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**Measurements and analyses in Environmental  
sciences and Radioenvironmental sciences**  
**Applications of nuclear technologies**  
**Medium-term perspectives of energetic  
development in SR and EU**

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## **The VIIIth Banská Štiavnica Days 2006**



**Measurements and analyses in Environmental  
sciences and Radioenvironmental sciences  
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Medium-term perspectives of energetic development  
in SR and EU**

**Banská Štiavnica**  
(The FEE campus, Banská Štiavnica, Kolpašská 9B)  
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## RADON IN THE ATMOSPHERE IN TWO DIFFERENT LOCALITIES OF SLOVAKIA

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### ABSTRACT

Radon activity concentration in the atmosphere can vary more or less according to the locality of the measurement. In this paper there are compared radon activity concentration (RAC) and equilibrium equivalent concentration (EEC) obtained in two different localities of Slovakia (Bratislava and Jaslovské Bohunice, respectively). The localities are about 55 km apart from each other. Data analyses for 5 months of the year 2005 are presented. A surprisingly good agreement between the localities was found on the variations and mean values. These results imply that the turbulent mixing of air in the atmosphere of both localities is very similar. Various EEC/RAC ratios were found for different months, which might indicate a change in equilibrium factor  $F$  during the year. There was also found out that the mean daily courses observed in the two localities are slightly shifted apart. This is probably caused by different orography of the area where the measurement devices are installed and because of an earlier incidence of solar radiation on the measurement area in Jaslovské Bohunice.

**Key words:** radon, activity concentration, equilibrium equivalent concentration, comparison

### INTRODUCTION

Radioactive noble gas  $^{222}\text{Rn}$  (further on also simply called radon) is formed in soil in the process of radioactive decay of  $^{226}\text{Ra}$ .  $^{226}\text{Ra}$  is an alkaline earth metal that is a member of  $^{238}\text{U}$  decay chain. Part of radon is released in the atmosphere.  $^{222}\text{Rn}$  decays with a half-life of 3.8 day, its progenies fix rapidly on aerosol particles present in air. Turbulent diffusion is the main process affecting the transport of radon and its daughters in the troposphere. In addition to that, radon concentration profiles are influenced by the decay of radon and its progenies and in case of radon daughters by wet and dry removal of aerosols from the atmosphere. Radon concentration in the atmosphere is sensitive to the changes of meteorological factors and is therefore

considered a suitable indicator mainly of the vertical exchange processes in the atmosphere [1]. Radon activity concentration show distinctive daily and seasonal variations [2, 3]. Research and improvement of radon models contributes to the better understanding of radon behaviour in the atmosphere and also to the understanding of important aspects of atmospheric dynamics [4]. Knowledge about radon behaviour in the atmosphere is also needed for a more precise assessment of public radiation exposure from radon.

Radon concentration in the atmosphere can vary more or less according to the locality of the measurement as it follows from the above mentioned facts. The main aim of this research was to compare radon related activities in two different localities that are about 55 km apart from each other, and to collect new data for



validation of atmospheric transport models at regional level.

## METHODS

Radon related activities for monitoring and scientific purposes are being continually collected on two different sites, the output is a  $^{222}\text{Rn}$  activity concentration on one site and an equilibrium equivalent concentration of  $^{222}\text{Rn}$  on the other site. The equilibrium equivalent concentration (EEC) of  $^{222}\text{Rn}$  is the radon concentration, in equilibrium with its short-lived daughters, that has the same potential alpha energy per unit volume as exists in a sample mixture. Radon activity concentration (RAC) and EEC are related as follows:

$$C_{\text{eqv}} = C \cdot F,$$

where  $C_{\text{eqv}}$  and  $C$  are values of EEC and RAC, respectively and  $F$  is the equilibrium factor, the typical value of which is between 0,5 and 0,7 [5]. The EEC can also be expressed in the following manner:

$$C_{\text{eqv}} = 0.105 C_1 + 0.515 C_2 + 0.380 C_3,$$

where the symbols  $C_1$ ,  $C_2$ , and  $C_3$  represents the activity concentrations of the decay progeny,  $^{218}\text{Po}$ ,  $^{214}\text{Pb}$ , and  $^{214}\text{Bi}$ , respectively. The constants are the fractional contributions of each decay product to the total potential alpha energy from the decay of a unit activity in the gas. In this way, a measured radon activity concentration  $C$  can be converted to an equilibrium equivalent concentration  $C_{\text{eqv}}$  and conversely if the equilibrium factor  $F$  and activity concentrations of the decay products are known.

Measurement of  $^{222}\text{Rn}$  activity concentration was carried out in the campus of the Faculty of Mathematics, Physics and Informatics, Comenius University (FMPI CU) on a hill above Karlova Ves in Bratislava. The air sampling was conducted at a height of 1,5 m above the earth's surface. Measurement of EEC was realized in outdoor air on the grounds of a nuclear power plant in Jaslovské Bohunice. The sampling sites are about 55 km apart from each other.

On the FMPI CU campus a large volume scintillation chamber with a volume of 4.5 litres [6] was used for the measurement of radon activity concentration. In the Jaslovské Bohunice sampling site there was used a silicon detector for the measurement of the activity concentrations of  $^{218}\text{Po}$ ,  $^{214}\text{Pb}$ ,  $^{214}\text{Bi}$  and  $^{214}\text{Po}$  [7]. Both devices worked in a flow regime.

A great amount of data about RAC and EEC was collected at both localities. From the data collected on the FMPI UK campus the radon activity concentrations related to two-hour intervals were determined using Ward method [8]. Equilibrium equivalent concentrations of radon in Jaslovské Bohunice were measured at irregular, mostly 25–40 minutes intervals. For the purpose of the comparison of both localities it was necessary to determine EEC values for 2-hour intervals. For this reason the data were linearly interpolated and EEC values belonging to 5-minute intervals were calculated. We got a new data set from which we picked up a group of four values belonging to half-hour intervals (e.g. 2:30, 3:00, 3:30, 4:00); subsequently these values were averaged. The obtained value was then assumed to be the EEC value belonging to 2-hour interval. Calculations were realised by a macro created in Visual Basic programming language.

## RESULTS AND DISCUSSION

In this paper there are presented data for 5 months of the year 2005. They were chosen because we had the largest amount of RAC and EEC data in these months and because they cover the period of the whole year. In our analysis we only used the days in which RAC or EEC data are presented during the whole 24-hour period.

Smoothed time-courses of RAC and EEC for February, April, June, September and October are presented in Figure 1. One can quickly see that a surprisingly good agreement exists between the two localities despite the fact the localities are approximately 50 km apart from each other. The correlation coefficient for non-smoothed data ranges from 0,37 in October to 0,77 in February, with an average value of 0,55. If the data are smoothed the correlation coefficients improve even more, ranging from the lowest value of 0,47 in October to the highest one 0,85 in February, in average 0,65. The correlation coefficients for smoothed and non-smoothed data are shown in Table 1, examples of correlations are given in Figure 2.

A particularly good agreement between the two localities was recorded in February 2005. In the period from 4 to 12 February 2005 there were observed distinctive variations and high concentrations of radon with a maximum on February 12 (Bratislava –  $17.2 \text{ Bq}\cdot\text{m}^{-3}$ , Jaslovské Bohunice –  $9.6 \text{ Bq}\cdot\text{m}^{-3}$ ), yet on the next day, February 13, a steep decrease with weak variations of

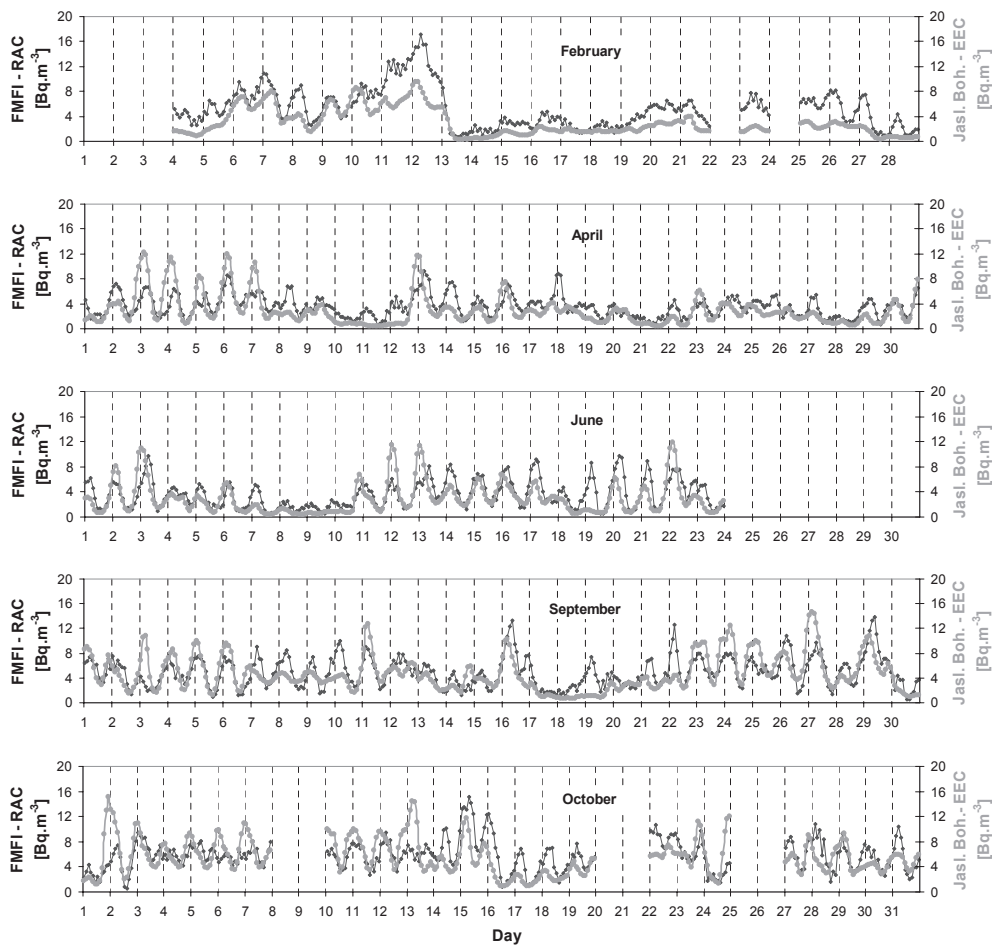


Fig. 1 Time-courses of  $^{222}\text{Rn}$  activity concentration (FMFI UK, Bratislava) and EEC (Jaslovské Bohunice) in various months of year 2005

Table 1. Correlation coefficients between EEC and RAC obtained in two localities of Slovakia for various months of the year 2005

Month	Correlation coefficient	
	non-smoothed data	smoothed data
February	0,77	0,85
April	0,51	0,64
June	0,56	0,66
September	0,52	0,64
October	0,37	0,47

radon concentration in both localities was observed. This situation lasted for about a week and after this period more distinct variations in both localities were observed once again. A good agreement on variations and mean values of RAC or EEC between the localities can also be seen in the other months of the year 2005.

One of the important findings of this research was that the ratio between EEC and RAC was not constant during the year. The ratio in autumn months was higher than that found in summer or spring. Similar dependency was also observed in [9]. Next, the mean monthly values of RAC were always higher than the

mean monthly values of EEC, yet in some days of the year 2005 the ratio was found to be opposite. Mean values and ratios are summarized in Table 2.

Mean daily courses of radon activity concentration and EEC are depicted in Figure 3. For better visual interpretation the data points were fitted by a curve, the parameters of which were determined by Fourier analysis in the Microcal Origin scientific application. Mean daily courses of RAC are always set higher than mean daily courses of EEC. The minima of the daily radon waves in February, April and June are more expanded in Jaslovské Bohunice than in Bratislava.

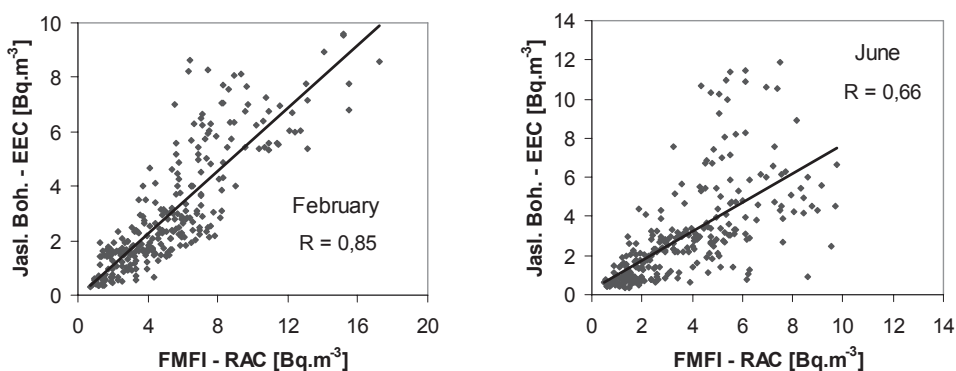


Fig. 2 Correlations between smoothed radon activity concentration (FMFI UK, Bratislava) and smoothed equilibrium equivalent concentration (Jaslovské Bohunice) in February and June 2005

Table 2. Mean values of activity concentration and equilibrium equivalent concentration for various months of the year 2005

Month	FMFI – RAC	Jasl. Boh. – EEC	EEC / RAC
	[Bq.m <sup>-3</sup> ]	[Bq.m <sup>-3</sup> ]	[ – ]
February	5,2	3,0	0,57
April	3,5	2,9	0,81
June	3,6	2,9	0,81
September	4,9	4,7	0,95
October	5,8	5,6	0,97

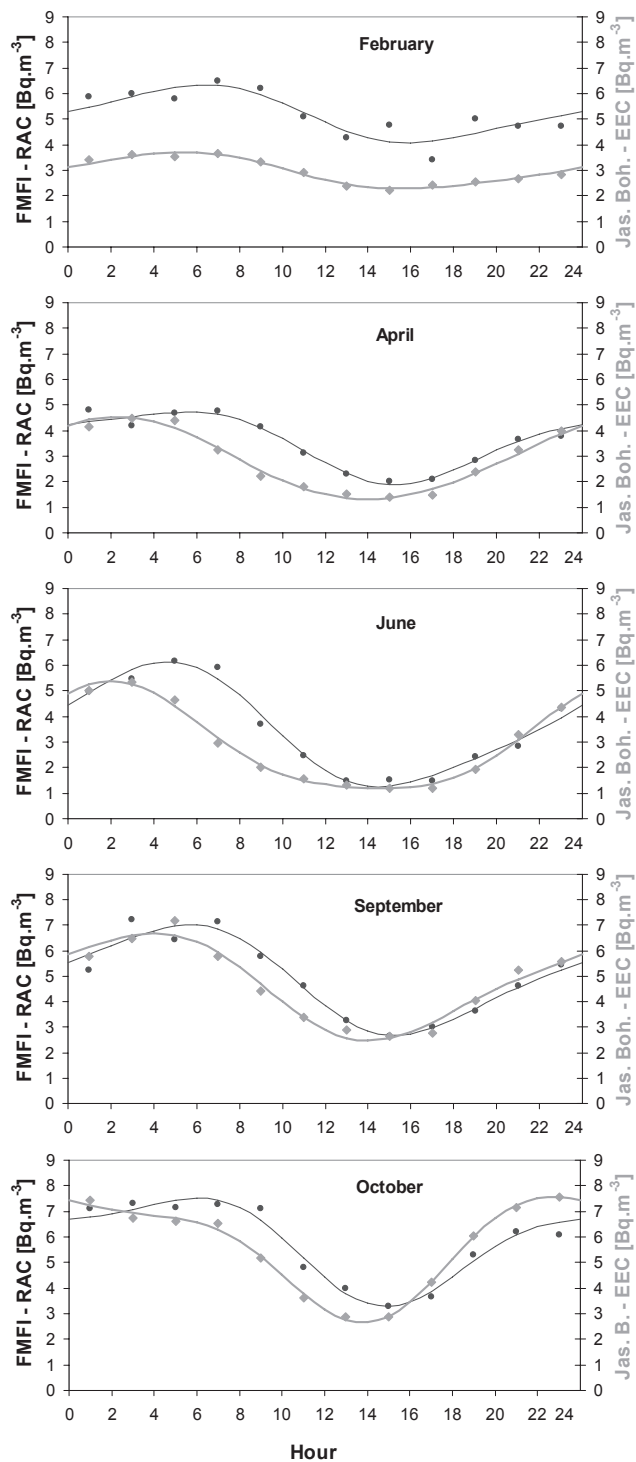


Fig. 3 Mean daily courses of <sup>222</sup>Rn activity concentration (FMFI UK, Bratislava) and EEC (Jaslovské Bohunice) in various months of year 2005

The amplitudes of mean daily courses of EEC are lowest in spring months and are along with the amplitudes of RAC recapitulated in Table 3. The results are in agreement with our previous measurements of radon in Bratislava air [10].

se of year. This might indicate a change of equilibrium factor F during the year, which is in agreement with our previous measurements [9, 11].

A slight, approximately 2-hour shift of data was found. This effect is probably caused by different

Table 3. Amplitudes of mean daily courses of activity concentration and equilibrium equivalent concentration for various months of the year 2005

Month	FMFI	Jasl. Boh.
	[Bq.m <sup>-3</sup> ]	[Bq.m <sup>-3</sup> ]
February	1,1	0,7
April	1,4	1,6
June	2,4	2,0
September	2,2	2,1
October	2,1	2,4

Table 4. Correlation coefficients between EEC and RAC obtained in two localities of Slovakia without shift and with 2-hour shift of data for various months of the year 2005

Month	Correlation coefficient			
	non-smoothed data		smoothed data	
	no shift	2-hour shift	no shift	2-hour shift
February	0,77	0,76	0,85	0,85
April	0,51	0,57	0,64	0,69
June	0,56	0,61	0,66	0,71
September	0,52	0,51	0,64	0,65
October	0,37	0,42	0,47	0,52

We can see from Figure 3 that the mean daily courses observed in the two localities are slightly shifted apart. This shift is particularly clearly visible in April, June, September and October. After a 2-hour shift of data we often observe an improvement of the correlation coefficients. The correlation coefficients for non-smoothed and smoothed data as well are listed in Table 4.

## CONCLUSION

A large amount of data about radon concentration were obtained in both localities. A surprisingly good agreement on the variations and mean values of RAC and EEC exists between the localities despite the fact the localities are approximately 50 km apart from each other. The agreement is confirmed by high values of correlation coefficients between the localities. These results imply that the turbulent mixing of air in the atmosphere of the localities is very similar. It was also found that the EEC/RAC ratio varies during the cour-

ography of the area where the measurement devices are installed and because of an earlier incidence of solar radiation on the measurement area in Jaslovské Bohunice [12]. The obtained data will be used for interpretations of <sup>14</sup>C measurements in both localities.

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## AN ENERGETIC ANALYSIS OF BIOMASS'S MATERIAL ELEMENTS

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### ABSTRACT

Energetic rate (content of combustion) of tree resin is so high, that the energetic rate of a spruce is  $38\,500\text{ J}\cdot\text{g}^{-1}$  and of a pine is  $38\,900\text{ J}\cdot\text{g}^{-1}$ . Differences between particular wood-pulps are irrelevant. An amount of macroergic substances in biomass can affect its energetic rate and production significantly.

Tree resin almost has a double higher energetic rate in comparison with content of wood's combustion without an expectation of a wood-pulp and it approaches refined hydrocarbon fuels.

**Key words:** energetic analysis, biomass, resin

### INTRODUCTION

New opinions on utilizing of energetic potentials changed energetic conceptions in regional and also international rank.

Recently the views of renewable energetic resources, especially the energetic valuation of biomass have been changed. Energetic valuation of biomass becomes a reality like a price of primary energy increases dramatically.

At the present times the research of biomass's energetic utilization is oriented at the technological mastering of biomass's energetic utilization and at the production quantity of biomass, too. Sometimes the qualitative side of energetic biomass is unnoticed.

An orientation of the research has to head to a quantity production as well as to a quality of energetic biomass to reach high biomass production with the highest energetic value of biomass. It further premarks an orientation for knowledge about production to reach maximal biomass production expressed in energetic measures.

Cellulose and lignin are standard substances of vegetal biomass. Biomass contains other substances, for example the macroergic substances (for instance tree resin), which are contained in biomass in miscella-

nous rates and they can significantly influence energetic level of biomass. Tree resin belongs between these macroergic substances and its volume can have an important influence of a biomass energetic level.

From physiological side the resins can be characterized as the excrets, the final products of the dissimilation reactions. These reactions are not split, because their energetic level is often very high.

From energetic side we the resins are considered as macroergic substances with high energetic content.

Resins originate from special tissues – resin canals in a similar way like essences. Physiological resin originates from metabolic activity. In trees pathological resin often originates as a consequence of wound.

From chemical point of view the resins are aromatic compounds of terpene character. In particular sorts of woods content and composition of resin depends on biochemical taxon of particular woods. The resins are made by two main groups of substances. The first group is derived from phenylpropane and the second group of substances is derived from terpene substances.

Resins don't dissolve in water, but they dissolve in organic solvents. Resins are not chemical individuals, but they are complicated mixtures of substances, that are compounded from carbon and oxygen. They are made in wood tissues.



BLAŽEJ and KOŠÍK (1985) state that the considerable differences of resin are not only between different woods, but also between woods of the same class. There is also a difference between compound of the physiological tree resin, which is found on healthy tree and the resin, which oozes after wound from injured bark. Pathologic resin comprises from terpenes and resin acids and it doesn't contain fats.

In different woods the resin content is assessed by value of alcohol-benzene or ethereal extract [1].

Chemical compound of resin is well-known and published in literature, but data about energetic analysis of resin as a macroergic substance absent. SIMANOV (4) marginally mentions energetic value of resin, but he doesn't inform about concrete rates and he only states that tree resin has higher heating capacity than wood.

Significance of energetic analysis of biomass components (in this case resin) hasn't importance only in an inquiry of information about reality. For high resin content in some woods and for high energetic level of resin there are chosen chemobiotaxons, which secure the highest energetic production of biomass already in a phase of a foundation of energetic plantations

## MATERIAL AND METHODS

As a fuel biomass is characterized by content of combustion and heating capacity. Content of combustion is heat, that comes up by complete burning of a weight unit of fuel including liquefied water vapor for water, whereby temperature of flues is 20,5°C after cooling down. The heat with upper heating capacity point is not used in an utilizing warmth from flues, because the condensation of water vapor is not be allowed in fuming gasses in a combustion equipment.

Combustion heat of analysed samples was detected by calorimeter, in which there can be burned solid, crystalline and squeezed samples.

Combustion heat was inquired on resin from spruce (*Picea abies* L.) and pine (*Pinus silvestris* L.). Resin was acquired by an exploitation of resin, a cutting, so we can characterize it as a pathologic resin. The trees were 30–40 years old. A thickness of tree was in  $d_{1,3}$  m 18–22 centimeters. Resin was acquired in the second half of summer.

The research was executed for 40 samples: for every wood there were inquired 20 samples. A number of samples was calculated as a minimal size of a file for parameter estimation – an arithmetic average of the

basic file with 95% reliability and 1% error.

## RESULTS

Combustion heat of spruce and pine is high. We can assort resin from spruce and spine to the macroergic substances: tree resin is probably substance with the highest content of energy in woods and plants. Adjusted value of combustion heat of pine is 38 900 J.g<sup>-1</sup> and of spruce is 38 500 J.g<sup>-1</sup> in an arithmetic average. Established differences between combustion heat of particular woods, pine and spruce are not significant.

Tree resin has almost double higher energetic value in a comparison with combustion heat of wood without difference, that is from 18,0 to 20,0 kJ.g<sup>-1</sup> [2,3,4] and it approaches refined hydrocarbon fuels. Established maximum values reach energetic value of heavy fuel oil, petrol and naphta. Another fossil fuels like black coal and coke reach energetic level of resin in the range 60–70% and brown coal in the range 30–35%.

Statistical distribution of combustion heat values doesn't noticeably differ from normal distribution and it is mildly levorotary.

As generally the biggest obstacle for wide using of biogenic fuels (particularly biomass) is considered its low energetic value. But this opinion doesn't stand up, because energetic value of wood is in general higher than brown coal, whereby particular substances and components of biogenic fuels are especially energetically abundant.

## DISCUSSION AND SUMMARY

With regard to world energetic trend it is justified to assume that importance of wood and other biomass as an energetic bearer will accrue because of economic, energetic and ecologic reasons. For European Union it is a very big challenge to fulfill its pledges of covering part of its energetic needs by biomass. An accomplishment of these promises is exceptionally difficult and long-termed.

In the present practice energetic measures come to the fore instead of volume or weight measures that pertinently enumerate quantity of produced biomass. Energetic value of biomass is qualitatively higher comparative equivalent whose importance permanently increases with a connection to biological and ecological sciences' development. By the weight and energetic measures we can compare production and productivity

of varied ecosystems (for instance agroecosystems, forest ecosystems, meadows or energetic agricultural and forest plantations).

