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TRIBOELECTRIC SEPARATION OF PE AND PP FROM MUNICIPAL WASTES

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ABSTRACT

Sisol M., Michalíková F, Kozáková I. & Kolesárová M. **Triboelectric Separation of PE and PP from Municipal Wastes**

Proportion of plastic waste in municipal solid waste accrues year after year. Recycling is the most effective method of plastic waste minimization. A condition of effectual plastic recycling is a source of rather clean plastics and the space opens from here for separation technologies that are making possible from plastic waste mixture to separate individual components and contaminants. The article deals with in separation of PP and PE. These two plastic separation is not possible by general gravitational methods because the specific gravities of the two polymers overlap. Electrostatic separation appears as a possible method at their separation. At this method the electric field that is created between positive and negative electrodes separates particles on the basis of charge size and polarity. By electrostatic separation of HDPE/PP mixture with particle size of 1×1 mm was made possible from negatively charged product to separate HDPE with recovery of 96.10 % and from positively charged product to separate PP with recovery of 97.52 %.

Key words: triboelectric separation, plastic wastes, polypropylene, polyethylene

INTRODUCTION

The mean of plastic waste minimization is its secondary utilization (recycling, thermal valorization or another utilization). The separation of several types of plastics is important for function of succeeding recycling technologies and for final quality of products from the recycling cycle. Several methods for plastic wastes identification and separation are known. Separation technologies are usually founded on chemical, optical, electrical or physical properties of separated plastics.

The separation of PP from PE by standard gravity separation methods is very difficult because a range of their specific weight blend together. According to obtained findings the electrostatic separation seems to be the potential method for separation of these two plastics.

Electrostatic separation

Methods of electrostatic separation are based on different electric properties of materials moving in the electric field on different trajectories and get to different products of sorting [1].

Utilizing forces of the electrostatic field for sorting of material mixtures differs in their electric properties and requires presence and mutual conditioning of two electric phenomena:

- the electric field with sufficient intensity which influences charged particles and changes their trajectory of movement,
- charged particles on which effect of the electric field can be shown.

A disadvantage of electrostatic separators is in action of electric forces which is lower in comparison with mechanical forces, hence is possible to assort only the material where the difference between mechanical and electrical forces is minor. Also it is eligible to assort a batch which is presequenced in a narrow range of granularity [1].

An advantage of electrostatic separation:

- independence from material density,
- dry process,
- low energetic consumption,
- high capacity,
- high cleanliness of the selected material [2].

The mechanism of particle charging

Ways in which solid particles can obtain an electric charge on their surface are:

- Ionization: a thin rod with a very large radius of curvature or several rods situated close by together, attached to high usually negative voltage cause brush discharge at which the air is being ionized. The space between ionizing electrode and earthed plate is filed by negative by charged ions which strike upon the surface of the earthed plate. Negative ions strike upon solid particles and give them a charge before they reach electrostatic field where the separation takes place.
- Influence (induction): conducting particles in contact with the positive by charged carrier electrode obtain electric charge with the same polarity as the polarity of contact electrode and they are separating from its surface and repulsing by Coulomb repulsive force.
- Triboelectric effect: by friction against a pad or mutual friction solid particles reach the specific electrical state – on their surface an electric charge with different value and polarity is shown up [3].

Triboelectric separation

The principle of triboelectric separation involves:

1. triboelectric charging of milled plastic particles,
2. transfer of electrified mixture through the elec–trostatic field which separates individual plastic particles by their size and polarity of electric charges which plastic particles obtain during triboelectric process [4].

If two different dielectric materials are in contact with each other the electric charge is transferred. One of the materials is charged negatively and another positively. The polarity of the electric charge is determined by the triboelectric line (Tab. 1). The polymer which is higher in the table in contact with the polymer situated lower in the table is charged negatively [5].

Properties affecting the electrostatic separation:

- **Particle size –** the charge which particle can obtain depends on the specific surface. Size of the charge increases if the size of particle decreases. Very small particles (smaller than 100 μm) with different polarities will, in consequence of effecting electrostatic forces, aggregate or tack on big particles of different plastics whereby the cleanliness of separated particles decreases. For the reaching of high cleanliness of separation the removal of small particles is needed to be done, e. g. by air washing process or screening.
- **Humidity** – the material has to be dry enough with low surface conductivity. Relative air humidity enfolding the separation unit has to be kept lower than 50 % [5].

Tab. 1: Triboelectric rows for plastics cited by several authors

Dodbiba [4]	Dodbiba [6]	Iugaa [8]	Brown [5]	Huanfu [7]	Fujita [9]	Coehn [9]
↑ negative charge						
PTFE PVC PE PS PET PC PP ABS	PVC PP PE PS PET PC ABS	PVC PP PET PE PMMA Al	PTFE PVC PE PP PS PET Lexan Acrylic	PTFE PVC PET PP PE PS	PTFE PVC PE PET PC PP ABS	PP PE PS PVC PET Polyacetate PMMA Celullose Nylon 66

- **Time charging** – is a critical parameter in triboelectric separation and it is given experimentally.
- **Mixture composition** – the two-part mixture with rate of 50:50 is charged approximately equally. However in mixtures with ratio of 95:5, the minority material is charged more strongly, because particles of the majority material are in contact with particles of the same material and they do not transfer the charge [10].

METHODS

The aim of experiments was to find out if it is possible to separate HDPE from PP electrostatically. Two types of waste plastics were used such as HDPE (foils, bottles of pharmaceutical waste products) and PP (food packaging, bottles of pharmaceutical waste products).

Two factors influencing electrostatic separation – *the way of charging and electrode voltage* – were considered.

Dependence of separation on charging of different charging plates

Samples of plastics (HDPE and PP waste bottles) were cut with scissors to 1×1 mm large-size particles. Average weight of HDPE particles was 0.0005 g and PP particles 0.0007 g. The mixture of plastics was achieved by mixing volumetric equal amount of HDPE and PP materials. The mixture was homogenized and subsequently separated by using the electrostatic separator with vibrating charging (Fig. 1). The charging of particles was realized on vibrating charging plate made of PET, HDPE, PVC and Cu. The charging time was 40 sec. Charged plastic particles were falling down by free fall in the electric field which was between Al electrodes (31.7×10 cm). Electrode voltage was 40 kV and the distance between electrodes was 14 cm.

Separated plastics were collected in the receiving jar. After electrostatic separation products were removed from individual dividers and then separated (visually according to colour of plastics) and weight on the analytical scales. Sequentially the recovery of HDPE and PP to individual products was determined.

The dependence of separation on electrode voltage

The mixture was charging on vibrating PET plate. The time of charging was 40 sec. Separation of HDPE/PP mixture was realized with electrode voltage of 40, 38, 35, 30 and 25 kV. During experiments Al electrodes (31.7 × 10 cm) were used and the distance between them was 18 cm.

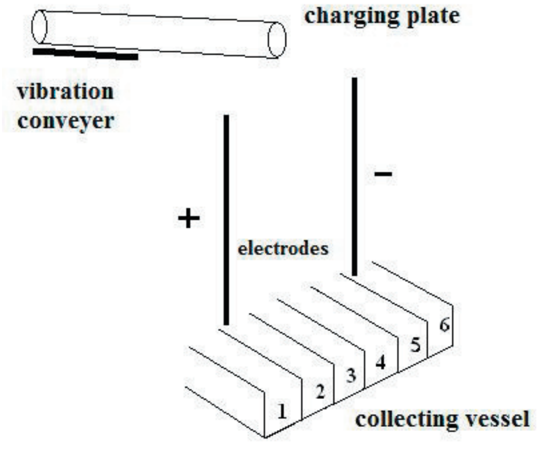

Fig. 1 Electrostatic separator with vibration charging

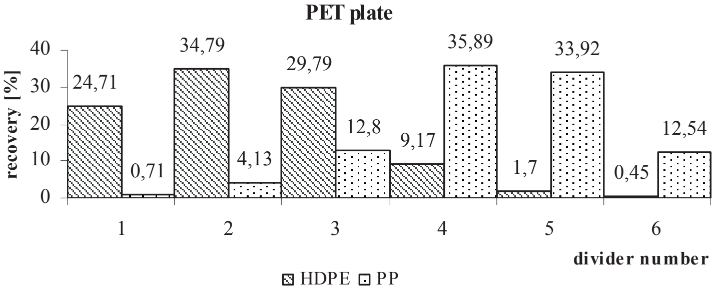

Fig. 2 Separation of HDPE/PP mixture with particle size of 1×1 mm charging on PET plate with electrode voltage of 40 kV

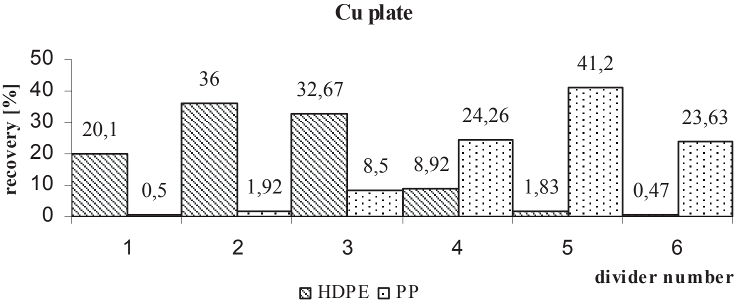

Fig. 3 Separation of HDPE/PP mixture with particle size of 1×1 mm charging on the Cu plate with electrode voltage of 40 kV

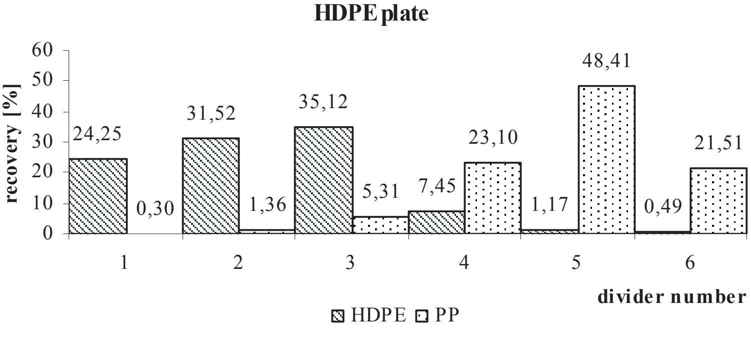

Fig. 4 Separation of HDPE/PP mixture with particle size of 1×1 mm charging on the HDPE plate with electrode voltage of 40 kV

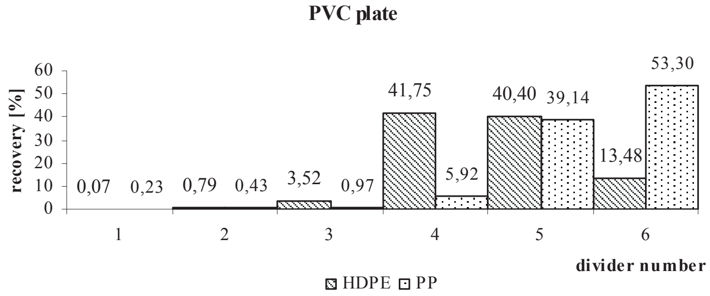

Fig. 5 Separation of HDPE/PP mixture with particle size of 1×1 mm charging on the PVC plate with electrode voltage of 40 kV

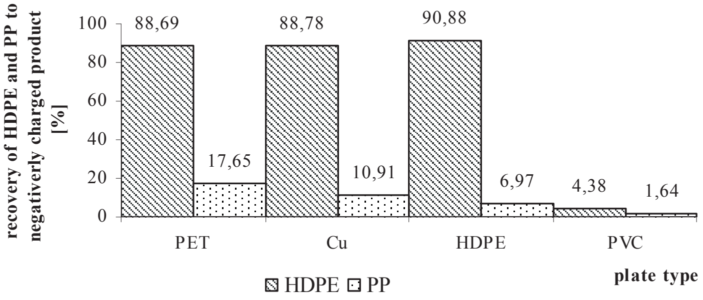

Fig. 6 Dependency of separation HDPE/PP mixture with particle size 1×1 mm on used charging plate with electrode voltage 40 kV

RESULTS AND DISCUSSION

The dependence of separation on charging of different charging plates

The dependence of plate on charging of plastic particles was minimal. The separation of HDPE/PP mixture charging on mentioned plates (except PVC plate) went ahead the same way. HDPE particles obtained their negative charge and were attracted to positive electrode, whereas PP particles were charged positively and were attracted to negative electrode. The best separation of HDPE/PP mixture was reached on HDPE plate. The recovery of HDPE in negatively charged product was 90.88 % and recovery of PP in positively charged product was 93.03 %.

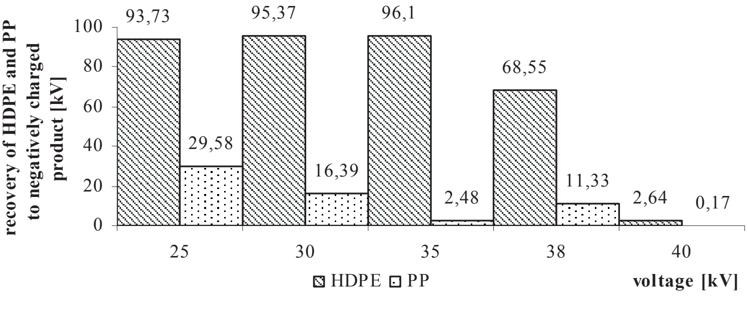

Fig. 7 Dependence of separation HDPE/PP mixture with particle size 1x1 mm on various electrode voltage (charging plate is PET)

The dependence of separation on electrode voltage

The electrode voltage influences the separation of plastic mixture. The best separation HDPE/PP mixture with particle size of 1×1 mm charged on the PET plate was reached on electrodes with voltage of 35 kV (Fig. 7). From the negatively charged product HDPE with recovery of 96.10 % and from the positively charged product PP with recovery of 97.52 % was obtained.

CONCLUSION

The work deals with electrostatic separation of plastics and aims mainly at separation of PE and PP. The separation of these plastic is problematic because they have almost the same specific weight and is not possible with different, economically profitable separation methods (as gravity methods).

All experiments were performed with real waste plastics. Two factors influencing electrostatic separation – the way of charging and electrode voltage – were considered.

According to results PP and PE particles were best charged on vibrating HDPE plate. The best separation was reached by separating of plastic's mixture with particle size of 1×1 mm with electrode voltage of 35 kV. On the part of economics would be better to separate mixtures with high particle size. It is possible to reach with using large electrodes with higher voltage. The results show that electrostatic separation with triboelectric charging has their application also in plastic separation.

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HEAVY METALS IN SOILS IN THE REGIONS WITH ENVIRONMENTAL LOAD IN MIDDLE SPIŠ

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ABSTRACT

Carach V., Vaľková M. & Kozáková Ľ. **Heavy Metals in Soils in the Regions with Environmental Load in Middle Spiš**

The soil samples from middle Spiš were collected and analyzed for releasable, mobilizable and mobile forms. Contents of heavy metals were judged according to determination of the MP SR no. 531/1994 – 540. Heavy metal contents were increased in comparison with highest acceptable concentration (A_1) and in a few samples indication values (B). Mobile fraction for lead was increased in comparison with copper and zinc in order: Pb > Zn > Cu. In the case of mobilizable forms there was the following order: Cu > > Zn > Pb.

Key words: contamination of soils, bioavailable form of heavy metals, copper, lead, zinc

INTRODUCTION

Heavy metals in soils are important problem. They are situated in the old environmentally load areas which used to be mining ones. Heavy metals can exist in variable forms. These forms have an impact on mobility and accessibility of plants. It is important to know the content of accessible forms on the part of advisement potentional treath. These forms determine risk of mobilization and transfer in other components.

Heavy metals in plants and their transfer to the food web will influence their bioavailability which depends on properties of soils, pH, cationexchangeable capacity and redox potential. Bioavailability of Zn, Pb, Cd decreases if pH of soils increases. Reduction of availability of metals is influenced by higher adsorption and precipitation in neutral and alkaline environment [1, 2].

Wang found out 30–60 multiple increase of Cu, Cd, Pb and Zn contents in soils and plants in copper mining area in compare with control [3]. This increase was found with studies of chemical forms of heavy metals in soils. Contents of heavy metals in clover hint as a positive signification of correlation with their exchangeable and organic forms in soils. Also these contents hint as a negative signification of correlation with Fe and Mn oxides and carbonate forms and they hint as no correlation with residual forms.

The region of middle Spiš was classified as the loaded region and hygienically badly following environmental regionalization. Dominant contaminants are heavy metals in this classification of components of the environment. Mining operations with following processing of complex metals and copper ores left negative effects in this region [4]. The region has three general locations of contamination: the industrial locality Rudňany, Krompachy and Spišská Nová Ves. Overload of limiting values of Hg, Cu, Zn, As, Cd and Pb was found in soils.

Heavy metals in soils

Lead in soils belongs to less mobile elements, especially when is bounded to carbonates and disulphates. Hydrosulphide is introduced as an indissoluiable form whose occurence is little likely (except soils over ores) [5].

As the most incident form of lead which occurs at solid phase of soils are $PbCO_3$ and $PbSO_4$. Ones of the main sources of lead in contaminated soils are imissions from smelters processing lead ores, smelters wastes and motoring [6].

Reducible and exchangeable forms of some heavy metals and also lead are immobilized by addition of humine matters. Solubility of compounds of lead is falling with the content of PO_4^{3-}. Influence of lead on soil microbial activity depends mainly on granularity and lead concentration [7, 8].

Copper exists in soils in a form of bivalent ions (nitrates, chlorides and disulphates), their compounds are very mobile. Solubility and mobility of copper are reduced by liming eventually after an application of phosphate fertilizer [9].

Soil mould binds copper dependence of his exchangeable sorptive capacity. Copper is released in a form of soluble salts after mineralization of soil organic matters. This metal is often cumulated in soils with high amount of manganese. Enormous high contents of copper in soils present risks of decreasing soil fertility and jeopardy of live organism status. Receiving of copper by plants influences pH of soils and the amount of organic matter [10, 11].

Zinc exists in soils wholly in the bivalent form. Majority of the present zinc (till 70 %) in soils is concentrated in overhead layer (4 cm). Mobility of zinc is influenced by value of soil reaction, thus pH. Zinc can form complex minerals in a form Zn_2SiO_4 and $ZnFe_2O_4$. An increase of basicity (pH > 7) raises also solubility of zinc as a consequence of zincates formation. Lower solubility of zinc in soils is in the range of pH: 5.5–6.9. Mould and its quality have considerable influence for on distribution of zinc in soils. Zinc belongs to biogenic elements but it is included in the list of weighty unfamiliar matters in agricultural soils as a biogenic element in surplus [12].

MATERIAL AND METHODICS

Soils were sampled from the region of middle Spiš (autumn 2006). Bioavailability of heavy metals in soils was estimated by implication of anthropogenic load.

Test samplings were realized by valid methodology. Samples of soils were drained at laboratory temperature. Soil was screened over the screen with the mesh 2 mm. This soil was prepared and used for estimating bioavailability of heavy metals in soils. One-shot extraction was used for isolation of single forms. Releasable forms were evaluated in extract 2 M HNO_3 by valid methodics. Mobilizable forms were evaluated in the extract 0.05 M EDTA and mobile forms in 0.1 M $CaCl_2$. 10 g soil was weight for extraction of both forms and 100 ml reagent was added. Then the sample was shaked in 1 hour [13]. Contents samples of components were evaluated by the method of absorption spectrometry with flame atomization in single extracts. Contents were presented in mg.kg^{-1} [14].

RESULTS AND DISCUSSION

Contents of heavy metals in releasable, mobilizable and mobile forms in soil samples of middle Spiš are listed at tables 1, 2 and 3.

Tab. 1: Contents of copper in soils of middle Spiš

No.	Place of consumption	Cu				
		2 M HNO_3 [mg.kg^{-1}]	0,05 M EDTA [mg.kg^{-1}]	0,05 M EDTA [%]	0,1 M $CaCl_2$ [mg.kg^{-1}]	0,1 M $CaCl_2$ [%]
1.	Richnava	112,40	88,90	79,1	0,80	0,7
2.	Kolinovce	114,00	86,60	76.0	0,60	0,5
3.	Kolinovce – Spišské Vlachy	29,00	24,20	83,4	0,50	1,7
4.	Spišské Vlachy – SNV	25,20	21,50	85,3	0,50	2,0
5.	Bystrany	16,00	14,00	87,5	0,50	3,1
6.	Spišský Hrušov	12,80	10,70	83,6	0,50	3,9
7.	Chrasť – Jamník	9,80	7,30	74,5	0,40	4,1
8.	Rudňany	54,90	48,10	87,6	0,50	0,9
9.	Rudňany – Matejovce	24,80	18,80	75,8	0,60	2,4

Tab. 2: Contents of lead in soils of middle Spiš

No.	Place of consumption	Pb				
		2 M HNO$_3$ [mg.kg^{-1}]	0,05 M EDTA [mg.kg^{-1}]	0,05 M EDTA [%]	0,1 M CaCl$_2$ [mg.kg^{-1}]	0,1 M CaCl$_2$ [%]
1.	Richnava	83,80	55,10	65,8	6,40	7,6
2.	Kolinovce	61,00	33,70	55,2	6,50	10,7
3.	Kolinovce – Spišské Vlachy	26,80	14,10	52,6	6,00	22,4
4.	Spišské Vlachy – SNV	29,00	14,20	50,0	6,00	20,7
5.	Bystrany	20,90	9,50	45,5	5,80	27,8
6.	Spišský Hrušov	19,60	9,30	47,4	5,90	30,1
7.	Chrasť – Jamník	15,70	3,90	24,8	5,80	36,9
8.	Rudňany	23,30	9,90	42,5	6,00	25,8
9.	Rudňany – Matejovce	16,00	4,50	28,1	5,90	36,9

Tab. 3: Contents of zinc in soils of middle Spiš

No.	Place of consumption	Zn				
		2 M HNO$_3$ [mg.kg^{-1}]	0,05 M EDTA [mg.kg^{-1}]	0,05 M EDTA [%]	0,1 M CaCl$_2$ [mg.kg^{-1}]	0,1 M CaCl$_2$ [%]
1.	Richnava	172,90	114,40	66,2	32,50	18,8
2.	Kolinovce	156,10	108,10	69,3	31,90	20,4
3.	Kolinovce – Spišské Vlachy	44,00	24,10	54,8	2,65	6, 0
4.	Spišské Vlachy – SNV	37,70	20,40	54,1	2,36	6,3
5.	Bystrany	35,50	20,10	56,6	1,52	4,3
6.	Spišský Hrušov	20,40	9,00	44,1	1,27	6,2
7.	Chrasť – Jamník	11,20	6,30	56,3	1,97	17,6
8.	Rudňany	66,60	38,80	58,3	1,28	1,9
9.	Rudňany – Matejovce	10,20	4,40	43,1	1,26	12,4

Contents of heavy metals were judged according to the Decision of the MP SR no. 531/1994 – 540. Reference value (A$_1$) valid for determination in extract of 2 M HNO$_3$ for copper is 20 mg.kg^{-1}, for lead is 30 mg.kg^{-1} and for zincs 40 mg.kg^{-1} of dry mass.

Indication value (B) for copper is 100 mg.kg^{-1}, for lead is 150 mg.kg^{-1} and for zinc 500 mg.kg^{-1} of dry mass.

Comparable contents of Cu, Pb and Zn with reference value (A$_1$) are given in at fig. 1, 2, 3.

Six samples of Cu exceeded reference value (A$_1$) and two samples exceeded indication value (B). Two samples of Pb had higher values as reference value and by Zn four samples exceeded reference value.

Average percentage representation of mobilizable forms is 81.4 % Cu, 24.3 % Pb and 55.9 % Zn. This high ratio suggests possible contamination of agricultural plants in this area. But ratio can increase the mobile forms of heavy metals in soils together with the change agrochemical properties of soils, in the first place of pH change. Therefore, it is important to monitor not only a releasable ratio but also mobilizable and mobile forms in all agricultural used soils in regions with environmental loads.

The higher ratio of mobile form has been recorded for lead in comparison with copper and zinc. The average percentage of the mobile form for lead is 24.3 %, for copper is 2.1 % and for zinc 10.4 %.

Individual forms for our monitored samples were compared each other. It can be seen that lead has a higher ratio of mobile form in soil samples in comparison with copper and zinc, in order Pb > > Zn > Cu. Order of metals is following: Cu > Zn > >Pb for mobilizable forms.

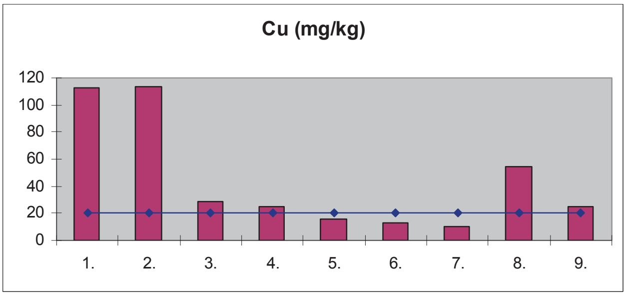

Fig. 1 Comparison of Cu content with the reference value (A_1)

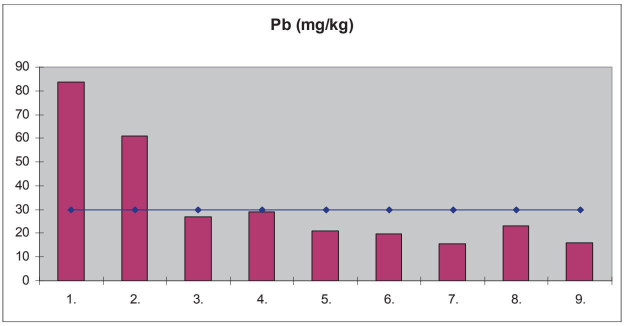

Fig. 2 Comparison of Pb content with the reference value (A_1)

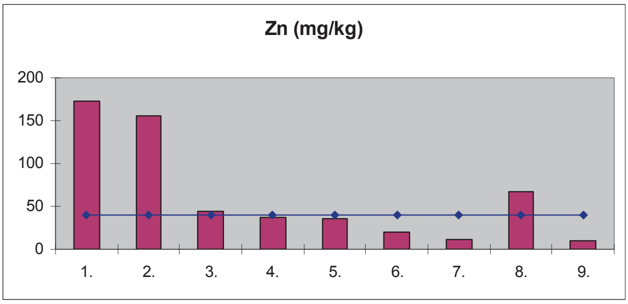

Fig. 3 Comparison of Zn content with the reference value (A_1)

The distribution of heavy metals in different forms of soils determines their behaviour in the environment: their mobility, bioavailability and toxicity. In soils, heavy metals can be found in several forms which influence their mobility and also availability for plants. According to reviewing the potential threat of the food chain as well as soil revitalization in environmentally polluted areas, it is important to know the proportion of bioavailable forms as well as soil properties for selection of suitable plants and selection of steps for decrease of these kinds of forms in soils.

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STRESS INFLUENCE ON AUTONOMOUS REGULATION OF HEART, FUNCTIONS AND RADIONUCLEODIC METHODS IN CARDIOLOGICAL DIAGNOSTICS

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ABSTRACT

Lacko A. & Komárek K. **Stress Influence on Autonomous Regulation of Heart, Functions and Radionucleodic Methods in Cardiological Diagnostics**

The study deals with to stress related problem and its psychological response in human body, such as influence of stress in the autonomous regulation of heart activity. The study has used the Stroop's test in order to determine the stress level. After that the spectral analysis of the heart rate variability was carried out in order to specify the impact of the stress on the regulation of the influence of the autonomous nervous system in the relation to the heart activity. Obtained results were compared with selected indicators of used psychodiagnostic methods (Stroop's test).

Cardio vascular diseases represent a serious problem which is trying to be resolved by health care professionals nevertheless it should also be a concern of each individual as well as the whole society. This disease continually affects younger age categories. From the medical point of view the ambition of early diagnosis with consequent therapy should influence this adverse trend. Diagnosis of cardiovascular diseases by the nuclear medicine method has a substantial place. These particular examinations represent about 40 % of performed examinations in units of nuclear medicine. This very fact has glanced off in conception of nuclear medicine by establishment of a new subdivision of "nuclear cardiology".

Key words: stress, autonomous nervous system, heart rate variability, spectral analysis, nuclear cardiology, radio nuclear method

INTRODUCTION

A human being had developed a variety of the defence mechanisms that would shield against the negative influence of the environment. When it comes to physiological conditions, non-specific and specific defence and adaptation mechanism respond quite well towards damaging signal and therefore ensuring optimal regime and vital functions. In pathological conditions, these mechanisms not only get activated but often fail and the human body becomes vulnerable to environmental influence. Maintaining homeostasis is a highly dynamic process in which our body constantly and promptly reacts to environmental changes (1).

Indency of so called civilisation stress (mental and psychic) triggered by inability to adapt oneselves to a new social calls in changes in human thinking as well as changes in a traditional lifestyle is continuously changing.

Importance of the pathological consequences depends on only the character make-up but also on seriousness of the overwhelming situation. The main aim of this study is objectivisation of the stress related situation in an educational and training process.

SUBJECTS AND METODS

During the research study: influence of the psychosocial factors of the stressful situation on a human being with a help of the psychological methods, reaction of examined participants has been monitored in order to determine their reaction according to the stressful situation. The most appropriate method, chosen for this particular testing, was the Stoop's test (2).

In a particular group of 16 students, members of the secondary medical school (age range of 18–19 years old) the Stoop's test has taken place. The aim of the Stoop's test was to induce a stressful situation using psychological methods and consequently to evaluate a resistance of the overwhelming situation. The test also included a fluency in reading, recognition of colours and interference. The principle of this method lies in the fact that setting an eye on a different colour from a written name of this particular colour (e.g. word „red" written by green colour) brings the examined person to a tendency to read a name and not actually answering the colour which is the word written in. This simple fact brings us into a stressful situation while a fluent reading (examined participant tends to read words not to name the colour). The score figures are measured in seconds. The lower the points are, the better the personal performance is. The interpretation compares the index with arithmetical averages found in the particular age group. An effective example of utilization during an overall evaluation of the student in a pedagogical-educational process would be judged on the basis of mental resistance of the student versus stressful situation, especially in the cases when it comes to a problematic student (3).

All 16 students were examined by VHF spectrum analysis. The first examination took place in the hospital clinic while on practice considering the optimal conditions. The second one took place while having graduation exams. Thus we have made a note on the autonomous nervous system in a particular time period, such as a stand-still position and during the stressful situation.

The method of a spectral analysis enables to distribute VHF (gradually from 300–900 intervals R-R – ECG using the fast Fourier's transformation) to a component determined by parasympatics (respiration peak of a high frequency in the spectrum of 0. 15–0.5 Hz) and component in which takes part also sympatics (peaks with a low frequency in the spectrum of 0.5–0.14 Hz). This is a configuration of R–R intervals concerning ECG of sinus curves according to the frequency and the power of their spectrum. The decrease in amplitude of a respiratory oscillation of a heart frequency or its disappearance manifests the decrease of the para-sympatics activity. The amplitude reduction of oscillation of a heart frequency with a low frequency or their disappearance demonstrates the low activity of sympatics (5).

The examined group consisted of 50 sound participants aged between 20–30 years (6).

For the diagnosis purposes the micro computer system was used specified for the telemetric non-invasive examination VHF, type VariaCardio TF4 by Simon Media Olomouc.

RESULTS

Having compared the scores of the students´ sub-tests in our particular group by the Stoop's test in comparison with average figures of particular age groups, we could state that achieved results of scores show an overall average performance of students. In a particular subtest of our students time scores (fluency in reading, identification of a colour, interference) indicates a mental competence, psycho-metric promptness and an ability to handle two or more different kinds of tasks at the same time. We are talking about prompt, dominant and demanding personalities. Anticipation anxiety had increased prior to testing in all students. Five out of them experienced somewhat a feeling of anxiety even after the test which pointed out a gradual decrease of a stress-related reaction. Comparing these particular indicators (VHF) in a relaxed situation with results of the exact and the same indexes in a stressful situation (such as the graduation exam) we have found out a significant decrease in an activity of parasympatics (drop in HF spectrum component score $p < 0,001$) and a majority of sympatics (LF spectrum components, pictures 1, 2, 3, 4).

The increased sympatics activity is followed by the latest structural changes which would be the one of the pathophysiological mechanisms in essential hypertension, cardiomyopathies, CAN. For examination of adrenergic innervation of heart by analogue of noradrenaline metaiodobenzylguanidin (MIBG) could bring a long new know-how into pathogeneses of these diseases. The total grasping of MIBG was calculated from planar pictures as a proportion between heart (mediastinum in the course of 4–24 hours after radiopharmaceutical treatment given). Medians S/M in these intervals are lower in ill patients compared with healthy individuals. The significant change can be located in grasping MIBG of myocardium. Presence of disintegrated adrenergic in nerves endings of heart, where it becomes clear in conjunction with endurance of ischemic myocardium (fig. 3, 4.)

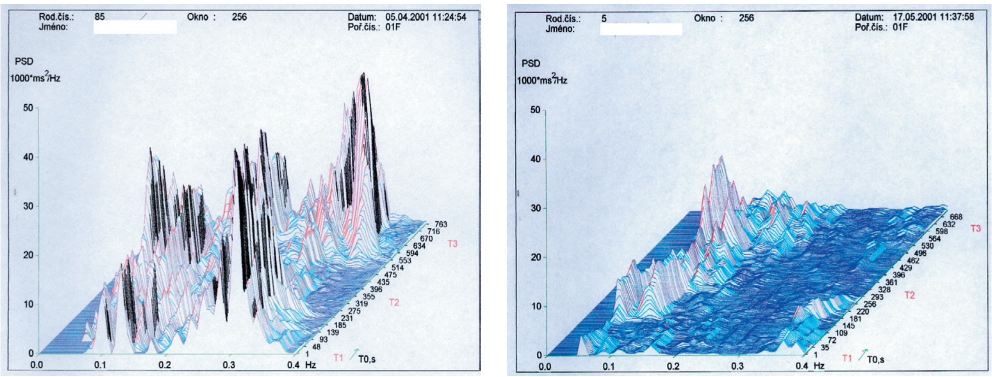

Fig. 1 VHF examined by spectral analysis with the student under relaxed conditions. VHF examined by spectral analysis with the student during an examination

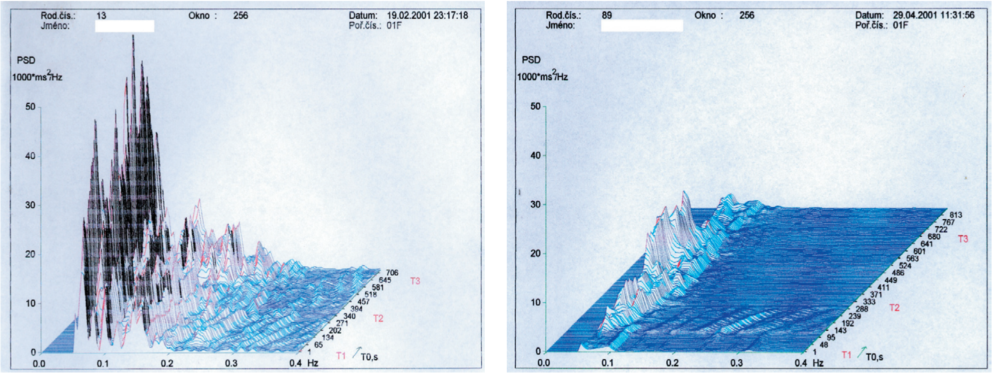

Fig. 2 Regular VHF examined by spectral analysis with the teacher. Altered VHF examined by spectral analysis with the teacher (view of chronic stress)

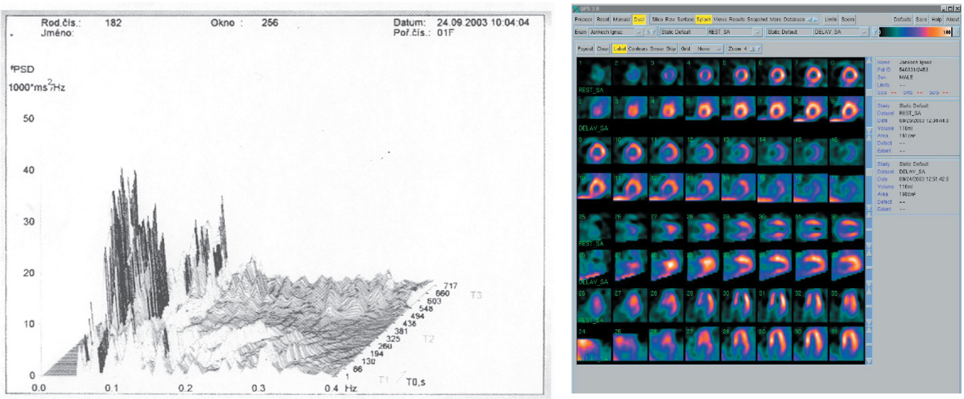

Fig. 3 VHF – spectral analysis and Myocardial examination ^{123}I-MIBG-ordinary diagnosis

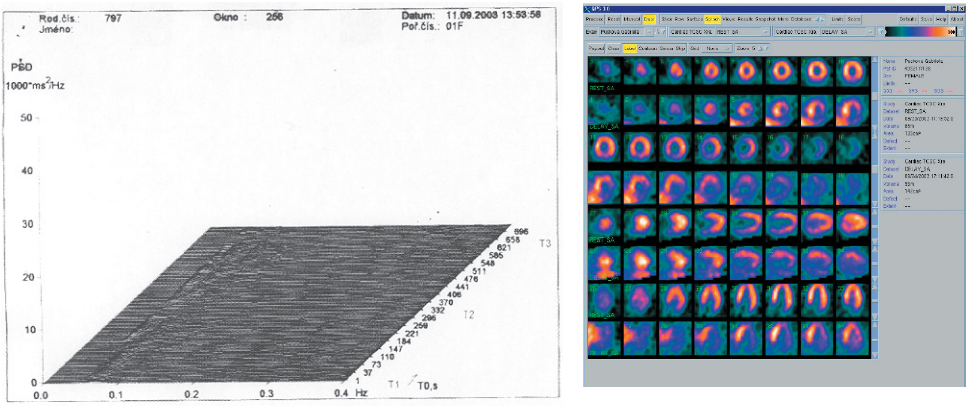

Fig. 4 VHF – SA and myocardial scintigraphy ^{123}I MIBG pathologic Detection systems

In a nuclear diagnosis tomography gamma cameras dominate. We distinguish 2 kinds of tomography examinations:

1. Single photon emission tomography (SPECT)
2. Positron emission tomography (PET)

The disadvantage of the PET examination is a need of four cyclotron work-units nearby, in order to produce positron radiation. The aim is to spread a similar technique outside the cyclotron centre, and this is why the construction of so called coincidental gamma camera took place. We are talking about coincidental detectors based on gamma cameras double heads, or usage of 511 KeV. Coincidental gamma camera would be able to perform in a classical nuclear medical diagnosis (with usage of single photon emission tomography) where it could also perform in the PET regime.

DISCUSSION

In our particular examining group of students we have found a positive relation between increased level of anxiety (anticipation anxiety before the test is present) and a satisfactory performance in the Stoop's test, which proves that one is able to get a stressful situation under control and by increased mobilization of effort perform well. All participants have proven to have a positive motivation towards the graduation exam study. This activity motivation that represents a complex of personal, changing abilities influenced by other factors, such as cognitive abilities, metric awareness, social attributes, etc.

Heart frequency and its changes are sensitive indicators of autonomic nervous system functions (ANS). Changes of tonization of sinus knot by sympatics vagus we mark as a variability of intervals R-R ECG (5, 6). The method is sensitive enough in order to monitor stress–related changes in a circular system seriously influenced by actual ANS state.

Nuclear cardiology takes advantage of 201T1, 99mTc. Out of the once we use would be from a group of cyclotron radio nuclides of 201T1, 111In, 123I type. From so far mentioned radio nuclides, 99mTc is the most appropriate one because of its clear gamma-radiator with a half time distraction of 6 hours. Because of this non-biogenic behaviour we cannot mark by it all metabolic actions or their disorders in a human body. Actual visual display of organs and pathological processes in a human body based on metabolic level would be possible due to a production of radio nuclides of biogenic elements (carbon, oxygen, nitrogen, hydrogen) with emission of positron radiation. They show very short half time of distraction and this is why they have to be used for examination exactly at the time of their regeneration. Instead of hydrogen, fluorum can be used (18F) with a half time of 120 minutes which would be possible to use units of nuclear medicine with the distance of few tens of kilometres.

CONCLUSION

Radio nuclear method plays a significant role in cardiologic diagnosis. Methods of cardial nucleology are considered as the most accurate ones in the cardiological diagnosis, due to functional and metabolite principle of heart imaging. The actual target of this submitted study is to point out their non-invasiveness and ability to uncover sub clinical myocardial perfusion and functional heart disorders (7).

Personal psychodiagnostic questionnaires determine some stable features in the personality structure. Examination VHF by spectral analysis points out a state that ANS (parasympatics and sympatics) is in an actual situation (also under stress). Having applied psychological methods along with examination by (VHF) spectral analysis appears to be an appropriate combination of mutually supplementing methods used in a medical psychological and pedagogical practice (8).

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MICROWAVE HEATING OF FLY ASH FROM MUNICIPAL WASTE INCINERATOR

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ABSTRACT

Kováčová M., Čuvanová S., Lovás M., Jakabský Š., Leonelli C., Veronesi P. & Boccaccini D. **Microwave Heating of Fly Ash from Municipal Waste Incinerator**

The paper is aimed at the research of microwave heating of the fly ash from the municipal waste incinerator in Košice. Before heating, two kinds of fly ashes (from filter and cyclon) were analysed by the XPS method. The samples were heated in the single mode furnace. The microwave heating was focused, the local melting of the samples was confirmed. The evolution of the gases was followed during heating.

Key words: fly ash, municipal waste incinerator, microwave heating, power

INTRODUCTION

In the developed countries, each inhabitant is estimated to produce more than 1 kg/day of municipal solid waste (MSW). Recycling, which implies a careful selection and classification of the waste, is suitable for only about 50 % of MSW, in principle glass and aluminium. The disposal of the non–recyclable fraction of MSW, generally involves dumping in landfills or incineration. Landfill disposal is more and more discouraged due to the possibility that the integrity of dumps might be lost (causing the leaching of materials into water beds), by more severe legal restrictions in all industrial countries (which impose the preliminary inertization of the residues) by the growing hostility of the populations and, above all, by the rising economic and environmental costs of landfill disposal.

The incineration of municipal waste is a way how to reduce their quantity. However, incineration also comes with their own problems, because the solid residues (fly ashes, bottom ashes and slag), which are produced in the proportion of 15–25 % of the MSW incinerated) may contain hazardous materials such as dioxines and heavy metals, and therefore need to be stabilized (1, 2).

The fly ashes used in experiments are from the municipal waste incinerator from Košice (Slovakia), where the production was 1896 t of fly ash in 2006 (this number is a sum of fly ash from cyclon, filters and additives).

According to the literature (3), the design of the applicators is critical to microwave heating because microwave energy is transferred to materials through the applicators. The type of applicators used in the microwave processing system often depends on the materials to be processed. The main difference between these systems consists of:

- single mode cavities tend to have one „hot spot“ where the microwave field strength is high (hot spot means local overheating of material due to selective heating of material and non-uniform electromagnetic field distribution). The size of single mode applicators is approximately one wavelength.

– multimode cavities are usually larger than one wavelength and support multiple modes, i.e. patterns of electromagnetic field distribution. The number of possible resonant modes increases with the increasing size of microwave cavity, which cause the higher occurrence of hot spots leading to a somehow better heating homogeneity.

The paper is aimed at the evaluation of microwave heating of MWI fly ash in single mode cavity at various power output. This configuration was chosen despite the expected unhomogeneity, because the electromagnetic field distribution in single mode applicators is known and the presence of impedance matching devices (short circuit, 3-stub tuner) can be used to compensate for samples properties variations, thus maximizing energy efficiency.

EXPERIMENTAL PART

Material

The fly ash from the municipal waste incinerator (MWI) from Košice (Eastern Slovakia) was used for the experimental study. Fly ash was caught in filters (flyashF) and cyclones (flyashC) during treatment of gases from the incineration process. The chemical analysis of fly ash by XPS (X-ray photoelectron spectrometry) is shown in Tab. 1.

Tab. 1: Chemical analysis of fly ash from filter and cyclon

Elements	Weight [at.%]	
	flyashF	flyashC
Si	4.21	0.75
Al	1.89	0
C	29.07	31.26
O	37.54	23.86
S	1.58	3.53
Mg	1.48	1.04
Ca	11.91	11.66
Na	1.36	1.36
K	1.51	3.13
Fe	0.41	0
F	1.7	0.48
Cl	6.19	21.67
Zn	1.07	1.13
Pb	~ 0.08	0.13

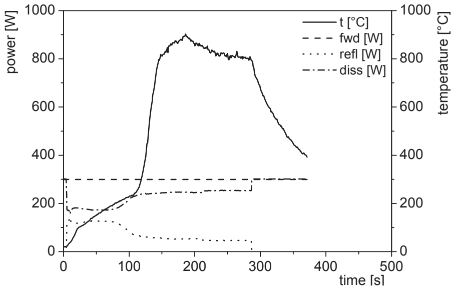

Fig. 1 Microwave heating of FlyashF-300 (single mode, power 300 W)

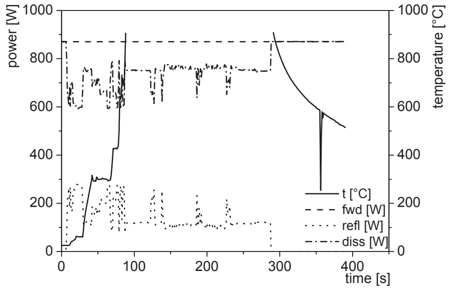

Fig. 3 Microwave heating of FlyashF-870 (single mode, power 870 W)

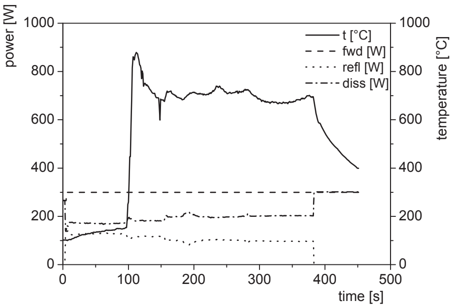

Fig. 2 Microwave heating of FlyashC-300 (single mode, power 300 W)

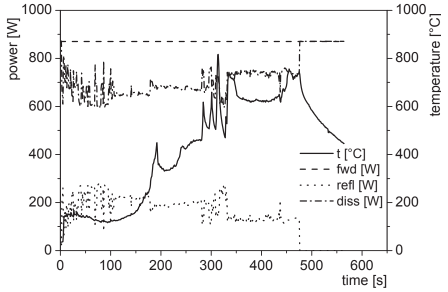

Fig. 4 Microwave heating of FlyashC-870 (single mode, power 870 W)

Methods

The XPS results were obtained with the electron spectrometer ESCA 310 (Gammadata Scienta, Sweden) equipped with the rotating anode of the special UHV design in Prague. Photoelectrons were excited using monochromatized Al K_α X-rays ($h\nu = 1486.6$ eV). The samples were spread on gold plates which were mounted on a sample probe by means of tantalum clips.

The microwave heating was carried out in the single mode microwave furnace based on the WR340 geometry, with output 300 W and 870 W at frequency 2.45 GHz. The heating time was from 300 to 500 seconds. The samples were heated in corundum crucibles. The applicator was tuned during the whole heating process, in order to follow the dielectric properties changes of the material.

Temperature was monitored in the 10 mm diameter spot using a non contact optical pyrometer (model IKS-T14-09, Sitel, Italy) focused on the central part of the load. Detection limit of the pyrometer was 900 °C. Reflected power measurements were performed using a directional coupler (Alter S.r.l., Italy) positioned along the transmission line. Temperature and reflected power measurements were acquired at 1 Hz frequency using an Agilent 34970A Multiplexer and thesoftware Agilent Benchlink Data Logger.

RESULTS AND DISCUSSION

The chemical analysis of fly ash from filter confirmed the higher content of Si, Al, Mg and Fe in fly ash from filter and lower content of C, S, K Cl, Zn and Pb in comparison with fly ashes from both processed (Tab. 1).

The fly ashes differ in grain size and colour visually. The grain size of fly ash from filter was 99 % under 500 μm and fly ash from cyclon was 90 % under 500 μm. The colour of fly ashes was grey before microwave heating and after heating has changed to brown colour (Fig. 5–8). During heating of the samples, the development of yellow gaseous products was observed and also the wall of crucible resulted coloured by yellow. It is assumed that it was sulphur.

Fig. 1–4 show the dependence of power (forward, reflected, dissipated) and sample temperature on time. Fig. 1–2 are referred to samples of fly ash from filter and cyclon heated at 300 W and Fig. 3–4 are samples of fly ash from filter and cyclon heated at 870 W.

During microwave heating, reflected power decreases after 100 s due to the more intensive absorption of microwave energy by the load (Fig. 1). In this point, the rapid increase of temperature also began (Fig. 1, 2). The sharp temperature rise corresponded to minima of reflected power. This could be ascribed to the load permitivity changes as it is progressively, and locally, heated. Fig. 3,4 present rapid changes in curves of reflected, dissipated power and temperature which are caused by exothermic reactions (combustion, oxidation) or by gaseous product evolution which tends to crack the cooler sample surface (exposed to air), thus exposing the inner hotter regions. The calculated value of absorbed energy in the single mode furnace are shown in Tab. 2. The results proved that the samples heated at 300 W had lower values of absorbed energy and samples absorbed more microwave energy during heating.

Tab. 2: Absorbed energy of flyashF and flyashC

Sample	Power output [W]	Absorbed energy [kJ]
FlyashF-300	300	63.11
FlyashC-300	300	72.32
FlyashF-870	870	204.61
FlyashC-870	870	325.62

The samples were melted in one point and from there the heat was spread to the surrounding parts of the sample. According to Fig. 5–8 it is obvious that a significant part of the samples remained in the powder form. Moreover, in the used experimental setup, the temperature measuring spot did not always correspond to the region of the sample subjected to melting. This is particularly evident comparing the time required to reach 800 °C in the graphs of figures 1–3 with the one in figure 4: such a difference can be explained noticing that in case of the graph of figure 4, melting started on the crucible side (Fig. 8), far away from the pyrometer spot, positioned in the centre of the sample. Moving the load, or stirring it, would solve this unhomogeneity problem, allowing also a better temperature control.

From the obtained results, it appears that it is necessary to add a susceptor (material with higher dielectric properties which improves the heating of fly ash and consequently whole mixture), to move the load during its exposure to focused microwaves or to provide a better thermal insulation, in order to homogenously increase the temperature of the whole sample.

Fig. 5 Microwave heating of FlyashF-300

Fig. 6 Microwave heating of FlyashC-300

Fig. 7 Microwave heating of FlyashF-870

Fig. 8 Microwave heating of FlyashC-870

CONCLUSION

The microwave heating of fly ash from the municipal waste incinerator in the single mode cavity was studied. The results confirmed that the samples were melted in one point – hot spot, which is typical for focused microwave heating. The results can be used for the next research of fly ash vitrification in the microwave furnace.

Acknowledgement

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STANDARDIZED PLANT TESTS FOR GENOTOXIC PHYTO-INDICATION OF RADIOACTIVE-CONTAMINATED SOIL FROM SITES AROUND NPP JASLOVSKÉ BOHUNICE

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ABSTRACT

Muriín G., Mičieta K., Chrenová J. & Kovařík P. **Standardized Plant Tests for Genotoxic Phyto-indication of Radioactive-contaminated Soil from Sites Around NPP Jaslovské Bohunice**

Radioactive-contaminated soil from sites around NPP Jaslovské Bohunice was evaluated by the standardized plant tests for genotoxic phytoindication. It confirmed conclusions from our previous tests with wild plants. Considering results from positive controls at *Vicia faba* and *Tradescantia paludosa 02* we may point at possible radioresistance. Sources of this effect are discussed.

Key words: radioactivity, contamination, plant tests, nuclear power plants

INTRODUCTION

The first (pilot) nuclear power plant A1 in the Slovak Republic situated in Jaslovské Bohunice site (60 km from Bratislava) with an electrical output of 143 MW was commissioned in 1972 and running with interruptions till 1977. A KS 150 reactor (HWGCR) with natural uranium as fuel, D20 as a moderator and gaseous CO_2 as a coolant was installed in the A1 plant. Refuelling was carried out on-line at plant full power.

The first serious accident associated with refuelling occurred on January 5, 1976 when a locking mechanism at the fuel assembly failed. The core was not damaged and following the reconstruction of the damaged technology channel, the plant continued in operation. Serious problems were occurring with the integrity of steam generators when the plant had to be shut down frequently due to failures and subsequent repairs. This accident caused death of two workmen.

The second serious accident occurred on February 22, 1977 when the fuel assembly was overheated with a subsequent release of D20 into the gas cooling circuit due to human failure in the course of replacement of the fuel assembly. Subsequent rapid increase in humidity of the primary system resulted in damages of fuel elements in the core and the primary system was contaminated by fission products (*1*).

Above-mentioned accidents in the power plant initiated the monitoring of possible radioactive impact on the environment. The biggest study of the area was done in the cooperation between the International Atomic Energy Agency (IAEA) and VÚJE (Výskumný ústav jadrových elektrární, Research Institute of Nuclear Power Plants) in Trnava. The 19 km long banks of the Jaslovské Bohunice NPP waste water recipient has been identified as contaminated by ^{137}Cs as a result of two accidents on the NPP-A1 unit in 1976 and 1977, respectively. In total, more than 67,000 m^2 of riverbanks have been found as being contaminated at levels exceeding 1 Bq ^{137}Cs/g of soil (*2*).

Collected soil samples from the vicinity of NPP Jaslovské Bohunice were evaluated under standard tests of *Vicia sativa, Vicia faba, Tradescantia* –

Tradescantia paludosa 02 test and *Tradescantia* 4430 test.

MATERIAL AND METHODS

Collection of samples at site was made thanks to the cooperation with the VÚJE in Trnava. The exposition was selectively measured for each sample and reached values between 46.7 – 57 – 196 – 507 – 571 pGy/sec. The shielded detector NB 3201 was used for measuring the dose rates. The detector was situated 30 cm above the sample of soil in the place of "hot spot". Control locality was chosen in the vicinity of the village Lieskovec – Podunajské Biskupice (60 km SW from Jaslovské Bohunice on the bank of the Danube River without radioactive contamination). Details are shown in Tab. 1.

Vicia sativa test was modified the way that swollen seeds in distilled water have not been cultivated at filtrate paper, but planted in observed soil samples. Control sample was cultivated in moist agroperlit and watered by distilled water.

