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FLOOD CONTROL MEASURES IN THE EAST OF THE APUSENI MOUNTAINS

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ABSTRACT. In the last period, the East of the Apuseni Mountains was affected by the floods which generated damages almost every year (75.624 mill. $., 1995-2006 reference period). For the mitigation of flood damages in the East of the Apuseni Mountains there was performed some specific flood control works. The most important of this are the permanent water reservoirs and temporary, the canalization works and embankments and torrent management works. This study focuses on the characterization of the major flood control works carried out in the east of the Apuseni Mountains in order to mitigate the flood-risk and highlight solutions to improve flood control system having regard to the main weaknesses reported.

Key words: *flood control works, water reservoirs, canalization works, embankments*

INTRODUCTION

More and more frequently, specialists in the field claim that the protection of population and of human build structures by achieving flood control works is an obsolete practice. Among the frequently stated arguments are the high costs associated to the construction and operation works, environmental balance disorder, and last but not least, increase of vulnerability to floods of the protected objectives temporarily sheltered by such works.

On the other hand it is doubtless that in some places and specific conditions, some structural measures are absolutely necessary in order to mitigate the damages associated to floods and inundations, although, these structural measures have to be supported by nonstructural measures known in the literature as "soft measures''.

The study is focused on the characterization of the main flood control works in the Eastern part of the Apuseni Mountains, in order to mitigate the flood-risk and on the highlight of the improvement solutions of the system taking into account the observed deficiencies.

STUDY AREA

The studied territory, respectively the Eastern part of the Apuseni Mountains, occupies the Western part of Central Romania, composed of the mountain basins of the Arieş and Someşul Mic rivers. The surface of the two drainage basins is 2903 km², while the average altitude of the territory slightly goes beyond 1000 m (Fig.1).

The high drainage density and the richness of natural resources leads to a relatively high population density for a mountain area, especially in ”Moților Country’’ region – 43.6 inh./km² (based on data from the National Census of the Population and Housing, 2002). The average settlements density for the entire region is 4.5 settlements/km², which classifies the area as one of the highest density of human settlements in Romania. Talking about a mountain region with high drainage density, relatively small basins with steep slopes, thin soils and rocks with low permeability, floods belong especially to the flash-flood type.

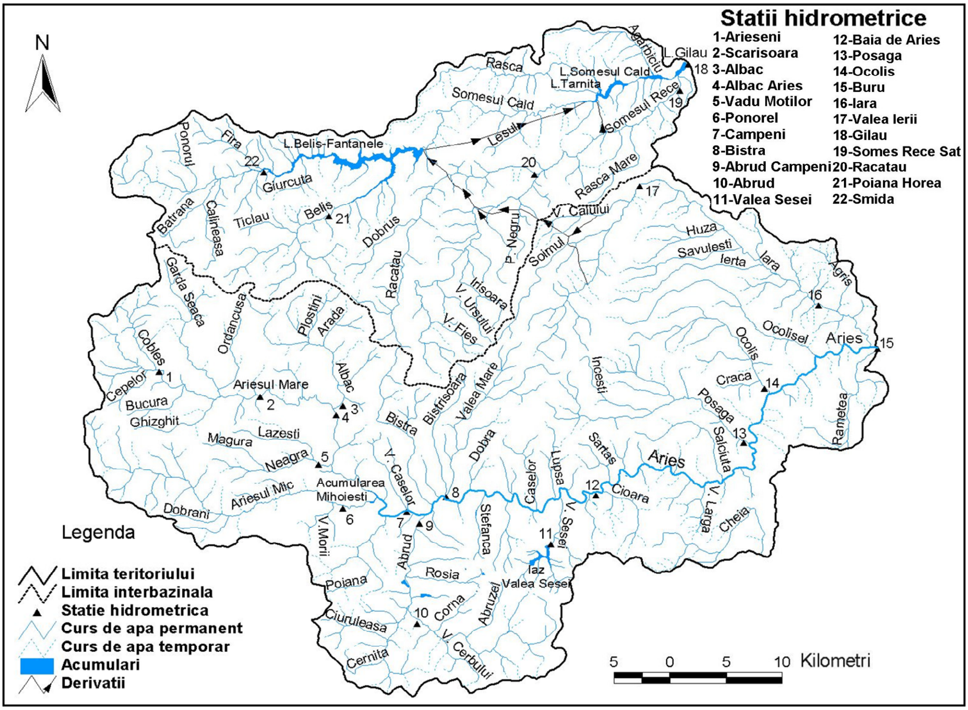

Fig. 1. *Hydrographical network of the studied area*

STRUCTURAL MEASURES FOR MITIGATION OF THE NEGATIVE IMPACTS INDUCED BY FLOODS

Among the natural risk phenomena, the floods are responsible for most of the damages and human casualties (Arghiuş, 2008). During the last period, the East of the Apuseni Mountains was affected by the floods which generated damages almost every year (75.624 mil. $., 1995-2006 reference period). For the mitigation of flood damages in the East of the Apuseni Mountains there were performed some specific flood control works. The most important of these are the permanent and temporary water reservoirs, the channelization works and embankments and torrent management works.

Permanent and temporary water reservoirs

Permanent and temporary reservoirs with important flood storage capacities play the most important role in mitigation of the intensity of flood events and their related consequences.

The most important reservoirs have been made in Someşul Cald basin, which provide flood protection for downstream localities (the most important is Cluj-Napoca city).

Among these one can notice particularly the Beliş-Fântânele (Fig.2) and Tarnița reservoirs which have been designed to include large volumes of flood water (Table 1).

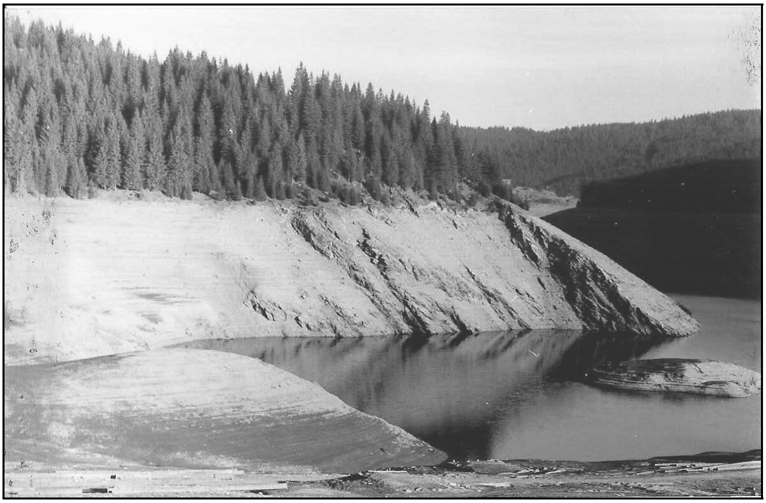

Fig. 2. *Fântânele Reservoir*

Table 1.

Characteristics of the main reservoirs in the mountainous part of Someşul Mic basin (Pop, 1996)

Nr. crt.	Reservoir / River	NSL* (masl)	Length (km)	Surface (ha)	Total volume NSL (mil. m³)	Flood storage capacity (mil.m³)
1.	Fântânele / Someş Cald	991.00	13.5	815	220	41
2.	Tarnița / Someş Cald	521.50	8.0	220	74	7,5
3.	Someş Cald / Someş Cald	441.00	3.7	85	7.47	1.97
4.	Gilău / Someş Mic	420.10	1.8	82	4	1.38

*NSL- Normal Storage Level

Maximum discharge values with different annual probability of exceedance related to reservoir's inflow water are given in Table 2.

Table 2.

Maximum discharge values with different annual probability of exceedance for Fântânele and Tarnița reservoirs (SGA Cluj, 2008)

Reservoir	Annual probability of exceedance			
	10 %	1 %	0.1 %	0.01 %
Fântânele	180	370	650	1010
Tarnița	170	262	504	922

Aries basin includes only one important flood-control reservoir (Mihoieşti temporary reservoir), located on the confluence of Arieşul Mare and Arieşul Mic rivers.

This temporary reservoir serves, at present, for flood attenuation and water supply of the Câmpeni town (Fig.3).

Fig. 3. *Mihoieşti reservoir during consolidation works for dam safety (Arieşul Mic)*

Construction works were started in 1981 and were finalized for the first stage in 1987. The second stage intended to be finalized is still ongoing due to the lack of funds. At present, consolidation works for dam safety are performed. The second stage will consist in raising the dam with 30 m, conditions in which the flood storage capacity will increase from 3.65 mil m³ to approx 20 mil m³ (SGA Turda, 2000).

The 1995 complex floods, which in some areas had an annual probability of exceedance of 2-3 %, (i.e. an average return period of 30-50 years) demonstrated the efficiency of these reservoirs. Fântânele reservoir was able to store almost the entire inflow water, while Gilău and Mihoieşti reservoirs only delayed for a while the flood, proved to be undersized (Fig. 4, Fig. 5).