Tree resin as a biomass substance probably won't play the role in an energetic utilizing, but its energetic importance is in complex content of combustible substances in biomass. Some woods have high content of resin in wood, for instance some northern woods have three times more resin than woods from southern regions.

From the said new questions arise for genetics, a topcross and a cultivation with precondition to secure such biological material which will have high energetic production. One way could be seeking and creating taxons which will have high content of macroergic substances apart from high weight production, thereby high energetic production of biomass will be adjusted.

Constant increasing of primary raw materials' consumption with parallel reduction their supplies lead to continual increasing their price and to the risk of the

lasting shortage and unattainableness. It opens a way for wide using of biomass as a renewable energetic carrier without an environmental deterioration, with a high using of solar radiation. The energetic using of biomass can be an important tool for a development especially country regions.

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## TOXICITY AND BIODEGRADATION OF PCBs IN CONTAMINATED SEDIMENTS

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### ABSTRACT

PCBs represent a serious ecological problem due to their low degradability, high toxicity, and strong bioaccumulation. Because of many environmental and economical problems, there are efforts to develop bioremediation technologies for decontamination of the PCB-polluted areas. In the locality of the former producer of PCB – Chemko Strážske a. s. – big amount of these substances is still persisting in sediments and soil. The goal of this study was to analyze the contaminated sediments from Strážsky canal and Zemplínska šírava water reservoir from several points of view. The study of ecotoxicity confirmed that both sediments were toxic for various tested organisms. The genotoxicity test has not proved the mutagenic effect. The subsequent step included microbiological analysis of the contaminated sediments and isolation of pure bacterial cultures capable of degrading PCBs. In order to determine the genetic potential for their biodegradability, the gene *bphA1* was identified using PCR technique in their genomes. This gene codes the enzyme biphenyldioxygenase, which is responsible for PCB degradation. The final goal was to perform aerobic biodegradation of PCBs in the sediments. The bacteria present in both sediments are able to degrade certain low chlorinated congeners. The issue of biodiversity is still open and has to be studied to reveal the real cooperation between bacteria.

**Key words:** biodegradation, contaminated sediments, polychlorinated biphenyls, PCBs, toxicity

### INTRODUCTION

Polychlorinated biphenyls (PCBs) are highly persistent pollutants that have been produced on the large scale in the past decades. The production was stopped after they had been proven to be toxic to humans. Once in the environment, PCBs tend to accumulate in different stages of the food chain and along with being toxic, they are also carcinogenic [1]. Environmental and economic reasons have urged the development of bioremediation technologies for the PCB removal from contaminated sites. A crucial step is the isolation or genetic

construction of microbial strains with biodegradation potential. Several aerobic microorganisms are able to biodegrade certain, usually less chlorinated, PCB congeners [2–5]. Although the complete PCB degradation is the ultimate goal, often only partial solutions of this complex problem can be reached resulting in elimination of the most harmful properties [6]. For PCBs, the top priority is to lower their bioaccumulation potential or, equivalently, their lipophilicity. In the aerobic biodegradation process, dioxygenases introduce hydroxyl groups into the PCB molecule, decreasing its lipophilicity and making the later cleavage easier [7]. The initial

oxidation and subsequent ring cleavage seem to be the rate-limiting steps of the process. In our recent publications, a simple apparatus for effective monitoring of the PCB evaporation kinetics in batch biodegradation experiments was described [8, 9] together with a simple mathematical model [10] that takes evaporation and biodegradation into account.

Slovakia is one of the countries where production of PCBs took place in the past. PCBs have been produced at the factory Chemko Strážske. Slovakia belonged to the eight largest world producers of commercial mixtures of PCBs. Through Regional Centre of UNDP, Slovakia has obtained a GEF grant to support implementation of the Stockholm Convention commitments and to elaborate the NIP within the project "Initial assistance to the Slovakia to meet its obligations under the Stockholm Convention on Persistent Organic Pollutants (POPs)". The production of PCBs was approximately 21,500 tons. About 46 % of the PCB production was exported mainly to the former East Germany. The rest (11,613 t) was used in former Czechoslovakia in dielectric fluids for transformers and power capacitors, as heat exchanger and hydraulic fluids, and as paint additives and lubricants. PCBs from damaged devices can easily enter the environment. At present, the use of PCBs in open systems is not allowed, however, in closed systems such as transformers and capacitors, they still can be used. Basing on extensive inventories, which were carried out in the years 2000–2002, current existence of about 3,500 tons of PCBs may be assumed in the territory of Slovakia [11].

Contamination at the factory Chemko Strážske surroundings belongs to the so-called "old environmental burdens". It can be considered as a hot spot and poses a serious problem in Slovakia. Contaminated areas are found inside the factory area well as in wider surroundings. The contamination is primarily spread through surface water by gradual release from contaminated sediments of an open sewer (effluent canal) that leads from the factory to Laborec River, and subsequently through the filling canal contaminates Zemplínska šírava water reservoir. This contamination resulted in increased values of PCB content in monitored components of environment as well as in the population of this district, comparing with the other parts of Slovakia. PCB concentrations in industrial canal fluctuate from grams to tens of grams of PCBs per kg of sediment dry weight, in some places in Laborec at hundreds of milligrams and in sediment of Zemplínska šírava in milligrams. Complex monitoring of PCB

contamination in the area surrounding a former production site has not yet been carried. Only partial data are available. For this reason, it is not possible to estimate exactly the amount of contaminated sediment and soils. Initial approximation assumes that at least 40,000 tons of PCBs are still adsorbed in the sediments of the effluent canal, Laborec River and Zemplínska šírava water reservoir. This sediment is an abundant PCB source causing the long-term contamination of the waters of Eastern Slovakia. As expected, the highest value of PCBs was found in a muddy part of the effluent canal flowing from the Chemko factory containing about 3–5 kg PCBs in 1 ton of dry mud. It is doubtless that the polluted effluent canal flowing into the Laborec River has caused the contamination. The Zemplínska šírava water reservoir that is partly filled from the Laborec River contains several hundred times higher PCB levels (100–2000 times) in comparison to a similar water reservoir (Domaša) in the background area (1.7 to 3.1 mg/kg compared to 0.007–0.01 mg/kg). PCBs determined in soil samples collected from the vicinity of the waste disposal sites of Chemko contained PCB levels much higher than those found in agricultural and forest soils. It should be stressed that, in general, PCB levels in Slovak human population are higher than those in other countries (with the exception of Czech Republic). Sediments from the area of former PCB production in Slovakia show high values even 21 years after the termination of the production – up to 4.1 mg.kg<sup>-1</sup> (on average, 0.3 mg.kg<sup>-1</sup>). PCB contents of the sediments from water bodies from other areas of Slovakia range between 0.01–2.8 mg.kg<sup>-1</sup> [12]. PCBs accumulated in sediments are only slowly mobilized into water. This situation will last probably until the start of remediation. Since estimated tens of tons of PCBs are adsorbed in the sediment of these water reservoirs, a flood, for example, might cause an ecological disaster. A possible solution involves the detailed examination of an extent of the pollution of the water reservoir, the removal of the contaminated sediment, and the decomposition or retrieval of PCBs by a suitable technology, e.g. incineration, thermal desorption, chemical dehalogenation, solvent extraction, or bioremediation.

The goals of the present work were: (1) to study toxicity and ecotoxicity of PCB-contaminated sediments from Strážsky canal and Zemplínska šírava water reservoir; (2) to isolate the microorganisms with degradative ability; and (3) to perform biodegradation of PCBs in natural and bioaugmented sediments.

## MATERIALS AND METHODS

### Chemicals

The following reagents were used: agarose (Bio-Rad, USA), bacteriological agar (Oxoid, UK), biphenyl (Sigma-Aldrich, USA), dibenzofuran (Sigma-Aldrich, USA), diethyl pyrocarbonate (Sigma-Aldrich, USA), DNA markers (Promega, USA), 100 bp ladder, 1 kb ladder, DNA polymerase (Finzymes, FI), ethidium bromide (Fluka, Germany), n-hexane (Chromservis, Czech Republic), IRS solution (Mo Bio Laboratories, USA), Luria-Bertani (LB) medium (Oxoid, UK), Plate Count Agar (PCA) (Oxoid, UK), primers (Biotech, Czech Republic), pyrophosphate (Sigma-Aldrich, USA), reaction buffer solution for DNA polymerase (Finzymes, FI), Trisma base (Lachema, Czech Republic), mixture of nucleotides (Promega, USA).

### Biological material and the environmental samples

Bacterial strains used were *Burkholderia* sp. LB400 (*bph* operon) [13, 14]; and the isolates from sediments. Sediments were sampled from Zemplínska šírava (ZŠ) and Strážský canal (Sk) according to the established protocol.

### Cultivation media

*LB medium*: 25 g LB in 1 l distilled water and 15 g.l<sup>-1</sup> of bacteriological agar.

*Minimal liquid medium (MM)*: 1 g (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>; 2.7 g KH<sub>2</sub>PO<sub>4</sub>; 10.95 g Na<sub>2</sub>HPO<sub>4</sub>·12H<sub>2</sub>O filled with distilled water to 1 l. After sterilization of the solution, salts containing particular trace elements sterilized by filtration were added: 250 µl FeSO<sub>4</sub>·7 H<sub>2</sub>O (2 g.l<sup>-1</sup>); 250 µl, Ca (NO<sub>3</sub>)<sub>2</sub>·4 H<sub>2</sub>O (6 g.l<sup>-1</sup>); and 250 µl MgSO<sub>4</sub>·7 H<sub>2</sub>O (40 g.l<sup>-1</sup>), each in 50 ml of the prepared medium.

*Minimal solid medium*: 5.37 g Na<sub>2</sub>HPO<sub>4</sub>·12 H<sub>2</sub>O; 1.30 g KH<sub>2</sub>PO<sub>4</sub>; 0.50 g NH<sub>4</sub>Cl; and 0.20 g MgSO<sub>4</sub>·7 H<sub>2</sub>O filled with distilled water to 1 l. To congelate the medium, 15 g.l<sup>-1</sup> of agar was added (Nobel Agar, Difco, UK).

*Plate Count Agar (PCA)*: 23.5 g PCA in 1 l of distilled water (the guide of Oxoid Company, UK).

*Phosphate buffer (pH 7.4)*: A: 13.8 g NaH<sub>2</sub>PO<sub>4</sub>·H<sub>2</sub>O filled with distilled water to 500 ml; B: 14.2 g Na<sub>2</sub>HPO<sub>4</sub> filled with distilled water to 500 ml. 60 ml of solution A and 440 ml of solution B were mixed;

*TBE buffer (pH 8.0)*: stock solution – 10 × concentrated: 54 g Tris, 27.5 g boric acid; 3.72 g EDTA, filled with distilled water to 1 l.

### Commercial sets

Nefermtest 24 – Lachema, Czech Republic (a biochemical test for identification of the strains of Gram-

-negative non-fermentative bacteria); QIAamp DNA Mini Kit – Qiagen, USA (a set for isolation of the total DNA from pure culture); UltraClean Soil DNA Isolation Kit – Mo Bio Laboratories, USA (a set for isolation of microbial DNA from soil).

### Determination of the inhibition effect

Specific inhibitory effects of PCBs on the bioluminescence of intact cells of the standard bacteria *Vibrio fischeri* NRRL-B-11177 were measured with the LumisTox method by using a luminometer Biocounter LUMAC 1500 (Perstorp, Netherlands). Toxicity was expressed as ID<sub>50</sub> value after 15 min incubation of bacteria in the presence of toxicant. To evaluate ecotoxicity, the criteria listed in Table 1 were used.

### Isolation of microorganisms from sediments

A mixture of 10 g sediment, 250 mg biphenyl, and 100 ml liquid mineral media was cultivated at 28 °C for 7 days. To determine the total number of microorganisms, solid LB medium was used. For isolation of potential degraders of biphenyl, mineral medium with Nobel agar was used. Microbial strains were cultivated in the presence of 250 mg of biphenyl placed in the cover of the Petri dish.

### Screening of the presence of 2,3-dioxygenase in the microorganisms

Microorganisms isolated from sediment were inoculated into solid minimal medium. Biphenyl and dibenzofuran were sprinkled on the cover of the Petri dish. Dibenzofuran, a substance structurally similar to PCB, is split by the enzyme dioxygenase to yield a so-called meta-cleavage product having yellow color. In this way, it is possible to detect bacteria producing dioxygenase, which indicates their potential to degrade PCBs [15].

Classification of microorganisms using Nefermtest24

The commercial set Nefermtest 24 is assigned for identification of Gram-negative non-fermentative bacteria. A bacterial culture cultivated on Plate Count Agar for 24 h at 28 °C was used. The procedure followed the guide for the use of the commercial set Nefermtest 24. The principle of this method lies in detection of the biochemical reactions of the tested strains with different substrates. To a specified dehydrated substrate, a suspension of the tested strain was added and after 48 h individual reactions were evaluated on the basis of a color reaction, and the particular strain was identified.

### Isolation of the bacterial DNA

Bacterial DNA of Gram-negative bacteria was

isolated by thermolysis. For isolation, a culture from solid media was used and incubated in 50 µl sterile distilled water for 10 min at 95 °C in a thermoblock. After thermolysis, the mixture was mixed and centrifuged at 1300 rpm. Sediment contains the obtained bacterial DNA.

#### **Amplification of the specific segments of DNA using PCR**

For detection and amplification of the genes of bacterial DNA, PCR method was used. Composition of the mixture: 34.5 µl sterile deionized water, 5 µl of polymerase buffer Finzymes, 1 µl dNTP (10 mM), 2 × 1 µl of primers, 2 µl BSA, 0.5 µl of polymerase Finzymes, 5 µl of DNA sample. 16s rDNA was isolated from the strain, in which the presence of the gene *bphA1* was demonstrated. By sequencing 16s rDNA it was possible to classify the unknown strains on the basis of the sequence of nucleotides in the amplified segment terminated by the primers F38GC and R518. DNA was stored at – 20 °C.

#### **Detection of the PCR products by gel electrophoresis**

The method was used for identification and detection of the fragments of DNA. The suitable concentration of the agarose gel was used: from 1 % (for fragments with number of bp higher than 100) to up 1.5 % (for fragments with number of bp below 100). Agarose gel was prepared by dissolving agarose in TBE buffer. Ethidium bromide was added into a gel for visualization of the DNA fragments (1 % solution) at a concentration 1 µl in 30 ml of gel. Before dabbing, 5 µl DNA was mixed with 2.5 µl of dab solution Blue/Orange 6×. The complex of DNA with ethidium bromide was visualized by UV radiation. Electrophoresis separation of the PCR products was performed at 120 V. To determine fragment size, a marker of 100 bp standard DNA was used [16].

#### **Biodegradation of PCBs in the natural sediments**

To assess aerobic biodegradation of PCBs present in contaminated sediments from Strážsky canal and Zemplínska šírava without additional bioaugmentation of natural isolated microorganisms, 10 g of sediments, 250 mg of biphenyl, and 50 ml of liquid minimal medium were added. Biodegradation was carried out for 14 days at 130 rpm and 28 °C. Negative control represents chemically sterilized sediment with 10 µl of diethyl pyrocarbonate in 10 ml sample.

#### **Biodegradation of PCBs in the sediments amended with the isolated microbial consortium**

Isolated microbial consortium from sediment was inoculated in 20 ml liquid minimal medium with biphenyl as the structure analogue of PCBs and incubated 48 h at 28 °C. To evaluate aerobic biodegradation of PCBs present in contaminated sediments from Strážsky canal and Zemplínska šírava with additional bioaugmentation of natural isolated microorganisms, 10 g of sediments, 250 mg of biphenyl, 5 ml of microbial consortia of 48 hour inoculum were used in the 45 ml of liquid minimal medium. Biodegradation was carried out for 14 days at 130 rpm and 28 °C.

#### **Determination of PCBs**

After biodegradation, the samples were extracted by n-hexane and measured by GC ECD (HP 5890). PCB indicator congeners recommended by EPA (Environmental Protection Agency) (US EPA Methods 8089/8081) were evaluated (IUPAC numbers 28, 52, 101, 138, 153, and 180). Quantitative evaluation of the results was performed on the basis of comparison of peak areas of the indicator congeners in the chromatogram of the sample and of the standard.

## **RESULTS**

#### **Determination of inhibition effect of the sediments**

The sediments from Zemplínska šírava water reservoir and Strážsky canal were sampled according to the protocol. Detected PCB concentrations are presented in Table 2. Toxicity of water and isopropyl alcohol extracts of sediments was determined using bacterial strain *Vibrio fischeri*. As can be seen from Figure 1, extracts of both sediments inhibited bioluminescence. The toxicity of isopropyl alcohol extracts was higher than of those of the water ones. It was caused probably by the compounds soluble in a non-polar solvent, which include also PCBs. The contact test of toxicity described in our previous work showed inhibitory effect of both sediments on growth of *Lactuca sativa* roots. Mutagenicity is a very important property of the environmental contaminants, which may complicate the use of the biological systems for decontamination. The extracts of both sediments were assessed by Ames test. The genotoxic effect of the sediments was not confirmed [17].

#### **The presence of biphenyldioxygenase in the isolated microbial consortium**

Microorganisms that grow on the minimal medium with biphenyl as the sole carbon source were



isolated from the samples of the sediments. Biphenyl is an inducer of the biphenyl operon and its presence causes induction of the so-called PCB “upper” degradation pathway. Microorganisms isolated by this procedure are potential degraders of PCBs. Along with detection of the bacterial growth on biphenyl there are many other screening methods, which enable to confirm the presence of biphenyldioxygenase – the first and one of the most important enzymes of the biodegradation pathway of PCBs. One of these pathways is the splitting of dibenzofuran. Dibenzofuran, a substance structurally similar to PCB, is split by the enzyme dioxygenase to yield a so-called meta-cleavage product having yellow color. In this way, it is possible to detect bacteria producing dioxygenase, which indicates their potential to degrade PCBs. On the basis of this screening, we have continued in the isolation of the pure strains, which were subsequently submitted to genetic analysis for the presence of the *bphA1* gene.

#### PCR – amplification of *bphA1* gene

A method of identification of the presence of a particular gene in the microbial cell is based on the use of the polymerase chain reaction and the knowledge of the sequence of the primers, short sequences of DNA, which enable replication of a particular gene and its amplification. We have based on the information that biphenyldioxygenase determines the specificity of PCB cleavage [18] and that being the first enzyme of the biphenyl pathway, it is the most suitable enzyme as an example of the genes of the biphenyl operon.

At amplification, the primers R350 a R674, that were previously defined and verified [19], were used. The results of amplification and identification of the *bphA1* gene are presented in the figures illustrating the gel electrophoresis. In the Figure 2, the gene for the total DNA is shown, which was isolated from the both sediments (Zš and Sk). The results indicate that in the microflora of the sediments the bacterial strains are present, which may express this gene. Figure 3 depicts the detected bands of *bphA1* gene for selected strains isolated from the both sediments. The used marker served for the detection of the number of the base-pairs of the detected product of PCR.

#### Classification of the bacterial strains with identified *bphA1* gene

The bacterial strains with the identified *bphA1* gene were detected using Gram method. All isolates were Gram-negative. The characterization of the strains was continued using the commercial Nefermtest 24

for detection of non-fermentative bacteria. Positive and negative results obtained with the tested substrates are listed in Table 3.

#### Aerobic degradation of PCBs in sediments

The mixture of the assessment of aerobic degradation of PCBs present in the sediments involves 10 g of the contaminated sediment, 50 ml of minimal mineral medium, and 250 mg of the biphenyl as the inducer of biphenyl and PCB pathways. To evaluate the experiments, an indicator standard (a mixture of six PCB congeners: 28, 52, 101, 138, 153, and 180) was used [20].

A decrease of the individual PCB congeners after 14 day aerobic biodegradation is presented in Figures 4 and 5. The results of the biodegradation processes were detached to control (sterile sediment without microorganisms), which represented abiotic transformation of PCB congeners. Figure 6 shows that in the sediments from Strážsky canal higher decrease of the PCB congeners were observed than in the sediments from Zemplínska šírava. In the sediments from Strážsky canal, the PCB congeners 28 (40 %), 138 (31%) and 180 (30%) were the most degraded congeners, while in the sediments from Zemplínska šírava it were the PCB congeners 28 (14 %) and 153 (13 %).

#### Aerobic degradation of PCBs in the sediments amended with the isolated microbial consortia

In this experiment, a 48 h inoculum of the microbial consortium obtained with from the particular sediment was added to the biodegradation system. The 14 day biodegradation of PCBs in the sediment with addition of the microbial consortium resulted only in a decrease of the amount of the PCB congener 28 from 20.38 to 2.41 mg kg<sup>-1</sup> of the sediment from Strážsky canal and from 3.18 to 2.72 mg kg<sup>-1</sup> of the sediment from Zemplínska šírava. The amount of all other studied PCB congeners increased. It is possible that the presence of the higher amount of microorganisms caused increased production of the biosurfactants and subsequently the release of sequestered PCBs from sediment structures. This probably caused the increase of PCB content in comparison with their initial amount. This fact requires an additional detailed study.

## DISCUSSION

The goal of the present study was to analyze the real samples of contaminated sediments from Strážsky canal and Zemplínska šírava water reservoir from several points of view. Both sediments are contaminated



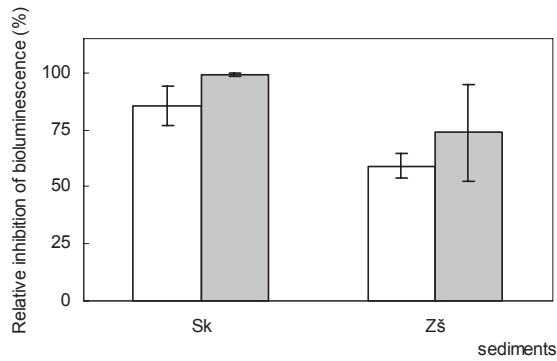
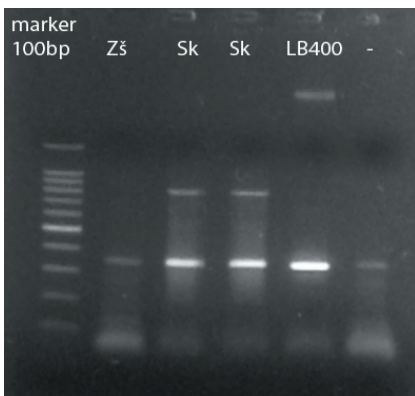
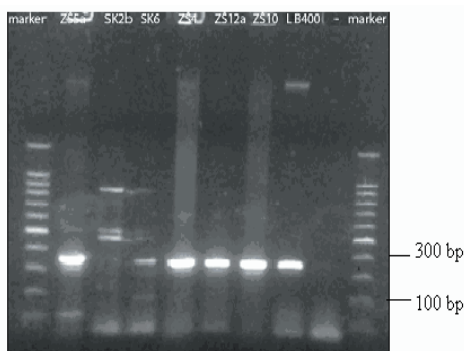


Fig. 1 Inhibition effect of the sediments from Zemplínska šírava (Zš) and Strážsky canal (Sk) on bioluminescence of *Vibrio fischeri*. □ water extract ■ isopropyl alcohol extract



Gel description	<i>bphA1</i> gene
Lane 1 marker100 bp	
Lane 2 Zš sediment	yes
Lane 3 Sk sediment	yes
Lane 4 Sk sediment	yes
Lane 5 LB 400	yes
Lane 6 negative control	no

Fig. 2 Gel electrophoretic proof (1.5 % gel) of the presence of *bphA1* gene in the mixed DNA isolated from both sediments, Sk and Zš



Gel description	<i>bphA1</i> gene
Lane 1 marker 100 bp	
Lane 2 Zš 5a	yes
Lane 3 Sk 2b	no
Lane 4 Sk 6	yes
Lane 5 Zš 4	yes
Lane 6 Zš 12a	yes
Lane 7 Zš 10	yes
Lane 8 LB400	yes
Lane 9 negative control	
Lane 10 marker 100 bp	

Fig. 3 Gel electrophoretic proof (1.5 % gel) of the presence of *bphA1* gene in the microbial DNA isolated from the sediments Sk and Zš

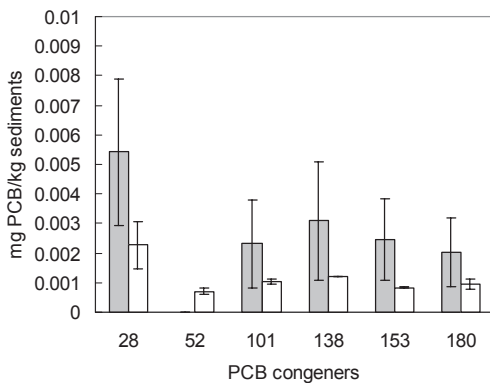


Fig. 4 Comparison of PCB concentrations in the sediments from Zemplínska šírava after 0  and 14  days of degradation

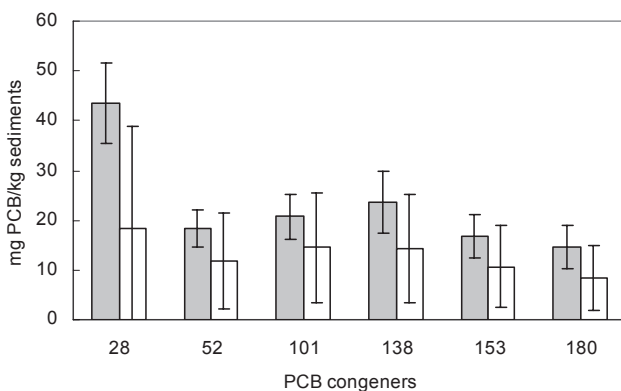


Fig. 5 Comparison of PCB concentrations in the sediments from Strážsky canal after 0  and 14 days  of degradation

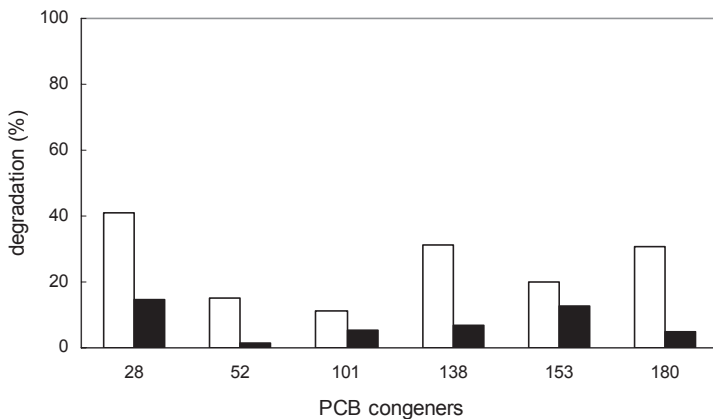


Fig. 6 Comparison of the results of 14-day biodegradation of the indicator PCB congeners in the sediments from Strážsky canal and Zemplínska šírava without amendment with the isolated natural microbial consortium. Strážsky canal  Zemplínska šírava

Tab. 1 Criteria for evaluation of ecotoxicity using assessment of an inhibition effect on the bioluminescence of the standard bacteria *Vibrio fischeri*

Relative inhibition H (%)	Ecotoxicity
0–5	Non-toxic sample
5–20	Potentially toxic sample
> 20	Toxic sample

Tab. 2 Concentration of selected PCB congeners in the sediments from Strážsky canal (Sk) and Zemplínska šírava (Zš) before degradation

PCB congener	Sk	Zš
	(mg.kg <sup>-1</sup> )	(µg.l <sup>-1</sup> )
8	81.1	208.3
28	124.5	187.8
52	40	26.3
101	55.3	29.1
118	58.1	44.3
138	40.6	19.2
153	50.2	22.5
180	209	< 2.5
203	15.1	6.9

Tab. 3 The microorganisms isolated from sediments of Zemplínska šírava and Strážsky canal

Sediment	Microorganism (Nefermtest 24)
Zemplínska šírava	<i>Pseudomonas fluorescens</i> <i>Ochrobacterum anthropi</i> <i>Pseudomonas aeruginosa</i>
Strážsky canal	<i>Agrobacterium radiobacter</i>

with PCBs and therefore were chosen for aerobic degradation by an indigenous microbial consortium and were also used as a source for isolation of bacterial strains with a potential to degrade PCBs.