Tradescantia micronucleus test (Trad MCN) was realized by the standardized method. Segments of standard cultivated plants *Tradescantia paludosa* clone 02 were covered by tested soil and 12 hours at 20 ºC exposed (ends of segments were closed in cotton wool which was damped by pabulum Hoagland 2). Frequency of micronucleus in tetrads with frequency of chromosome aberrations in ana-telophases of I and II meiotic division were observed.

For positive control at *Vicia faba* seeds GammaCell device with dose rate of 11.5 Gy/h was used. For broader spectra of results a scale of differently aged *V. faba* seeds were treated by emissions of different doses (2,5; 5; 10 Gy/h) of ^{60}Co. Doses were measured by Fricke dosimetre.

For positive control at *Tradescantia paludosa* the exposure from homogenous source of ^{137}Cs with dose rates of 0.17 and 0.34 μGy.h^{-1} for 96 hrs (with recovery time of 96 hrs) was used.

Tab. 1: Studied soil samples from the vicinity of NPP Jaslovské Bohunice

Locality No.	Site of sampling	Dose rates ^{137}Cs pGy/sec
1	Manivier drainage, 30 m from the bridge (the village Žlkovce), downstream	507
1a	Manivier drainage, 1 m apart of the spot above (the village Žlkovce), downstream	46.7
2	Manivier drainage, 500 m from the bridge (the village Žlkovce), downstream	571
3	Bučany, 15 m from the Dudváh river, downstream	196
3a	Bučany, 30 m from the Dudváh river, downstream	57
4	Sediment of old river-bed of the Váh river, grassy bottom of the Siladice river	9.50

RESULTS

Vicia sativa test – Simultaneous test of phytotoxicity and mutagenicity

Test was realized at all monitored soil samples. The results are shown in Tab. 2.

Tab. 2: Results of the *Vicia sativa* test

Sample	IC in %	No of ana-telophases	Frequence of aberrations in %
1	0	500	0.4 ± 0.4
1a	0	500	0.2 ± 0.2
2	0	500	0
2a	0	500	0.2 ± 0.2
3	0	500	0.4 ± 0.4
4	0	500	0.2

Vicia faba test

For our study the test was modified by the following method:

- 2 hours of exposition, evaluation immediately after treatment, ana-telophases;
- 2 hours of exposition, evaluation 26 hours after treatment (3 hours of pretreatment by 0.05 % colchicine, c-metaphases;
- 24 hours of exposition, evaluation immediately after treatment, ana-elophases;
- 24 hours of exposition, evaluation 26 hour after treatment; c-metaphases.

Only the sample with the highest dose of radioactivity was evaluated and the results are shown in Tab. 3.

Positive control of *Vicia faba* seeds

To compare impact of radioactivity from samples collected around NPP Jaslovské Bohunice with radiation from the standardized source under standardized conditions we have used in co-operation with the Faculty of Nuclear Sciences and Physical Engineering (the Czech Republic) Gamma-Cell device with emissions of different doses ^{60}Co. For broader spectra of results a scale of differently aged *V. faba* seeds was used. The results are shown in Tab. 4 and 5.

Tradescantia test

Taking and evaluation of samples were realized by the following method:

Tab. 3: Results of the *Vicia faba* test

Sample No.	Activity ^{137}Cs pGy/sec	Exposition in hrs	No. of evaluated ana-telophases *c-metaphases	Frequency of aberrations in %
2	571	2/0	300	0.3
2	571	2/26	*300	0.3
2	571	24/0	300	0.6
2	571	24/26	*300	0.3

- 12 hours of exposition, evaluation 20 hours after treatment, evaluation of micro-nucleus frequency per 1000 tetrads;
- 12 hours of exposition, evaluation immediately after treatment, evaluation of 500 ana-telophases I.;
- 12 hours of exposition, evaluation 30 hours after treatment, evaluation of 500 ana-telophases II.

In case of the clone *Tradescantia paludosa* 02 we completed the cytogenetic test in meiosis and the micronucleus test in the tetrads.

The results are shown in Tab. 6.

Tab. 4: Results of positive control of *Vicia faba* seeds (vitality)

Age of seed samples in years	Exposition in Gy/h	Length of roots in mm		
		48 hrs	72 hrs	96 hrs
22	Blank	3.44 ± 1.48	7.11 ± 2.96	11.67 ± 4.86
	2.5	4.67 ± 1.22	18.55 ± 3.36	24.78 ± 4.73
	5	4.89 ± 2.02	12.00 ± 4.40	15.67 ± 5.60
	10	6.67 ± 1.37	17.78 ± 3.28	23.89 ± 4.65
14	Blank	10.22 ± 1.02	36.22 ± 2.05	48.89 ± 2.19
	2.5	10.56 ± 1.09	27.89 ± 0.87	39.11 ± 1.01
	5	11.44 ± 1.19	30.44 ± 3.13	41.00 ± 4.22
	10	8.89 ± 0.68	21.55 ± 1.89	29.44 ± 2.63
2	Blank	13.78 ± 1.50	24.56 ± 3.24	29.22 ± 4.18
	2.5	14.89 ± 0.54	28.44 ± 1.78	38.56 ± 3.56
	5	12.00 ± 1.53	22.67 ± 3.30	32.89 ± 4.67
	10	14.56 ± 0.87	27.44 ± 1.34	36.89 ± 2.06
Control (2-year old)		12.54 ± 0.56	27.09 ± 1.48	36.64 ± 2.86

Tab. 5: Results of positive control of *Vicia faba* seeds (genotoxicity)

Age of seed samples in years	Exposition in Gy/h	No. of evaluated ana-telophases	Frequency of aberrations in %
22	Blank	430	0.70
	2.5	500	0.60
	5	328	1.83
	10	281	1.07
14	Blank	500	0.40
	2.5	500	0.60
	5	448	0.89
	10	499	1.00
2	Blank	181	1.10
	2.5	444	0.70
	5	451	1.11
	10	390	1.54
Control (2-years old)		500	0.40

Tab. 6: Results of the micronucleus test *Tradescantia paludosa* 02

Sample No.	Activity ^{137}Cs pGy/sec	Exposition in hrs/recovery time	No. of evaluated *I. ana-telophases ^{x}II. ana-telophases ^{o} tetrades	Frequency of aberrations and MCN^{o} in %
2	571	12/0	*500	3.6 ± 0.4^{+}
2	571	12/30	^{x}500	2.4 ± 0.4^{+}
2	571	12/30	^{o}1000	^{o}4.5 ± 0.2^{+}
Negative control	9.5	12/0	500	1.8 ± 0.2
Positive control (diffusive exposition)	1000	12/0	500	8.9 ± 1.2
	1000	12/12	500	4.8 ± 0.4

+ without recovery time (with recovery time clastogenicity was not increased)

Tab. 7: Results of the *Tradescantia* test 4430 SHM system

Sample No.	Activity ^{137}Cs pGy/sec	SHM mutations in % 9. 10. day after exposition
1	507	0.26 ± 0.06
1a	46.7	0.30 ± 0.05
2	571	0.36 ± 0.07
3	196	0.26 ± 0.04
3a	57	0.23 ± 0.05
4	9.50	0.16 ± 0.04

Tradescantia test 4430 SHM system

Tradescantia color-mutation test (Trad-SHM) was performed by the protocol where segments were exposed 24 hours at 20 °C similarly at clone 4430 in Trad-MCN test.

The results are shown in Tab. 7.

DISCUSSION

Collected soil samples from the vicinity of NPP Jaslovské Bohunice were evaluated under the standard tests of *Vicia sativa, Vicia faba, Tradescantia* – T*radescantia paludosa* 02 test and *Tradescantia* 4430 test. Results of these tests confirmed our previous results at wild plant species (3). With use of the results from positive controls at *Vicia faba* and *Tradescantia paludosa 02* we may point at possible radioresistance (4). In positive controls at *Vicia faba* radiation of differently aged seeds showed almost stimulative effect at the oldest and youngest samples, while the level of chromosome aberrations were insignificant against the control. The same it was with *Tradescantia paludosa 02*. The explanation may be in existence of "check point" in the mitotic cycle that is not allowing heavily damaged cells to continue in growing and therefore seeds to germinate. The same effect was reported after the Chernobyl nuclear disaster at other species. From our results it seems to be clear that ability of plants to adapt or resist to higher doses of radioactivity may be a result of long-term evolutionary selection of the most durable species. Natural selection of the most adapted genotypes of *Stipa capillata* was observed within almost half a century of their exposure to a low dose rate of ionizing radiation on the Semipalatinsk nuclear test site in Kazakhstan (5). The yield of cytogenetic damage in leaf meristem of agricultural crop plants such as rye and wheat grown in the 10-km zone of Chernobyl NPP was evaluated by Geraskin et al. (6) and found to be dependent on the level of radioactive contamination. Their analysis of experiments with genetic variability in three sequential generations of rye and wheat revealed increased cytogenetic damage in plants exposed to chronic irradiation during the 2nd and 3rd years. In case of standard laboratory tests we may then confirm that these processes are somehow universal in plants.

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POSTIRRADIATIONAL CHANGES IN HEMATOLOGIC PARAMETERS AND IN INTESTINAL MICROFLORA IN RATS

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ABSTRACT

Beňová K., Strišková K. & Dvořák P. **Postirradiational Changes in Hematologic Parameters and in Intestinal Microflora in Rats**

A decrease in the defense capacity of the body combined with penetration of intestinal microorganisms through the intestinal wall causes severe, often lethal complications of the acute radiation disease. We followed the clinical symptoms, the changes of hematological parameters and the changes of the composition of intestinal microflora in laboratory rats irradiated by a single, whole–body dose of 15 Gy gamma-rays. An increase of the common microflora in duodenum, liver and in oral cave and leucopoenia in peripheral blood have been observed in all time intervals followed. The changes in red blood cells were characterized by anemia, manifesting clinically in hemorhagies and bloody diarrhea.

Key words: ionizing radiation, clinical symptoms, hematological changes, microflora, rats

INTRODUCTION

The wide use of nuclear technologies in various areas of human activities made necessary to work out methods of radioprotection. Therefore, it is important to know the detailed mechanisms of the biological action of radiation and that of the pathogenesis of radiation disease. Up to now a huge amount of knowledge about the radiation effects on living organisms have been accumulated, but a unifying theory of their mechanisms is still lacking [1, 2].

Post-irradiational changes in peripheral blood and in hematopoesis in mammals and birds are often followed in literature [7, 9, 14]. The evaluation of these changes belongs to the basic diagnostic methods of the radiation disease. Based on clinical symptoms, hematological parameters and changes in microflora the severity of radiation disease and the prognosis of pathogenesis could be estimated.

The aim of our work was to investigate the changes in hematological parameters and in intestinal microflora in rats irradiated with a supralethal dose of gamma-rays and observe the dynamics of overall clinical symptoms during 9 days after irradiation.

MATERIAL AND METHODS

Male Wistar rats, aged 3 months were used in the experiments. Before the experiment, the animals were kept for 1 week in a previously disinfected room to acclimatize to experimental conditions [5]. They were housed in plastic cages on wood shavings at 22–24 °C and 65 % relative humidity of air. The animals had a free access to pelleted standard food and tap water [13].

After the adaptation period the rats were irradiated by a single whole-body dose 15 Gy of gamma-rays from a ^{60}Co-source (irradiation apparatus CHISOSTAT, Chirana, Prague, Czech Republic) by a dose rate of 0.117 Gy.min^{-1}. The animals were then divided into experimental groups (n = 6), analyzed 3, 6 and 9 days after irradiation. From animals fasting overnight a swab of the oral mucus was taken, then they were sacrificed by fast decapitation and samples of blood, liver and duodenum were taken in sterile conditions. Hematological parameters (the total erythrocyte number – RBC, the hemoglobin content – Hb, the hematocrit value – PVC, the total number of leucocytes – WBC and the differential blood picture – leucogram) were determined by standard methods [3]. For examination of microbiological parameters culture medium for faecal streptococci and the agar medium No. 2 were used [8]. Parallel to each experimental group, groups of sham-irradiated controls of equal size were analyzed. The results were statistically evaluated by non-pared t-test.

RESULTS

The clinical symptoms in irradiated animals observed from the 2nd post-irradiational day were: diarrhea, apathy, somnolence, piloerection and hemorrhages on eyes. The first mortalities occurred on the 3rd day. Beginning with the 5th day the animals took no food and bloody diarrheas were observed. Comparing with controls, they were markedly cachectic. None of irradiated animals survived the 10th day after irradiation. The number of *E. coli* in duodenum increased with time (Tab. 1).

In liver the presence of *E. coli* was observed on the 3rd and 9th days after irradiation. In controls the livers were sterile. In oral cave, except of the common respiratory flora we found in irradiated animals *E. coli* on the 6th and 9th days after irradiation. The results of post-iradiational changes of hematological parameters are given in Tab. 2. On the 3rd day after irradiation both the total erythrocyte count (TEC) and the content of hemoglobin in erythrocytes (EHC) were statistically non–significantly increased. The haematocrit value (HT) was statistically significantly increased ($P<0.05$), too. On the 6th post-irradiational day the increase of EHC and HT persisted, but the TEC was decreased ($P<0.01$). On the 9th day all the three hematological parameters were statistically significantly ($P<0.01$) decreased in comparison with controls.

In white blood picture marked changes were observed already on the 3rd day after irradiation. The observed leucopoenia ($P<0.01$) had neutropenic ($P<0.01$) and concurrently lymphopenic ($P<0.01$) characteristics in all post irradiation intervals. The parallel occurring eosinopenia and monocytopenia were not statistically significant.

Tab. 1: Changes of the population size of *E. coli* in duodenum of irradiated rats

	control	**3. day**	**6. day**	**9. day**
E. coli	**–**	**1.10^3**	**17.10^3**	**2.10^7**

Tab. 2: Changes of hematological parameters in rats after irradiation with a single whole-body dose of 15 Gy gamma-rays

Hematologic parameter	**SI**	**Control**	**Days after irradiation**		
			3 days	**6 days**	**9 days**
Erythrocytes	T.l	6.57	7.39	4.43**	1.61***
Hematocrit	l.l	0.40	0.55*	0.48	0.20**
Hemoglobín	g.l	121.60	136*	130.7	44**
Leucocytes	G.l	6.07	0.4***	0.97***	0.93***
Neutroph. segm	%	32.1	95***	83***	88***
Neutroph. rods	%	1	0	2	1
Juveniles	%	1	0	1	0
Lymphocytes	%	60.66	5***	14***	11***
Eosinopfiles	%	1.66	0	0	0
Monocytes	%	0.66	0	0	0
Basophiles	%	0	0	0	0

***$P<0.001$ **$P<0.01$ *$P<0.05$

DISCUSSION

The ionising radiation exerts profound effects on the mucous lining of the gastrointestinal tract: as a result of its impact on the dividing enterocytes in the crypts the continuous replacement of the dying and desquamating cells on the top of the enteric villi is interrupted. This state leads to the interruption of the regeneration processes of the gut mucous and to the loss of its functions. Clinically, this state manifests in diarrhea and in a subsequent cachexia. The damage of the barrier functions of the intestinal mucous caused by the high radiosensitivity of the enterocytes, along with the disruption of the impermeability of blood capillaries conditioned by the high radiosensitivity of endothelial cells belong to the typical symptoms of the radiation disease [10]. The increased permeability of blood capillaries leads to development of hemorrhagic diatesis as it was observed in our experiments on the eyes of the irradiated rats and on the presence of bloody diarrhea.

Microorganisms commonly present in the gastrointestinal tract penetrate after irradiation through the intestinal mucus and the damaged capillaries of the intestinal wall into the blood circulation, where they acts as antigens. In irradiated organisms, however, because of lymphopenia and monocytopenia caused by radiation the immunoligical response is strongly suppressed. This can lead to further reproduction of bacteria and to the development of bacteremia and of subsequent toxinemia. The prolonged depression of immunological reactions as a result of radiation leucopenia leads to sepsis, followed by death of the animal.

From the point of view of the early diagnostics of the radiation disease the most important are the changes in white blood cells. In our experiments in all irradiated individuals a statistically significant decrease of the total number of leucocytes and an increase of neutrophils in comparison with controls occurred. Shortly after irradiation leucopenia characterized by lymphopenia and neutrophilia was observed. The changes in the white blood picture are caused not only by the damage of the bone marrow, but also of the lymphoid tissues with myelopoetic functions, like thymus, the lymphatic nodes, and the *Bursa fabricii* in birds [6, 12]. The lymphocytes, on the other hand, show a high degree of direct radiosensitivity and their number in peripheral blood decreases as a result of their direct extinction. The immunosuppressive effect of radiation could be critical for the irradiated organism, as much it becomes sensitive not only to various infections, but also to the common microflora, which leads to postradiation bacteremia [1].

In the total number of erythrocytes as well as in the hemoglobin content a statistically non-significant increase was recorded 3 days after irradiation. The increase of the hematocrit value was in this time interval statistically significant. Starting with the 6th day after irradiation a statistically significant increase in CPE was recorded, which was prolonged up to the 9th day. The hemoglobin content was increased still on the 6th day after irradiation, however, on the 9th day a marked decrease of this parameter in comparison with controls occurred. The hematocrit values decreased only on the 9th day after irradiation. The following changes in the red blood picture are due to the high radiresistence of the erythrocytes and also due to the fact that the body disposes with large reserves of these blood cells deposited in the spleen and in liver [4, 7]. The anemia which belongs to the basic symptoms of the radiation disease manifest itself as the latest of the hematological changes. The extent of the hypoplastic or aplastic anemia and the degree of damage which are documented after irradiation depend, except of the radiosensitivity of cells, also on the exposition dose and on the dose rate, the regeneration capacity of the cells, e.g. Subakov et al. [11] using chronical irradiation with a total dose of 0.9 Gy of gamma-rays recorded an increase of the number of reticulocytes in the peripheral blood, which is an evidence of an increased erythropoesis in the bone marrow. In the case of the dose applied by us irreversible changes in the bone marrow can be assumed, which leads to the development of the anemia described above. The normal tissue is replaced by the fat tissue which is unable to produce differenciated blood cells. Also the destruction of existing cells (karyorexis, karyolysis) and cytogenetic damage of cells occur (4).

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DETERMINATION OF EQUIVALENT MIXING HEIGHT AND ATMOSPHERIC STABILITY ASSESSMENT

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ABSTRACT

Šimon J., Bulko M. & Holý K. **Determination of Equivalent Mixing Height and Atmospheric Stability Assessment**

Atmospheric stability is an indicator that reflects the intensity of boundary layer mixing processes. This feature of the atmosphere is especially important since it defines dispersive atmospheric conditions and provides information on how effectively the anthropogenic pollution will be transferred to the higher levels of the atmosphere. The assessment of atmospheric dispersiveness plays a crucial role in the protection of air quality and public health in big cities. The presented paper deals with determination of atmospheric stability via so called *Equivalent Mixing Height (EMH)* quantity using a radioactive noble gas ^{222}Rn. A method of deriving a link between ^{222}Rn activity concentration, eddy diffusion coefficient and EMH using fluid mechanics is also outlined in this work.

Key words: Equivalent mixing height, stability, ^{222}Rn

INTRODUCTION

Laminar and eddy flows are the main mixing mechanisms occurring in the horizontal as well as vertical direction. Laminar flows are initiated by pressure gradients, whereas eddy flows are generated by gradients of substance concentrations. Although present physics is on a high level of knowledge, eddy diffusion is still a terra incognita and the only way to describe it qualitatively and quantitatively is to use parametric models. One of them is a model based on a modified continuity equation, which is presented in this paper. The modified continuity equation is a discrete analogue of the principle of conservation of matter. Its mathematical formulation is grounded on the assumption that the relevant block of atmosphere can be substituted by an idealized cell with dimensions Δx, Δy, h (see fig. 1) [1,2]. Due to mixing processes we are allowed to suppose a zero gradient of the substance concentration inside the cell. Laminar advective flow described by a simple vector field and a constant exhalation rate of a substance from the ground are assumed as well. Under the above-mentioned conditions the principle of conservation of matter has the following form:

$$\frac{d\rho}{dt}=\frac{\phi}{h}-\lambda\rho-\frac{u}{\Delta x}\left(\rho-\rho_0\right)-\alpha\frac{1}{h}\frac{dh}{dt}\left(\rho-\rho'\right)$$

[3, 4]. (1)

Here ρ stands for the concentration of the substance, ρ´ is the substance concentration above the cell, ρ_0 is the substance concentration beside the cell (see fig. 2), ϕ is the surface exhalation rate of the substance, λ is the radioactive or chemical decay constant, **Δx** is the horizontal dimension of the cell in the direction of wind flow, α is the discontinuous function:

$$\alpha=\begin{matrix}1 \text{ if } \dfrac{dh}{dt}>0\\[2ex] 0 \text{ if } \dfrac{dh}{dt}\le 0\end{matrix}\qquad(2)$$

and **h** is so-called *equivalent mixing height* (*EMH*).

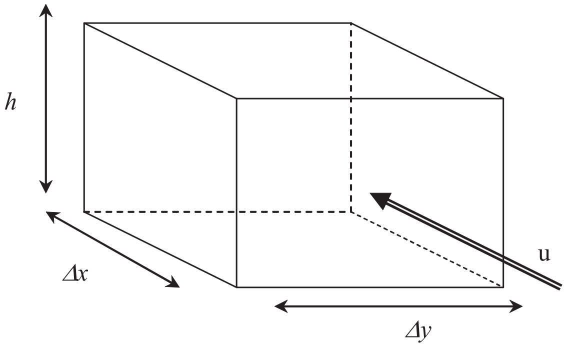

Fig. 1 Scheme of a simplified cell

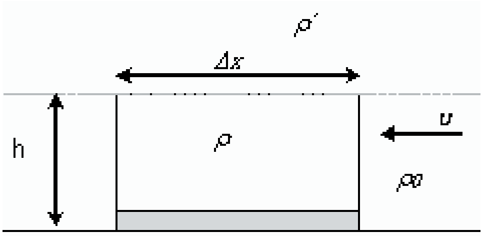

Fig. 2 Description of symbols in equation (1)

As one can see, equation (1) depends on the quantity *h* quite strongly and possible temporal changes of *h* could induce variations of concentration, too. The 'natural' use of equation (1) would be the computation of the temporal course of a substance concentration. However, if the temporal course of concentration is known, we can turn equation (1) in such a way that we can use it for computing of the parameter *h*. After several algebraic steps we obtain the basic equation for EMH:

$$\alpha\left(\rho-\rho'\right)\frac{dh}{dt}+\left[\frac{d\rho}{dt}+\lambda\rho+\frac{u}{\Delta x}\left(\rho-\rho_0\right)\right]h-\phi=0 \quad [4] \quad (3)$$

EMH represents the height of the atmosphere where intensive mixing takes place and to a large degree reflects the intensity of atmospheric exchange processes. To put it simply, the higher EMH, the more intensive mixing and the lower stability index. Finally, it should be pointed out that there is a possibility of linking the EMH with atmospheric stability (characterized by the eddy diffusion coefficient **K**).

By analogy to the phenomenon of molecular diffusion, it is customary to describe the eddy diffusion by the partial differential equation:

$$\frac{\partial\rho}{\partial t}=K\frac{\partial^2\rho}{\partial z^2}-\lambda\rho+q \quad [5], \qquad (4)$$

where **q** stands for the substance supply rate, **K** is the eddy diffusion coefficient and the remaining symbols have the same meaning as in the previous text. When a constant continual flat source and a time invariant **K** are supposed, the solution of (4) is:

$$\Delta\rho=\frac{\phi}{2\sqrt{K_z\lambda}}e^{-\sqrt{\frac{\lambda}{K_z}}z}\left[1+\mathrm{Erf}\left[\sqrt{\lambda\tau}-\frac{z}{2\sqrt{K_z\tau}}\right]-\right. \\ \left.-e^{\sqrt{\frac{\lambda}{K_z}}2z}\left(1-\mathrm{Erf}\left[\sqrt{\lambda\tau}+\frac{z}{2\sqrt{K_z\tau}}\right]\right)\right]. \quad (5)$$

Here τ is the time of substance aggregation (the time interval between the two subsequent measurements of substance concentration).

If one accepts Fontan's [1, 2] definition of EMH:

$$h(t)=\frac{\int_0^\infty \Delta\rho(z,t)\mathrm{d}z}{\Delta\rho(0,t)}, \qquad (6)$$

then after placing (5) into (6) one obtains the link between EMH and eddy diffusion coefficient *K*:

$$h=\sqrt{\frac{K_z}{\lambda}}\frac{1-e^{-\lambda\tau}}{\mathrm{Erf}\sqrt{\lambda\tau}}, \qquad (7)$$

or after a few algebraic procedures:

$$K_z=h^2\lambda\frac{\mathrm{Erf}\sqrt{\lambda\tau}}{1-e^{-\lambda\tau}}. \qquad (8)$$

The most appropriate substance for the purposes of EMH computation is a radioactive noble gas ^{222}Rn. It excels in advantageous physical and chemical characteristics. From the wide list we pick just the most important ones:

^{222}Rn is produced by radioactive decay of ^{226}Ra in the soil grains. Part of the produced ^{222}Rn gets into the soil air. Then it is transported mostly by diffusion processes into the atmosphere. Decay products of ^{222}Rn remain in the soil because they are solid state metals. The amount of ^{222}Rn that escapes from the soil to the atmosphere depends on the depth where radon was created and on the permeability of the surrounding soil. Radon present in the atmosphere is created mostly in the top 10 m of the soil [6].

Exhalation rate of ^{222}Rn generally depends on ^{226}Ra content in soil, diffusion and emanation coefficient and soil properties. Average exhalation rate has been estimated to be 0.7–1.3 atoms. $cm^{-2}s^{-1}$. ^{222}Rn exhalation from oceans is 2–3 orders of magnitude lower than from the ground surface [6]. Significant variations in ^{222}Rn exhalation rate have not been proved yet.

^{222}Rn gets to the atmosphere also by emanation from ground water. The mechanism is simple. After the ground water enters the atmospheric environment, the majority of radon is released. Other ^{222}Rn sources, mostly of anthropogenic origin, are negligible when compared to the previously mentioned ones [7].

METHODS

Continual measurements of ^{222}Rn activity concentration in the outdoor atmosphere has been carried out since 1991 at the Faculty of Mathematics, Physics and Informatics. Samples are collected above an open grassy area in front of the faculty building at a height of 1.5 m above the earth's surface. A high-volume scintillation chamber has been used for the measurement of ^{222}Rn activity concentration. The detector itself is a cylinder made of brass, with a diameter of 12 cm and with a length of 40 cm. The chamber volume is approximately 4.5 l. ZnS(Ag) has been chosen as a scintillation material. At each side of the detector there is a glassy window and a photomultiplier tube. The drawn-in air enters the peripheral sectors first and then, passing near the windows, it goes to the inner sector and finally it is drained out. The air flow through the detector is 0.5 l/min.

Before the air enters the detector itself, firstly it passes through a high-volume tube where ^{220}Rn ($T_{1/2}$ = 55 s) decays completely. In the next step there is a system of freezing traps and silica gel boxes where the H_2O vapour is removed from the sucked air at a temperature of –20 °C. Just before the detector there is a membrane filter used for collecting aerosols with deposited ^{222}Rn decay products. Using this experimental setup it is ensured that only pure air and ^{222}Rn enters the scintillation chamber [8].

RESULTS AND DISCUSSION

Because of the huge datasets that have to be processed, the direct EMH numerical computations are out of question. For example to solve equation (3) numerically for a single year takes approximately 4300 calculations. The only effective solution is the use of PC along with an appropriately programmed code. From several programming languages suitable for our purposes we chose the MATHEMATICA 5 package. The results of the numerical computation could be presented in a form of tables or by synoptic charts. To be as clear as possible, we have chosen the second way.

Equivalent mixing height was computed in the time interval from 1.1.2004 to 31.12.2004. Because of the limited space available we cannot present the full results here. In order to be brief we present just illustrative example results for summer as well as winter season. As one can see in figure 3, the courses of ^{222}Rn activity concentration and EMH anticorrelates nearly ideally (when the ^{222}Rn volume activity is high, EMH gets low and vice versa).

Statistical summary of numerical results offers interesting conclusions. Firstly, daily variations of EMH are observed. It is clear that the EMH reaches a maximum in the afternoon between 2–4 p.m. and a minimum just before sunrise. This pattern is especially well visible in the summer season when the amplitude of the temperature is high enough to boost the eddy diffusion and convective turbulence.

To obtain an evidence of the presence of annual EMH variations we carried out the harmonic Fourier analysis of the averaged diurnal EMH waves. The tested Fourier series were restricted to the first two harmonic terms:

$$f(x) = A + B\sin\left(\frac{\pi}{12}t + \pi\varphi\right) + C\sin\left(\frac{\pi}{6}t + \pi\psi\right) . \tag{10}$$

Function (10) is used for characterization of the time courses of ^{222}Rn activity concentration and for

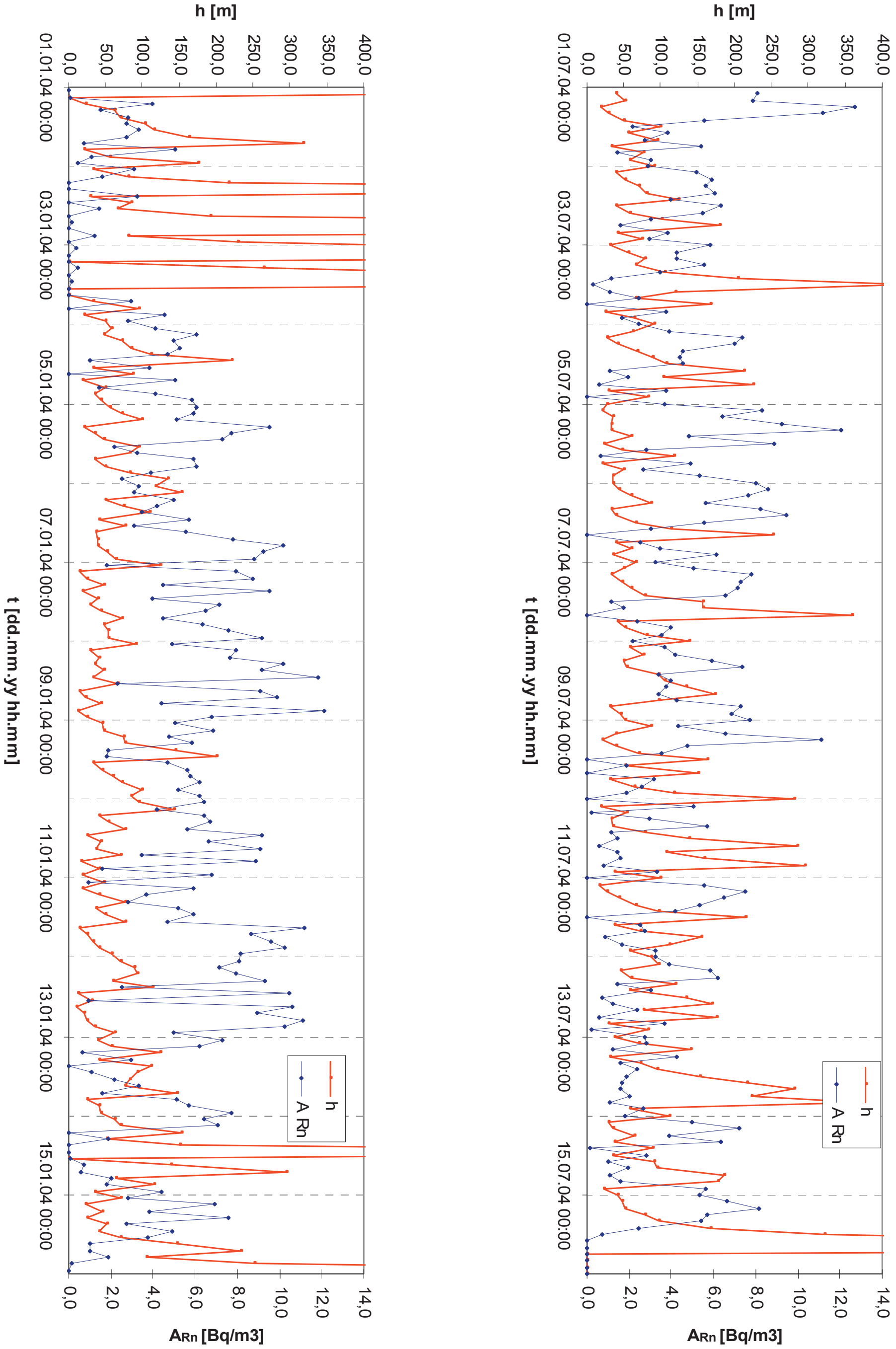

Fig. 3 Comparison of EMH and ^{222}Rn volume activity in outer atmosphere during January 2004 (left) and July 2004 (right)

this reason we also picked of this function for the characterization of EMH. Our choice has also been influenced by the work [9]. By means of nonlinear regression the coefficients A, B, φ, C and ψ were obtained to fit daily average waves for each month within year 2004. The package Microcal ORIGIN 6.0 was used for this purpose. Results are depicted in figures 4–8 and they lead to interesting conclusions. The annual mean value of EMH $\overline{h}$ remains approximately constant during the whole year at a level of 123.4 m. However, a potential by small variation cannot be rejected due to weak statistics. Deviations from the mean value are at a level of 26 %. The coefficient B, representing a 24 h oscillation amplitude, varies inversely to the coefficient A. It reaches the minimum in September and the maximum at the beginning of January. The variation of the coefficient B deviates from its mean value at the level of 86% and significantly anti-correlates with ^{222}Rn activity concentration. It is not easy to draw a conclusion about the coefficient C because of rather big uncertainties at a level of 50 % as well as due to weak statistics. Anyway, we can state that the annual average value $\overline{C}$ is at a level of –26 m and the deviations are about 100 %.

The variation with the period of 24 h can be regarded as the dominant one since its amplitude is 2.3 times higher than the variation with the period of 12 h. Finally, the values of the parameter φ (ψ) oscillate around the mean value 0.25π (0,9π) with the variation at a level of 100% (55%). From figures 7 and 8 it is also obvious that the minimum of EMH is shifted from 2:30 a.m. in summer to 8:30 a.m. in winter and depends fairly well on sunrise time.

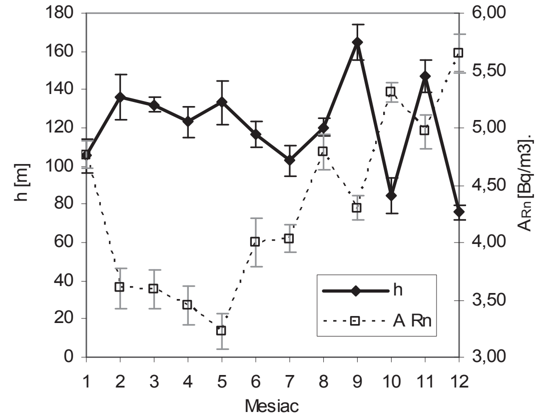

Fig. 4 Annual course of coefficient A (10) for EMH and ^{222}Rn volume activity

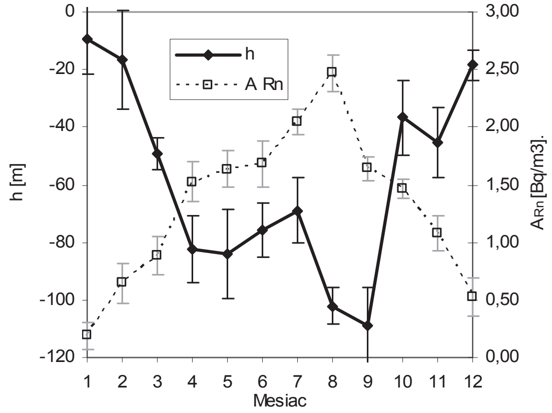

Fig. 5 Annual course of coefficient B (10) for EMH and ^{222}Rn volume activity

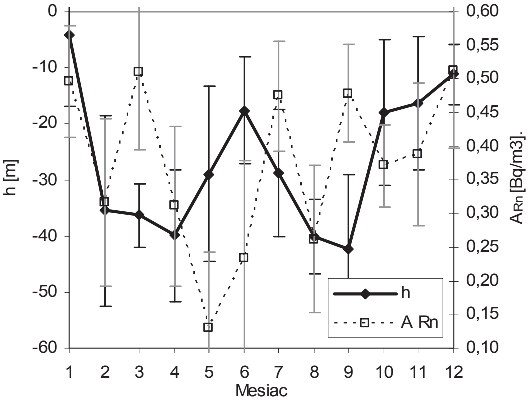

Fig. 6 Annual course of coefficient C (10) for EMH and ^{222}Rn volume activity

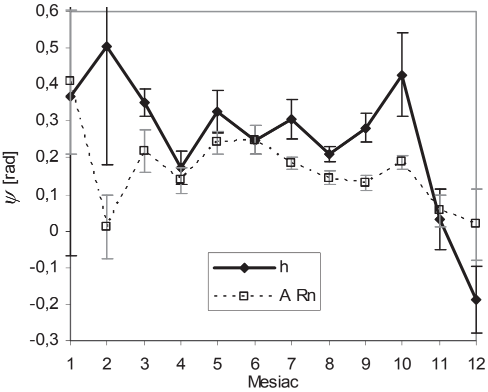

Fig. 7 Annual course of coefficient φ (10) for EMH and ^{222}Rn volume activity

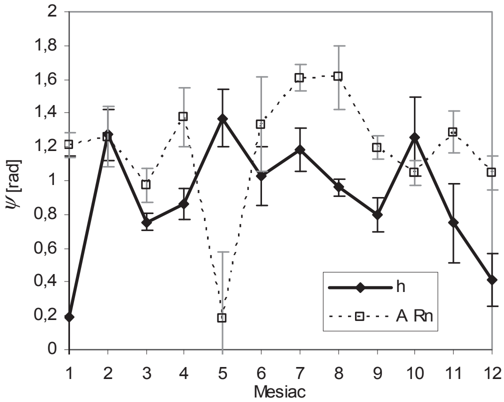

Fig. 8 Annual course of coefficient ψ (10) for EMH and ^{222}Rn volume activity

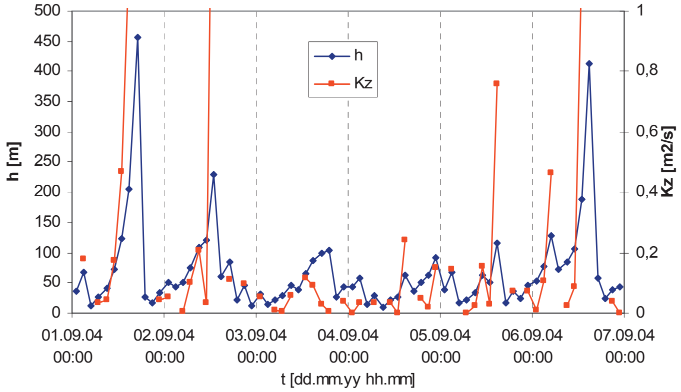

Fig. 9 Comparison of EMH and eddy diffusion coefficient K_z, counted using (8) within 1.–7. 9. 2004

Finally, the relation (8) between EMH and eddy diffusion coefficient K is depicted in fig. 9. One must bear in mind that the validity of equation (8) is restricted only to situations when $\frac{dh}{dt} > 0$.

CONCLUSIONS

Theoretical and experimental results regarding the monitoring of ^{222}Rn activity concentration and numerical computing of the equivalent mixing height are presented in this paper. Mathematical formalism linking together the EMH and eddy diffusion coefficient based on numerical solution of ordinary differential equations has been developed and presented. Furthermore, there are also presented statistical summaries of the results for the year 2004, leading to the conclusion that both EMH and K_z have diurnal and annual periodicity. The diurnal waves are simple variations with maximum in the afternoon and minimum just before sunrise. Regarding annual wave besides the main variation with the period of 1 year we must also take into account the second harmonic component with a period of 6 months, which demonstrates itself mostly in winter season.

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DETERMINATION OF ANTIMONY BY ON-LINE ELECTROCHEMICAL PRECONCENTRATION/GFAAS

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ABSTRACT

Manová A., Tropp M., Čacho F. & Beinrohr E. **Determination of Antimony by on-line Electrochemical Preconcentration/GFAAS**

The aim of this work was to develop an on-line coupling of electrochemical preconcentration to the AAS method and the utilization of the developed system for the determination of ultra-trace amounts of Sb in water samples. A flow-through electrochemical analyzer EcaFlow (Istran, Bratislava) was used as the preconcentration unit with the two-electrode cell. The working electrode was an RVC electrode coated with gold. The AAS spectrometer Spectraa 400 with the graphite furnace atomizer (Varian) was used to measure the preconcentrated Sb species. The preconcentration parameters for the electrochemical process were optimized. The deposition runs at a constant current of – 8000 the μA and the optimum stripping current was found to be 150 μA.

Key words: Antimony, GFAAS, electrochemical, preconcentration

INTRODUCTION

The increasing of concentration of the toxic element (As, Hg, Cd, etc.) and their compounds in the water, soil and air present serious problem for humans. Toxic properties of the elements could be transferred from the soil to the foodstuff and mammals by erosion cycles. Consequences of medical research indicate that the many compounds exhibit like injurants at inconsiderable amounts as was supposed years ago. Determination of the toxic elements represents a typical problem of ultra-trace analysis. In this work we have focused on determination of Sb(III).

Atomic absorption spectrometry (AAS)

Atomic absorption spectrometry (AAS) is one of the most widespread analytical methods. The principle is hidden in absorption of radiation by free atoms in gaseous state (produced in atomizer).

This work is aimed at coupling of atomic absorption spectrometry with electrochemical preconcentration of the analyte, in our case – antimony.

The sub-goal of this work was to develop a suitable method for the determination of antimony by GFAAS without matrix modification. Determination of antimony without modification is still problematic [1–3]. Detection limits for determination of antimony by “quartz atom trap” is 0.053 $\mu g.dm^{-3}$ [4]. Interference emerges as a big problem in the determination too. The standard technique for the determination of antimony is HGAAS. Detection limits for this technique could be between 0.03 až 0.05 $\mu g.\ dm^{-3}$ [5].

Flow through chronopotentiometry (FTC)

Determination of Sb was done by GFAAS, but with the preconcentration of electrochemical unit. We inspected considerable decreasing limit of detection and influence of interferences could be removed, too. On the surface of working electrode will be deposited quantitatively only Sb(III). The deposit is that stripped in off-line system to the graphite cuvette of the electrothermal atomizer.

On-line coupling FTC and GFAAS

On-line takes advance of coupling of two steps to one's. At the first step, analyte is deposited on working electrode from flowing sample. At the second step, the analyte is then quantitatively determined by the suitable analytical method.

The main topic of the preconcentration step is to maximize the concentration of the analyte with the simultaneously suppressing the effect of interference.

MATERIALS AND METHODS

GFAAS

The AAS spectrometer Spectraa 400 with the graphite furnace atomizer (Varian) was used to measure the preconcentrated Sb species.

FTC

The flow-through electrochemical analyzer EcaFlow (model GLP 150, Istran, Bratislava) was used as the preconcentration unit with a two-electrode cell. The working electrode was a RVC electrode coated with gold (Fig. 1).

Scheme of the on-line coupling FTC-GFAAS

The 6-way valve was connected with sampling loop with sampling volume 83.9 µl. Thereby on-line connection of electrochemical analyzer EcaFlow could by make by coupling with GFAAS over the 6-way valve (Fig. 2).

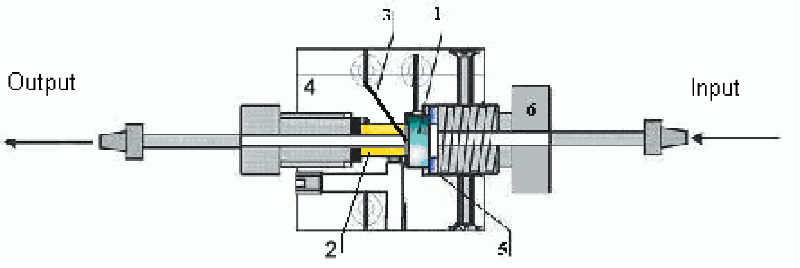

Fig. 1 Scheme of the flow-through cell with dual electrode connection

Legend: 1 – working electrode E-53 Au, 2 – inert inset, 3 – auxilliary Pt electrode, 4 – plexi glass body, 5 – packing, 6 – screw

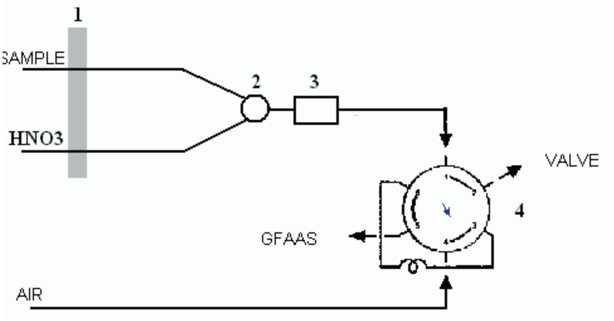

Fig. 2 Scheme of the flow–through system FTC-GFAAS

Legend: 1 – pump, 2 – valve, 3 – preconcentration cell, 4–6-way valve with sampling loop calibrated to the sampling volume 83.9 µl

RESULTS AND DISCUSSION

For validation of the process of the new developed coupling FTC-GFAAS were chosen three different feeding volumes of the sample and complete validation set were survey for all feeding volumes. The linear range, limit of detection and limit of quantification were appointed, respectively. Finally were assessed repeatability, reproducibility and accuracy by analyzing the standard reference material.

Linear ranges

Linear ranges are summarized in Tab. 1. Listed results show broad ranges, parameters of the calibration curves, coefficients of determination and regression coefficients for different feeding volumes.

Limit of detection (LOD) and limit of quantification (LOQ)

Assessed values for limit of detection and limit of quantification for determination of Sb (III) are listed in Tab 2.

Repeatability

Fig. 3 represent the dependence of measured concentration of the Sb(III) against measurement order (significance level 0,05, selected concentration was 20 μg.dm^{-3}). Repeatability characterized by RSD was 1.8 % (n = 20).

Tab. 1 Linear ranges, equations of the linear regressions and their coefficients for different feeding volumes Sb(III)

Feeding volume [ml]	Linear range [μg·dm^{-3}]	Equation of regression	R^2
1	4,2–800	$\tau = 1{,}467+0{,}268*c$	0,9993
5	1,2–250	$\tau = 6{,}184+1{,}229*c$	0,9970
10	0,4–250	$\tau = 6{,}434+2{,}690*c$	0,9958

Tab. 2 Summarized values of slopes and increments for assessement of LOD and LOQ over ULA-2 aproach [7]

volume [ml]	LOD [μg.dm^{-3}]	LOQ [μg.dm^{-3}]	Equation of regression
1	1,4	4,20	$\tau = 0{,}637+0{,}208*c$
5	0,39	1,17	$\tau = 0{,}480+1{,}703*c$
10	0,12	0,36	$\tau = -0{,}024+2{,}948*c$

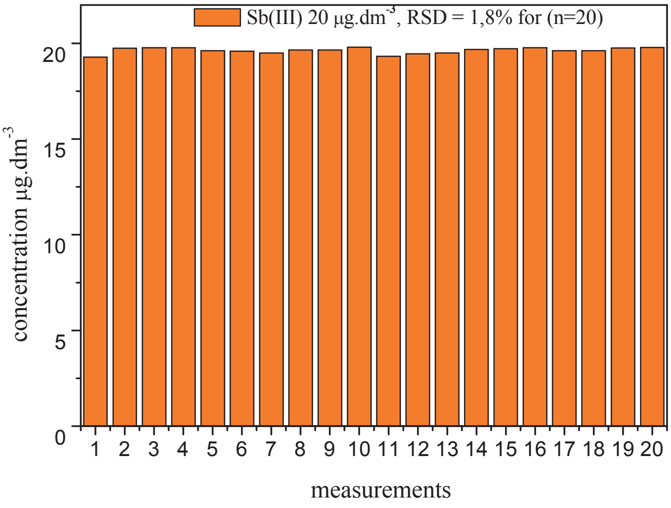

Fig. 3. Repeatability of the determination of the Sb(III) (ρ = 20 μg.dm^{-3}, feeding vol. 2 ml)

Trueness

Trueness was determined in standard reference material CRM 12-3-10 by on-line FTC-GFAAS of the total Sb.

The FTC-GFAAS technique developed at these conditions have some limitations. It is suitable only for determination of Sb(III) species and total Sb must be converted to the Sb(III) form. Many publications were pointed to the selective reduction of total Sb to Sb(III) form. As appropriate procedure for selective reduction step seems to be utilizing L-cysteine [8].

CONCLUSIONS

The aim of this work was to develop an on–line coupling of electrochemical preconcentration to the AAS method and the utilization of the developed system for the determination of ultra-trace amounts of Sb in water samples. The flow-through electrochemical analyzer EcaFlow (model GLP 150, Istran, Bratislava) was used as the preconcentration unit with a two-electrode cell. The working electrode was a RVC electrode coated with gold. The AAS spectrometer Spectraa 400 with the graphite furnace atomizer (Varian) was used to measure the preconcentrated Sb species. The preconcentration parameters for the electrochemical process were optimized. The deposition runs at a constant current of –8000 μA and the optimum stripping current was found to be 150 μA.

The deposition was made from the hydrochloric acid solution, which was then on-line replaced by a diluted nitric acid facilitating the AAS measurement of Sb. The advantage of the used preconcentration system was in an automatic and reliable matrix exchange facility. Optimum electrolyte concentrations were found to be 1 mol.dm^{-3} HCl and 2 mol.dm^{-3} HNO_3 for the deposition and stripping/AAS measurement, respectively.

Acknowledgement

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GENERATION OF SINGLET OXYGEN BY MODIFIED NATURAL ZEOLITES AND MONTMORILLONITES

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ABSTRACT

Šeršeň F., Pavlíková S., Jesenák K. & Čík G. **Generation of Singlet Oxygen by Modified Natural Zeolites and Montmorillonites**

This work deals with the generation of singlet oxygen by modified natural zeolites and montmorollonites. In the work natural zeolite from the deposit of Nižný Hrabovec (Slovak Republic) and montmorillonite from the deposit of Stará Kremnička – Jelšový Potok (Slovak Republic) were used. Both natural aluminosilicates were doped with Fe^{3+} and thiophene or pyrrole. It was found that all four forms of prepared natural alumininosilicates are able to produce singlet oxygen in chloroform suspensions under visible light. It was also found that all prepared forms of natural aluminosilicates decomposed 4-chlorophenol in water surroundings. We suppose that the singlet oxygen formation causes decomposition of 4-chlorophenol. This effect of thus modified natural zeolites and montmorillonites can be exploited to decontamination of the environment polluted by chlorophenol compounds.

Key words: chlorophenol decomposition, montmorilonote, singlet oxygen, zeolite

INTRODUCTION

Singlet oxygen ($^1O_2$) belongs to reactive oxygen species. Essentially, it is an oxygen molecule O_2 in excited state. $^1O_2$, despite not being a radical, is very reactive and easily initiates various radical reactions. $^1O_2$ can be generated by several physical, chemical, photochemical or biological reactions [1]. Photoexcitation is the most frequently used method for generation of $^1O_2$. Because, molecular oxygen does not exhibit serious absorption in UV–VIS radiation, its excitation is carried out indirectly by photosensible compounds [2]. For that purpose, organic dyes [3] or oligomers of thiophene derivatives [4] are used.

Zeolites are porous aluminosilicates with nets of channels and cavities, which are composed of the AlO_4^{5-} and SiO_4^{4-} tetrahedrons [5]. Montmorillonite belongs to dioctahedral phylosilicates. Its structure is composed of two tetrahedron and one–octahedron layers; the negative charge of the layers is compensated by various cations (for instance Na^+, Ca^{2+}, Mg^{2+}, Fe^{3+}) [5]. It is known that iron doped zeolites form thiophene oligomers in channels or cavities and on the surface of the zeolite [6,7]. Also, montmorillonites are able to form thiophene oligomers [8].

The goal of this work is to demonstrate the possibility of generation of singlet oxygen by modified natural zeolites and montmorillonites and their use for photodecomposition of 4-chlorophenol in water solution.

MATERIAL AND METHODS

Chloroform (p.a.) was purchased from Centralchem (Slovak Republic). Pyrrole, thiophene and 4-chlorophenol were purchased from Lachema (Czech Republic). Pyrrole and thiophene were freshly distilled before experiments. 2,2,6,6-tetramethyl piperidine (TEMP) was purchased from Sigma-Aldrich (Germany).

In this work was used volcanic tuff from the deposit of Nižný Hrabovec (Slovak Republic) with mineral composition: 40–56 % clinoptilolite, 6.3–8.7 % feldspar, cristobalit 7.8–10.7 %, quartz 2.3–3.2, biotite 1% and amorphous phase 22.5–40 % [9]. The zeolite was pulverized (grain ~1 mm) and then by ion-exchange reaction doped with Fe^{3+} by water solution of $FeCl_3$ (c = 0,2 mol dm^{-3}). Thus doped zeolite was dried and treated with pyrrole or thiophene. The guest molecules are bounded in the cavity or on the surface of the zeolite during this treating.

Montmorillonite was isolated from 4 % water suspension of bentonite from the deposit of Stará Kremnička – Jelšový Potok (Slovak Republic). This bentonite contains calcium-magnesium montmorillonite. The chemical composition of this calcium montmorillonite is $[Si_{7,95}\ Al_{0,05}]\ [Al_{3,03}\ Fe_{0,22}\ Mg_{0,75}]0_{20}(OH)_4(Ca_{0,42}Mg_{0,04}Na_{0,01}K_{0,01})$ [10,11]. Dopations by iron and then by thiophene or pyrrole were carried out as in the case of the zeolite.

The singlet oxygen was generated in suspension, which was composed of 2 ml of 10^{-3} mol dm^{-3} chloroform solution of TEMP and 20 mg of modified aluminosilicates by the visible light (~100 $W.m^{-2}$) from a 250 W halogen lamp passed through a 10 cm water filter. All suspensions were irradiated 15 min. at continual stirring by the magnetic stirrer.

The experiment of 4-chlorophenol decomposition was carried out in glass Erlenmeyer flasks which contained 10 ml water solution of 4-chlorophenol (10^{-4} mol dm^{-3}) and 100 mg modified aluminosilicates by continual irradiation with visible light (12 W m^{-2} by 36 W TLD Philips neon tubes).

The spectra of electron paramagnetic resonance (EPR) were registered by ERS 230 apparatus (ZWG Berlin, Germany), which operates in X-band (~ 9.3 GHz), with modulation amplitude 0.1 mT and microwave power 5 mW. The UV-VIS spectra were recorded by the spectrophotometer Hewllet-Packard Diode Array 8254. All experiments were carried out at the room temperature (25 °C).