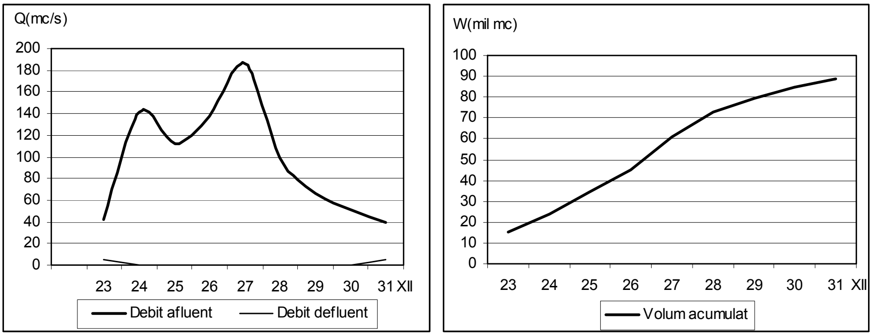

Fig. 4. *The influence of Fântânele reservoir on the December 1995 Flood* (data processed from S. C. Hidroelectrica S. A., Sucursala Cluj)

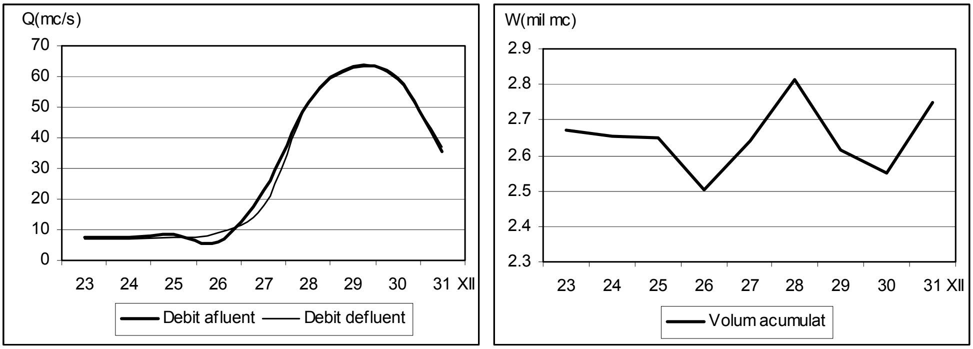

Fig. 5. *The influence of Gilău and Mihoieşti reservoirs on the December 1995 Flood* (Şerban, 2004)

The channelization works

The oldest works are described in the ancient name of ,,gătaşe'' and date back from the Middle Age period, being carried along Aries river, subsequently to the catastrophic flood event occurred around 1500. The purpose of the works was to prevent the development of new river channels in the floodplain sector. The works consisted of short embankments, built of large stone blocks, whose remnants can still be seen today in the Lupşa-Bistra sector (Şerban and Năsăleanu, 1981).

Some channelization works as rerouted and enlargement of river channel (recalibration) give the best short-term results in the efforts of attenuating the high flood level, and thus on the water overflow from stream channels.

Local embankments and bank consolidation are useful in order to avoid the inundations frequency, bank protection and generally consist in building dikes parallel to river channel. The bank protective works, especially on the concave sectors of the meanders, in the nearby of road are very useful, while more than 70% of the damages produced between 1995-2006, respectively 55 mil. $ are associated with roads (Arghiuş, 2008).

In the Eastern part of Apuseni Mountains a series of channelization works and embankments were performed, the most important along the main course of Arieş river (Table 3, Fig. 6).

Table 3.

The main characteristics of channelization works

Locality/ river	Flood control methods	Length	Year	Protected objectives
Lunca Arieşului village-Arieş	Embakments, Recalibration Bank protection works	2.20 km 2.42 km 0.865 km	1997	Lunca Arieşului, 2 km of 75 National Road, 2 hectares of agricultural land, a bridge
Baia de Arieş town-Arieş	Bank protection works	1.3 km right side	2001	Baia de Arieş, 100 m of 75 National Road, a bridge
Câmpeni town-Caselor Valley	Bank protection works Channelization works	1.3 km	1964	1294 m of road, 3 bridges, Avram Iancu Museum
Ponorel village-Arieşul Mic	Bank protection works	0.18 km	1966	Ponorel, 180 m of road

Locality/ river	Flood control methods	Length	Year	Protected objectives
Abrud town - Abrud	Channelization works Bank protection works	2.5 km 5.0 km	1972	Abrud flood-plain residential area 1.0 km of road, 2 bridges, 2 socio
Valea Ierii village-Iara	Recalibration Bank consolidation	1.72 km 0.70 km right side and 0.445 km left side	1978	35 households, 10 ha of agricultural land, 500 m of county road
Măguri Racătău village-Someşul Rece	Recalibration Bank consolidation	1.5 km 0.545 km left side		Măguri Racătău

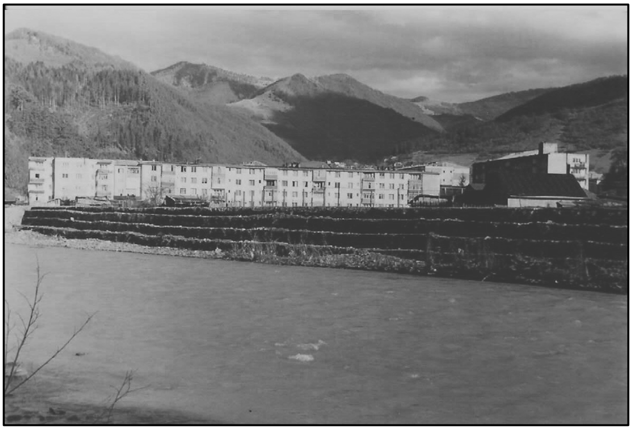

Fig. 6. *Right bank protection work along the Arieş River in Baia de Arieş town*

Subsequent to the flash floods in the summer of 2006, on several tributaries of Aries middle basin, recalibration works were started in the proximity of confluences. Such works are located in the administrative territory of the localities Baia de Aries (Ciorii Valley, Negoiu Valley), Salciua (Largă Valley, Matri Valley) and Ocolis (Ocoliş river).

In many sectors of the middle Arieş River silting phenomena were observed, especially at confluences. This phenomenon was possible due to massive sediment accumulation carried by torrents during flash floods, as the Aries river was not subjected to massive floods on the middle sector since 2000. In this context, a practical and efficient solution for recalibration works consists in concession of the gravel islands for gravel exploitation. According to the measurements performed using GIS techniques and detailed cartographic support on 51 km of the total 74 km of the middle course of the Aries river, in terms of normal levels, a total fluvial islands surface of 14.8 ha resulted, representing 7.5 % of the total river channel surface. At present, several river islands are undergoing exploitation, especially on the lower sector of the Aries river, the material being used in the construction of the Braşov - Borş Highway.

The efficiency of channelization works was demonstrated for regular floods but in the case of high intensity floods accompanied by inundations such works proved to be vulnerable, suffering important damages. Thus, the historic flash flood produced on Abrud River in December 1995, affected a large part of the bank protection works in the Abrud town, with total damages of 1.5 mil USD at that time.

Torrent management works

Torrent management works are performed in order to decrease the destructive power of torrential stream. The large power of the torrential stream flow results from the rapid runoff concentration of rainfall water loaded with solid materials.

In the Apuseni Mountains classical measures of torrent control are more frequently used, consisting in the reduction of the longitudinal slope and modification of the base level through the performance of transversal works in the stream channel. In the vicinity of localities and of roads dams are constructed with increased sediment storage capacity.

In the Eastern part of the Apuseni Mountains, torrent control works are more frequently used in the Southern and Eastern part of the Muntele Mare Massif. This is a region with high intensity rainfalls, basins with steep slopes and settlements concentrated on the bottom of the valleys, on the alluvial fans (Fig. 7).

Fig. 7. *Torrent control works: right tributary of Iara River (left); Brăzeşti Valley (right)*

CONCLUSIONS

Analyzing the situation after the high intensity flood events of the last years (1995, 2000, 2001), it is ascertained that the most important damages are produced in the same sectors, location in which funding is needed in order to implement protective measures. Many of the existing works are poorly maintained or undersized, consequently these often do not achieve the objective for which they were made. In this context, at present, some specific flood control works are under construction, such as embankments (6.067 km), channelization works (6.96 km) and bank protection works (4.04 km) inside the localities Lunca Arieşului, Câmpeni and Baia de Arieş. Works are in development also at Mihoiesti reservoir for the increase of the dam safety. On the main course of the Arieşul Mare river, relocation works on a higher level of the 75 National Road (upstream Albac) are in progress.

Also a series of structural measures is integrated in the future plans of authorities. The most important of these are the channelization works in Avram Iancu and Vidra (Ponorel - Tarsa sector), Garda de Sus, Bistra, Sălciua, Abrud and Baia de Arieş localities, starting the works for elevating the Mihoiesti dam, torrent control measures in the sectors Scarisoara - Baia de Aries and in Iara basin, unsilting the river channels in the bridges sectors and last but not least, consolidation and raising of the dikes in order to cope with the new conditions generated by foreseen climatic global changes.

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ASPECTS CONCERNING THE NANO - SEDIMENTS COMPOZITION AND DISTRIBUTION IN ST. ANA LAKE - ROMANIA

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ABSTRACT. The shore sand sample collected from St. Ana Lake shows a wide range size particles, from 500 µm to less then 10 µm to the nano-scale one, particles being sustain by water strata as nano - sediments. The shore sand is formed by andesine amorphous volcanic glass with potasic hornblende and feldspar with traces of potasic biotite, muscovite and hydrate silicate, belonging to the surface formation without any deeper compounds. The identified minerals were found in wide range size particles even at nano-scale. Water samples were collected from surface, 1 m, 2 m, and 3 m deep, deposed on glass layer and investigated with AFM in order to observe the nano-particle distribution. It was found in surface water sample rounded nano-particles with 80 nm average diameters increasing proportional with water deepness. At 1 m was found 125 nm, at 2 m 200 nm, and at 3 m deep, the average diameter was around 300 nm presenting the same morphology as observed for identified minerals. The values obtained indicate a parabolic variation of particle diameter associated with a Gaussian distribution of percentage particle density in each investigated water sample. These aspects can establish a new sedimentation model specific to inland water ecosystems applied also to St. Ana Lake.