Toxicity of sediments depends on their physico-chemical properties (dilution in water, evaporation, polarity). These properties influence adsorption of PCBs on sediment particles or their arrangement in particular phase (water, solid matrix, air). The sensitivity of tests in water solution is very low especially for organic compounds with low solubility in water [21]. At the beginning, the ecotoxicity and genotoxicity of water and isopropyl alcohol extracts of the sediments were studied. The results confirmed that both sediments, mainly their isopropyl alcohol extracts were toxic for various tested organisms. Chemical analysis alone is

not sufficient for determination of the environmental risk. Sometimes, the byproducts are more toxic than the initial compound. Lovecká et al. [22] and Vrana et al. [23] proved higher toxicity of chlorobenzoic acids, which are bacterial degradation products of PCBs produced by the higher degradation pathway. Tests with water solutions did not render unambiguous results due to the hydrophobic character of some toxic compounds, e.g. PCBs [24]. A test performed with bacteria *Vibrio fischeri* demonstrated different effects of the water and isopropyl alcohol solutions on the bioluminescence of the tested organism. It is obvious that toxicity was expressed more markedly in the case of less polar solution. The genotoxicity assay (Ames test) of the water and isopropyl alcohol extract has not proven any mutagenic effects. It has been confirmed that sediments

contaminated with PCBs represent a source of the adverse effects on live functions of the microorganisms in the environment.

The next step was a microbiological analysis of contaminated sediments and isolation of pure bacterial cultures able to degrade PCBs in the environment. In order to determine the genetic potential for biodegradability of the isolated strains, the gene *bphA1* was identified using PCR technique in the genomes of several selected strains. This gene codes the enzyme biphenyldioxygenase, which is responsible for higher PCB degradation rate. DNA was isolated from the both sediments and the presence of *bphA1* gene was determined. This gene codes a small subunit of biphenyldioxygenase, which is the specific enzyme of the “higher degradation pathway”. After confirmation of its presence we continued the isolation of pure strains. In the end, one strain from the sediments Strážsky canal and four strains from the Zemplínska šírava water reservoir were identified as expressing *bphA1* gene. All strains were subjected to other identification procedures as Gram-test and Nefermtest 24. The 16s rDNA was isolated as well, which for each strain has a conserved sequence of nucleotides, on which basis it is possible to taxonomically determine the strain. Using this method for a rapid screening of dioxygenase, it was confirmed that the isolated strains that possess this enzyme in their outfit produce yellow coloration in the presence of dibenzofurane. This visual proof of cleavage with dioxygenase was manifested during the growth of colonies in Petri dishes with solid minimal medium as well as in liquid medium throughout degradation.

The final goal of the work was to carry out aerobic biodegradation of PCBs in the contaminated sediments, as well as to perform aerobic biodegradation with the bioaugmentation by natural microorganisms isolated from these sediments. PCB biodegradation produced positive results. The microorganisms present in both sediments are capable of degrading certain low chlorinated congeners. The issue of biodiversity is still open and must be studied to reveal the real cooperation between degrading bacteria. Biodegradation of PCBs by intact sediments, i.e. without an amendment of additional microbial inoculum was significantly higher in sediments from Strážsky canal in comparison with those of the Zemplínska šírava water reservoir. We supposed that in the course of aerobic degradation, bioaugmented sediments would degrade PCBs faster and more effectively in comparison with the non-bioaugmented sediments. This fact was confirmed only in the case of PCB

congener 28 (2,4',4-trichlorobiphenyl), which content was markedly reduced by both sediments. This phenomenon can be explained by the effect of amendment of sediment by a fresh microbial consortium and an increase of biosurfactants production, which may release sequestered PCBs from the soil particles and in the end, the concentration of PCBs increased. It is also possible that dechlorination of higher chlorinated PCB congeners were dechlorinated to lower chlorinated ones. Last but not least, it is necessary to take into account possible competition of microorganisms in the substrate. It caused inhibition of the growth of microorganisms responsible for degradation of the mentioned congeners. Therefore, it is indispensable to determine microbial diversity of bacterial consortium and its coexistence. The bacterial strains isolated from Zemplínska šírava water reservoir produced more positive results in comparison with those isolated from Strážsky canal, where the concentration of PCBs was one order higher.

#### Acknowledgement

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## ARCHIVE-MAGNETISM IN BANSKÁ ŠTIAVNICA

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### ABSTRACT

The paper presents the first results of re-measurements of directions of the old mining works which were oriented by a mining compass. The measurements were performed for the purpose of investigating the change of magnetic declination. The old mining maps, as well as the maps of artificial water reservoirs from State Central Mining Archives in Banská Štiavnica, were used for comparison of historical and present local values of magnetic declination. The obtained results showed an eastern deviation of the present magnetic North from the North in historical ages.

**Key words:** mining maps, water reservoirs, geomagnetism, magnetic, declination, State Central Mining Archives in Banská Štiavnica

### INTRODUCTION

The geomagnetic field as an inseparable part of the environment is not static. It is a dynamic system changing in time and space. Its substantial part is generated in the core of the Earth. The interaction of Earth's magnetosphere with the so called solar wind shapes the outer part of the geomagnetic field. Both parts are submitted to temporal variations. While outer geomagnetic field presents irregular short-periodic changes, the characteristic attribute of the inner geomagnetic field are its regular long-periodic variations. The short-periodic changes, including the so called magnetic storms, are sufficiently known from observations on the Earth's surface, as well as from permanent space stations. The direct observations of long-periodic changes of the Earth magnetic field have been carried out for several centuries only. The longest observational series exists for London and Paris, since 16<sup>th</sup> and 17<sup>th</sup> century respectively. The geomagnetic field changes consist of changes in the orientation and the intensity. The change of orientation dwells in shifting the main magnetic dipole as related to geographical coordinates. In other words, the rotational and magnetic axes of the Earth do not coincide. For instance the north magnetic pole lies in the area of Northern Alaska, which means that the

deviation between the rotational and magnetic axes is approximately 11°. Regarding the changes of intensity of geomagnetic field, they are caused by complicated magnetohydrodynamical processes in Earth's core. It follows from the present knowledge that the intensity of the geomagnetic field in geological history regularly changed approximately in the interval from 0.2 to 1.8 multiple of the present value. Many results of rock magnetism indicate that from time to time the polarity reversal of the geomagnetic field occurred, while the period of one polarity lasted for about several million years.

### Measurement of geomagnetic field in Banská Štiavnica

One of the possibilities to recognize the orientation changes of the geomagnetic field in the past is offered by the re-measurement of the old line buildings, or constructions, orientation of which was appointed by compass, and their schemes, plans and maps are preserved till now in the archives. For this purpose such objects as old mining corridors, and surface mining constructions such as artificial lakes or water reservoirs (the so called 'tajchs') are ideal. The old-time mine town Banská Štiavnica was in the Middle Ages one of



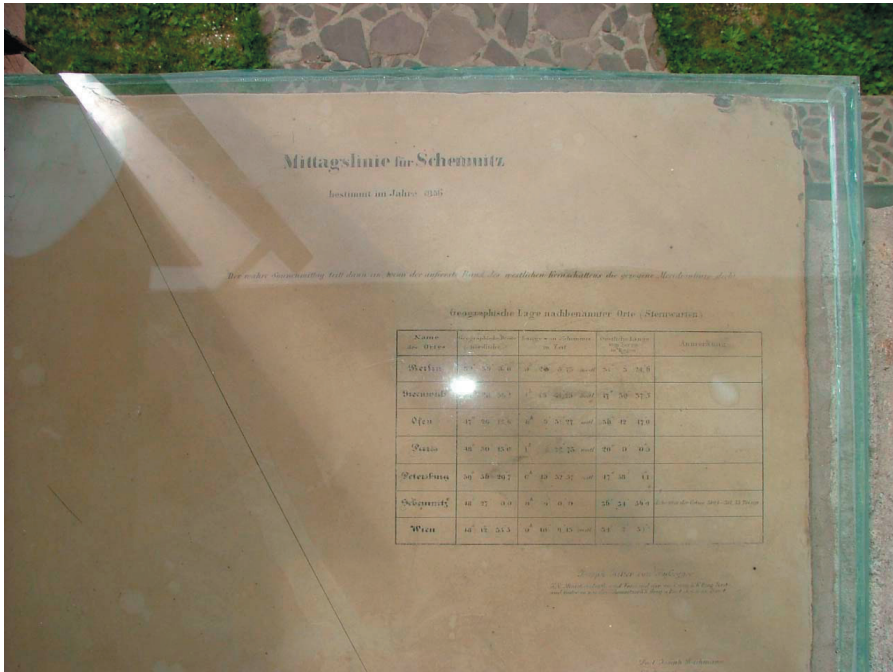


Fig. 1 Marker of geographical meridian of the Banská Štiavnica, located in the former Main Mining Office (today Mining Museum), according of which the mining compasses were calibrated

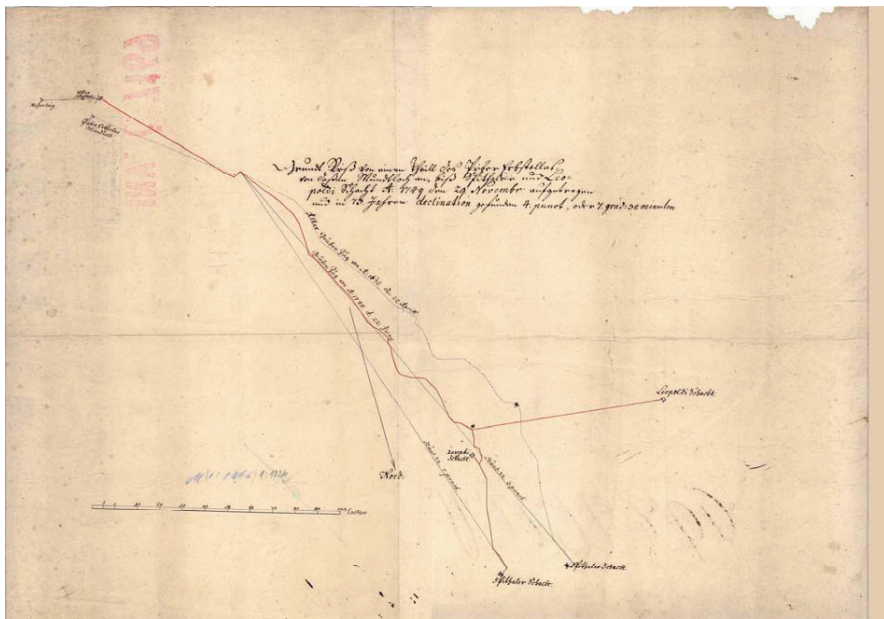


Fig. 2 Historical map of mine Spittaler. The measurements of mining corridor orientation in the years 1675 and 1748 provided information about magnetic declination changing during cca 100 years

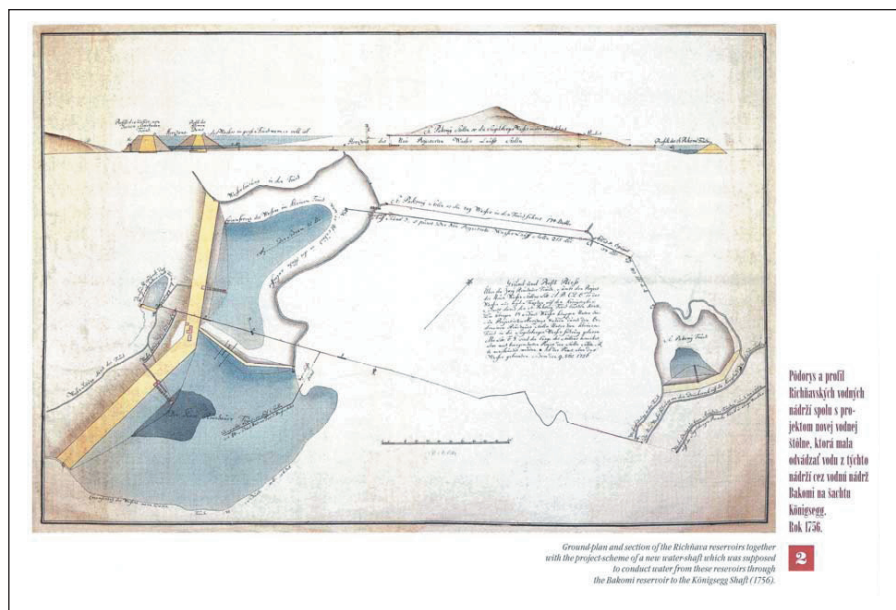


Fig. 3 Map of water reservoir Richňava

Tab. 1 Results of direction measurements on the old mining works. Tajch – water reservoir. Deviation means angular difference between present North direction ( $N_p$ ) and such one in the time of map construction ( $N_H$ ). Capp. E means, that present magnetic meridian is moving to the East. The numbers refer to difference between present and historical magnetic declination

Mine	Year of map origin	Deviation ( $N_p - N_H$ )
Anton Padua	1795	19° E
Schöpfer	1820	14° E

Tajch	Year of map origin	Deviation ( $N_p - N_H$ )
Richňava	1746	12° E
Počúvadlo	1770	4° E
Siglisberg	1778	14° E
Rozgrund	1790	9° E
Bakomi	1792	9° E
Brenner	1795	16° E
Belá	1821	10° E



the most important cities of the Austrian Empire. In the year of 1762 the first mining university in the world, called Banská Akadémia, was established there [1]. It educated not only the specialists for prospecting and exploitation of raw material deposits, but also mining surveyors and draughtsmen of mining maps. They were using mine compass for determinations of direction and regulation of mine corridors. Compass was described by J. Agricola in 1556 in 'The Twelve Books of Mining' [2]. The first mention about compass surveying in Slovakia dates back to 1535 in Špania Dolina. In Banská Štiavnica area the compass was used in 1555 at the Altrádschaft in Hodruša. Mining plans and maps were archived [2]. In 1856 an astronomical measurement was taken by professors of Banská Akadémia university Bachmann and Ruscéger who determined a meridian for Banská Štiavnica. It is marked on stone lithographical board on the arcade Kamerhof house, the present Mining Museum (Fig. 1). It served for measuring magnetic declination and for calibration of mining compasses. Actual declination was published and the surveyors improved the mining maps accordingly [1, 2].

Some mines were later re-measured, and it was found out that new measurements showed new direction with smaller or greater deviation from older measurements. An example of that, where the direction characteristics changed during 100 years, is a map of the schaft Spittaller in Fig. 2 [3].

In the middle of the 19<sup>th</sup> century, a well-known physicist Ch. Doppler taught at the Banská Akadémia university. He referred to the fact that temporal changes of direction measurement reflect the local changes of magnetic declination, which is the deviation between geomagnetic and geodetic meridians. Ch. Doppler proposed a project of systematic re-measurement of old mines, but after his death nobody continued this project, and no results of these measurements are preserved [4].

The State Central Mining Archives in Banská Štiavnica keeps one of the largest collection of old mining maps over the world [5]. Many of mining works mapped on them are reachable and re-measurable till now. Beside maps of mining corridors, also valuable maps of artificial water reservoirs exist [6]. On them the excellent line buildings are the dam barriers (Fig. 3).

The Department of geomagnetism of the Geophysical Institute SAS decided to revitalize the Doppler's idea and use the map plenitude of the Slovak

State Mine Archive for investigating long-periodic variations of the magnetic declination for the last 2–3 centuries. The first measurements from two corridors and seven reservoirs are presented in Tab. 1.

## RESULTS AND DISCUSSION

From a very limited amount of measurements it is not possible to do far extending conclusions, but in spite of this, we can deduce from the obtained results some regularity. All refer to the eastern deviation of the present magnetic North to the North in historical age. It corresponds to a present trend of changing magnetic declination on the territory of Slovakia. Very raw approximation is that measurements of mines provided average deviation of about 16°, and measurement of water reservoirs average deviation of about 11°. When we consider that in the region of Banská Štiavnica there is one of the biggest magnetic anomalies in Slovakia, and that many authors of geomagnetic maps do not define the magnetic declination there, the obtained results look promising. We plan to extend such measurements to all available mining works of which the archive documents exist, and in such a way to explore this valuable archive material.

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# MAGNETIC SUSCEPTIBILITY MAPPING OF SOIL POLLUTION

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## ABSTRACT

Fast and cost-effective detection of industrial pollution can significantly promote its ecological, economic and social assessment. A magnetometric method, used for qualitative determination of anthropogenic contamination, meets these requirements but needs further development in more quantitative terms. It could be used successfully in numerous cases when heavy metals coexists with strongly magnetic iron oxide particles in the source dust.

We presented a magnetic study which examines the utility of magnetometric techniques for rapid, qualitative detection of metallic pollutants in soils. In the present paper we tested the use of rock-magnetic method designed to access the degree of pollution of soil taken from Nováky situated in the south-western of Slovakia. The aim was to identify magnetic particles and to link magnetic pollution, to trace distribution and concentration of contaminants in soil. About 40 years the rainwater overflow the dump and flooded out the ash waste from the brown coal power plant in Nováky. Soil samples have been taken from 3 horizons (20, 40 and 60 cm) and measured by KLY–kappabridge in the Slovak Academy of Sciences, in Geophysical Institute in Bratislava.

Our results clearly demonstrate that magnetic anomalies can be explained by human activity.

**Key words:** heavy metals, magnetic susceptibility, pollution

## 1. INTRODUCTION

Magnetic properties of soil and recent sediments are sensitive to presence of ferro(i)magnetic minerals. Present instruments and methods enable very sensitive determination of concentration of strong ferrimagnetics (for instance magnetite), in the order of ppm. Ferrimagnetics in soils are of both primary (e.g., lithogenic magnetites) and different forms of secondary origin. Possible mechanism of magnetic enhancement of soils due to increased concentrations of secondary ferrimagnetic minerals are discussed in, e.g. [1,2,3,4]. Besides pedogenic and biogenic processes, atmospherically deposited ferrimagnetic particles of anthropogenic origin contribute to a great deal to concentration-dependent magnetic particles of top soil such as low-field magnetic susceptibility e.g. [5,6]. Practically all industrial

fly ashes contain significant fraction of ferrimagnetic particles. Most important sources of anthropogenic ferromagnetic particles include fly ashes produced during combustion of fossil fuel, e.g. [7,8]. Moreover, other sources, such as iron and steel works, cement works, public boilers and road traffic contribute to contamination by anthropogenic ferrimagnetics, e.g. [9,10,11]. In contrast to particles of pedogenic origin, anthropogenic ferrimagnetics are characterized by specific morphology and distinct magnetic properties. They are most often observed in the form of spherules with magnetic spherules. Prevailing ferro(i)magnetic phases are Fe-oxides, namely magnetite and maghemite [12].

Recently, rock-magnetic methods have been applied to modern soils in several environmental studies for overview see, e.g. [13]. Application of comparatively simple technique of measurements of magnetic

susceptibility enables to outline areas with concentrations of deposited anthropogenic ferrimagnetics significantly above the background values. Magnetic mapping represents thus a rapid, sensitive and cheap tool of targeting areas of interest. Afterwards detailed, more time consuming, expensive and laborious chemical analysis should be carried out in order to quantify the pollution levels. Measurements of low-field magnetic susceptibility of surface soils have been applied recently around local pollution sources, e.g. [11,14,15]. On larger, regional scale, mostly areas in Poland and Great Britain were investigated [16,17,18]. These studies proved that in polluted areas magnetic susceptibility of surface soil layers is considerably elevated and, at the same time, typical ferrimagnetic particles of anthropogenic origin were identified.

Up to now, magnetic methods have been primarily used in areas with rather high concentration of anthropogenic particles in soils. For example, in areas with high concentration of industry, the annual amount of atmospherically deposited dust reaches several thousands of tons. A single coal-burning power plant can produce hundreds of tons of fly ashes per year e.g. Considering the fact that such power-plant fly ashes contain some 10% of ferro(i)magnetic particles [15], it is obvious that these particles influence significantly magnetic properties of soils in the surrounding areas).

## 2. MATERIAL AND METHODS

The study area covers about 5 km<sup>2</sup> of Nováky situated in the south-western part of Slovakia. The main pollution source is a coal-burning power plant. The 14 soil samples were collected and gathered at different distances from the main pollution source. The grid was 0.5 x 0.5 km. Soil sampling was done after removing the vegetation layer, which consists of typical grasses. Soil material was sampled from 3 soil horizons (20, 40 and 60 cm). All samples were air-dried and then sieved through 2 mm to remove refuse and small stones. Low-field magnetic susceptibility was measured in the Geophysical Institute, in the Slovak Academy of Sciences in Bratislava, using KLY-2 kappabridge (Agico). Maps of magnetic susceptibility distribution were processed using SURFER for WINDOWS software.

## 3. RESULTS AND DISCUSSION

Effect of dust deposition can rapidly be monitored by magnetic measurements of soil. These material, how-

ever, accumulate magnetic particles over a long period. We were searching for an equally rapid and economical methods to determinate pollution in soil. And soil samples seems to be promising.

Our aim was to verify how the value of the magnetic susceptibility will be change from the distance of source pollution. The concept of statistically significant relationship between magnetic susceptibility and content of heavy metals in soil confirmed for one source of emission. Changes in low-field magnetic susceptibility along typical soil vertical profiles are shown in Fig. 1. Significant increase of magnetic susceptibility in the deeper layers was observed. Values of magnetic susceptibility varied between 0.8 and 141.1 m<sup>3</sup>/kg SI units. The Fig. 2 demonstrate the increase of magnetic susceptibility. Our results show that this area is obviously very suitable for the purpose of magnetic monitoring of contamination due to deposition of industrial dust.

