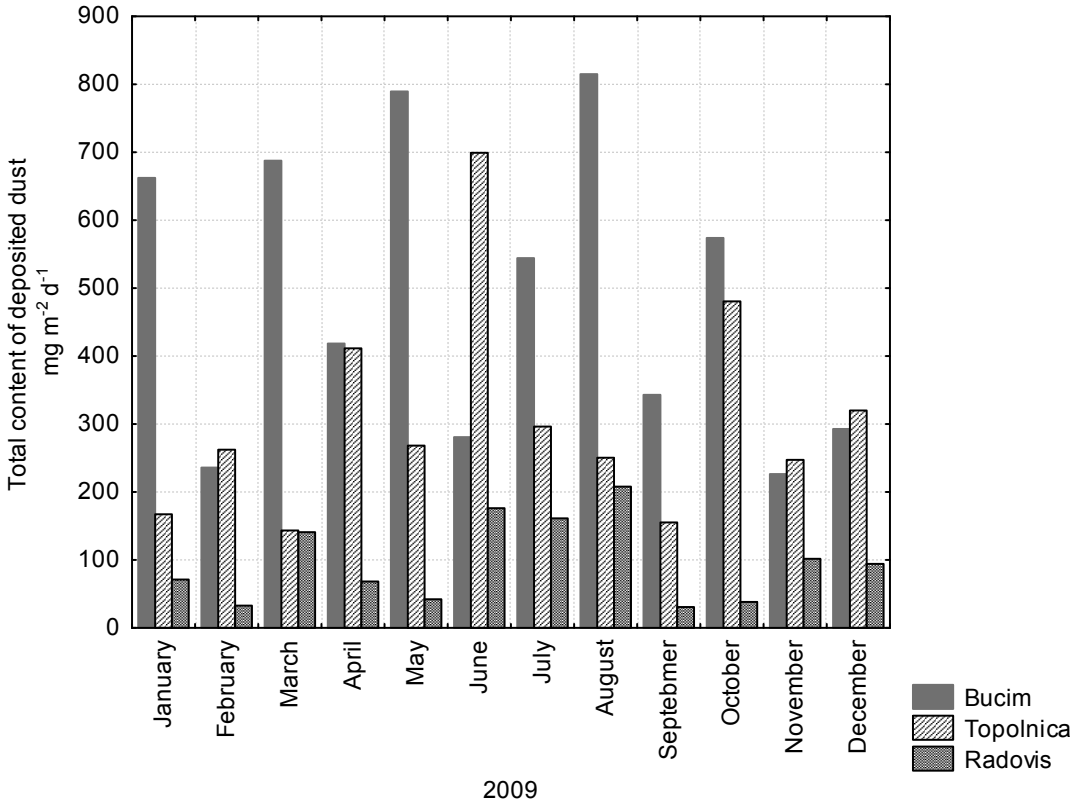

Fig. 2. The total content of deposited dust

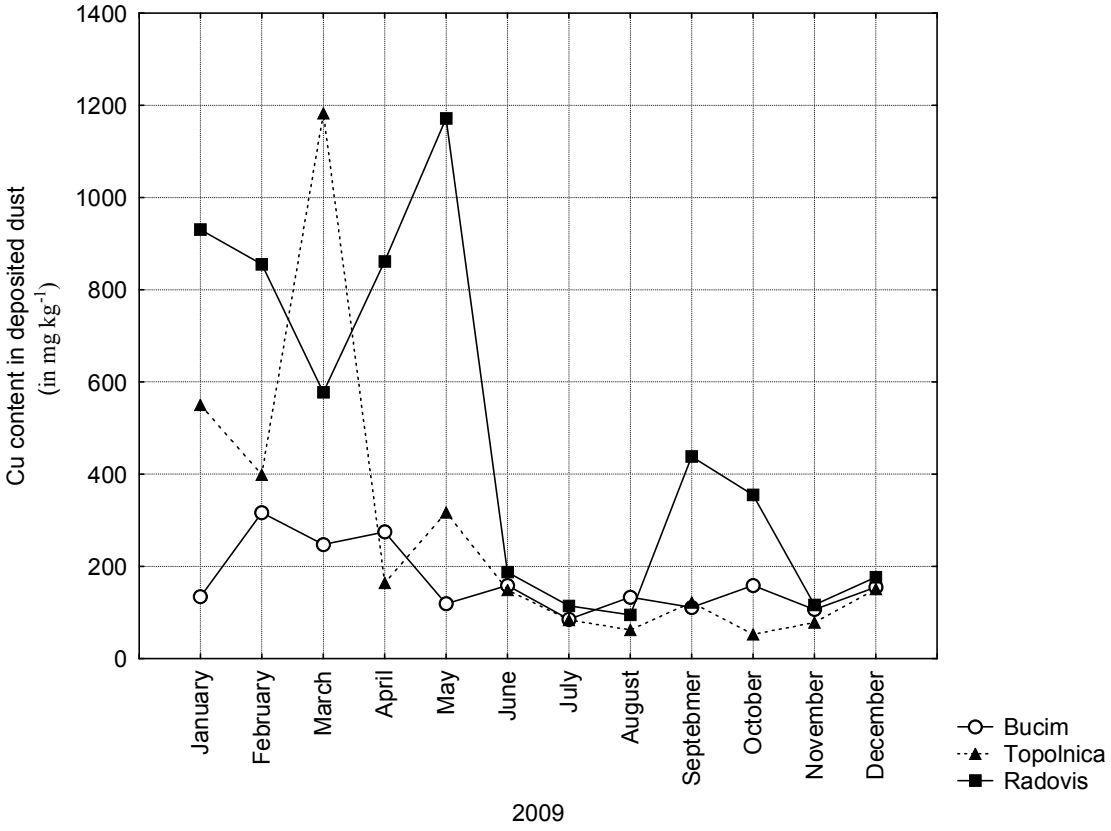

Fig. 3. Trends of copper content in deposited dust through the whole year

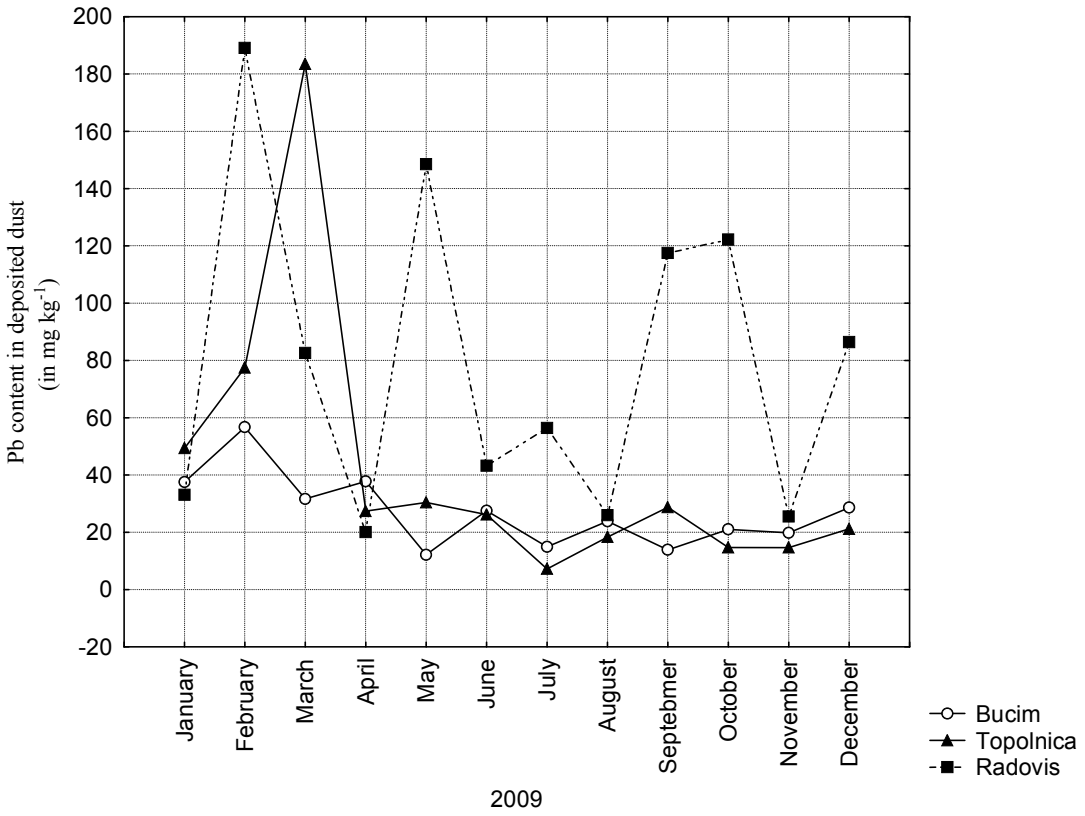

Fig. 4. Trends of lead content in deposited dust through the whole year

Conclusion

Conducted monitoring with deposited dust samples fortify that anthropogenic introduced elements (Cu and Pb) deposit in higher contents in close vicinity of their hot spots (open ore pit, ore waste and flotation tailings landfill). In the copper mine environ, there are some values above the national maximum permitted amount of sedimental dust (300 mg m^{-2} d^{-1}); annual average for the total deposited dust in the vicinity of the Bučim village - 489 mg m^{-2} d^{-1}, for Topolnica - 309 mg m^{-2} d^{-1} and for Radoviš - 97 mg m^{-2} d^{-1}. Maximum value for the Cu content was obtained from Topolnica village (settlement near by the flotation tailings landfill). In the town of Radoviš deposited dust was not above the maximum permitted amount for dust powder, but higher contents of Cu and Pb were obtained (with monthly variations in results). The high contents of Cu