RESULTS AND DISCUSSION

The incorporation of pyrrole and thiophene into modified zeolites and montmorillonite was accompanied by change of the colour, initially orange aluminosilicates turned black. This black colour is caused by formation of oligomers of pyrrole or thiophene, respectively in the modified aluminosilicates [6–8]. The presence of oligomers in the Fe--zeolite with pyrrole and thiophene was documented by registration of polarons in their EPR spectra (Fig. 1). These polarons have one unpaired electron and so exhibit the EPR signal in the free radical region. The spectroscopic constants for polarons were g = 2.0012 and ΔB_{pp} = 0.5–1.5 mT. The individually modified aluminosilicates contained 2.3 10^{16}–6.6 10^{18} spin per gram (Fe-montmorillonite with thiophene 2.3 10^{16} and 6.6 10^{18} with pyrrole, Fe-zeolite with thiophene 6.3 10^{16} and 9.9 10^{17} with pyrrole).

The generation of $^1O_2$ was detected indirectly via its reaction with TEMP. It is known that the result of the reaction of TEMP with $^1O_2$ is the 2,2,6,6--tetramethyl piperidine-N-oxide radical (TEMPO) [12]. In Fig. 2 is documented the formation of TEMPO by visible light irradiation in chloroform suspensions of our modified aluminosilicates. These EPR spectra consist of three lines of hyperfine interaction of an unpaired electron with the nuclear spin of ^{14}N. The g factor of all central lines was 2.0032 and the constants of hyperfine splitting were 1.58 mT.

In our previous work [7] it was demonstrated that ZSM-5 zeolite doped with Fe and thiophene decomposed 4-chlorophenol in water solution under the visible light. Now we attempted to find out if prepared modified natural zeolites and montmorillonites are able to decompose 4-chlorophenol. We found that natural zeolites and montmorillonites doped with Fe and pyrrole and thiophene are able to decompose 4-chlorophenol too. The decomposition of 4-chlorophenol by modified natural aluminosilicates in the visible light was documented spectrophotometrically (Fig. 3). The decrease of absorption bands (226 and 280 nm) of 4-chlorophenol is evident after irradiation by visible light of 4-chlorophenol water solution in the presence of the modified zeolites and montmorillonites. The most effective in the decomposition of 4-chlorophenol were Fe-zeolite doped with pyrrole and Fe-montmorillonite doped with thiophene.

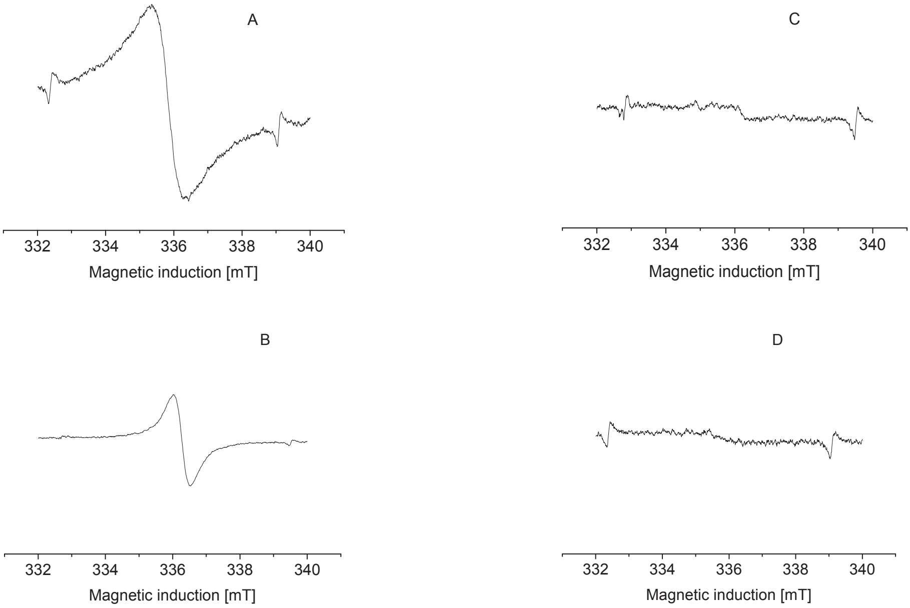

Fig. 1 EPR spectra of Fe-zeolite with pyrrole (A), Fe-montmorillonite with pyrrole (B), Fe-zeolite with thiophene (C) and Fe-montmorillonite with thiophene (D). Spectra C and D were recorded at 4-times higher amplification as spectra A and B. The marginal peaks belong to Mn^{2+} standard

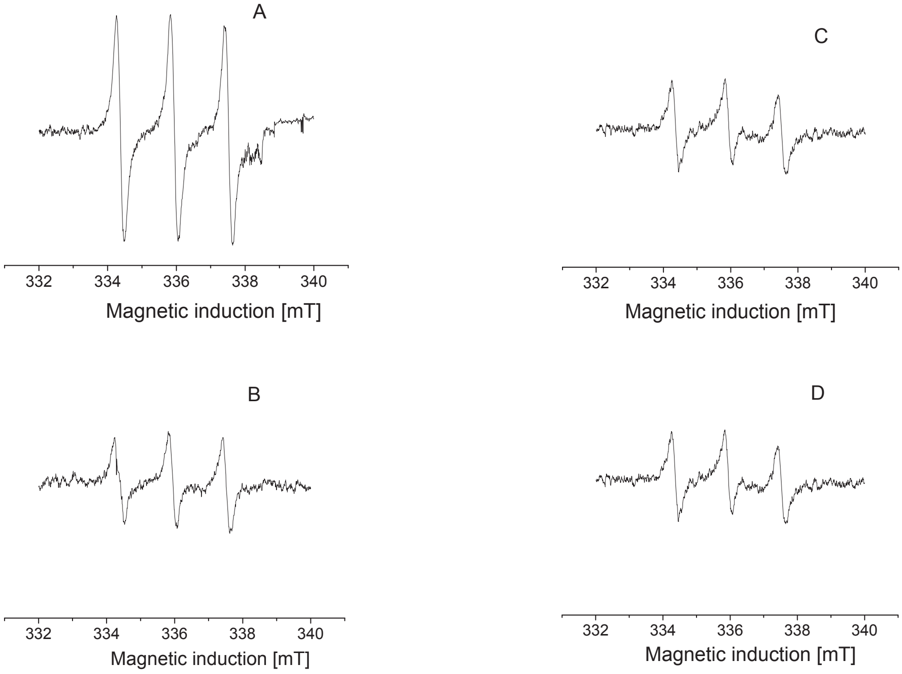

Fig. 2 EPR spectra of TEMPO radicals generated in chloroform suspensions of Fe-montmorillonite with thiophene (A), Fe-zeolite with thiophene (B), Fe-zeolite with pyrrole (C) and Fe-montmorillonite with pyrrole (D)

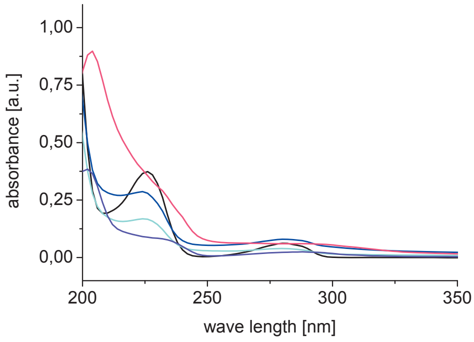

Fig 3 Absorption spectra of 4-chlorophenol solutions (10^{-4} mol dm^{-3}) after 48 hours of irradiation by visible light (black line); in the presence of Fe--zeolite with thiophene (blue line); Fe-zeolite with pyrrole (green line); Fe-montmorillonite with thiophene (violet line) and Fe-montmorillonite with pyrrole (red line)

We suppose that the first step of 4-chlorophenol decomposition is the formation of the singlet oxygen in 4-chlorophenol water solutions with the modified zeolites and montmorillonites. ${}^1O_2$ then can enter reactions with molecular oxygen which is present in water and therefore other reactive oxygen species (hydroxyl and superoxide anion radicals) are produced. These radicals can react with 4-chlorophenol and cause its decomposition. This effect of modified natural zeolites and montmorillonites can be exploited to decontamination of the environment polluted by chlorophenol compounds.

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VOC EMISSIONS AND TVOC EMITTED TO THE AIR BY THE INTERIOR EQUIPMENT

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ABSTRACT

Tesařová D., Čech P., Haraslínová L. & Meloun M. **VOC Emissions and TVOC Emitted to the Air by the Interior Equipment**

In the article there are solved the problems of the VOC and the TVOC measurements in indoor (air) and the influences that have a great impact on them. The influence of the

Use of gypsum plasterboards, furniture sets and floor covering made from PVC and glued by the rubber solvent glue on the quality of indoor air especially with the dependence of time. The reached results of the work show the significant influence of the PVC floor covering on the amount of TVOC and the quality and quantity of benzene, toluene and xylenes in the indoor air. Results of the measurements prove to use the rooms with floor covering glued by rubber solvent glued is not very good for human health.

Key words: PVC flooring, TVOC, VOC, gypsum plasterboard, GC/MS

FOREWORD

The interior environment creation and interior conservancy are nowadays the main topics of international importance. This problematic came in to the forefront of public interest. We know that the amount of chemicals in the atmosphere has grown exponentially since the sixties and not only quantitatively but also qualitatively. Middle aged people are the first generation which have been daily exposed to the influence of these chemicals since they were born. Some of these materials need a long time before some impact on human health is proved. The nowadays middle aged people are the first testing group for discovering of the effects of these materials. Now we can detect the first illnesses which are connected with the polluted indoor air.

Healthy indoor environment is very important. It was found out that indoor pollution can be from two to five times (sometimes ten times) more concentrated than outdoor atmosphere. It is known that people stay there up to 90 % time of the day (EPA, 1998) and it brought the first illnesses connected to buildings (Building Syndrome SBS a Building Related Illness BRI). One of the main causes of the SBS and BRI are Volatile Organic Compounds VOCs which are emitted into the air by the constructional material, furniture and other equipment. VOCs are also products of people, animals, microorganisms and their metabolism. Their indoor concentration can be significantly changed by the dwellers' activity. Some of the volatile organic compounds are carcinogenic and dangerous for the human health and to the fetus.

The indoor VOCs are one of the biggest problems of environment. There have been identified and measured from 50 to 300 volatile chemicals in the air of interiors. Concentrations of these compounds are only rarely higher than 50 µg/m^3.

For the indoor emissions there were mandated limits for some seriously dangerous organic chemicals in the standard MZČR 6/2003. Emissions limits are in the Table no. 1.

Tab. 1: Rrequirements determinating for Limits of VOC concentrations in indoor air of residence rooms (regulation of MZČR – standard MZČR č.6/2003)

Volatile organic compounds	Formula	NPK (highest concentration) long-term [μg.m^{-3}]
Benzene	C_6H_6	7
Toluene	$C_6H_5.CH_3$	300
o,m,p-Xylene	$C_6H_4.(CH_3)_2$	200
Styrene	$C_6H_5.CH.CH_2$	40
Ethylbenzene	$C_6H_5.CH_2CH_3$	200
Formaldehyde	HCHO	60
Trichlorethylene	$CCl_2.CHCl$	150
Tetrachlorethylene	$CCl_2.CCl_2$	150

In connection to the term VOC there is the new term TVOC (total volatile organic compounds) which is used to describe, the total amount of volatile organic compounds in the indoor atmosphere. The TVOC value indicates the level of indoor air pollution.

The term TVOC is used for measuring of indoor air composition and for determinating the total amount of organic compounds in the air. The TVOC value can be obtain on the gas chromatograph and it is defined as the sum of all peak areas of all VOCs which are emitted between hexane and hexadecane. The sum of areas is then calibrated to the value which is equivalent to toluene.

This paper concentrates on VOC emissions sources in a newly built and equipped room. Material used for building was gypsum board. The PVC material used for floor covering was glued by the rubber solvent glue. Furniture in the room was made from laminated particleboard.

Goal of the Research

The main goal of the research was to find dependency of qualitative and quantitative contribution of VOCs emissions on time. We tried to determine the impact of all interior components (used building material, PVC flooring and glue used for flooring gluing, furniture) on indoor air pollution and its changes in time.

MATERIALS, EQUIPMENT AND METHODS

Measured space – newly built room with PVC flooring glued by the rubber solvent glue.

- dimensions of the room 4880 mm x 3170 mm x x 3770 mm; two windows and one door which were closed during the testing
- dimensions of flooring: 3170 mm x 4880 mm; with ratio 1 m^2 to 3.77 m^3 of the room space

Tab. 2: Requirements determinate for the amount of TVOC in indoor air of residence rooms (Jokl, 2002 – standard MZ ČR č.6/2003)

Toxic VOC	NPK average [μg.m^{-3}]		NPK optimal [μg.m^{-3}]		Annotation
	short-term	long-term	short-term	long-term	
Formaldehyde	120	60	60	60	
TVOC	600	300	300	300	Constituent VOC could not exceed the limit mandated in the standard MZČR 6/2003

Samples measured in small-space chamber with inner space 1 m^3:
gypsum plasterboard brick with the surface of 0,2819 m^2

- for testing there were three bricks with the sum of surfaces 0.8457 m^2 given in to the small-space chamber; VOC emissions emitted by bricks were recalculated to the surface 1 m^2 (according to ISO 16000-1); ratio 1 m^2 to 1 m^3 of air in the chamber

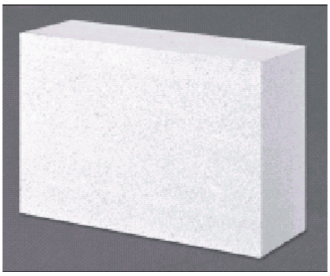

Fig. 1 Gypsum plasterboard

Samples measured in great-space chamber with the inner space, of 40 m^3

- measuring of emissions emitted by furniture set 28 days after construction;
  ratio 40 m^2 to 40 m^3 of air in chamber

Used equipment

- short path thermal desorption tube, Silco trated Thermal Desorption Tube 786090-100, inner diameter 4 mm, fill in with 100 mg of Tenax TA (Scientific Instrument Services company) for collection of VOCs emissions emitted from tested samples in to the air in chamber
- air sampler Gilian – LFS 113 SENSIDINE with the air flow 6 l.h^{-1}. and 12 l.h^{-1}; the pump has been calibrated in ČMI
- gas chromatograph Agilent GC 6890 N with MS (mass spectrometer) detector 5973 with cryofocusation, thermal desorption and library of spectra NIS 05, column type HP – 5 (AGILENT USA)
- VOC equipment small-space chamber (Smýkal company)
- Great-space chamber (Weiss)

Technical parameters of great and small-space chamber for VOCs testing

Inner dimensions of great-space chamber	40 m^3 (5.9 m x 2,82 m x 2,4 m)
Inner dimensions of small-space chamber	1 m^3 (0.7 m x 2,82 m x 2,4 m)
Adjustable range of temperature in chamber	15 to 50 °C
Regulation accuracy of temperature in chamber	>0.5 °C
Adjustable range of humidity in chamber	45 % to 55 %
Regulation accuracy of temperature in chamber	>2 %
Air changing rate in great-space chamber	40 m^3 per 1 h
Air changing rate in small-space chamber	1 m^3 per 1 h
Air speed over the tested samples	0.1 to 0.3 m.s^{-1}

Tab. 3: Conditions of emissions VOC sampling in small space and great space chamber

Conditions of sampling	Great-space chamber	Small-space chamber
Time of starting of furniture testing after construction	28 days	28 days
Time of acclimatization of samples in chamber before testing	72 h	72 h
Surface of tested samples	40 m^2	1 m^2
Inner volume of chamber	40 m^3	1 m^2
Ratio of tested surface to inner volume of the chamber	1/1	1/1
Temperature during the testing	23 °C	23 °C
Relative humidity in chamber	50 %	50 %
Air changing rate per hour	40 m^3	1 m^3
Air speed in chamber over the samples	0,1 to 0,3 m/min	0,1 to 0,3 m/min
Time of air sampling	6 h	6 h
Volume of air pumped through the desorption tube during sampling	36 l	36 l

Methods of VOC testing were set accoding to the following standards:

ČSN P ENV 13419	Determination of emission volatile organic compounds in building products, which consists of three parts and the fourth part is under preparation:
ISO 16000: 2004	Indoor air
ISO 16000-1: 2004	General aspects of sampling strategy
ISO 16000-5: 2005	Measurement strategy for volatile organic compounds (VOCs)
ISO 16000-11: 2004	Determination of the emission of volatile organic compounds – sampling, storage of samples and preparation of test specimens

VOC samplings in great/small-space chambers were done according to:

ISO 16000-6: 2005	Determination of volatile organic compounds indoor and test chamber air by active sampling on Tenax TA® sorbent, thermal desorption and chromatography using MS/FID
First part ČSN P ENV 13419-1	Emission test chamber Method
ISO 16000-9: 2004	Determination of the emission of volatile organic compounds-Emission test chamber method

VOC samplings in the room were done according to:

Metodical instructions No. 6 from 16. 12. 2002	NRL for indoor and outdoor air SZÚ Prague
ISO 16000-6: 2005	Determination of volatile organic compounds indoor and test chamber air by active sampling on Tenax TA® sorbent, thermal desorption and chromatography using MS/FID

RESULTS OF MEASURING

The results of measuring of qualitative and quantitative composition of VOC emission, total sum of VOC and TVOC emitted in room after building finishing and floor covering are listed in Table 4.

Influence of the Gypsum plasterboard was measured in small-space chamber. Material was tested 28 days after production. The results of qualitative and quantitative measuring of VOC emissions emitted by gypsum plasterboard are given in Table 5.

The influence of furniture set with surface 40 m^2 to air condition in room was tested in the great-space chamber. Furniture was made from laminated particleboard DTD-L with pattern of cherry wood. Testing was done 28 days after the furniture construction. The results are in Table 6.

Tab. 4: VOC and TVOC emissions emitted by the floor covering after the gluing in the new built room

Time of measuring after gluing of flooring	Blank	3 h	24 h	72 h	168 h	432 h	648 h
VOC	µg m^{-3}	µg m^{-3}	µg m^{-3}	µg m^{-3}	µg m^{-3}	µg m^{-3}	µg m^{-3}
Formaldehyde	0	0	0	0	0	0	0
Ethyl acetate	0	80.9	4.9	4.6	1.0	5.5	0.7
Benzene	0.4	6.9	1.6	1.6	0.5	0.4	0.4
I-methoxy-2-propanol	0.6	2.3	1.8	2.8	0.9	1.6	0.7
Pentanal	0.6	79.4	16.3	14.2	1.8	2.9	0.6
Toluene	15.9	2440.1	643.4	724.0	145.6	152.9	32.2
Capronaldehyde	1.2	10.5	4.5	5.6	1.1	2.2	0.4
n-Butyl acetate	5.7	0.0	0.0	0.0	0.5	0.0	1.5
Ethylbenzene	3.3	52.9	53.9	41.1	4.6	8.5	4.6

Tab. 4: Continued

Time of measuring after gluing of flooring	Blank	3 h	24 h	72 h	168 h	432 h	648 h
VOC	µg m^{-3}	µg m^{-3}	µg m^{-3}	µg m^{-3}	µg m^{-3}	µg m^{-3}	µg m^{-3}
M,p-Xylene	9.9	186.1	69.0	53.6	5.9	10.9	5.8
Styrene	0	0.5	0.2	0.2	0.0	0.0	0
o-Xylene	1.8	27.7	10.9	9.0	1.1	2.2	1.1
Butoxy-Ethanol	0	0.1	0.1	0.2	0.0	0.0	0.1
A-Pinene	0.1	0.4	0.6	0.8	0.2	0.4	0.2
Camphene	0	0.3	0.1	0.1	0.1	0.0	0
3 or 4-Ethyl-Toluene	0.2	7.0	2.8	2.9	0.5	0.8	0.1
1,3,5-Trimethyl-Benzen	0.3	7.4	2.9	2.9	0.5	0.9	0.1
β-Pinene	0.1	2.1	0.3	0.3	0.1	0.0	0.1
2-Ethyl Toluene	0.2	6.8	2.6	2.7	0.4	0.8	0.1
Myrcene	0	2.7	0.9	1.1	0.2	0.3	0.1
1,2,4-Trimethyl-	1.2	29.9	10.9	11.0	1.9	3.2	0.3
α-Phelandrene	0.3	0.6	0.2	0.2	0.0	0.1	0.3
3-δ-Carene	0.3	0.6	1.1	2.8	0.9	2.8	0.3
1,2,3-Trimethyl–	0.4	5.4	2.4	3.0	0.7	1.2	0.1
Limonene	0.1	0.3	0.3	0.5	0.1	0.1	0
γ-Terpinene	0	0.1	0.0	0.0	0.0	0.0	0
Bornyl Acetate	0.1	0.3	0.1	0.1	0.0	0.1	0
Σ VOC	42.8	2950.7	831.6	885.1	168.5	197.9	50.0
TVOC	73	7986	1822	1817	311	386	87

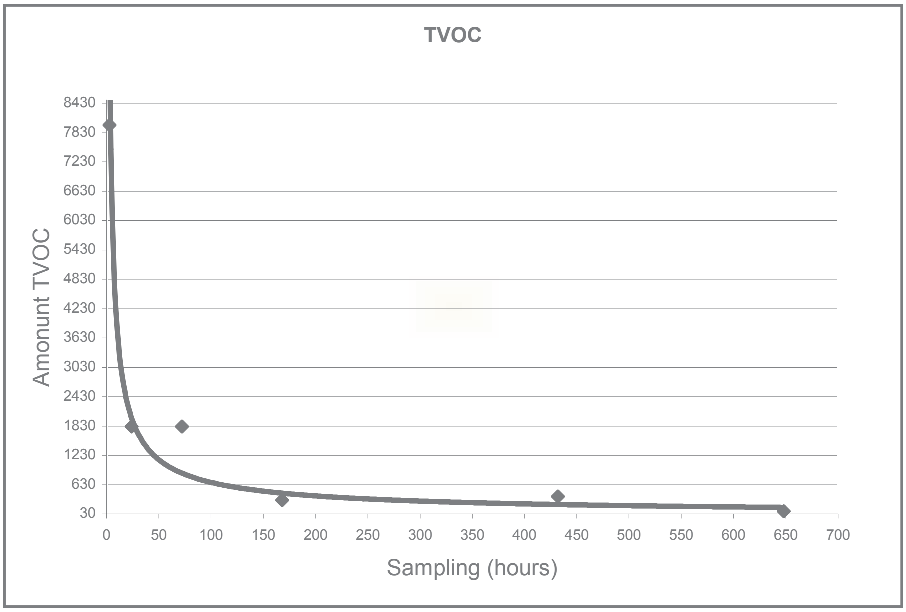

Fig. 2 Dependence of TVOC amount emitted by floor covering on the time of gluing

Tab. 5: VOC Concentrations emitted by the gypsum plasterboard

Matter	VOC emissions concentration emitted by 1 m^2 of gypsum plasterboard		
	Samples with background	Background	Results
	µg.m $^{-3}$	µg.m $^{-3}$	µg.m $^{-3}$
Ethyl acetate	0.34	0.05	0.29
Benzene	0.87	0.26	0.60
I-methyl-2-propanol	0.43	0.22	0.21
Valeraldehyde	0.22	0.09	0.13
Toluene	18.04	6.46	11.57
Capronaldehyde	0.20	0.17	0.02
n-Butyl acetate	4.22	1.63	2.59
Ethylbenzene	1.74	0.64	1.10
m,p-Xylene	5.29	1.97	3.33
Styrene	0.02	0.01	0.01
o-Xylene	1.10	0.41	0.69
Butoxy-ethanol	0.05	0.01	0.03
α-Pinene	0.10	0.04	0.06
Camphene	0.00	0.00	0.00
3 or 4-Ethyl-Toluene	0.08	0.03	0.05
1,3,5-Trimethyl-Benzene	0.08	0.04	0.04
β-Pinene	0.03	0.03	0.00
2-Ethyl Toluene	0.08	0.04	0.04
Myrcene	0.00	0.00	0.00
1,2,4-Trimethyl-Benzene	0.32	0.18	0.15
α-Phelandrene	0.64	0.19	0.45
3-δ-Carene	0.61	0.19	0.42
1,2,3-Trimethyl-Benzene	0.10	0.05	0.05
Limonene	0.10	0.06	0.05
γ-Terpinene	0.01	0.00	0.00
Bornyl acetate	0.09	0.02	0.07
Σ VOC	34.74	12.79	21.95
TVOC			67

Tab. 6: VOC emissions emitted by the furniture set 28 days after productions

	Samples with surface 40 m ^{2} with background	Background	Results
VOC	µg.m $^{-3}$	µg.m $^{-3}$	µg.m $^{-3}$
Formaldehyde	8.9	7.3	1.7
Ethyl acetate	0	0	0
Benzene	0	0	0
Valeraldehyde	0	0	0
Toluene	2.0	2.9	0
Capronaldehyde	0	0	0
n-Butyl acetate	0	0	0
Ethylbenzene	0.5	0.9	0
m,p-Xylene	1.4	3.0	0
Styrene	0	0	0

Tab. 6: Continued

	Samples with surface 40 m ^{2} with background	Background	Results
VOC	μg.m $^{-3}$	μg.m $^{-3}$	μg.m $^{-3}$
o-Xylene	0.5	0.5	0
Butoxy-Ethanol	0.1	0.1	0.1
A-Pinene	0	0	0
Camphene	0	0	0
p-Cymene	0	0	0
B-Pinene	0	0	0
Eucalyptole	0	0	0
Myrcene	0	0	0
α-Phelandrene	0	0	0
3-δ-Carene	0	0	0
Fenchone + Linalool	0	0	0
Limonene	0	0	0
Carvone	0	0	0
Bornyl Acetate	0	0	0
Σ VOC	13.4	14.9	0

Measuring accuracy was continuously evaluated thanks of according to regulation diagrams of TVOC and VOCs for which are set limits in the Standard 6/2003 (tab. 1).

DISCUSION

As we can see in Table 5, the gypsum plasterboards which are made from inorganic and porous material do not emit VOCs in to the tested indoor air.

Analysis of furniture brought quite similar results. There were not found any high VOCs concentrations (table 6).

The biggest source of VOC emissions in newly equipped room was the PVC flooring glued by the rubber solvent glue. Values of TVOC were 3 hours after floor covering 27 times higher then WHO recommended limits. The highest values reached toluene which was 3 hours after floor gluing 10 times higher than limits and three days later still 3 times higher than limits.

All values of VOC and TVOC were below the limits in 28 days after finishing the room. Figure 2 shows that there is a very strong dependency of the amount of emissions on time.

CONCLUSION

Our research proved that the biggest source of VOC emissions was PVC flooring glued by the rubber solvent glue.

Equipment of the newly built room with the glued flooring emitted amounts of VOCs higher than are the limits not only after 3 hours but also after 72 hours. These results signify that rooms with newly glued floor covering are at least for 250 hours not convenient for living.

All other equipments in the room did not have too much high level of emissions.

At this work we proved that there is dependency between TVOC values and values of chemicals from the standard 6/2003.

Acknowledgement

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OUTDOOR RADON AS AN INDICATOR OF ATMOSPHERIC STABILITY

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ABSTRACT

Bulko M., Holý K., Polášková A., Hrvoľ J. & Šimon J. **Outdoor Radon as an Indicator of Atmospheric Stability**

This work deals with the potential use of radon as an indicator of atmospheric stability. Stability of the atmosphere is a parameter that can be used e.g. for quantitative assessment of pollutant dispersion in the ground layer of the atmosphere. A rather good agreement was found between the courses of radon activity concentration and stability indexes determined by modified Turner classification of atmospheric stability. The courses of radon concentration tend to lag behind the courses of stability indexes; this lag is of the order of hours. It can be caused by the fact that unlike radon activity concentration in the ground layer of the atmosphere, the reaction of stability indexes to the change of meteorological parameters is immediate, because they are defined by table values. Several analyses presented in this paper also showed that there is a close connection between the time change of radon activity concentration and the time change of stability indexes. Then radon seems to be a good indicator of vertical mixing processes in the atmosphere, but further research on this issue is needed to confirm these results.

Key words: outdoor radon, atmospheric stability, stability index

INTRODUCTION

Development of industry and engineering has had many adverse effects on the environment. A need for controlling the environment pollution and its impact on the earth‘s biosphere is therefore still topical. It is known that the aggregation of pollutants in the lowest layers of the atmosphere occurs under especially stable atmospheric conditions. Hence the degree of atmospheric stability is one of the most important parameters for evaluation of air pollution [1].

Atmospheric stability can be determined on the basis of meteorological parameters like the intensity of solar radiation, cloudiness, cloud height, visibility, period of day (daytime or night-time), wind speed and possibly temperature gradients. Numerous studies [2, 3, 4] have shown that concentration of gas (e.g. radon gas) in the atmosphere depends mainly on vertical atmospheric stability. For this reason, monitoring of ^{222}Rn activity concentration can bring information about stability of the atmosphere in polluted area. ^{222}Rn is especially suitable for this purposes since the radon exhalation rate from soil is approximately even, half-life of radon is long enough so that radon is able to escape by means of molecular diffusion from soil air into the atmosphere and because radon activity concentration can be measured with sufficient accuracy.

The aim of this study was to examine closely the relation between ^{222}Rn activity concentration and indexes of stability determined by modified Turner method of atmospheric stability classification. At least certain agreement between the quantities can be expected because some studies indicate that the variations of radon activity concentrations and the variations of quantities used for determining the stability indexes are also in good mutual agreement [1].

METHODS

^{222}Rn activity concentrations were measured at the Faculty of Mathematics, Physics and Informatics, Comenius University (FMPI CU) campus, Bratislava. The sampling air was collected at the height of 1.5 m above the earth's level and sucked through a large volume (4.5 l) scintillation chamber with a flow rate of 0.5 l/min [5]. Subsequently, radon activity concentrations belonging to two-hour intervals were determined from the recorded count rates using the Ward method [6].

Meteorological parameters required for determining the stability indexes were acquired at the Division of Meteorology and Climatology, FMPI CU. The stability indexes were determined by Turner's method of atmospheric stability classification modified by Nester and Reuter [7]. This classification comprises 7 degrees of atmospheric stability: 1 – extremely unstable, 2 – unstable, 3 – slightly unstable, 4 – neutral conditions, 5 – slightly stable, 6 – stable, 7 – extremely stable. Due to strong vertical mixing caused by global solar radiation, unstable conditions are likely to occur during the day, while stable ones during the night when temperature inversions are in effect.

RESULTS AND DISCUSSION

For the purposes of evaluation of the relationship between radon activity concentration and stability indexes there were carried out thorough analysis of 6 months (August, September and October of the years 1994 and 1998). Due to limited space available we provide in this paper only the analysis of a single representative month – August 1998.

In the picture below (Fig. 1) there are depicted smoothed courses of radon activity concentration and calculated stability indexes.

The correlation between these time courses is rather weak (R = 0,38). However, after a closer look one can see that the variations are mutually shifted. We therefore decided to shift the stability indexes 2, 4 and 6 hours forward in time, respectively. The highest degree of correlation was achieved by a 4-hour shift of stability indexes against radon activity concentration (Fig. 2). The correlation coefficient improved from 0.38 to 0.64, which attests that there is a good agreement between the courses. This approximately 4-hour shift was also confirmed for the rest of the analysed months.

Fig. 3 clearly shows the main difference between variations of radon activity concentration and stability indexes. While the mean daily values of stability indexes remain virtually constant during the month, the mean values of radon activity concentration show a significant degree of variability.

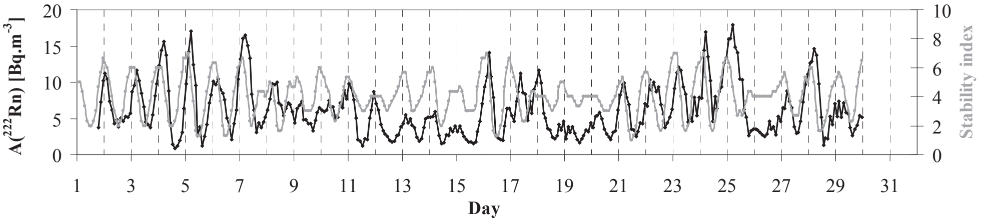

Fig. 1 Variations of smoothed courses of radon activity concentration and stability indexes in August 1994

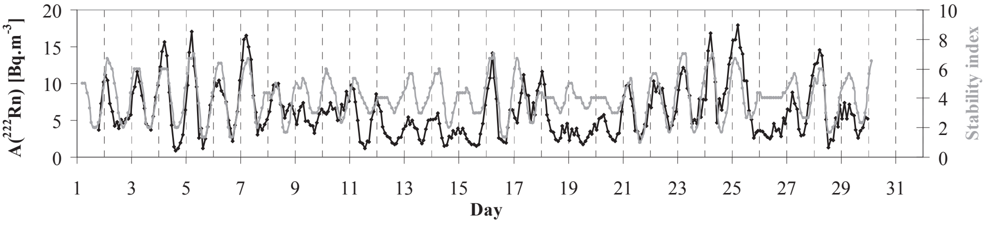

Fig. 2 Variations of smoothed courses of radon activity concentration and stability indexes in August 1994.
Time-courses of stability indexes are shifted 4 hours forward in time

One of the possible explanations is that radon is more sensitive to changes of meteorological parameters than indexes of atmospheric stability. The thing is, Turner classification is an indirect method of atmospheric stability determination – it uses a set of basic meteorological parameters like cloudiness, intensity of solar radiation and wind speed as an input, and gives a discrete degree of atmospheric stability as an output. On the other hand, radon is a natural part of the atmosphere and therefore it can react far more flexibly and to a greater extent to the changes of mixing processes in the atmosphere (and thus to the changes of atmospheric stability).

Low variability of mean daily values of stability indexes, in contrast with high variability of mean daily values of ^{222}Rn activity concentration, led us to the examination of deviations from their mean daily values (DfMDV). As one can see in Fig. 4, such courses are very much alike, for example after the period of relatively small DfMDV (August 8–15) we observe significantly higher deviations of both stability indexes and radon activity concentration the following day. In a similar fashion, in the period from August 19 to August 25 we observe gradually increasing of DfMDV. A high correlation coefficient (R = 0.74) also attests that there is a good agreement between the courses.

The next picture (Fig. 5) shows the mean daily courses of radon activity concentration and stability indexes obtained in August 1994. Mutual shift of the courses is now even more visible, we again observe that the change of radon activity concentration does not immediately follow the change of atmospheric stability (the mutual shift is of the order of hours and the best agreement of the courses was achieved by a 4 hour shift of data).

This shift can possibly be caused by an immediate reaction of stability indexes to a change of meteorological parameters (because they are defined by table values), which is in contrast with the fact that naturally it must take some time until the change in radon concentration occurs. As an illustrative example let us imagine a situation when after a long period of overcast conditions the sun started to shine again. Stability indexes will react on such a change immediately, yet it always needs some time until the sun rays heat the ground, subsequently the ground will heat the adjacent air until the air temperature rises to such an extent that a volume of air near the ground will start to rise upwards and as a result we will observe a decrease in radon activity concentration near the surface.

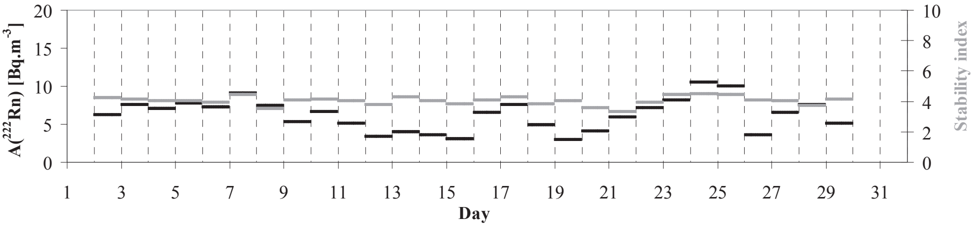

Fig. 3 Variations of mean daily values of radon activity concentration and stability indexes in August 1994. The time courses of stability indexes were shifted 4 hours forward in time

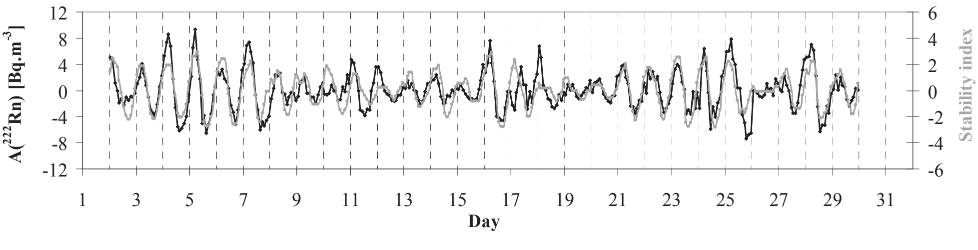

Fig. 4 Deviations from mean daily values of ^{222}Rn activity concentration and stability indexes in August 1994. Smoothed data. Time courses of stability indexes were shifted 4 hours forward in time

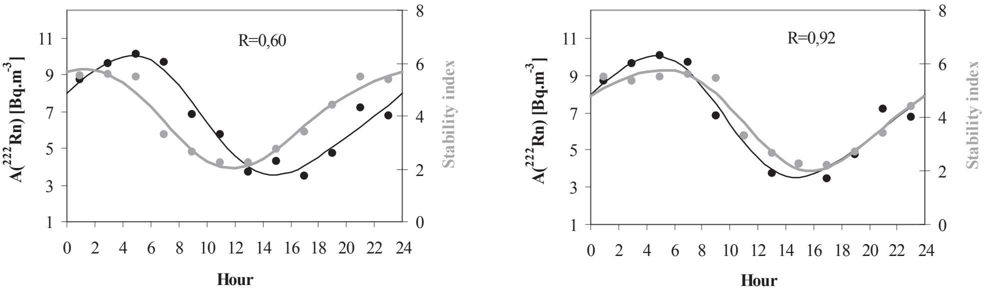

Fig. 5 Mean daily courses of radon activity concentration and stability indexes in August 1994. The picture on the left shows the real (not shifted) courses, at the right picture the courses of stability indexes are shifted 4 hours forward in time

We wanted to study the relation between radon activity concentration and stability indexes more thoroughly, especially if these quantities were proportional to each other, and if so, to find out what type of proportionality it was. Some authors [8] did not find any dependence between these quantities (but it should be mentioned that they did not use ^{222}Rn but its daughter products for testing). The data from August were therefore subjected to further analyses; geometrical means (the frequency distribution of radon concentration was found to be log-normal) of radon activity concentrations belonging to individual stability classes were calculated and depicted in the chart.

When the data were not shifted, the linear coefficient of correlation was low (R = 0.37). However, when we analyzed the data set where the stability indexes are shifted 4 hours forward in time, the coefficient of correlation improves to 0.61 (Fig. 6, left). If the averaged radon data belonging to individual stability indexes are fitted by a power function of the type

$$y = a + b.x^{c}, \tag{1}$$

we obtain the exponent c = 2.7, which implies a rather nonlinear relationship between the analysed quantities (Fig. 6, right).

A similar nonlinear relationship was also found when the impact of stability indexes on the change of radon activity concentration was evaluated. In this case, the exponent c in function (1) was approximately equal to 2.1.

However, if we plotted a change of radon activity concentration in a given interval against a change of stability indexes in a previous interval, we got the results that are different from what we see in Fig. 6. In this case, we got a nearly linear dependency (Fig. 7). The fit result was a straight line that very nearly passed through the origin of coordinates. These results indicate that there is a close

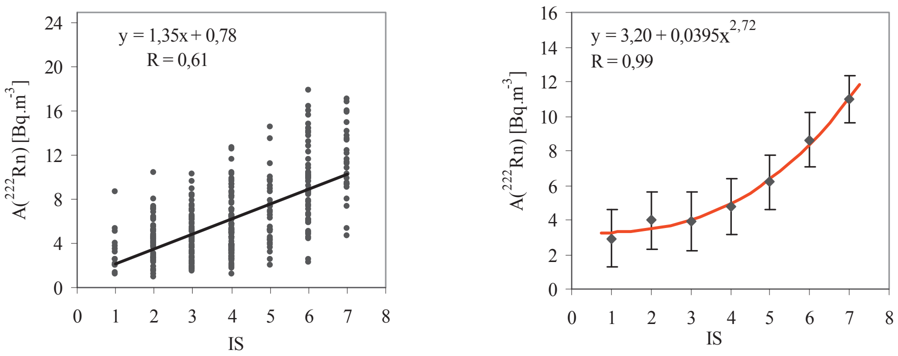

Fig. 6 Influence of atmospheric stability on ^{222}Rn activity concentration (August 1994). The courses of stability indexes are shifted 4 hours forward in time. At the left picture all data are shown, at the picture on the right geometrical means of radon activity concentration corresponding to individual stability indexes are depicted

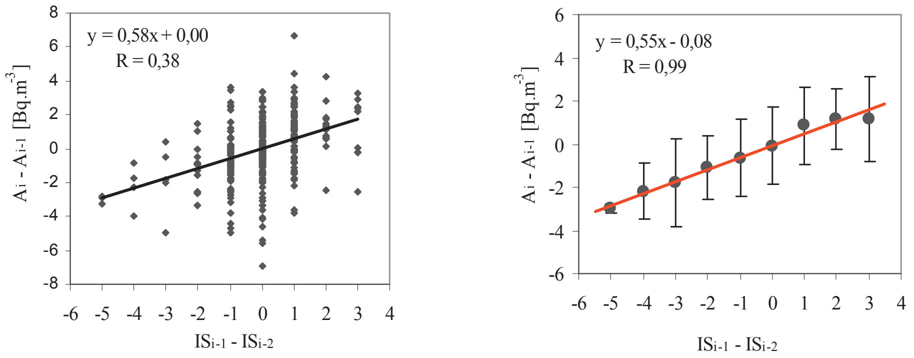

Fig. 7 The dependence between the change of ^{222}Rn activity concentration in given interval and the change of stability indexes in previous interval (August 1994). In the left picture all data are shown, in the picture on the right arithmetical means of changes of radon activity concentration corresponding to the changes of stability indexes are depicted

relation between the change of atmospheric stability and the change of radon activity concentration.

CONCLUSION

This work deals with the potential use of radon as an indicator of atmospheric stability. There was found a rather good agreement between the courses of radon activity concentration and stability indexes calculated on the basis of modified Turner classification. Moreover, it was found that the courses of radon concentration lag behind the courses of stability indexes. This lag is of the order of hours. Best agreement was found when the courses of stability indexes was shifted 4 hours forward in time. A possible cause of this is that while the reaction of stability indexes to a change of meteorological parameters is immediate (because they are defined by table values), it must obviously take some time until an appropriate change in the atmosphere and in radon concentration occurs.

It was also found out that, unlike the mean daily values of radon activity concentration, the mean daily values of stability indexes do not vary significantly during the month. This led us to the examination of deviations from their mean daily values. A very good agreement was found between such courses.

Further analysis showed that the dependence between radon activity concentration and stability indexes is not completely linear. A similar trend was observed when the impact of stability indexes on the change of radon activity concentration was examined. However, a nearly linear dependency was obtained when we examined the change of radon activity concentration in the given interval against the change of stability indexes in the previous interval, which suggests that there is a close connection between these quantities.

To sum up, radon gas seems to be a suitable indicator of vertical mixing processes in the atmosphere. However, drawing any final conclusions should be avoided until more extensive research about this matter has been conducted.

Acknowledgments

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SELECTED METALWORKING FLUIDS BIODEGRADABILITY AND ECOTOXICITY EVALUATION

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ABSTRACT

Gerulová K., Hostin S. & Michalíková A. **Selected Metalworking Fluids Biodegradability and Ecotoxicity Evaluation**

Metalworking fluids (MWFs) have been introduced into the cutting process with the purpose to improve the characteristics of the tribological processes which are always present on the contact surfaces between the tool and the workpiece. Significant amounts of lubricants are lost into the environment which potentially affects plants, animals and human life.

The main aims of this study were to evaluate the level of biodegradation of selected metalworking fluids standards and samples from the plant by Zahn-Wellens test (OECD 302B) for inherent biodegradability, evaluate potential adsorption after 3 hours of cultivating and assessment applicability of the test for measuring the biodegradability, evaluate the potential of activated sludge from the sewage treatment plant to degrade the selected MWFs and preliminary study to evaluate the ecotoxicity by *Lemna minor*.

Evaluated level of tested MWFs (Emulzin H, Ecocool, BC 25) standards biodegradation by Zahn-Wellens test achieved 80% in 10 days, so they have a potential to ultimate degradation. Tested MWFs samples from the plant pass higher level of starting COD concentration instead of this, in the case of Emulzin H and Ecocool sample 2 the level of degradation pass 80% degree.

Preliminary study of ecotoxicity measuring by *Lemna minor* shows effective concentration of Emulzin H at the rate of 93 mg/L, for Ecocool 99 mg/L and for BC 25 about 150 mg/L. Small concentrations of testing fluids indicate the hormetic effect. It is required to test Emulzin H, Ecocool and BC 25 by semi-static or flow-through condition.

Key words: metalworking fluids, biodegradation, EC_{50}, machining

INTRODUCTION

Metalworking fluids have been introduced into the cutting process with the purpose to improve the characteristics of the tribological processes which are always present on the contact surfaces between the tool and the workpiece [12, 13, 14].

A wide variety of chemicals may be used in each of the metal working fluid classes, and the risk these chemicals pose to workers may vary because of different manufacturing processes, various degrees of refining, recycling, improperly reclaimed chemicals, different degrees of chemical purity, and potential chemical reactions between components through the usage [3]. Exposes of the working environment to fluids may cause significant contamination to the environment and health hazards for the workers [8].

Future lubricants have to be more environmentally adapted, have a higher level of performance, and lower total life cycle cost (LCC) than presently used lubricants [1]. The use of rapidly biodegradable lubricants could significantly reduce environmental pollution. Environmental friendly alternatives are available for a large variety of mineral oil based lubricants [2]. The most interesting group for formulation of environmentally adapted lubricants are base fluids such as vegetable oils, synthetic fluids (polyglycols, polyalpha olefins (PAO), synthetic ester) [1, 3, 4, 10]. These oils can offer significant environmental advantages thanks to resource renewability, biodegradability and nontoxicity [4].

In Europe predominantly vegetable oils such as rapeseed oil and sunflower oil are used [3,1]. Chemically these are esters of glycerin and long–chain fatty acids (triglycerides) [2,1,5]. Natural triglycerides are very rapidly biodegradable and are highly effective lubricants. The use of vegetable oil in metalworking applications may alleviate problems faced by workers, such as skin cancer and inhalation of toxic mists in the work environments [6]. Biodegradable synthetic esters have much better performance than natural oils especially in the field of low and high temperature application and oxidation stability, but they are more expensive [4].

Properties related to the environmental fate of metalworking fluids

Significant amounts of lubricants are lost into the environment which potentially affects plants, animals and human life [7]. Definitions and examples of test methods for environmentally related properties can be found in a number of studies, such as [1].

Consequently, considerable attention has been given to lubricant parameters such as [1]:

- toxicity (non toxic against to human beings, fish, bacteria etc.) [5],
- degree of biodegradability,
- bioaccumulability and biomagnification,
- relative content of renewable raw material.

In [5] the consideration of the environment aspects of lubricants is focused on health hazards and water hazards.

Ecotoxicity of metalworking fluids

Ecotoxicity to aquatic organisms is generally used to reveal potentially adverse environmental effects of a compound or product [10]. Toxicity means the acute and chronic influences of a chemical on the functions of organisms [8]. Experience has shown that the ecotoxicologic properties of fully formulated lubricants are related to those of the base fluid and additive components. The measured toxicity of mixtures is found to be close to the sum of component toxicities [1]. Regarding the toxicological potential of lubricants, base oils and additives have to be regarded. Toxicity can be measured e.g., by means of an LC_{50} value (i.e., lethal concentration, 50 %), EC_{50} (effective concentration) or a WGK value (i.e., German water hazard class) [8].

It is widely recognized that the ecotoxicologic effects of the main MWFs components (biocides, corrosion inhibitors, extreme pressure and anti wear agents, emulsifiers, and surfactants) cause a major problem regarding the disposal of MWFs and their environmental impact. Established pollution parameters – such as Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD) and total organic carbon (TOC) – although important for effluent monitoring, are not sufficient to describe the impact of wastewater constituents on the environment [9].

Much scientific research indicates the need for wider toxicologic monitoring of industrial effluents and receiving waters. Toxicity bioassays can also be applied as promising tools for evaluating the efficacy of unit operations in industrial wastewater treatment (toxicity reduction evaluation, TRE) as well as for identification of toxic substances in effluents (toxicity identification evaluation, TIE) [9].

Toxicity of a substance is generally evaluated by conducting an acute toxicity test. The most common test methods used by the lubricant industry for evaluating the acute toxicity and European ecolabelling board of their products are EPA 560/6-82-002 (Sections EG-9 and ES-6); and OECD 201 (Algae growth inhibition test), OECD 202 (Daphnia acute immobilization test) and OECD 203 (Fish acute toxicity test) [3, 8, 10, 15]. The tests are used to determine acute toxicity, and do not evaluate adverse effects after long time exposure. Even so, problems arise from poor water solubility of the test substance. If a hydrophobic compound that is poorly soluble in water is discharged into the natural environment, it will probably end up in sediment and soil rather than remain in the water phase. Development of assays for sediment and soil are underway. The following scales of toxicity have been used: $EC_{50} < 1$mg/L highly toxic, 1–10 mg/L toxic, 10–100 mg/L hazardous, and >100 mg/L without acute toxicity [10].

Biodegradability

The great variety of biodegradation processes in the natural environment and in the technical plants for treating waste water and solid wastes gave rise to a rather large number of test methods based on different test principles [16].

Biodegradability of lubricant industry recognized the following test OECD 301 B – Modified Sturm test, ASTM D 5864 Standard Test Method for Determining Aerobic Aquatic Biodegradation of Lubricants and CEC L-33-T-82 Biodegradability of Two-Stroke Cycle Outboard engine Oils in CH_2 groups Water [17, 3], and approved the test method CEC-L-33-A-93 (1995) [18, 19, 5, 20]. In 2005/360/ES the biodegradability shall be determined for each constituent substance in the lubricant separately by test methods specified as OECD 301 A–F for readily biodegradation [1] and OECD 302 C or ISO 14 593 (CO_2 headspace test) for inherently biodegradable substances [8]. In [5] is for evaluating biodegradability cited also OECD 302 B – Zahn-Wellens test.

Screening tests for ready biodegradability (OECD 301 A-F) indicate if a compound is degradable under natural conditions without any problem [22, 23]. The biodegradation is monitored as the degree of mineralization, by means of summary parameters such as oxygen uptake, carbon dioxide production or elimination of dissolved organic carbon (DOC). Without employing ^{14}C techniques this is only possible if the test compound is the sole carbon and energy source for microorganisms. The test duration is 28 days, allowing some adaptation of the microorganisms to the compound but mineralization as a test criterion adds some extra stringency as it prevents chemicals to pass the test which are only converted into persistent products [22]. These informative tests basically discriminate readily biodegradable compounds from others, but they often underestimate the potentiality of degradation in environmental systems. Therefore when the result is negative, inherent (potential) biodegradability tests are required [23].

Many lubricants, particularly those based on mineral oils, are not readily biodegradable and data on their inherent biodegradability (i.e. potential to be biodegraded) is perhaps more useful when assessing their likely environmental impact. There are currently three internationally accepted guidelines for assessing inherent biodegradability: OECD 302 A (`Modified SCAS Test', Inherent Biodegradability, 1981a), OECD 302 B (Zahn-Wellens/EMPA Test, 1992) and OECD 302 C (`Modified MITI II Test', Inherent Biodegradability, 1981b). However, two of these tests (OECD 302 A and B) measure biodegradation as the loss of DOC and are therefore unsuitable for testing lubricants which usually have a very low solubility in water (however, in OECD 302B biodegradation can be realized also with COD) [18]. However, this method is not suitable for testing substances that are poorly soluble, volatile or adsorb to activated sludge, since the DOC or COD analysis it encompasses does not allow a clear differentiation between biodegradation and elimination by abiotic processes. Modification of the Zahn-Wellens test by continuous measurement of oxygen consumption (pressure measurement) and carbon dioxide (conductivity measurement) production was discussed in [26, 27]. It is a closed test system consisting of a culture flask, a carbon dioxide adsorption flask, a pump as well as integrated measuring and control instruments. The air circulating within the test system causes the carbon dioxide present in the test solution to be striped out completely and directly absorbed by the adsorption solution. This new test system also facilitates to test poorly soluble, adsorbing and volatile substances for inherent biodegradability and constitutes an appropriate complement to the standardized Zahn-Wellens test [26].

The third test (OECD 302 C) measures biodegradation as O_2 uptake and could therefore be applied to insoluble substances. However, with the exception of Japan, the OECD 302 C is reported to have hasfallen into disuse, and has technical limitations concerning the need for a ThOD value and a (needlessly) complex inoculum [18].

Bioremediation

To conform to all European legislation all spent metalworking fluids are to be disposed of as hazardous waste. The internal disposal of used emulsions via the waste water is not allowed; therefore all used metal working fluids as well as cleaning water are disposed of as waste [28].

The wide variety of organic MWFs constituents, which are susceptible to biodegradation partially or in whole, and the presence of water render O/W emulsions an ideal environment for some microorganisms to [9]. Although microbial deterioration of MWFs is a problem, such deterioration can be used to advantage for the disposal of operationally exhausted fluids. There is growing interest in exploiting the biocatalytic potential of micro-organisms to biodegrade MWFs in bioreactor-based processes [25]. The most common extracted bacterial isolates are *Pantoea agglomeraus, Citrobacter freundii, P. aeruginosa, Actinobacillus liginieresii* [10].

Van der Gast and colleagues have also carried out a series of waste MWF treatment studies. In their work, the indigenous bacterial communities have been identified. Also comparisons of the overall performance among activated sludge from municipal sewage works, indigenous communities and bacterial consortia have been made. They proved that introducing specific bacterial consortia was more effective. The technique of bacterial inoculation is named bioaugmentation, which is where additional organisms are added to enhance the treatment level when the existing microorganisms are not degrading the pollutant satisfactorily [24].

In the CEC-L-33-T-82 is as the extracting solution used 1,1,2-trichloro-1,1,2-trifluoroethane which affect the ozonosphere. Potential alternative carbon tetrachloride is well-known human carcinogen.

The main aims of this study were:

- Evaluate the level of biodegradation of selected metalworking fluids standards and samples from the plant by Zahn-Wellens test (OECD 302B) for inherent biodegradability.
- Evaluate potential adsorption after 3 hours of cultivating and assessment applicability of the test for measuring the biodegradability.
- Evaluate potential of activated sludge from sewage treatment plant to degrade the selected MWFs.
- Preliminary study to evaluate the ecotoxicity by *Lemna minor*.