## 4. CONCLUSION

Magnetic mapping has been recently successfully used in pollution studies primarily in areas with intensive industrial activity and major pollution sources. Measurements of the magnetic susceptibility provided complementary information about pollution of soils for the estimation of environmental situation in the study area. The mapping technique permitted to determine groups of elements (heavy metals) which influenced the variation of the magnetic susceptibility. The level of magnetic susceptibility is a result of complex influence of natural ferrimagnetic mineral and the contribution of magnetic particles into soil as a result of industrial pollution. The contamination of soils by iron, iron minerals and heavy metals in the area lead to an increase of the magnetic susceptibility. It is only a preliminary study which aim was to check out new method in environmental studies. Our endeavour is now to refill a net of area with another samples and to compare our results with the results from geochemical map. Our preliminary results confirm that over the whole area in the top soil layer can be reliably determined as being magnetically enhanced in terms of magnetic susceptibility.

Because the magnetic method of soil-pollution monitoring is sensitive, fast and relatively cheap, it can be applied over large regions.

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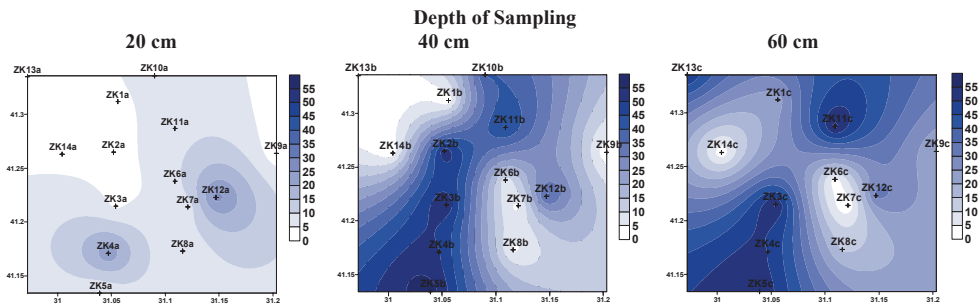


Fig. 1 Maps of MS distribution

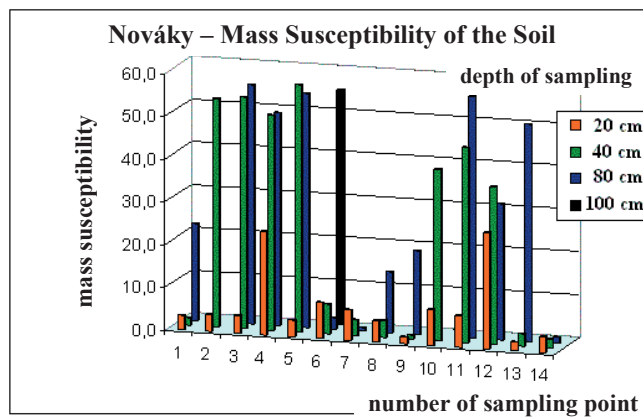


Fig. 2 The increase of soil pollution

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# INTEGRATION OF ENVIRONMENTAL APPROACH TO STRATEGY OF PRODUCTION ENTERPRISES – ENVIRONMENTALLY ORIENTED QUALITY OF PRODUCTION

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## ABSTRACT

In the paper there is presented system approach, applied in Slovak transformed production enterprises, which solve questions of closing the so called industrial cycle from the side of the wastes' producers, especially from the side of energetically solid wastes producers – fly ashes and slags. The quality of processes and final products is connected not only with the technological chain itself and with outputs from it – the utility product, but also with the load of the environment, with wastes care.

**Key words:** system approach, production and environmental policy, solid wastes from energetic enterprises, fly ashes and slags, utilization, quality of environment

## INTRODUCTION

If the production or an enterprise at present causes harms to the environment, its existence is endangered because

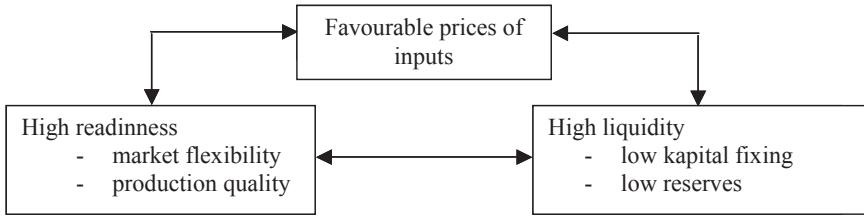
- the public opinion starts to turn against,
- strict regulations for a certain time/totally will disable its operation, out of which follow two even antagonistic principles:
  - permanently to take into consideration the relation of the enterprise and its acting on the environment,

- permanently to have an appropriate profit with a cardinal importance for its existence.

In the relation “economical interests versus environmental requirements” there exist contradictory points of view:

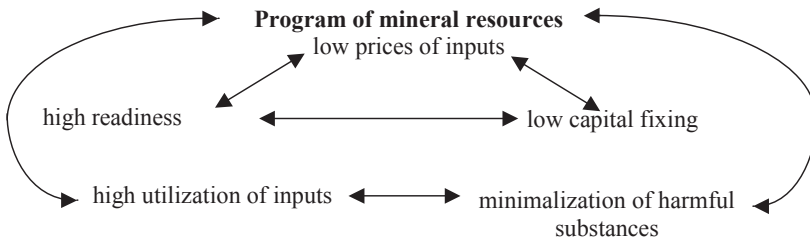
- the principal conflict between the economy and ecology/ environment,
- strained relations between the economy and environment,
- preferring the environment to economy.

The entrepreneurial and environmental conflict follows from their different aims. For a production enterprise of the first importance is:



From environmental views its needed to solve mainly contradiction interim consumption production from to survive defensible development/impact human intervention on earth stability. In 1992 Lorentz define 5 axioms affecting coexistence of system nature – society. They Are that: dynamic, interactivity, hierarchical, creative brittleness. Solvability of the given conflict requires the linear thinking to be replaced by a system, process one. Target of environment oriented, system, is find a harmony between human and society, technics and environment.

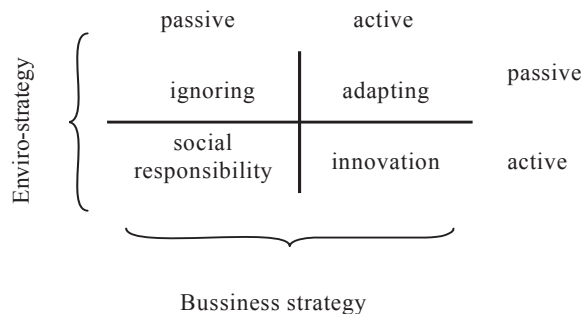
- **so called input-output concept**, which at the production takes into account the care of:
  - a) protection of resources,
  - b) avoiding forming the wastes,
  - c) decreasing the “occurrence” of wastes,
  - d) change of wastes on a harmless substance,
  - e) utilisation of wastes,
  - f) diffusion or wastes on less concentrated/diluted form, namely trough e.g. adjusting the production program, adjusting the technology, recycling, active protection of the environment etc.



Strebel [13] formed two system approaches to the production policy of the environment:

- **so called triple concept for the production:**
  - a) favourable for the environment,
  - b) loading the environment as low as possible,
  - c) being interested in “neighbourhood” environment (outside the enterprise),

In both these approaches the protection of the environment is considered as the product, which means that in each partial production aim must be achieved the aim environmental as well. It means to switch from inactive protection of environment – the first rate is the production, to active protection of the environment – the first-rate is the social responsibility – quality of life.





Enterprise entrance to environmental question manifest at four strategy:

It would be probably wrong to give an absolute priority to one of the systems. There most exist a “rational balance” among the human principle (self realisation, self-confirmation, and humanisation of work), principle of minimum load of the environment (saving resources, decreasing, even preventing the load of the environment) and economical principle (maximum profit at minimum costs).

The task of mining and mineral processing industry is not only

- decreasing of the “exploitation” of mineral resources, but also,
- ecological-environmental responsibility for general quality of the environment.

Besides economical interests the enterprises have to take into consideration also the social responsibility, thus e.g.: If it is necessary to process raw materials, making harm to the environment, it is necessary to take expenses that are formed by loading the environment by their production (Law on wastes, Law on fees for storing wastes, Decree of the government of the SR on registering wastes, Decree of the government of the SR on waste management, Edict of the ministry of the environment on programs of the waste economy, Edict on establishing categorisation of wastes and catalogue of wastes, Law of environmentally oriented management and audit, Law of integrated pollution and prevention control, etc.).

Environmental understanding of enterprises must be concentrated on:

- limitation of raw materials’ resources and not expansiveness of needs,
- maintaining the stabilisation of the ecosystem and energetic needs,
- alternatives, how to decrease even remove the devastation mining and restrict at present used harmful technologies,
- environmentally favourable technologies and development of concepts, aimed at recycling, and reusing,
- rebuilding the industry in the direction of the tactfulness to the public (clean and best available technologies and decreasing robustness of products).

Solving these problems, however, inevitably increases costs, by which are formed conflicts between

- increase of costs and prices,
- taking responsibility for certain financial losses at environmentally friendly production,
- frequency of consumption and saving.

The institutional enactment of the “environmental thinking” of enterprises acts more as **correcting** the existing state and environments as **forming** (the strategy of an enterprise). So-called waterfall chain of {exploitation-processing-utilization of earths resources} are not sufficient entrenched rights in its last part (e.g. obligation of liquidation/reusing/utilization of production processes wastes, or. wastes by life cycles products ending. Individual measures, however, must be integrated especially from the point of view of impacts on the environment, into a unit. Necessary is mainly:

- to support the motivation for protection of the environment,
- to improve technologies favourable for the environment or to strive for their innovation from the point of view of loading the environment,
- to plan, control and improve (technical) measures from the point of view of enterprise’s protection of the environment,
- to judge costs on the protection of the environment as commentary with costs for the production,
- to keep regulations standard conditions and safeguard optimum management with wastes.

The example, close to the presented attitudes is the way of dealing with the energetical waste – fly ash from burning the black semi-anthracite coal – caught in electrostatic separators. In the following part there are given the possibilities of its utilisation.

## POSSIBILITIES OF UTILISATION OF SOLID WASTES FROM ENERGETICAL ENTERPRISES

The world trend – the utilisation of industrial wastes – is motivated by economical advantages especially saves of raw materials, energies and necessity of the protection of the environment. This trend is connected with solid wastes from the power industry as well. Their making harmless is a difficult thing.

Of a rather great interest are especially fine-grained fly ashes because they are bulk, accessible, cheap raw material, often with such utility properties that at processing on certain products do not act harmfully on man as well as environment. At present this waste is being stored on a plane dump in the form of stabiliser.

### The utilisation of fly ashes is conditioned by their properties

- **physical** – granulometry, or area of the surface, morphology, specific, loose and bulk density, hardness, compactness, freezing, fusibility, swelling, etc.,



- **chemical** – content of chemical environments, utility separable components (e.g. magnetite form of the Fe component, residuals of non-burnt coal – loss by annealing), metal elements (Al, Ge), harmful elements (S, B, Cd, As, Pb, ...) and radioactive elements (Ra, Th, Rn, U, K).
- **mineralogical** (during thermal processes there are formed mineral novelties, many with puzolane properties).

#### **Possibilities or utilisation of solid wastes from energetic:**

1. **Direct utilisation**, without interference to the “natural composition” of the solid waste.
2. **Utilisation after the treatment** when the direct utilisation does not come into consideration from reasons of exceeding the content of some component, the content of which is limited by standards. It is for example the content of sulphur or residuals of non-burnt coal, i.e. the content or the loss by annealing.

#### **Direct utilisation:**

- **In mining:** the fly ashes are used as cement-free bond, fill and thermo-insulation material.
- **In mineral processing:** the magnetite powder, acquired by the application of mineral processing technologies – by wet low-intensity magnetic separation – it can be used as heavy medium at coal and metals separation in heavy suspensions,
- **In metallurgy:** for the production of insulation layers and mixtures for the production or exothermic and thermo-insulation inserts used at casting the steel
  - a) as fill substances at casting the steel,
  - b) as cenospherical mixtures together with graphite powder,
  - c) as insulation fill mixtures-microspheres with coke powder,
  - d) as thermo-insulation plates.

#### **Other possibilities of using the fly ashes:**

- at the production of sonic-absorption mixtures used in the automobile industry,
- at cleaning waters -as catchers of oils,
- fillings at robber and paint production.

#### **In the civil engineering and industry or construction materials:**

The fly ashes often comprise residuals of non-burnt coal, the content of which is from almost zero to 15 % and more. This content is expressed by the loss ignition (I.i.).

The set of the STN standards from 722060 to 722070 limits the loss by annealing in individual kinds of fly ashes. E. g.:

- for the fly ash as the active components of mortars (STN 722062) the allowed loss by annealing is 4 %,
- for the fly ash from burning the brown coal or the coal from the mixture of brown and black coal for the production of porous concrete the allowed loss by annealing is 4 %, for the fly ash from burning the black coal 7 % (STN 722067),
- for the fly ash as non-active component into the concrete the allowed loss by annealing is 10 %.

Wastes from energetic – fly ashes and slags – can be used in these main areas of the civil engineering:

At the production of sinter of the Portland cement. The example is the utilisation of the slag-fly ash mixture (SFAM) from the plant of Energetic in the VSŽ Košice. On the basis of the results of laboratory tests in 1992 was realised the operation verification of its utilisation at the production of cement sinter in the firm of CETU. 1200 t of the SFAM – from the dry heap was in the relation 1 : 1 mixed with clay. The experiment was carried out without principal changes in the technological procedure. The results showed its successfulness. The presence of residuals of non-burnt coal in the SFAM (15 % of the I.i.) improved the energetic balance of the process – the gross calorific value of the SFAM was determined on 4 284 kJ/kg<sup>-1</sup>. Another favourable factor is the Fe content (7–10 %) in the SFAM, in the result of which it is not necessary to add the iron into the process. The operational results confirmed good ability of the SFAM to react in the cement mixture so that they **can replace a part or extracted silicates**.

- At the production of cement – in France in the cement industry the fly ashes are used as the component of raw materials<sup>3</sup> mixture, or as hydraulic admixture to the sinter. This fly ash has to meet the same requirements as is defined in the STN 722062 standard.
- In the production of porous concrete the best application finds the brown coal fly ash from the ENO Nováky and the black coal fly ashes imported from the Czech Republic. From the Slovak black coal fly ashes only those that meet the STN 722067 standard. The production of the porous concrete in Slovakia in recent years used 4,25 Mt of the fly ash from the ENO Nováky, which is a plumbless service for the environment, because this quantity would fill the deposit with the area of 52 ha to the height of 10 m.

- At the production of **light porous aggregates**, for example by the cold peletisation. The Dutch firm of Aerding BV has also developed the technology for the production of non-calcinated aggregates on the basis of the ash.
- In the production of small-size wall elements from concrete with the hydraulic bond.
- As fine-grained filling – replacement of fine shares or aggregates in concretes. This question is from the research point of view solved and verified also in the operational conditions in our country as well as abroad. The fly ash at the same time acts not only as the aggregate, but also as the active component, partially replacing the cement. At the same time the water tightness and resistance against aggressive waters is increased. The utilisation of fly ashes is suitable especially for transport concretes, massive concrete constructions of foundations, supporting walls and water workings. The suitability of the fly ash applying into the concrete is however, necessary to be verified on one hand from the point of view of their **quality** and on the other hand from the point of view of required technological properties of the concrete. For quality of the fly ashes at the production of concrete an important role-plays the fact that the **higher temperature or burning the coal** (1400–1500 °C in smelting boilers), thus occurrence of particles with characteristic morphology and mineral novelties, **acts favourably for the quality of concrete**. In our country the fly ash concrete is used mainly at the construction or water workings and for the production of transport concrete. The first larger utilisation of fly ashes in the former CSFR was at the construction of the Orlik dam, where the recipe 50 kg of the fly ash per 1 m<sup>3</sup> of the concrete, by which 60 kt of cement was saved, while a better quality of the concrete was achieved. Another advantage of the fly ashes' concretes is higher density and resistance against sulphate corrosion.
- At the stabilisation of foundations in road construction engineering cinders and fly ashes are used either in the care of the bank or in layers of sandwich banks. The fly ash has to meet the STN 722060 standard (Fly ash for construction purposes) or the ON 736133 standard. For the fly ash in the condensed base layer in the function of bond the puzolane property is of importance, defined as the reaction of the silicon dioxide SiO<sub>2</sub> and aluminium oxide Al<sub>2</sub>O<sub>3</sub> in the fly ash with the calcium hydro-

xide Ca(OH)<sub>2</sub>, while calcium silicate and calcium aluminate hydration products are formed.

- In the common production of aluminium and cement. Prof. Grzymek patented this technology in 1934 at the Lvov Polytechnics in Poland. Till 1991, non-stop, worked the plant for the common production of the Al(OH)<sub>3</sub> and cement at Groszowice (province Opole). Its annual production was 12 kt of Al(OH)<sub>3</sub> and 200 kt of cement.
- In the production of ceramic products the fly ash becomes a permanently used component, the most often at the production of bricks, seldom at the production of dark ceramics.
- Another utilisation of fly ashes is in the production of concrete covering, in the production of thermo insulation materials, for fill thermal insulations, for the production of mineral wool, as filling to the epoxy and polyurethane substances of polyester resins, in the production of the polystyrene concrete.

Not all methods and forms of the utilisation of solid wastes from the energetic are published. Many plants protect their technologies.

## CONCLUSIONS

General system approaches, used already for several years in industry of advanced countries are in recent years actively applied in our transforming production enterprises. The presented possibilities of utilisation of a typical bulk waste – waste from enterprises producing power by burning fossil fuels – show the increasing responsibility of waste producers for their further “destiny” – existence, survival on the market, social accountability of enterprise and improved quality of life. The largest area of the utilisation of the energetical wastes on the basis of detailed knowing their physical, chemical and mineralogical properties is the civil engineering and the industry of construction materials.

### Grateful

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# ENVIRONMENTAL STUDY OF THE AMBIENT AIR QUALITY IN KREMNICA MONITORING AREA

## PART I. DATA EVALUATION OF HEATING SEASON

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### ABSTRACT

The ambient air samples were collected in monitoring area Kremnica on six localities. Four indicators were estimated in 24-hours samples: fraction of solid aerosol  $PM_{10}$ ,  $PM_{2.5}$ ,  $NO_2$  and  $NO_x$ . The values were measured in the heating period (March 2006) on six measuring localities. These values were compared after statistical evaluation with the limits of concentrations for the assessment of the air quality in this locality.

**Key words:** size fractions of solid aerosol ( $PM_{10}$ ,  $PM_{2.5}$ ),  $NO_2$ ,  $NO_x$ , collection, of air samples

### INTRODUCTION

In the connection with planning opencast gold and silver mining in the Šturec locality close to historical centre of Kremnica began wide discussion about negative environmental feedback from the mining with using of toxic cyanides, noise coming and apprehension from disaster of similar activities e.g. in Romania. Corporation Envigeo Banská Bystrica was ordered collection and measurement of ambient air samples from area Kremnica. These samples were determined in the Regional Institute of Public Health (RIPH) in Banská Bystrica. There were chosen four chemical indicators in connection with the damage of public health from planned mining: two size fractions of solid aerosol ( $PM_{10}$ ,  $PM_{2.5}$ ),  $NO_2$  and  $NO_x$ . The sample collection was realized in terms of environmental appreciation on six measuring localities: thereof three localities were directly in Kremnica (corporation Tournigan Gold, municipality and City Stadium), and three localities were in closely settlements (Lúčky, Kremnické Bane and

Kopernica). There were 24-hours samples of ambient air collected in the heating season from 1. March to 23. March 2006. Measured values were evaluated after statistical processing and compared with limit values in home and/or foreign legislation.

### MATERIALS AND METHODS

All the air samples were collected 24 hours. The aerosol size fractions  $PM_{10}$  and  $PM_{2.5}$  were collected with high volume pump in connection of two Harvard impactor to separation of thoracic fraction  $PM_{10}$  and high risk respirable fraction  $PM_{2.5}$ . The applied aerosol fractions were collected on fiberglass filter with the constant flow rate 10 l/min which guarantees thoracic or respirable convention on given type of impactor in accordance to STN ISO 7708 [1–3].

The air flow was controlled with calibrated aerometer and air volume was re-counted on status conditions (293 K). Weight of size fractions  $PM_{10}$  a  $PM_{2.5}$  was evaluated with gravimetric method.

The air samples for determination of  $\text{NO}_2$  and  $\text{NO}_x$  were collected with passive method outgoing from principle of molecular diffusion in accordance with Fick law on OGAWA passive sampler (equipment preserved with American-Japan patent) enabling simultaneous bleeding of  $\text{NO}_2$  (collection pads PS134) and  $\text{NO}_x$  (collection pads PS124) [4]. OGAWA samplers

were exposed 24 hours coupled with blank and all the samples were analyzed on contents of  $\text{NO}_2$  and  $\text{NO}_x$  with spectrophotometric method for determination of nitrites using N-(1-naphtyl)-ethylenediamine and sulphanyl acid.

Table 1 shows important climatic conditions for counting of calculation of measured concentrations.

Tab. 1 24-hours averages of air temperatures, humidity and air pressure in Kremnické Bane (data were offered by SHMÚ Bratislava)

Date of sampling	Air temperature (°C)	Humidity (%)	Air pressure (hPa)	Date of sampling	Air temperature (°C)	Humidity (%)	Air pressure (hPa)
1. 3. 2006	-7,0	90	920	13. 3. 2006	-4,3	70	940
2. 3. 2006	-7,2	69	922	14. 3. 2006	-5,5	83	938
3. 3. 2006	-3,5	72	920	15. 3. 2006	-3,2	72	936
6. 3. 2006	-6,0	64	927	16. 3. 2006	-3,0	81	937
7. 3. 2006	-5,7	62	930	17. 3. 2006	-2,1	85	935
8. 3. 2006	-6,5	74	931	20. 3. 2006	0,6	73	926
9. 3. 2006	-4,8	88	922	21. 3. 2006	1,8	61	925
10. 3. 2006	0,7	95	920	22. 3. 2006	4,2	75	924

## RESULTS AND DISCUSSION

Summary term for ambient air aerosol with size below  $100 \mu\text{m}$  is total suspended particles (TSP). It is very heterogeneous group for flying particles by size and by quality which gets to air from various resources, e.g. emissions from industry, combustion of fuel (coal, petroleum, bio-fuel), transport, agriculture, mining etc. For characterization of aerosol particles impact to public health is dominant their size and chemical composition. The particles larger than  $10 \mu\text{m}$  are eliminated from human body e.g. by cough, and to respiratory system penetrate only particles smaller than  $10 \mu\text{m}$ . There are e.g. viruses, bacteria, particles from anthropogenic sources (sulphate and nitrate aerosols originated from secondary atmospheric transformations of acidic gases). Fine particles – fraction  $\text{PM}_{2,5}$  – easy penetrate to lung alveoli where they are blocking the exchange of breathing gases – oxygen and carbon dioxide. The air-borne dust has number of various type of negative impact to the people health: the increase of prevalence of cardiovascular diseases, the increase of premature death, chronic cough, chronic phlegm, shortness of breath, setback by asthmatics, they are irritable on mucous membrane of respiratory system, etc. [5–9]

The most significant sources of nitrous oxide are gas-engines, thermal power stations and industry. High

concentrations of  $\text{NO}_2$  (below  $10\,000 \mu\text{g}\cdot\text{m}^{-3}$ ) produce serious inflammatory diseases, pneumonia, cold, headaches, significantly increase the incidence of acute respiratory symptoms, especially of children and old people (asthmatics) [11, 12].

The assessment results of air-borne dust fractions ( $\text{PM}_{10}$  and  $\text{PM}_{2,5}$ ),  $\text{NO}_x$  and  $\text{NO}_2$  from six measuring localities are summarized in table 2.

Statistical processing of measured yields is listed in table 3, where are also listed the number of measuring, maximum, minimum and average values. There are compared with limit values and number of exceeding values is presented.

Systematic monitoring of air-borne dust – fraction  $\text{PM}_{10}$  and  $\text{PM}_{2,5}$  – has taken place in our country via SHMU since 2000. The limit value is  $50 \mu\text{g}\cdot\text{m}^{-3}$  in accordance to Ministerial Order No. 705/2002 about ambient air quality [10]. This value was exceeded once on the all measured localities (in Kopernica four times – this is the most polluted locality), except Kremnické Bane where was exceeded limit value not once. The results of measurements are showed in graphs 1 and 2.