and Pb are not only due to mining works, but also the town works, traffic, industry and developed technological processes which aloud emission of higher amounts of these heavy metals in air.

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RESULTS OF MEASUREMENTS OF SOIL ACTIVITY, SOIL GAS AND INDOOR RADON CONCENTRATIONS IN PRILEP AND SKOPJE

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Abstract: The preliminary measurements of radon and thoron concentrations in the soil gas were done, using short term active method. Field measurements were made at a distance of 1-2 m away from the randomly selected houses in Skopje and Prilep. Ten series of short-term (10-minutes) measurements were made. The arithmetic mean values of radon and thoron concentrations in the soil gas were found to be 15.9 ± 5.6 kBq m^{-3} and 5.3 ± 2.3 kBq m^{-3}, respectively. Activity concentrations of ^{40}K, ^{226}Ra and ^{232}Th in soil were evaluated from gamma spectrometry analysis on the soil samples that were collected from the same locations. Indoor radon concentrations were measured in the houses of the same locations.

1. Introduction

Radioactivity is a part of our everyday's life and as such, it is present in every medium of the living environment. The study of radioactivity in the living environment is a crucial segment of radiation protection, but at the same time, it is a useful tool in the exploration of the transport processes which originate from the nature itself.

In the period of 2007-2009, a survey of natural radioactivity was carried out in whole regions of Republic of Macedonia (1-6). Attempts were made in all investigates areas to identify populations receiving elevated natural exposures that might serve as potential groups for a planned future health study.

From human perspective, indoor radon (^{222}Rn) and its progeny are one of the most significant natural sources of radiation exposure to the population. As an inert gas, radon freely diffuses through the soils and reaches the atmosphere where it could migrate into structure of dwellings to pose a health hazard. The national survey of indoor radon concentration in 2008 was done. Indoor radon concentration was measured in 413 dwellings by using CR-39 detectors, with a total 1652 measurements. Detectors were deployed in four seasons in living room or bedroom of each house, where inhabitants spent the most of the time (5,7).