MATERIALS AND METHODS

1. Preliminary biodegradability study – Zahn-Wellens test.

Metalworking Fluids Source

In experiments were used four types of metalworking fluids standards and samples from the plant – Emulzin H, Ecocool and Blascocut BC 25 that were obtained from ZVS Dubnica nad Váhom. In the test were used concentrations of cutting fluids that affect 1000–1400 mg/L of COD.

Preparing Samples for COD Measuring

5 ml of sample was filtered in frit S4. In leachate was measuring the content of chemical oxygen demand. The measurements of chemical oxygen demand were realized in thermoreactor and spectrophotometer by fi. Merck.

Source and Preparing of Inoculum

As an inoculum was used fresh activated sludge from thesewage treatment plant Volkswagen in Bratislava on the same day as the experiment started (or the day before) and leave in dark or diffuse light and cold place. Inoculum was washing twice with tap water. The sludge was separated by settlement. The activity of the sludge was controlled by the procedural control using a reference compound. As a reference substance was used ethylenglycol. In each test was used 0.5 g of dry matter/L in final volume. Volume of inoculum was evaluated after drying the special amount in the drying plant type HERAEUS to the constant weight at 60 °C. Samples of MWFs from the plant were contaminated by microorganisms at the rate 10^5–10^6 (contamination by moulds and yeast were not achieved).

Sample preparation

It was tested metalworking fluids samples prepared from concentrate diluted to required concentration with mineral medium prepared by [29] and samples from the plant ZVS in Dubnica nad Váhom with concentration in the range 0.5–5 Vol.% that were also diluted to the required concentration of COD in the test up to 1400 mg/L. Samples were cultivated in diffuse light at the temperature range 20–25 °C. Mix of inoculum, mineral medium and test or reference substance were aerated continuously by the membrane pump M401 and aeration pumps.

Validity of the tests and measuring parameters

The test is considered valid if the control shows the removal of the reference compound by at least 70 % within 14d and if the removal of COD. If it is reached 80 % of degradation in the test substance before 28d, the test considers finished. If the degradation starts of late days, the test will be elongated until the biodegradation is completed. The biodegradation can be calculated as the percentage of COD (or DOC) decrease by:

$$D_t = \left[1 - \frac{C_t - C_B}{C_A - C_{BA}} \right] \bullet 100$$

D_t – percentage degradation at time t;

C_A – concentration (mg/L) of COD (or DOC) in the test suspension measured after 3h ±30 min. of incubation;

C_t – mean concentration (mg/L) of COD (or DOC) in the test suspension at time t;

C_{BA} – mean concentration (mg/L) of COD (or DOC) measured in the blanks after 3h ± 30 min. of incubation;

C_B – mean concentration (mg/L) of COD (or DOC) measured in the blanks at time t.

Value determined after 3 h ± 30 min. of incubation gives the information about adsorption on activated sludge. Total decrease of COD (or DOC) of testing substation $D_t{}'$ could be calculated as the additional value in cases where is observed more than 20 % of adsorption.

From the displayed data on the biodegradation curve it can be evaluated:

Lag phase t_1 – time from inoculation until the biodegradation percentage increases up 10% from initial COD (or DOC). Lag phase is variable and repeated with difficulties. It is measured in days. *Ultimate biodegradation degree* – it is the degree of biodegradation, above no other biodegradation occurs. *Biodegradation time t_2* – degradation time from the end of the lag phase until 90 % of biodegradation occurs.

2. Preliminary study of ecotoxicity evaluation by *Lemna minor*

Ecotoxicity Testing Organisms

As the organism for ecotoxicity testing was used *Lemna minor* (duckweed) that was obtained from the ECOTOX s.r.o. Bratislava. *Lemna minor* was cultivated in Hoagland E medium by [21] in the axenic condition before the test started. As the end point, was selected the number of fronds

Lighting and Temperature Condition

Lemna minor was cultivated in the continuous constant light condition and illumination was in the range of 7200–10 000 lx. Lightening was provided by 6 cold neutral white illumination bulbs. Temperature was regulated to the range of 25 ± 2 °C by the blower.

Concentrations of Testing Substances – Range Finding Test

In the preliminary study of metalworking fluid ecotoxicity was chosen the concentration range from 0.01 mg/L, 0.1 mg/L, 1 mg/L and 10 mg/L of Emulzín H, Ecocool and Blascocut BC25. After were tested concentrations of 1 mg/L, 10 mg/L, 50 mg/L, 80 mg/L, and 100 mg/L and finally were tested concentrations of 80 mg/L, 150 mg/L, 250 mg/L, 350 mg/L, and 400 mg/L. For evaluating EC_{50}value was applied linear regression. Inhibition was calculated by the area under the growth curve to control groups as it is described in [21].

RESULTS AND DISCUSSION

Biodegradability evaluation

Validity and interpretation of the test is considered valid if the procedural control shows the removal of the reference compound by at least 70 % within 14 day and if the removal of DOC (or COD) in the test suspension took place relatively gradually over days or weeks, since this indicates biodegradation. Ultimate degradation degree of a reference compound was 95 % in 10 days window (started concentration of COD was in the required range up to 1000mg/L and was 772 mg/L of COD).

Starting concentration of MWFs samles from the plant passed 1101 mg/L for Emulzin H standard, 1125 mg/L for Ecocool standard and 1043 mg/L for BC 25. As it is presented in the Fig. 1 all tested cutting fluids satisfy 80 % of degradation in 10 days. *Lag phase* were shown in the cases of Emulzin H and Ecocool and extend of 2 days. All tested MWFs standards show to be good ultimate degradability by the Zahn-Wellens test even when the concentration of COD was higher about 43–125 mg/L than is required for this test.

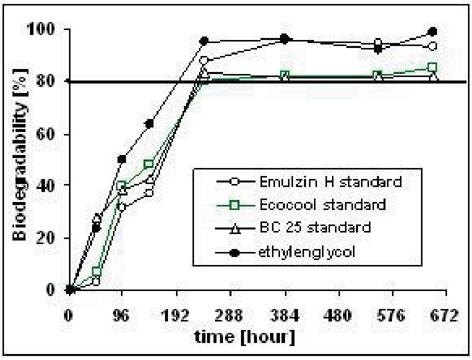

Fig. 1 Biodegradation curves of MWFs standards – Emulzin H, Ecocool and BC 25 using Zahn-Wellens Test

Starting concentration of MWFs samples from the plant was also higher than 1000 mg/L of COD and pass 1496 mg/L for Emulzin H sample, 689 mg/L for Ecocool sample 1 and 1225 mg/L for sample 2; and 1043 mg/L for BC 25. Figure 2 shows iodegradation kinetics of these tested cutting fluids. 80 % of biodegradation rate pass only the sample of Emulzin H and Ecocool sample 2. Ecocool sample 1 passes only about 70 % and BC 25 sample only 60 % of degradation instead both starting concentrations of COD pass criterion for this test, they show worse potential to ultimate biodegradability. *Lag phase* was observed only in the case of BC 25 sample and extended 4 days.

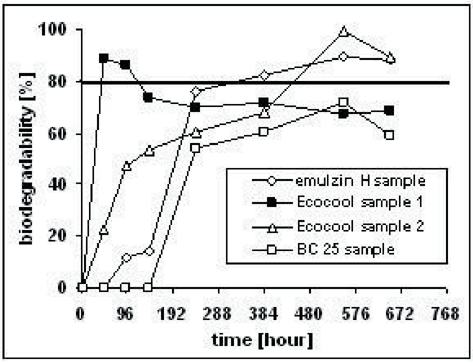

Fig. 2 Biodegradation curves of MWFs samples from the plant using Zahn-Wellens Test

However, physico-chemical adsorption can, in some cases, play a role and this is indicated when there is a complete or substantial removal in the first 3 h and the difference between blanks and test solutions remains at an unexpected low value. In such cases additional information is obtained from the comparison between the 3 h value and initial value of the test measured before the inoculum is added. If a more precise distinction between biodegradation (or partial degradation) and adsorption is to be drawn, carry out further tests, preferably a respirometric test for ready biodegradation, using the supernatant of the acclimatized sludge as inoculum.

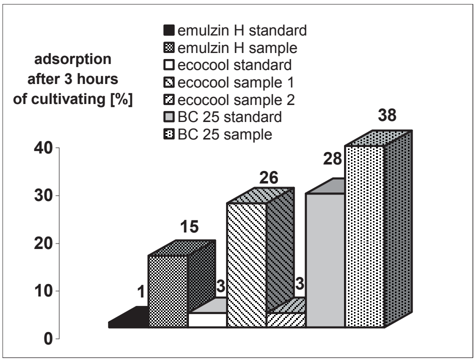

Fig. 3 Adsorption of the MWFs after 3 hours of cultivating

Figure 3 shows the adsorption of tested emulsions after 3 hours of the test (+/– 30 min.). Chemical oxygen demand – COD of tested standards and samples were higher than 20 % in Ecocool sample 1, where presented 26 % of COD decrease and on both of BC 25 standard and sample from the plant (28 % and 38 % of COD decrease), so there were no possibility to evaluate if the decrease was realized with the microbial activity, or by another adsorption kinetics. It is required to evaluate the level of biodegradation by other biodegradation method for BC 25 e.g. OECD 301 B or by CEC-L-33-A-93. Emulzin H and Ecocool standards has the decrease of COD in the limits of Zahn-Wellens test validation (<20 %). Treated (after 28 days of cultivating) and non-treated tested MWFs (before adding activated sludge) standards and samples from the plant are shown in Fig. 4.

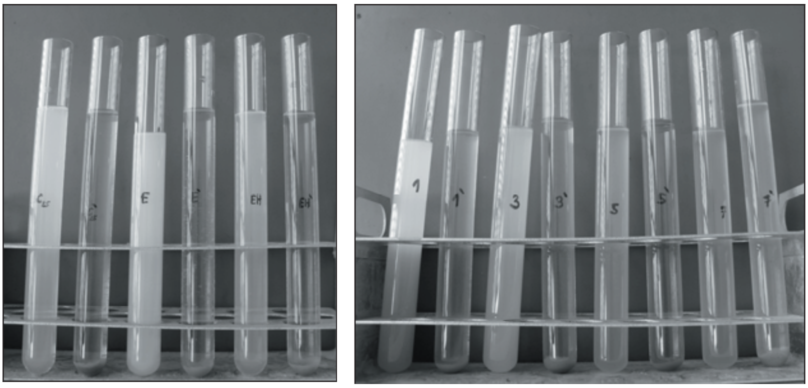

Fig. 4 Treated (after 28 days of cultivating) and non–treated MWFs standards and samples.
BC 25 – standard before, BC 25´ standard after, E – Ecocool standard before, E´– Ecocool standard after,
EH – Emulzin H standard before, EH´– Emulzin H standard after,
1 – Emulzin H sample before, 1´– Emulzin H after, 3 – BC 25 sample before, 3´– BC 25 sample after, 5 – Ecocool sample 1 befere, 5´– Ecocool sample 1 after, 7 – Ecocool sample 2 before, 7´– Ecocool sample 2 after.

Ecotoxicity evaluation

Preliminary study of selected MWFs ecotoxicity on *Lemna minor* is shown in the Fig. 5a-c. For the test to be valid, the doubling time of frond number in the control must be less than 2,5 days (60 h), corresponding to approximately a seven–fold increase in seven days and an average specific growth rate of 0,275 d^{-1}. Average specific growth rate were evaluated for all tests in the range 0,23–0,24 d^{-1} and pass the criteria for the test.

In the concentration of 0,001 mg/L; 0,01 mg/L; and 0,1 mg/L of all tested cutting fluid were observed hormesis – stimulatory effect on growth. Effective concentration of tested MWFs that effect 50 % of growth inhibition was evaluated from the area under the growth curves and for Emulzin H was about 93 mg/L, for Ecocool 99 mg/L. BC 25 has affect lesser inhibition in compare to the others – about 150 mg/L.

The test was realized in the static condition but it shows to be advantageous to study effect on *Lemna minor* in semi-static or semi-static and flow--through condition with renewal of testing solution due to observed little precipitation during the test.

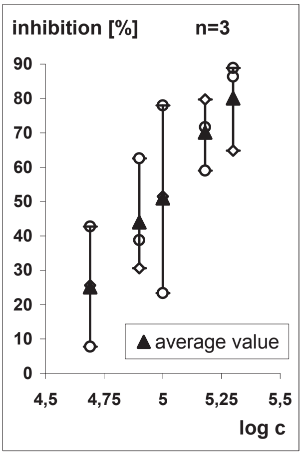

Fig. 5a EC$_{50}$ evaluation of Emulzin H with *Lemna minor*

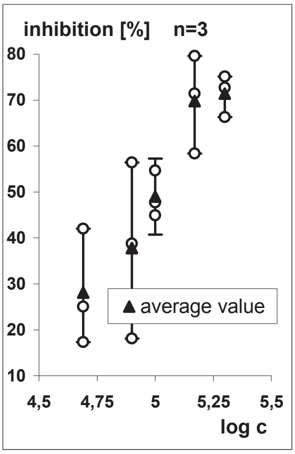

Fig. 5b EC$_{50}$ evaluation of Ecocool with *Lemna minor*

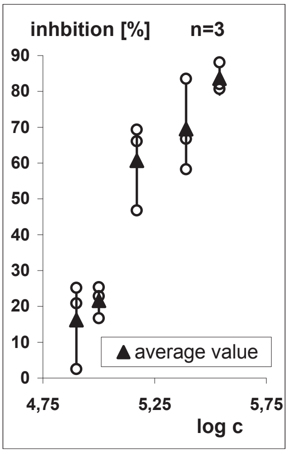

Fig. 5c EC$_{50}$ evaluation of BC 25 with *Lemna minor*

CONCLUSION

Evaluated level of tested MWFs (Emulzin H, Ecocool, BC 25) standards biodegradation by Zahn-Wellens test achieved 80 % in 10 days, so they have potential to ultimate degradation by this test. Tested MWFs samples from the plant pass higher level of starting COD concentration instead of this, in the case of Emulzin H and Ecocool sample 2 the level of degradation pass 80 % degree.

Disadvantages of Zahn-Wellens test are DOC measurement by which it is not able to evaluate all presented organics, even when they are in insoluble form (in the case of COD there is evaluating with oxidable forms also inorganics). At high rate of adsorption it is impossible to differentiate between biotic degradation and another form of abiotic elimination, which was shown in the case of BC 25 (28 and 38 % of COD decrease after 3 hours of cultivating). This method is also discontinual. It will be in the next study, use the modified test method of Zahn-Wellens test, by the measuring of CO_2 production and O_2 consumption, by continual measuring.

Substances that are created in the fluid during machining operations and adding biocides or other impurities such as tramp oil, can affect level of biodegradation. It is required to study also qualitative content of cutting fluids and degradation products, to evaluate the potential hazard to humans or the environment.

Microbial contamination during usage can reduce lifetime of MWFs (and also affect workers health), but on the other hand, there is a possibility to utilize nonpathogenic microorganisms, that are presented in fluids, to degrade them. In the next study it will be isolated microbial consortium presented in specific plant and realize experiments to degrade MWFs at higher concentration rate with focusing also on the rising products.

The preliminary study of ecotoxicity measuring by *Lemna minor* shows effective concentration of Emulzin H at the rate of 93 mg/L, for Ecocool 99 mg/L and for BC 25 about 150 mg/L. Small concentrations of tested fluids indicate hormetic effect. It is required to test Emulzin H, Ecocool and BC 25 by semi-static or flow-through condition.

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MOBILITY OF MERCURY IN THE SOILS USING SEQUENTIAL EXTRACTION FROM THE RUDŇANY LOCALITY

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ABSTRACT

Šestinová O., Hančuľák J., Bobro M., Fedorová E. & Brehuv J. **Mobility of Mercury in the Soils Using Sequential Extraction from the Rudňany Locality**

Many sequential extraction methods were elaborated for the evaluation of elements mobility. They are different in number of the extraction steps, used extraction solvents or/and extraction procedure. The one-step extraction can be used for fast indication of changes in the mercury mobility in the contaminated environment. The goal of our study was the quantify of released, potentially mobile and mobile mercury forms in the contaminated soil in the area of the former Rudňany mining plant and the former mercury plant in Štefánska Huta, with the assumed influence of Kovohuty Krompachy. The one-shot extraction of the sequential leaching (according to Tessier et al., 1979) was used for the isolation of individual forms. The extraction was based on already known concentrations of total mercury content which has been observed for long time.

Key words: sequential extraction, soils, mercury, environment, pollution

INTRODUCTION

Heavy metals in soil occur in various forms and bonds depending on soil properties. The most marked influence has the soil reactivity, the content of organic matter and soil granularity. Their binding forms show various mobility degrees, various forms of transport to subterranean and surface waters and bio-facility for plants and animals as well. Except the released forms, the metals can be fixed also in the potentially mobile and mobile forms that have most importance for evaluation of the soil bio-toxicity. These metals may come directly from the weathering process of the rocks, where the soil-forming process influences their concentration and distribution. Moreover, they also come into the soil as result of the anthropogenic human activity as well. Nowadays, the mercury and mercury compounds are considered to be one of the most important pollutants of the environment. Mercury is a trace element which creates the large number of the inorganic and organic compounds. These compounds are toxic almost in every case. Natural and/or geochemical sources include the volcanoes, geological deposits and sea fumes. The anthropogenic mercury input into the environment is more miscellaneous compared to the natural one. The main sources are for example: mining dumps, ore transport, metallurgy/contamination from exhalates, aerosols, agriculture, electronics, batteries, teeth fixtures and waste facilities. Subsequently, mercury and mercury compounds enter into atmosphere, hydrosphere and pedosphere, where they change during its cycles and the result of these processes is the increase of toxicity.

High ecological risk of mercury comes from its specific properties. Mercury influences mainly areas with mining industry and/or thermal treatment of ores containing mercury. Siderite deposit of Rudňany belongs to risk localities.

Many sequential extraction methods were elaborated for the diversification of particular forms of mercury in the soil that differ in a number of the extraction steps, extraction solvensts or/and extraction procedures. The gradual washing of individual solid phases from soil and metals associated with these phases occurs during the sequential extraction leachate contains a group of elementary forms with similar physical and chemical properties. The specificity can be increased by using of suitable extract solvent into extraction sequence where thefollowing agent extracts the rest of one extraction step. Extraction process evaluates the strength of bond of metal forms to different soil phases, to ion-renewable, carbonated, reducible, oxidable and finally to resistant residue [1]. The most known is the five-step sequential extraction of soil published by McLaren and Crawford [2] and Tessier [3]. This method can differentiate heavy metals fixed on the sediments in five fractions. Sequential extraction methods are the most suitable form for evaluation of element mobility in the sediments and soil mediums and they are also acceptable by the IRMM (Institute for Reference Materials and Meassurements) as standard procedures of certified reference material. Nowadays, the assessment of pollutant mobility starts to be a part of European procedures. It is necessary to think about involving of one-step extractions into complex solvents that are an economic (time-saving) alternative to the supplement reference IRMM. They can be the form for quick indication of changed element mobility in the monitored locality [4].

The goal of our work was to determine released, potentially mobile and mobile mercury forms in the contaminated soils in the area of the former Rudňany minig plant and the former mercury plant in Štefánska Huta with the influence of Kovohuty Krompachy. The one-shot extraction of sequential leaching according to Tessier procedure [3,5] was used for isolation of individual forms. The extraction was based on already known concentrations of total mercury content which has been observed for years.

MATERIAL AND METHODS

The soil samples from eight localities (Rudňany and Štefanska Huta) were used for the analysis. Biota and assimilation organs (two years old needles of spruce and cedar, birch leaves) were also taken. Taking of samples was realized in November 2006 and the total content of mercury was determined in the sample. The soil was taken according to law (220/2004 Z.z. section no. 2) from various areas to keep representativeness. Soil samples from grass coppice and forest soils (depth was 0.05–0.20 m) were used for one-shot sequential extraction. The atomic Spectrometer determined mercury concentration in the soils directly, without mineralization, from dried, quartered and mechanically worked samples (granularity – up to 2 mm). Presented sort of tree species were selected from the reason of their most frequent occurrence in the monitored areas as well as for a possibility of the comparison of mercury content and its mobility in the soils and biota. Biota samples were washed by distillate water, then dried, homogenized and then analyzed by the trace mercury analyzer (TMA 254).

The sequential extraction was used for extraction of the soil samples:

Fraction: A (free forms) was determined in the extract of extraction solvent – 2M HNO_3.5g of the sample was mixed with 50 ml of the extraction solvent and shaken for 60 minutes in the mechanic shaker at the room temperature and 300 rpm. After this procedure the sample was fleeced for 15 minutes and supernatant was filtered and filtrate was filled up to 100 ml. The rest was washed by deionized water and it was used in the second step. This fraction contains metals bonded to sulphide and phosphate.

Fraction: B (potentially mobile forms) was determined in the extract of extraction solvent – 0.05 M EDTA (ethylen-diamine-tetra-acetic acid). The solution was shaken and fleeced at the same conditions as a fraction A. Fraction contains metals in the ion-changing form and bonded to carbonates.

Fraction: C (mobile forms) was determined in the extract of extraction solvent 0.1 M $CaCl_2$ at the same conditions as a fraction A and B. This fraction contains metals in ion-changing form that creates only a fragment of the element portion to its total content in the soil.

Fraction: D (residual rest) presents extracted phase, e. g. metals bonded to the silicate structure and to crystal lattice of the primary minerals. The rest was dried at room temperature. After drying and homogenizing TMA 254 measured the sample.

RESULTS AND DISCUSSION

Active soil reaction (pH) is presented in Table 1. It shown that only samples 1 and 3 are slightly alkaline and the rest are acid soils. It is supposed that in the acid soils the Hg^{2+} is bonded to organic matter. The influence of Rudňany mining plant ŽB (iron ore mining) Fig. 1 is evident from the extremely high total mercury concentration in the samples 1, 4, 5, and 6. In the past, for whole centuries, this locality was the center of mining industry and ore treatment. At the present time, there are forested stacks and forest soils, which are located under_sampling_biota and it contained the highest content of humus and organic compounds. For example, according to law [7] the limit value for mercury content in agricultural soil is depending on type of soil from 0.15 to 0.75 mg/kg.

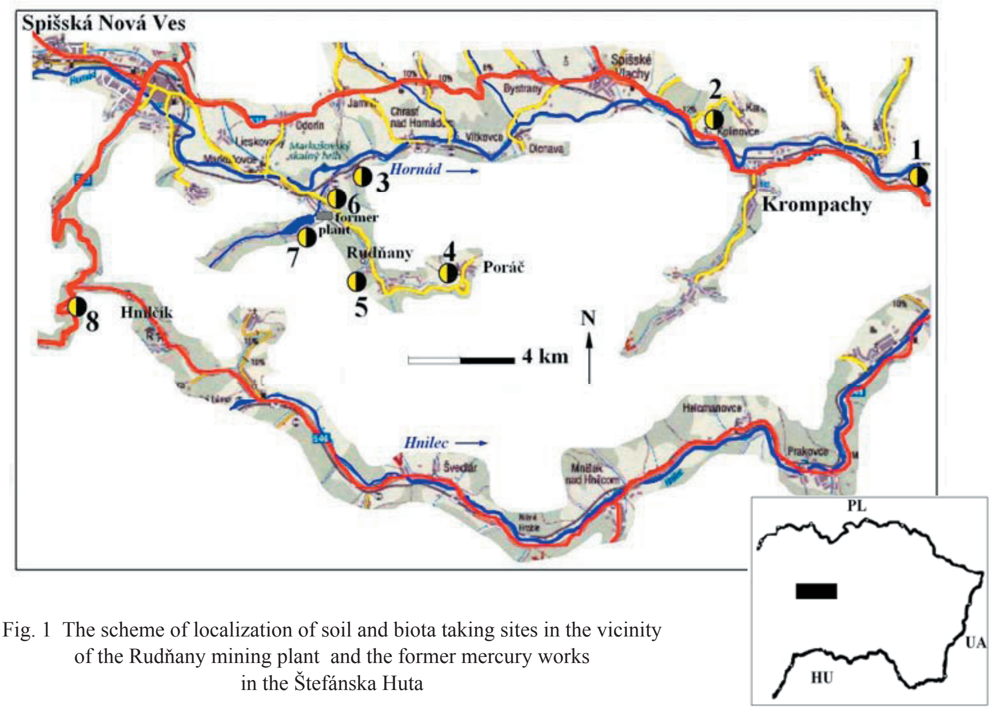


Fig. 1 The scheme of localization of soil and biota taking sites in the vicinity of the Rudňany mining plant and the former mercury works in the Štefánska Huta

Tab. 1 Description of sampling places and the chemical composition of soils taken in the area of Rudnaňy in November 2006

No.	Locality	pH	Redox potential	Organic portion [%]	Total content of Hg [ng/g]
1	Štefanská Huta	7.25	506	6.70	122 440
2	Kolinovce	3.78	661	1.51	3 700
3	Matejovce	7.46	554	7.71	7 160
4	Poráč	4.84	627	10.02	116 500
5	Rudňany – winter valley	3.57	695	9.29	48 600
6	Rudňany – opposite to manufactory	3.91	686	5.40	80 620
7	Rudňany – sludge bed	4.06	673	9.82	11 810
8	Hnilčík – winter valley	3.43	637	30.06	1 195

Mercury content determined in individual fractions A-D after sequential extraction of soils and percentage content of mercury (the yield) is presented in Table 2, where in each sample it is determined the highest content of mercury in fraction D (residual rest). Percentage content of mercury in this fraction varied from 73.65 to 146.9 %. In the sample 3 there was probably made an mistake in the determination of mercury content. Determined mercury content in the fraction A was mainly under the value of detection limit for TMA 254. The mercury content determined in fractions B-C was very low, which corresponds to percentage yield content.

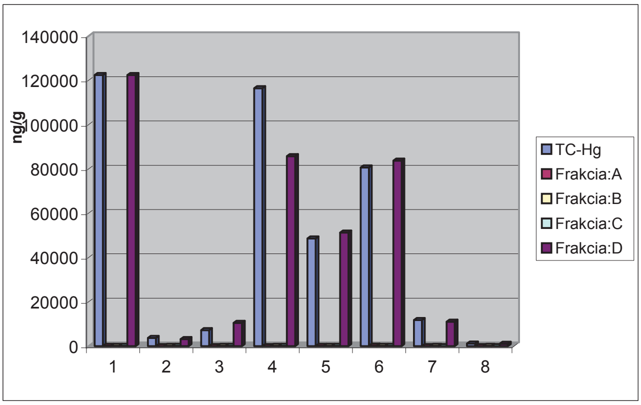
The Figure 2 shows that particular fractions i.e. free, potentially mobile and mobile forms do not contain mercury bonded in bio-permissible form. On the contrary, all mercury remains in the rest.

In the samples taken from assimilation organs of trees were measured very low values of mercury (approximately 27–380 ng/g). These results were obtained even though the content of total mercury in the soils were high (Table 3). Correlation relationship

Tab. 2 Mercury content determined in extraction solvents after extraction of soils and the yield of used sequential extraction

No.	**Fraction A** **[ng.g^{-1}] /Y [%]**		**Fraction B** **[ng.g^{-1}] /Y [%]**		**Fraction C** **[ng.g^{-1}] /Y [%]**		**Fraction D** **[ng.g^{-1}] /Y [%]**	
1	33.3	0.027	33.3	0.027	33.3	0.027	122 381	99.95
2	PD	0	49.4	1.330	49.4	1.330	3 152	85.19
3	PD	0	33.3	0.460	33.3	0.460	10 520	146.90
4	PD	0	33.3	0.028	33.3	0.028	85 800	73.65
5	33.3	0.069	66.7	0.137	33.3	0.069	51 300	105.50
6	148	0.180	49.4	0.060	98.8	0.122	83 780	103.91
7	PD	0	49.4	0.420	24.7	0.210	10 983	92.99
8	PD	0	49.4	4.130	PD	0	1 030	86.19

Y[%] – yield of used sequential extraction, where 100 % is total mercury content in the soils
UDL – concentration of Hg under the value of detection limit
Fractions A – D:
A – free forms were determined in the extract of extraction solvent 2M HNO_3
B – potentially mobile forms was determined in the extract of extraction solvent 0.05M EDTA
C – mobile forms were determined in the extract of extraction solvent 0.1M $CaCl_2$
D – solid residual rest, where was determined mercury content bonded in the structure of silicates and in the crystal lattice of primary minerals



TC-Hg: total mercury content

Fig. 2 Comparison of total Hg content with Hg content in the particular fractions A-D in the soils was not confirmed. Maximum of mercury concentration was detected in the leaves of birch. Proportion of total mercury contents in the soil to assimilated mercury in the biota was the highest in the birch sample from Hnilčík – Winter Valley and was three times higher.

Tab. 3 Comparison of mercury content specified in biota: birch, cedar, spruce and soil from Rudňany area

No.	Locality	**Birch** [ng.g^{-1}]	**Spruce** [ng.g^{-1}]	**Cedar** [ng.g^{-1}]	**Total content of Hg in the soil** [ng.g^{-1}]
1	Štefanská Huta	161	119	230	122 440
2	Kolinovce	72	105	51	3 700
3	Matejovce	37	136	65	7 160
4	Poráč	68	110	84	116 500
5	Rudňany – Winter Valley	271	63	31	48 600
6	Rudňany – opposite to manufactory	370	216	27	80 620
7	Rudňany – sludge bed	–	124	124	11 810
8	Hnilčík – Winter Valley	380	52	38	1 195

On the basis of the results we can state that mercury is not bonded in the form bio-accessible for plants, but it remains fixed on crystal lattice and in structure of mineral matrix. This conclusion is consistent with results reached by Závadská et al. [1]. Correlation relationship between the total mercury content in the soil compared to that in biota was monitored in this locality but it was not confirmed. The mercury from the anthropogenic human activity (like the Rudňany area) is in such environment superimposed to its geochemical background, while high concentration of mercury in the local scale may arise with its dangerous impacts on the environment.

Acknowledgements

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CONCLUSION

The one-shot sequential extraction that characterized individual forms of mercury bonds in the soil was used for determination of mercury mobility in the contaminated soils from the Rudňany area.

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THE COMPARATIVE STUDY OF URANIUM ISOTOPES BY ALPHA SPECTROMETRY AND SECONDARY ION MASS SPECTROMETRY. PRELIMINARY RESULTS

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ABSTRACT

Kuruc J., Harvan D., Galanda D., Mátel Ľ., Aranyosiová M. & Velič D. **The Comparative Study of Uranium Isotopes by Alpha Spectrometry and Secondary Ion Mass Spectrometry. Preliminary Results**

The paper presents the preliminary results of the first comparative measurements of uranium isotopes by two techniques – alpha spectrometry and secondary ion mass spectrometry (SIMS). Samples with specific activity of uranium isotopes were prepared by electrodeposition from aqueous solution of $UO_2(NO_3)_2.6H_2O$, not directly from natural environment. We obtained linear correlation between SIMS intensities of uranium ions and their alpha activities. These correlations give a possibility to obtain linear correlation between SIMS intensities of uranium ions and surface weights of uranium isotopes. Preliminary results indicate the possibility to use SIMS for quantitative analysis of surface contamination by uranium isotopes. The obtained results are presented in this article.

Key words: alpha spectrometry; secondary ion mass spectrometry; uranium isotopes; electrodeposition; correlations; regression analysis; radiochemical analysis; radiometric analysis

INTRODUCTION

Principle of SIMS technique

Secondary ion mass spectrometry (SIMS) is a method founded for chemical composition analysis of different substances and materials [1]. It is not limited by origin or type of material. Basic principle of SIMS is resided in atomic bombardment of sample surface with high-energy primary ion beam (consisting from I^+, Cs^+, Au^+ i.e.). Primary ion beam penetrates by material, it transfers its energy to hit atoms and generates collision cascade. The result of collision cascade is emission of atoms, molecules and clusters from the surface. Emitted or sputtered particles convert into ions as secondary ions and secondary ions are analyzed in mass spectrometer.

The SIMS, with system for separate particle weights by time of fly (TOF–SIMS), is simple and the most effective. It works in pulse mode. Emitted secondary ions are extracted to time-of-fly column with potential, which are dispensed by the same kinetic energy. If the mass of ion is lower, then this ion flies faster through the column to the detector. This is the basic principle of separation of ions with TOF system. Measure of the depth profile is another possibility of analysis of sample surface. Depth profile affords information about composition inside the sample. It creates a three-dimensional picture of the sample.

Advantages [2]:

- High sensitivity (ppm, ppb)
- 1 nm depth resolution
- Collateral detection of all masses

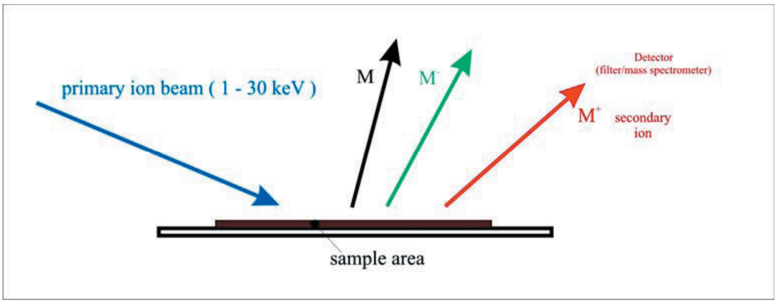

Fig. 1 Schematic diagram of atomic bombardment of sample surface by high-energy primary ion beam

- Weight range to 10000
- 100 nm laterally resolution in measure of two-dimensional distribution.

SIMS in nuclear research

In 1978 Shilling J.H. [3] was investigating to use this technique for analysis of trace elements and he showed that SIMS is not a universally appreciated analytical method. But this method found its utilization in most areas of research, especially in dating of surfaces, detection and migration of isotopes, isotopic analysis, contamination analysis of surfaces, and compositional changes in materials. SIMS found widely application in coupling with other analytical or nuclear methods such as XRF (X-Ray Fluorescence) [4], GC-MS (Gas Chromatography-Mass Spectrometry) [5], TIMS (Thermal Ionization Mass Spectrometry) [4], ICP-MS (Ion Coupled Plasma-Mass Spectrometry) [6], AMS (Accelerator Mass Spectrometry) [7], NAA (Neutron Activation Analysis) [8], PIXE (Particle Induced X-Ray Emission) [9]. These methods were used for determination (especially isotopes ratios) of ^{238}U [10], ^{232}Th [11], lead isotopes [9, 12] and other isotopes [13].

METHODS AND EXPERIMENT

The most common procedures are co-precipitation and electrodeposition for preparation samples [14]. Radionuclides are deposited by electro-chemical procedures on metallic plate in deposition cell by the effect of electrochemical process in solution by electrical flow [15]. Metallic plate is a disc (sample for measure) and electrode, too. Frequently used discs are platinum, tantalum, nickel discs and stainless steel discs. Uniform distribution of particles on disc's surface is an advantage and it is the most

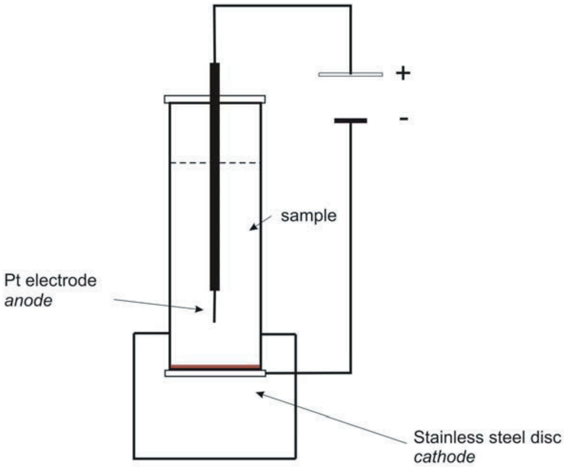

Fig. 2 Schematic diagram of electrodeposition cell [14]

important for SIMS measurement. Losses are low as uncertainty of weighting [14]. Brightening stainless steel discs were used in this experiment. Electrodepositing cell is presented in Fig. 1.

Preparation of discs with electrodeposited uranium was performed by methodology from Galanda D. [14] and Eichrom Industries, Ltd. [16]. After preparation, discs were measured by low-level alpha spectrometer. Recovery of electrodeposition was accepted as a value 86 % in accordance to literature [16]. Our calculations of weights of deposited uranium confirmed this value. Weights of deposited uranium isotopes were calculated from their alpha activities. After alpha spectrometry, discs were analyzed by the machine TOF-SIMS IV at International Laser Center in Bratislava.

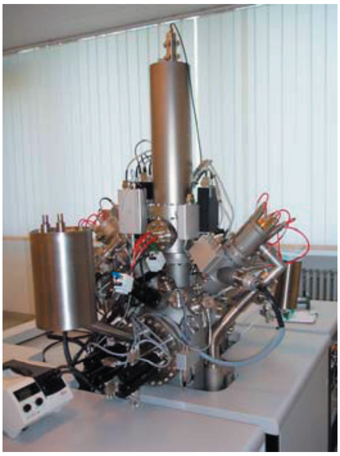

Fig. 3 TOF-SIMS IV at International Laser Center in Bratislava [1]

Characteristics of the used instrument:

Alpha spectrometry

Instrument: Ortec Dual Alpha Spectrometer 576 A – 919 (Ortec®, U.S.A.); Efficiency: Discs 1–3, $\varepsilon = 0.18$, Discs 4, 5, $\varepsilon = 0.203$; Background: <30 counts/day; 300 to 450 mm^2 active area, <40 counts/day, 600 mm^2 active area; Measure time: Discs 1–3, $t = 60000$ s, Discs 4, 5 $t = 3000$ s; Software: AlphaVision 32.

SIMS:

Instrument: TOF-SIMS IV (ION TOF GmbH, Germany); Ion gun: Au; Primary ions: Bi^+; Ion energy: 25 keV; Samples current: 1 pA; Area: 150×150 mm^2; Number of ions: 5×10^{12} ions·cm^2; Polarity: positive; Software: IonSpec.

RESULTS AND DISCUSSION

In accordance to the method described in part Methods and experiments, discs with electrodeposited isotopes of uranium from solution of uranyl nitrate $UO_2(NO_3)_2.6H_2O$ were prepared. Tab. 1 shows the basic properties of natural uranium isotopes [17, 18]:

The Figure 4 shows the disc after electrodeposition.

Fig. 4 Stainless disc after electrodeposition

Tab. 1 Basic properties of natural occurrence of uranium isotopes

Uranium isotopes	***Natural occurrence [%]***	***Relative atomic weight***	***Half time of decay***	***Emitted radiation; Energy [MeV]***	***Decay product***
^{234}U	0.0055	234.0409456	245500 y	α ; 4.859	^{230}Th
^{235}U	0.7200	235.0439231	$7.038\cdot10^8$ y	α ; 4.679	^{231}Th
^{238}U	99.2745	238.0507826	$4.468\cdot10^9$ y	α ; 4.270	^{234}Th

Alpha spectrometry

Alpha spectrometry with Dual alpha spectrometer was realized before SIMS analysis. Activities were obtained from counts and calculated from Equation 1:

$$A = \frac{\left(n_d - n_b\right)}{\varepsilon . R}, \qquad (1)$$

where A is an activity of sample [Bq]; n_d is a count rate of isotope [s^{-1}]; n_b is a count rate of background [s^{-1}]; ε is efficiency of detector; R is recovery of electrodeposition (R = 0.86 according to [16]). Uncertainities of alpha activity measurements were calculated from Equation 2:

$$u_A = \pm \frac{A}{\sqrt{N_D}} .1.96, \qquad (2)$$

where A is alpha activity [Bq]; N_D is number of counts obtained from alpha spectrometry measurements. Results obtained from Eq. 1 and Eq. 2 are described in Tab. 2:

Relatively high difference between relationships ^{234}U/^{238}U and ^{235}U/^{238}U are caused by low activities of uranium isotopes at low-active samples. These low-active samples were close to background.

Conversions of activities to weights by Eq. 3 are summarized in Tab. 3:

$$m = \frac{A . A_r}{N_A . \ln 2} . T_{1/2}, \qquad (3)$$

where m is weight of uranium isotope [g]; A is activity [Bq]; A_r is relative atomic weight; N_A is Avogadro's constant; $T_{1/2}$ is half time of decay [s]. Surface area after electrodeposition was 2.97 cm^2. Values of surface's weights of uranium in g.cm^{-2} are summarized in Tab. 3.

SIMS results

Discs prepared by electrodeposition after alpha spectrometry were measured at the International Laser Center in Bratislava by TOF-SIMS IV

Tab. 2 Results from alpha spectrometry

		^{234}U	^{235}U	^{238}U	$^{234}U/^{238}U$	$^{235}U/^{238}U$
Disc # 1	**A** [Bq]	**0.0068**	**0.0002**	**0.0042**	**1.619**	**0.0476**
	u$_\mathrm{A}$ [±Bq]	0.0017	0.0003	0.0013		
Disc # 2	**A** [Bq]	**0.0124**	**0.0003**	**0.0102**	**1.216**	**0.0294**
	u$_\mathrm{A}$ [±Bq]	0.0023	0.0004	0.0021		
Disc # 3	**A** [Bq]	**0.0202**	**0.0014**	**0.0173**	**1.168**	**0.0809**
	u$_\mathrm{A}$ [±Bq]	0.0029	0.0008	0.0027		
Disc # 4	**A** [Bq]	**0.5687**	**0.0153**	**0.5152**	**1.1038**	**0.0297**
	u$_\mathrm{A}$ [±Bq]	0.0646	0.0090	0.0615		
Disc # 5.	**A** [Bq]	**1.086**	**0.0267**	**1.128**	**0.9628**	**0.0237**
	u$_\mathrm{A}$ [±Bq]	0.089	0.0127	0.091		

Tab. 3 Values of weights and surface's weights of uranium isotopes

Disc No.	^{234}U		^{235}U		^{238}U	
	m [g]	**m$_\mathrm{s}$** [g.cm^{-2}]	**M** [g]	**m$_\mathrm{s}$** [g.cm^{-2}]	**m** [g]	**m$_\mathrm{s}$** [g.cm^{-2}]
Disc # 1	**$2.95\cdot10^{-11}$**	**$2.93\cdot10^{-12}$**	**$2.69.10^{-9}$**	**$9.07.10^{-10}$**	**$3.38.10^{-7}$**	**$1.14.10^{-7}$**
Disc # 2	**$5.38.10^{-11}$**	**$1.81.10^{-11}$**	**$4.04.10^{-9}$**	**$1.36.10^{-9}$**	**$8.23.10^{-7}$**	**$2.77.10^{-7}$**
Disc # 3	**$8.79.10^{-11}$**	**$2.96.10^{-11}$**	**$1.75.10^{-8}$**	**$5.90.10^{-9}$**	**$1.39.10^{-6}$**	**$4.70.10^{-7}$**
Disc # 4	**$2.47.10^{-9}$**	**$8.32.10^{-10}$**	**$1.91.10^{-7}$**	**$6.44.10^{-8}$**	**$4.14.10^{-5}$**	**$1.39.10^{-5}$**
Disc # 5	**$4.72.10^{-9}$**	**$1.59.10^{-9}$**	**$3.34.10^{-7}$**	**$1.13.10^{-7}$**	**$9.07.10^{-5}$**	**$3.06.10^{-5}$**

with Au ion gun. Bi^+ ions with energy 25 keV and sample current 1 pA were used. The result of measurement is mass spectra with intensity vs. m/z. Figures 5 and 6 show some examples of these SIMS spectra.

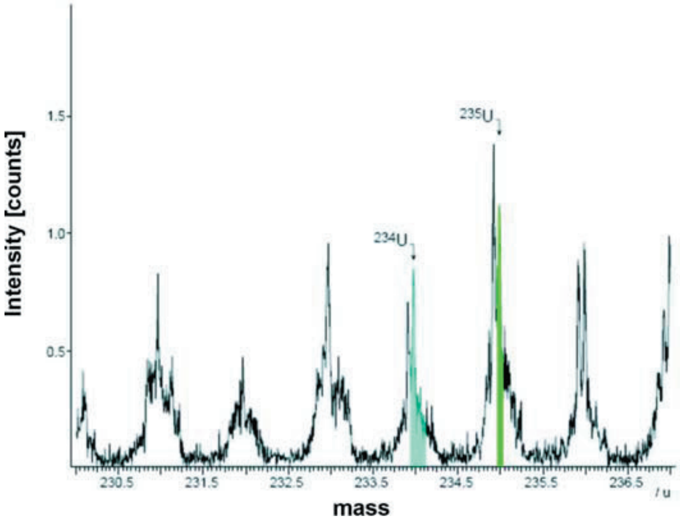

Fig. 5 SIMS spectrum of ^{234}U and ^{235}U

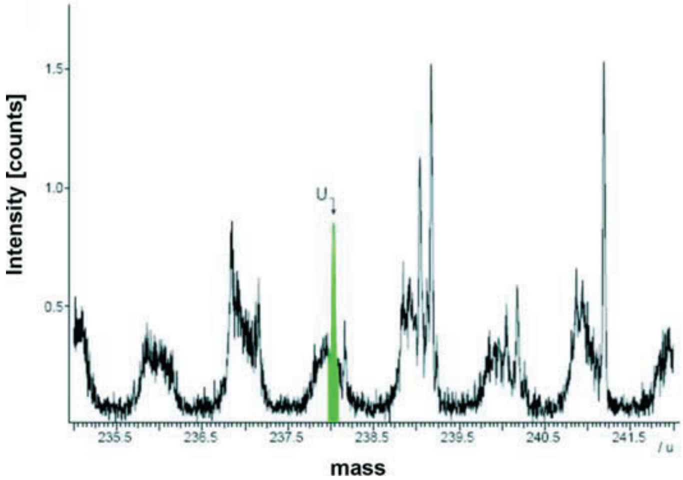

Fig. 6 SIMS spectrum of ^{238}U

We studied SIMS intensities of ^{234}U, ^{235}U and ^{238}U ions in dependence with its activities obtained from alpha spectrometry and its calculated surface's weights. Intensities (counts) were obtained by using of IonSpec software. Figure 7 shows the linear correlation of SIMS intensity vs. activities of uranium isotopes.

In the Tab. 4 the results of dependence of SIMS intensity of ions of uranium isotopes on surface weights of uranium isotopes are presented.

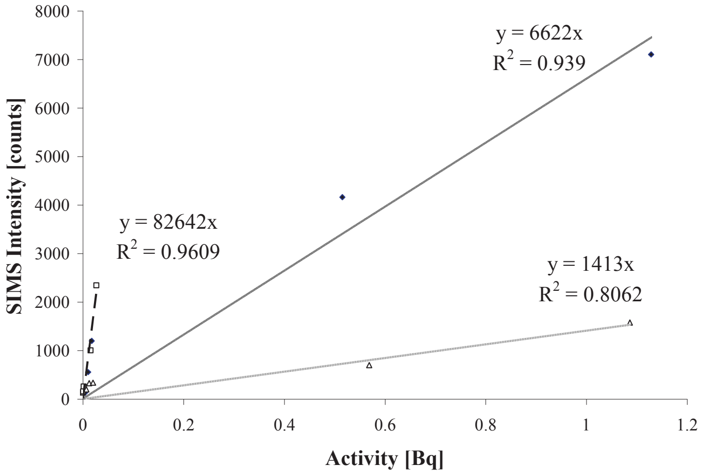

Fig. 7 The correlation between SIMS intensity of ions with m/z = 234 vs. ^{234}U alpha activity

Tab. 4 Table with correlated values SIMS intensity vs. Uranium isotopes surface´s weights

Isotope	m_s [g·cm^{-2}]	Intensity [Counts]	Linear correlation	
^{234}U	**2.93.10^{-12}**	**202**	*y = b·x* **y = 965.42x**	*R*^{2} **0.8065**
	1.81.10^{-11}	**331**		
	2.96.10^{-11}	**339**		
	8.32.10^{-10}	**701**		
^{235}U	**1.59.10^{-9}**	**1578**	**y = 19.63x**	**0.9607**
	9.07.10^{-10}	**134**		
	1.36.10^{-9}	**162**		
	5.90.10^{-9}	**263**		
	6.44.10^{-8}	**1003**		
^{238}U	**1.13.10^{-7}**	**2347**	**y = 244.52x**	**0.9389**
	1.14.10^{-7}	**132**		
	2.77.10^{-7}	**560**		
	4.70.10^{-7}	**1200**		
	1.39.10^{-5}	**4165**		
	3.06.10^{-5}	**7105**		

As we can seen, it's possible to plot the calibration curves of SIMS intensities [counts] vs. surface's weights of uranium isotopes by Equation 3, which permits to use the SIMS measurements as a quantitative method for measurement of surface contamination by uranium isotopes.

CONCLUSIONS

The main objective of the paper is to find the correlation between two sensitive techniques–alpha spectrometry and SIMS for natural isotopes of uranium and to determine the possibility of using of SIMS for quantitative measurement of uranium isotopes and contaminated metal surfaces by natural uranium. Linear correlation between the SIMS maximum ion intensity vs. alpha activity as well as of SIMS maximum ion intensity vs. surface's weight were obtained according to Fig. 7 and Tab. 4, respectively. We can see from these correlations the deviation from linearity of low-level activity discs, which is caused by low count rates in SIMS. These are evidently near background of SIMS device. Measurements of minimal detection mass (MDM) of uranium isotopes and uncertainties of the counts in SIMS need to carry out additional experiments, but they were not realized for time demandingness yet. Preliminary results indicate the possibility to use SIMS for quantitative analysis of surface contamination by uranium isotopes. From SIMS measurement it may be expected the acquirement of information about depth profiles of distribution of uranium as well as about distribution uniformity on a metal surface.

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CONTAMINATION OF THE WATER AND SEDIMENT LOAD FROM THE DRAINAGE BASIN OF THE SLANÁ RIVER BY INFLUENCE OF FORMER AND PRESENT MINING ACTIVITIES

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ABSTRACT

Brehuv J., Špaldon T., – Šestinová O., Slančo P., Hančuľák & J. Bobro M. **Contamination of the Water and Sediment Load from the Drainage Basin of the Slaná River by Influence of Former and Present Mining Activities**

The paper contains information on occurrence and content of selected elements, mostly heavy metals, in samples of waters and sediment load procured from localities with former mining and subsequent treatment and metallurgic activity. Samples were procured from spots of mining water outflows from abandoned shafts or tunnels and outflows from active and old mining sludge basins including selected profiles on streams in the reservoirs of waterworks (WW), in drainage basin of the Slaná River. The chemical composition of waters and sediment load in 2 WW reservoirs of drainage basin of the Slaná River is markedly influenced by water from near–by drainage basin of the Hnilec River. Sampling was carried out within projects that focused on study of the treatment of bottom sediments of watercourses in areas with current and finished mining activity and observation of current state of sediment load in chosen places of sampling.

Key words: reservoir of waterworks, mining water, sediment load, sludge basin and heavy metals

INTRODUCTION

The oldest news about extraction and operating of metals in drainage basin of the Slaná River, which is till 1918 known as Gemer, led us to the 1st century A.D. and continues in the 21st century. In more detail data run about mining in this territory are from 14st century. There are mined and operated silver, copper and iron primarily. Primal extraction of iron metals was situated to surface mouth of ore seams. This was called “iron hats” and they were created by limonite, iron mineral, which arose by weathering of siderite. The most important iron mineral for emerge ting metalwork in Gemer was siderite, which was for long centuries mined in the deposits in the surroundings of Železník, Hrádok, Rožňava, Nižná Slaná and Dobšiná. In underground were mined minerals by means of the hammer and curling irons to the end of 17st century, when gunpowder began to used in mining. Here were mined and operated the hematite ores, too and magnesite in the surroundings of Tisovec in the past.

The extraction and operating of magnesite to final products is executing still today in this region in the industrial plants of SLOVMAG joint stock company Lubeník and SMZ joint stock company Jelšava.

The extraction and operating of iron ore-siderite is executed still today in the industrial plant of SIDERIT Nižná Slaná, which looks like a mining plant mining the iron ore by the underground way.

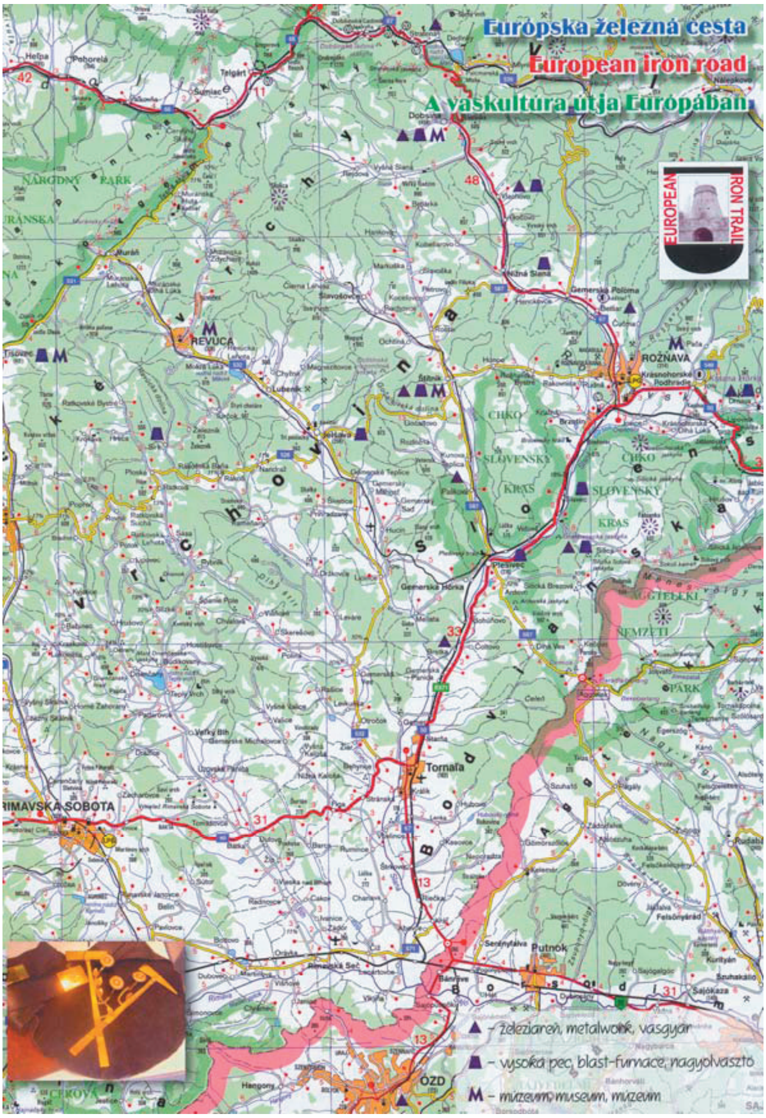

Fig. 1 The general map of the Slaná River drainage basin in the territory of the Slovak Republic, till 1918 known as Gemer, part of the European iron road – according to (1)

The rich deposits of iron minerals became the raw material basis for iron working in the Slovak ovens, which have been built in Gemer from 10th century. The iron production is developing especially in the surroundings of deposits Železník, Hrádok, Rožňava and Dobšiná. In all the drainage Basin of the Slaná River are on a large number building pit-part Slovak ovens. For the iron working plants, exploiting waterpower, in this region in the year 1344 began. It looked like the first in the Hungarian kingdom built “the hamor” in Štitnik, which made use of the water wheel on the drive the bowers in ovens and the hammers on forging the reduce iron. The Slovak ovens worked in Gemer above half a millennium and the last from them finished melting of iron in the year 1853 in Lúčka. Building the oven of hitting type, namely in the trot round of the stream Turiec in the surroundings of Kameňany, in the beginning of 18th century started. In Dobšiná was stated the first blast furnace in

Gemer according to the German model in the year 1772. Here works 33 high ovens and Gemer became the metallurgical base of the Hungarian part of Habsburg monarchy, in the half of the 19th century. This region was connected to the European market of iron.