Fine particles  $\text{PM}_{2,5}$  are very important from health point of view because they penetrate deeply to respiratory tract and therefore are also more dangerous. No limit value exists in our country therefore measured values should be compared only with foreign limits in

Tab. 2 Values for PM<sub>10</sub>, PM<sub>2,5</sub>, NO<sub>2</sub> and NO<sub>x</sub> on six measured localities KR1–KR6

Measured locality	Date of sample collection	PM <sub>10</sub> [µg/m <sup>3</sup> ]	PM <sub>2,5</sub> [µg/m <sup>3</sup> ]	NO <sub>2</sub> [µg/m <sup>3</sup> ]	NO <sub>x</sub> [µg/m <sup>3</sup> ]
KR1 Kremnica – residence of corp. Tournigan Gold	01.03.06	69,1	48,4	ND	15,2
	02.03.06	51,3	40,2	116,0	116,0
	06.03.06	13,3	12,1	<LOQ	10,1
	07.03.06	22,5	21,8	ND	<LOQ
	08.03.06	45,0	38,0	22,0	22,0
	09.03.06	30,2	38,2	17,0	20,4
KR2 Kremnica – municipality	01.03.06	61,9	56,9	22,5	40,3
	02.03.06	30,6	21,5	<LOQ	20,2
	06.03.06	22,5	20,1	ND	<LOQ
	07.03.06	34,6	30,4	ND	<LOQ
	08.03.06	42,8	40,5	16,7	19,1
	09.03.06	48,3	40,4	50,3	50,3
KR3 Lúčky	01.03.06	55,4	33,8	15,7	23,9
	02.03.06	30,7	23,3	<LOQ	<LOQ
	06.03.06	13,6	12,2	ND	ND
	07.03.06	25,9	21,6	ND	<LOQ
	08.03.06	45,3	41,3	22,3	22,3
	09.03.06	42,9	36,4	<LOQ	<LOQ
KR4 Kremnické Bane – sanatorium Slniečko	13.3.2006	48,7	47,6	<LOQ	14,6
	14.3.2006	42,4	35,0	21,5	23,8
	15.3.2006	41,0	35,7	<LOQ	<LOQ
	16.3.2006	32,6	31,7	18,3	18,3
	20.3.2006	30,7	24,2	<LOQ	<LOQ
	21.3.2006	33,6	26,6	18,5	18,5
KR5 Kopernica – private house	13.3.2006	62,1	40,4	24,4	24,4
	14.3.2006	43,2	36,3	29,0	29,0
	15.3.2006	60,9	56,0	17,3	17,3
	16.3.2006	36,5	33,3	18,9	18,9
	20.3.2006	60,2	55,1	18,9	18,9
	21.3.2006	57,6	51,9	35,9	35,9
KR6 Kremnica – City Stadium	13.3.2006	49,7	37,4	17,9	21,9
	14.3.2006	47,2	43,5	19,6	56,8
	15.3.2006	50,5	44,9	49,9	49,9
	16.3.2006	32,6	31,0	37,5	37,4
	20.3.2006	42,5	40,3	29,2	31,0
	21.3.2006	45,1	35,3	24,6	34,0

ND – values below limit of detection, &lt;LOQ – values below limit of quantification

Tab. 3 Statistical processing of measuring yields on particular localities in Kremnica and surrounding

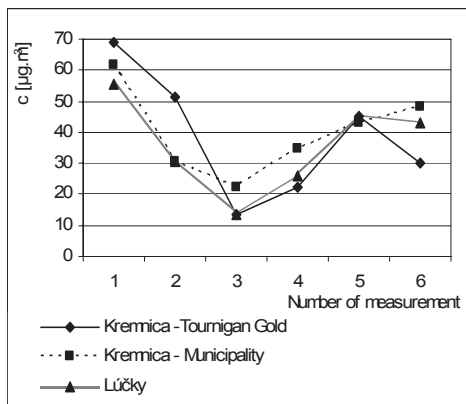
Indicator on measured locality	Number of measuring	Max value	Min value	Average value	Limit*	Number of limit exceeding
PM <sub>10</sub>	n	µg.m <sup>-3</sup>	µg.m <sup>-3</sup>	µg.m <sup>-3</sup>	µg.m <sup>-3</sup>	n
Kremnica – Tournigan Gold (KR1)	6	69,1	13,3	38,6	50/24 h	1
Kremnica – municipality (KR2)	6	61,9	22,5	40,1	50/24 h	1
Lúčky (KR3)	6	55,4	13,6	35,6	50/24 h	1
Kremnické Bane – Slniečko (KR4)	6	48,7	30,7	38,2	50/24 h	0
Kopernica (KR5)	6	62,1	36,5	53,4	50/24 h	4
Kremnica – City Stadium (KR6)	6	50,5	32,6	44,6	50/24 h	1
PM <sub>2,5</sub>						
Kremnica – Tournigan Gold (KR1)	6	48,4	12,1	33,1	25/24 h	4
Kremnica – municipality (KR2)	6	56,9	20,1	35,0	25/24 h	4
Lúčky (KR3)	6	41,3	12,2	28,1	25/24 h	3
Kremnické Bane – Slniečko (KR4)	6	47,6	24,2	33,5	25/24 h	5
Kopernica (KR5)	6	56	33,3	45,5	25/24 h	6
Kremnica – City Stadium (KR6)	6	44,9	31	38,7	25/24 h	6
NO <sub>2</sub>						
Kremnica –Tournigan Gold (KR1)	6	116	4,5	29,4	40/rok	0
Kremnica – municipality (KR2)	6	50,3	4,5	18,5	40/rok	0
Lúčky (KR3)	6	22,3	4,5	12,2	40/rok	0
Kremnické Bane – Slniečko (KR4)	6	21,5	13,5	16,5	40/rok	0
Kopernica (KR5)	6	35,9	17,3	24,1	40/rok	0
Kremnica – City Stadium (KR6)	6	49,9	17,9	29,8	40/rok	0
NO <sub>x</sub>						
Kremnica – Tournigan Gold (KR1)	6	116	10,1	36,7	40/rok	0
Kremnica – municipality (KR2)	6	50,3	16,7	32,5	40/rok	0
Lúčky (KR3)	6	23,9	22,3	23,1	40/rok	0
Kremnické Bane–Slniečko (KR4)	6	23,8	14,6	18,8	40/rok	0
Kopernica (KR5)	6	35,9	17,3	24,1	40/rok	0
Kremnica – City Stadium (KR6)	6	56,8	21,9	38,5	40/rok	0

\*in accordance to legislation [10], only for PM<sub>2,5</sub> limit value is in accordance to limit in state California, USA

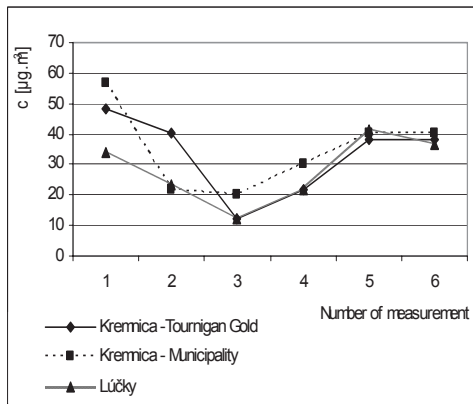
USA. Here several limit values exist, e.g. in state California 24-hours limit is 25 µg.m<sup>-3</sup> while federal limit is 65 µg.m<sup>-3</sup>. In light of federal limit the measured value was exceeded not once whereas California's limit value was exceeded practically in all events (the least polluted locality is Lúčky, the most polluted locality is Kopernica). The level of pollution with PM<sub>2,5</sub> on separate localities is practically replicated with level of size-

fraction PM<sub>10</sub> what is evident from graphs 1–5.

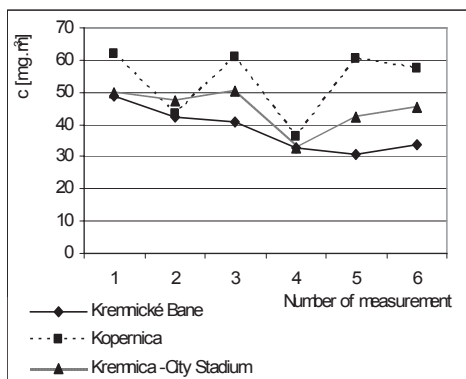
Concentrations of nitrous oxide (NO<sub>2</sub>) and oxides of nitrogen (NO<sub>x</sub>) on watched localities reach to relatively low values. The limit value wasn't exceeded in accordance to legislation [10]. The maximum 24-hours value 116 µg.m<sup>-3</sup> was measured in Kremnica on residence of corporation Tournigan Gold. It is probably accidental concentration from random emission



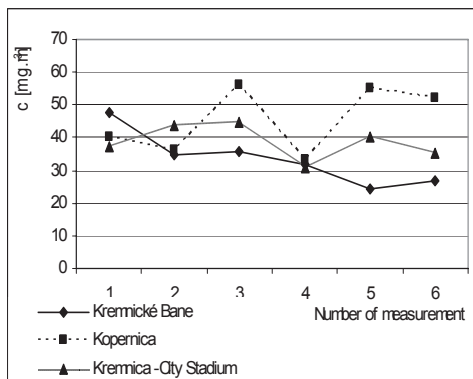
Graph 1. Size fraction of PM<sub>10</sub> on first two weeks



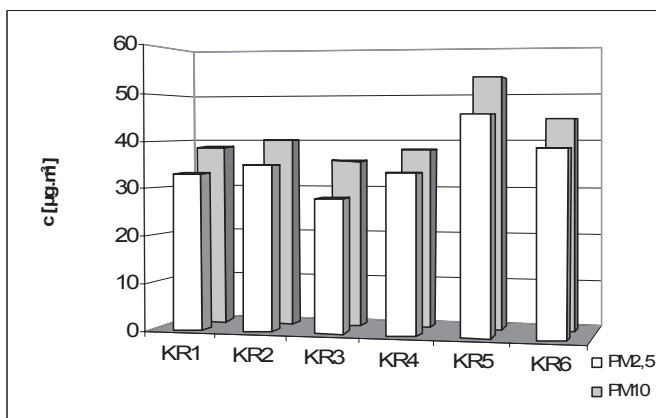
Graph 2. Size fraction of PM<sub>2.5</sub> on first two weeks



Graph 3. Size fraction of PM<sub>10</sub> on second two weeks

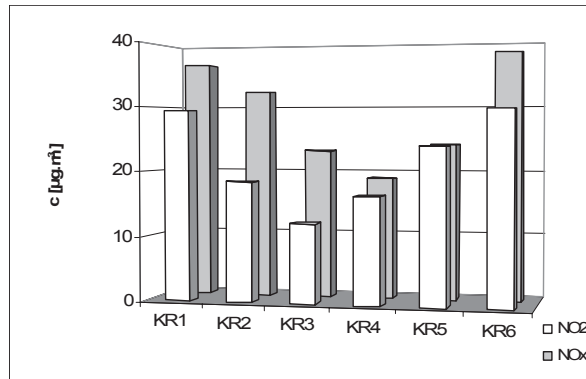


Graph 4. Size fraction of PM<sub>2.5</sub> on second two weeks



Graph 5. Average concentrations of PM<sub>10</sub> and PM<sub>2.5</sub> from the all measurements





Graph 6. Average concentrations of NO<sub>2</sub> and NO<sub>x</sub> from the all measurements

nearby place of collection in the time of measuring. The highest average levels were observed already on this place and on city stadium what is apparent from graph 6.

## CONCLUSION

The most polluted locality for air-borne dust indicator is Kopernica (limit value in accordance to legislative [10] was repeatedly exceeded). The least polluted is locality Lúčky. The highest concentrations of NO<sub>2</sub> were observed in residence of corporation Tournigan Gold and on City Stadium, vice versa the lowest concentrations of NO<sub>2</sub> were observed again in Lúčky.

Statistical budget of current measurements is very sensitive to extreme values therefore is necessary to perform additional series of measurement to establishment of pollution trends and to compare results from heating season and non-heating season during the year. The results published on this paper are insufficiently representative due to they are too small collection of measurements. They will be consequently subject of the additional research in non-heating season for more comprehensive establishment of pollution in Kremnica monitoring area.

## Acknowledgement

Authors thank RIPH for realization of measurements and corporation ENVIGEO for agreement to publication of measured results.

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## THE $^{222}\text{Rn}$ ACTIVITY CONCENTRATION IN BOREHOLE WATER AND ITS CORRELATION TO RAINFALL – A PRELIMINARY RESULTS

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### ABSTRACT

The  $^{222}\text{Rn}$  activity concentration changes in borehole water from the three boreholes V-1 (10 m), V-2 (40 m) and V-3 (10 m) have been studied. In V-3 also the continual measurements of the  $^{222}\text{Rn}$  activity concentration in borehole air have been performed. The results since January to June 2006 are discussed. The changes of the radon concentration have been studied in relation to the water level changes in boreholes and to the precipitation amount. Also the water level changes in relation to precipitation were studied. The first results show that the radon concentration and the water level in V-1 and V-3 boreholes are significantly affected by precipitation, in V-2 borehole this phenomenon is not clearly observed.

**Key words:** radon activity concentration, borehole, water level, precipitation

### INTRODUCTION

The application of radon for geodynamical processes monitoring needs the precise knowledge of the influence of various meteorological parameters on the radon activity concentration in the borehole air [1].

In our former investigations the influence of temperature and pressure on the  $^{222}\text{Rn}$  activity concentration in borehole air was studied [2].

The subject of this contribution was the study of the influence of the precipitation on the  $^{222}\text{Rn}$  activity concentration in borehole water and borehole air.

### METHODS

The studied samples of water have been taken from the three boreholes V-1, V-2 and V-3, drilled in the Lower Triassic quartzites at the area of Astronomical and Geophysical Observatory of Comenius University at Modra – Piesky (Modra AGO) [3]. The sampling have been carried out obviously three times a week since January 2006. At the same time, the water level at

each borehole was measured.

The radon from water was transferred into the scintillation cell of Lucas type. The samples were measured at the laboratory of Department of Nuclear Physics and Biophysics at Faculty of Mathematics, Physics and Informatics of Comenius University in Bratislava [4].

Since August 2003 the continual measurement of  $^{222}\text{Rn}$  in borehole air have been performed in V-2 and V-3 boreholes [3]. In October 2005, the detector from V-2 borehole was transferred into new measuring site.

### RESULTS

The  $^{222}\text{Rn}$  activity concentrations in water in every borehole were calculated and evaluated in relation to the water level changes and rainfall data. In the case of V-3 borehole also the interdependence of  $^{222}\text{Rn}$  activity concentrations in water and in borehole air were studied. We investigated also the influence of rainfall to the changes of water level and  $^{222}\text{Rn}$  activity concentrations in borehole air.

In V-1 borehole the clear anticorrelation between water level and  $^{222}\text{Rn}$  activity concentrations in water was observed, the value of correlation coefficient was equal to 0,68. The water level was strongly affected by rainfall. If the rainfall was more like 20 mm, the water level increased up to 3 m. This increased level was durable approximately three weeks, then it decreased to the former state. This high amount of water was connected with the decrease of  $^{222}\text{Rn}$  activity concentration in water. Later than the water level decreased, the activity concentration in water started to rise. The changes of  $^{222}\text{Rn}$  activity concentration between minimal and maximal value were about 70–80  $\text{kBq/m}^3$ .

At the last decade of June, the water level in V-1 borehole started to decrease rapidly, about 3 m during ten days. It was caused by hot weather and low amount

of rainfall. Usually in summer months this borehole lost the water first of all every year. Together with the decrease of water level, the  $^{222}\text{Rn}$  activity concentrations in water decreased too.

The deepest borehole V-2 was not affected by rainfall such significantly like V-1. Because in this borehole the water level was very deep under the surface, probably, the rainfall water could not reach the borehole water and enrich it with radon. But water created by melting of snow influenced this borehole markedly. Before the melting of snow, the water level was approximately 28 m under the surface. During the melting it had increased about 5m, then the water decreased to the level of 26 m. Since then it have been slowly increasing. No significant correlation between the  $^{222}\text{Rn}$  activity concentrations in water and the water level was observed.

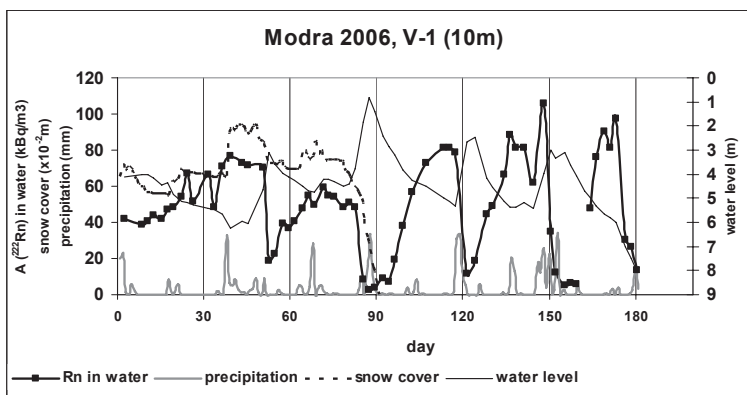


Fig. 1 The courses of the  $^{222}\text{Rn}$  activity concentration in water, precipitation amount, the state of the water level and snow cover in V-1 since January to June 2006

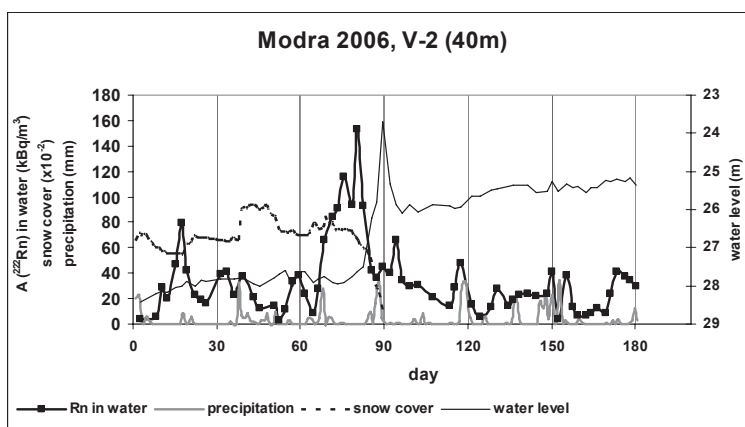


Fig. 2 The courses of the  $^{222}\text{Rn}$  activity concentration in water, precipitation amount, the state of the water level and snow cover in V-2 since January to June 2006

However, the increase of water level caused by melted snow was followed with the decrease of the  $^{222}\text{Rn}$  activity concentration in water, equally like in V-1 borehole. On the contrary to the V-1, the beginning of melting was accompanied with rising of the  $^{222}\text{Rn}$  activity concentration in water.

In V-3 borehole initially the correlation between the water level changes and the  $^{222}\text{Rn}$  activity concentrations in water was observed. After the melting of snow it turns to anticorrelation, because the transport of the created high amount of water was too quick for enriching the borehole water with radon.

The influence of rainfall on the  $^{222}\text{Rn}$  activity concentrations in water was confirmed in this borehole, similarly like in V-1. Also the rise of water level

was observed after raining. But the changes in activity concentrations were lower like in V-1, only about  $10\text{--}20\text{ kBq/m}^3$ .

Only in this borehole, the  $^{222}\text{Rn}$  activity concentrations in borehole air was continually measured. When the study area was covered by snow, the course of  $^{222}\text{Rn}$  activity concentration was different in comparison with following months. After the melting of snow, the values of  $^{222}\text{Rn}$  activity concentrations in borehole air significantly decreased. But some days after the raining the increase were observed and the radon activity concentration peaks in maximum reached values comparable to the values of radon activity concentration in period with snow cover.

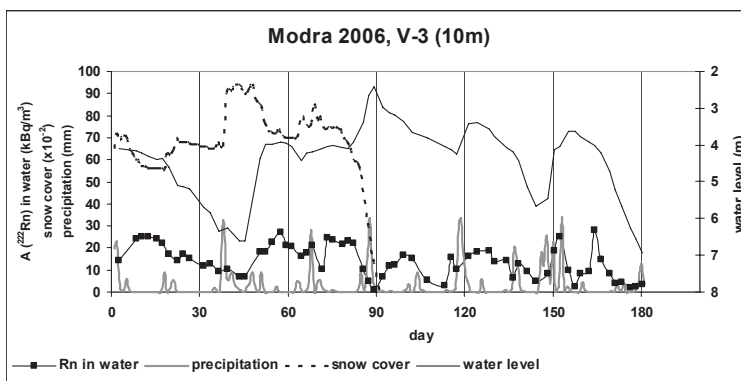


Fig. 3 The courses of the  $^{222}\text{Rn}$  activity concentration in water, precipitation amount, the state of the water level and snow cover in V-3 since January to June 2006

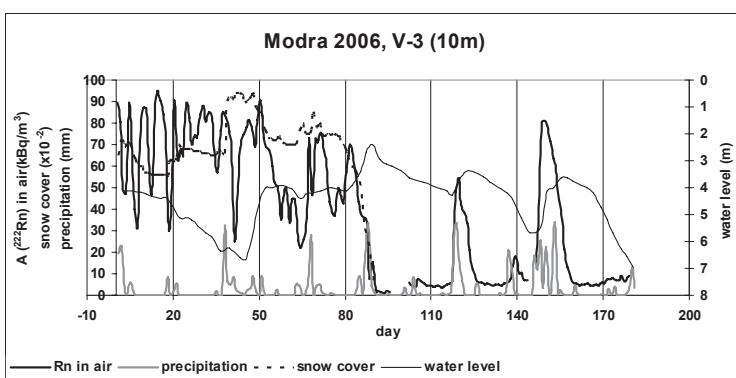


Fig. 4 The courses of the  $^{222}\text{Rn}$  activity concentration in borehole air, precipitation amount, the state of the water level and snow cover in V-3 since January to June 2006

The courses of the  $^{222}\text{Rn}$  activity concentrations in borehole air and water were not completely the same. The values of the  $^{222}\text{Rn}$  activity concentration in water were significantly lower. But the decrease during the melting of snow appeared at the same time, equally the increases after the raining were visible.

## DISCUSSION

Since January to the end of March 2006, the study area was covered by thick layer of snow, the snow cover reached approximately 0,60–0,90 m. At the end of March the snow started to melt and it disappeared completely during approximately ten days. This rapid and sudden melting created an extensive volume of water, who permeated through fissures in rock and the water level significantly increased in every borehole. On the contrary, the  $^{222}\text{Rn}$  activity concentrations in water decreased. We assume, that the transport of water through soil cover and rock beneath the soil into the boreholes was in this case too quick for enriching of the borehole water with radon.

Only the V-1 and V-3 boreholes were evidently affected by precipitation. Rainfall induced the distinct increase of water level and related changes of  $^{222}\text{Rn}$  activity concentration in water.

In V-1 the clear anticorrelation between the state of water level and  $^{222}\text{Rn}$  activity concentrations in water was observed. The situation in V-3 was partially different. The rainfall increased the water level like in V-1 and the courses of water levels in both boreholes were almost the same. But the growth of  $^{222}\text{Rn}$  activity concentration in V-3 was lower and shorter like in V-1, the maximal value appeared approximately after 10 days. Also the increased values returned to the previous state sooner like in V-1, after 15 days. In V-1 the maximum appears later, roughly 20 days after raining. It seems, that the rapid decrease of  $^{222}\text{Rn}$  activity concentrations in water in V-1 was probably caused by subsequent raining.

At the end of June the water level in V-1 significantly decreased and simultaneously the  $^{222}\text{Rn}$  activity concentration in water descended. The hot and dry weather caused drying up the water from soil pores and rock fissures and cut off radon transport by water through rock environment to the borehole water.

The values of the  $^{222}\text{Rn}$  activity concentrations in water at V-3 borehole were considerably lower in comparison to V-1. The V-1 borehole is situated at the base of a small hill, during the raining, rainfall water flows

down the slope. Therefore the increase of water level in V-1 is caused not only by rainfall water, but also by draining of water from hill. That is why the changes of water levels were steeper like in V-3, up to 3m, while in V-3 only about 2 m. Immediately after raining, the  $^{222}\text{Rn}$  activity concentrations in water decreased. After some days it started to rise up, because the water, slowly infiltrated through the soil and rock into the borehole, was enriched in radon occurred in rock and soil pores.

Similarly the  $^{222}\text{Rn}$  activity concentration in borehole air in V-3 was affected by rainfall water. The maximal values of  $^{222}\text{Rn}$  activity concentration in borehole air occurred after the raining, when probably infiltrating water displaced the air rich in radon from surrounding rock's pores and fissures into the borehole air. The  $^{222}\text{Rn}$  activity concentration in borehole air decreased on the initial state after approximately five days, probably in consequence of borehole ventilation.

The V-2 borehole was not markedly influenced by precipitation. The depth of this borehole is too deep for infiltration of rainfall water. Rainfall did not give a rise to the increase of a water level and therefore did not cause any change of  $^{222}\text{Rn}$  activity concentrations.