Some researches even believe that measurements of radon in the soil gas can be used to predict indoor radon level. In addition, numerous activities in the field of radon measurements in soil have been published (8-11). In order to give a more comprehensive evaluation of exposure and to identify sources of indoor radon concentrations in Skopje and Prilep, some measurements in 16 dwellings were undertaken in 2010. In this paper, we report the results of these measurements, with the emphasis on their correlations.

2. Study area

In order to investigate the concentrations of ^{40}K, ^{226}Ra and ^{232}Th in soil, radon and thoron concentrations in the soil gas and indoor radon concentrations, as well as to test its correlations, 16 testing sites were selected randomly for this study. These sites are situated a two towns Prilep and Skopje.

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3. Measuring procedure

3.1. Activity concentrations in the soil

The soil samples were collected on two different depths (0-20 cm and 20-100 cm). All samples were grinded and then dried at 105°C temperature until the moisture of the sample was completely evaporated. After homogenization, the samples were transferred in 500 ml Marinelli beaker which was used for the gamma spectrometry measurements. The containers were closed and sealed hermetically and kept aside for a month, in order to achieve a secular equilibrium between ^{226}Ra and its daughters.

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 with software GENIE 2000 for spectrum evaluation.

From the gamma spectrum the activity of the following radionuclides: ^{40}K, ^{226}Ra and ^{232}Th was determined. The activity of ^{40}K was determined from its 1460 keV line. The activity of ^{226}Ra was determined from the gamma lines associated with the short-lived daughters of: ^{214}Pb (295.22 keV, 351.93keV) and ^{214}Bi (609.31 keV, 1120.29 keV, 1764.49keV). Finally, the activity of ^{232}Th was determined from the gamma lines of ^{228}Ac (338.32 keV, 911.2 keV, 968.97 keV), ^{208}Tl (583.19 keV).

3.2. Indoor radon concentrations

The indoor radon concentration was measured at the same position locations during the four seasons (4 times a year with the same time of exposure, 3 months) in period 2008-2009.

The measurements were performed with commercially available RSKS passive track detectors. The detector consists of a CR-39 chip placed in a cylindrical diffusion chamber with dimensions 25 mm x 40 mm.

The detectors were set either in the living rooms or the bedrooms inside the houses, at a height of 1 to 1.5 m above the floor, at a distance greater than 0.5 m from each wall (to avoid influence of ^{220}Rn originating from the building materials, which contributes negligibly to the room interior, due to the low diffusion length) and, minimum 20 cm away from any other object in the room.

At the end of each seasonal cycle, the detectors were returned to the laboratory for analysis.

3.3. Radon and Thoron concentrations in soil gas

The measurement set-up consisted of the SARAD (RTM2100) radon monitor and soil gas sampling system. The RTM2100 - semiconductor detector combined with the alpha spectrometry analysis measured simultaneously radon and thoron concentrations by the short living daughter product (^{218}Po and ^{216}Po). The measurement locations were set at the house's courtyards for which the indoor concentrations of radon were measured as they were randomly selected, in Prilep and Skopje. Attention was payed that the selection was made from different town sections. The measurements in a selected location were made at a 1-2 m distance from each selected house.

A one meter (1 m) deep hole with 7 cm diameter was drilled. The soil sampler was carefully inserted into the bore-hole and connected directly to the instrument (connected to internal pump) by a flexible PVC tube. Ten series of short-term (10-minutes) measurements were made, and each result was recorded and kept for further processing.

4. Results and discussion

The results of the gamma spectrometry measurements of the soil samples, taken from holes on different depths (0-20 cm and 20-100 cm), are presented in Table 1. The activity concentration as well as the total combined uncertainty at the 68% confidence level of ^{40}K, ^{226}Ra and ^{232}Th are in Bq kg^{-1}.