Due to more than one thousand years lasting mining activity and the following processing, metallurgic or iron making activities have left many different dumps during centuries. The oldest dumps have been covered with forests. The dumps and mine rubbish being 150 to 50 years old, but in particular the sludge basins built in the last 50 years can be seen in the area also today.

The material stored in the above dumps or sludge basins, especially due to rain water and mining waters flowing from the old mining works influence the content of different elements in the water and in the bottom deposits of surface streams and in the two water reservoirs of this basin.

The exploring works aimed to find out by procuring of samples of water and bottom deposits (sediment load) the content of selected elements in the individual sampling places in the drainage basin of Slaná.

EXPERIMENTAL WORKS

Sampling of water was carried out on glass bottles with the amount of 1 litre. The sampling localities are described in Tab. 1 and 2 and their situation is explained in Fig. 1. The sampling water underwent a chemical analysis using the AAS method for the selected elements. The analysis results contained in Tab. 1 and 2 are compared with the valid standard (*2*).

The sediment load was taken to glass sampling containers from the surface layer with the thickness of 10 cm using the sampling set. The methodology is suitable for large-scale sampling from the sediment load surfaces or from the depth of 3 m under the water surface. The sampling places were identical with the ones of sampling of water. The samples of several localities – due to their grain size – were not suitable for the analysis. The procured samples underwent a chemical analysis using the AAS method, preferable for heavy metals. The analysis results contained in Tab. 3 and 4 were compared with the valid standard being the Methodological Instruction of the Ministry of the Environment of the Slovak Republic No. 549/1998–2 to assess the risks from polluted sediment load of streams and water reservoirs (*5*).

RESULTS AND DISCUSSION

Water

Results of the analysis of procured samples of waters are contained in Tab. 1 and 2. The content of selected elements in samples is compared with the valid standard (*2*). Sampling of water was carried out in spring and summer with a view to take samples during anticipated maximum and minimum flow rates in the streams as well as in the outflows of mining waters.

The waters were taken excluding the selected profiles of streams and reservoirs also from localities with current and old mining loads (Tab. 1) that can influence or contaminate the surface waters also in case of higher flow rates. In summer the attention was enlarged to the old sludge bed of "Čučma" in Rožňava, the outflow of the mining water and selected profiles of streams in the basin of the river Slaná (Tab. 2).

Chemical analyses of samples of water procured in 8 sampling places in April (Tab. 1) have shown that only the water from the brook flowing to the reservoir of WW Vlčia Dolina containing Cu and the water flowing from the left toe drain of the sludge basin of Nižná Slaná containing Zn and Cu exceed the limit values permitted by the valid standard. The content of the selected elements in the remaining 6 samples of the surface waters is lower than required by the above standard.

Tab. 2 contains results of analyses of water samples procured in July from 16 sampling places during the dry period. The results show that 13 out 16 samples showed the contents of selected monitored elements lower than the limit value. The remaining 3 samples can be characterised as follows: water sample no. 8 procured from the surface of the current sludge bed of Nižná Slaná containing higher values of Fe, Mn and As than required by the valid standard does not meet the requirements for water quality in surface streams. Sample no. 10 from the mining waters from the abandoned mine "Mária" in the cadastral area of Rožňava does not meet the requirements of the above standard due to higher values of Fe and Co, but especially due to high contents of Mn, Cu and Ni.

Sample no. 11 taken from the outflow canal of the old sludge basin of „Čučma“ in the cadastral area of Rožňava does not meet the requirements of the valid standards due to higher contents of Fe and Mg as well as the higher contents of Sb and As.

Results in Tab. 1 and 2 prove that sources of high contents of some selected elements (Fe, Mg, Mn, Zn, Cu, Co, Ni and As) are outflows of waters from old mining shafts and drifts, mining sludge beds and dumps. After the water has flown from the contamination source it is often largely dilluted as soon as it flows to the surface stream or the river Slaná. That is why the contents of the selected elements in the samples from localities of the surface streams are lower than the limit values of the valid standard (*2*) for water in surface streams.

The basin of Slaná is special due to the fact that the water in the water reservoir of WW Vlčia Dolina and the water reservoir in Dobšiná (Fig. 1 and 2) that is the balancing reservoir is in fact the water from the basin of Hnilec. It is caused by the fact that the pump-storage power station in Vlčia Dolina being an integral part of the water reservoir of WW Vlčia Dolina generates the electrical energy using the energy of water brought by pressure piping from the water reservoir of WW Palcmanská Maša in the basin of Hnilec. In the basin of Hnilec above the water reservoir of WW Palcmanská Maša up to the spring of the river of Hnilec there are old abandoned mining works and places of processing of extracted ores up to the final product – metal having the area of 84.5 km^2.

Due to the transfer of water from the basin of Hnilec to the basin of Slaná through the above pressure piping there have been assessments of water quality made in the 3 water reservoirs of the waterworks. The third water reservoir is in, or betters under Dobšiná town (Fig. 2), since 1956 focusing on the water management point of view. What is assessed is the quality of water. Results of chemical analyses are not published.

Brief characteristics of this water reservoir (*4*) say that there is water accumulated having the characteristics corresponding to the water quality of lower horizons in the water reservoir of WW Palcmanská Maša. The basic chemical structure excluding the concentration of the total Mn and Fe corresponds with the chemical composition of the

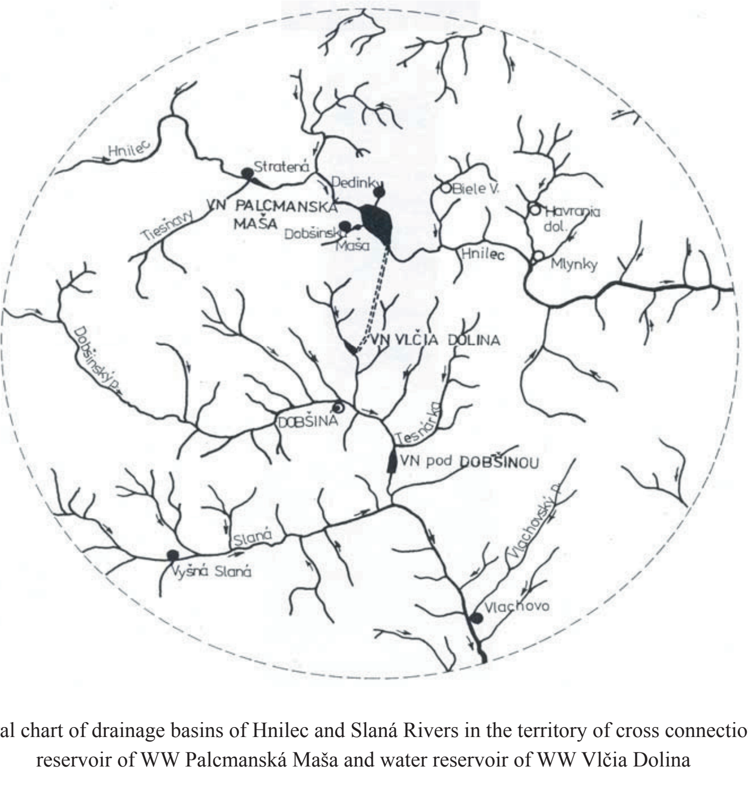

Fig. 2 General chart of drainage basins of Hnilec and Slaná Rivers in the territory of cross connection of water reservoir of WW Palcmanská Maša and water reservoir of WW Vlčia Dolina

Tab. 1 Results of the chemical analysis of water samples out of the Slaná river basin, from Vlčia Dolina – brook to Nižná Slaná, (sampling – April 2006) and comparison with the Governmental Regulation of the SR No. 296/2005 Coll., Annex No. 1

No. of sample	**LOCALITY**	**pH**	**Fe**	**Ca**	**Mg**	**Mn**	**Al**	**Zn**	**Cu**	**Co**	**Ni**	**Pb**	**Sb**	**Cd**	**Cr**	**As**	**Hg**
			[mg . l^{-1}]				**[μg . l^{-1}]**										
1	Vlčia Dolina – brook	7.38	0.55	62.1	10.0	<0.03	< 400	30	90	< 2	12	3	< 5	< 0.2	44	15	–
2	WW Vlčia Dolina – near the dam	7.42	0.63	86.4	6.2	0.06	< 400	20	< 20	< 2	8	4	< 5	0.5	20	10	–
3	Water Reservoir – in Dobšina	7.46	0.16	49.7	8.8	<0.03	< 400	80	< 20	< 2	7	4	< 5	0.7	4	16	–
4	Dobšina – brook – under Reservoir	7.62	0.81	70.7	5.3	0.1	< 400	40	< 20	< 2	7	4	< 5	0.3	5	8	–
5	Slaná, over inflow of Dobšina – brook	7.35	0.15	83.0	7.0	<0.03	< 400	60	< 20	< 2	11	4	< 5	1	7	8	–
6	Sludge basin Nižná Slaná – left toe drain	7.37	0.25	86.1	6.9	<0.03	< 400	1 630	60	< 2	8	5	< 5	0.2	5	7	–
7	Sludge basin Nižná Slaná – surface	7.11	0.1	80.8	4.9	<0.03	< 400	50	< 20	< 2	18	4	< 5	0.2	5	6	–
8	Slaná river – under Sludge basin N. Slaná	7.39	0.39	69.0	9.0	<0.03	< 400	30	< 20	< 2	10	3	< 5	0.2	4	8	–
GR SR No. 296/2005 Coll.		–	2	200	100	0.3	200	100	20	50	20	20	–	5	100	30	0.2

Tab. 2 Results of the chemical analysis of water samples out of the Slaná river and Slaná River Basin, from Vlčia Dolina – brook to the village of Bretka, (sampling – June 2006) and comparison with the Governmental Regulation of the SR No. 296/2005 Coll., Annex No. 1

No. of sample	LOCALITY	pH	Fe	Ca	Mg	Mn	Al	Zn	Cu	Co	Ni	Pb	Sb	Cd	Cr	As	Hg
			[mg . l^{-1}]				[µg . l^{-1}]										
1	Vlčia Dolina – brook	7.83	0.16	30.63	6.12	< 0.03	< 400	30	< 20	< 2	< 3	< 1	< 2	< 0.2	< 1	< 3	–
2	WW Vlčia Dolina – near the dam	7.85	0.16	36.56	10.04	0.06	< 400	30	< 20	< 2	< 3	< 1	3.5	< 0.2	< 1	5	–
3	Water Reservoir – in Dobšiná,	7.86	0.11	36.75	11.01	< 0.03	< 400	30	< 20	< 2	< 3	< 1	< 2	< 0.2	< 1	12	–
4	Dobšina – brook – under Reservoir	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
5	Slaná, over inflow of Dobšiná – brook	6.09	0.79	14.48	5.27	0.08	< 400	30	< 20	< 2	< 3	< 1	< 2	< 0.2	< 1	< 3	–
6	Slaná, under inflow of Dobšiná – brook	7.64	0.34	9.62	9.33	0.05	< 400	30	< 20	< 2	< 3	< 1	< 2	< 0.2	< 1	8	–
7	Sludge basin Nižná Slaná – left toe drain	7.60	0.24	12.96	5.45	< 0.03	< 400	30	< 20	< 2	< 3	< 1	5,5	< 0.2	< 1	27	–
8	Sludge basin Nižná Slaná – surface	7.67	2.91	93.75	5.24	1.74	< 400	30	< 20	< 2	< 3	< 1	11.7	< 0.2	< 1	129	–
9	Slaná river – under Nižná Slaná	6.56	1.04	27.5	18.6	0.14	< 400	30	< 20	< 2	3,3	< 1	< 2	< 0.2	< 1	12	–
10	Rožňava – Mária mine –mining water		5.47	64.02	55.5	28.9	< 400	60	240	143.1	149.5	< 1	< 2	< 0.2	< 1	< 3	–
11	Sludge basin Čučma – outflow from drain	7.24	2.27	78.84	112.6	0.26	< 400	40	< 20	2.8	< 3	< 1	120	< 0.2	< 1	600	–

Comment: Sample No. 4 was broken (abolished)

Continuation of Tab. 2 Results of the chemical analysis of water samples out of the Slaná River and Slaná River Basin, from the Water reservoir in Dobšina to the village Bretka, (sampling – June 2006) and comparison with the Governmental Regulation of the SR No. 296/2005 Coll., Annex No. 1

12	Slaná river – over village Bretka	7.74	1.08	3.07	8.55	0.13	< 400	30	< 20	< 2	< 3	< 1	12	< 0.2	< 1	8	–
13	Muráň brook – under fort (castle)	7.74	< 0.05	55.34	5.77	< 0.03	< 400	20	< 20	< 2	< 3	< 1	< 2	< 0.2	< 1	< 3	–
14	Lubeník, W. Reservoir – on the Muráň brook	8.31	< 0.05	28.27	8.3	< 0.03	< 400	20	< 20	< 2	< 3	< 1	< 2	< 0.2	< 1	< 3	–
15	Muráň brook, over the junction with Slaná	6.95	0.59	50.48	15.17	0.08	< 400	20	< 20	< 2	< 3	< 1	< 2	< 0.2	< 1	< 3	–
16	Slaná – under village Bretka	–	0.85	111.1	15.73	0.7	< 400	20	< 20	< 2	< 3	< 1	< 2	< 0.2	< 1	< 3	–
GR SR No. 296/2005 Coll.		–	2	200	100	0.3	200	100	20	50	20	20	–	5	100	30	0.2

water in the water reservoir of WW Palcmanská Maša (*4*).

Sediment load

Results of analyses of the samples of sediment load (bottom sediments) procured from the streams in the basin of the River Slaná, WW Vlčia Dolina, the water reservoir in or better under Dobšiná town, as well as from the places of outflows from sludge beds, shafts and drifts in this basin are contained in Tab. 3 and 4. The values gained by the analysis were compared with the standard being the Methodological Instruction of the Ministry of the Environment of the Slovak Republic No. 549/98-2 (*5*).

Tab. 3 contains results of the chemical analysis of samples of deposits taken in April from three localities. Each of the localities is specific in terms of the basin of the River Slaná. The sediment load from the brook bottom in Vlčia Dolina before it flows to the reservoir of WW Vlčia Dolina reflects the impact of relics of old mining, processing and iron–making activities in the remote past on both banks of this brook. Out of 10 selected elements for which the standard used has 3 limit values the contents of 5 elements – Pb, Sb, Cd, As and Hg – do not reach the maximum testing value (TV), the contents of 3 elements – Zn, Cu and Co – exceed the TV limit, but do not reach the maximum permitted concentration (MPC). The contents of 2 elements – Ni and Cr – significantly exceed the MPC as well as the intervention value (IV) showing that the content of the element is according to the standard used undesirable and correcting the measures are needed.

The contents of the elements in the sediment load from the bottom of the water reservoir in Dobšiná serving as the balancing reservoir for the reservoir of WW Vlčia Dolina is very similar to the one from the deposits from the brook bottom in Vlčia Dolina. Out of 10 selected elements the contents of 3 elements – Pb, Sb and As – in the sample do not reach the testing value (TV), the content of 7 elements – Zn, Cu, Co, Ni, Cd, Cr and Hg – in the sample exceed the TV to different extents, but the contents of 3 elements – Cu, Ni and Cr – in the sample exceed also the MPC and the elements Ni and Cr also the IV.

The sample from the locality of the left toe drain of the sludge basin of Nižná Slaná has a similar content of the selected elements as the preceding two localities. The contents of 4 elements – Zn, Co, Pb and Cd – in the sample do not reach the TV, whereas Cu and Hg exceed it significantly. However, the contents of 4 elements – Ni, Sb, Cr and As – significantly exceed all 3 limit values (TV, MPC and IV).

The contents of heavy metals in the sediment load (sediments) from the locality – left toe drain of the sludge bed of Nižná Slaná – from the basin in

Tab. 3 Results of the chemical analysis of sediment load samples in the Slaná River Basin, from Vlčia Dolina – brook to Nižná Slaná, (sampling – April 2006) and comparison with the Methodical Instruction of the ME the SR No. 549/1998-2

No. of sample	**LOCALITY**	**Zn**	**Cu**	**Mn**	**Co**	**Ni**	**Pb**	**Sb**	**Cd**	**Cr**	**As**	**Hg**
		[mg . kg^{-1}]										
1	Vlčia Dolina – brook	141.5	51.9	1 000	12.3	650.9	28.3	<2	0.75	533.0	<2	0.20
3	W. Reservoir – in Dobšiná	196.4	104	1 100	13.3	552.1	26.7	2,2	1.11	489.1	5.2	0.40
6	Sludge basin Nižná Slaná – left toe drain	85.0	59.5	7 900	4.3	531.5	20.4	680.3	0.60	731.3	24 660	2,52
MI ME SR No. 549/ 1998-2	TV	140	36	–	9	35	85	3	0,8	100	29	0.3
	MPC	620	73	–	19	44	530	15	12	380	55	10
	IV	720	190	–	–	210	530	–	12	380	55	10

TV – Testing value; MPC – Maximum permissible concentration; IV – Interventional value;
Annotation: The samples from localities No. 2, 4, 5, 7 and 8 due to their grain size, were not suitable for the analysis.

Vlčia Dolina and from the reservoir of WW Dobšiná contained in the Tab. 3 shows a high extent of exceeding of all limit values of the contamination of sediments with elements of Ni, Sb, Cr and As in the individual localities.

Tab. 4 contains the results of the chemical analysis of samples of sediment load taken in July from 11 localities.

Tab. 4 Results of the chemical analysis of sediment load samples out of Slaná river and in Slaná river basin, from Vlčia Dolina – brook to village Bretka, (sampling – July 2006) and comparison with the Methodical Instruction of ME SR No. 549/1998-2

No. of sample	LOCALITY	Zn	Cu	Mn	Co	Ni	Pb	Sb	Cd	Cr	As	Hg
		[mg . kg^{-1}]										
1	Vlčia Dolina – brook	129.0	< 10	1 100	65.8	95.7	13.9	15.3	3.34	81.2	12.9	0.33
2	WW Vlčia Dolina – dam	194.2	< 10	2 900	66.0	107.1	55.0	9.5	2.84	104.2	31.3	0.28
3	Water Reservoir – in Dobšiná	197.1	< 53	1 500	62.5	139.9	57.7	14.4	2.40	105.8	21.2	0..6
5	Slaná river – over Dobšiná brook	73.7	< 10	400	11.1	44.4	23.4	8.7	0.91	86.7	6.5	0.09
6	Slaná river – under Dobšiná brook	81.4	< 10	700	14.6	65.9	24.4	13.6	1.22	90.9	11.8	0.16
7	Sludge basin, Nižná Slaná – left toe drain	41.8	< 10	6 600	7.9	326.7	11.6	1200	1.02	20.9	19 500	4.21
9	Slaná river, – under Nižná Slaná	94.3	< 10	1 500	16.3	79.0	10.1	22.7	1.43	83.9	17.8	0.20
12	Slaná river – over Bretka	66.6	< 10	700	10.1	29.3	23.0	1.5	0.52	48.9	3.3	0.19
14	Muráň brook, estuary to reservoir in Lubeník	102.3	< 10	900	14.9	36.5	46.5	5.5	0.87	55.0	3.4	–
15	Muráň brook, over junction with Slaná river	112.5	< 10	1 300	14.5	49.8	26.1	30.6	0.54	86.4	40.9	0..2
16	Slaná river – in Bretka	91.3	< 10	800	13.6	41.5	25.6	5.5	0.87	59.3	4.1	–
MI ME SR No. 549/ 1998 –2	TV	140	36	–	9	35	85	3	0.8	100	29	0.3
	MPC	620	73	–	19	44	530	15	12	380	55	10
	IV	720	190	–	–	210	530	–	12	380	55	10

TV – Testing value; MPC – Maximum permissible concentration; IV – Interventional value;
Annotation: The samples from localities no. 4, 8, 10, 11 and 13 were not picked-up

Localities of sampling of sediment load no. 1, 2 and 3 although being located in the basin of the Slaná River are directly influenced by the basin of the River Hnilec due to the pressure water supply from the water reservoir of WW Palcmanská Maša to the water reservoir of WW Vlčia Dolina. Out of 10 assessed elements for which limit values exist 6 elements, namely Zn, Cu, Pb, Cr, As and Hg, show lower concentrations or concentrations very close to the TV limit in those 3 localities. 4 elements, namely Co, Ni, Sb and Cd, show concentrations reaching or exceeding the limit value of MPC, however, being deep under the IV.

Sample of sediment load no. 7 from the locality of the sludge basin of Nižná Slaná from the left toe drain shows the concentration of Ni being higher than the IV. The content of Sb in this locality exceeds the maximum limit value of concentration 80 times, the content of As even 355 times.

The samples of sediment load no. 4, 8, 10, 11 and 13 were not picked-up. The remaining 7 samples of sediment load (no. 5, 6, 9, 12, 14, 15, 16) taken from the bottom of the River Slaná and the bed of the brook of Muráň on different localities showed concentrations of the selected elements largely similar to the TV. Only the contents of the elements Ni in samples no. 6, 9 and 13 and Sb in samples no. 9 and 13 exceeded the MPC value. The content of the selected elements in those 7 samples was deeply under the limit IV.

A high level of contamination of sediment load by the selected elements exceeding the limit MPC values as well as the IV is according to Tab. 3 and 4 shown especially in the sediment load of the water reservoir of this basin and in the deposits in the left outflow drain from the sludge basin of Nižná Slaná.

CONCLUSION

The results of analyses of the water and sediment load (bottom deposits) samples, picked up in the selected localities, influenced by old and present mining activities and their assessment may state the following:

- The outflow of mining waters from old mining works in the basin of the River Slaná, especially the outflow from the Mária mine and the outflow from the old sludge “Čučma“ in Rožňava may have a negative impact on the level of water contamination in the River Slaná in case of minimum flow rates by several selected elements. However, after flowing to the River Slaná and mixing with its water the analyses of the samples procured have shown that the content of the selected elements was on the level that is in accordance with the valid requirements for the quality of the surface water.
- Analyses of samples of water from the outflow of the left toe drain and from the surface of the active sludge basin of Nižná Slaná have shown that this sludge basin may also have a negative impact on the content of several elements in the water of the River Slaná, especially in case of minimum flow rates.
- However, the samples of sediment load (bottom deposits) procured in the same localities as the samples of water that were thanks to their granulometry suitable for the chemical analysis have shown that almost all analysed samples have the content of the selected elements close to the level of the TV of the valid standard for the environment or they slightly exceed it. It is true especially for the content of Hg from the locality of Vlčia Dolina – brook up to the river of Slaná in Nižná Slaná,
- almost two thirds of elements from the majority of localities exceed the value of the maximum permitted concentration – MPC,
- elements Co, Ni, Sb, Cr in the monitored localities of water reservoirs and in the left toe drain of the sludge basin of Nižná Slaná significantly exceed the intervention value – IV of the valid standard for the environment,
- keeping of water in water reservoirs contributes to the increase of the contents of selected elements in the sediment load (bottom deposits).

Monitoring of contamination of water and sediment load in the selected profiles in the basin of Slaná as well as Hnilec need to be continued by sampling and analysing of samples.

Acknowledgements

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INPUTS OF NITROGEN BY PRECIPITATION INTO THE SOIL IN THE AGRICULTURAL REGION OF THE SOUTHWESTERN SLOVAKIA

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ABSTRACT

Babošová M., Noskovič J. & Palatická A. **Inputs of Nitrogen by Precipitation Into the Soil in the Agricultural Region of the Southwestern Slovakia**

In the years 2005 and 2006 atmospheric precipitation was caught on the experimental base of the Slovak University of Agriculture in Nitra – Dolná Malanta. Concentrations of N-NO_3^-, N-NH_4^+ a N-NO_2^- were evaluated. The experimental base of the Slovak University of Agriculture in Nitra – Dolná Malanta is situated cca 5 000 m east of the area of the SUA Nitra, 48º 19´20´´ of the northern latitude and 18º 8´5´´ of the eastern longitude. The results were presented in mg.l^{-1} and inputs of nitrogen into the soil in kg.ha^{-1}. The average concentration of nitrate nitrogen, ammonium nitrogen and nitrite nitrogen were 2.61 mg.l^{-1}, 1.0 mg.l^{-1} and 0.08 mg.l^{-1} respectively for the whole monitored period. On the average 14.90 kg.ha^{-1} of nitrate nitrogen, 6.18 kg.ha^{-1} of ammonium nitrogen and 0.05 kg.ha^{-1} of nitrite nitrogen were infiltrated into the soil in the monitored area. The total sum of N-NO_3^- + N-NH_4^+ + N-NO_2^- is made up 71.02 % of N-NO_3, 26.78 % N-NH_4^+ and 2.20 % of N-NO_2 for the whole monitored period. About 21,50 kg.ha^{-1} of nitrogen was infiltrated into the soil during the years 2005–2006.

Key words: atmospheric precipitation, nitrate nitrogen, ammonium nitrogen, nitrite nitrogen, inputs of nitrogen by precipitation into the soil

INTRODUCTION

Atmospheric water contains dissolved gases which form normal composition of the air (oxygen, nitrogen, carbon dioxide and rare gases), gaseous pollutants of the air (sulphur dioxide and sulphur trioxide, nitrogen oxides, ammonium, etc.) as well as solids (particles of dust, smoke, plants, microorganisms) (Tölgyessy, et al., 1997). Anions of strong mineral acids are very important components of polluted atmospheric waters because they can substantially increase natural acidity of atmospheric precipitation, particularly sulphate ions. There are fewer amounts of nitrates in atmospheric precipitation but their concentration has the rising tendency over the last years (Minďáš, Kunca, 1997). They are formed during the contact of atmospheric nitrogen oxides with water (Noskovič, Gábriš, 1995). Under normal conditions, nitrogen oxides represent a very small amount in the air, hundredths of milligrams (www.referaty.atlas.sk). Nitrogen compounds (nitrogen monoxide, nitric oxide and nitrogen dioxide) are typical components of the atmosphere in cities and industrial sites. They are formed during fuels combustion; they are in exhaust gases of motor vehicles and air pollutants from some chemical factories. They are formed during electric discharges in the atmosphere, too. Nitrogen monoxide mainly comes from natural sources; it is formed in microbial denitrification in soil and water. Nitrogen oxides are transformed to nitric acid by photochemical oxidation. Another compound, which is found in precipitation, is ammonium. It is released from microbial decomposition of organic matter and leaks from fertilizers, animal excrements and combustion processes. In agricultural areas, ammonium nitrogen ratio dominates over other sources (www.fpv.umb.sk).

MATERIAL AND METHODS

In the years 2005–2006 atmospheric precipitations were caught on the experimental base of the Slovak University of Agriculture in Nitra – Dolná Malanta. The experimental base of the SUA in Nitra – Dolná Malanta is situated cca 5 000 m east of the area of the SUA Nitra, geographic coordinates are 48º 19´20´´ N and 18º 8´5´´ E. The area is situated in western part of Žitavská upland. Locality of the experimental base has a lowland character with undistinguished gradient to the south and it is at an altitude of 175–180 m asl. In term of agriculture the base belongs to the maize cropping region.

As for the climate, the territory of the experimental base of the SUA Nitra belongs to the very warm region. The annual average temperature is 9.7 °C and the average precipitation represents 561 mm. In 2005 the average temperature was 9.6 °C and precipitation represented 638.2 mm. In 2006 the average temperature was 10.1 °C and precipitation represented 507.1 mm. In winter months precipitations fall in the form of snow, rain with snow or rain.

A tank made of inert material was used for catching the precipitations. The amount of fallen precipitations was ascertained by a rain gauge. There were also some precipitations during both years of the monitored period whose amounts were so low that they could not be analyzed. In 2005 it was 0.1–1.1 mm and 0.1–1.0 mm in 2006. In 2005 the precipitations represented 1.7 mm what makes up 0.27 % of the total amount of fallen precipitations, in 2006 it was 4.5 mm what makes up 0.89 % of the total amount of fallen precipitations.

Nitrate nitrogen (spectrophotometrically using WTW-nitrospectral in concentrated sulphuric acid), ammonium nitrogen (spectrophotometrically using indophenol blue – Berthelot reaction) and nitrite nitrogen (spectrophotometrically using sulphanilic acid and 1-naphthylamine) were determined in collected precipitations. The results were given in mg.l^{-1}. Inputs of nitrogen given in kg.ha^{-1} into the soil were calculated according to N-NO_3^-, N-NH_4^+, N-NO_2^- concentrations and the amount of fallen precipitations.

RESULTS AND DISCUSSION

Results obtained by the analysis of rainfall waters showed that the concentration of nitrate nitrogen in precipitations fluctuates. In 2005 its average value ranged from 1.80 (July) to 3.53 mg.l^{-1} (January), the average concentration was 2.68 mg.l^{-1}. In 2006 it ranged from 1.30 (September) to 3.95 mg.l^{-1} (February) and the average concentration was 2.54 mg.l^{-1}. The average N-NO_3^- value for the whole monitored period represented 2.61 mg.l^{-1} (Fig. 1, 2). From the results it follows that there was higher fluctuation of nitrate nitrogen concentration in 2006 in comparison with the year 2005. The values of average nitrate nitrogen concentration are analogical with the Budská results (2004) which ascertained its average value of 2.84 mg.l^{-1} at the Hřeběcí boudy station and 2.68 mg.l^{-1} at the Rýchory station. Obtained data showed that N-NO_3^- concentrations did not exceed 4 mg.l^{-1} which is the boundary value of permissible limit in atmospheric precipitations according to Tužinský (1995).

Inputs of N-NO_3^- by precipitations into the soil is shown in Table 1. From the results it follows that the highest average month value of N-NO_3^- inputs was in December 2005 (3.71 kg.ha^{-1}) and in May 2006 (2.37 kg.ha^{-1}). This could be caused by higher amount of precipitations in these months (113.2 mm in December 2005 and 95.6 mm in May 2006). The lowest value was in March 2005 (0.08 kg.ha^{-1}) and in September 2006 (0.17 kg.ha^{-1}). It can be stated that there was no seasonal regularity in N-NO_3^- concentrations during the monitored years. Generally in 2005 17.09 kg of N-NO_3^-.ha^{-1} infiltrated into the soil by precipitations and in 2006 it was 12.70 kg of N-NO_3^-.ha^{-1}. During the monitored

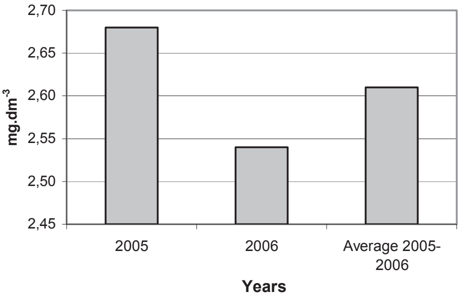

Fig. 1 The average concentrations of N-NO_3^- (mg.l^{-1}) in atmospheric precipitations in 2005–2006

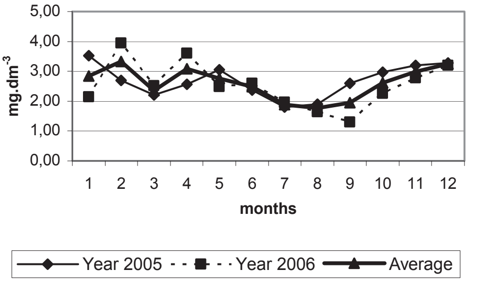

Fig. 2 The average concentrations of $N\text{-}NO_3^-$ (mg.l^{-1}) in atmospheric precipitations in each month over the years 2005–2006

period 14.90 kg of $N\text{-}NO_3^-$.ha^{-1} infiltrated into the soil by precipitations on the average per year. Noskovič, Gábriš (1995) found out that 5.71 kg of $N\text{-}NO_3^-$ got into the soil in surroundings of Nitra. This implies that the amount of $N\text{-}NO_3^-$ which got into the soil in Dolná Malanta over the monitored years depended on their concentrations in precipitations and also on the efficiency of precipitations.

Nitrate nitrogen ratio made up of 68.19 % of the total sum $N\text{-}NO_3^- + N\text{-}NH_4^+ + N\text{-}NO_2^-$ (mg.l^{-1}) in 2005 and in 2006 it made up to 78.84 %. Its average ratio represented 71.02 % of total sum $N\text{-}NO_3^- + N\text{–}NH_4^+ + N\text{-}NO_2^-$ over the whole period (Table 2).

In 2005 the average concentrations of ammonium nitrogen fluctuated from 0.48 (February) to 2.50 mg.l^{-1} (July) and its average concentration was 1.18 mg.l^{-1}. In 2006 the average concentrations of $N\text{-}NH_4^+$ ranged from 0.23 (May) to 1.84 mg.l^{-1} (August) and the average concentration represented 0.81 mg.l^{-1}. The average concentration of $N\text{-}NH_4^+$ was 1.0 mg.l^{-1} (Fig. 3, 4) over the whole monitored period. It agrees with Dubová, Bublinec (1998) opinion who state that ammonium nitrogen creates half of $N\text{-}NO_3^-$ deposition. The detected average value of ammonium nitrogen corresponds with Dubová, Bublinec results (1997) who ascertained its average value 1.15 mg.l^{-1} in precipitations in chosen localities of the protected landscape area Muránska planina. Analogous to nitrate nitrogen there was no seasonal regularity in $N\text{-}NH_4^+$ concentration.

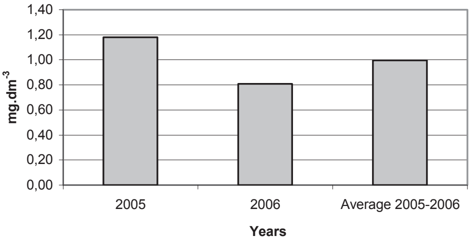

Fig. 3 The average concentrations of $N\text{-}NH_4^+$ (mg.l^{-1}) in atmospheric precipitations in 2005–2006

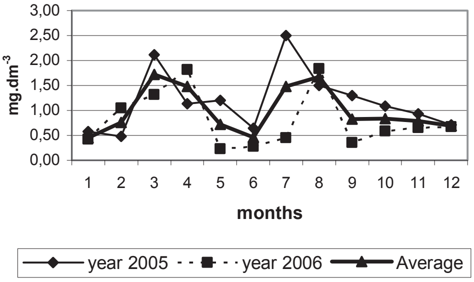

Fig. 4 The average concentrations of $N\text{-}NH_4^+$ (mg.l^{-1}) in atmospheric precipitations in each month over the years 2005–2006

In 2005 the amounts of ammonium nitrogen infiltrated into the soil ranged from 0.07 (March) to 1.48 kg.ha^{-1} (July) and the average amount of $N\text{-}NH_4^+$ represented 7.47 kg.ha^{-1} over the whole experimental year. In 2006 inputs of ammonium nitrogen by precipitations into the soil fluctuated in interval from 0.05 (September, December) to 1.55 kg.ha^{-1} (August) and the average amount represented 4.88 kg.ha^{-1} (Table 1). On the average 6.18 kg of $N\text{-}NH_4^+$.ha^{-1} got into the soil by precipitations during the whole monitored period. It corresponds with Noskovič, Gábriš results (1995) who found out that 7.00 kg of $N\text{-}NH_4^+$.ha^{-1} infiltrated into the soil by precipitations in surroundings of Nitra.

Ammonium nitrogen ratio made up 30.03 % of the total sum $N\text{-}NO_3^- + N\text{-}NH_4^+ + N\text{-}NO_2^-$ (mg.l^{-1}) in 2005 and in 2006 it was 23.54 %. The average value was 26.78 % over both experimental years (Table 2).

In 2005 concentrations of nitrite nitrogen in precipitations fluctuated in interval from 0.03 (February, April, June) to 0.17 mg.l^{-1} (July) and the average value represented 0.07 mg.l^{-1}. In 2006 the concentrations ranged from 0.03 (September) to 0.29 mg.l^{-1} (March) and the average value was 0.09 mg.l^{-1}. Its average value per two experimental years represented 0.08 mg.l^{-1} (Fig. 5, 6). It follows that there was no seasonal regularity of N-NO$_2^-$ concentrations.

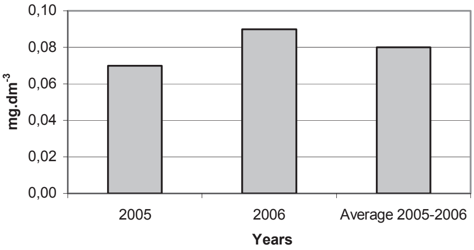

Fig. 5 The average concentrations of N-NO$_2^-$ (mg.l^{-1}) in atmospheric precipitations in 2005–2006

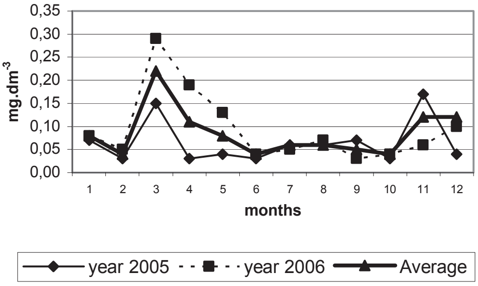

Fig. 6 The average concentrations of N-NO$_2^-$ (mg.l^{-1}) in atmospheric precipitations in each month over the years 2005–2006

Inputs of nitrite nitrogen by precipitations into the soil fluctuated from 0.004 (October) to 0.07 kg.ha^{-1} (November) in the first monitored

Tab. 1 Inputs of N-NO$_3^-$, N-NH$_4^+$ and N-NO$_2^-$ (kg.ha^{-1}) into the soil by precipitations 2005–2006

	Year 2005				
Months	**Precipitations**	**N-NO$_3^-$**	**N-NH$_4^+$**	**N-NO$_2^-$**	**N-NO$_3^-$+ N-NH$_4^+$ + N-NO$_2^-$**
January	36.4	1.28	0.21	0.03	1.52
February	58.3	1.57	0.28	0.02	1.87
March	3.4	0.08	0.07	0.01	0.16
April	78.7	2.02	0.89	0.02	2.93
May	60.9	1.86	0.73	0.02	2.61
June	31.5	0.75	0.20	0.01	0.96
July	59.0	1.06	1.48	0.04	2.58
August	94.5	1.80	1.03	0.06	2.89
September	47.1	1.22	1.08	0.03	2.33
October	12.1	0.36	0.30	0.004	0.66
November	43.1	1.38	0.40	0.07	1.85
December	113.2	3.71	0.80	0.04	4.55
Σ	**638.2**	**17.09**	**7.47**	**0.35**	**24.91**
	Year 2006				
Months	**Precipitations**	**N-NO$_3^-$**	**N-NH$_4^+$**	**N-NO$_2^-$**	**N-NO$_3^-$+ N-NH$_4^+$ + N-NO$_2^-$**
January	57.4	1.23	0.24	0.05	1.52
February	39.0	1.54	0.41	0.02	1.97
March	35.2	0.89	0.46	0.10	1.45
April	48.1	1.73	1.36	0.09	3.18
May	95.6	2.37	0.22	0.12	2.71
June	63.9	1.66	0.18	0.03	1.87
July	23.7	0.46	0.11	0.01	0.58
August	84.0	1.38	1.55	0.06	2.99
September	12.7	0.17	0.05	0.004	0.22
October	15.3	0.34	0.09	0.006	0.44
November	24.4	0.68	0.16	0.02	0.86
December	7.8	0.25	0.05	0.008	0.31
Σ	**507.10**	**12.70**	**4.88**	**0.52**	**18.10**

year and the average value represented 0.04 kg of N-NO_2^-.ha^{-1}. In the second year inputs of nitrite nitrogen ranged from 0.004 (September) to 0.12 kg. ha^{-1} (May) and the average value was 0.06 kg of N-NO_2^-.ha^{-1}. The average value per two experimental years represented 0.05 kg of N-NO_2^- .ha^{-1}.

Based on inputs of N-NO_3^-, N-NH_4^+ and N-NO_2^- it was determined that in 2005 24.91 kg of N.ha^{-1} got into the soil by precipitations in the monitored area and in 2006 it was 18.10 kg of N.ha^{-1}. From the obtained data it follows that on the average 21.50 kg of N.ha^{-1} per year was infiltrated into the soil by precipitations. It corresponds with Dubová, Bublinec results (1998) who measured 10–40 kg of N.ha^{-1}. Noskovič et al. (2000) ascertained that 13.72 kg of N.ha^{-1} got into the soil by wet deposition in surroundings of Nitra.

In 2005 nitrite nitrogen ratio made up 1.78 % of the total sum N-NO_3^- + N–NH_4^+ + N-NO_2^- (mg.l^{-1}), in 2006 it made up 2.26 % and its average value per two years represented 2.20 % (Table 2).

Acknowledgement

This research was conducted thanks to grant project VEGA 1/2444/05.

Tab. 2 Ratio of individual forms of nitrogen making the total sum of N–NO_3^- + N–NH_4^+ + N–NO_2^-

Year	Sum of N–NO_3^- + N–NH_4^+ + N–NO_2^- [mg.l^{-1}]	Ratio of nitrogen forms making the total sum [%]		
		N-NO_3^-	N-NH_4^+	N-NO_2^-
2005	3.93	68.19	30.03	1.78
2006	3.44	73.84	23.54	2.62
Average	**3.68**	**71.02**	**26.78**	**2.20**

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MONITORING AND EVALUATION OF CONCENTRATIONS OF SULPHATES AND CHLORIDES IN THE WATER OF THE NATURAL RESERVE ŽITAVSKY LUH

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ABSTRACT

Noskovič J., Babošová M. & Palatická M. **Monitoring and Evaluation of Concentrations of Sulphates and Chlorides in the Water of the Natural Reserve Žitavsky luh**

Over the years 2003–2004 the concentrations of sulphates and chlorides were evaluated in the water of the Natural Reserve (NR) Žitavský luh. Taking of water samples in the NR was realized in regular monthly intervals from 5 sampling sites. The obtained data showed that during the monitored period the regularity in seasonal dynamics of sulphates was not manifested. The highest mean value for the whole period was in January (65,2 mg.l^{-1}) and the lowest mean value was in July (43,9 mg.l^{-1}). Depending on sampling site the highest mean SO_4^{2-} concentration (74,7 mg.l^{-1}) for the whole period was in the site of ending of the underground channel which transports the water from the river Žitava to NR. The lowest mean concentrations for the whole period (51,8 and 53,8 mg.l^{-1}) were determined in sampling sites which are characterized with shallow standing water level and rich layer of organic sediments above the bed. The reason of sulphates falling in these sampling sites was probably, especially in summer season, creating of anoxic conditions suitable for the reduction of sulphates. Depending on sampling time their highest mean concentrations for the whole period were recorded mostly in autumn and winter season. The maximum mean value was in September (46,8 mg.l^{-1}) and the minimum in March (26,8 mg.l^{-1}). The increase of their concentration in September was probably caused by chlorides in applied potash fertilizers (KCl) on agricultural lands situated in the surroundings of NR. Depending on sampling site the highest mean concentration of chlorides for the whole monitored period (38,9 mg.l^{-1}) was in sampling site situating on the open water area near floodgate controlling of the water from NR and the lowest mean value (35,2 mg.l^{-1}) was in the site of ending of the underground channel.

Key words: chlorides, sulphates, water quality, wetland

INTRODUCTION

Sulphur occures in form of different inorganic and organic compounds in waters (Tölgyessy et al., 1997). Energy stable sulphated anion SO_4^{2-} forms the largest amount of sulphur in rivers and small water reservoirs (Lellák, Kubíček, 1991).

Sulphates get into waters especially from gypsum and anhydrit as well as by oxidation of sulphide minerals (Pitter, 1999). Their concentrations in rivers are increased by waste water disposal with the content of inorganic and organic sulphur compounds. Some mineral waters are extra rich in sulphates (Tölgyessy, Melichová, 2000). The source of sulphates in surface waters is also atmospheric precipitations (Lellák, Kubíček, 1991).

Chlorides together with hydrogen-carbonates and sulphates are the main anions in waters. They are in different rocks from which they get into the soil after their weathering. Anthropogenic sources of chlorides are sewerages and some effluents waters of organic origin (Biskupič, 1991, Pitter, 1999).

Pitter (1999) considers the road salting in winter season and using of potash fertilizers in agriculture as the main source of chlorides.

MATERIAL AND METHODS

The Natural Reserve was established in 1980, and originally it represented a wetland with the area of about 140 ha. The actual area is 74.69 ha, situated at an altitude of 132–133 m a. s. l. Geographic coordinates are: 48°12' N and 18°19' E. As for the climate, the territory belongs to the warm and dry region with mild winter and the average annual temperature of 9.5 °C. The annual precipitation total represents 600 mm. In term of geologic standpoint the research area belongs to older Quaternary (pleistocene). This area is created by extensive and ground level of Pleistocene sediments, primarily calcium loess, which create a base rock (bedrock) of large soil amounts. The territory of the Reserve comprises parts of three cadastral zones belonging to the villages Maňa, Kmeťovo and Michal' nad Žitavou (district Nové Zámky). The original side channel of Žitava crossing the southern and western part of the territory in 600 m long and belongs to the catchments area of the Žitava River, the training bank of the river represents the western boundary. The northern boundary is identical with the boundaries of the districts Nitra and Nové Zámky. The lowest parts on southeast of the considered wetland are typical marshes. The source of water is the surface water of the regulated Žitava River transported along an underground channel, from which the water periodically penetrates to the wetland surface. Until 1994, higher situated, periodically flooded meadows (cca 35 ha) were regularly mowed with machines.

The locality represents a significant habitat, especially because it serves as a foraging and breeding site for several endangered wetland bird species, both nesting and migratory. There have been confirmed 39 at-European-level endangered bird species occurring in this area: 7 critically endangered, 16 endangered and 4 migratory (Danko et al., 1995). The locality represents one of the most significant occurrence places of species *Porzana porzana, Anas querquedula* and *Circus aeruginosus*. Svobodová (1992) confirmed 262 upper plant species, 36 from them was being endangered species of Slovak flora. The critically endangered taxon of high ecosozological value is *Adonis flammea,* endangered rare taxons: *Clematis integrifolia, Papaver albiflorus, and Viola pumila.* From the endangered species we list here: *Adonis vernalis, Carex melanostachya, Carex paniculata, Catabrosa aquatica, Nepeta pannonica, Taraxacum palustre, Tithymalus salicifolius, and Veronica longifolia.* The succession of the main vegetation formation of *Glyceria maxima, Typha latifolia* is in progress and has a significant impact on the decrease in the nesting bird species. Wood vegetation in the southern part of the Reserve consists of associations and communities of *Salicion albae*, with expanding an invasive North American species – *Negundo aceroides*. At present, the riverine vegetation can only be found in the rest of original, non regulated flow of Žitava. The dominant woody plants are: *Salix alba*, *Salix fragilis*, *Salix cinera*, *Alnus glutinosa* and *Populus alba*. The shrubs are represented by *Crategus monogyna*, *Rosa canina* and *Rubus caesius*.

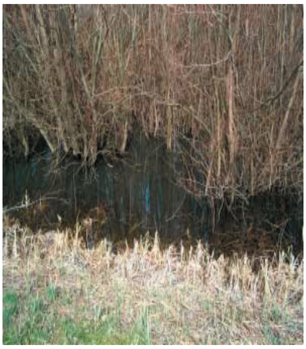
The water from the wetland was sampled regularly, over the whole period of years 2003–2005, monthly, always around the date of the 15th. The layout of the sample sites system was proposed in such a way as to obtain the best possible data for evaluation of the changes in bivalent and univalent alkaline cations concentrations in dependence on space and time. We have established the following five sites:

1. The beginning of the old original bed of the Žitava River. It is the collection spot of the water transported from the Žitava River through the underground channel to the western part of the Reserve during spring and summer months.
2. Pursuing original meander of the old Žitava River with the protective levee on the southern bank.
3. An open water area, with the water outfall regulated with a floodgate to control the flood water level in the southeastern part of the Reserve.
4. and 5. The sample sites situated on the open water area in the southeastern part of the wetland, with marshy character, adjacent to a road.

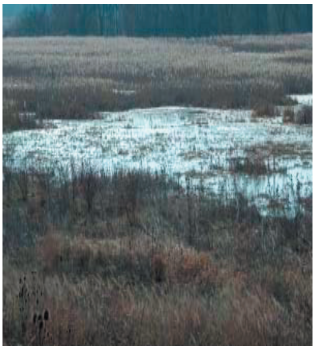
In taking water samples sulphates were determined volumetrically by lead nitrate and chlorides were determined volumetrically according to Mohr (Gábriš, Noskovič, 1988). The results were given in mg.l^{-1}.

Sample site 1

Sample site 2



Sample site 3



Sample site 4

Sample site 5

The water in the individual sampling sites was ranked in the categories of surface water quality. It was performed by comparison of the calculated characteristic value of the indicator and the corresponding system of limit values which are stated by the STN 75 7221 (The quality of water – Classification of the surface water quality).

RESULTS AND DISCUSSION

Over the monitored years the mean concentrations of sulphates were from 41,0 (2005) to 69,1 mg.l^{-1} (2003) and the average value was 58,4 mg.l^{-1} for the whole period (Fig. 1).

Based on their concentrations in dependence on sampling time (Fig. 2) it can be stated that the regularity in their seasonal dynamic was not manifested during the monitored period. The concentrations of SO_4^{2-} ranged from the minimum average value in September 2005 (32,8 mg.l^{-1}) to the maximum average value in January 2003 (78,3 mg.l^{-1}). Klopatek (1978; In Patten, 1990) found out the range of the average concentrations of SO_4^{2-} from 15 to 99 mg.l^{-1} in riverine wetland of Wisconsin. The highest mean value over the whole period was recorded in January (65,2 mg.l^{-1}) and the lowest average value in July (43,9 mg.l^{-1}). The decrease of SO_4^{2-} concentrations in summer months is probably connected with the low concentration of dissolved oxygen in the water (Beňačková, 2007). Pitter (1990) states that the sulphates in water are subjected to biochemical reduction under anaerobic conditions. After the reduction sulphide and its ionic forms are created. The reduction is caused by desulphurating bacteria *Desulfovibrio* finding in ground waters, riverine sediments, putrescent surface waters and sewerages. Nevertheless, the presence of few amounts of organic substances as hydrogen donors is needed. Polanski a Smulikowski (1971) state that during oxygen deficiency the remains of organisms cumulating on the bed are decomposed by putrescent bacteria. During this process sulphide and other toxic substances are formed. Sulphide diffuses into higher parts of

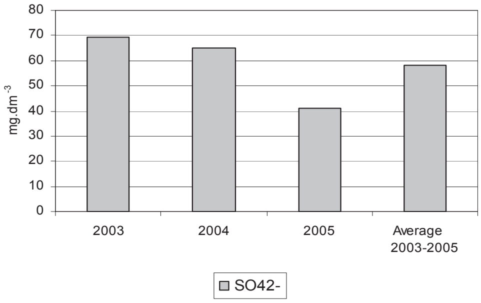


Fig. 1 The average concentrations of SO_4^{2-} in mg.l^{-1} over the years 2003–2005

water column. Dissolved oxygen can oxidate by anorganic way or sulphide is oxidated into free sulphur by aerobic sulphur bacteria which can oxidate it up to sulphates.

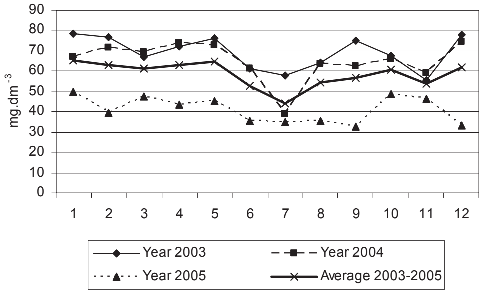


Fig. 2 The average concentrations of SO_4^{2-} in dependence on sampling time

In dependence on sampling site the concentrations of SO_4^{2-} in the monitored years were different (Fig. 3). The concentrations of sulphates decreased with every following year. The lowest concentrations were recorded in 2005 with the minimum average concentration in sampling site No. 5 (34,7 mg.l^{-1}). The highest concentrations were in 2003 with the maximum in sampling site No. 1 (74,7 mg.l^{-1}). The highest mean sulphate concentration for the whole period was also in sampling site No. 1 (65,0 mg.l^{-1}) and the lowest concentration in sampling site No. 5 (51,8 mg.l^{-1}). The second lowest concentration was in sampling site No. 4 (53,8 mg.l^{-1}). The reason of lower SO_4^{2-} concentrations in sampling sites No. 4 and 5 which are characteristic with shallow standing water level and rich layer of organic sediments above the bed was probably caused by creating of anoxic conditions suitable for the sulphate reduction, especially during summer season. According to Tölgyessy and Melichová (2000) the concentrations of sulphates occuring in surface waters are not of hygienic importance.

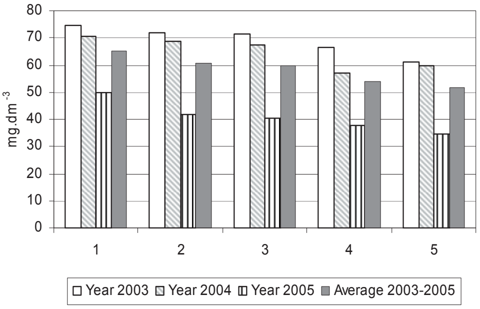


Fig. 3 The average concentrations of SO_4^{2-} in dependence on sampling site

Based on calculated characteristic SO_4^{2-} values for the whole monitored period and according to the standard STN 75 7221 the water in sampling sites No. 1, 2 and 3 was ranked into the 2nd class of the water surface quality (clean water) and in sampling sites No. 4 and 5 into the 1st class of the water surface quality (very clean water).