## CONCLUSION

The melting of snow at the end of March significantly affected the state of water level in all three investigated boreholes.

The results obtained from six months of our investigation show, that only shallow boreholes V-1 and V-3 were significantly affected by precipitation. The water level increased immediately after the raining. The  $^{222}\text{Rn}$  activity concentration in water initially decrease, but after several days increased, because of the slow transport of water through soil and rock pores. Equally the  $^{222}\text{Rn}$  activity concentration in borehole air in V-3 was affected by rainfall, its rapid increase was observed after the raining.

No changes in  $^{222}\text{Rn}$  activity concentration in water or in the state of water level caused by precipitation were observed in V-2 borehole.

## Acknowledgement

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The authors are indebted to the staff of the Modra AGO for provision of the rainfall data measured at this locality.

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# POLYCYCLIC AROMATIC HYDROCARBONS IN THE SAMPLES OF ENVIRONMENT

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Translated by Martin Divočoš

## ABSTRACT

Polycyclic aromatic hydrocarbons (PAHs) represent one group of toxic organic substances in the environment. We determined PAHs in the samples of water and river sediments from river Zolna, in the samples of soils and plants from surrounding of Zolna. The river Zolna flows directly through woodprocessing factory area. The impregnation division together with associated impregnated materials store is considered the most important source of PAH contamination in the surrounding area. We analysed the 16 compounds (PAHs) by List of the priority pollutants by EPA by the HPLC method.

**Key words:** Polycyclic Aromatic Hydrocarbons (PAHs), contamination of environment, determination of PAHs

## INTRODUCTION

The field of ecology has gained a higher importance after entering into European Union. Emphasis has been placed not only on the new and actual damages to the environment, but also on the ones caused in the past, which often present frequent and very complex problems.

The contribution presents results of polycyclic aromatic hydrocarbon contamination research of the river Zolná basin on the grounds of town of Zvolen.

Polycyclic aromatic hydrocarbons (PAH) belong to the highly toxic compounds present in all components of the environment. A small part of PAHs are created by natural processes which take part in nature (geological synthetic processes, volcanic activity, biosynthesis of some species of sea-grass and higher plants). A higher amount of PAHs enter the environment through antropic activities. The main process causing the creation of polyaromates is incomplete burning of organic substances, they are part of fossil fuels and fossil fuel products, we may find them in the roasted or charbroiled meat, cigarette smoke, roasted coffee, caramelized sugar.

## MATERIAL AND METHODS

The main producers of polycyclic aromatic hydrocarbon pollution in the town of Zvolen are the heating power complex, home hearths, transport and wood impregnation department of the wood processing company, through which river Zolná flows. These are the mean ways how PAHs pollute the atmosphere and they either directly or gradually enter the water and soil. PAHs enter the environment from the wood processing complex directly during the process of impregnation (leakage of impregnation oil), but polyaromates are also often washed up from the impregnated materials in the adjoined warehouse.

We determined polycyclic aromatic hydrocarbons in the samples of water, river sediments, soil and also in the plant samples.

In order to gain samples, we chose two sampling localities:

1. before the wood processing company in the flow direction of river Zolná,
2. behind the wood processing company in the flow direction of river Zolná.



Water samples were taken in accordance with STN ISO 5667 – 6 (75 7051).

Sediment samples were taken at places with minimum water flow, where the segment sedimentation is likely to be higher.

Soil samples were sampled from the adjacent bank of the river using a soil pit up to 20 cm depth.

*Baldingera arundinacea* was chosen as a plant sample as it appeared on the both sampling places. The above-ground part of the plant was sampled.

Samples were processed in the laboratory at the same day or most at the next day after sampling. They were conserved in a dark and cold place (to 4°C) up to the day when the analysis took place.

Suspended particles have been removed from the water through filtration. PAHs have been isolated with the use of extraction by n-hexane.

Coarse aggregates and eventually some organic parts (parts of lose plants or animals, accidentally sampled living organisms) were removed from the samples of sediments and soils. Air dried samples were extracted by n-hexane.

Plant material was processed fresh. Sample portions together with the extracting material were processed with the use of a disintegrator.

All acquired extracts were then processed in a standard way. Abundant water was removed by adding calcite carbonate, the extracts were condensed using a vacuum rotary evaporator and in the stream of nitrogen they were steamed off. Evaporate was than dissolved in acetonitrile and analyzed by the method of high performance liquid chromatography.

Conditions of chromatographic analysis:

- column: Lichrospher PAH (Merck)
- mobile phase: A: acetonitrile (gradient grade), B: water
 

0 min:	A: 50%,	B: 50%
5 min:	A: 50%,	B: 50%
12 min:	A: 100%,	B: 0%
30 min:	A: 100%,	B: 0%
33 min:	A: 50%,	B: 50%
- flow speed: 1 cm<sup>3</sup>.min<sup>-1</sup>
- temperature: 35 °C
- detector: Diode Array Detector L – 7455 (Merck – Hitachi)
- detection: UV – 250 nm

Qualitative and quantitative determination of particular PAHs was performed by the method of external calibration. The backing standard was a mixture of 16 polycyclic aromatic hydrocarbons (SUPELCO), which are allocated in the environment according to the List

of main pollutants EPA (US – Environmental Protection Agency): *Naphthalene (Naft)*, *Acenaphthylene (Acnft)*, *Acenaphthene (Ace)*, *Fluorene (Flu)*, *Phenanthrene (Fen)*, *Anthracene (Ant)*, *Fluoranthene (Flt)*, *Pyrene (P)*, *Benzo(a)anthracene (BaA)*, *Chrysene (Chry)*, *Benzo(b)fluoranthene (BbF)*, *Benzo(k)fluoranthene (BkF)*, *Benzo(a)pyrene (BaP)*, *Dibenzo(a,h)anthracene (DBA)*, *Benzo(g,h,i)perylene (BghiP)*, *Indeno(1,2,3-cd)pyrene (IP)*.

Particular PAHs were identified in the samples by comparison of their ultraviolet spectra with spectra of standard substances. Concentration of allocated compounds was determined according to height of peaks.

## RESULTS AND DISCUSSION

Measured results are stated in the table no. 1. Higher amounts for all matrices of the environment were measured at the second sampling place. The most PAHs were found in the sediments. A low concentration was found in the samples of water and sediments. Water is a less stable matrice, which is easily affected by external factors. There is just a small portion of water soluble PAHs, polyaromates which are usually found in water are absorbed into particles. They settle into sediments according to their size and weight and by these means they disappear from the water.

Sediments are more stable, the external influences are not so important in such a rate for them. Particles with absorbed PAHs tend to settle rather quickly, but when affected by certain factors (increased appearance of humic acids, stronger water flow) they may be washed up again. Matrice, which characterizes pollution of a locality with PAHs in the most precise way is soil, material with relatively stable chemical structure.

During the detailed study in the given field, rather lower values have been found. Blaho, Kačík [1] were examining and determining oil substances as well as polyaromatic hydrocarbons in the sediments of the river Zolná. In the areas behind the department of impregnation, they found oil substances reaching values more than 400 mg.kg<sup>-1</sup>, and the amount of PAHs was about ¾ of the overall value. During the research 2001–2002 [2, 3] the samples of water and sediments were sampled. Amount of PAHs in the sediments approximated to value 2000 mg.kg<sup>-1</sup>.

Plant samples are meanwhile a less examined material concerning PAH amounts. The reasons for this are mainly difficult analytical methods and ambiguity of gained results. It is questionable whether

Tab. 1 Measured PAH values in the samples of environment

PAH	water [ $\mu\text{g}\cdot\text{dm}^{-3}$ ]		sediments [ $\text{mg}\cdot\text{kg}^{-1}$ a.s.]		soil [ $\text{mg}\cdot\text{kg}^{-1}$ a.s.]		plants [ $\text{mg}\cdot\text{kg}^{-1}$ a.s.]	
	1	2	1	2	1	2	1	2
Naft	–	–	–	–	–	–	–	–
Acnft	–	–	–	–	–	–	–	–
Ace	1,81	6,69	1,474	10,671	1,512	10,467	–	–
Flu	–	–	–	18,952	–	–	–	–
Fen	–	–	–	23,138	–	0,3724	–	–
Ant	–	–	–	–	–	–	–	–
Flt	–	0,39	0,0827	35,542	0,0804	4,115	–	1,949
P	–	0,28	0,0533	18,523	0,0548	2,650	–	1,044
BaA	–	–	0,0143	4,335	0,0342	1,294	–	–
Chry	–	–	0,0115	3,536	0,0359	1,830	–	–
BbF	–	–	–	1,185	0,0238	0,600	–	–
BkF	–	–	–	–	–	–	–	–
BaP	–	–	–	0,285	0,0328	0,199	–	–
DBA	–	–	–	–	–	–	–	–
BghiP	–	–	–	–	–	0,0847	–	–
$\Sigma$	1,81	7,36	1,6358	116,167	1,7739	21,6121	–	2,993

1 – the sample from locality no. 1

2 – the sample from locality no. 2

a. s. – amount of PAHs in absolute dried material

“–” – not measured

given compounds come from the internal structure of the plant, or from the leaf pores into which they get through the air pollution. In our experiment we determined PAHs in the plants from the second sampling place. Measured values allow us to assume, that they entered the plant structure through the contaminated water, whereas by air pollution also plants from the first sampling place would be polluted. These findings are preliminary and they present a part of the research project which is still ongoing.

It is also remarkable to compare the qualitative composition of founded PAHs in the given dies (figures 1–3). In the water samples, mainly PAHs with a lower molecular weight were found, in the sediments and soil PAHs were “heavier”, which are rather quickly removed from water actually by sedimentation thanks to their higher molecular weight [4]. This fact points out the “lurking” danger of PAH washing up from the sediments.

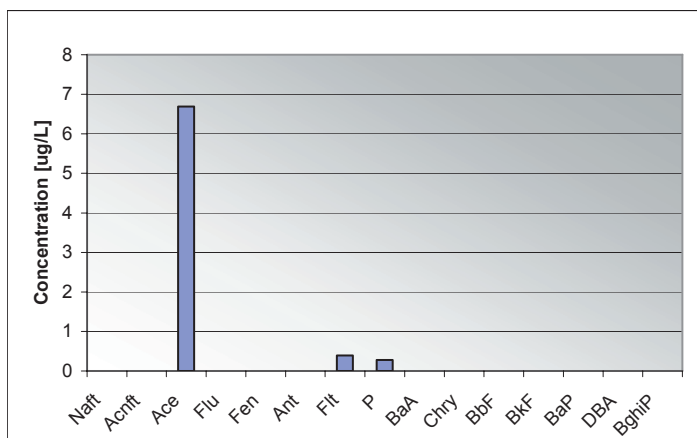


Fig. 1: Graph of amount of PAHs in the water – sample 2

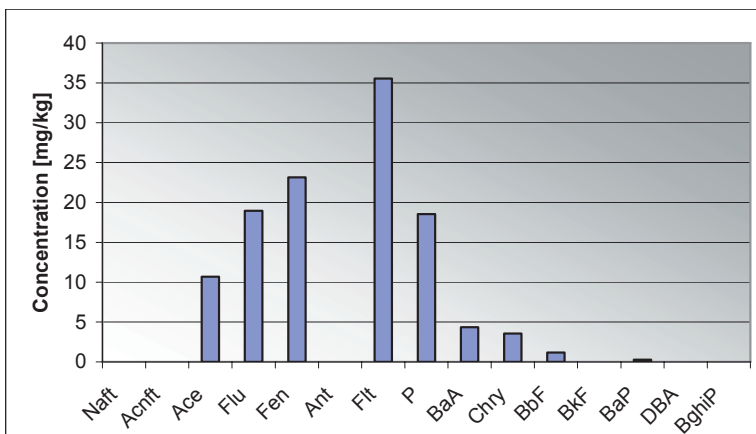


Fig. 2: Graph of amount of PAHs in the sediment – sample 2

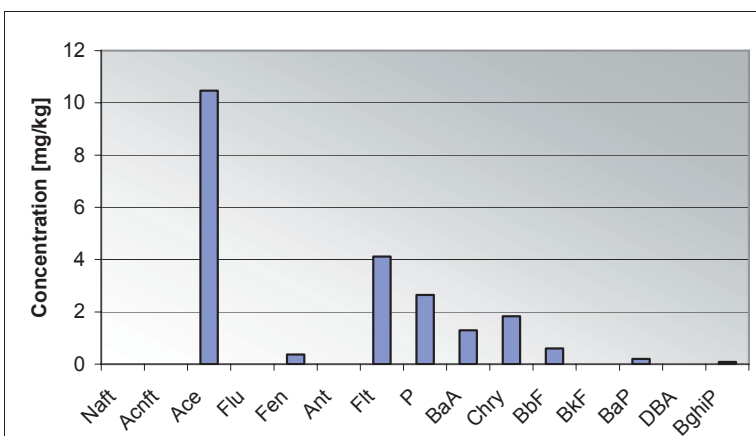


Fig. 3: Graph of amount of PAHs in the soil – sample 2

## CONCLUSION

The paper presents the results of the study of polycyclic aromatic hydrocarbons in the environment. The gained results definitely prove the influence of the wood processing company on the PAH values in the closest surroundings. The highest values were found in the sediment samples. The highest values were measured for acenaphthene, fluoranthene and pyrene.

## Acknowledgement

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# EXAMINATION OF EXPRESS DETERMINATION OF $^{226}\text{Ra}$ IN BUILDINGS MATERIALS USING GAMMA SPECTROMETRY

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## ABSTRACT

In the article is presented the proposal of express method for evaluation of radium concentration in building material. The method is based on estimation function of time dependence of achievement of equilibrium radon daughter products radioactivity with the  $^{226}\text{Ra}$ . The obtained results from one selected sample of building material (porous concrete brick) show, that estimation of radium concentration on acceptable confidence level is possible obtain during some days.

**Key words:**  $^{226}\text{Ra}$ , buildings materials, express method, daughter products

## INTRODUCTION

$^{222}\text{Rn}$  and its decay products are dominant resources of the population radiation dose. Inhalation of short lived radon decay products represents nearly half of the effective population dose from the all natural radiation sources [1]. One of the main problems in radiation protection consist in formation of the lung cancer affected by this radionuclides, therefore reduction of this cancer type probability to the minimal level is very actual question.

Possible radiation sources can be found in buildings, in which we live or work, because there we spend most of time of our life.  $^{226}\text{Ra}$  present in building materials is the main producer of the  $^{222}\text{Rn}$  in dwellings. Some of the natural raw materials (lime, clay, sand, gravel etc.) used in building industry, release radon according to their geological origin, composition and graininess. This is documents for example, by results of measurements of samples of building material with different structure and graininess presented in [2] which show different concentration of  $^{226}\text{Ra}$ , in gravel 5,5 Bq.kg<sup>-1</sup>, in sand 8,5 Bq.kg<sup>-1</sup> a in cement 28,2–46,9 Bq.kg<sup>-1</sup> (concentration are different for various kinds of cement). Radon exhalation from building commo-

dity influence except amount,  $^{226}\text{Ra}$  concentration and exhalation rate of used materials also technology of the processing. For example using fly ash in production of the building materials causes that concentration of  $^{226}\text{Ra}$  reached the value of 85–222 Bq.kg<sup>-1</sup> [3].

The very frequently used method for radium concentration determination in various materials is based on measurement of concentration of radon daughter products in radioactive equilibrium with radium activity. Achieving of such equilibrium requires, due to radon half life, for hermetized samples spent time approximately about four weeks. After elapse such time interval, the radioactive equilibrium is on acceptable level enables evaluation of radium concentration. Presented express method can enable shorten the necessary time for radium concentration estimation based on above described method. This method should help with effective and time undemanding monitoring of the  $^{226}\text{Ra}$  concentration in building materials.

## MATERIALS AND METHODS

For demonstration of using express method was used brick from porous concrete (“Porobeton”) that was divided into eight separate parts. Blocks of brick

were measured by semiconductor HPGe 280 cm<sup>3</sup> detector in the low background shield [4] that is situated in laboratory of gamma spectrometry of Department of Nuclear Physics and Biophysics of Comenius University Bratislava. <sup>226</sup>Ra concentration was evaluated from its daughter products gamma lines – <sup>214</sup>Bi (609,3 keV) and <sup>214</sup>Pb (351,9 keV).

When brick was separated into eight homogenous parts, they were separately measured on the HPGe detector. After the first measurement, blocks were separately hermetical packed into the plastic wrap and measured again in various time intervals after packing for a one month. After a month became radioactive equilibrium in packed samples and the activity of <sup>226</sup>Ra was determined from activity its daughter products.

The four most suitable brick parts were chosen and separately grinded on the ball grinder. The parts were grinded to different graininess. Crushing enlarge the surface from which the <sup>222</sup>Rn is released to air volume [5], [6]. Modified samples were putted into the cylindrical chambers and hermetically enclosed. The chambers were measured in various time intervals from hermetically enclosing. After radioactive equilibrium became, the activity was determined.

$$A = \frac{N}{I \cdot \epsilon} \quad 1$$

where

A [Bq] – activity of the sample

N [s<sup>-1</sup>] – counts per second

I – number of emitted gamma rays per decay

ε – efficiency of detector

The detection efficiency of various geometry detector-sample was specified by Monte-Carlo simulation [7].

## RESULTS AND DISCUSSION

Concentration of <sup>226</sup>Ra in solid materials was evaluated by its daughter products after radioactive equilibrium in hermetically closed samples. The sample was separated into eight parts and seven was measured with and without hermetic seal. The results are in Table 2. Diversity of activity in single samples is caused by leakage of plastic wrap that brick was packed in.

After measurement of the seven whole samples, four samples of Porobeton brick were grinded to various graininess and were measured for a one month.

On Fig. 1 is presented percentage difference between the counts from grinded opened and enclosed brick for daughter products of <sup>226</sup>Ra.

Fig. 2 and Fig. 3 show fitted curves of activities time dependences of the <sup>222</sup>Rn daughter products <sup>214</sup>Bi and <sup>214</sup>Pb, respectively. The volume of sample should be much larger than volume of the air in chamber because <sup>222</sup>Rn will concentrate in this air and the air volume will change the efficiency of detection. After approximately seven half lives (means approximately one month) become radioactive equilibrium. Express method means that we actually know the function of time dependence of the daughter products concentration and could from its progress predict concentration in any time after the sample was hermetically enclosed that means soon as after a month.

The smaller grains show the faster grow activity to the total value that means for express method is most suitable as smallest as possible granularity of building material sample. The simulation of efficiency assume homogenous material and equally allocation of <sup>222</sup>Rn atoms in all volume of the sample. Growing of the curves on Fig.2 and Fig.3 is caused by uneven distribution of <sup>222</sup>Rn atoms in closed chambers and formation of radioactive equilibrium. After hermetization of the samples are atoms of <sup>222</sup>Rn mainly in soil

Table 1 Physical characteristic of grinded samples

Mark	Graininess	Weight [g]	ρ <sub>vz</sub> [g.cm <sup>-3</sup> ]
sample 1	0,1–1 cm	608,4	0,56172
sample 2	0,1–0,5 cm	595,8	0,5658
sample 3	0,05–0,1 cm	575,8	0,88239
sample 4	0,01–0,05 cm	680	0,64576

Table 2 Activity [ $\text{Bq}\cdot\text{kg}^{-1}$ ] measured in opened and closed bricks

Sample	Opened	Hermetized
Brick 1	$64,6 \pm 1,7$	$73,4 \pm 1,6$
Brick 2	$63,7 \pm 1,6$	$78,3 \pm 1,8$
Brick 3	$65,6 \pm 1,7$	$72,3 \pm 1,8$
Brick 4	$71,8 \pm 1,4$	$76,6 \pm 1,5$
Brick 5	$69,6 \pm 1,8$	$78,3 \pm 2,0$
Brick 6	$70,5 \pm 1,9$	$72,9 \pm 1,8$
Brick 7	$69,1 \pm 1,8$	$69,7 \pm 1,8$

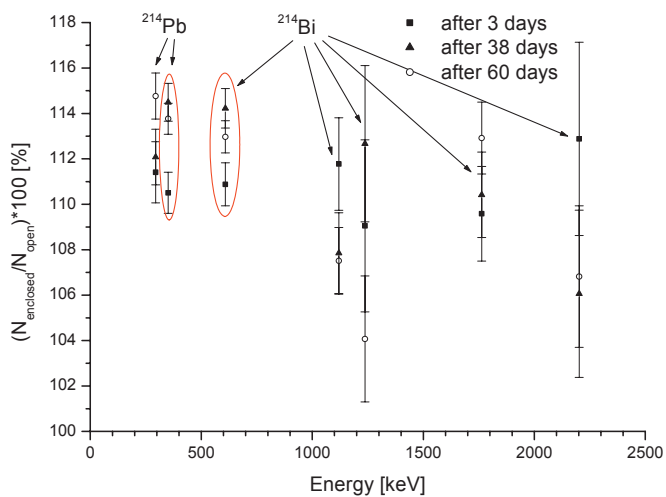
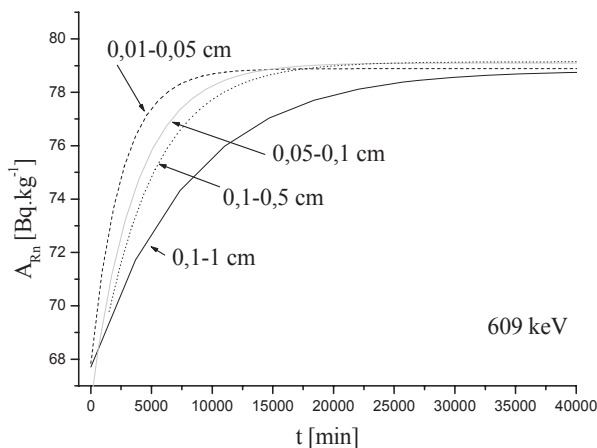


Fig. 1 Percentage differences between counts measured enclosed and opened grinded Sample 3 (graininess 0,05–0,1 cm) for various time intervals from closed

Fig. 2 Growing of activity  $^{214}\text{Bi}$  in closed chambers

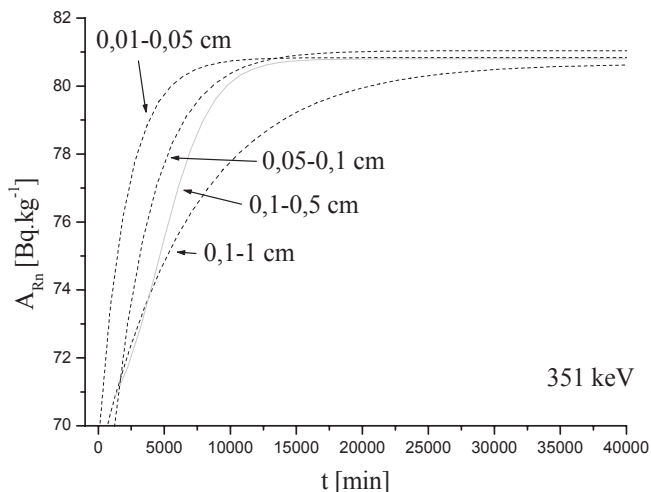


Fig. 3 Growing of activity  $^{214}Pb$  in closed chambers

grains, during the measurement they fill the air volume up. Allocation of  $^{222}Rn$  atoms at the same level as in the simulation became in sample with smaller grains faster than in sample with large grains.

Measured radioactivities values of brick parts are presented with  $1\sigma$  confidence level.

## CONCLUSION

The activities of  $^{214}Bi$  and  $^{214}Pb$  in four grinded and hermetically enclosed samples were measured during one month. After the month was determined concentration of  $^{226}Ra$  in Porobeton brick as  $80 Bq \cdot kg^{-1}$  with 3,5 % uncertainty. The uncertainty of measured data after about 5 days is about 1,5 % and of fitted function is about 3 %, whereby the agreement of all results is good (table 3). The systematic uncertainty of

used express method varied with the graininess and the time passed after closing. For example measurement of sample4 (granularity 0,01–0,05 cm) after a few (3–4) hours after closing has systematic uncertainty about 13 %, but after 5 days is systematic uncertainty about 3 %. In measurement of sample1 (granularity 0,1–1 cm) is systematic uncertainty after few hours of closed also about 13 %, but after 5 days is still about 7 %. From the measurement of activity follows that activity in sample with the smallest grains grows faster than from the sample with biggest grains. This variation is caused by different geometry of simulation of the efficiency and production of radioactive equilibrium.

The presented results are only introductory, the better verification of this method required more measurements of substantially more samples from various materials used in building industry.