Key words: *nano-dispersion, AFM microscopy, X – ray diffraction*

INTRODUCTION

The particulate matter sedimentation presents some special features in the volcanic cone lakes like St. Ana Lake because of their special water supply: only from precipitation, without any spring source, and interaction with volcanic emanations (Aeschbach-Hertig, W.M. et al., 1999; Martinez, M. et al., 2000, Mastin, L.G. and Witter, J.B., 2000). St. Ana Lake is the only volcanic cone lake in Southeastern Europe located in Oriental Carpathians – Romania in Ciomatu massive as part of volcanic chain Gurghiu – Harghita, figure 1. Some of geological research performed on the Ciomatu Massive reveals that is formed by andesine volcanic glass with hornblende and biotite in the surface layers and andesine with pyroxene in deeper formations (Slavoaca, D. and Avramescu, C., 1956; Lazar, A. and Arghir, E., 1964; Seghedi, I. et. al., 1995).

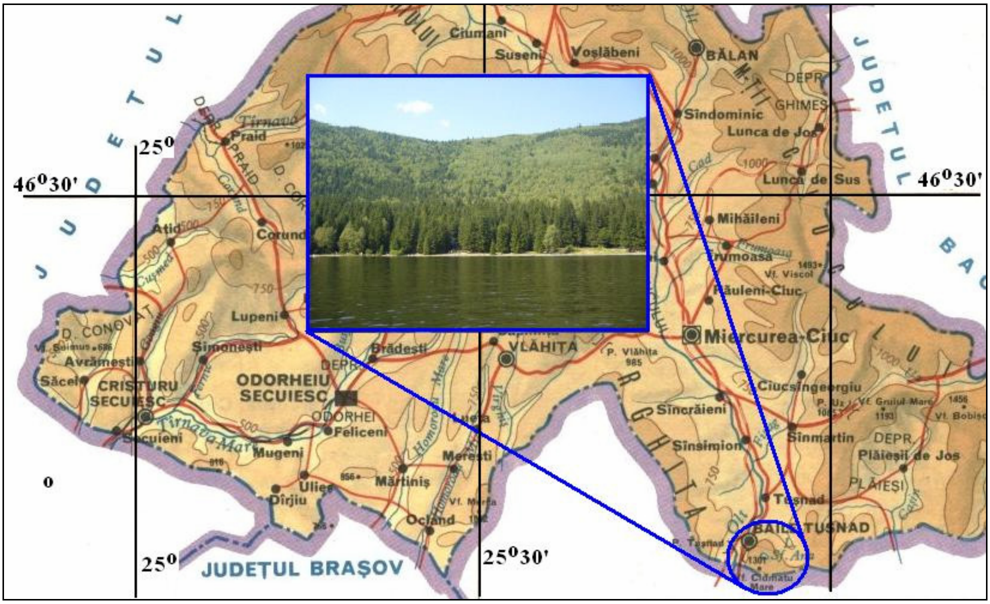


Fig. 1. *St. Ana Lake's geographic position, part of Harghita county – Romania, with detailed image from the middle of the lake.*

St. Ana Lake formed in the volcanic cone during years collecting water from local precipitation. The action of water flood eroded surface volcanic soil and carried resulted particles to the bottom of the lake. These movements influence the particle shape and size, a representative sample of this soil eroding process is represented by the shore sand. Secondly those particles getting in the wet environment are subjected to the natural sedimentation process.

Chemically, the water from St. Ana Lake should be similar to distilled water but the local environmental conditions such as eroding process might affect the water purity from micro scale to nano scale dispersions. The aim of present article is to investigate the nano-particles pattern in several water strata related to the possible anthropologic pollution in the natural sedimentation process.

RESULTS AND DISCUSSION

St. Ana Lake is a closed environmental water system. Precipitation represents the only water source. The water floods during rain and melting snow in spring erode the volcanic rocks of the cone and carry into the lake depositing them on the lake's bottom and shore. The shore sand represents the average characteristic of particulate mineralogical sample, which could easily form nano - sediments.

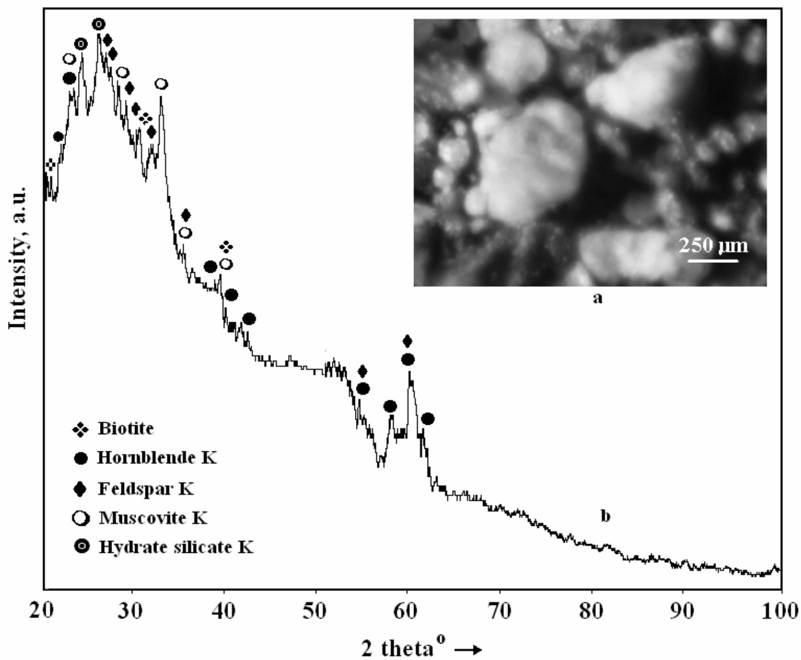


Fig. 2. *The sand sample colected from St. Ana Lake's shore characterisation: a) morphologic aspect on dark field optical microscopy and b) crystal phase identification on the X ray spectrum.*

It was collected a representative sand sample from the lake shore and was morphologically and structural investigatigated. The sand is formed by a various size range of microparticles, figure 2a, from larger ones, arround of 500 µm to smaller ones, less than 10 µm and even more fine particles. Last mentioned ones appear in figure 2a as a very fine dust covering the larger particles. The particle presents rounded shapes and volumes at each observed scale as a long interaction with water.

The sample was also investigated with X-ray diffraction, figure 2b, resulting that is a mixture of volcanic amorphous glass and crystal components. In figure 2b can be observed that the amorphous phase affects the shape of the X-ray pattern in a typical manner (Arghir, G. and Ghergari, L.M., 1989; Chicinaş, I. et al., 2001) and over that, the crystal phase peaks are observed. The major crystal components are identified using proper Match PDF file (***, Biotit, 1997; Nagelsmidth, L.Z., 1934; ***, Feldspar potasic, 1999; ***, Hornblende - potasic, 1997; ***, Hydrate potasic silicate, 1997). It was found the following compounds: potasic hornblende and feldspar with traces of biotite, potasic hydrates silicate and potasic muscovite.

The minerals identified with X-ray diffraction are part of complex silicates type, like filo-silicates (biotite, muscovite) or tecto-silicates (hornblende and feldspar). These minerals, under constant water action, disaggregate in very fine particles, with an average diameter below 1 µm. In order to observe the particle pattern in the lake water, samples were collected from the surface, 1 m, 2 m and 3 m deep to investigate with AFM.

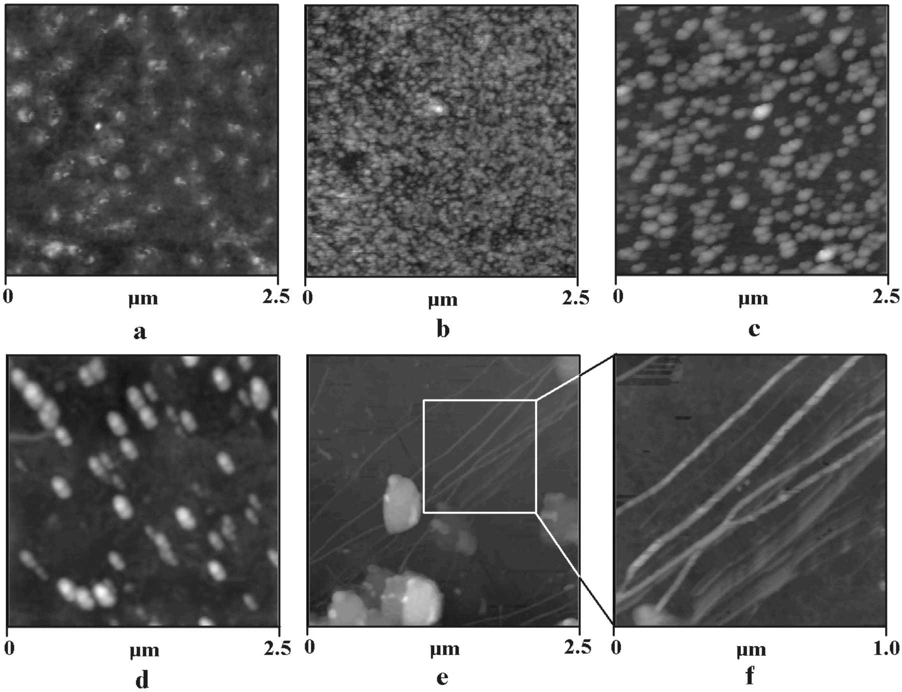


Fig. 3. *AFM topography images: a) glass substrate, b) surface water sample, c) 1 m deep water sample, d) 2 m deep water sample, e) 3 m deep water sample, and f) image detail for 3 m deep water sample.*

The AFM samples were prepared putting each water sample as a drop on optical glass. The prepared AFM samples were drained at room temperature and investigated in tapping mode on a NanoScope AFM microscope using tapping mode silicon nitride tip NSC 12 Micromasch. It was acquired topographic images of 2.5 x 2.5 μm^2 scanned area performing some detailed scans when needed, figure 3.

First of all it was investigated the bare glass substrate to observe the possible influence on the samples measurements, figure 3a. It results that the substrate is very plane with a roughness of 0.79 nm corresponding to the maximum features height of 9 nm, suitable for AFM thin films investigation. At the first sight the surface water sample features very much small particles lied in a uniform film indicating a very populate dispersion, figure 3b.