The arithmetic mean (± standard deviation of the mean value) of the activity concentration of ^{40}K, ^{226}Ra and ^{232}Th on the (0 - 20)cm were (585 ± 33) Bq kg^{-1}, (38 ± 3) Bq kg^{-1} and (38 ± 2) Bq kg^{-1}, respectively. The activity of ^{226}Ra ranges from 19 to 56 Bq kg^{-1} and from 20 to 57Bq kg^{-1} on the (0-20)cm and (20 – 100)cm deeps respectively The range of measured activity on the (0-20)cm of ^{232}Th was 24-52 Bq kg^{-1} and 26-53 Bq kg^{-1} on the 20-100cm deep. The ranges of measured activity of ^{40}K on the (0-20)cm and (20-100)cm deeps were ranged from 319 to 761 Bq kg^{-1} and 332 to 807 Bq kg^{-1}, respectively.

Table 1. Activity concentraction of ^{40}K, ^{226}Ra and ^{232}Th in soil samples

N	Location	0-20cm						20-100cm					
		^{40}K		^{226}Ra		^{232}Th		^{40}K		^{226}Ra		^{232}Th	
		A*	u(A)**	A	u(A)	A	u(A)	A	u(A)	A	u(A)	A	u(A)
1	Prilep	761	10	53	0,4	49	0,6	765	10	54	0,7	53	0,6
2	Prilep	576	8,0	42	0,4	36	0,5	611	8,3	42	0,4	37	0,5
3	Prilep	749	9,9	42	0,4	41	0,5	807	10	41	0,4	39	0,5
4	Prilep	685	9,2	44	0,4	43	0,5	707	9,4	43	0,4	47	0,5
5	Prilep	659	9,2	47	0,4	42	0,5	728	9,6	57	0,5	51	0,6
6	Prilep	682	9,3	56	0,5	52	0,6	731	9,5	52	0,4	49	0,5
7	Prilep	609	11	47	0,6	47	0,8	555	7,8	49	0,4	45	0,5
8	Prilep	732	9,7	52	0,4	52	0,6	727	9,7	49	0,4	48	0,6
9	Prilep	559	7,7	44	0,4	47	0,5	569	7,7	46	0,4	53	0,5
10	Skopje	505	7,5	22	0,3	30	0,5	491	30	21	0,4	31	0,7
11	Skopje	604	8,5	30	0,3	30	0,4	715	9,7	25	0,3	34	0,5
12	Skopje	625	8,6	38	0,4	33	0,5	639	8,6	35	0,3	32	0,5
13	Skopje	434	6,2	21	0,2	29	0,4	457	6,6	25	0,2	32	0,4
14	Skopje	379	5,9	31	0,3	24	0,4	403	6,4	25	0,3	26	0,4
15	Skopje	319	6,1	19	0,2	26	0,4	332	5,4	20	0,2	28	0,4
16	Skopje	488	7,5	25	0,3	29	0,4	488	7,5	25	0,3	38	0,5

*activity concentration in Bq kg^{-1}.
**total combined uncertainty (σ=1) Bq kg^{-1}.

It seems useful to examine the downward distribution for ^{40}K, ^{226}Ra and ^{232}Th in surface soil to obtain an insight into mixing near the surface. For this purpose, radioactivity ^{40}K, ^{226}Ra and ^{232}Th, was compared for each sample taken from the two depths of each hole (12). A nonparametric linear regression analysis was performed, and the Spearman correlation coefficient was 0.94 for ^{40}K, 0.96 for ^{226}Ra and 0.87 for ^{232}Th, at the level of significance p=0.05.

From the statistical analysis, the results of the gamma spectrometry analysis of the soil samples, taken from holes, showed statistically insignificant differences between activity concentration of ^{40}K, ^{226}Ra and ^{232}Th from different depths (0-20cm and 20-100cm). On Figure 1 are presented the mean values of ^{226}Ra and ^{232}Th at 0 -100 cm depth.