Table 3 Activity [ $Bq \cdot kg^{-1}$ ] of the daughter products and  $^{226}Ra$  in hermetical enclosed grinded sample obtained by measurement on detector after a month (classic method CM) and using fitted function after a 5 days (express method EM)

	$^{214}Bi$ (EM)	$^{214}Pb$ (EM)	$^{226}Ra$ (CM)
Sample1	$76,5 \pm 1,2$	$74,3 \pm 1,3$	$78,8 \pm 1,9$
Sample2	$80,5 \pm 1,5$	$78,31 \pm 1,3$	$78,9 \pm 1,6$
Sample3	$78,6 \pm 2,0$	$76,5 \pm 2,3$	$81,2 \pm 0,9$
Sample4	$79,4 \pm 1,9$	$77,4 \pm 1,4$	$82,3 \pm 2,2$
Average rate (after month)	$81,6 \pm 2,2$	$78,1 \pm 2,1$	$80 \pm 2,8$

### Acknowledgement

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## VARIATION OF $^{222}\text{Rn}$ ACTIVITY CONCENTRATION IN WORKPLACE

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### ABSTRACT

The aim of this report was to demonstrate the impact of different approaches to determining of the average radon activity concentration for the calculation of effective dose from radon. Continual set of data for modelling of temporal variations was obtained. We found out that frequency distributions of measured radon activity concentration differ for various parts of day and year.

**Key words:** Indoor radon, frequency distribution, daily and annual variation, effective dose, mean activity concentration.

### INTRODUCTION

Protection of the population against ionizing radiation is now among the most discussed topics. It is the radon ( $^{222}\text{Rn}$ ) that is the most important natural source of radiation exposure of the population. Hence an appropriate care is taken in the field of radon radiation protection. Residential areas are the greatest source of radon population exposure.

Measurement of indoor radon and its daughters allows us to better understand the mechanisms influencing radon concentration, test the models describing its variations, identify and quantify the sources of radon in residential areas, specify the procedures for measurement of radon concentration by means of integral methods and for evaluation of data from these measurements, control the efficiency of anti-radon measures etc. For the estimation of radiation exposure the measurements carrying the information about average radon activity concentrations are needed. Such measurements can be done either by year-long or by short-term measurements and then, with the utilization of radon models, the average annual radon activity concentration can be determined. Integral or continual measurements of radon are suitable for this purpose.

### Behaviour of radon in enclosed areas and effective dose from radon

Under the term ‘indoor air’ we understand the air inside a flat, house or other enclosed area. Main sources of radon in buildings are: underlying rock, building material, outdoor atmosphere and, to a lesser extent, the tap water and natural gas [1].

Radon gets into enclosed spaces by exhalation from the floor, walls, items in the room, natural gas, water used in the household and by the air entering the room from the outside. Radon indoor concentration varies in time. Under the assumption of homogenous distribution of activity concentration inside a building, the temporal change of activity concentration can be described by the differential equation [2]:

$$\frac{dA(t)}{dt} = \frac{R}{V} - A(t)(\lambda + \lambda_v) \quad (1)$$

where:

$A(t)$  – radon activity concentration in the room at the time  $t$  [ $\text{Bq}\cdot\text{m}^{-3}$ ],

$R$  – radon entry rate [ $\text{Bq}\cdot\text{s}^{-1}$ ],

$V$  – volume of the room [ $\text{m}^3$ ],

$\lambda$  – radon decay constant [ $\text{s}^{-1}$ ],

$\lambda_v$  – air exchange rate [ $\text{s}^{-1}$ ].

For a steady state condition  $\frac{dA(t)}{dt} = 0$  and under the assumption  $\lambda_v \gg \lambda$  (because:  $0,1 \text{ h}^{-1} < \lambda_v < < 3 \text{ h}^{-1}, \lambda = 7,6 \cdot 10^{-3} \text{ h}^{-1}$ ) we get the mean  $^{222}\text{Rn}$  activity concentration in the room:

$$A = \frac{R}{\lambda_v \cdot V} \quad (2)$$

Let us consider three interpretations of equation (2) (depicted in Fig. 1 [3]), in dependency  $R$  on  $\lambda_v$  and:

a)  $R = \text{const.}, \lambda_v \sim \Delta T$  ( $\Delta T$  is indoor-outdoor temperature difference)  $A$  is indirectly proportional to  $\Delta T$  with a maximum in the afternoon and minimum during the night

b)  $\lambda_v = \text{const.}, R \sim \Delta T$

$A$  is proportional to  $\Delta T$  with a minimum in the afternoon and maximum during the night

c)  $R(\Delta T), \lambda_v(\Delta T)$

for  $A$  we can write  $A \approx \frac{R(\Delta T)}{\lambda_v(\Delta T)}$ ,  $A$  can rise or fall as a function of  $\Delta T$

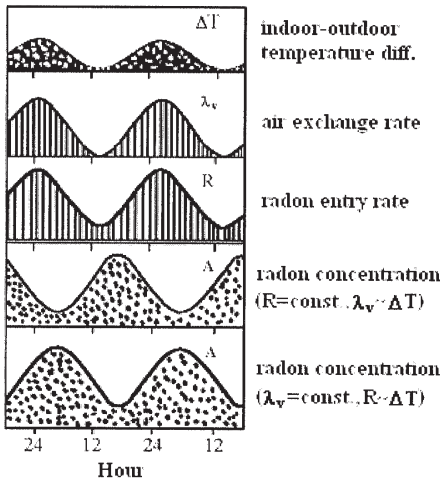


Fig. 1 Variations of indoor radon as a function of  $R$  and  $\lambda_v$  [3]

From a structural and building utilization point of view, two aspects play a key role in affecting the radon activity concentration [1]. The first one is the ventilation system that may have an influence on the air pressure difference between inside and outside, forcing the air to flow inside. The second one is the foundation construction that affects the flow of air between the soil and the building [4]. Other factors are meteorological effects (barometric pressure, temperature, wind speed)

as well as residential activities (heating, ventilating).

From the  $^{222}\text{Rn}$  activity concentration it is possible to determine the effective dose rate from  $^{222}\text{Rn}$  in indoor air by the equation [5]:

$$\dot{E} = a_{Rn} \cdot F \cdot f \quad (3)$$

where:

$a_{Rn}$  – average indoor  $^{222}\text{Rn}$  activity concentration [Bq.  $\text{m}^{-3}$ ],

$F$  – equilibrium factor characterizing the degree of radiation equilibrium between radon and its short-lived daughters ( $F \sim 0,4$ ),

$f$  – dose conversion factor  $\left[ f = 9 \frac{\text{nSv}}{\text{Bq} \cdot \text{h} \cdot \text{m}^{-3}} \right]$ .

For the annual effective dose we can write:

$$E = \dot{E} \cdot t_{in} = a_{Rn} \cdot F \cdot f \cdot t_{in} \quad (4)$$

where:

$t_{in}$  – the total time spent indoors during the year [h].

## MEASUREMENT DEVICE DESCRIPTION

For the monitoring of radon activity concentration in indoor air the radon monitor AlphaGUARD developed by Genitron company is used at the Department of Nuclear Physics and Biophysics, Faculty of Mathematics, Physics and Informatics, Comenius University, Bratislava. The detector itself is a cylinder-shaped ionization chamber with an active volume of 0,56 liters. The air gets inside the chamber by means of passive diffusion through an aerosol fibre-glass filter. The ionization chamber sensitivity is about 0,05 imp.  $\text{min}^{-1}$  for 1  $\text{Bq} \cdot \text{m}^{-3}$  of  $^{222}\text{Rn}$  activity concentration. The background signal is lower than 1  $\text{Bq} \cdot \text{m}^{-3}$  [6]. The monitor can record the  $^{222}\text{Rn}$  activity concentration, temperature, pressure and humidity of the room in 1-hour intervals.

## RESULTS AND DISCUSSION

Radon concentration in a room at FMPI CU was monitored during a period of one year (April 2004 – March 2005). The room is situated on the second floor, with north-oriented windows, and is shielded against direct influence of wind by other parts of the building.

Meteorological conditions, building materials and building construction are among the important factors affecting radon activity concentration in indoor air.

According to these factors, indoor radon activity concentration shows daily and seasonal variations.

The daily variations obtained by us have a shape of a regular wave with a maximum in the early morning and minimum in the afternoon. The daily wave calculated on the basis of all radon data obtained during

the course of one year show a maximum in the early morning (at about 04–06 hours) and a minimum in the afternoon (at about 15–17 hours) (Fig. 2).

Seasonal variations show a minimum in summer months (June – August) and a maximum in late autumn and winter months (October – February). The yearly

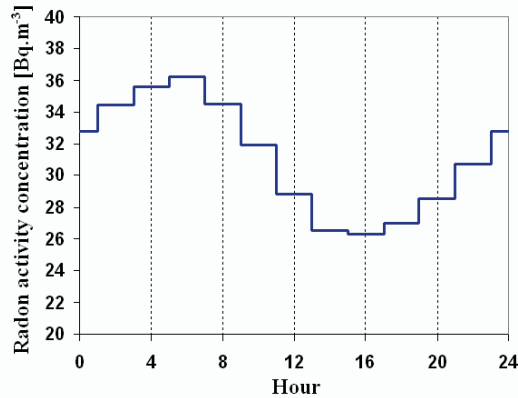


Fig. 2 Mean daily course of  $^{222}\text{Rn}$  activity concentration obtained in investigated room in the period from April 2004 to March 2005

course obtained by us is depicted in Fig. 3.

High values of radon activity concentration in winter months are caused by high minima of average daily waves in this time period; low monthly mean values in summer months are caused by low placed minima as well as low maxima of average daily waves

in these months. The highest amplitudes of daily waves were observed in summer months ( $\sim 6 \text{ Bq/m}^3$  and  $A_{\text{Rn,max}}/A_{\text{Rn,min}} \approx 1,8$ ), the lowest in winter months ( $\sim 3 \text{ Bq/m}^3$  and  $A_{\text{Rn,max}}/A_{\text{Rn,min}} \approx 1,2$ ) (Fig. 3).

Comparison of summer period (April – September) and winter period (October – March) can be

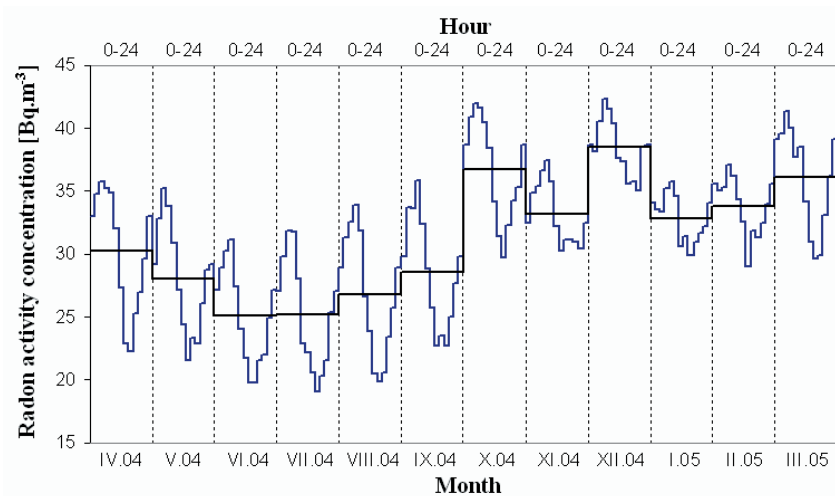


Fig. 3 Average monthly values and daily courses of  $^{222}\text{Rn}$  activity concentration in indoor air (time period April 2004 – March 2005)

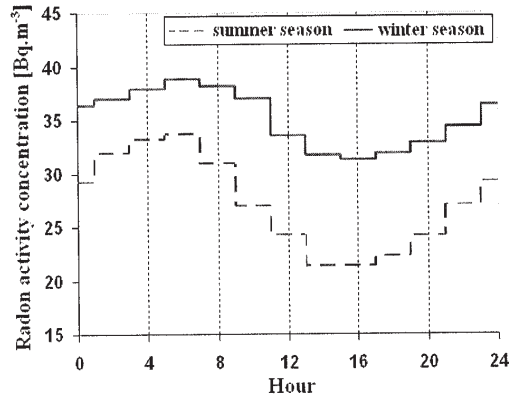


Fig. 4 Comparison of average daily waves for summer (April – September) and winter period (October – March)

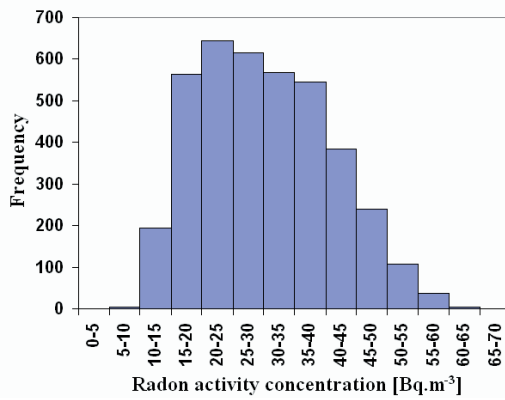


Fig. 5 Frequency distribution of <sup>222</sup>Rn activity concentration in investigated room in the period from April 2004 to March 2005

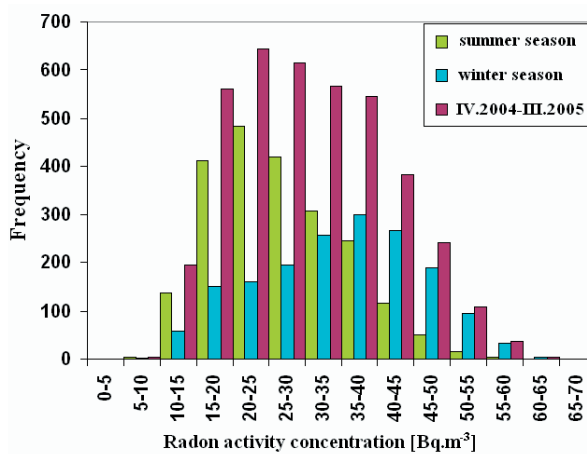


Fig. 6 Comparison of the frequency distribution of <sup>222</sup>Rn activity concentration in investigated room in summer and winter period along with the frequency distribution for the whole year

seen in Fig. 4. The mean daily wave of  $^{222}\text{Rn}$  activity concentration in winter period has one-half the amplitude of the mean daily wave in summer.

Frequency distribution of all  $^{222}\text{Rn}$  activity concentrations measured in indoor air is close to log-normal distribution (Fig. 5).

However, the frequency distributions of activity concentration obtained in different periods of year are different; the frequency distribution in winter is close to normal, while in summer it is close to log-normal (Fig. 6).

If we split the day in summer or winter period into two parts (first part covers the period from 09:00 to 21:00 hours, the second one covers the period from 21:00 to 09:00 hours), we can compare how the frequency distributions differ for various parts of day. As we can see in Fig. 7, the frequency distributions for daytime and nighttime are close to normal in winter period. In summer period the frequency distribution for a

period from 21:00 to 09:00 hours is normal, however, for a period from 21:00 to 09:00 hours the frequency distribution is log-normal.

The frequency distribution results led us to compare the annual courses of radon activity concentration calculated by three different methods (Fig. 8):

1. arithmetic mean during the whole year
2. geometric mean in summer period and arithmetic mean in winter period
3. geometric mean in summer period and arithmetic mean in winter period, but only the data from 09:00–21:00 hours were taken into account

The last method is justified from an employee point of view because it covers the usual working time period.

As follows from Fig. 8, the key factor in determining the effective dose rate – average monthly radon activity concentrations – are lower using the 3rd method. The greatest differences between average

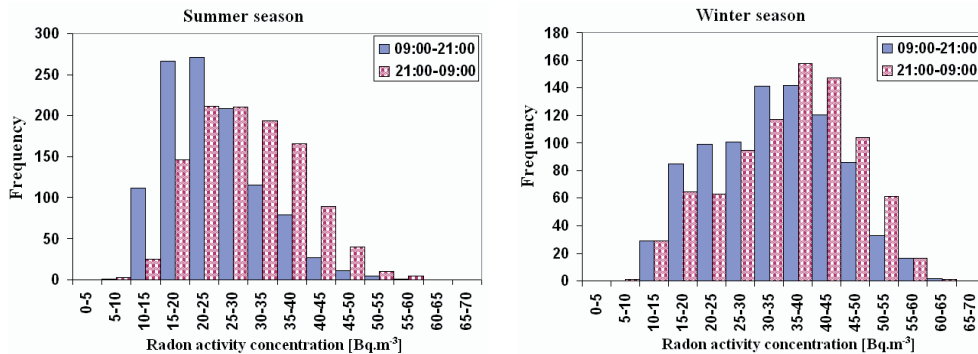


Fig. 7 Comparison of the frequency distribution of  $^{222}\text{Rn}$  activity concentration in investigated room for a period from 09:00 to 21:00 hours and for a period from 21:00 to 09:00 hours for summer and winter months, respectively

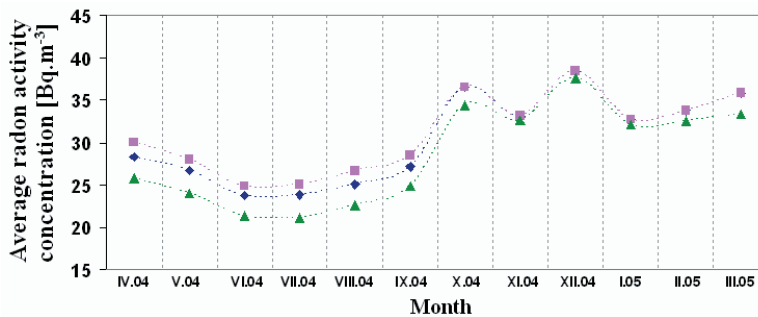


Fig. 8 Average monthly radon activity concentrations calculated by means of: 1 arithmetic mean (■); 2. geometric mean in summer period and arithmetic mean in winter period (◆); 3. after taking into account that it is a workplace, only the period from 09:00 to 21:00 hours was considered, and geometric mean in summer period and arithmetic mean in winter period were used (▲)

monthly radon activity concentrations calculated by different methods, up to 20%, were found in spring and summer months.

On the basis of the average radon activity concentration for individual months during daytime, the annual course of effective dose rate was calculated and compared with the annual course of effective dose rate calculated from all radon activity concentration data (Fig. 9). As one can see, the effective dose rate in winter months is about 1,5 times higher than that in summer months.

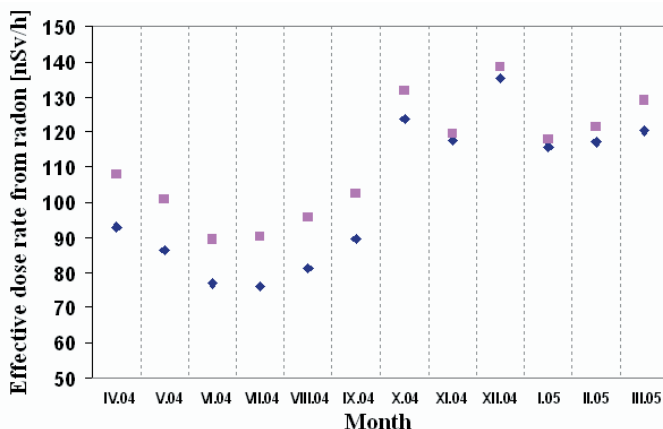


Fig. 9 Comparison of the average  $^{222}\text{Rn}$  dose rate for individual months in indoor air for a period from April 2004 – March 2005 calculated on the basis of all data (■) and on the basis of the data obtained during 09:00-21:00 hours (◆)

According to UNSCEAR [5], the average indoor occupancy  $t_m$  is 7000 hours per year. If we assume only average radon activity concentrations during daytime when determining the annual effective dose rate, then according to (4) we get  $E \sim 0,7$  mSv. This value is about 20 % lower than that obtained by a conservative guess based on average monthly radon activity concentrations.

## CONCLUSION

Knowledge concerning of variations of radon activity concentration were obtained. Daily variations show a maximum in the morning and a minimum in the afternoon, seasonal variations show a minimum in summer months (June – August) and a maximum in late spring and in winter (October – February).

Unlike the expected variations of activity concentration (when the character of the room is taken into account) as a function of thermal gradient  $\Delta T$  and not a time-dependent function of  $R$ , the courses of daily and seasonal variations of radon activity concentration are just opposite. This effect will be thoroughly studied in the future.

Frequency distribution of activity concentrations was found to be different for various parts of day and year. The impact of these distributions on a calculated dose rate is lower than 20 %. Short-term measurements

of radon activity concentration carried out in various parts of year may have more significant impact on the accuracy of the calculation of effective dose rate, when even an uncertainty of 100 % can be produced.

## Acknowledgement

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## SEASONAL VARIATIONS OF $^{13}\text{C}$ AND $^{14}\text{C}$ IN SOIL $\text{CO}_2$

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### ABSTRACT

Long-term measurements of carbon-13 and carbon-14 content in soil  $\text{CO}_2$  are presented. Temporal  $^{14}\text{C}$  and  $^{13}\text{C}$  variations with period of one year has been observed and discussed in two soil levels (exhaled  $\text{CO}_2$  and  $\text{CO}_2$  in depth 0,8 m). Analyses shows that there are significant differences in phase shifts of variations and in fractionation rates at different soil levels.

**Key words:**  $^{13}\text{C}$ ,  $^{14}\text{C}$ , soil, atmosphere,  $\text{CO}_2$ , variations

### INTRODUCTION

There are two major sources of  $\text{CO}_2$  in soil. Partly it is the root respiration of plants and partly the bacterial decomposition of organic matter [1, 2, 3].  $\text{CO}_2$  starts to flow in the opposite direction of the concentration and pressure gradient to reach the thermodynamic and mechanic equilibrium. Such a flow, if measured on the soil surface, is called “the soil respiration” [1]. Root and bacterial respiration plays the key role in  $\text{CO}_2$  production in underground environment. In metabolically active seasons both of them pumps carbon-dioxide into soil capillaries.

This paper deals mostly with temporal changes of relative isotope ratios in soil  $\text{CO}_2$ , defined as

$${}^iR = \frac{[{}^iC]}{[{}^{12}C]}$$
. Here  $[{}^iC]$  stands for concentration of rare carbon isotope ( $i=13,14$ ) and  $[{}^{12}C]$  is concentration of abundant carbon isotope. The more useful and widely used expression of  ${}^iR$  is the “delta-notation”

$$\delta^iC = \frac{{}^iR}{{}^iR_S} - 1$$
. Here the symbol  ${}^iR_S$  stands for the tabulated isotope ratio in reference standard.

A typical temporal pattern of presented data is a variation with a period of 1 year. This period originates mostly from cyclic temperature and moisture chan-

ges as well as from photosynthesis processes variability during the year. Moreover, the isotopic ratios are affected by isotopic fractionation in metabolism of plants and bacteria, diffusion processes and also by carbon-14 enrichment due to the “bomb effect”.

### METHODS

The radiocarbon samples in  $^{14}\text{CO}_2$  chemical form were collected in the area of Faculty of Mathematics, Physics and Informatics, Comenius University, Bratislava (48° 9' N, 17° 7' E, 164 m.a.s.l.). Soil at the sampling area is of type sandy clay [4]. The samples from a depth of 0.8 m have been continually collected by the method of dynamic absorption of  $\text{CO}_2$  in NaOH solution [5,6]. The  $\text{CO}_2$  released from the soil has been collected by ordinary diffusion in the NaOH, surrounded by an accumulation container. In the next step the  $\text{Na}_2\text{CO}_3$  has been precipitated by  $\text{BaCl}_2$  and subsequently the  $\text{BaCO}_3$  was filtered out. The  $\text{CO}_2$  in the gaseous state has been released by  $\text{HPO}_3$  and a small amount of gas was taken to determine the  $\delta^{13}\text{C}$  using mass spectrometry. For the higher stability of  $^{14}\text{C}$  measurement, carbon dioxide released in the previous reaction is converted to  $\text{CH}_4$ . A high-volume gaseous proportional counter with cylindrical symmetry has been used to measure  $^{14}\text{C}$  activity per volume unit. After the isotopic fractionation

correction, the results are presented as  $\Delta^{14}\text{C}$  with standard deviation of 6 ‰. The uncertainty of  $\delta^{13}\text{C}$  measurements is at the level of 1 ‰.

## RESULTS AND DISCUSSION

Although the  $^{13}\text{C}$  and  $^{14}\text{C}$  content in the soil air has been measured since 1997 at FMFI UK, the simultaneous measurements of exhaled air began only in 2000 (see Fig. 1, 2). The separate monitoring of soil and exhaled  $\text{CO}_2$  seems to be justified since there are significant differences between the temporal courses of  $^{13}\text{C}$  and  $^{14}\text{C}$ .