In figure 3c can be observed the nano-dispersion of particles at 1 m deepness, which appear sensibly greater particles than the surface featuring an almost rounded shape, very similar with the microstructure observed in figure 2a. The arrangement of nanoparticles in this case is uniform but the density is obviously decreased. This tendency is also observed in figure 3d on the sample of 2 m deepness. A major change in this tendency is observed in figure 3e, because of greater particles related to relatively less density and also there appears a nano-biological formation.

Those biological formations cam be observed better in 1 x 1 μm^2 scanned area detail in figure 3f.

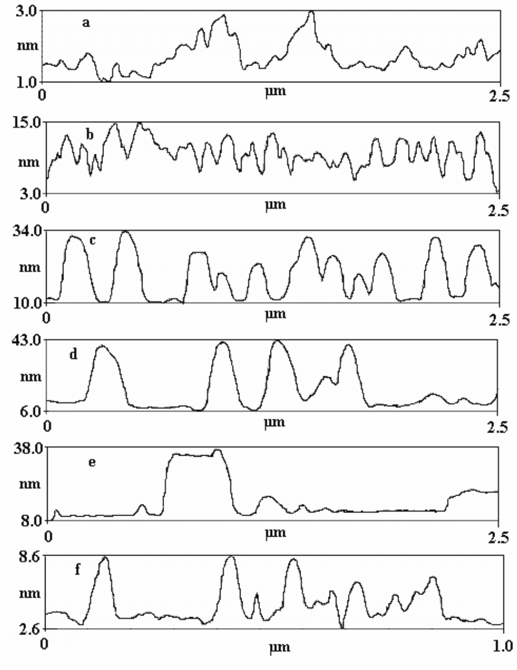


Fig. 4. *Horizontal profile detail on the high particle density on each AFM image: a) glass substrate, b) surface water sample, c) 1 m deep water sample, d) 2 m deep water sample, e) 3 m deep water sample, and f) image detail for 3 m deep water sample.*

The morphology of particulate matter is also changed form relatively round shape into grater formations, probably aggregates of mineral particles bonded with organic materials from observed biomass. At water sample collecting was noticed that at 3 m deepness appeared traces of lake mud.

At the second sight on the AFM topographic images were made special measurements and representations. It was taken on each AFM image a horizontal detailed profile on the particle high density zone, the result is presented in figure 4.

These representations allow us to measure the particle's average diameter. It was measured also the roughness on those detailed profiles and the surface properties for each entire image such as surface height and roughness; their variation versus water deepness are presented in figure 5.

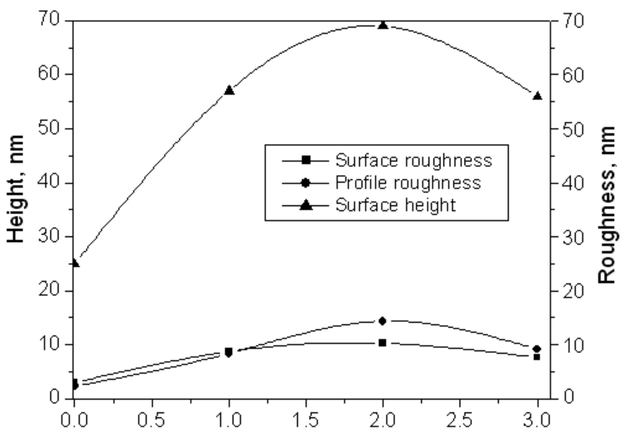


Fig. 5. *Surface height, surface and profile roughness versus collected sample deepness.*

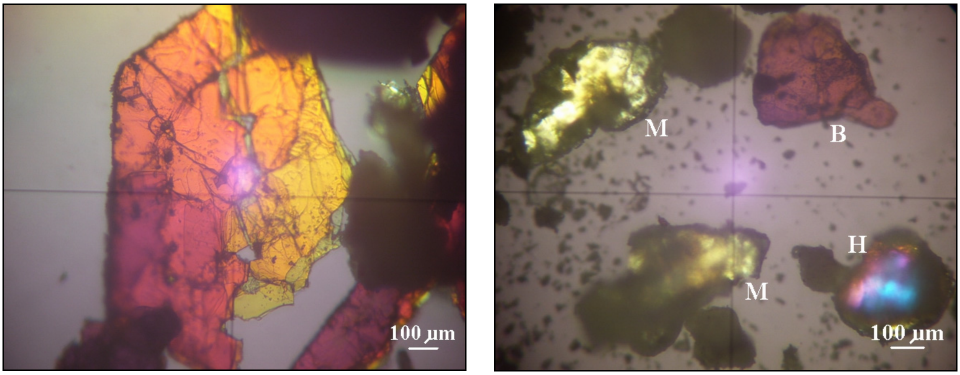
Figure 5 shows that at the surface sample particles induce a total height of 25 nm which causes a 3 nm roughness.

The roughness in the detailed profile taken through the maximum density zone of the AMF image of surface water sample is sensible lower which means a uniform packing.

This kind of packing is specific to very fine complex silicates particles distributed in water mass. At one meter deep it can be observed that the maximum sample height is about 55 nm corresponding to 8 nm roughness. The total roughness value coincides with the one in detailed profile. This fact points out a uniform particle distribution in the investigated surface unit but with quite long separation distances. This is because of the bigger particle medium diameter caused by several crystal layers still being welded between them.

At two meter deep, the maximum height sample's variation is observed at 70 nm because of the volume consistence of complex silicate particles which can be taken as spheres with irregular surface. This fact induces an increasing roughness on the profile taken through high density zone in comparison with the roughness investigated in whole area. This is because of the reduced number of particles.

The sediment aspect modifies at 3 meters deep where organic bonding fibers are among particles, actually from here starts the influence of the bottom of the lake. The aspect is distinguished by larger particles in plane, but a much lower height, about 55 nm. This morphology is specific to clay particles like muscovite and biotit, pointed out at micro-structural scale with crossed polarised light microscopy, figure 6. It can be observed in figure 6a for biotit as in figure 6b for muscovite a particle morphology similar to the one observed in figure 3e.

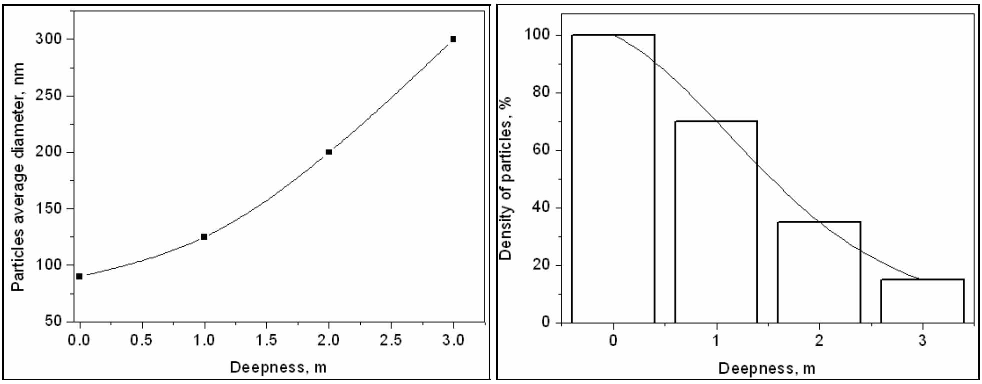


a b

Fig. 6. *Microstructural cross polarised light optical characterisation of St. Ana particulate matter: a) biotite lamellae, b) multicomponent feature: M – muscovite, B – biotite and H - hornblende*

The difference is only dimensional. The fact that at 3 m we find in plane larger particles but flat (specific to clay) has direct implication to the roughness observed, being in a slow decrease. The obvious modification in particle pattern at 3 m makes this level as an emergence limit of fine micro-structural particles.

A more precisely measure of particle distribution being suspended in water samples investigated is given by the particle average diameter, quantitive determined based on detailed profiles taken through maximum density zones in each AMF image. Therefore it was represented particle average diameter variation with water depth, figure 7a. It can be observed that the surface particles fit to nano-crystal domain with an 80 nm diameter. At 1 m deep is recorded a 125 nm value, near the limit between nano-crystal domain and micro-crystal domain. Therefore, the material particle dispersion in St. Ana Lake from surface to 1 m depth is similar with a colloidal soil of complex silicate particles. At 2 m deep is recorded 200 nm for average particle diameter, inferior limit in micro-crystal domain and at 3 m depth is obtained a value of 300nm.



a b

Fig. 7. *Particle distribution versus water deepnes:*
a) particle average diameter and b) the density of particles in observed area.

Taking in consideration that the nano-crystal domain is defined as being lower than 100 nm (Jumate, N. et al., 2002), from figure 7a is observed that nano-dispersoids distribution in St. Ana Lake has a wide parabolic shape which makes the connection between nano-crystal domain from surface and micro-crystal domain specific to mud accumulation area.

From AMF images was determined percentage density of particles for each water sample, figure 7b. While particle diameter have a parabolic distribution, the particle density shows a Gaussian distribution with a maximum at water surface corresponding to smallest identified particles. The crossover particles from nano to micro-crystal domain, the ones from 3 m depth are less dense but have bounds with organic fibers shown in figure 3f.

These revealed aspects show the strong connection between particulate matter from rocks desegregation of volcanic cone surface layers and nano-particle dispersion from lake water layers. This parabolic distribution of particle average diameter and Gaussian distribution of particle percentage density can establish a new model of static sedimentation with no horizontal driven current available in balanced weather conditions without precipitation. It is worthy of note that these nano-particles very well distributed in water layers are remains after larger micro-particle deposit and driven by water currents formed when precipitation fall.