In comparison with sulphates the concentrations of chlorides were lower. The average concentrations in the monitored years ranged from 35,1 (2004) to 41,8 mg.l^{-1} (2003) and the average concentration for the whole period represented 37,4 mg.l^{-1} (Fig. 4). Similar values were found out by Klopatek (1978; In Patten, 1990) in riverine wetland in Wisconsin (17–54 mg.l^{-1}). Bologová (2003) found out the average value of chlorides 46,2 mg.l^{-1} in wetland communities of Abrod.

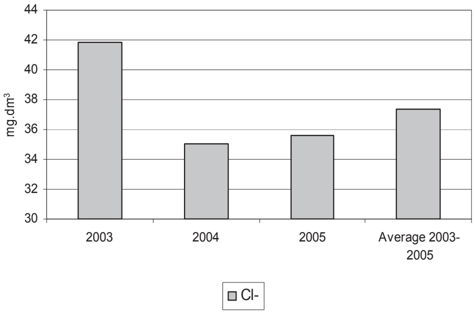


Fig. 4 The average concentrations of Cl$^-$ in mg.l^{-1} over the years 2003–2005

As for the sampling time (Fig. 5) the highest average concentrations of chlorides for the whole monitored period were recorded in principle during autumn and winter season with the maximum value in September (46,8 mg.l^{-1}). The increase of their concentration in September was probably caused by chlorides in applied potash fertilizers (KCl) on agricultural lands situating near the Nature Reserve. Cey et al. (1999) state that Cl^- concentration in waters is influenced by agricultural activities which are probably the reason of raised concentrations of chlorides in summer and autumn months. Chlorides are poorly adsorbed by soild phase of the soil. They are washed out from the soil and they are chemically and biochemically stabled in the water environment. They can get into the environment as contaminants or as products of wide scale of human activities (sewerage, effluent waters of organic origin, the use of potash fertilizers in agriculture (KCl), road salting during winter season) (Pitter, 1999). The minimum average concentration of Cl^- for the whole monitored period in dependence on sampling time was in March (26,8 mg.l^{-1}).

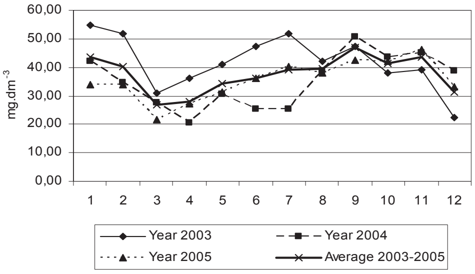


Fig. 5 The average concentrations of Cl^- in dependence on sampling time

The influence of sampling sites on the concentrations of chlorides in the monitored years (Fig. 6) was not so strong. The highest mean concentration was in sampling site No. 1 in 2003 (44,4 mg.l^{-1}). In 2004 the lowest mean concentration was also recorded in this sampling site (28,9 mg.l^{-1}) (Fig. P29). The maximum average value for the whole monitored period was in sampling site No. 3 (38,9 mg.l^{-1}). The minimum value of the whole period was recorded in sampling site No. 1 (35,2 mg.l^{-1}).

Based on calculated characteristic values of chlorides and according to the standard STN 75 7221 the water in sampling site No. 4 was ranked into the 1st class of the water surface quality (very clean water) and in sampling sites No. 1, 2, 3 and 5 into the 2nd class of the water surface quality (clean water).

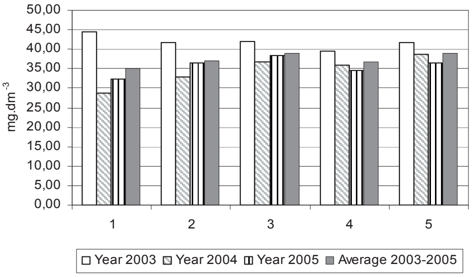


Fig. 6 The average concentrations of chlorides in dependence on sampling site

Acknowledgement

This research was conducted thanks to the grant project VEGA 1/0196/03 a 1/2444/05.

Table 1: Calculated characteristic values and the water surface quality

Sampling site	1.		2.		3.		4.		5.	
Indicator	SO_4^{2-}	Cl^-	SO_4^{2-}	Cl^-	SO_4^{2-}	Cl^-	SO_4^{2-}	Cl^-	SO_4^{2-}	Cl^-
Unit	mg.l^{-1}	mg.l^{-1}	mg.l^{-1}	mg.l^{-1}	mg.l^{-1}	mg.l^{-1}	mg.l^{-1}	mg.l^{-1}	mg.l^{-1}	mg.l^{-1}
Calculated characteristic value	86,4	51,5	85,7	53,2	86,4	53,2	79,8	49,7	75,5	51,0
Class of quality	II.	II.	II.	II.	II.	II.	I.	I.	I.	II.

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EVALUATION OF DISSOLVED OXYGEN AND ORGANIC SUBSTANCES CONCENTRATIONS IN WATER OF THE NATURE RESERVE ALUVIUM ŽITAVY

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ABSTRACT

Palatická A., Noskovič J. & Babošová M. **Evaluation of Dissolved Oxygen and Organic Substances Concentrations in Water of the Nature Reserve Aluvium Žitavy**

In 2006 concentrations of dissolved oxygen and organic substances were evaluated in water in the Nature Reserve Aluvium Žitavy (indirect method based on their oxidation by $K_2Cr_2O_7$ was used). The results are represented in mg $O_2.l^{-1}$. Taking of samples took place in 6 sampling sites in regular month intervals. Based on obtained data and according to the standard STN 75 7221 (Water quality – The classification of the water surface quality) water in individual sampling sites was ranked into the classes of the water surface quality.

From the data it is clear that the concentrations of dissolved oxygen and organic substances in the Nature Reserve Aluvium Žitavy changed in dependence on sampling sites and time. The highest mean concentrations of dissolved oxygen in dependence on sampling time were found out in spring months and the lowest concentrations in summer months. They ranged from 1.6 mg $O_2.l^{-1}$ (July) to 9.0 mg $O_2.l^{-1}$ (March). Falling dissolved oxygen values can be related to successive increase of water temperature, thus good conditions were created for decomposition of organic matter by microorganisms in water and sediments in which they use dissolved oxygen. In dependence on sampling place the highest mean concentration of dissolved oxygen was in sampling site No. 4 (6.0 mg $O_2.l^{-1}$) which is situated in the narrowest place in the NR. The lowest value was in sampling site No. 2 (3.6 mg $O_2.l^{-1}$) which is a typical wetland ecosystem. High mean values of COD_{Cr} in dependence on sampling time were determined in summer months and low values during winter moths. Dependence of COD_{Cr} values on sampling site was also manifested. The lowest mean value was obtained in sampling site No. 4 (59.5 mg.l^{-1}) and the highest value in sampling site No. 5 (97,1 mg.l^{-1}) which is also a typical wetland. Based on the results and according to the STN 75 7221 we ranked water in all sampling sites into the 5th class of the water surface quality (very strongly polluted water).

Key words: dissolved oxygen, chemical oxygen demand, organic substances, surface water quality, wetland

INTRODUCTION

Oxygen is the basic indicator of water environment features. Total revival of aquatic ecosystems as well as majority of chemical and biochemical processes depend on content of dissolved oxygen (Hudec, 1996). The concentration of dissolved oxygen in water depends on temperature and partial pressure of oxygen in gaseous phase (Šálek, 1999). Water is able to receive more oxygen when the temperature is lower and the pressure is higher (Strauss, 1992). The amount of dissolved oxygen also decreases with the depth of water**.** In critical situations on the ground it can decrease below the value of 1,0 mg.l^{-1} (Brvenník et al. 2003). Oxygen is used in respiration of aquatic organisms, especially decomposers and consumers. When there are favourable weather conditions during the day it is produced in the process of photosynthesis by producers. It is also gained due to a contact of water level with atmosphere (Šálek, 1999). In high productive waters, such as shallow lakes, ponds and slowly flowing rivers with many macrophytes and enough nutrients, there is a higher concentration of oxygen and lower amount of carbon dioxide during the day. At night there is the opposite situation (www.fns.uniba.sk).

There are lots of different organic substances in waters. The source of these substances are products of photosynthesis of algae and aquatic vegetation, losses through photosynthesis, organic compounds which are released in hydrolysis and as a result of decomposition of dead animals by microorganisms. Increased content of easy degradable organic substances deplete large amount of oxygen from the water and thus it can fall up to zero (Kubíček, Lellák, 1991).

Individual determination of individual organic substances is very complicated and therefore the methods were sought to make possible to use representation of the total organic substances concentration in the water and to describe the rate of total water pollution (Gábriš et al., 1998). Most of them are subjected to biochemical oxidation which is conected with oxygen consumption. Some substances are not oxidated biochemically but they are oxidated chemically (Streďanský et al., 2005).

Indirect laboratory methods based on chemical or biochemical oxidation are usually used to determine the organic substances in waters. From chemical methods we use the oxidation with permanganate potassium (Kubelova method) and the potassium dichromate method. However, permanganate potassium does not oxidize all organic substances (weaker oxidizer). Therefore, the dichromate method is more suitable and it is also called the chemical oxygen demand (COD).

MATERIAL AND METHOD

The Nature Reserve (NR) Aluvium Žitavy is situated in cadastral land of the village Martovce, 22 km north of the district Komárno. The area lies in Podunajská Lowland, on the bottom land of the rivers Žitava and Nitra, at an altitude of 107–112 m asl (www.dunajsko.sk). It belongs to the catchments area of the river Nitra which joins the river Váh. Aluvium Žitavy was established as the Nature Reserve in 1993, mainly for protection of biotopes of European importance (riverine willow-poplar and alder wood forests) and other species of European importance (*Proterorhinus sp.*, *Rhodeus amarus*, *Gobio albipinnatus*, *Bombina bombina*, *Lutra lutra*, *Citellus citellus*) (www.martovce.sk). Aluvium is the part of CHKO Dunajské luhy (www.chu.enviroportal.sk). Its area is 32,53 ha. Its larger part is flooded along the year, but especially in spring. There are different biotopes, aquatic, wetland and riverine vegetation. Riverine forests, particularly willow stands, almost along Aluvium provide suitable ecological conditions for nesting of avifauna as well as hiding places. There are more than 76 bird species occurring in this area (www.zitava.sk).

As for the climate, the territory belongs to dry or slightly dry region and is ranked among the driest regions in Slovakia. The average annual temperature is 9.9 °C, the coldest month is January (with an average month temperature –2.1 °C) and the warmest month is July (with an average month temperature 20.5 °C). The average annual precipitations represents 550–600 mm, most of it falling in May, June and July (www.martovce.sk).

In term of geology, the area is created by quaternary, recent and alluvial sediments. Only in the eastern part of the area there are quaternary Pleistocene blown sands and sand dunes.

Concerning the hydrogeology quaternary sands and gravels superimposed with loess form a base rock (bedrock). Haplic chernozems, haplic gleysols and mollic fluvisols are the main soil types (www.martovce.sk).

The research area belongs to the agricultural region with high productivity specialized in growing cereals, oilseeds, sugarbeet and trifolium. Animal production is focused on pig and poultry breeding (www.martovce.sk).

NR Aluvium Žitavy has a high biological value and observes an important function for preservation of fauna and flora gene pool. The rarest living avifauna species are for example *Ardea sp., Remiz sp., Botaurus sp., Circus sp., Anas sp., Acrocephalus sp., Charadrius sp., Locustella sp. Leucojum aestivum* grows in the NR and protected *Nuphar lutea* occurs on the water level. *Limna minor* forms green cover on the water level. There are wetland species of flora, from which stands of *Phragmites australis,* *Typha latifolia, Carex sp.,* Scirpus *sp.,* etc. dominate, among two fill slopes (www.zitava.sk).

Taking of water samples was realized from 6 sampling sites in the NR. Water samples were taken regularly during the whole year, 15th day of each month. The sampling sites were proposed to obtain the best possible data for the evaluation of the changes in concentrations of dissolved oxygen and organic substances in water in dependence on space and time. We have established the following six sampling sites:

1. Inflow of the river Žitava into the Aluvium. *Phragmites australis* and *Salix sp.* grow along the river Žitava and they are also typical for the whole area of the NR. The average depth is 0.32 m.
2. and 3. The sampling sites are typical wetland ecosystems. There is a very dense stand of *Phragmites australis* and *Salix sp.* in this part of the NR. Water level is covered by *Lemna minor*. Water in these sites flows very slowly and its high changes in dependence on weather during the year. The average depth is about 0,30 m.
4. It is situated near the bridge on which there is a road to the village Martovce. It is also the narrowest part of Aluvium; therefore water flow reaches the highest speed in the river Žitava. There are typical stands of *Phragmites australis, Salix sp., Alnus sp.* on the banks of the river. The average depth is 0.40 m.
5. and 6. They are characterized as typical wetland ecosystems. The river Žitava flows out of its watershed here while rapid snow melting during spring months and intensive precipitation amount in summer months. In comparison with the second and the third sampling site the river floods the whole area between two slopes. The water level decreases about few meters during dry weather in summer months. This part of Aluvium is mostly represented by an open water area. *Typha latifolia, Phragmites australis, Alnus sp.* and *Salix sp.* grows along the river. The water level in the sixth sampling site is covered with *Lemna minor* which forms a typical green cover. This sampling site is situated about 120 m from the place where the river Žitava joins the river Nitra. The average depth in the 5th sampling site is 0.26 m and 0.39 m in the 6th sampling site.

In taken water samples the concentrations of dissolved oxygen were determined by inoLab Multi Level 3 with galvanic oxygen sonde StirrOx G. The concentrations of organic substances were determined by an indirect method based on their oxidation with dichromate potassium by means of solutions of Merck spectrophotometrically. The method is analogical with ISO 6060, EPA 410A. The results of dissolved oxygen and organic substances concentrations are given in mg $O_2.l^{-1}$.

The water in the sampling sites was ranked in the categories of surface water quality. It was performed by comparison of the calculated characteristic values of indicator and the corresponding system of limit values which are stated by the standard STN 75 7221 (Classification of the surface water quality). According to the standard STN, the characteristic value of indicator is the value with the probability of non-overfullfilment of 90 % in COD_{Cr} and with the probability of overfullfilment 90 % in dissolved oxygen.

RESULTS AND DISCUSSION

From the results of average concentrations of dissolved oxygen in water of the NR Aluvium Žitavy in dependence on sampling time shows that the highest values were during winter and early spring months. The maximum value was meausred in March (9.0 mg $O_2.l^{-1}$). Since April there was a tendency of successive decrease of average concentrations of dissolved oxygen. The minimum value was measured in July (1.6 mg $O_2.l^{-1}$) (Fig. 1). This fall is probably related to successive increase of water temperature. Thus good conditions were created for decomposition of organic matter by microorganisms in water in which they use dissolved oxygen. We supposed that very low average concentration of oxygen in July is connected with the highest temperature of water (22 °C) measured in this month in the NR (Fig. 2). It is known from literature (Losos et al., 1984, Pitter, 1999) that the dissolubility of oxygen in water subsides with rising water temperature. Beňačková, Noskovič (2005) found out similar dependence between dissolved oxygen concentration and water temperature in the NR Žitavský luh.

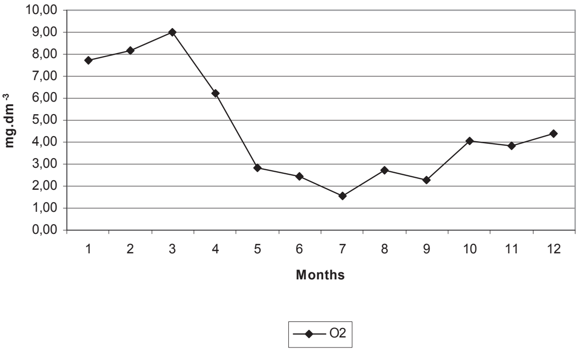

Fig. 1 Concentrations of dissolved oxygen in mg.l^{-1} in dependence on sampling time

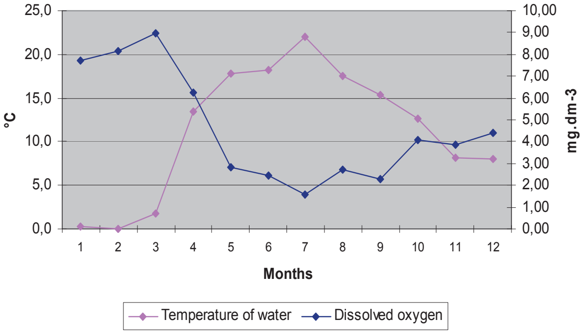

Fig. 2 Relation between the average temperature of water and dissolved oxygen concentration

As for the sampling place the highest average concentrations of dissolved oxygen were measured in sampling sites No. 1 (6.0 mg O_2.l^{-1}) and No. 4 (5.5 mg O_2.l^{-1}). Sampling site No. 1 is situated on the inflow of the river Žitava into the Nature Reserve and sampling site No. 4 is situated on the narrowest place of the NR where water flow has the highest speed. These sites are characterized by permanent water flow. Lower values of dissolved oxygen were in sampling sites No. 2, 3, 5 and 6 (Fig. 3) because these sites are typical wetland ecosystems. They are overgrown by aquatic plants and there is a huge amount of organic matter from extinct plants in sediments thus good conditions for accumulation of organic substances in water are created. Different conditions in sampling sites No. 2, 3, 5 and 6 were probably the reason of lower concentrations of dissolved oxygen compared with sampling sites No. 1 and 4 Beňačková, Noskovič (2005) and Sedláková (2004) measured low concentration of dissolved oxygen in similar localities (the NR Žitavský luh and the NNR Parížske močiare respectively).

Based on calculated characteristic values of dissolved oxygen and according to the standard we ranked all sampling sites into the 5th class of the water surface quality (very strongly polluted water).

Total content of organic substances in water in the NR Alúvium Žitavy was evaluated according to COD_{Cr} values. In dependence on sampling time the highest values were determined in summer months with the maximum in August (129.3 mg O_2.l^{-1}). Beňačková, Noskovič (2005) measured the highest values of COD_{Cr} in August in the NR Žitavský luh, too. High values of COD_{Cr} in summer months are obviously related to intensive decomposition of organic matter. The lowest values were measured in winter season with the minimum in December (52.7 mg O_2.l^{-1}) (Fig. 4). The fall of COD_{Cr} values in winter can be connected with unsuitable thermal conditions for decomposition of organic substances in water. Similar results in seasonal dynamics of organic substances concentration were detected by Pivokonský et al. (2001), Sedláková (2004), Beňačková, Noskovič (2005).

Influence of sampling sites on COD_{Cr} values was opposite in comparison with influence of sampling sites on dissolved oxygen concentrations. Higher values were in sampling sites No. 2, 3, 4, 5 and 6 and the lower ones were in sampling sites No. 1 and 4 (Fig. 5). Organic substances which got into the water through the decomposition of extinct

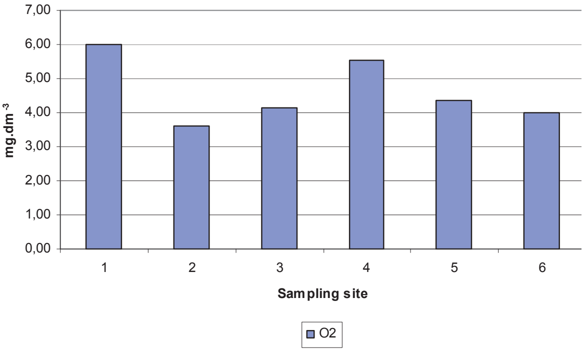

Fig. 3 Dissolved oxygen concentrations in mg.l^{-1} in dependence on sampling site

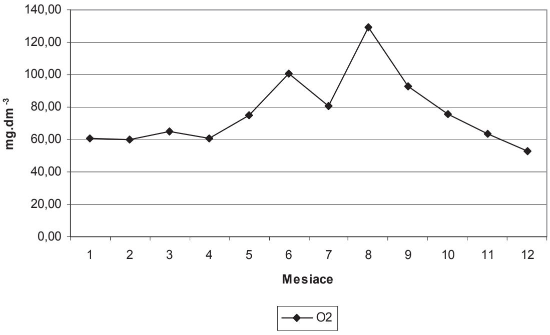

Fig. 4 COD_{Cr} values in mg.l^{-1} in dependence on sampling time

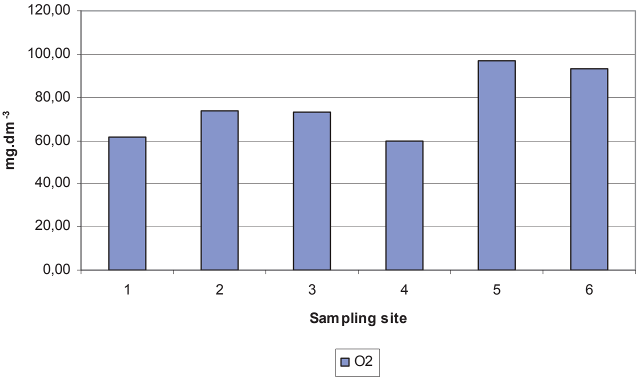

Fig. 5 COD_{Cr} values in mg.l^{-1} in dependence on sampling site

Tab. 1 Ranking of water in sampling sites into the classes of the water surface quality according to the standard STN 75 7221

Sampling site	**1.**		**2.**		**3.**		**4.**		**5.**		**6.**	
Indicator	O_2	COD_{Cr}	O_2	COD_{Cr}	O_2	COD_{Cr}	O_2	COD_{Cr}	O_2	COD_{Cr}	O_2	COD_{Cr}
Unit	mg $O_2.l^{-1}$	mg $O_2.l^{-1}$	mg $O_2.l^{-1}$	mg $O_2.l^{-1}$	mg $O_2.l^{-1}$	mg $O_2.l^{-1}$	mg $O_2.l^{-1}$	mg $O_2.l^{-1}$	mg $O_2.l^{-1}$	mg $O_2.l^{-1}$	mg $O_2.l^{-1}$	mg $O_2.l^{-1}$
Calculated characteristic value	2,6	98,5	1,2	88,0	1,2	88,3	0,6	74,4	0,6	246,8	0,9	205,7
Class of quality	V.	V.	V.	V.	V.	V.	V.	V.	V.	V.	V.	V.

hydrophytes can be considered as the main reason of the increase of COD_{Cr} values in sampling sites No. 2, 3, 5 and 6.

Based on the calculated characteristic values of COD_{Cr} and according to the standard STN 75 7221 all sampling sites are ranked into the 5th class of the water surface quality (very strong polluted water).

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MAGNETIC SUSCEPTIBILITY MAPPING OF ROADSIDE POLLUTION

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ABSTRACT

Kľučiarová D. & Gregorová D. **Magnetic Susceptibility Mapping of Roadside Pollution**

In the last years, several proxy methods have been used to outline increased levels of pollution. One of them is based on measurements of the concentration of (ferri)magnetic minerals of antropogenic origin. This approach was successfully applied in several European cities and has shown that magnetic parameters (mainly magnetic susceptibility) can be used as a proxy for heavy metals pollution in topsoils.

The aim of our study was to trace the distribution and concentration of contaminants (heavy metals) in the soil along the road carrying appreciable traffic by using magnetic proxies. The area of this study was the part of the main road between Pezinok and Pezinská Baba. We tested how far magnetic measurement of soil samples can give information about road soil pollution. The soil samples (very close to the road, 0.5 m and 2m from the road) were collected each 50 m on the 3km long way, air-dried, sieved and measured for the bulk magnetic susceptibility on the Kappabridge (KLY–2).

The results show that the soil samples near the road are characterized by enhanced magnetic susceptibility, with highest values and that the magnetic susceptibility decreases with increasing distance from the road. The geochemical analyses revealed the high positive correlation. Therefore the measurement of magnetic susceptibility of soils can be – in this case – used as a supplemental method to the geochemical mapping; method, which allows to assess, in a simple, cheap and rapid way, the level of soil pollution in sites, where the geochemical data are missing.

Key words: magnetic susceptibility, heavy metals, magnetic screening, pollution of roadside soils

INTRODUCTION

Pollution of soils and sediments significantly reduce environmental quality and affect human health. As a condition for effective protection and remediation actions, the screening and detection of soils and sediment pollution has become increasingly important. The pollutants of most concern are heavy metals and organic contaminants.

Magnetic techniques were shown to be highly useful in investigating industrial pollutants and other atmospheric aerosols. The intention of magnetic studies of aerosols has been the discrimination of fly–ash from other aerosols based on the characteristic magnetic properties of anthropogenic dusts. Recent studies (Strzyszcz, 1993; Strzyszcz and Magiera, 1998; Petrovský et al,. 1999) demonstrate how a combination of simple magnetic susceptibility measurements can help identify regions where soils contain higher than average concentrations of fly-ash and other anthropogenic dusts. In addition to fly-ash, there are other numerous atmospheric pollutants such as vehicle and aircraft emissions or dust from cement production, open pit mining, and steel production. Vehicle emissions have been suggested to be a significant source of magnetic pollutants (Hunt, 1986). However, details about the origin and the composition of these particles are presently unknown.

Preliminary studies indicate a possible correlation between magnetic susceptibility measurements and atmospheric contaminants. Particles below the

PM 10 limit (10μm) can significantly affect human health as they can easily be transported into deeper parts of the respiratory tract and accumulated in the alveoli (LfU – Landesanstalt für Umweltschutz, 1998). It is well known that due to their specific surface, such particles are excellent absorbers and carriers of pollutants such as heavy metals. Magnetic methods provide an inexpensive and quick diagnostic alternative to other techniques for (direct) analyzing pollutants and are extremely sensitive to magnetic particles of the above mentioned grain sizes (Hoffmann et al,; 1998, Leven et al., 1998).

Sediments and soils can act as natural storage for many types of pollution. Magnetic proxies represent powerful means for routine screening and detecting contamination due to heavy metals.

Here, we report results of our investigations focused on pollution screening using magnetic susceptibility on roadsides. The main aim of this study is to test the applicability of the magnetic mapping method.

ENVIRONMENTAL MAGNETISM – MAGNETO-SCREENING OF POLLUTION

Overview

A description of the method of environmental magnetism including a few results demonstrating the capabilities of this technique are presented below (more detailed reviews are found, e.g. in (Oldfield, 1991; King and Chanell, 1991; Strzyszcz, 1993, Dearing, 1994; Heller and Evans, 1995; Verosub and Roberts, 1995; Reynolds and King, 1995; Petrovský and Elwood, 1999).

In environmental magnetism, magnetic properties of materials such as soils, sediments and dusts are investigated. Such measurements provide powerful tools for approaching environmental problems of concern such as climate and environmental changes and, more recently, environmental pollution. The high sensitivity of magnetic measurements allows the detection of very low quantities of magnetic material which often act as proxies for the underlying environmental processes. Anthropogenic pollution can also have a strong magnetic signature and magnetic techniques have proven to be capable of discriminating between different sources of pollution. Magnetic techniques have been applied successfully in studies of climate changes, soil erosion, analyzing of atmospheric (e.g. by detecting high fly-ash) and pollution produced by historical or active mining and other anthropogenic activities. The sensitivity of magnetic techniques is suited for rapid measuring of very small quantities of magnetic particles in bulk samples (in general equivalent to ppb in chemical analyses). Magnetic parameters are capable of discriminating the ferromagnetic component of atmospheric dust derived from soil-sizes particles from different source areas as well as fly-ash from different industrial sources (e.g. Hunt et al,. 1984; Chester et al., 1984; Oldfield and Robinson, 1985; Hunt, 1986).

Although magnetic studies have been successful in providing proxies for environmental processes, the fact that many of the environmental magnetic results rely on bulk techniques means that only average magnetic parameters are obtained from many measurements.

Methods

The principle of the method of environmental magnetism, namely of the magnetic-proxies technique which is used in this study for the screening and detection of pollution can be summarized as follows:

(1) All rocks, sediments and soils contain a certain, mostly accessory portion of ferri(o)magnetic minerals.

(2) These phases are: Fe-oxides (magnetite, $Fe_3O_{4,;}$ maghemite, γ-$Fe_2O_{3;}$ hematite, α-Fe_2O_3), Fe--hydroxides (goethite, a-FeOOH), Fe-sulfides (pyrrhotite, Fe_7S_8; greigite, Fe_3S_4) or similar phases.

(3) In addition, aerosols and dust of anthropogenic origin containing different ferri(o)magnetic phases with Fe partly substituted by other cations like Ni, Co, Cr, Ti, Al, Mg are deposited and accumulated in soils and sediments.

(4) With the help of magnetic proxies such as susceptibility, potentially polluted areas can be mapped in the field (so-called magnetometry): 2D-mapping.

(5) Only the magnetic signal related to the secondary ferri(o)magnetic phases of anthropogenic origin is of interest.

(6) A series processes are known to result in an enhancement of the magnetic signal in soils or sediments (Maher, 1998). Therefore, the anthropogenic magnetic signal must be discriminated

from the background (derived from lithogenic and other secondary ferri(o)magnetic mineral phases.

(7) Proper magnetic parameters can be used as proxies for the detection of environmental pollution.

(8) Anthropogenic ferri(o)magnetic phases mainly consist of highly magnetic spherules produced during processes such as combustion (fly-ash), welding, steel production, smelting and others (Hoffmann et al., 1998; Knab et al., 1998; Leven et al., 1998).

MAGNETIC MAPPING OF ROADSIDE POLLUTION

The area of this study is the main road from Pezinok Pernek to Pezinská Baba. Fig. 1 represents the part of the way which was chosen as the first test side for detailing magnetic susceptibility mapping because: (1) a high level of pollution can be expected along this road (high traffic density per day, place where are very frequent motorbike racing, (2) vehicles are the only significant source of pollution in this area, (3) there is only grass land on both sides of the road (the magnetic signal is not disturbed by agricultural processes such as ploughing, (4) the present road-line is many years old and an undisturbed accumulation of the pollution due to traffic can be expected for this time span, (5) to our best knowledge, the soil on both roadsides has not been disturbed significantly within the last few years.

Two emission-components are largely responsible for the roadside environmental contamination: (1) vehicles and (2) materials used for the road construction (asphalt, bitumen being most important). A large variety of solid, gaseous are emitted into the environment. These pollutants accumulate in the topsoil, migrate to the water system (penetration to ground-water), or are taken up and accumulated by plants or microorganism. Only solid particles are responsible for the enhancement of the magnetic signal in the topsoil. These include soot particles, metallic or fly-ash particles produced by abrasion (e.g. brake system), rust or paint particles due to corrosion.

The soil samples were collected each 50 m on the 3 km long way in 3 distances (near the road, 0.5 m and 2 m from the road) and measured on

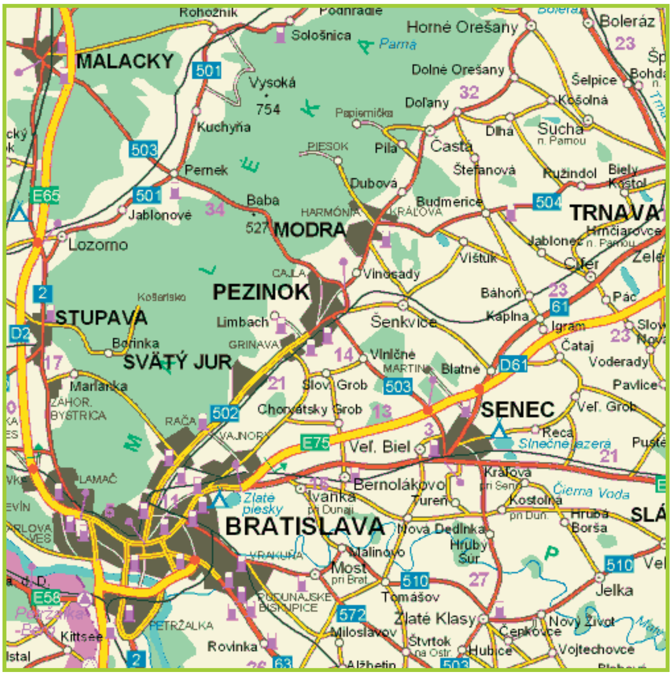

Fig. 1 The investigated area

the kappabridge KLY-2 (AGICO, Brno) in the Geophysical Institute of SAS. A single test profile was measured in order to qualitatively determine the degree of magnetic pollution along a road with high traffic density.

SUMMARY AND CONCLUSIONS

Magnetic susceptibility mapping was used in the field in order to trace potentially contaminated area along the road. Clearly enhanced values of the magnetic susceptibility were found on the roadsides. In order to highlight the trend of susceptibility vs. distance on the roadside is that the soil samples near the road are characterized by enhanced magnetic susceptibility with the highest values ($7.64.10^{-6}$ m^3.kg^{-1}) and that the magnetic susceptibility decreases with increasing distance from the road ($2.27.10^{-6}$ m^3.kg^{-1}) how it is presented in Fig. 2. The preliminary study has shown that magnetic mapping was demonstrated to provide a rapid, cheap, efficient and highly sensitive alternative method for investigating of potentially contaminated area. For the correlation with the heavy metals is necessary to refill the magnetic susceptibility data with chemical analyses (AAS).

Magnetic mapping can help significantly reduce the cost (time) in comparison with direct analyses of pollutants. We propose that magnetic screening should be performed as a first step of determining environmental pollution and the tracing of its potential sources.

Magnetometry provides a proper base for more systematic sampling which in practice means preselection in order to reduce time-consuming and expensive laboratory analyses to a reasonable level.

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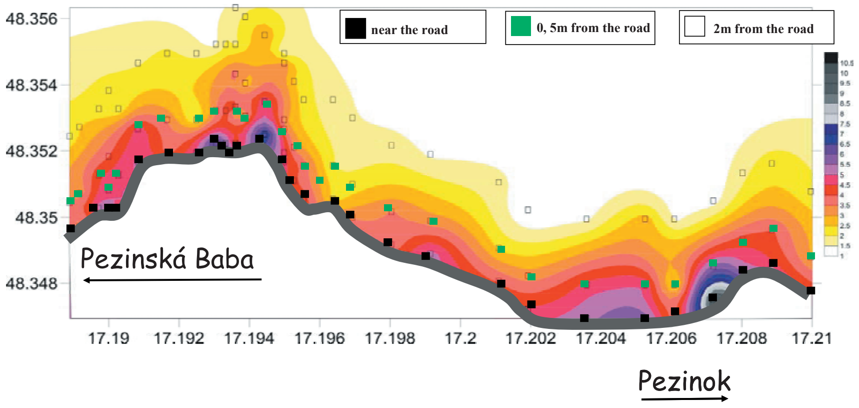

Fig. 2 The values of magnetic susceptibility

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CONCENTRATIONS OF ^{222}RN AND ITS PROGENY ^{210}PB IN LOWER ATMOSPHERE IN BRATISLAVA

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ABSTRACT

Ješkovský M., Holý K., Sýkora I., Merešová J., Müllerová M., Bulko M. & Polášková A. **Concentrations of ^{222}Rn and its Progeny ^{210}Pb in Lower Atmosphere in Bratislava**

Monitoring of atmospheric radioactivity in Bratislava has been carried out by the Department of Nuclear Physics and Biophysics of Faculty of Mathematics, Physics and Informatics of Comenius University. Air activity concentration of gaseous ^{222}Rn and its progeny ^{210}Pb, bound to aerosol particles, were measured. The concentrations of ^{222}Rn varied from 0.59 to 11.1 Bq.m^{-3} (average value 3.73 ± 0.17 Bq.m^{-3}) and concentrations of ^{210}Pb from 0.22 to 2.37 mBq.m^{-3} (average value 0.83 ± 0.02 mBq.m^{-3}). Temporal variation with seasonal behaviour was observed. The correlation study has been carried out between the meteorological factors and concentrations of radionuclides.

Key words: seasonal variations, ^{222}Rn, ^{210}Pb, air radioactivity

INTRODUCTION

The atmospheric pollution is a very topical problem at present. Study of emission processes and chemical-physical transformations of pollutants, associated with meteorological processes of turbulent diffusion and transport is therefore important. Useful tools to study these processes are radon and its progeny, even if are measured at ground level, because the atmospheric processes are dependent on the dynamic evolution of the boundary layer.

^{222}Rn originates from the decay chain of ^{238}U, which is a component of rocks and soils since nucleosynthesis. Radon is produced in soil and after that is exhalated to the ground level of atmosphere where is decayed and its progeny are bounded to the atmospheric aerosols. The ^{222}Rn exhalation rate depends on the soil type and concentration of ^{226}Ra in soil. The variations of exhalation rate are caused by precipitation and soil moisture. The variations of ^{222}Rn air concentrations and subsequently of its decay products are induced mainly by atmospheric mixing. Air activity concentration of ^{222}Rn shows seasonal variations with maximum values in winter and minimum in summer [1]. It also exhibits diurnal variations with the maximum in the night hours and the minimum in the afternoon [2].

The radon daughter product with half-live long enough to stay in the atmosphere longer than few hours is ^{210}Pb. It is transported through the atmosphere bounded to aerosol particles and precipitated back to the Earth surface by dry or wet deposition. The level of volume activity of ^{210}Pb is influenced by several meteorological factors.

The aim of this paper is to present the results of the long-term measurement of radioactivity concentration in low level atmosphere [3–6]. In particular it is concerned with ^{222}Rn and ^{210}Pb, compared with basic meteorological parameters.

EXPERIMENTS

For determination of ^{222}Rn and ^{210}Pb concentrations in lower atmosphere were used the following methods.

Concentrations of ^{222}Rn have been measured by the continual method using the scintillation chamber. Data have been obtained every half-hour and averaged for two-hour interval [3] and for one-week interval.

The atoms of ^{210}Pb are attached to the aerosol particles at ground level of atmosphere. Aerosols were collected by pumping of the air on the nitro-cellulose filters with the hole of 0.85 μm in diameter. The exposed filters were changed every week. Concentrations of ^{210}Pb on filters were estimated by the gammaspectrometric measurement using HPGe detector situated in the low-background laboratory [4–6].

RESULTS AND DISCUSSION

The seasonal trends of measured ^{222}Rn and ^{210}Pb concentrations during the period from January 2005 to September 2006 are presented in Fig. 1. During the period of 21 months were 82 sets of nitro-cellulose filters collected. The mean value of ^{222}Rn concentrations is 3.73 ± 0.17 Bq.m^{-3} and the mean value of ^{210}Pb concentrations is 0.83 ± 0.02 mBq.m^{-3}, respectively.

Concentrations of radionuclides show a seasonal variation with maximum in the autumn to winter period and minimum in the spring to summer period. The increase of concentration in the cold season is attributed to frequent inversion conditions of the surface air layer. The decrease in the warm season is a result of intensive air mixing during these months.

Correlation analysis between concentration of these two radionuclides was carried out and correlation coefficient was found to be 0.72 (Fig. 2) in a weekly period and 0.88 in a monthly period, which implies a strong correlation between air concentrations of ^{222}Rn and ^{210}Pb. The correlation between air concentrations of radionuclides and meteorological parameters is presented in Tab. 1. The values of correlation coefficients are comparable for both of the radionuclides and for whole year data did not show any significant correlations between studied meteorological factors and concentrations. Comparison of the temperature data and concentrations of radon shows a shift between their variations. If only data from summer months (from May to September) were chosen for the correlation analysis between temperature and concentrations of ^{222}Rn and ^{210}Pb, correlation coefficient for ^{222}Rn was found –0.71 and for ^{210}Pb –0.59.

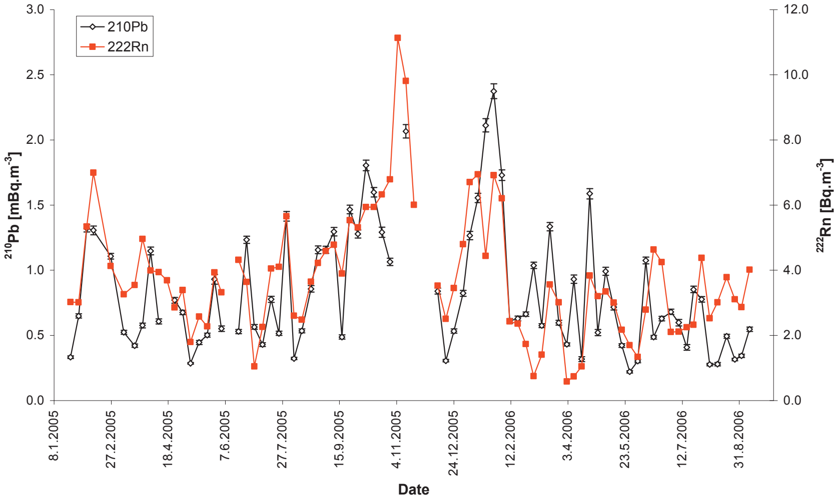

Fig. 1 Air activity concentrations of ^{222}Rn and ^{210}Pb in the atmosphere

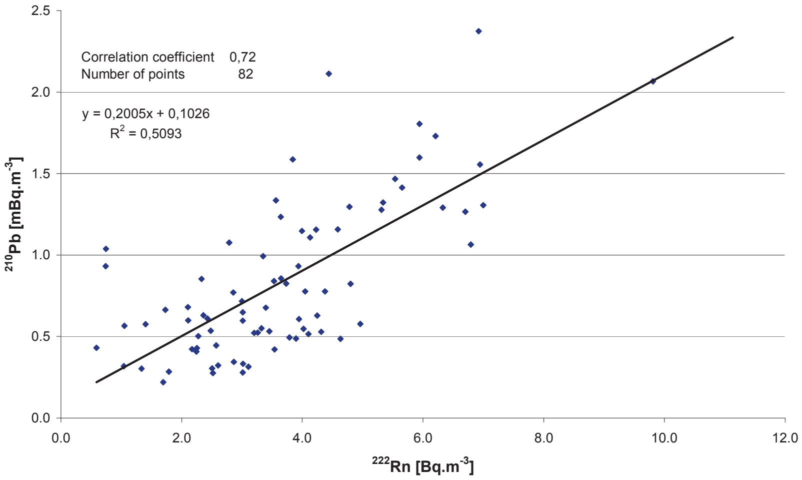

Fig. 2 Correlation between air activity of ^{222}Rn and ^{210}Pb in a week period

Tab. 1 Correlation coefficients between air activityconcentrations of radionuclides and meteorological parameters

	Air temperature	Air pressure	Air humidity	Precipitation
^{222}Rn (week period)	–0.19	0.44	0.31	–0.22
^{222}Rn (month period)	–0.28	0.57	0.41	–0.42
^{210}Pb (week period)	–0.31	0.37	0.14	–0.36
^{210}Pb (month period)	–0.38	0.48	0.50	–0.39

CONCLUSION

The concentrations of gaseous ^{222}Rn and ^{210}Pb in the ground level of atmosphere indicate seasonal variations in Bratislava region. Correlation coefficients between radionuclides were found 0.72 for a weekly period and 0.88 for a monthly period. The high coefficients prove relations between ^{222}Rn and ^{210}Pb in air at the ground level of the atmosphere. The concentrations of ^{222}Rn and ^{210}Pb ranged from 0.59 to 11.1 Bq.m^{-3} with average 3.73 ± 0.17 Bq.m^{-3} and from 0.22 to 2.37 mBq.m^{-3} with average 0.83 ± 0.02 mBq.m^{-3}, respectively. These are typical values of air activity concentrations of ^{222}Rn and ^{210}Pb for the European area [7–9]. The correlation study between air concentrations of radionuclides and meteorological parameters was carried out and shows correlation between temperature and concentration of radon in summer months.

Acknowledgement

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EVALUATION OF BOTTOM SEDIMENT QUALITY IN SELECTED SMALL WATER BASIN

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ABSTRACT

Kovaliková N. & Bálintová M. **Evaluation of Bottom Sediment Quality in Selected Small Water Basin**

Erosion processes in watersheds belong to serious ecological and economical problems because of negative consequences in terms of soil and water deterioration as well as on the environment as a whole.

Sediments, originated by water erosion, cause silting of the small water basins, that belong among crucial problems in water management mainly due to the reducing of the basin's accumulation capacity. Besides quantity, quality of sediment affects, also downstream areas and thus the water quality because they act as a potential sink for many hazardous contaminants.

The aim of this paper is assessment of bottom sediment quality in small water basin Kľušov in the east of Slovakia.

Key words: sediment quality, water basin, nutrient

INTRODUCTION

Changes in land use, started centuries ago, have increased the rate of many erosion processes. Increased soil erosion causes a rise in sediment supply to rivers, and is also of concern for the sustainable use of soils for agriculture. Soil erosion affects about 17 % of the total land area in Europe.

Erosion is one of the most important pathways of sediment and nutrient entries into river systems. The release of nutrients (particularly nitrogen and phosphorus), which predominantly originate from agriculture and domestic sewage, can significantly affect the balance of the aquatic ecology and often produce algal blooms throughout the body of water and at the surface, resulting in eutrophication of lakes and rivers [1].

Although such sources of pollution as sewage discharges may contribute significantly to nutrient enrichment in some regions, diffuse sources – particularly agriculture – are the major contributors.

About 80 % of the nitrogen in rivers is present as nitrate. Nitrate concentrations in rivers are linked to the proportion of arable land in the upstream catchment (figure 1) – the highest levels occur where large amounts of nitrogenous fertilisers and animal manure are used. In 2001 nitrate levels in rivers where arable land covers more than 50 % of the upstream catchment area were three times higher than in catchments with arable land cover of less than 10 % [2].

Agriculture also contributes to phosphorus loading of surface water. As with nitrogen, intensive farming methods produce a surplus of phosphorus in the soil.

Not only water quality but also sediment quality monitoring is necessary for ecological status assessment of water ecosystems.

Sediment as a pollutant is harmful itself and is even more when combined with contaminants, such as heavy metals, nutrients, pesticides and other organic micro-pollutants.

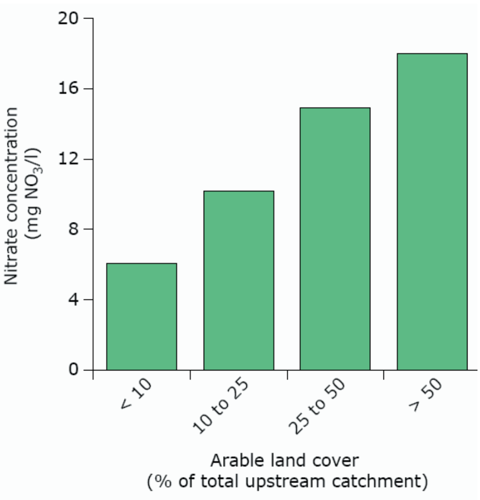

Fig. 1 Nitrate concentrations in catchment

Significant amounts of nutrients can be contained in sediment, and its release can significantly influence the quality of the body of water [3].

MATERIAL AND METHODS

Bottom sediment quality was monitored in small water basin (SWB) Kľušov, which is situated at the Tisovec stream, in district of Bardejov, in the east port of Slovakia. It was built for fishing, irrigations, recreation and for retention of high water. Its basic attributes are shown in table No. 1.

Tab. 1 Basic attributes of small water basin (SWB) Kľušov

Altitude [m above SL]	**Average depth [m]**	**Surface area [ha]**	**Total capacity [m^3]**
343.00	3.5	2.20	72 128

According to the last measuring, the quantity of sediments in the Kľušov reservoir was approximately 24 507.30 m^3. This fact resulted in decreasing the capacity of SWB about 33 %. For the reason of sediment quantity and requirement for dredging the reservoir is being discharged the water off at present.

For the assessment of bottom sediment quality, there was realized the sampling of bottom sediments and also sampling of arable land in vicinity of reservoir.

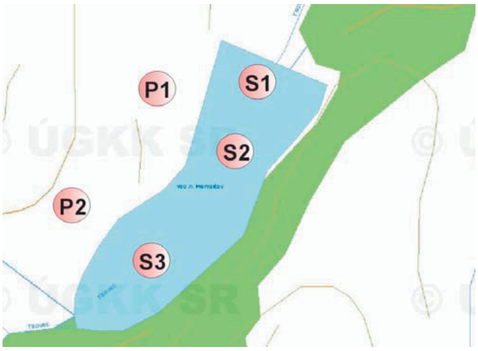

Fig. 2 Points of taking sediment and soil samples

Sediment samples were taken from the reservoir in June 2006. One composite sample was taken from each selected locality. Previous research has shown that it wasn't necessary to collect samples more times, because sediment quality in the reservoir, which is run the water off, isn't evidently varying. Samples were collected to plastic bucket. Localities for taking of sediment samples are shown in figure No. 2.

The weight of the collected composite samples represented about 3 kg. The samples were air dried at room temperature, any coarse lumps were crushed and samples were homogenized. Sediment samples were sieved through a 0,063 mm sieve.

Collection of soil samples from arable land in vicinity of reservoir was realized in accordance with [4]. Two composite samples – P1, P2, consisting of 30 subsamples – were taken using a soil probe (figure 2). Soil samples handling were identical with the handling of sediment samples.

Samples of bottom sediments and soils were analyzed for total N, P, K. The analyses of the taken samples were made in the average sample and also in the sample with grains smaller than 63 µm. Chemical analyses were realized in laboratory of State Geological Institute of Dionyz Stur Spišská Nová Ves.

RESULTS AND DISCUSSION

Table 2 gives the results of chemical analysis of followed compounds (N, P, K) in average sample of sediments and soil.

From chemical analysis, given in table No. 2, it shows that concentrations of P, N, K in separate sediment samples are diverse. The reason is irregular sediment deposit in the reservoir, because coarse sediments settle down on an inlet to the reservoir and fine sediments are deposited close to the dam.

Tab. 2 Concentration of N, P, K in soil and in bottom sediments of SWB Kľušov

Measured parameters	**Unit**	**SWB Kľušov**				
		Soil from the field		**Sediment from the reservoir**		
		P 1	**P 2**	**S 1**	**S 2**	**S 3**
P total	**[%]**	0.069	0.065	0.113	0.09	0.07
N total	**[%]**	0.08	0.12	0.24	0.2	0.14
K	**[%]**	1.80	1.67	2.42	2.05	1.71

Because the fine sediments have a high surface area, they carry have the most pollutants and the highest values were detected in collection locality No. 1, that means close to the dam.

Nutrient concentration in sediments is nearly 2-fold from this in the soil. This increase may depend on the nutrient content in the water, or it depends on the finest particles of soils, because of carrying the most of pollutants [5].

In a follow-up research, content of P, N, K was followed in the finest particles (with grains smaller than 63 µm) of sediment sample S1 and soil samples P1, P2 (Tab. 3).

Sample P1 contained 72,7 % and the sample P2 80,2 % particles with grains smaller than 63 131 µm. Sediment sample S1 represented 100 % particles with granularity below 63 microns. Literary information [5] about higher concentrations of the followed compounds (N, P, K) in samples P1, P2 and in fraction below 63 microns were not confirmed. This fact comes from the values confrontation given in tables 2 and 3. The granularity impact of soil particles on the concentration of the followed compounds are the object of the further research.

CONCLUSION

For ecological status assessment of water ecosystems, it is necessary to study not only surface water quality but also sediment quality and quality of soils, which are taken from hillslopes during the soil erosion.

The results from chemical analyses confirmed the information from scientific papers, that the concentrations of P, N, K in the chosen sediment samples are diverse due to irregular sediment deposit

Tab. 3 Concentration of N, P, K in the arable land and in bottom sediment of SWB Kľušov

Measured parameters	**Unit**	**SWB Kľušov**		
		Soil from the field (fraction < 63 µm)		**Sediment from the reservoir (fraction < 63 µm)**
		72,7 %	**80,2 %**	**100 %**
		P 1	**P 2**	**S 1**
P total	**[%]**	0.068	0.066	0.110
N total	**[%]**	0.09	0.13	0.24
K	**[%]**	1.77	1.68	2.22

in the reservoir. These concentrations increase with proportion of the finest particle fraction, because pollutants are preferentially attached to the finest particles. From chemical analysis also follows, that nutrient concentration in sediment samples in the reservoir is nearly 2-fold from this in the soil.

Considering that the sediment has been accumulating in the reservoir for 18 years, this fact can be connected with fertilizing in previous period of time, which is the object of the further research.

Acknowledgements

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5. Metodický pokyn Ministerstva životného prostredia Slovenskej republiky č. 549/98 – 2 na hodnotenie rizík zo znečistených sedimentov tokov a vodných nádrží.

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THE VARIATIONS OF ^{222}RN ACTIVITY CONCENTRATION IN BOREHOLE WATER – A COMPARISON BETWEEN THE FIRST HALVES OF 2006 AND 2007

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ABSTRACT

Smetanová I., Holý K., Müllerová M. & Polášková M. **The Variations of ^{222}Rn Activity Concentration in Borehole Water – a Comparison between the First Halves of 2006 and 2007**

Three boreholes V-1 (10 m),V-2 (40 m) and V-3 (10 m) have been drilled in the Lower Triassic quartzite at the area of Astronomical and Geophysical Observatory in Modra-Piesok. Since January 2006 the sampling of borehole water has been performed three times per week for the ^{222} Rn activity concentration analyses. Radon concentration in water has been studied in comparison to the water level changes in the boreholes, the precipitation amount and the height of snow cover. The variations of ^{222}Rn activity concentration in borehole water measured since January to July in 2006 have been compared with those measured in the same period in 2007. It was observed that radon concentrations in V-1 and V-3 boreholes were changing when the precipitation amount was more than 20 mm in both years of thestudy. A similar variation was recorded in the state of water level in those boreholes. The effect of the precipitation was not observed in V-2 borehole for both periods of our research. The melting snow caused the increase of water level and the decrease of radon concentration in all three boreholes. The courses of water level and the values of ^{222}Rn activity concentration were not the same for compared months, because of the significantly lower precipitation amount in 2007.

Key words: radon activity concentration, borehole, precipitation, water level, snow cover

INTRODUCTION

Radon concentration in underground water depends on many factors, mainly on the uranium content and mineral composition of surrounding rock environment and on radium dissolved in underground water. The diameter of connected fractures in rock massif, the possibility for radon degassing from water and also the hydrodynamic factors, that control the mobility of underground water, influence the radon content in water [1, 2].

Underground water can move through rock via connected crack and fissures of various diameters. The position of the underground water level is not stable. The continuous flow of groundwater to the valley results in a general lowering of water level except after the periods of significant precipitation. The seasonal rise of water level during winter months is observed due to the slight of evapotranspiration [3]

During the seasonal falling stage of the water table, some of the radon dissolved in water of the large fractures likely remains in the water as it recedes to a lower position. Much of the radon reverts to vapor in the interconnecting fractures when water drains down. Radon clinging to fracture walls is free to move as the water moves out and also radon that was held in pores that are too small for water to penetrate can now move out into the larger air-filled fractures. As the water table rises seasonally, the airborne radon is pushed upward and outward. A large amount of precipitation may cause a rise of the water level and entrapment of air with an airborne radon by the downward infiltrating water [3].

In this paper we present the results of radon concentration monitoring in water from boreholes. We will compare the interdependence among the variations of ^{222}Rn activity concentration in borehole water and water level changes with precipitation from January to July in both years 2006 and 2007 of our investigation.