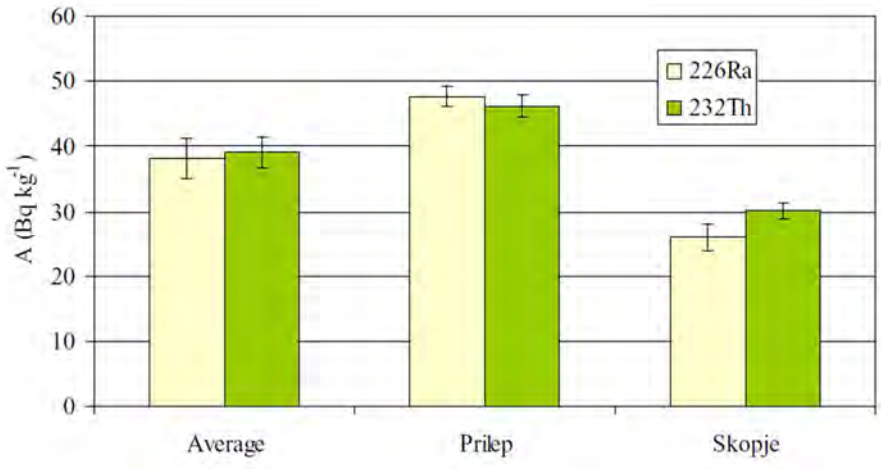

Figure 1. Mean values and 95% LSD intervals of the ^{226}Ra and ^{232}Th concentration at 0-100 cm depth

In Tabe 2, the results of indoor radon concentration measured in different season are present. The annual average indoor concentration is estimated as an arithmetic mean value of measured results in four seasons. All results are presented in Bq m^{-3}.

As can be seen from Table 2, the maximum value of radon concentration was 956 Bq m^{-3} and the minimum 16 Bq m^{-3} measured in winter and summer respectively. The indoor radon concentrations are subjected in seasonal variation. This could be attributed to the applied passive techniques, which are advantageous due to averaging of the seasonal variations caused by the long measurement period. The annual radon concentrations were ranged between 40 and 552 Bq m^{-3}.

Table 2. Results of indoor radon concentration ^{222}Rn

		^{222}Rn (Bq m^{-3})				
N	Location	Winter	Sping	Summer	Autumun	Annual average
1	Prilep	112	70	33	51	**66**
2	Prilep	300	221	117	198	**209**
3	Prilep	89	44	52	43	**57**
4	Prilep	117	95	41	69	**80**
5	Prilep	59	47	42	58	**51**
6	Prilep	323	178	73	154	**182**
7	Prilep	54	41	29	35	**40**
8	Prilep	72	79	64	43	**64**
9	Prilep	956	478	128	647	**552**
10	Skopje	45	51	16	50	**40**
11	Skopje	127	60	38	114	**85**
12	Skopje	335	157	171	301	**241**
13	Skopje	738	331	53	294	**354**
14	Skopje	291	173	38	293	**199**
15	Skopje	274	141	59	202	**169**
16	Skopje	104	49	39	94	**71**

The active method was used to determine the radon and thoron concentrations in the soil gas. The meteorological parameters: air temperature, pressure and relative humidity were measured with the same device because it is known that they can influence radon concentration. Therefore it seems important to know under what

conditions the short-term radon measurements were carried out (13). The average values of air temperature, air pressure and relative air humidity ranged from 19 °C to 46 °C, 932 hPa to 980 hPa and 26% to 73%, respectively. The results of the soil gas measurements on the same locations are presented in Table 3.