CONCLUSIONS

The investigations made in order to establish the nano-sediment composition at St. Ana Lake – Romania reveals a strong connection between particle structure and mineral composition and their distribution in water strata. Using X-ray diffraction method was determined material particle composition which can appear suspended in water as it follows: potasic hornblende and feldspar with traces of biotit, potasic hydrate silicate and potasic muscovite associated with volcanic non-crystalline glass (andesine). The microscopic investigation of these particles show specific morphologies joined with a wide range particle dimensions from 500 μm to less then 10 μm. There were collected samples from surface, 1, 2 and 3 m depth being prepared for AMF investigation. The AMF images points out mineral particle specific morphology identified with X-ray diffraction, fact confirmed by the similarity observed with optical cross polarized light microscopy investigation. It points out an 80 nm diameter particles at surface, at 1 m deep the medium diameter is 125 nm the limit of nano-crystal domain, at 2 m a 200 nm diameter and 300 nm at 3 m deep. These results enter in a parabolic evolution related with a Gaussian distribution of particle density in water layers, the surface one being denser with particles similar to colloidal soils. These revealed aspects can establish a new sedimentation model specific to inland water ecosystems.

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RESEARCHES REGARDING THE FORESTRY ECOSYSTEMS EVOLUTION FROM O.S. BAIA MARE

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ABSTRACT. The present paper presents a detailed analysis, on a long time period, 1972-2002, of the coppice that is in the responsibility of O.S. Baia Mare. The field activity proved that a cost-benefit analysis for the forest ecosystem from our country is difficult to be made, but an analysis of the productivity of the ecosystem is easier to be done and can also be presented briefly. These analyses can be used by teams of economists and ecologists in order to present the quality of the environmental factors, of the processes of degradation or amelioration for a specific area, and to suggest an environment protection strategy that is going to be developed on a long time period. For O.S. Baia Mare, the indirect economic value of the forest ecosystem is not presented in official documents. Through this paper we measure the value of the forest ecosystem, the nature and the intensity of the destabilization factors and we conclude that the diversity of the coppice has decreased, but the local species of forest have not disappeared, generating new phase of succession of the ecosystems.

Key words: *pollution, forest ecosystems, intrinsic economic value*

INTRODUCTION

The daily concerns have evolved during time from the work that was to provide the stern necessities, to the rush after profit and social prosperity. During the last decades, the human society has become more aware of the harmful effects resulted form acting with the strict purpose of obtaining profit, so the basic preoccupation has now become the discovery of a way that combine profit obtaining actions with a minimum impact over the environment. But the long time period in which humanity followed strictly the obtaining material benefits has generated environment problems that are difficult or impossible to be solved in a short time period.

As it is known, Baia Mare is a city high polluted with different compounds of sulfur and heavy metals. The flux of polluted gasses damages the human health and disturbs the protection and production functions of the forest ecosystems. But these ecosystems are part of the durable development strategy and have a key role in the polluted areas (Cherecheş, 1999).

To remediate the harmful effects generated by the economic activities the first step is attracting highly trained in ecological reconstruction personal. In Romania forestry science has developed experts in environment protection and reconstruction. Nowadays, environment protection is being made by specially trained personal, the results being faster and more efficient environment protection activities.

THE OBJECT OF RESEARCH

The paper makes an integrate analysis on a long time period, 1972-2002, of the coppice that is in the responsibility of the Baia Mare forestry administration area (O. S. Baia Mare). For this area, as for the other Romanian ones in general, the indirect economic value of the forest ecosystem is not mentioned in official documents (Amenajament, 1982, 1992, 2002).

THE PLACE OF RESEARCH

From a geographic point of view, Ocolul Silvic Baia Mare is framed by the Baia Mare Depression. The natural frame of the depression is generated by the following factors:

- **Non biotic factors:**
  - Geomorphologic (low mountains, loose valleys, sinuous manes, small intern and marginal depressions, altitude fields, sunny exposures and all types of slopes);
  - Geologic, volcanic rock types prevail (andesite, basalt, dacites etc);
  - Climatic, a moderate thermal regime, high precipitations during the year, mild winters and weak winds.
  - Soils and stationary (acid soils, middle and superior productivity stations);
  - Hydrographic – characterized by a high density of rivers and streams with relatively small debits, small natural lakes and a vast capacity human made lake.
- **Biotic factors:**
  - Flora favorability, a high grade of forest covered zones in the north of the depression, fruit tree cultures, wine cultures, grass and hay zones on the south versants and agricultural cultures in the south of the depression;
  - Fauna favorability characterized by the wild life, fishing, aquaculture (trout) and the livestock farms.
- **Factors that imply human activity:**

  The intensive pollution with gazes that contain sulfur dioxide and dusts with high content of lead and heavy metals from the last decades has generated numerous polluted sites:
  - The crumble and destruction of vegetation: Dealul Crucii (U.P.I, u.a.84), Ferneziu (U.P.II, u.a.15) and Bulat (U.P. VI, u.a.97);
  - Tailing damps: Valea Borcutului: halda Vilhelm (U.P.I, u.a. 29); Valea Neamțului: halda Iojica (U.P.I, u.a.36), halda Borzaş (U.P.I, u.a.41); Valea Roşie (U.P.I, u.a. 61); Dealul Crucii (U.P.I, u.a.85); Herja (U.P.VI, u.a. 81).
  - Areas that lack soil after human exploitations: Valea Sfântului Ioan (U.P.I, u.a.79, 84); Limpedea (U.P.VI, u.a.52);

WORK METHOD

We have used a comparative analysis method for the principal forest types registered in the reports of the Baia Mare forestry administration area from 1972 to 2002. Also, we have identified and registered the main factors of destabilization and limitation from this area.

RESULTS

Table 1

Types of station and types of forest managed by O.S. Baia Mare

Station type	Forest type	Year 1982			Year 1992			Year 2002		
		Forest total (ha)	Empty areas total (ha)	TOTAL (ha)	Forest total (ha)	Empty areas total (ha)	TOTAL (ha)	Forest total (ha)	Empty areas total (ha)	TOTAL (ha)
0	**0**	-	-	-	-	364,8	364,8	-	342,8	342,8
4121	**4191**	104,6	-	104,6	-	-	-	-	-	-
4311	**4151**	15,6	-	15,6	-	-	-	-	-	-
	4161	70,4	-	70,4	630,8	-	630,8	494,1	-	494,1
4322	**4113**	3,5	-	3,5	-	-	-	-	-	-
	4114	3798,4	19,2	3817,6	1929,8	6,3	1936,1	3140,7	-	3140,7
	4121	37,4	-	37,4	-	-	-	-	-	-
	4141	367,2	-	367,2	-	-	-	-	-	-
4323	**4151**	177,9	-	177,9	36,7	-	36,7	-	-	-
4324	**4141**	362,0	-	362,0	1502,7	-	1502,7	-	-	-
4420	**4114**	3070,8	3,2	3074	2839,6	1,1	2840,7	2716,6	-	2716,6
	4121	59,9	-	59,9	73,1	2,7	75,8	-	-	-
	4131	46,6	-	46,6	-	-	-	-	-	-
5232	**4212**	4	-	4	-	-	-	-	-	-
	4231	128,6	-	128,6	169,1	-	169,1	-	-	-
	4281	3125,2	3,7	3128,9	2062,8	31,4	2094,2	1470,7	21,7	1492,4
	4312	70,2	-	70,2	-	-	-	-	-	-
5233	**4221**	14,6	-	14,6	7,8	-	7,8	-	-	-
5252	**9713**	-	-	-	-	-	-	2,3	-	2,3
5253	**9722**	18,3	-	18,3	8,8	0,5	9,3	14,5	-	14,5
	9821	8,0	-	8,0	-	-	-	-	-	-
5254	**9911**	0,5	-	0,5	-	-	-	-	-	-
5255	**4212**	-	-	-	-	-	-	2,1	-	2,1
	4281	-	-	-	-	-	-	1,3	1,1	2,4
7331	**6143**	32,2	-	32,2	-	-	-	-	-	-
7332	**6141**	31,7	-	31,7	-	-	-	-	-	-
	6142	69,0	-	69,0	-	-	-	-	-	-

Table 2

Evolution of the composition of the forest species managed byO.S. Baia Mare

Year of the development	Proportion of the species (%)									
	FA	GO	MO	CA	ME	CAS	DR	DT	DM	TOTAL
1962	71	7	-	7	-	-	6	8	1	100
1972	68	7	8	-	3	1	2	10	1	100
1982	68	5	11	4	4	1	4	2	1	100
1992	72	3	15	3	-	-	1	5	1	100
2002	76	4	14	2	2	1	-	1	-	100

The analyze of the tables

All three tables present the status of the forest ecosystem in the key moments from the changing of the exploitation method, generating a clear image over the influence of the human will over the ecosystems that present a potential of capitalization on the economic market.

Table number one presents a pronounced diminution of the forest types. In 1982 there were existing twenty three principal types of forest, diversity being one of the characteristics of the Baia Mare Depression forest ecosystems. In 1992 the variety has decreased, the number of the forest types being below half of the one measured in 1982 (only ten forest types), the diminution appeared without a development of new species. The most visible transformation appears in the analyze from 2002. The number of initial forest types has decreased even more (only five have survived over the time), and new types have timorously emerged: 9713 – *Anin negru de productivitate superioară* (2.3 ha), 4212 – *Făget de deal pe soluri schelet cu flori de mull* (2.1 ha), 4281 – *Făget de deal cu Festuca drymeia* (2.4 ha). Although the number of forest types has drastically decreased in a very short time period, the signs of change in the structure of the ecosystems begin to be more and more obvious. The development of new species, although on small surfaces, has proved to be the sign that foretells a great change in the composition of the ecosystem (the development of new forest types), but also a change from the point of view of managing the resources and exploitation of the new natural resources.