As we can see at Fig. 3, the  $\Delta^{14}\text{C}$  in the exhaled  $\text{CO}_2$  and the  $\text{CO}_2$  in a depth of 0.8 m obeys the common

one year period cycle. The minima occur in winter or in early spring and maxima in late summer. The mean value of  $^{14}\text{C}$  annual variation as well as its phase are just slightly shifted, contrary to  $^{13}\text{C}$  with significant differences in both mentioned parameters. Considering the papers [7,8], the best way to describe the variations of this type is by using the equation:

$$\Delta^{14}\text{C}(t) = A + B \cos \left[ 2\pi \left( \frac{t}{T} + \varphi \right) \right]. \quad (1)$$

Here symbol  $A$  stands for annual  $\Delta^{14}\text{C}$  mean value,  $B$  represents amplitude of variation,  $T=12$  months is period of variation and finally  $\varphi$  is the phase shift. The semiempirical form (1) is a result of two-compo-

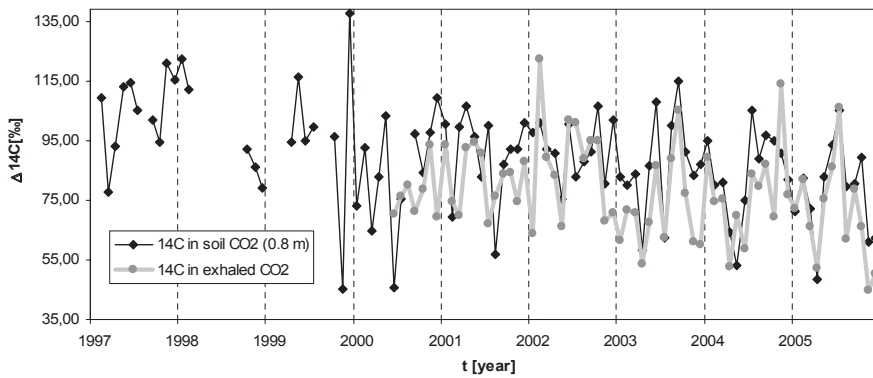


Fig. 1  $\Delta^{14}\text{C}$  at different soil levels

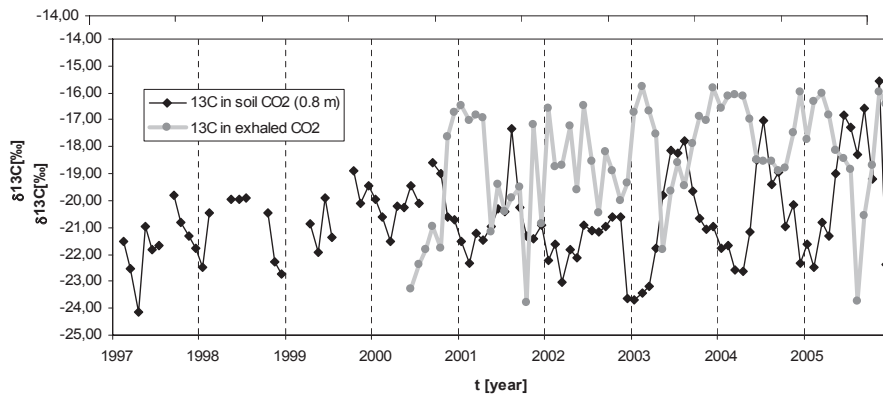


Fig. 2  $\delta^{13}\text{C}$  at different soil levels

ment box-model theory. A strong agreement of (1) with experimental atmospheric data convinced us that (1) is a good choice for our purposes. Comparing the results, one will find that the soil  $\text{CO}_2$  is more depleted of  $^{13}\text{C}$  relatively to atmosphere than it is in the case of  $^{14}\text{C}$  (Fig. 3,4).

The relative difference between the  $\delta^{13}\text{C}$  in a depth of 0.8 m and the  $\delta^{13}\text{C}$  in the atmosphere is nearly 92 % of atmospheric value in the years 2001–2005, whereas it is only 17 % in the case of carbon-14. In all likelihood, it can be explained by isotopic fractionation (systematic discrimination) of  $^{13}\text{CO}_2$  molecules in photosynthesis and other metabolic processes of plants and

bacteria.

The above-mentioned phenomenon, the fractionation of isotopes, is taking place if molecules of the same type, but of different masses act in a diffusion or chemical reactions. The molecules of  $\text{CO}_2$  containing  $^{13}\text{C}$  are partly discriminated in a plant respiration process, so  $\delta^{13}\text{C}$  is at lower level in the soil air than in atmospheric one.

If one carries out the harmonic analyses of measured data, he will obtain the coefficients A,B and  $\varphi$ , demonstrated at Fig. 5–10.

An interesting conclusion (showed at Fig. 5) is that  $\Delta^{14}\text{C}$  in the atmosphere is nearly of the same co-

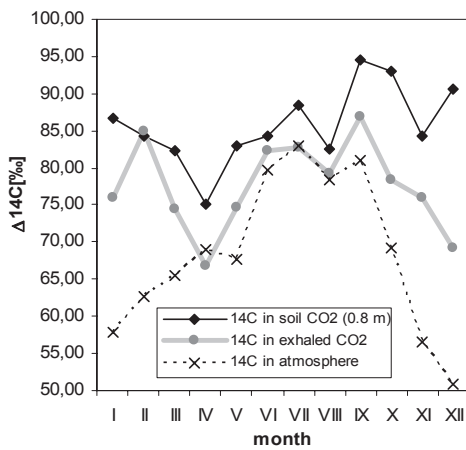


Fig. 3 Average  $\Delta^{14}\text{C}$  variation in soil  $\text{CO}_2$  during years 2000–2005

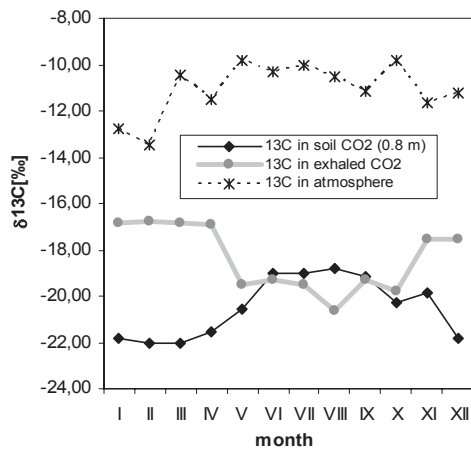


Fig. 4 Average  $\delta^{13}\text{C}$  variation in soil  $\text{CO}_2$  during years 2000–2005

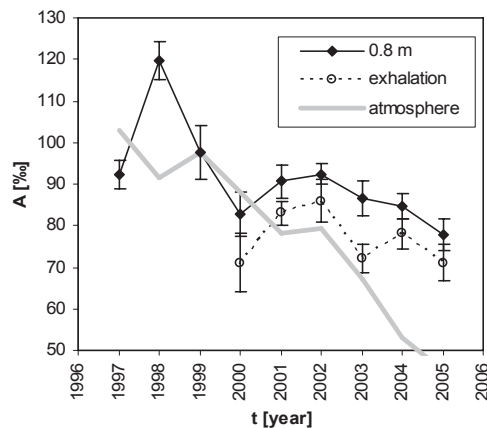


Fig. 5 Temporal courses of coefficients A (equation (1)) for  $^{14}\text{C}$  at different depth levels, comparatively to atmospheric data

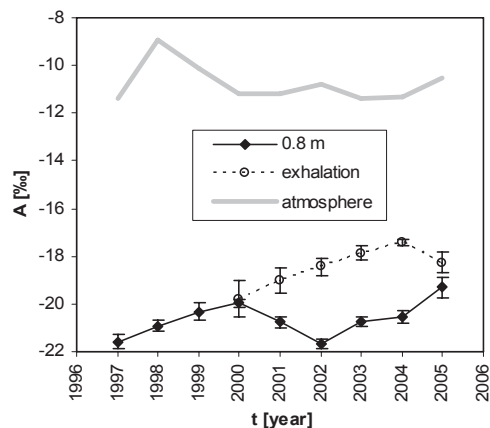


Fig. 6 Temporal courses of coefficients A (equation (1)) for  $^{13}\text{C}$  at different depth levels, comparatively to atmospheric data

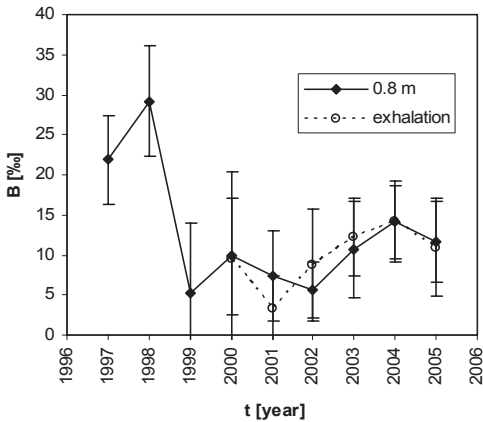


Fig. 7 Temporal courses of coefficients  $B$  (equation (1)) for  $^{14}\text{C}$  at different depth levels

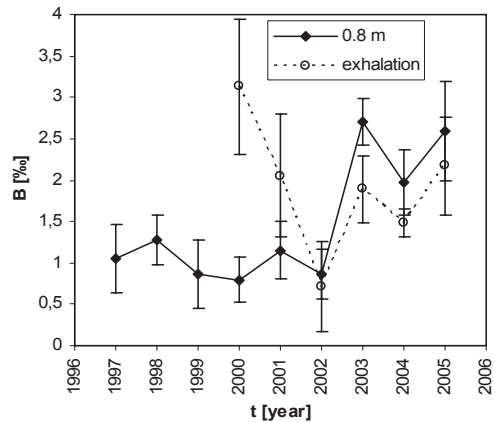


Fig. 8 Temporal courses of coefficients  $B$  (equation (1)) for  $^{13}\text{C}$  at different depth levels

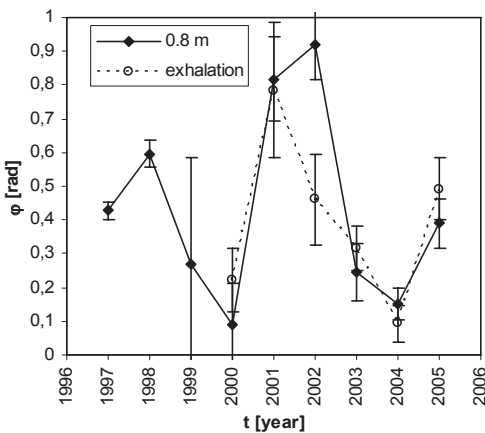


Fig. 9 Temporal courses of coefficients  $\varphi$  (equation (1)) for  $^{14}\text{C}$  at different depth levels

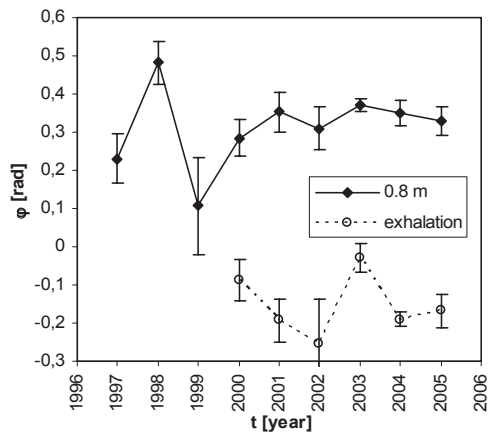


Fig. 10 Temporal courses of coefficients  $\varphi$  (equation (1)) for  $^{13}\text{C}$  at different depth levels.

urse as  $\Delta^{14}\text{C}$  in both of involved depths. But there is a completely different situation if we take a look at Fig. 6. Although atmospheric  $^{13}\text{C}$  content is almost constant in time, the soil environment has been slowly enriched by  $^{13}\text{C}$ . Significant differences in temporal courses have been encountered also for parameter  $\varphi$ . While in the case of  $^{14}\text{C}$  the data from different soil levels are synchronous, there is an obvious phase shift in  $^{13}\text{C}$  data.

As one can see (Fig. 10), the phase shift increases gradually with depth in the case of  $\delta^{13}\text{C}$ . Since bacteria are the main contributors to  $\text{CO}_2$  in deeper soil levels and their metabolism is temperature dependent, the shift can be explained by the delay of the temperature

wave due to the heat conduction through soil. The observed delay is 5.6 months (nearly half a year).

## CONCLUSIONS

Carbon-13 and Carbon-14 content in the soil environment has been measured at two soil levels (exhaled  $\text{CO}_2$  and  $\text{CO}_2$  in a depth of 0.8 m). Results of measurements and several analyses are presented in this paper. Temporal  $\Delta^{14}\text{C}$  and  $\delta^{13}\text{C}$  variations with a period of one year have been observed. As follows from the previous section, there are significant differences in temporal and spatial courses of various carbon

isotopes. The most obvious difference is the phase shift between the  $\delta^{13}\text{C}$  of  $\text{CO}_2$  from 0.8 m depth and the  $\delta^{13}\text{C}$  of  $\text{CO}_2$  exhaled from the soil surface. The measured and analysed data are useful for applications connected to the greenhouse effect.

### Acknowledgement

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# SOIL MAGNETIC SUSCEPTIBILITY AS INDICATOR OF RADIOACTIVE CONTAMINATION

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## ABSTRACT

Measurement of magnetic susceptibility is a method, which is used in many areas of research. The locality AK-Tjuz is typical example of old ecological load. One of the negative effects represents radioactive contamination. This situation is caused by environmental disaster in 1964. For useful reparation it is really necessary to determinate the surface range of contamination. And measurement of the magnetic susceptibility could be the suitable method for that kind of monitoring.

**Key words:** Magnetic susceptibility, Ak-Tyuz, Th, environment contamination

## INTRODUCTION

Mining and mineral dressing activities present one of the most important influences on environment. The impact on environment is really intensive. Beside those, there are some other kinds of influence – for instance disasters, which damage the environment hard. This is the case of locality Ak-Tjuz (Kyrgyzstan). In 1964, there was ruptured one of the sludge beds in the mineral dressing factory.

### The Locality Ak-Tjuz

The ore department is situated about 150 km Eastern from Biskek, Kamenina county, Cchujchujaska district. It covers important ore measures of noble earths, which contains Th, Be, Zr, Hf, Nb etc. and polymetallic ores. Localities of research contain the measures AK-Tjuz (polymetallic ores and rare earths elements), Kuperlisai (rare earths plus Th), Kolesai (Be) and the most important measures Kutesai (rare earths, Th, Y, Sc, Ta, Nb, Zr, Hf a Pb), where is situated open strip mine with huge mining mineral waste banks [1].

## RESEARCH AREA

The project was running in locality Ak-Tjuz (Kyrgyzstan). Firstly, the whole area was surveyed in

project Geoenvironmental research and evaluation of ecological load and risk in surroundings of the mining – mineral dressing complex of buildings in Kirgyszstan. The most contaminated area presents a former stock of radioactive extracts, which is built partly from bricks, partly from cement concrete, with concrete bottom.

In that stock, there are situated unsecured remains of Th – extract about c. 15–20 m<sup>3</sup>, which embodies the barched input even 1200 µR/h. By spectral measurements was identified the highest content Th 2280 ppm.

In the territory left of the stock left of the road to Ak-Tjuz are on deposit the remains of radioactive waste coming from the sludge beds, which were imported here within “cleaning” after the dam of the sledge bed number 2 was ruptured in 1964. This contaminated materials have typical light brown-violet colour, it is different from the rest of the materials in the surroundings and is characterized by the radioactivity higher than the limits – c. 100–150 µR/h and even higher in some places.

It is unnecessary to claim, that the range of dangerous and unsecured radioactive waste imported from the sledge beds to some places in this locality is even higher and it presents very high danger for environment.

The waste is situated also right of the road to Ak-Tjuz, where it intervenes to the river Kitchi-Kemin.



This river takes the waste away down to the valley. Cubage in this place is really huge – in thousands of m<sup>3</sup>.

Research of radioactive pollution was provided not only in stock of radioactive extracts, but in the surroundings – whole area was c. 400 x 100 m.

The border points – the profiles – of the profile net (for radioactivity measurement) were signalized. Profiles (number 1 to 21) were orientated in the North-South direction, the distance of profiles was 20 meters, the step of measurement was 10 meters.

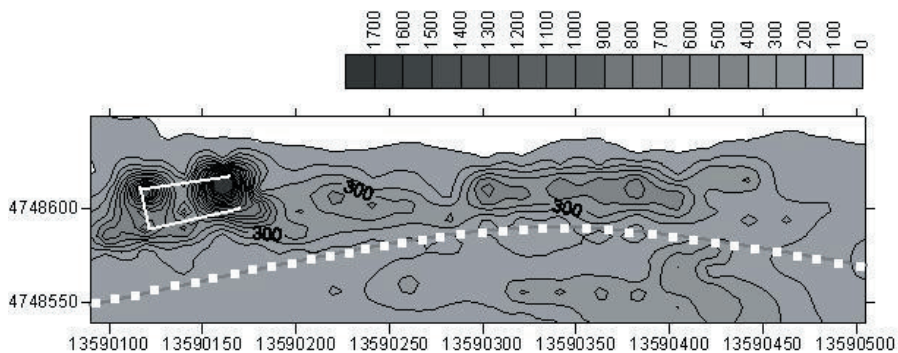
**Contamination surveying**

At the profiles, the gamaspectrometric measurement was provided – it means to determinate the content of Th (ppm), U (ppm), K (%) and total  $\gamma$ -activity. The Canadian instrument GR 130 was used for that measurement, total time of measurement was 600 seconds. In the end, 195 points were measured out. The final products, came up from the results of the measurement, present The digital radiometric maps of Ak-Tjuz locality.

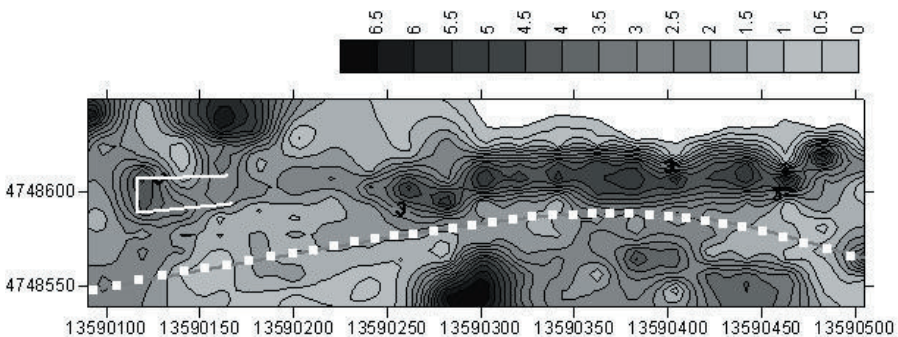
The results confirm, that the main source of strong radiation is Th. Very high values were measured out by Kallium K 40, a little value was identified by U. Radioactivity distribution shows Map of total  $\gamma$ -activity. All values are in distinctively positive correlation.

In the same time what the radiometric research was running, in the same profile net was measured of the magnetic susceptibility. The point of that measurement was to verify the premise that the potential heavy metals contamination coincides with the higher value of magnetic earth susceptibility. For the measurement was used Canadian handheld field instrument KT 9. The final value measurement of magnetic susceptibility at each point is an average of 10 measured values within 1 meter circle of that point.

Considering that the main contamination part presents Th, the most important meaning represent measurement of magnetic susceptibility and Th. In confrontation of both of the maps we can see some areas with different predicative value – vide pictures No. 1 and 2.



Picture No. 1:  $\gamma$  – spectrometry – Th distribution (white colour represents in-process store Th – extract, dash represents the road)



Picture No. 2: Measurement of magnetic susceptibility (white colour represents in-process store Th – extract, dash represents the road)

## Evaluation

In distribution map we can unambiguously see really tight correlation between higher and abnormal values of measurement of magnetic susceptibility and anomalous values of radioactivity in surveying area (see Picture No.3). This is evident especially in the middle and eastern part of surveying area, where the anomalies are bound on radioactive waste came from damaged sludge bed No. 2. The explanation is quite easy – anomalies of measurement of magnetic susceptibility are caused by high content of magnetite in the waste after ore modification in Ak-Tjuz and Kutesaj localities.

In research of heavy mineral extracts from the samples came from the sludge bed No.1 was found that the whole ferromagnetic fraction is framed just with magnetite, which in 10-litres sample reached the weight 11 g. It means content about 1100 g/m<sup>3</sup>.

The coincidence of radioactivity anomalies and magnetic do not happen in the stock area with the remains of pure extract, where enormous Th anomalies can be identified, but measurement of magnetic susceptibility does not reach to high values (vide Picture No. 4). That happens, because in contrast to the mineral-dressing factory is Th magnetite extract considered as undesirable element and thrown away.

Very interesting is anomaly of measurement of magnetic susceptibility at the end No. 3 to 5. It is caused probably by the present of minerals with the high content of accessory magnetite, eventually of pyrrhotite. Considered could be amphibolites, amphibolite gneisses and mica schists.

## CONCLUSION

The results of measurement of magnetometric measurements could be considered as really beneficial. Tight correlative relation between measurement of magnetic susceptibility and radioactive materials came from the damaged sludge bed shows that this could be the potentially used in application for environmental survey the valley of the river Kitchi-Kemin.

The article came into being on the basis of Project foreign development cooperation of The Czech Republic: **Geoenvironmental research and evaluation of ecological load and risk in surroundings of the mining- mineral dressing complex of buildings.**

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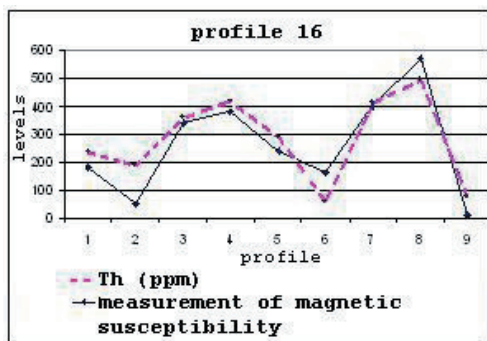


Fig. No. 3: Comparing measurement of magnetic susceptibility and  $\gamma$  – spectrometry Th distribution in profile No. 16.

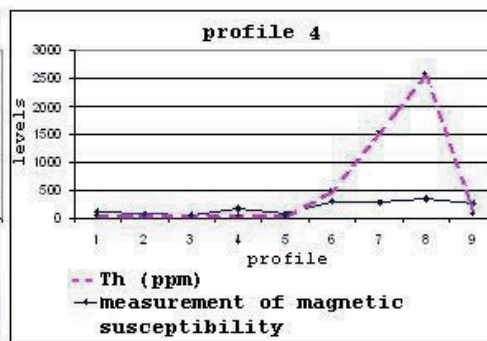


Fig. No. 4: Comparing measurement of magnetic susceptibility and  $\gamma$  – spectrometry Th distribution in profile No. 4.

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tel. 044 / 433 16 21, 433 16 22 (spoj.)



*Poskytuje služby:*

### **DODÁVKA VODY**

Výroba, úprava a dodávka vody je zabezpečovaná pracovníkmi **Hospodárskeho strediska VODOVODY**.

**Hospodárske stredisko Vodovody poskytuje odberateľom nasledovné služby:**

- montáž nových vodovodných prípojok pre odberateľov,
- montáž nových vodomerov,
- vytyčovanie rozvodov vodovodov na objednávku pre investorov, projektantov a pod.,
- vyhľadávanie porúch na vodovodnej sieti,
- konzultačnú činnosť spojenú s prípravou a realizáciou rekonštrukcií vodovodných sietí, s realizáciou prekládok vodovodov a zariadení vodovodnej siete a ďalšou inžinierskou činnosťou, taktiež konzultačné činnosti spojené so zriaďovaním nových odberných miest, montážou prípojok a vodomerov.

**Hospodárske stredisko KANALIZÁCIE zabezpečuje predovšetkým odkanalizovanie odpadových vôd (splaškové a iné komunálne, vody z povrchového odtoku – tzv. zrážkové) a ich čistenie.**

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- vývoz žump,
- vytýčenie trás kanalizácie v správe a. s.,
- dodávka a montáž kanalizačných prípojok (v spolupráci so strediskom, vykonávajúcim stavebnú činnosť).

### **VYJADROVACIA ČINNOSŤ**

V zmysle Zákona č. 442/2002 o verejných vodovodoch a verejných kanalizáciách v znení neskorších predpisov je prevádzkovateľ verejného vodovodu a verejnej kanalizácie povinný:

- poskytnúť za odplatu technické podklady na zriaďovanie alebo odstraňovanie vodovodnej prípojky/kanalizačnej prípojky,
- vyjadrovať sa za odplatu k projektovej dokumentácii týkajúcej sa výstavby rodinných domov, sídelných celkov alebo inej investičnej činnosti, ako aj k zmenám vo výrobnom procese fyzických osôb alebo právnických osôb z hľadiska požiadaviek na zásobovanie pitnou vodou/odvádzania a čistenia odpadových vôd do 30 dní odo dňa vyžiadania,
- Na žiadosť projektanta alebo stavebníka za odplatu zakresľuje smer a výšku podzemného potrubia verejného vodovodu alebo verejnej kanalizácie do jeho dokumentácie do 15 dní odo dňa vyžiadania.

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