METHODS

Three boreholes V-1 (10 m), V-2 (40 m) and V-3 (10 m) have been drilled at the area of Astronomical and Geophysical Observatory of Comenius University in Modra-Piesok (AGO Modra) in the Little Carpathian Mts (40 km NE from Bratislava). The inner diameter of those boreholes is 80 mm, they are cased with a PVC pipe with 10 % perforation along the whole length. All of them have been drilled in the Lower Triassic quartzites folded in the granodiorite of the Modra massif [4, 5].

Since August 2003 the investigation of radon concentration in borehole air has been performed in V-2 and V-3 borehole [6]. The continual monitoring of the atmospheric temperature is also performed in Modra AGO from 2003 [6]. Since 2006 the study of the ^{222}Rn activity concentration changes in borehole water has been performed in all three boreholes [7].

The sampling of water from boreholes has been carried out regularly three times a week by plastic bottle. Simultaneously the state of water level has been measured. The ^{222}Rn activity concentration analyses have been executed at the laboratory of the Department of Nuclear Physics and Biophysics at Faculty of Mathematics, Physics and Informatics of Comenius University in Bratislava. The scintillation cell of Lucas type DS 401M with volume 125 ml have been used for the measurements of radon concentration in water [8].

The precipitation amount and the height of snow cover have been regularly measured at the observatory and which was kindly available for our investigation.

RESULTS

In this paper were studied the results obtained from January to July (respectively to August in the case of V-1 borehole) for two years of the investigation of ^{222}Rn activity concentration in borehole water at AGO Modra. This time period was selected to comparise of the results because since summer there is no water in V-1 and V-3 borehole each year.

It is interesting and very useful, that those two years of our research were completely different for the sake of different atmospheric temperature, precipitation amount and height of snow cover (Fig. 1). Generally, in 2006 the winter temperatures were significantly lower than in 2007. Equally the precipitation amount in winter and spring months was higher in comparison with 2007. Since January to March the study area was covered by a permanent thick layer of snow in 2006. On the contrary, there was almost no snow in 2007. Those different conditions allowed us to compare the courses of radon concentration in borehole water and the changes of water level in diverse situations.

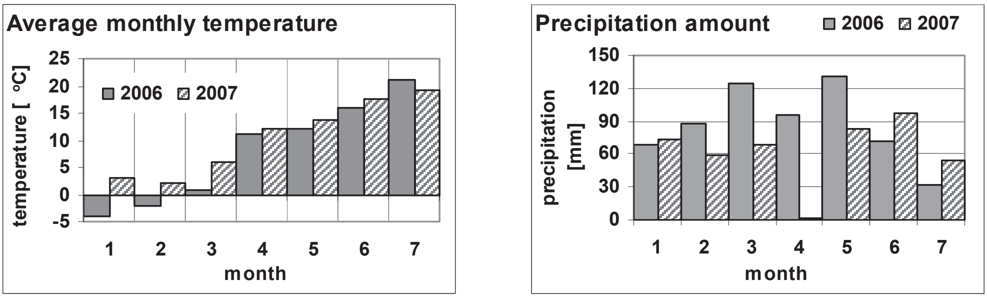

Fig. 1 The comparison between the average monthly atmospheric temperature and the precipitation amount at AGO Modra for the years 2006 and 2007

V-1 BOREHOLE

The courses of ^{222}Rn activity concentration and water level in V-1 borehole were very similar during both years of our research. After a significant rainfall (20 mm and more) the water level in borehole increased up to 3 m, on the contrary, the radon concentration in water decreased sharply. As the water level was falling to the stage before raining, radon concentration in water started to rise. The changes of ^{222}Rn activity concentration between minimal and maximal value were about 70–80 kBq/m^3 in 2006 and 20–60 kBq/m^3 in 2007.

In 2006 the study area was permanently covered with a snow layer up to 1m for the period of three months. After the melting of this snow cover, the water level increased rapidly up to 5 m. The situation in 2007 was completely different. There was nearly no snow, only for a few days each month. The height of the snow cover was no more than 0,15 m. After the melting of snow in January, the water level increased up to 4 m. The rise of water level in February and March was only up to 1,5 m, due to a thinner snow cover.

Since the end of June 2006 there was no water in the borehole until the raining in the middle of August. An intense growth of water table was observed after the precipitation amount of 40 mm. A very similar case occurred in June 2007. Because in 2007 the precipitation amount was significantly lower than during the same period in 2006, the water in V-1 borehole started receding since the beginning of April. The water vanished from this borehole at the end of May. After the strong precipitation in June the water level ascended from the level under the borehole bottom to almost 5m. Since the middle of July there has not been water in borehole again.

The negative correlation between the ^{222}Rn activity concentration and the state of water level was observed in both years of our research. This negative correlation turns to correlation when the water level was less than 6m under the surface.

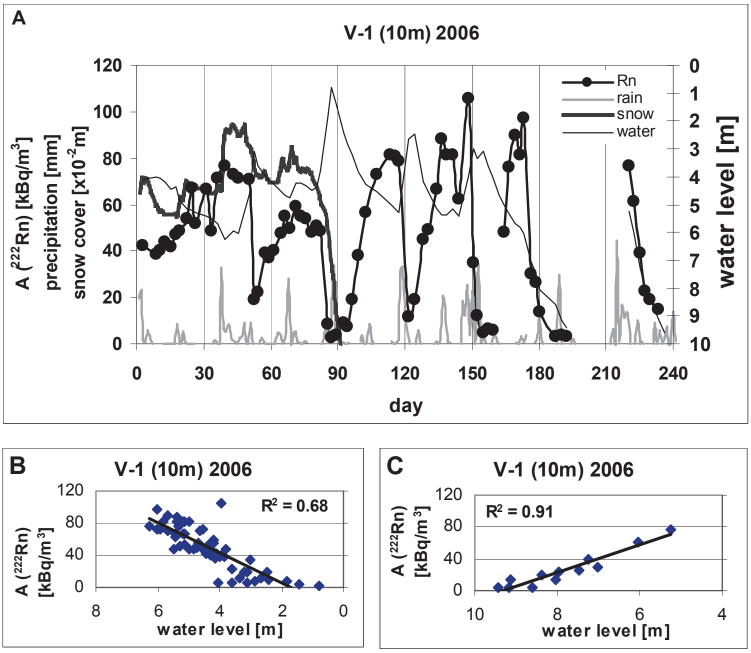

Fig. 2 The courses of the ^{222}Rn activity concentration in water, precipitation amount, the state of the water level and snow cover in V-1 since January to August 2006 (A). The negative correlation between ^{222}Rn activity concentration in water and the state of water level in borehole was observed (B). If the water level in borehole was less than 6m, the positive correlation between those variables appeared (C)

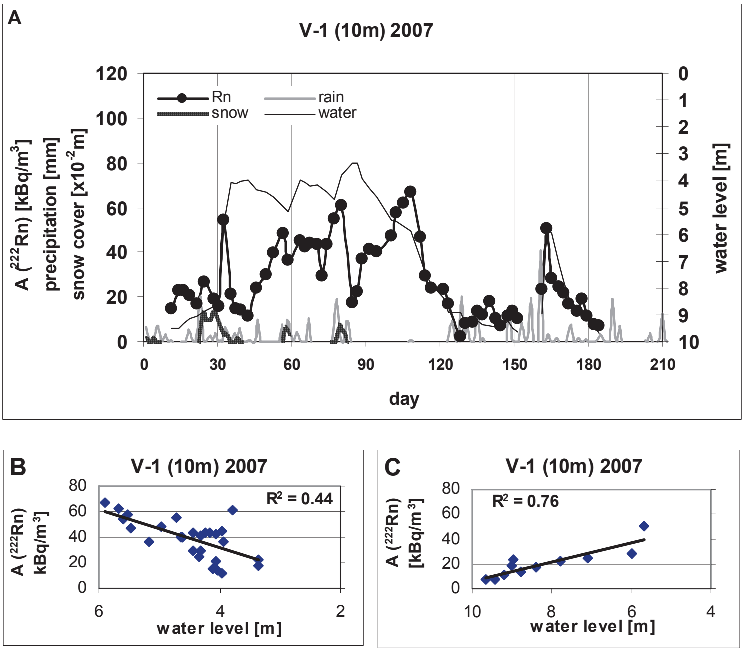

Fig. 3 The courses of the ^{222}Rn activity concentration in water, precipitation amount, the state of the water level and snow cover in V-1 since January to July 2007 (A). The negative correlation between ^{222}Rn activity concentration in water and the state of water level in borehole was observed (B). If the water level in borehole was less than 6 m, the positive correlation between those variables appeared (C).

V–2 BOREHOLE

The V-2 borehole is the deepest one and it contained water during the whole studied period during both years of our research. The radon concentration in borehole water reached the highest values among all investigated samples.

No perceptible influence of precipitation to the state of water level or to the changes of radon concentration in water was recognized in this borehole.

From January to July 2006 one conspicuous maximum of ^{222}Rn activity concentration was noticed. It was observed in March, at the beginning of the snow cover melting. Radon concentration in borehole water attained more than 150 kBq/m^3.

A rapid snow melting, lasting approximately ten days in March 2006, created a large amount of water that increased the water level in this borehole about 5 m. Simultaneously, the radon concentration in water decreased. Since April the water level in borehole stayed at the level about 2 m lower in comparison to previous state before snow melting.

During the studied period in 2007 a very expressive maximum of ^{222}Rn activity concentration appeared. The values of radon concentration reached up to 240 kBq/m^3. It was not connected with snow melting or precipitation. Those high values lasted during whole April, since then the radon concentration started to fall. The previous state was reached approximately after three months. The decrease of radon concentration was much smaller in comparison to the radon decay.

In 2007 no significant rise of water caused by snow melting was observed, due to the lack of snow. Similarly, the characteristics of the V-2 borehole were not affected by precipitation likewise than in the previous year, only with one exception. A strong precipitation with 40 mm amount of water per day increased the water level about 1 m for one day in June. Equally the radon concentration in borehole water increased after this rainfall. After that both the values of ^{222}Rn activity concentration and the height of water level returned to the previous state quickly.

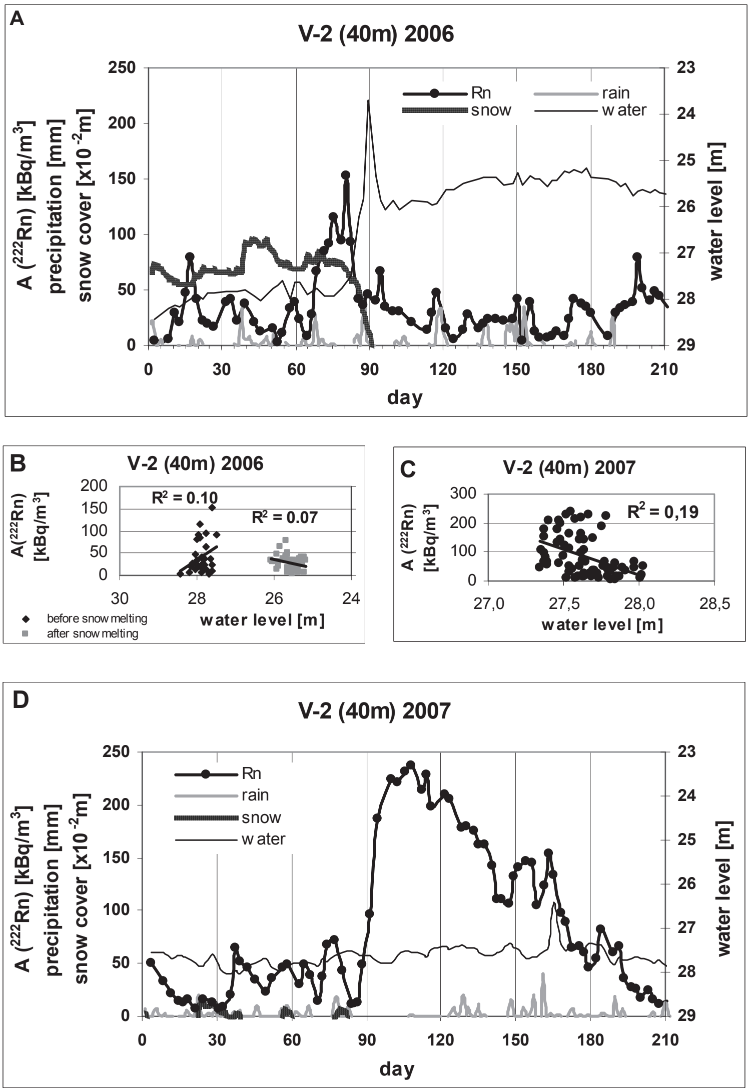

Fig. 4 The courses of the ^{222}Rn activity concentration in water, precipitation amount, the state of the water level and snow cover in V-2 borehole from January to July in 2006 (A), in 2007 (D). No correlation of ^{222}Rn activity concentration in water and the state of water level in borehole was observed (B, C)

V-3 BOREHOLE

In V-3 borehole the lowest values of the ^{222}Rn activity concentration in water were measured. The positive correlation between radon concentration in water and the state of water level in this borehole appeared in both periods of our investigation.

The snow melting in 2006 caused the rise of water level in V-3 borehole at the end of March 2006, but it was not so conspicuous like in the same time in V-1 and V-2 boreholes.

In comparison with previous year, there was no water in V-1 borehole during January 2007, because of the precipitation deficiency last autumn. The first snow melting at the beginning of February brought the increase of water level from the state under the bottom of this borehole to nearly 4 m. Following snow meltings increased the water level to the 3 m.

After significant precipitation (20mm), identically like in V-1 borehole, the water level started to rise. However, the growth of water level was slower and much lower in comparison with V-1, it reached only up to 2 m. In 2007 the increase of the water level after the precipitation was only negligible, up to 1 m.

During both years of our study, the radon concentration in V-3 borehole increased when the amount of precipitation was more than 20 mm. The higher values of ^{222}Rn activity concentration lasted approximately for 20 days in 2006 and for 15 days in 2007. Since May 2007 the influence of precipitation has not been clearly observed.

From April 2007 the water level started receding considerably due to precipitation deficiency. Equally the radon concentration in water started to decrease. The falling of water level in 2007 was more rapid than in 2006, because of the precipitation shortage in spring months.

At the end of July there was no water in V-3 borehole in both years of our research. Identically, the radon concentration in borehole water was very low. Similarly, the strong precipitation with amount of 40 mm occurred a few weeks ago, was not able to convert this situation in the both compared periods.

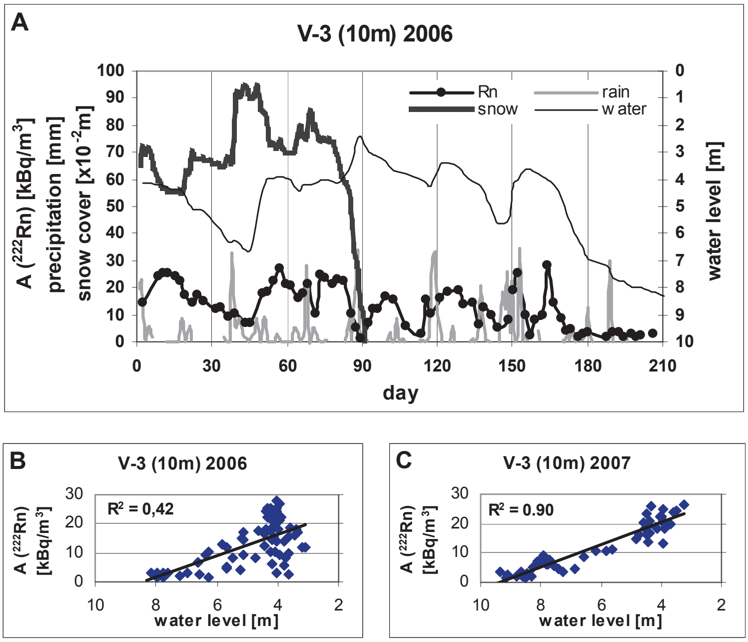

Fig. 5 The courses of the ^{222}Rn activity concentration in water, precipitation amount, the state of the water level and snow cover in V-3 borehole since January to July in 2006 (A), in 2007 (D). The positive correlation between ^{222}Rn activity concentration in water and the state of water level in borehole was observed (B, C)

DISCUSSION

The responses of all three boreholes V-1, V-2 and V-3 to the precipitation were not of the same type. It was confirmed in both years of the monitoring.

The results obtained during both years of the research show that both V-1 and V-3 boreholes were affected by precipitation, if the precipitation amount was more than 20 mm per day. The infiltrated water increased immediately the water level in those boreholes. In V-1 borehole the growth of water level was approximately one meter higher than in V-3, due to the different position of those boreholes. All three boreholes are situated on the slope of the hill above the observatory. The V-3 borehole, together with V-2, is situated about 9 m higher than V-1. During the raining a part of water soaks into the soil, another part flows down the hill and this way could contribute to the higher increase of water level in V-1 borehole. As the groundwater drains away to the valley, the water level in V-1 and V–3 boreholes is falling until the next intense precipitation.

At the beginning of summer the water level in V-1 and V-3 boreholes started to decrease rapidly because of warm weather and stronger evapotranspiration. Usually in summer the groundwater level is under the bottom line of those two boreholes. In 2007 this process started earlier, because of a precipitation deficiency in spring months. Neither the heavy raining with precipitation amount of about 40 mm per day could not change the water level falling.

In V-2 borehole no influence of the precipitation to the water level changes was observed. Only in June 2007, after the heavy raining, the water level increased about 1 m, but it decreased rapidly. The water level in this borehole is too deep under the surface to be affected by precipitation.

The precipitation significantly influenced also the radon content in borehole water in V-1 and V-3, but not in the same way. While in V-1 the negative correlation of the ^{222}Rn activity concentration to the increase of water level after the precipitation was observed, in V-3 the positive correlation was found out. The possible explanation of this phenomenon is in the different way of enrichment of borehole water with radon. While in V-1 and V-2 radon transport from the underlying granodiorite body is prevailing, in V-3 the radon supply comes from the radon transported by precipitation water from air of soil and rock fissures.

All three boreholes were drilled in the quartzite, folded in granodiorite. The maximal thickness of quartzite is about 50 m. The bottom of V-1 and V-2 borehole is located much lower in comparison with V-3. We suppose that granodiorite is the main source of radon in water for V-1 and V-2 boreholes, because their bottoms are closely to the granodiorite body. Radon created in mineral grains of granodiorite is transported upwards through the rock fissures filled with groundwater. Therefore radon concentration in borehole water is much higher in comparison with V-3 borehole.

The bottom of V-3 borehole is situated in higher level above granodiorite than V-1 and V-2. Probably the connection of rock fissures is also not advantageous for a radon transport from below. On the other hand the enrichment of borehole water after the precipitation was noticed. The rainfall water during the soaking catches radon from the air of soil pores and rock fissures and brings it to the borehole water.

In V-1 borehole was observed, that the precipitation reduces radon concentration in borehole water, because infiltrated water has a lower activity concentration in comparison with groundwater in this borehole. As the water in V-1 is sinking, the transport of radon from granodiorite prevails and radon concentration in borehole water is restored to the previous stage until next rain.

The variations of ^{222}Rn concentration in V-2 borehole were not connected with precipitation. In 2006 the maximum appeared in the beginning of snow melting. It was probably caused by water transport to the borehole. When the whole area was covered by a thick layer of snow and the upper layer of soil was frozen, the exhalation rate of radon from soil was very low. The radon could not escape to the atmosphere and it was accumulated in soil and rock pores and fissures. The soaking water from melted snow could enrich the borehole water with radon this way. The explanation of a very expressive maximum in 2007 is difficult. The rise of radon concentration was very quick, but the decrease lasted for three months. It was connected neither with snow, nor with precipitation. The decrease was much slower in comparison to the radon decay.

The influence of the snow melting to the water level changes and radon content in borehole water was noticed in all three boreholes. In 2006 a large amount of snow covered the whole study area for three months. The snow melting intensively increased the water level in boreholes to the higher state of the year in V-1 and V-2 borehole. The increase in V-3 was not so significant. Simultaneously the radon concentration in water decreased due to infiltration of non active water into a borehole. Contrary to 2006, in 2007 the snow cover was very poor. However, the snow melting increased the water level in V-1 and V-3 boreholes. Also the radon concentration in those boreholes was changed, similarly like after the precipitation.

CONCLUSION

The values of ^{222}Rn activity concentration in all studied boreholes were very different in both years of the investigation. The highest radon concentrations were measured in V-2 borehole, the lowest in V-3.

The different responses of the studied boreholes to the precipitation were confirmed in both years of our research. While V-1 and V-3 boreholes were significantly affected by precipitation with an amount more than 20 mm, in V-2 borehole this phenomenon was not observed.

The precipitation caused the rapid increase of water level in V-1 and V-3 boreholes. In spite of this, the courses of the ^{222}Rn activity concentration were not the same. In V-1 the negative correlation of radon concentration in water to the water level in borehole was observed, in V-3 the positive correlation. This phenomenon is probably caused by the different type of an enrichment of borehole water with radon. While in V-1 the radon comes mainly from underlying granodiorite body, in V-3 the radon is supported by infiltrated precipitation water from the air of soil pores. In the case of V-1 borehole, infiltrated precipitation water reduces radon concentration in borehole water.

In V-2 borehole no influence of precipitation was observed with one exception after the strong precipitation in June 2007. Similarly like in V-1, the borehole water is enriched by radon from granodiorite.

All three boreholes were affected by snow melting. It was clearly observed in 2006, when the snow cover was massive. After the melting of snow, the water level increased rapidly, simultaneously the radon concentration in borehole water decreased in every borehole. In 2007 snow melting affected only V-1 and V-3 boreholes, due to not permanent and poor snow cover. The effect was the same like in the case of precipitation.

Because of hot weather and strong evapotranspiration, during the July/August the groundwater level in V-1 and V-3 decreased under the borehole bottom in both years of the research. In V-2 the water occurred permanently.

Acknowledgement

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CONTINUOUS MONITORING SYSTEMS FOR INDOOR RADON MEASUREMENT: CONSTRUCTION AND RESULTS OF THEIR TESTING

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ABSTRACT

Műllerová M., Holý K., Bujnová A., Polášková A. & Holá O. **Continuous Monitoring Systems for Indoor Radon Measurement: Construction and Results of their Testing**

Two continuous radon monitoring systems were built on the basis of the scintillation chambers. The first system used the large volume scintillation chamber with the volume of 4.5 liters and the second one the commercial scintillation chamber with the volume of 1 liter as the detectors for radon concentration measurement. Both systems were calibrated by Ward–Borak method. The detection limits of monitoring systems are 2.9 $Bq{\cdot}m^{-3}$ and 5.1 $Bq{\cdot}m^{-3}$ respectively, at – 2 hour counting period and 30% statistical uncertainty.

The radon monitoring systems and the professional radon monitor AlphaGUARD were tested in real conditions of working room. The testing showed that long-term courses of radon activity concentrations obtained by all three monitors are highly correlated ($R^2 \sim 0.95$). Also the average values of radon activity concentrations calculated on the basis of measured data are identical in the scope of counting errors already at the measurement of the radon activity concentrations in the range of (10–120) $Bq{\cdot}m^{-3}$.

Key words: indoor radon, radon monitor, radon variation, continual measurement, calibration

INTRODUCTION

Under the term ‘indoor air’ we understand the air inside flats, houses or other enclosed areas. Main sources of radon (^{222}Rn) in buildings are underlying rocks, building materials, outdoor atmosphere and, to a lesser extent, the tap water and natural gas.

Radon gets into enclosed spaces by exhalation from the floors, walls and cracks in the rooms. Radon concentration in the indoor atmosphere is not stable. As a rule in the indoor air the radon concentration is being changed in a relatively short time [1]. The measurement and the study of these changes are possible by means of the continuous radon monitors [2–6]. A correct calibration and verification of their operation in the environment with changing radon concentration is a precondition of their successful utilization. This paper describes constructions and results of testing three continuous radon monitors which are used for radon diagnoses of inhabited buildings.

RADON MONITORS

The first radon monitor (SCH 1L) is built on the basis of the scintillation chamber of Lucas type with the volume one liter. The inner wall of the chamber is coated with ZnS(Ag). Scintillations are collected through the glass window to a photomultiplier tube which is placed at one end of the chamber. The flow rate of the air through the chamber is 0.6 $l{\cdot}min^{-1}$. The sensitivity of the scintillation chamber is 0.06 cpm at 1 $Bq{\cdot}m^{-3}$ of ^{222}Rn concentration.

The chamber background measured at the stable flow of the inactive air through the chamber is about 0.1 cpm.

As the second radon monitor was used AlphaGUARD monitor (AG) developed by Genitron Company [7]. In AlphaGUARD cylindrical ionization chamber in combination with DSP-technologies is used for radon concentration measurement. The active volume of the ionization chamber is equal to 0.56 liters. The measured gas enters the ionization chamber via a large surface glass fiber filter in a diffusion mode. The sensitivity of the detector is 0.05 cpm at 1 Bq·m^{-3} of ^{222}Rn concentration. The background signal due to an internal detector contamination is less than 1 Bq·m^{-3}. AlphaGUARD was operated in the flow mode at the flow rate of the air through the monitor of 0.6 l·min^{-1}.

The third radon monitor (LSCH) is built on the basis of the large scintillation chamber. The chamber has a cylindrical shape. The inner diameter is 120 mm and its length is 400 mm. The volume of the chamber is 4.5 liters. To achieve good geometrical conditions for radon detection the inner space of the chamber is divided into 9 sectors. The walls of the sectors are coated with ZnS(Ag). Scintillations are collected through two glass windows placed at the ends of the chamber to two photomultiplier tubes. At the flow rate of the air through the chamber of 0.5 l·min^{-1} and with an aerosol filter closely outside the chamber inlet the sensitivity of the scintillation chamber is 0.3 cpm at 1 Bq·m^{-3} of ^{222}Rn concentration. The chamber background measured at the stable flow of the inactive air through the chamber is about 2.4 cpm.

RESULTS AND DISCUSSION

For the comparison of an operation of radon monitors the radon concentration was measured in the same unventilated room. During the measurement the air was being sucked in with the flow rate of 0.6 l·min^{-1} through one liter scintillation chamber and simultaneously through AlphaGUARD and with the flow rate of 0.5 l·min^{-1} through a large scintillation chamber. For the large and one liter scintillation chamber the radon activity concentrations corresponding to the time interval of 2 hours were calculated on the basis of every 30 minutes records according to the method published by Ward and Borak [4]. AlphaGUARD monitor was operated in flow mode with a 10-minute lasting measuring cycle. On the basis of the recorded data the average radon activity concentrations corresponding to the time interval of 2 hours were calculated.

In Fig. 1 the air supply line for one liter scintillation chamber and AlphaGUARD is shown and in Fig. 2 for the large scintillation chamber. In the Fig. 3 there are shown courses of the radon activity concentration measured by all three monitors. For an illustration there was chosen such case of measurement where the course of the radon activity concentration was not regular during the whole measured interval. The radon activity concentration shows noticeable changes. The regular variations with the low amplitude and low average values of the radon activity concentration measured an 27/3/2007 – 1/4/2007 and 6/4/2007 – 13/4/2007 correspond to the unventilated room. In the time period from 1/4/2007 till the 6/4/2007 an additional radon source to the room was brought in. The regular variations showed larger amplitudes than in previous days. In the time interval from 8:00 a.m. till 10:00 a.m. of April 4th, the room was ventilated by opening the windows.

Further, as can be seen in Fig. 3, the courses of the radon activity concentration measured by means of all monitors are almost identical. Even in some details it is possible to find the same responses of all the monitors. All three devices recorded a growth during the 1/4/2007 and also an intense

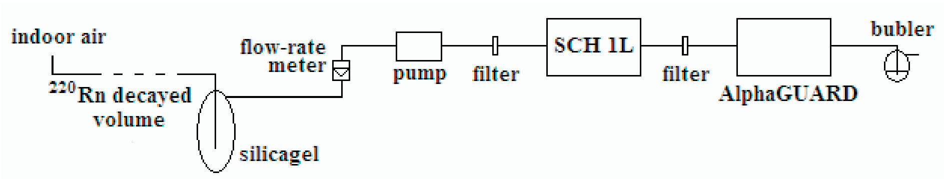

Fig. 1 The continuous monitoring system for the ^{222}Rn measurement in indoor air on the basis of one liter scintillation chamber and AlphaGUARD monitor

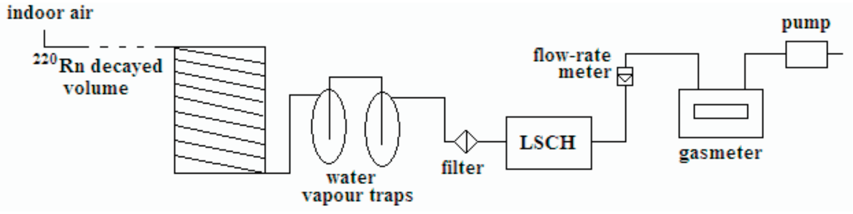

Fig. 2 The continuous monitoring system for the ^{222}Rn measurement in indoor air on the basis of the large scintillation chamber

decrease on 4/4/2007 during the time interval 8:00–10:00. The average value calculated from the radon activity concentration measured during the whole period is (50.7 ± 7.6) Bq·m^{-3} for AlphaGUARD monitor, (47.0 ± 7.1) Bq·m^{-3} for one liter scintillation chamber and (42.9 ± 6.4) Bq·m^{-3} for the large scintillation chamber, which is a good agreement in the scope of counting errors.

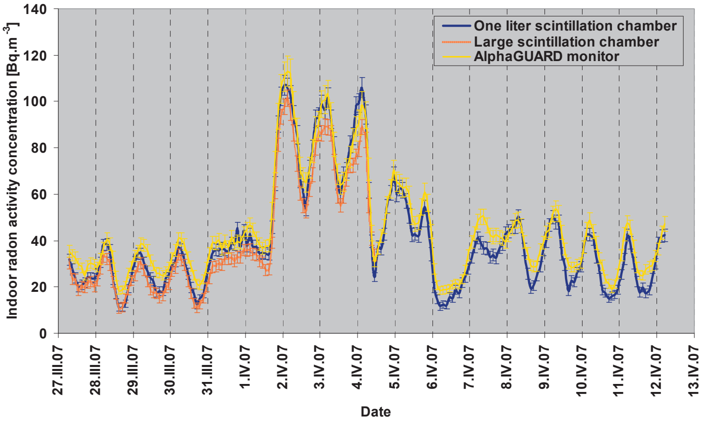

Fig. 3 ^{222}Rn activity concentration in the room measured by three radon monitors

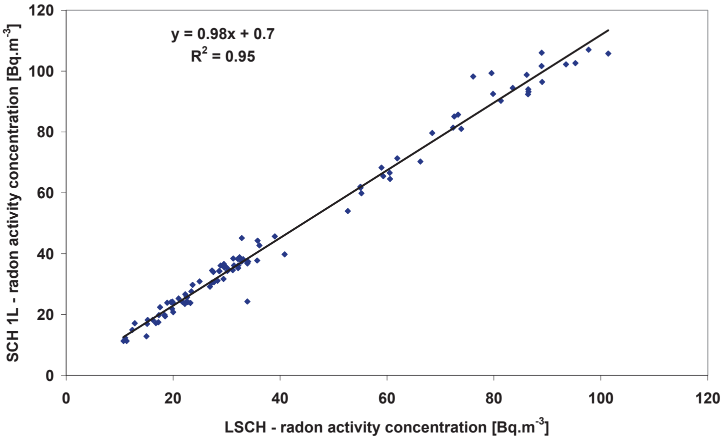

Fig. 4 Correlation plot of the ^{222}Rn activity concentration measured by a large scintillation chamber and by one liter scintillation chamber

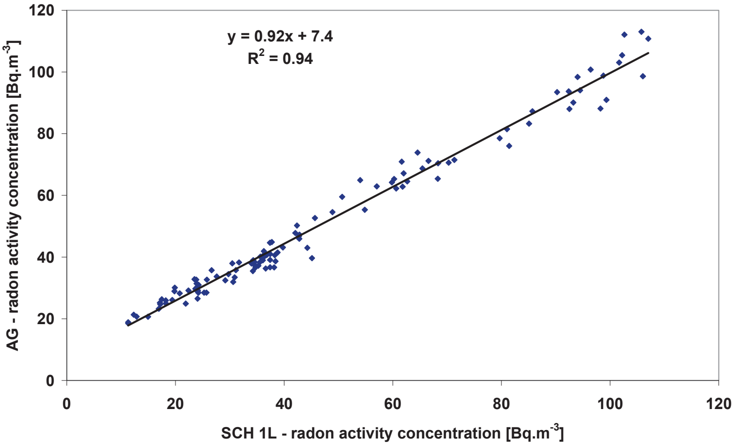

Fig. 5 Correlation plot of the ^{222}Rn activity concentration measured by one liter scintillation chamber and AlphaGUARD monitor

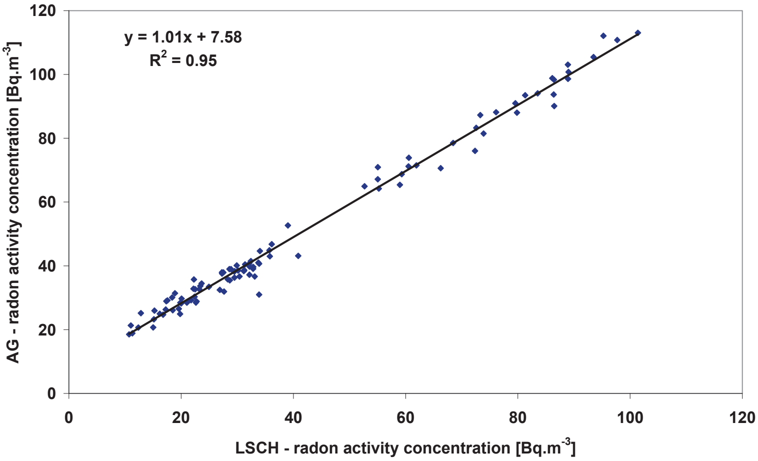

Fig. 6 Correlation plot of the ^{222}Rn activity concentration measured by a large scintillation chamber and AlphaGUARD monitor

The figures 4, 5 and 6 show the correlation plot of radon concentrations measured by one liter scintillation chamber and the large scintillation chamber, one liter scintillation chamber and AlphaGUARD monitor, and the large scintillation chamber and AlphaGUARD monitor, respectively. The relations between radon activity concentrations measured different radon monitors are linear and the correlation coefficients are very high ($R^2 \sim 0.95$). However, as can be seen in Fig. 5 and 6, AlphaGUARD records radon activity concentrations a few percent higher than the other two monitors. It is caused mainly by the difference in the measurement of daily variations where AlphaGUARD provides higher values of radon activity concentrations in their minima than scintillation chambers (Fig. 7).

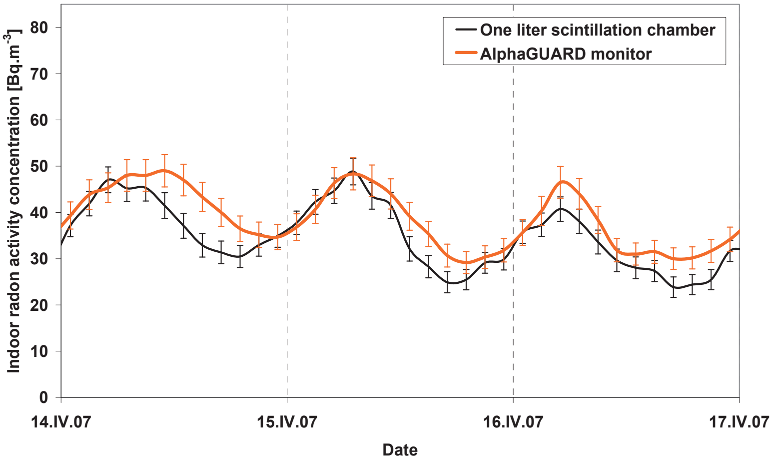

Fig. 7 The courses of the ^{222}Rn activity concentration measured by one liter scintillation chamber and AlphaGUARD monitor

Tab. 1 Detection limits of radon monitors for 2 h counting period and 30% statistical uncertainty

Monitor	AG	SCH 1L	LSCH
Detection limit [Bq·m^{-3}]	4.6	5.1	2.9

The detection limits of radon monitors for 2-hour counting period and 30 % statistical uncertainty are shown in Tab. 1. As can be seen the highest sensitivity has the monitor built on the basis of the large scintillation chamber. The sensitivities of other two monitors are mutually comparable. Compactness and high sensitivity are advantageous features of the AlphaGUARD monitor but monitors based on scintillation chambers are better adaptable for different conditions of radon measurements.

CONCLUSION

We built two radon monitoring systems on the basis of scintillation chambers and compared the operation of three continuous radon monitoring systems in the real conditions. The results of tests show that the records of radon activity concentrations of all three monitors are very similar and average values of radon concentrations calculated on the basis of the measured data are identical in the scope of counting errors. Moreover, it was found out that AlphaGUARD provides radon activity concentrations a few percent higher in minimum of daily radon variations than other two monitors. All three monitors can be successfully used for solving different problems of radon diagnosing of inhabited buildings starting from the level of radon concentration of some Bq·m^{-3}.

Acknowledgments

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INFLUENCE OF THE DUMP SITES ON DEVELOPMENT OF SELECTED PLANT TISSUES AT THE ĽUBIETOVÁ AREA (SLOVAKIA)

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ABSTRACT

Andráš P., Mamoňová M., Ladomerský J., Turisová I., Lichý A. & Rusková J. **Influence of the Dump Sites on Development of Selected Plant Tissues at the Ľubietová Area (Slovakia)**

Natural installation and development of plant species such as *Pinus sylvestris, Betula pendula, Quercus petraea, Salix fragilis, Mentha longifolia, Acetosella vulgaris, Juncus articulatus* can be observed at the old mine waste dumps in the Ľubietová – Podlipa (Zelená Valley, Slovakia) area, specific to the local chemical conditions such as low content of essential nutrients and high content of heavy metals (Fe, Cu, As, Sb, Cd and others). Content of heavy metals and landscape features of the dump material are not appropriate for the vegetation development. The individual parts of the plant tissues (roots, branches/stems, leaves/needles, flowers/fruits) are contaminated by heavy metals and tissues are damaged differently, respectively.

Key words: mining dumps, heavy metals, contamination of plant tissues

INTRODUCTION

First written evidence about mining activity in the Ľubietová area came from the Anjou monarchy time in 1340 [1]. Ľubietová deposit was historically important by mining of copper ores. Gold was obtained in small amount as well. The biggest boom of mining activity was in the fifteenth and the sixteenth century and lasted for almost 200 years. This period ended by Turkish invasions in 1571–1588. In the eighteen century, iron became the main component for mining production.

The revival of mining activity was in 1810 and the attenuation in 1863. In the period 1860–1870 decline of the European copper mining activity due to competition of oversea ore deposits caused the stopping of mining activity in the Ľubietová area for more than 100 years and mining dumps were interesting only for researchers and mineral collectors [2]. Hydrothermal ore mineralization is evolved at 3 deposits: Podlipa in the east border of village, Svätodušná and Kolba in the closure of the Peklo Valley, 5 km east of village where cobalt, silver and nickel are observed besides iron and copper.

The most important Podlipa deposit dump-field, which represents about 2 km^2 area, is situated 1 km east of the village center, at the south slope of the Vysoká spot height (995.5 m), in western direction from the Zelená Valley (Fig. 1). It is situated in the Ľubietová crystalline complex of Permian age which consists of greywackes, arcose schists and conglomerates [1]. The deposit was exploited by 18 adits from 570 to 700 m (Fig. 1), from the bottom adit Empfängnis to the top adit Francisci [3]. Copper content in manually graded ore was about 4–10 wt. %. Copper content in dump waste material was 0.9–2.4 wt. % [1, 4].

Heavy metals can reach plants from the soils due to their higher content in the base rocks or from the sources of different anthropogenic activities. Heavy metals from the air pollutants can reach plants through pores/water or soil solution [5]. Their penetration influences soil-ecological conditions such as soil types, soil pH, concentrations and bonds of heavy metals, humus content in soil, oxidative-reductive conditions around root system connecting with microbial decomposition of inorganic and organic substances, soil moisture, temperature, utilized fertilizes and preparations for plant protection [6].

Natural installation of mine waste dumps by plants is inhibited due to fine-grained soil flushing from the slopes and fast draining of rain water from the surface into the basal level of dumps or into the impermeable sub-soil by soil-forming substratum. Therefore only several large mine waste dumps provide the possibility to enroot to resistant plants in depressions or at local plains after centuries. Many authors have devoted to the study of plant contamination at the mine waste dumps in recent years [7–12].

The main aim of the presented work was the monitoring of heavy metal pollution in different plant tissues. We sampled also the stream water, drainage water (both from the reference and contaminated sites), and water from wetland situated beneath the dump-field to get sense about the source of the studied heavy metals and about their migration.

MATERIAL AND METHODS

The samples (of about 10 kg weight) of sediments from the dumps and soils from the 15–20 cm depth, surface water (stream water, drainage water, and water from wetland) were collected for the characterization of components of landscape contamination. To each water sample of 1 000 ml volume was added 10 ml of HCl Following reference sites were selected for comparison of territories loaded by heavy metals and non-contaminated natural environment: planes A and B (Fig. 1) are situated outside of geochemical anomalies of heavy metals and represent graywakes of Permian age, similar to material at the dump-field. The samples of plant material were collected from the contaminated planes C, D, E, F (Fig. 1). Planes C and D are situated on the terrace of the highest dump, plane G is below the dump of the Empfängnis adit and plane E is the wetland below the dump-field.

The realization of the plant sampling was difficult at the contaminated planes C and D due to missing vegetation cover. Vegetation creates small isles and is enrooted in few depressions which have enabled limited soil-forming process. The selection of plant species was performed so that it could be possible to compare all identical plant species from the contaminated planes with plants from the reference sites. The samples of hardwood species (*Betula pendula, Quercus petraea, Salix fragilis*), coniferous species (*Pinus sylvestris, Abies alba, Picea abies*) and herbs (*Juncus articulatus, Mentha longifolia*) were studied. The samples of *Acetosella vulgaris* were collected at the contaminated planes. At everyone site 10 individuals of each plant species were sampled to get average sample Five coniferous individuals of approximately same age were sampled for branches (in case of *Picea abies* also needles) from the fourth or fifth spike with approximate length of segment from 10 to 15 cm. In the case of *Pinus sylvestris* were analysed two-years old needles. Roots of the same length and with 2–3 cm diameter were obtained from the surface soil level. Similar mode of sampling was used for hardwood species: 3–4 years old branches were sampled from the lower limbs. The samples were dried at laboratory temperature and then homogenized.

The samples of technogenous sediments from the dumps and soils were dried and 0.25 g of sample was heated in HNO_3-$HClO_4$-HF to fuming and taken to dryness. The residue was dissolved in HCl. Solutions were analysed by ICP-MS analyse in the ACME Analytical Laboratories (Vancouver,

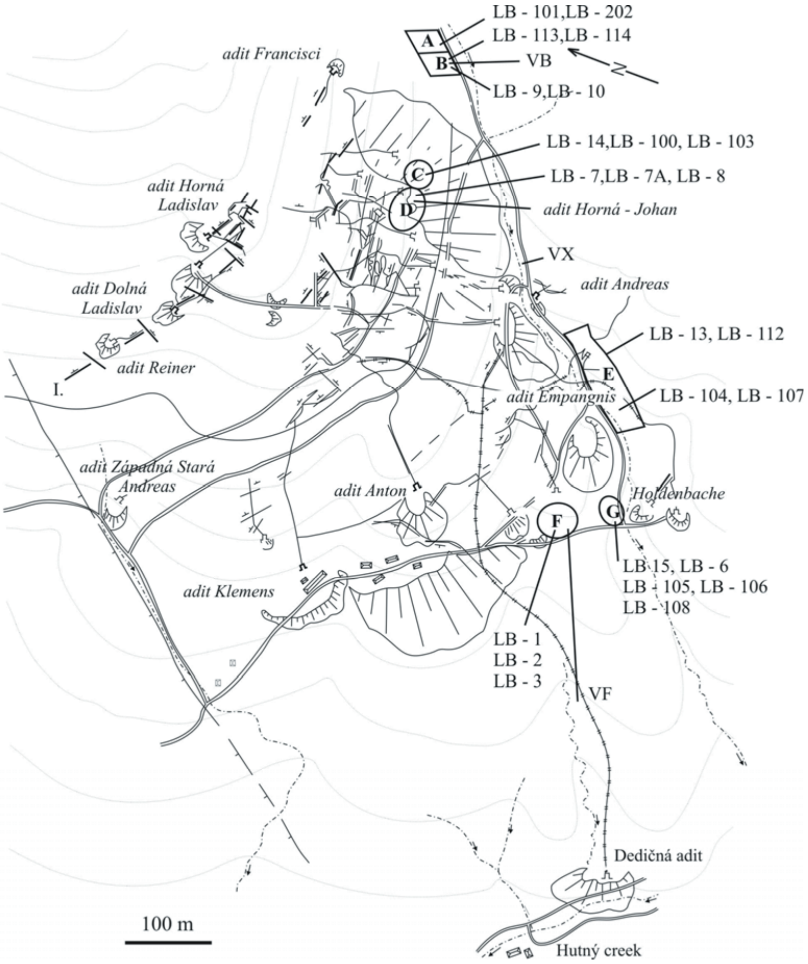

Fig. 1 Podlipa dump-field

Canada). Plant samples were divided into roots, branches/stems, leaves/needles and flowers/fruits. 0.5 g of vegetation sample was after split digestion in HNO_3 and then in Aqua Regia analysed by ICP-MS for ultralow detection limits. The contamination of live and dead parts was compared in several plants. Plants were analyzed in the same laboratory as sediments. As and Sb were analysed in the laboratories of Geological Institute of the Faculty of Natural Sciences, Comenius University, Bratislava. The samples were pressure-decomposed in Aqua Regia and analysed using electrotermic atomization. The water samples were analyzed in the National Water Reference Laboratory for Slovakia at the Water Research Institute in Bratislava. Microscopical analyses of plant tissues were realized in the laboratories of the Department of Wood Science and Technology of the Technical University Zvolen.

RESULTS AND DISCUSSION

Sediments and drainage water contamination by heavy metals

Table 1 presents concentrations of Fe, Cu, Zn, Pb, Ag, Cd, Ni, Co, As and Sb in the sediments from the reference sites A and B and contaminated planes C – F. Soil from the reference site A contains surprisingly the highest Zn concentrations. Sediments from the dump plant C contain the highest concentrations of Fe, Pb, Ag, Ni, Co, As and Sb. Site E shows the highest Cu and site C the highest Co concentrations. Sediment from the wetland (plane E) contains mostly Cu (6766 ppm). Sediment from the plane F is mostly contaminated by Cd and Zn (with exception of the Zn concentration in reference site A).

Water sample VX from the Zelená Valley below mine waste dumps has the lowest pH from the collected surface water (tab. 2). This sample has the highest concentrations of Fe and Cd. Sample VF has pH 6.7 and the highest concentrations of Cu (810 µg/ml), Zn (30 µg/ml), Ag (2 µg/ml), Ni (8 µg/ml) and Sb (0.2 µg/ml) and Co (7.0 µg/ml). The comparison of water from the reference plane with other water samples shows its gradual saturation by heavy metals from the dump material. Concentrations of heavy metals culminate in the wetland where is assumed partial precipitation of metals.

Plant tissues contamination by heavy metals

The knowledge of content of heavy metals in plants is important from the point of foot cycle contamination. The intensity of plant contamination by heavy metals is necessary to critize dependence up on plant species.

Leaves are the most contaminated part of *Mentha longifolia* in case of all observed heavy metals at the dump-field and reference site (tabs 3 and 4). As and Sb analysis shows higher contamination of flowers where As content is 1.44 ppm and Sb content is 2.07 ppm. Similarly. the highest concentrations of heavy metals (with exception of As. Sb. Cu and Ag) were determined in leaves of *Acetosella vulgaris* from the valley below the dump-field besides As and Sb (tab. 3). Plant roots are the most contaminated part of *Juncus articulatus* from the wetland besides Cu and Sb (tab. 3). The highest

Tab. 1 Ľubietová, analyses of the dump-field sediments

	Fe	Cu	Zn	Pb	Ag	Cd	Ni	Co	As	Sb
Sample	**%**	**ppm**								
A	1.38	25	39	16.1	0.1	0.1	8.5	5.1	7	10.4
B	1.12	390	36	13.6	0.3	0.1	7.8	7.1	32	17.5
C	2.58	541	20	24.1	1.6	0.1	31.6	53.6	294	39.2
D	2.14	1977	23	7.9	0.3	0.1	17.1	36.2	34	15.6
E	2.25	6766	19	17.7	0.7	0.1	25.8	34.9	153	26.4
F	1.61	1388	29	16.2	0.6	0.3	16.6	15.1	85	17.7

Explanations to the tab. 1–4: localization of samples is marked at fig. 1

Tab. 2 Ľubietová, spectrochemical analyses of surface and drainage water

Sample	pH	**Fe**	**Cu**	**Zn**	**Pb**	**Ag**	**Cd**	**Ni**	**Co**	**As**	**Sb**
		ppb									
VB*	6.3	221.0	14.2	0.0	0.0	0.2	0.2	2.7	0.0	0.00	0.0
VB**	6.5	299.0	25.8	0.0	0.0	0.6	0.4	5.3	0.0	0.02	0.0
VB***	6.5	260.0	20.0	0.0	0.0	0.4	0.3	4.0	0.0	0.01	0.0
VX*	5.7	342.5	34.1	4.3	0.0	1.0	0.3	5.1	2.6	0,00	0.1
VX**	7.1	297.7	35.9	5.3	0.1	1.2	0.7	5.3	3.0	0.01	0.1
VX***	6.4	320.2	35.0	4.8	0.1	1.1	0.5	5.2	2.8	0.01	0.1
VF*	6.5	164.2	795.3	34.6	0.0	1.6	0.5	7.7	6.2	0.01	0.1
VF**	6.9	156.4	824.7	25.4	0.0	2.4	0.5	8.3	7.8	0.01	0.3
VF***	6.7	160.3	810.0	30.0	0.0	2.0	0.5	8.0	7.0	0.01	0.2

Explanations:

** sampled on June 2006 after rainfall*
*** sampled on June 2007 in dry season*
**** average sample*

concentrations of Fe. Cu. Cd. Ni. As and Sb were determined in the plant tissues from the reference site in root system (tab. 4).

Concentrations of Zn, Pb, Ag and Co are the highest in leaves and stems. *Quercus petraea* shows an important contamination by heavy metals in roots at the dump-field (tab. 3). The exception is a moderate As increase (0.77 and 0.64 vs. 0.50 ppm) in its leaves and branchess.

Contamination of *Salix fragilis* from the wetland below the dump-field is significant in leaves (tab. 3). Cu, Co, As, Zn and Sb are concentrated in roots. The highest Ag concentrations are in branches. Leaves of *Betula pendula* from the dump-field are the most contaminated part (tab. 3). Exception is the preferential contamination of Pb. As and Sb in roots. *Pinus sylvestris* from the dump-field and reference plane tends to preferential contamination of leaves (tabs. 3

Tab. 3 Analyses of plant tissues from dump-field Ľubietová – Podlipa

Plant	Site Sample	Part of the plant	Fe	Cu	Zn	Pb	Ag	Cd	Ni	Co	As	Sb
			ppm									
Betula pendula	D LB-7	a	91.7	7.1	16.80	24.1	0.02	0.08	5.80	0.90	2.14	2.90
		b	158.5	6.6	16.70	18.6	2.90	0.04	3.50	0.70	1.50	0.30
		b_2	308.9	8.6	71.30	75.6	16.90	0.15	10.70	6.70	0.50	0.10
		c	380.0	25.3	35.40	3.8	8.20	0.08	10.90	3.40	1.29	0.14
Quercus petraea	C LB-100	a	274.6	9.2	59.00	57.1	40.10	0.10	11.80	3.50	0.50	0.25
		b	204.1	0.0	41.70	4.7	2.04	0.10	4.70	1.00	0.64	0.09
		c	85.2	8.1	10.30	28.6	30.30	0.06	3.70	1.00	0.77	0.11
		d	210.0	6.5	14.60	17.1	0.02	0.05	3.00	1.10	0.37	0.07
Pinus sylvestris	C LB-103	a	156.8	28.1	15.00	14.5	0.70	0.03	2.70	2.30	0.42	0.50
		b	164.6	2.9	15.70	32.2	3.04	0.03	2.50	1.30	0.56	0.13
		b_2	143.0	0.0	16.70	20.5	0.10	0.03	2.30	1.10	0.62	0.11
		c	148.5	59.9	44.30	38.3	8.00	0.10	4.90	2.50	0.15	0.04
		d	95.4	6.8	12.80	15.2	0.04	0.03	2.70	1.60	0.41	0.10
Picea abies	C LB-14	a	221.8	7.5	32.40	38.6	0.07	0.07	6.10	6.10	3.14	0.53
		b	158.2	12.1	16.05	2.0	0.82	0.04	9.20	0.80	0.59	0.12
		b_2	–	–	–	–	–	–	–	–	0.19	0.12
		c	134.1	10.1	14.60	1.9	0.70	0.03	9.20	0.80	0.85	0.19
Abies alba	D LB-8	a	125.2	10.8	22.14	15.4	3.10	0.06	6.20	1.25	0.49	0.96
		b	221.6	8.0	27.70	15.5	1.40	0.05	5.40	1.80	1.34	0.34
		c	73.2	8.7	8.70	31.5	20.80	0.04	5.42	1.60	2.24	1.14
Juncus articulatus	E LB-1	a	358.0	37.2	85.10	51.4	225.1	0.20	10.20	8.70	19.70	1.52
		b	209.4	70.1	33.20	37.9	4.70	0.10	4.90	2.60	1.40	1.67
		c	208.0	68.3	32.01	35.9	4.00	0.10	4.92	2.55	1.28	1.60
		d	–	–	–	–	–	–	–	–	3.64	0.44
Mentha longifolia	E LB-112	a	246.0	100.4	23.30	16.0	0.20	0.06	4.70	1.20	0.57	0.21
		b	89.4	14.3	13.10	11.4	0.04	0.04	2.40	0.50	0.05	0.08
		c	593.6	173.3	38.30	41.2	2.40	0.10	7.60	3.30	0.76	0.26
		d	–	–	–	–	–	–	–	–	1.44	2.07
Salix fragilis	E LB-2	a	415.6	63.5	84.00	6.0	0.20	0.20	13.00	9.70	2.84	0.21
		b	131.3	0.0	20.80	6.3	5.30	0.05	3.70	0.60	0.26	0.15
		c	565.9	0.0	74.10	98.6	0.80	0.20	21.00	6.20	0.52	0.11
Acetosella vulgaris	E LB-13	a	184.0	133.7	22.30	4.6	0.30	0.06	9.40	5.7	17.31	3.46
		b	176.8	72.9	31.10	23.1	7.40	0.08	12.00	7.70	13.08	3.30
		c	701.0	46.5	185.80	135.1	0.38	0.42	36.30	25.60	12.97	3.27

Explanations to tab. 3 and 4: a – roots; b – live branches and stems; b_2 – dead branches; c – leaves and needles; d – flowers and fruits and 4). Higher contamination by heavy metals (Fe, Cu, Co, As and Sb) in other plant parts is mostly a weak increase of their concentrations compared with concentrations in leaves, e.g. Cu concentrations 8 vs.7. As concentrations 0.16 vs. 0.13. Co concentrations 2 vs. 1.3 ppm in plant from the reference site.