Another factor of maximum importance is the surface covered by forest. In 1982, the 11616.6 ha represented the forest covered surface of the forest administration zone. 1992 presented a descendent trend, the forest covered surface being only 9261.2 ha. The sensitive reduction of the forest covered area cumulated with the spectacular reduction of forest types demonstrates a predilection for systematic and unsustainable exploitation of some forest types. In 2002 the exploitation method is continues, as a result, the forest covered surface dropping to 7842.3 ha, approximately two thirds of the surface registered in 1982. The drastic reduction of the forest types, in full, eight, from which only five have survived from the twenty three identified in 1982, mark two aspects of the ecosystem: the man caused pauperism of the forest types and the power to rebirth.

Table 3

The surfaces affected by the destabilization and limitative factors from the area managed byO.S. Baia Mare

The nature of the factors	% from the S of the forest area	The affected surface (2002)											
		TOTAL	Manifesting grade										
			Weak		Moderate		Powerful		Extremely powerful		Excessive		
Name	17373,7	ha	ha	%	ha	%	ha	%	ha	%	ha	%	
Wind flooring	27	4682,0	3419,7	73	1159,3	25	93,7	2	9,3	-	-	-	
Drying	6	1106,7	446,0	40	374,6	34	167,4	15	118,7	11	-	-	
Pests attacks	2	288,5	97,3	34	88,2	31	103,0	35	-	-	-	-	
Destructions caused by fire	-	72,2	33,2	46	39,0	54	-	-	-	-	-	-	
Wind and snow brakes	3	444,6	245,6	55	156,2	35	30,6	7	12,2	3	-	-	
Exploitation harming	1	161,1	117,5	73	40,0	25	-	-	3,6	2	-	-	
Harms produced by wild beasts	-	5,8	-	-	3,0	52	-	-	2,8	48	-	-	
Pollution	45	7847,1	5240,8	66	2204,3	28	355,7	5	46,1	1	-	-	
Run downs	1	93,6	47,7	51	37,2	40	7,7	8	1,0	1	-	-	
The extending of swamps	-	20,2	-	-	15,3	76	4,9	24	-	-	-	-	
Surface erosion	1	174,4	68,0	39	105,5	60	0,9	1	-	-	-	-	
Deep erosion	-	12,4	8,6	69	3,8	31	-	-	-	-	-	-	
Erosion - total	1	186,8	76,6	41	109,3	59	0,9	-	-	-	-	-	
Rock at the surface	18	3083,9	-	-	-	-	-	-	-	-	-	-	
Unhealthy stem	3	566,3	-	-	-	-	-	-	-	-	-	-	

The last factor, the empty areas, prove the unremitting extending of the human habitats and atrophic areas. In 1982 have been registered as empty areas 26.1 ha, the empty areas have doubled in 1992. As we can see, in 2002 the total surface of forest which covered zones is decreases and the empty areas also sufferer a decrease (22.8 ha).

Table number 2 presents the evolution of the composition of the ecosystem from the species of wood point of view. From the presented data it is easy to observe that the species are developing constantly, generating over time an almost identical model of forest. Analyzing the data we can conclude that valuable species (from the economic point of view) have been the same over time.

Table number 3 presents the factors that cause destruction or incapacity of development of the monitored types of forest. The factor that has the main influence is pollution, affecting 7847.1 ha and being responsible for 45% of the causes of destruction in the forest ecosystems located in the Baia Mare Depression. The data also shows that low and moderate intensity pollution usually affect the development of the forest types. Negligence in human actions, that should be oriented in keeping the environment as close as possible to the ideal of untouched nature, manifests by continuous decrease of the variety of forest types. As a consequence, the indirect value of the forest ecosystems, for both, the interest of human health, and direct economic value, is decreasing drastically, or becoming impossible to obtain because the exploited type of forest has disappeared.

Another significant perturbation factor is wind flooring. This factor causes approximately 27% from the destructions suffered by the ecosystem, affecting 4682.0 ha. The moderate and strong intensity of wind usually cause damages, transforming wind from a natural resource indispensable in seeds dispersal and pollination into an element that causes chain destructions. Wind becomes one of the natural causes in ecosystems destruction, but it also remains an indispensable tool in the reproduction process of wooden and herbal vegetation.

Another factor that causes a limitation of possibilities in ecosystems growth is the existence of rock on surface. This impossibility of the ground to support complex vegetation can appear because of natural hazards, or because of irresponsible human activities. The natural causes are multiple: the soil can be washed from the rock in the course of a massive inundation, or the soil might have never formed because of the unfriendly natural conditions, but this type of soil problems are to appear as a result of pollution and massive exploitation that is not followed by activities in replanting a young forest. If the corrective actions are not applied the soil remains without its intrinsic support made from roots and it is exposed to soil run downs, inundations (usually caused by the perturbation of the water circle in nature as a result of massive deforestation) and because of a sum of natural factors. The presence of rock at the surface is to be conceived as a natural element, impressive by the age and beauty of the rock, or as an effect of excessive exploitation. The second cause generates many of the unprecedented natural hazards, emphasizing the way in which human activities affect the environment.

In conclusion, the three tables present the modifications that appeared in one of the most effervescent periods from the Romanian society. The possibility to exploit natural resources with minimum restrictions has transformed the forest ecosystems into a frenetic fight to benefit from the natures wealth in strict financial way. These caused a brutal decrease in a very short time period of the number of forest types and forest covered areas.

CONCLUSIONS

Analyzing the actual and passed number of types of forest from the Baia Mare Depression forest ecosystems shows a diminution of biologic and coppice diversity.

The profound manifestation of destabilization and limitation factors has imposed protective activities for forest ecosystems influencing the evolutional ecologic processes from these areas.

The forest protection technologies, through the maturity of the processes and the universal applicability, represent secure and close to the natural models (in ameliorating the effects of pollution and ecological reconstruction) methods. Optimum results can be expected after a long time period, monitoring and efficient personal organization is also needed.

One of the decisive factors in the success of an ecological reconstruction program is interdisciplinary research. This activity is of great interest for the moment, but in this research faze it cannot cover the need of integrate effects of human activity, provide solutions or prepare citizens to develop a healthy life style.

The lack of implication of economic and social environment in voluntary activities has proved to be a problem due to the actual legal frame through which founds and benefits are given.

A stabile legislative frame in the environment protection domain would transform the past successful environment reconstruction actions (done in the absence of a legal frame) into trusted models of action for present and future.

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ATOMIC ABSORPTION SPECTROMETRY (AAS) VS. ATOMIC EMISSION SPECTROMETRY WITH INDUCTIVELY COUPLED PLASMA (ICP) IN MONITORING HEAVY METALS IN SOIL AND VEGETATION

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ABSTRACT. In the current social context of environmental issues have taken on particular importance. A growing number of studies show the devastating effects of pollution on the environment, quality of life and health, and the need for knowledge and monitoring of environmental factors. Making monitoring systems require detailed technical and economic studies in order to get through their efficiency and maximum quality with minimum costs.

This paper has proposed to prove the correctness of the choice of atomic absorption spectroscopy as a technique used in systems for monitoring heavy metals soil and vegetation. Study was conducted on a total of 33 deep-surface soil samples and vegetation simultaneously analyzed by atomic absorption spectrometry (AAS) and atomic emission spectrometry with inductively coupled plasma (ICP). To compare the results have been used in specific processing techniques and statistical indicators, namely indicators of trends and indicators of dispersion adaterilor. In addition to their a study using minimal cost-benefit argument defining the choice of method.

The data processing showed that, while PCI is a technique more sensitive to the needs of monitoring and nilelurile concentrations of heavy metals in soils, ASA is the preferred technique.

Key words: *monitoring, soil-vegetation, heavy metals, AAS, ICP.*

INTRODUCTION

Soil is a natural resource just as important as water or air. As man can not live without water and air, so he can not live without soil as the basis for it`s entire existence or without food plants and animals that evolve and live on soil.

Soil characteristics vary from one area to another depending on a big number of factors such as climate and altitude. For each climate area there is a certain type of soil. In temperate zones, there are many black and high fertility chernozems, brown soils and forest podzolurile related parts. There are about 720 different types of soil, each having own characteristics.

From many industrial activities result poluttant emission in different forms suchs as liquid, solidor gas, rich in heavy metals. Various scientific sources (***, EMEP/ CORINAIR, 2008; ***, CEC - B.A.T. for Air, 2005; ***, O.M. 756, 1997) shows that from many human activities (like the steel and metallurgical, mining, chemical, etc..) there results emissions rich in heavy metals. These metals pollute all environmental components (air, water, soil and vegetation, biodiversity) in wich they are found in significant quantities. To these industrial activities are added pollutants from road transport, which supplements, sometimes in a significant way, the amounts of heavy metals.

With the soil pollution near industrial facilities and the possibility of the tranfer of pollutants from contaminated soil becoming reality, monitoring soil becomes a necessity.

The regular space and time analysis of environmental indicators characteristic to both environmental factor and to the specific socio-economic area, can provide clear elements and concrete data on the level of pollution and possible sources of pollution. The analysis and the interpretation of the data from the space-time monitorisation considering the manner in wich the heavy metals in soil accumulate and migrate can bring important and necessary infromation that are used for making a corect and relevant decision.

Establishing a network monitorisation structure and the methods of analysis that are most appropriate to the monitoring is a complex, painstaking and difficult work, but there are several important information that depend on it (the value of the data, accuracy of estimates, forecasts and especially the conclusions and guidelines correctness of programs and plans related to the quality and soil management and food quality).

Achieving and maintaining these monitoring networks involves a research work to establish accurate and adequate monitoring locations and frequency, and involves significant costs for maintenance and operation. Determinations are made with manual systems, which involves taking samples from certain locations, transportation, training and specialised analysis.