Table 3. Radon and Thoron concentrations in soil gas

		^{222}Rn		^{220}Rn	
N	Location	C (kBq m^{-3})	u(C) (kBq m^{-3})	C (kBq m^{-3})	u(C) (kBq m^{-3})
1	Prilep	57,6	0,9	9,5	0,3
2	Prilep	23,4	0,4	5,2	0,2
3	Prilep	2,6	0,1	0,4	0,0
4	Prilep	3,3	0,1	2,5	0,1
5	Prilep	4,5	0,3	1,0	0,1
6	Prilep	3,7	0,2	0,5	0,1
7	Prilep	2,9	0,2	3,7	0,3
8	Prilep	2,8	0,1	2,2	0,1
9	Prilep	0,8	0,1	0,9	0,1
10	Skopje	20,7	0,4	38,6	0,1
11	Skopje	57,1	0,8	8,2	0,3
12	Skopje	62,5	0,7	7,3	0,2
13	Skopje	0,2	0,0	0,2	0,0
14	Skopje	6,1	0,2	1,4	0,1
15	Skopje	1,0	0,1	0,6	0,1
16	Skopje	5,0	0,2	2,5	0,1

The values of radon concentration in soil gas using short-term measurements obtainned using active devices varied from 0.2 kBq m^{-3} to 62.5 kBq m^{-3}. Obtained results for thoron concentrations in soil gas were found to vary from 0.2 kBq m^{-3} to 38.6 kBq m^{-3}. Nonparametric linear regression analysis of radon (^{222}Rn) and thoron (^{220}Rn) concentrations in soil gas has showed a statistically significant positive correlation with the Spearman correlation coefficient R=0.81 (p=0.0003). The mean values and 95% LSD intervals of the concentration of radon and thoron in soil gas are presented on the figure 2.

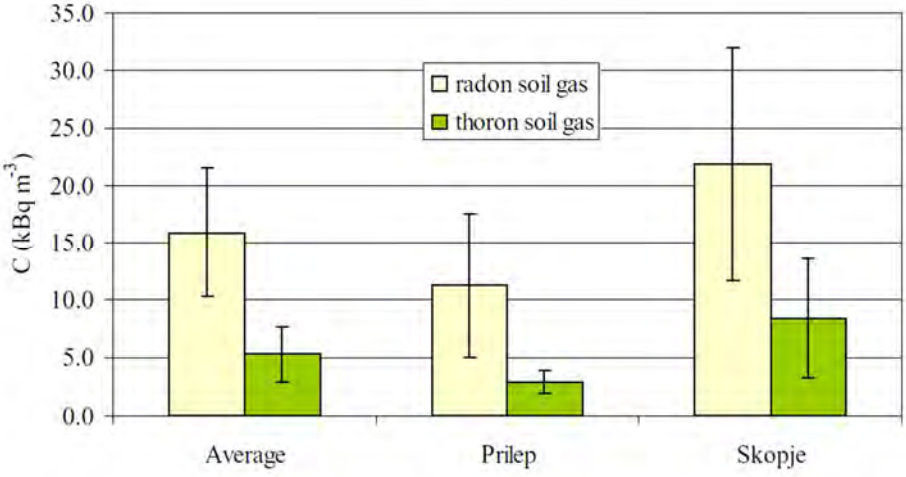

Fig. 2. Mean values and 95% LSD intervals of the radon and thoron concentration in soil gas

Furthermore the correlation between the ^{226}Ra content in the soil and the radon concentration in the soil gas were observed. There is no statistically significant

correlation between radon concentration in soil gas and activity concentrations of ^{226}Ra in soil (p=0.805). Correlation between thoron (^{220}Rn) concentration in soil gas and soil activity concentrations of ^{232}Th, as well as correlation between the indoor radon concentration of and radon concentration in soil gas were statistically insignificant.

5. SUMMARY

A limited number of measurements of radon and thoron soil gas concentrations in the soil gas in Skopje and Prilep led to conclusion that there is a correlation between radon and thoron concentrations in soil gas, as well as a correlation between activity concentrations of ^{40}K, ^{226}Ra and ^{232}Th in soil is confirmed. Possibilities for other correlations are not excluded. However, the number of the data points is too small to allow generalization of the last conclusion. These results can be utilised to set up the methodology for a more systematic investigation to radon concentration in the soil gas.

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