The comparison of additive concentrations of heavy metals in individual types of plant tissues (roots, branches/stems and leaves/needles) was carried out to obtain more complex contamination model of the plant tissues. The comparison was performed with the following wood species and herbs: *Betula pendula, Quercus petraea, Picea abies, Abies alba, Pinus sylvestris, Juncus articulatus, Mentha longifolia*. It was possible to collect their samples from the dump-field and reference site, respectively. The study showed (Fig. 2) that the highest concentrations of Fe, Pb, As, Sb and Zn were determined in the root system. Cu contaminates leaves and needles in preference. Fe probably enters leaves and needles up to certain concentration level in preference. When this concentration level is exceeded, Fe accumulates in root system after it cannot enter leaves and needles.

The contamination of plant tissues of live and dead branchess was compared in several plants from the dump-field (*Betula pendula, Pinus sylvestris, Picea abies*) and reference site (*Betula pendula, Quercus petraea*) (tabs 3 and 4). *Betula pendula* from the dump-field (tab. 3) showed higher As and Sb concentrations in live branches. Higher concentrations of Fe, Cu, Zn, Pb, Ag, Cd, Ni and Co were determined in dead branches. *Pinus sylvestris* (tab. 3) showed higher concentrations of Fe, Cu, Pb, Ag, (Cd), Ni, Co and Sb in live branches

Tab. 4 Analyses of plant tissues from the reference site Ľubietová – Podlipa

Plant	Site Sample	Part of the plant	Fe	Cu	Zn	Pb	Ag	Cd	Ni	Co	As	Sb
			ppm									
Betula pendula	B LB-10	a	192.0	2.0	27.10	19.20	0.02	0.06	5.10	2.30	0.31	0.20
		b	107.7	3.5	16.90	14.80	1.30	0.02	3.00	7.70	0.12	0.27
		b_2	108.8	5.6	41.30	75.60	1.90	0.12	1.70	6.70	0.20	0.05
		c	209.0	6.9	25.50	3.10	5.40	0.07	4.70	1.80	0.14	0.04
Quercus petraea	B LB-9	a	174.2	4.2	32.00	31.10	0.08	0.06	7.82	1.53	0.35	0.19
		b	67.1	0.0	25.40	2.00	0.02	0.04	3.40	1.80	0.06	0.04
		b_2	158.6	3.2	36.30	30.40	0.20	0.06	3.80	1.00	0.63	0.07
		c	123.2	3.1	27.50	22.20	0.05	0.03	2.80	1.30	0.16	0.09
Pinus sylvestris	A LB-101	a	111.1	8.1	10.20	10.80	0.05	0.02	2.00	2.00	0.16	0.51
		b	84.0	0.0	12.80	11.40	1.20	0.02	2.20	0.30	0.04	0.03
		c	136.8	6.6	22.90	17.00	0.10	0.06	4.50	1.30	0.13	0.06
Picea abies	A LB-202	a	121.6	4.5	22.40	28.60	0.04	0.05	4.11	4.10	0.33	0.52
		b	95.2	8.1	10.20	1.15	0.55	0.60	7.10	5.10	0.07	0.06
		c	90.8	7.4	10.01	1.11	0.48	0.52	7.00	4.20	0.17	0.08
		d	84.1	2.1	8.63	0.98	0.60	0.02	8.20	0.70	0.57	0.16
Abies alba	B LB-113	a	98.1	3.4	19.70	10.00	0.80	0.04	5.13	1.11	0.39	1.20
		b	112.8	4.6	20.00	11.80	0.80	0.04	4.30	1.40	0.07	0.03
		c	41.7	3.0	17.20	22.40	3.50	0.03	4.90	0.70	0.15	0.11
Juncus articulatus	B LB-114	a	199.5	34.1	39.50	4.30	0.20	0.08	5.10	1.00	0.59	0.18
		b	103.2	8.8	42.90	15.40	0.50	0.05	3.00	1.30	0.16	0.07
		c	100.4	8.0	38.12	15.41	0.49	0.03	2.99	1.30	0.17	0.05
		d	–	–	–	–	–	–	–	–	0.31	0.06
Mentha longifolia	B LB-101	a	246.0	100.4	23.30	16.00	0.20	0.06	4.70	1.20	0.57	0.21
		b	89.4	14.3	12.10	11.40	0.04	0.04	2.40	0.50	0.05	0.08
		c	593.6	173.3	38.30	41.20	2.40	0.10	7.60	3.30	0.76	0.26
		d	–	–	–	–	–	–	–	–	1.44	2.07

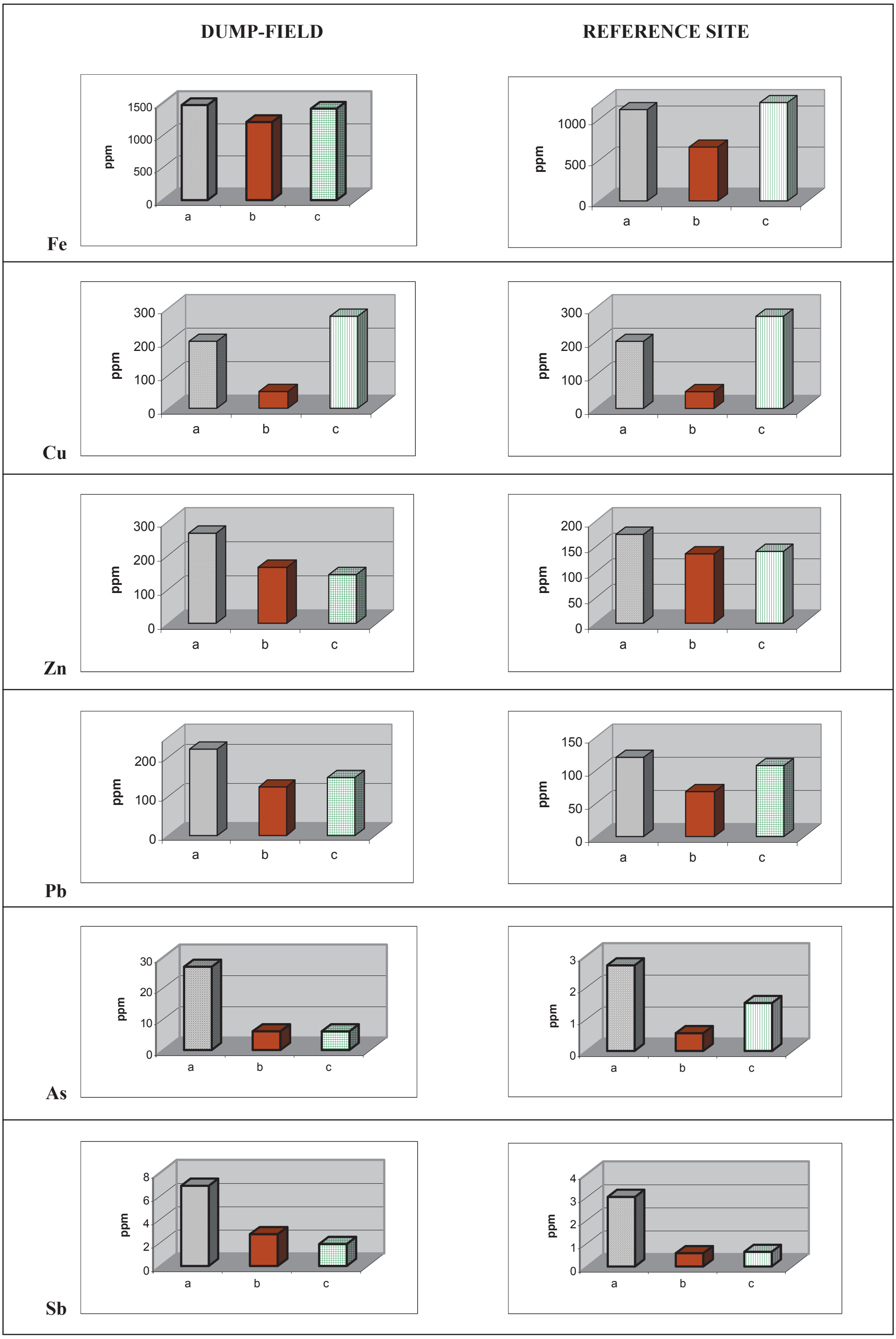

Fig. 2 Cumulative heavy metal concentrations in individual types of plant tissues
a – roots b – branches/stems c – leaves/needles

and higher concentrations of Zn, (Cd), As in dead branches. As and Sb concentrations were possible to compare in *Picea abies* (tab. 3).

Higher As concentrations were in living branches (0.59 vs. 0.19 ppm). Sb concentrations were equal in living and dead branches (0.12 ppm). *Betula pendula* from the reference site (tab. 4) showed higher concentrations of Ni, Co and Sb in living branches. Increased concentrations of Fe, Cu, Zn, Pb, Ag, Cd, Co and As were in dead branches. *Quercus petraea* (tab. 4) showed higher Co concentrations in living branches and higher concentrations of Fe, Cu, Zn, Pb, Ag, Cd, Ni, Co, As and Sb in dead branches.

Plant tissues

Plants at the mine waste dumps have lack of organic nutrients and moisture besides higher concentrations of heavy metals. They mainly populate depressions or weathered parts of the dumps. Permanent plants prevail at the old mine waste dumps. Annual and biennial plants are rare. Year shoots in living branches of *Pinus sylvestris* from the dump-field are narrow (Fig. 3). Anomalous thin-walled tracheides (weak summer wood) were determined in several year shoots from 1994–1999. It shows that secondary coarsening of cell-wall did not pass off and bond between secondary cell-walls of tracheides of reaction wood weakened and exfoliation of summer tracheide cell-wall layers (fig. 4) was described.

Lack of moisture (mostly in summer) is probably the main reason of this state besides contamination of tissues by heavy metals. It is probably the reason of insufficient soil-forming at the dumps. Formation of pressure reaction wood was determined in tissues from 1995–2007 (Fig. 5). Formation of very narrow year shoots has been observed in dead branches of *Pinus sylvestris* from the dump-field over the last 13 years (Fig. 3). Occurrence of numerous calluses with near formation of numerous resin canals was confirmed. Cell-wall coarsening of the summer tracheides is completely missing in the last year shoots. Tracheides of reaction wood in live branches from the reference site are relatively regular.

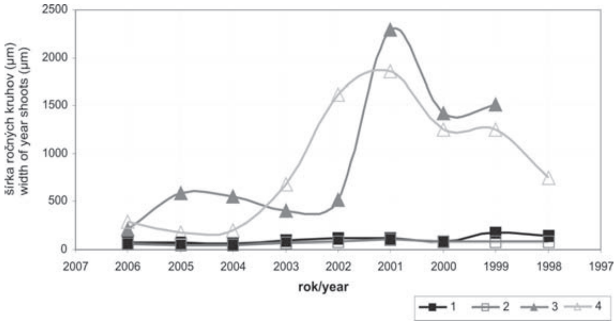

Fig. 3 Comparison of the current year shoots in analysed samples of the ***Pinus sylvestris.***
Dump-field – sample LB-103: 1 – living branches. 2 – dead branches; Reference site – sample LB–101: 3 – living branches. 4 – dead branches

In some samples of *Betula pendula* is visible zonal occurrence of thick-walled fibres (Fig. 7). Exfoliation of secondary cell-wall of summer tracheides is possible to observe in the cross-section. This trend weakened in 1999–2000. Marks of weaken cohesion of secondary cell-wall and its exfoliation extreme narrow year shoots are possible to observe in the cross-section of dead branches.

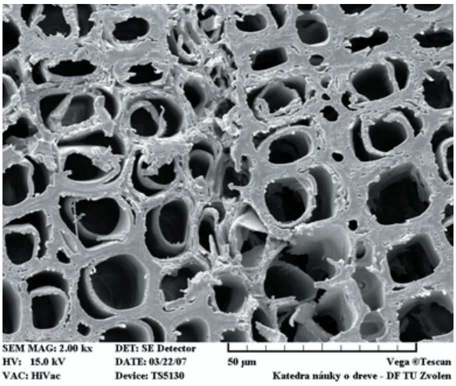

Fig. 4 The living branches of the ***Pinus sylvestris*** from the reference site: exfoliation of summer tracheide cell-wall layers

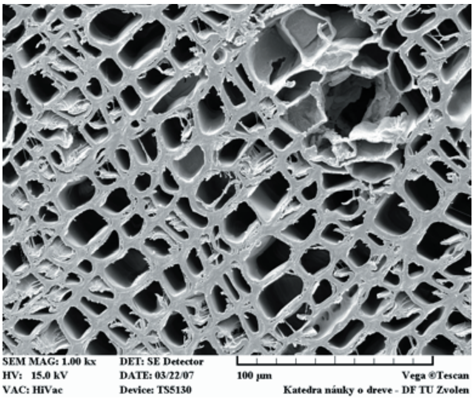

Fig. 5 Compression of wood formation during the 1995–2007 period in the living branches of the ***Pinus sylvestris*** from the dump-field

Fig. 8 shows comparison of width of year shoots from the analyzed samples of *Betula pendula* from the dump-field and reference site. The width of year shoots is narrower in sample from the dump-field. It suggests more stressful conditions for vegetation at the dump-field. The zonal occurrence of thick-walled and thin-walled libro-shaped fibres, scalar perforation and hyphae in vessels is possible to observe in the cross-section of living branches of *Betula pendula* from the dump-field by detail enlargement (Fig. 9). In living branches of *Betula pendula* membranes of axial parenchyma and parenchyma of medullary ray are enzymatic decomposable and parenchyma of medullary ray is without stock substances. Irregular width of year shoots and preferential setting of vessels into radial groups is possible to be observed in the cross-section of live branches from the reference site. Membranes of thinned parenchyma of medullary ray were enzymatic decomposabled.

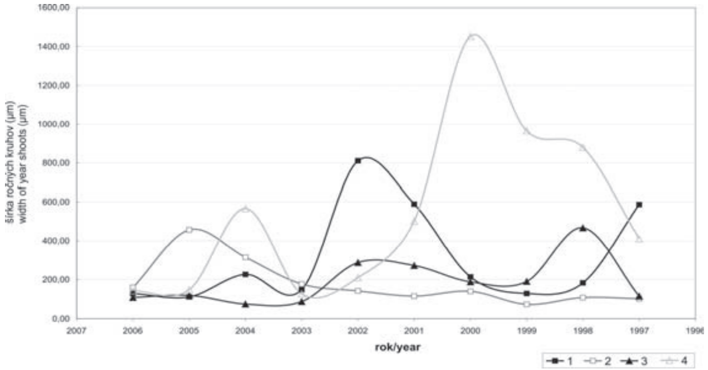

Fig. 6 Comparison of the current year shoots in analysed samples of the ***Betula pendula.*** Sample LB–7 from the: 1 – living branches. 2 – dead branches; sample LB–10 from reference site: 3 – living branches. 4 – dead branches.

Changes of pH and oxidative-reductive potential affect the release and precipitation of heavy metals. It causes the heavy metals transfer into the bottom sediments, solution or soil/rock environment. Bowen [13] states that Ag, As, Cd, Cu, Pb, Sb and Zn metals have the tendency to accumulate in the upper soil horizon due to vegetation recycling, atmospheric deposition and adsorption by organic mass. Fe, Co and Ni metals usually accumulate in higher concentrations in dislocated clay minerals and autigene sesqui-oxides in lower horizon of the soil profile enriched in clay and oxyhydroxide components.

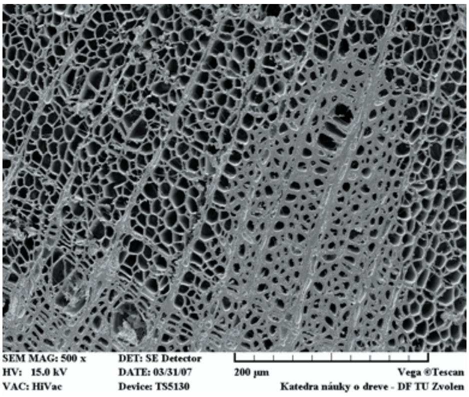

Fig. 7 Living branches of ***Betula pendula*** from dump-field; zonal occurrence of thick-walled fibres.

Plant contamination by Fe causes the atrophy of plant tops and the root coarsening [14]. It has been observed by *Picea abies* where the deformation of tree tops and the formation of „stork nests" has been occurred. Plant contamination by Cu causes the formation of dead stains on lower leaves at steam, purple and violet stem coloring (*Acetosella vulgaris*), atrophy of the root system and leaf chlorosis with green veining.

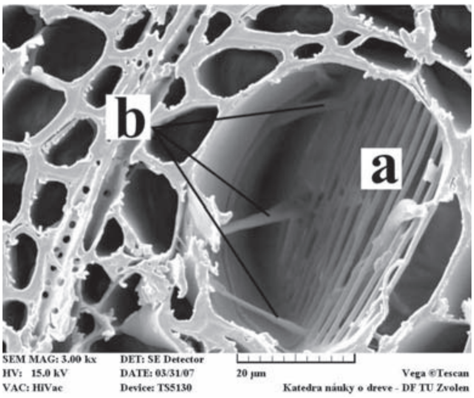

Fig. 8 Reference site dead branches of ***Betula pendula***; a – scalar perforation in vessels.. b – hyphaes

Cannon [14] states that the flora loading by Zn causes the abundant occurrence of plants with leaf chlorosis with green veining (*Picea abies, Betula pendula*), dead stains on leaf-tips (*Acetosella vulgaris*) and rudimentary root system (*Picea abies*). Plant loading by Ni and Co causes the formation of white stains [14]. White stains were described by *Salix fragilis*. Plants receive Cd mostly by roots [15, 16] in Cd^{2+} form [17] by diffusion due to metal chelatation by organic acids secreted by plant root system [18]. Hagrini [15] states that the highest Cd contents are in roots, lower in leaves and then in stems and fruits. The lowest Cd contents are in seeds. Our research of plant tissues from the dump-field and reference site confirmed these statements.

Higher Cd contents cause several diseases such as leaf chlorosis [19], root darkening [20] and formation of violet-brown stains on leaves [21] which is probably caused by the change of phenols metabolism [22]. Diseases have been observed at the studied locality by *Picea abies* (needle chlorosis), *Quercus petraea* (root darkening), *Acetosella vulgaris* (formation of violet-brown stains on leaves). Shedding of leaves and needles is present frequently as well. Lack of Cd causes the increase of biomass formation. High Cd content causes unproportional growth of leaves and roots, cell extension and stagnation of cell division [23]. For instance, needle length is ultra small by *Pinus sylvestris* (only 2 cm) at the mine waste dumps in Podlipa.

Pitter [24] states that in neutral and alkaline area which is typical in Ľubietová. The following complexes can form in higher concentrations: $[Pb(CO_3)_2]^{2-}$, $[Pb(OH)_2(aq)]^0$ and $[PbOH]^+$. Pb shows the affinity to form complexes with insoluble mould substances. It causes Pb fixation in the upper humus layer [25]. Extracellular uptake based on ion exchange and complex formation with ligands of cell-wall predominates in Pb uptake by organisms [26]. Pb accumulates mostly in roots if Pb uptake by roots predominates [25]. This statement was confirmed in our study. It is possible to observe in contaminated plants the atrophic plant growth (*Picea abies, Quercus petraea, Betula pendula*), leaf chlorosis and drying, root damage and decrease of wood reproduction ability.

Lagerwerff [27] states that the content of Cd, Pb, Mn, Zn and Co decreases in plant tissues with increasing pH in case of their identical concentrations in soil. This explains the relatively low contamination level observed in plants at the Ľubietová locality. Generally, As toxicity increases in the following order: organic compounds of As^{5+}, arsenates – inorganic compounds containing As^{5+}, organic compounds of As^{3+}, arsenites – inorganic compounds of As^{3+}, arsanes [28]. Arsenates and arsenites can form methylane compounds whereby they merge into the lower toxic forms [29]. Specific anomalous of flora caused by As and Sb contamination were not determined.

Concerning the plant distribution it was not possible to obtain the identical plant species from each plane A-F (Fig. 1). It was impossible to compare the contamination level of plant tissues with the contamination level of soils and sediments from the planes, neither with contamination level of surface water.

CONCLUSIONS

It was determined that at the Podlipa locality the concentrations of heavy metals in plant tissues decrease in the following order: Fe, Zn, Pb and Cu. The comparison of contamination of individual plant tissues showed that the highest concentrations of heavy metals have roots and then leaves and stems. Flowers, seeds and fruits have the lowest concentrations of heavy metals. Plant tissues are considerably damaged at the dump-field and increments of year shoots are extremely narrow. Anomalous cell-wall coarsening, occurrence of calluses, resin canals and numerous hyphaes in vessels suggest defense mechanism of plants which are exposed to stress factors at the dump-field such as contamination by heavy metals, soil and moisture deficiency, movement of incohesive material down the slope.

Acknowledgements

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IDENTIFYING DISPARITIES IN THE PODKRUŠNOHOŘÍ ROCK ENVIRONMENT

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ABSTRACT

Blažková M. **Identifying Disparities in the Podkrušnohoří Rock Environment**

Rock environment is a fundamental part of the overall environment; however the necessary indicators for its evaluation do not exist. This paper is an introduction of defining them and gives directions for their elaboration. To identify them, the environs in Northern Bohemia were chosen, where the rock environment, along with Northern Moravia, is the most afflicted. A predominant amount of the known factors disrupting the rock environment are represented here to an exceptional degree of accumulation. It concerns the disparities of the region under investigation in contrast to other regions in the Czech Republic.

Key words: rock environment, indicators, disparity, mineral mining

INTRODUCTION

The area of Northern Bohemia, especially the North Bohemian brown coal basin, is known for the enormous anthropogenic disturbances to the Earth's surface. A qualified estimate pouts it at 90 % of the surface in the districts of Chomutov, Most, Teplice and Ústí nad Labem.

The anthropogenic changes to the surface arise due to human activities or are corrected with man's assistance. Their classification is genetic according to how and why man made them. The intensity of the disturbances depend on several factors such as the settlement density, the location of industries, the occurrence and deposition of raw materials, the type of usage of the agricultural and forest soils, etc.

CLASSIFYING THE INTENSITY OF THE DISTURBANCES TO THE ROCK ENVIRONMENT

For an overall appraisal of the disturbances to the rock environment it is necessary to combine the individual processes and not to appraise them separately. It concerns the changes by mutually connected stimuli and the mediated effects and consequences.

For the Czech Republic were determined 5 categories [1, 2] especially for mechanical and then chemical disturbances. Levels 1–5 classify relationships from mild to extreme disturbances.

Mechanical disturbance to the rock environment is based on phenomena such as erosion and sedimentation, slope movement, karstic features, mining mineral materials, old mines, building and ground work.

On a territory classified in the 5th level of mechanical disturbance more than 50 % of the surface is afflicted by marked relocation of large volumes of rock and earth. The surface and underground mining and sites are undermined with the threat of surface subsidence. It is densely populated, has frequent slope movements, strong erosion and the resulting sedimentation and a large concentration of industrial activities.

Chemical disturbance to the rock environment is defined by pollution of underground water and soils, agricultural activities, an excessive occurrence of nitrates, heavy metals, contaminated mine water, atmospheric deposition affecting soils and plants, radon emanations, etc.

Areas assessed at the 5th level have a catastrophic level of underground and surface water pollution by risk elements in above the limit concentrations. Soils are contaminated by anthropogenic activities on the surface and atmospheric deposition. There is an occurrence of radon anomalies etc..

In general both of the above-mentioned types of disturbance to the rock environment, i.e. mechanical and chemical, work in simultaneously.

According to this classification of disturbance to the rock environment it is estimated that 8–15 % of the Czech Republic's area has strongly disturbed rock environment. More than 5 million inhabitants live here [2]. The most serious are those afflicted areas with the most intensive mining activities and the largest concentration of industry. In the Czech Republic's territory there are the areas of Northern Moravia and Northern Bohemia, where live over 3 million inhabitants.

Therefore evaluating the environment with the focus on the rock environment is one of the most important criteria. In the official methodologies this criterion only manifests itself in connection with devastation of the surface. Thus one of the most important aims of the project is to specify the disparity in the rock environment in the most distinct example, those at Podkrušnohoří territory of Northern Bohemia.

FORMULATING THE FACTORS OF THE ROCK ENVIRONMENT IN THE INVESTIGATED AREA OF NORTHERN BOHEMIA

Through the study of the available information and the field survey in the territories of the Chomutov, Most and Teplice districts the following rock environment factors were found and specified.

A predominant part of these factors are those negatively influencing the rock environment.

The factors are significantly disparate in comparison with other regions in the Czech Republic. The disparity primarily concerns their exceptional accumulation in this territory. The factors do not act individually but in various combinations and thus more intensively.

The following table presents an overview of the factors influencing the rock environment.

Factor	Weight/extent*	Negative effect	Positive effect	Notes
Surface mining	1	yes	no	
Underground mining	1	yes	no	
Anthropogenic geomorphology	1	yes	yes	New landscape formations
Stability of the mining pit slopes	1	yes	no	
Stability of the spoil bank slopes	1	yes	no	
Old mine pit	2 – 3	yes	no	
Sinks and mining pools	3	yes	yes/no	Used during land reclamation
Seismic activity in the area	3	yes	no	
Occurrence of radon	3	yes	no	
Radioactive ash from energy emissions	2	yes	no	Rarely measured
Mine water (by quality)	2	yes	yes/no	Used when flooding hollows
Waste deposition	2	yes	no	
Geothermal energy	2 –3	no	yes	Low water temperature but locally very substantial
Mineral reserves	1	no	yes	Mineral wealth

*weight/extent – 1) very significant, 2) significant, 3) slightly significant

SPECIFIC EXAMPLES OF FACTORS THAT ARE PART OF THE ROCK ENVIRONMENT AND INFLUENCE IT

The examples are given for factors indicated by weight and extent of 1, i.e. very significant factors.

Underground and surface mining

The territory under investigation is the part of the North Bohemian Basin (NBB) and the major mining activity here is brown coal.

In the Podkrušnohoří, the coal has been mined in an industrial way for more than 150 years and in the period from 1945 to 1998 alone almost 3.4 billion tonnes of brown coal were mined; but in the period up to the Second World War brown coal mining in this area only occasionally exceeded 20 million tonnes per year. However in the post war period brown coal mining grew drastically. In essence for every five-year-plan period it grew by more than 10 million tonnes and in the mid 80's the North Bohemian Brown Coal-field was mined 74.6 million tonnes a year [3].

In 1991 the Czech government accepted decision to suppress Czech mining, especially coal. The result was the issuing of the government resolutions on territorial environmental mining limits. The Governmental Resolutions affecting the Podkrušnohoří brown coal basin block almost 3.5 billion tonnes of usable brown coal reserves.

This inhibitory variant on the development of mining means a definite and irreversible end to brown coal mining in the Northern Bohemia by the end of 2150.

Open pit coal mining takes place in the following localities:

- Vršany Mine and Československé armády Mine, they are owned by the Mostecká uhelná společnost (MUS) in Most
- Nástup Tušimice Mines with the quarries Merkur and Libouš and Bílina (formerly Maxim Gorkij) owned by Severočeské doly based in Chomutov.

The last underground mine in the territory is the Centrum Mine (MUS)

Anthropogenic geomorphology

The anthropogenic accumulations have arisen in the North Bohemian brown coal basin since the start of coal mining and intensive industrial activities. Anthropogenic accumulations are understood to be the external and internal spoil banks of surface mines, sludge settling lagoons for power plant ash, various dumps, slag heaps and landfills.

In the territory of the North Bohemian brown coal basin anthropogenic changes to the morphology of the rock environment as a result of mining unequivocally dominate.

However the phenomena that have arisen in connection with the activities of a number of large industrial enterprises are also significant. In the investigated territory there is a number of industrial formations.

The most significant of the external slag heaps are currently merged into the landscape and the landscape has even gained something from it. These, for instance, are the Lochočická slag heap near Ústí nad Labem, Radovesická near the town of Bíliny, Obránců míru and Velebudická slag heaps, which tie into the built up area of the city of Most. In the most west parts of the territory under investigation the Merkur and Březno slag heaps near Chomutov are also significant.

From the geomorphological standpoint these slag heaps are protuberant. The territory's morphology is also formed by anthropogenic depressions which are the new lakes and those being newly built.

The present lakes, used for recreation, are Barbora near Teplice, or Matylda and Benedikt near Most. Currently, with a time horizon of 2–3 years, the lakes of Chabařovice and Most – Ležáky will be ready for use.

Stability of the slopes in coal mines and slag heaps

An example of monitoring, defining warning states and limiting the expansion of the mining areas is the section of the main Krušnohory slope between Vysoká Pac and Horní Jiřetín, with the width of about 5 km, which is, without doubt, the most problematic area in the forefront of advanced mining in the NBB. It is the highest and the steepest and also has specific geological conditions.

The huge coal mine Čs. armády was expanded from the central area of the basin to the foothills of the Krušné Mountains by the end of the 70's.

The most critical sites are below Jezeří Castle and the Jezerka nature reservation.

A stabilising buttress and the monitoring system ensure the slope's stability even in the subsoil of the Jezeří Castle. The rest of the castle's lower park the "arboretum", is within the range of the stabilising buttress and it is in the monitoring system's area.

Mining using the opencast system in a pit over 200 m deep under the slope of the mountain made of a tectonically distressed and porous crystalline complex has no parallel in the world.

Research into the slopes of the slag heaps was realised on modelled localities of the Merkur, Libouš, Chabařovice slag heaps and the old slag heaps in the area of the Varvažovská Basin near Ústí nad Labem.

The research was aimed at measuring the geomechanical properties of the spoil material through field methods and in site measurement (permeability, aeration and pore pressure).

The results of the research led to the following conclusions:
- the main source of the pore pressure is the Earth's own weight;
- developments in pore pressure are conditional on the amount and extent of the structural changes in the backfill;
- the nonlinear development of the pore pressure is caused by the heterogeneity of the backfill's creep over time.

CONCLUSIONS

The information given here is the summary of general mapping of the significant factors in the rock environment.

In the next stages the problem will be further studied and a specification of the factors for indicators of the rock environment will be made. With the regards to the fact that such indicators do not, as yet, exist, these will be supported by further research and specific information.

Acknowledgement

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MODELLING STOMATAL OZONE FLUX AND DEPOSITION TO CONIFEROUS AND DECIDUOUS FOREST IN THE CZECH REPUBLIC

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ABSTRACT

Zapletal M. & Chroust P. **Modelling Stomatal Ozone Flux and Deposition to Coniferous and Deciduous Forest in the Czech Republic**

There are presented the estimates of ozone concentration and deposition flux to coniferous and deciduous forest in the Czech Republic on a 1 x 1 km grid during growing season (April – September) in 2006. Ozone deposition flux was derived from ozone concentrations in the atmosphere and from its deposition velocities. To quantify the spatial pattern in surface concentrations at 1 km resolution incorporating topography, empirical methods are used. The procedure maps ozone concentrations from the period of the day when measurements are representative for the forest areas of countryside. The effects of boundary layer stability are quantified using the observed relationship between the diurnal variability of surface ozone concentration and altitude. Ozone deposition velocities were calculated according to the multiple resistance model incorporating aerodynamic resistance (R_a), laminar layer resistance (R_b) and surface resistance (R_c). Surface resistance (R_c) comprises stomatal resistance (R_{sto}). R_{sto} was calculated with the respect to global radiation, surface air temperature and land cover.

Key words: ozone concentration, ozone deposition, resistance model, stomatal fluxes, topographic effects, ozone

1. INTRODUCTION

Photooxidants with ozone as the major compound have been the concern for vegetation in Europe for long time. There is an evidence that the ambient ozone concentration found in Europe can cause a range of effects to vegetation, including visible leaf injury, growth and yield reductions [1]. Ozone is an air pollutant of great consequence for sustainable development of forest in the Czech Republic.

Level I ozone critical levels for forest trees were based upon the AOT40 concept [2]. Level I aproach has a number of serious problems if the aim is to assess the likely ozone damage to vegetation. AOT40 is calculated only on the basis of ambient ozone concentrations regardless of whether this ozone is actually absorbed by the plant or not [3]. On European scale, the application of an uptake based approach for assessing the possible risk of O_3 causing damage to vegetation requires the availability of models capable of calculating the seasonal and diurnal courses of O_3 flux on vegetated surfaces [3, 4, 5]. Ozone flux is a fuction of ozone concentration above plant canopy and the resistance to ozone transfer from there into the sub-stomatal cavity of an individual leaf. This resistance is a function of a number of factors, including atmospheric turbulence, canopy height and structure, species-specific phenology, and the effects of factors such as irradiance, soil moisture deficit and vapor pressure deficit on the stomatal component of the resistance.

The results of the evaluation of the relationship among ozone concentration, AOT40 exposure index and the flux to coniferous forest in Hrubý Jeseník

Mountains in 1998 in the Czech Republic were presented in [6]. The results of evaluation of relationship between AOT40 exposure index and the total ozone flux to coniferous and deciduous forest in the Czech Republic in 2001 were presented in [7, 8].

Estimates of ozone concentration and deposition flux to coniferous and deciduous forest in growing season (Apríl–September) for the year 2006 in the Czech Republic on a 1x1 km grid are used. Ozone deposition flux to forest was estimated from the monitored and modelled ozone concentrations in the air and from its deposition velocities. The data of ozone concentration from the Czech Hydrometeorological Institute database were used [9]. Empirical methods to quantify the spatial pattern in surface concentrations at 1 km resolution, incorporating topography, are used.

2. MATERIAL AND METHODS

2.1 Ozone concentrations

For this study were used the databases of the Air Quality Information System of the Czech Republic [9]. At present the measurements of ozone concentration are carried out at 60 automated ambient air quality stations representing rural, mountainous and urban areas. Automatic monitoring stations operate continuously on a 30 minutes time resolution. The ozone concentration measurement is based on ultraviolet absorption photometry. Some of the stations, within the meteorological monitoring framework, also record global solar radiation.

For this study were used the monitoring data from rural areas (23 automated rural monitoring stations for ozone concentrations measurements and 73 meteorological monitoring stations for wind speed, global radiation, air temperature and relative humidity measurements).

Ozone concentrations during afternoon in the vegetation period, when the planetary boundary layer is well developed, were compared on the rural monitoring sites. Listing of daily mean ozone concentration, mean ozone concentration in the period from 11 to 17 o´clock UTC from April to September 2006 and the altitude of monitoring station are presented in Table 1.

Tab. 1 Listing of daily mean ozone concentration, mean ozone concentration during the period 11 to 17 o´clock UTC, during April to September 2006 and the altitude of monitoring stations

Site name	Altitude (m a.s.l.)	Mean ozone concentration ($\mu g\ m^{-3}$) from April to September 2006	
		Daily mean	11 –17 UTC
Kuchařovice	334	77	99
Mikulov – Sedlec	245	79	98
Churáňov	1122	103	110
Kocelovice	519	75	95
Svratouch	735	77	87
Krkonoše Rýchory	1001	91	95
Šerlich	1011	79	86
Hojná Voda	818	102	113
Kostelní Myslová	569	84	101
Košetice	534	76	94
Přebuz	904	81	93
Souš	771	79	97
Jeseník	625	89	99
Přimda	745	85	96
Ondřejov	514	74	89
Bílý Kříž	890	87	93
Červená	749	79	86
Studénka	231	62	95
Lom	265	67	96
Rudolice v Horách	840	90	100
Sněžník	588	87	100
Tušimice	322	71	95
Štítná n.Vláří	600	94	103

The methods developed to incorporate the effects of topography into the map of rural mean ozone concentration are described in [10] and the underlying theory is examined in [11]. The map was produced by interpolating the afternoon value of the variable from rural sites then modifying the resulting grid cell values to account for the diurnal cycle in ozone concentration. Afternoon average O_3 concentrations (the concentration during the period from 11 to 17 o´clock UTC) at the rural monitoring sites are interpolated accross forest area ecosystems by applying a minimum curvature interpolation algorithm [12] that produces gridded data at 1 x 1 km resolution. Minimum curvature is used as ozone varies quite slowly across the landscape during the average period and this interpolation method provides a smooth fitted surface. For the 24 hour mean ozone concentration this is done using the variable ΔO_3 (the difference between the seasonal average ozone concentration during the period from 11 to 17 o´clock UTC and the daily mean concentration). This variable was then related to the altitude (h) of the monitoring station. This effect is quantified in Fig. 1 as the relationship between altitude of monitoring station and ΔO_3.

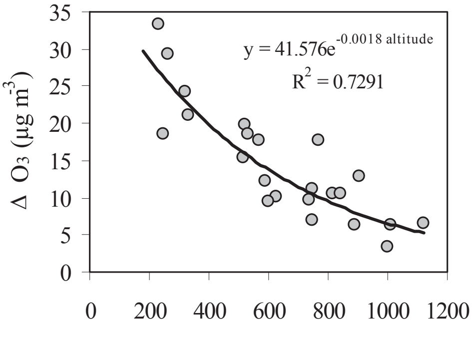

Fig. 1 Relationship of seasonal ΔO_3 (difference of seasonal 2006 average O_3 concentration in the period from 11 to 17 hours UTC and seasonal 2006 24 average O_3 concentration) at rural sites to the sites altitude

The relationship:

$$\Delta O_3 = 41.576e^{-0.0018\ \text{altitude}} \tag{1}$$

was used with an altitude map of country to obtain ΔO_3 for each 1 x 1 km grid square of the forest area. The afternoon value in each grid square is adjusted for the diurnal cycle using relationship (1).

2.2 Ozone deposition flux

2.2.1 Description and application of the ozone deposition flux model

Since no simple method was available for the direct measurement of ozone deposition flux, the deposition flux was estimated from measured concentrations of ozone in the air multiplied by the corresponding deposition velocities:

$$F = V_d(z)C(z) \tag{2}$$

where F is the deposition flux of the component to a unit area (e.g. m^2), V_d is the deposition velocity of the ozone and $C(z)$ is concentration of the ozone at height z above surface.

The ozone deposition model differentiates the stomatal and non-stomatal deposition components and estimates ozone deposition according to vegetation-specific parameterisation. Deposition velocity for ozone was calculated by using the resistance analogy. Deposition velocity V_d may be expressed by the inverse of the sum of three resistances:

$$V_d(z) = \frac{1}{R_a(z) + R_b + R_c} \tag{3}$$

The three resistances represent three stages of transport: the aerodynamic resistance, R_a, for the turbulent layer, the laminar layer resistance, R_b, for the quasi-laminar layer, the surface or canopy resistance, R_c, for the receptor itself. In this study the aerodynamic resistance, R_a, is calculated from micrometeorological relations suggested by [13] and [14] and the quasi-laminar layer resistance, R_b, is calculated from micrometeorological relations suggested by [14]. R_a and R_b may be assessed on the basis of known wind velocity and a surface roughness. The annual average values of the surface roughness, z_0, for different surface types were derived from the literature [13, 15]. Annual averages of the surface roughness, z_0, were related to the corresponding surface characteristics in the forest territory of the Czech Republic according to the CORINE Land Cover classes [16]. Land Cover classes used were coniferous forest (*Picea abies*) and deciduous forest (*Fagus sylvatica*).

The surface resistance (R_c) comprises the plant canopy (described using a “big leaf” formulation) and the underlying soil. Surface resistance was calculated using the following equation:

$$R_c = \left(\frac{1}{R_{sto} + R_m} + \frac{1}{R_{inc} + R_{soil}} + \frac{1}{R_{ext}} \right)^{-1} \quad (4)$$

R_c was calculated on the basis of known global radiation, surface temperature, relative humidity and land cover according to Eq. (4) using the results and assumption obtained from literature (Table 2), for calculating and parameterization of the land-cover specific canopy stomatal resistance (R_{sto}), the mesophyll resistance (R_m), the canopy cuticle or external leaf resistance (R_{ext}), the soil resistance (R_{soil}), and the incanopy resistance (R_{inc}), respectively.

The stomatal resistance (R_{sto}) includes dependence upon global radiation and surface air temperature. Here we use the following generalized function to estimate the canopy stomatal resistance [17]:

$$R_{sto}=R_i\{1+[200(G+0.1)^{-1}]^2\}\{400[T_s(40-T_s)]^{-1}\} \quad (5)$$

where R_i is input resistance in s m^{-1}, G is the global radiation in W m^{-2} and T_s is the surface air temperature (ºC). We only extract values of R_i from Wesely´s (1989) table [17] that are pertinent to the present study (Table 2).

The incanopy resistance (R_{inc}) for vegetation was modelled with [21]:

$$R_{inc}=bLAIh/u_* \quad (6)$$

where *LAI* is the one leaf area index, *h* the vegetation height, *b* an empirical constant taken as 14 m^{-1} and u_* is a friction velocity. The current parameterization that was used to calculate the surface resistance (R_c) for coniferous forest (*Picea abies*) and deciduous forest (*Fagus sylvatica*), is summarised in Table 2.

In this article are presented calculations for the growing season in 2006. The resistance model of the ozone deposition velocities calculation under conditions on the forest territory of the Czech Republic was applied as follows: the forest area of the Czech Republic was divided into 41 forest natural regions, and the seasonal average horizontal wind velocity, u_z, for the growing season at 73 meteorological stations, was extrapolated for all these regions. The value R_a and value R_b were calculated from the micrometeorological relations by [13] and [14] by using the average value, z_0, according to individual surface type and seasonal average values, u_z, in the different regions.

Tab. 2 Vegetation – specific parameters used in the ozone deposition model

Parameter	Coniferous forest	Coniferous forest References	Deciduous forest	Deciduous forest References
LAI	8.6	[15]	5	[18]
R_i (s cm^{-1})	2.5	[17]	1.4	[17]
R_m (s cm^{-1})	0	[17]	0	[17]; [19]
R_{soil} (s cm^{-1})	3[a]	[20]	3	[20]
R_{ext} (s cm^{-1})	20[a]	[20]	20	[20]

[a] For mixed forest

The seasonal average deposition velocities, $V_d(z)$, of ozone at a 10 m reference height for individual surfaces (grid cells 1 x 1 km), represented in regions surrounding the 73 meteorological stations on the Czech forest territory were calculated by diurnal averages of the values R_a, R_b and R_c from Eq. (3). Each grid cell (1 x 1 km) was assigned the dominant surface type.

Seasonal average value of ozone deposition flux, FO_3, was calculated from seasonal average concentration, $C(z)$, seasonal average deposition velocity, $V_d(z)$, and time, t, in a 1 x 1 km grid resolution.

3. RESULTS AND DISCUSSION

3.1 Ozone concentrations

The hourly mean ground level concentration of ozone in rural sites in the Czech Republic vary between 0 and 205 µg m^{-3}, but generally lie in the range 40 to 120 µg m^{-3}. Days with the concentration maxima exceeding 100 µg m^{-3} can be taken to imply photochemical episodes, when the ozone concentration is raised above the background level by a combination of anthropogenic precursor emissions and weather conditions [7, 8].

The effects of wind on ozone concentration are to reduce the effects of depletions at the ground on surface concentrations. As wind speeds and turbulent mixing processes are enhanced on hills, it follows that surface depletion effects are less on hills than sheltered lowland sites [7, 8]. The effects are illustrated by neighbouring monitoring stations which differ substantially in an altitude, as in an example Studénka (STU) and Bílý Kříž (BKR) (The Beskydy Mts) differ by 659 m in the vertical yet are within 39 km horizontally (Fig. 2). These show almost identical concentrations during the period 11–17 o´clock UTC (respectively 12–18 o´clock CET) in growing season while the night time concentrations differ by 40 % or more.

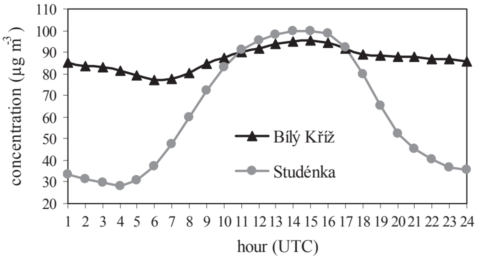

Fig. 2 The effects of altitude on ozone concentration at Studénka (STU) and Bílý Kříž (BKR) from April to September 2006

Diurnal average cycles at rural monitoring stations from April to September 2006, plotted in 3 groups by site altitude are shown in Fig. 3.

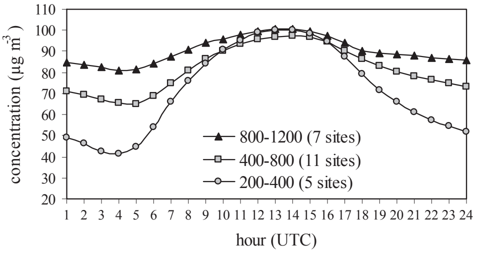

Fig. 3 Diurnal cycles at rural monitoring stations from April to September 2006, averaged into 3 groups by site altitude

The magnitude and timing of mid-afternoon peak is very similar at all sites, showing that rural concentrations are generally comparable over the wide geographical area during this period. The diurnal cycles in ozone for summer period show that during the afternoon many of the monitoring stations in the same region (within 100 km of each other), show similar concentrations despite considerable altitude differences within the boundary layer. These effects may be seen in the whole rural monitoring network in the Czech Republic [7, 8]. Similar effects on rural areas in the United Kingdom were described by [10] and [11]. The very similar concentrations during the afternoon period of the day with the most effective vertical mixing for neighbouring rural monitoring stations show that during this period the rural monitoring stations are providing data which are representative of a much larger geographical area than during the night when local effects of shelter etc. generate great horizontal variability [7, 8].

The rural monitoring network contains 23 sites to define the spatial patterns and simple direct interpolation between the sites fails to predict the pronounced effect of topography on the pattern of surface ozone concentration.

The attribute of the minimum-curvature algorithm is a tendency to maintain the recorded values at the monitoring stations as much as possible. The incorporation of an altitude enhancement at 1 x 1 km scale (according to [10]) provides a realistic picture of the variation in ozone concentration with undulating topography of the Czech Republic. In the case of the seasonal average ozone concentration, there is a perfect agreement between the measurements and the map (Fig. 4).

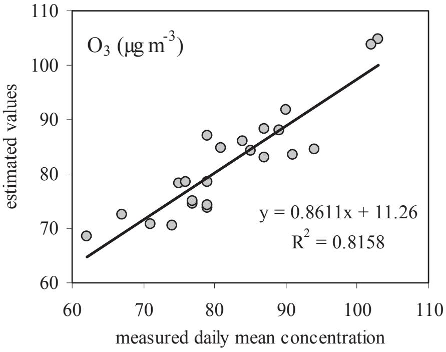

Fig. 4 Plot of the measured daily mean ozone concentration from April to September 2006 versus the estimated values in the grid squares containing the monitoring site

Spatial distribution of the mean ozone concentration over the forest territory in the Czech Republic in April – September is shown in Fig. 5. Ozone concentration values are ranging from 57 to 116 µg m^{-3}. Mean ozone concentration is 79 µg m^{-3}.

The highest values of ozone concentrations were recorded in the borderline of mountain regions (higher altitudes), in the Krušné Mts in the northwest part of the country, the Jeseníky Mts in the northern part of the country and the Šumava Mts in the south. The locations in higher altitudes are more exposed to ground ozone and are less affected by night inversion conditions. Thus the concentration values of ground ozone in the open grow up with an increasing altitude. The highest values of ozone concentrations were localised in higher altitudes of the mountain areas.

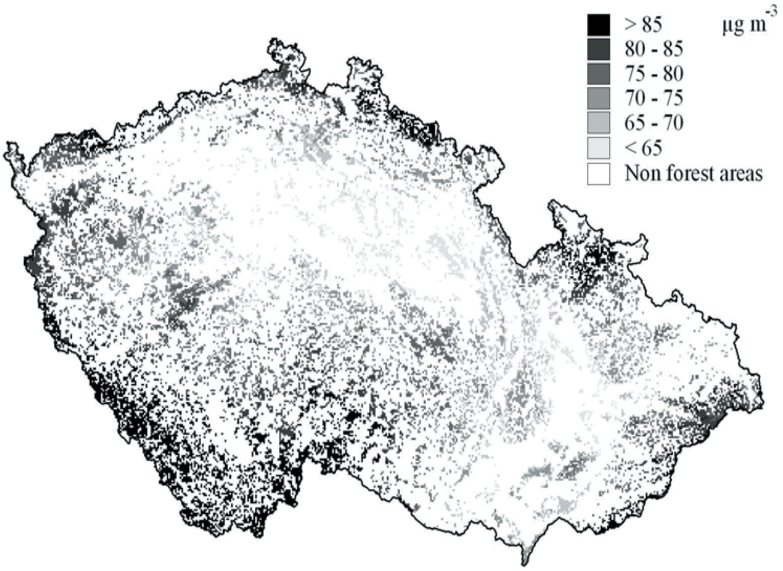

Fig. 5 Mean ozone concentration (µg m^{-3}) in forest in the Czech Republic on a 1 x 1 km grid in April – September 2006

3.2 Ozone deposition flux

Spatial distribution of mean total and stomatal fluxes of ozone to coniferous and deciduous forests over the Czech Republic in April – September are shown in Fig. 6. The highest values of total fluxes of ozone were recorded in higher altitudes of mountain areas, in Krušné Mts in north-west, the Šumava Mts in the south and the south-eastern parts of the Czech Republic.

Ozone deposition model statistics are presented in Table 3.

Calculated deposition velocities of ozone for coniferous and deciduous forest were compared with observations based on the data from literature (Tab. 4). The modelled data are in good agreement with the observed ones.

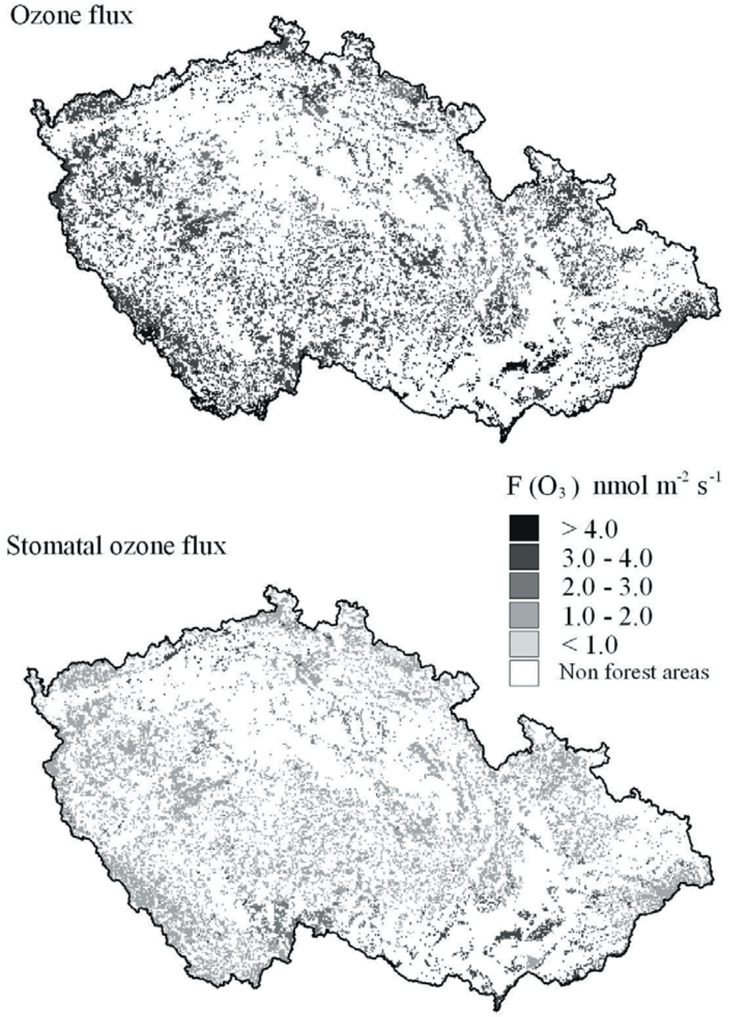

Fig. 6 Mean total and stomatal fluxes of ozone (nmol m^{-2} s^{-1}) to forests in the Czech Republicon a 1 x 1 km grid in April – September 2006

Tab. 3 Ozone deposition model statistics for coniferous and deciduous forest in the Czech Republic in April – September 2006

Surface	Ozone flux nmol m^{-2}s^{-1}			Stomatal ozone flux nmol m^{-2}s^{-1}			Deposition velocity cm s^{-1}		
	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max
Spruce	3.27	2.29	4.33	1.71	0.67	2.32	0.26	0.1	0.65
Beech	4.26	2.71	5.95	3.07	1.79	4.22	0.34	0.1	0.8

Tab. 4 Comparison of observed and modelled dry-deposition velocities (cm s^{-1})

Surface	Observation				Model calculation for Czech Republic		
	Mean	Range	Reference	Condition	Mean	Range	Condition
Spruce		0–0.7	[23]	June	0.26	0.1–0.6	April – September
Beech	0.4	0.1–0.7	[24]	April – May	0.34	0.1–0.75	April – September

4. CONCLUSIONS

This study describes the modelling of ozone concentrations and deposition to a coniferous and deciduous forest on 1 x 1 km for the territory of the Czech Republic. The deposition has been assessed from the measured and modelled concentrations of ozone in the atmosphere.

The effects of boundary layer stability were quantified using the observed relationship between the diurnal variability of surface ozone concentration and altitude. Climatic conditions in higher altitudes differ from those in lower altitudes. The locations in higher altitudes are more exposed to ground ozone and are less affected by night inversion conditions. Thus the concentration values of ground ozone in the open grow up with an increasing altitude of mountain areas of the Czech Republic.

It seems clear that patterns of ozone concentration and pattern of ozone deposition are different. The difference between ozone concentrations and ozone deposition is largely due to the fact that in the central Europe, the meteorological conditions favour ozone formations (high temperatures and high vapour-pressure deficits) tend to inhibit stomatal conductance and hence uptake.

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