There are several techniques used to identify metals. Chemical instrumental analysis is preferred because of the speed and the quality of the results. From the most common instrumental analysis techniques we mention (Hodişan T. et al., 1999; Pleniceanu, M. et al., 2007): atomic absorption spectofotometry with flame and/or in graphite furnace, atomic emission - inductively coupled plasma, the technique of ion exchangers, X-rays - fluorescence spectrometry, Polarography, thin layer chromatography / densitometry, column liquid chromatography / mass spectrometry, gas chromatography techniques / mass spectrometry.

For multiple and various tests, necessary for implementing a monitoring system, choosing the proper method of analysis is essential. This choice depends on the quality of the determinations (method sensitivity, detection limits, interference and eliminating their opportunities, technical characteristics and performance of the device used) and on the costs (analyzer cost, consumables cost, reagents cost, depreciation period expenses for equipment).

Atomic absorption spectometer AAS (Atomic Absorption Spectrometer) relies on the fact that in the ground state, the atoms can absorb specific radiation emitted by a source spectrum. The Frequency of the source indicates the nature of species M. The degree of reduction of radiant power of the light output after passing through the flame (absorption), measured by spectrometer, gives us quantitative indications of species M. During the The atomic absorption spectrometry, absorption phenomena are produced by a population of free atoms which arise from the dissociation of molecular sample.

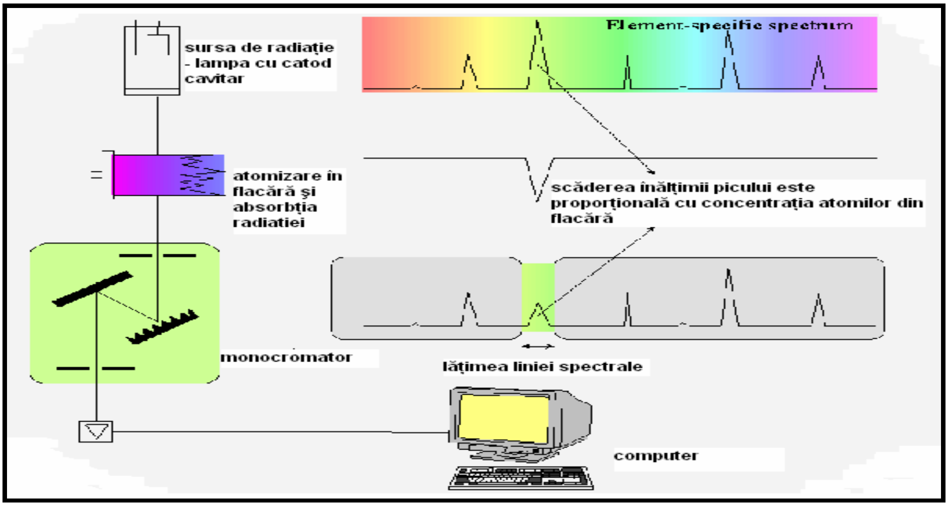


Fig. 1. *Working principle of atomic absorption sectrometer (AAS)*

When we determine the heavy metals through atomic absorbtion spectometry with flame, the results depend on: the technique for sampling, storage time, storage method, pH, clean containers for samples, color samples, the method of purification and concentration, analytical reagents used, environment in which to place analysis, method and equipment used, etc. Atomic absorption is a comparative technique, so the quantitative measurement accuracy depends largely on the quality of information in the standard that is used (Hodişan T. et al., 1999; Pleniceanu, M. et al., 2007).

Atomic emission spectrometry with inductively coupled plasma ICP (Inductively Coupled Plasma) is an analytical technology used to detect traces of metal (at the molecular level). Elements are determined to deliver a specific light to which corresponds a particular wavelength that can be measured. The ICP device is designed to generate plasma in an argon environment using a radio frequency generator and an induction coil. The base of CPI is made by the three concentric tubes, called the outer cylinder (outer loop), the intermediate cylinder (intermediate loop), inner cylinder (inner loop), which together form the "torch" (torch). The gas circulating through the inner tube carries the sample in the plasma. Plasma support gas is tangentially introduced through the outer tube. The gas that is inserted through the middle tube controls the height at which the plasma is produced. Coil creates an alternating magnetic field that induces an alternating current of ions and electrons in the plasma support gas.

In atomic emission spectrometry the sample, placed in an inductively coupled plasma, is the source of emissions, and considering that each atomic species has it`s own well defined wavelengths that emit radiation, it can be easily identified by the use of some separation and detection optic sistems(Hodişan T. et al., 1999).

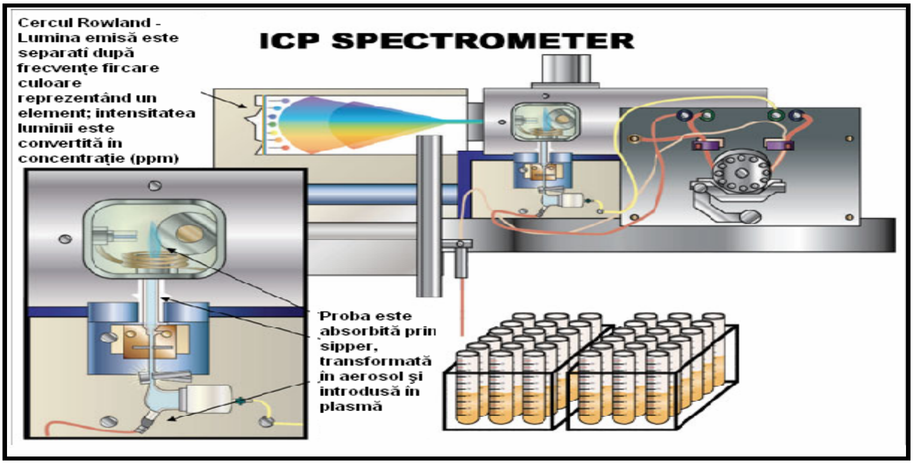


Fig. 2. *Working principle of atomic emission spectrometer with inductively coupled plasma(ICP)*

METHODS AND MATERIALS

The purpose of the study is to determine which of the two techniques of instrumental analysis is more suitable to be used in a monitoring system, to obtain a set of concrete data.

For atomic absorption spectrometry it has been used a spectrometer AAS GBC 932 Plus (Australia) with double beam, with hollow cathode lamps as the source of radiation, spray atomization system with variable flow type pneumatic, fog room and laminar flow burner with Premixture with long, built entirely of titanium, air-acetylene flame, approx. 23000C

For atomic emission spectrometry with inductively coupled plasma it has been used a spectrometer ARL ICP ACCURIS simultaneously. We used the same calibration solutions as the ASA, for each determination being made 5 consecutive readings.

Estimated standard deviations were 0.01 ppm for Cd, 0.05 ppm for Cr, 0.002 ppm for Cu, 1 ppm for Pb and 0.0024 ppm for Zn.

To achieve the calibration curves it had been used standard reference solutions with 5 points of concentrations. Absorbance value, meanning the metal concentration from the extraction solution has been achieved by mediating three consecutive readings.

Samples (11 surface soil samples, 11 depth soil samples and 11 samples of deep-soil vegetation related question) were taken and mineralized with a mixture of nitric acid / hydrochloric acid according to SR ISO 11466/1999.

RESULTS

To determine which of the two laboratory techniques is most appropriate for a soil and vegetation monitoring system, there were analyzed in parallel, by both methods, a total number of 33 samples - 11 surface soil samples, 11 deep soil samples and 11 samples from vegetation.

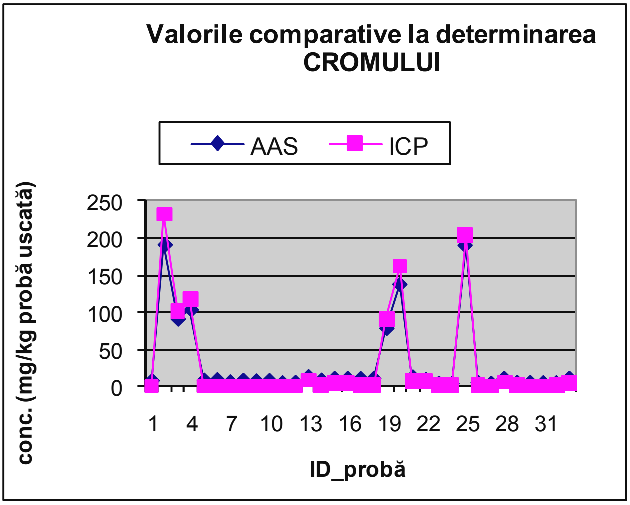
Qualitative characteristics of two instruments are similar, with a slight superiority of the ICP, as it was exemplified by the correlation coefficients and standard deviation estimated.

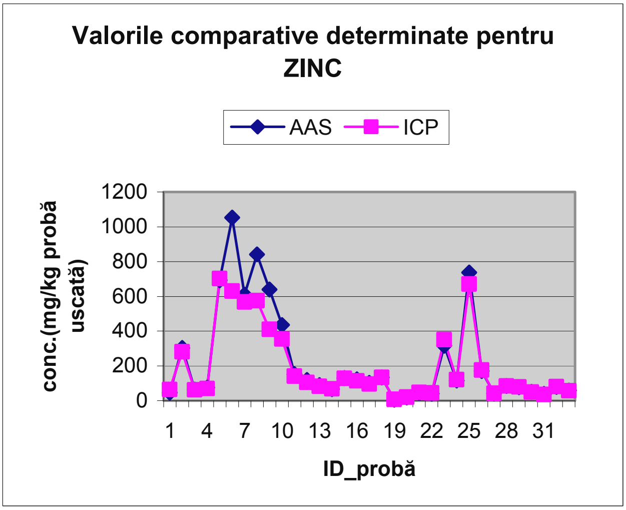
Table 1.

Qualitative characteristics of analyzers

instrument		AAS	ICP
coeficienti de corelație R^2	Cd	0,999	0,998
	Cr	0,999	0,999
	Cu	0,988	0,999
	Pb	0,999	0,999
	Zn	0,987	0,998
abaterea standard estimata	Cd	0,01	0,01
	Cr	0,09	0,05
	Cu	0,008	0,002
	Pb	0,01	0,06
	Zn	0,003	0,008

By direct comparison of the values obtained for the 33 samples analyzed by the two methods, it is noted that for the indicators for copper, zinc and chromium the values obtained by the two methods are very close.





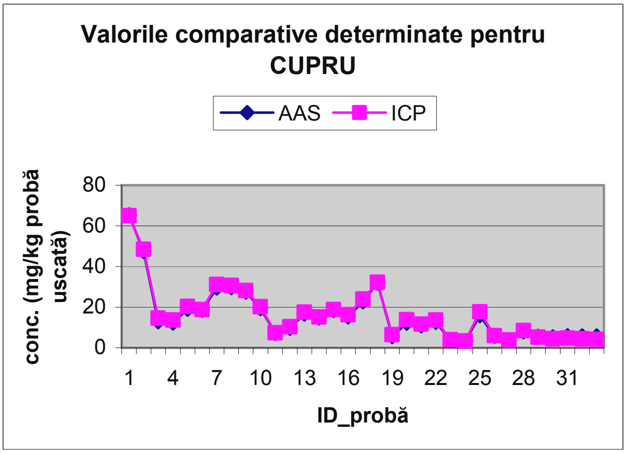


Fig. 3. *Comparative graphical representation of the values obtained from analysis of samples by AAS and ICP indicators copper, chromium and zinc*

To establish the correlation between the sets obtained and to be able to draw final conclusions fair, we turned to a statistical study by using a series of proper indicators (Pleniceanu, M. et al., 2007; Rouessac, M. and Rouessac, A., 2007; http://www.winstat.com/; http://www.chem.utoronto.ca/coursenotes/analsci/StatsTutorial/index.html; Harris, D.C., 2006; Rojanschi, V. et al., 2002). Starting from the two sets of data we determined: direct average, linear average deviation (d) and the square deviation or standard (Std. ad., σ) and then through Excel statistical functions, the coefficient of variation, the covariation and variation of deviations:

Table 2.

The values of statistical indicators

indicator	coeficient de corelație	covarianța	varianța abaterii medii	varianța abaterii standard
Zn	-0,133217	-0,6099678	17,369067	17,369067
Cd	0,3605973	0,0014839	0,0011668	0,0011668
Pb	0,7046469	5,7333226	7,9937453	7,9937453
Cr	0,9975381	4,9484157	0,0226283	0,0226283
Cu	0,9987658	0,2883151	2,669E-33	9,172E-05

To compare the two sets of data we calculated coefficients and we made specific statistical representations by WinSTAT program.

➢ t-test (known as Student's test) is one of the most common statistical test, used to compare standard deviations of data series. After we aplied this test to the data series, we obtained the following values:

Table 3.

The road test results of Kolmogorov-Smirnov distribution

Test of Normal Distribution - Kolmogorov-Smirnov test			
	N	**D**	**P**
Zn	35	0,175331	**0,232168**
Pb	35	0,344645	0,00049
Cd	35	0,314491	0,001969
Pb	35	0,260355	0,017392
Cr	35	0,163541	**0,30645**
Cu	35	0,145255	**0,45124**

The high value of the P coefficient (probability of occurrence of the value of D as the maximum distance from the actual distribution curve concentrations) in Cu, Cr and Zn it denotes a normal distribution.

➢ The linear correlation between two data series is well defined by the coefficient of correlation. Pearson Chromium and copper have a good correlation of data, according to the values determined for the correlation coefficient.

Table 4.

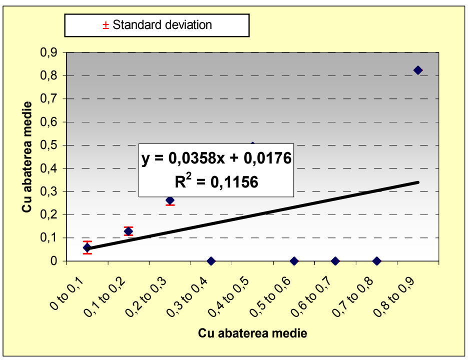
Sheet calculation results of Pearson correlation coefficient

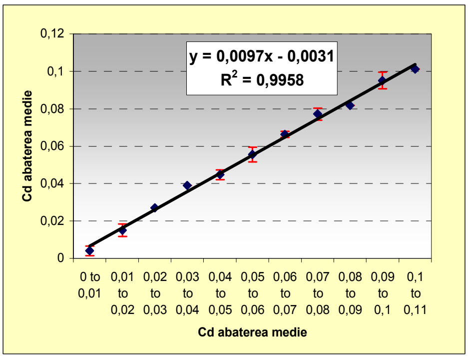
Cr conc.ICP	**Cr conc.AAS**
Correlation coefficient	**0,997538128**
valid cases	35
one-sided significance	5,6679E-40
Cu conc.ICP	**Cu conc.AAS**
Correlation coefficient	**0,998438453**
valid cases	35
one-sided significance	3,11931E-43
Pb conc.ICP	**Pb conc.AAS**
Correlation coefficient	**0,70464693**
valid cases	35
one-sided significance	1,15126E-06
Cd conc.ICP	**Cd conc.AAS**
Correlation coefficient	0,360597348
valid cases	35
one-sided significance	0,016667432
Zn conc.ICP	**Zn conc.AAS**
Correlation coefficient	-0,133216749
valid cases	35
one-sided significance	0,222759011

➢ By applying the Mean function over the data series representing the average deviation calculated for the tests that were carried out, we obtained the data and the graphics below

	N	Mean	95% Conf. (±)	Std.Error	Std.Dev.
Cu	35	0,010573	0,002387	0,001175	0,00695

	N	Mean	95% Conf. (±)	Std.Error	Std.Dev.
Cd	35	0,043426	0,011906	0,005858	0,034657

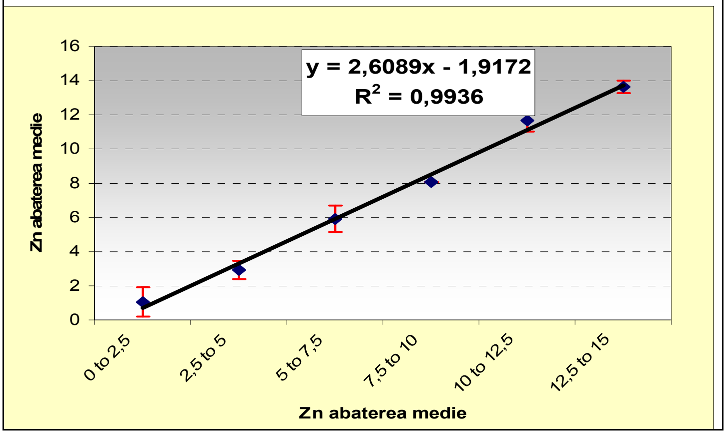




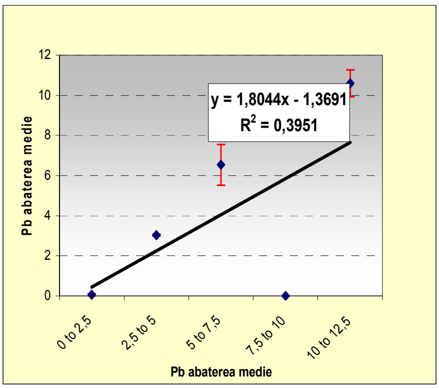
The function calculated the values for the probability of distribution of the average deviation for a confidence level of 95% and the graphic representations of the madium dispersion term also included a linear trend with the proper function. It is proved through this statistical test that for copper, cadmium and zinc the correlation data obtained for the same samples by the two techniques is good to very good.

For a maximum acceptable deviation, according to SR EN ISO 17025 (including requirements for competence of laboratories testing and calibration) of 0.1% between the values obtained for the same indicator between two different laboratories, we have a 100% correlation of results for chromium and copper. Likewise the calculation of correlation for zinc and 93.94% for chromium is 54.56%.

	N	Mean	95% Conf. (±)	Std.Error	Std.Dev.
Zn	35	3,407309	1,452581	0,714741	4,228466



	N	Mean	95% Conf. (±)	Std.Error	Std.Dev.
Pb	35	1,197646	0,985434	0,484882	2,868598



	N	Mean	95% Conf. (±)	Std.Error	Std.Dev.
Cr	35	0,138226	0,05243	0,025798	0,152623

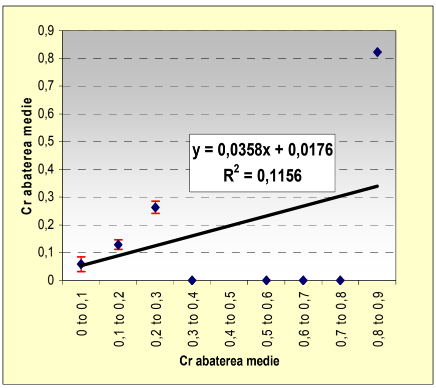


Fig. 4. *Graphical representation of the variance standard deviations*

Taking as a basis for calculating the values determined by AAS for copper indicator for example, the deviation% of the values obtained by ICP has a range of spread between -14.978% and 25.20179% which means changes of concentration in the extraction solution between -- 0.0698 ppm and 0.0562 ppm.

For the indicators of led and cadmium the situation is the same for small values of concentration but at higher concentrations recorded in soil samples (over 400 mg / kg soil) the values obtained by AAS are bigger. This difference may arise from this error brought on serial dilutions that were necessary to fit us in the calibration curve or due to matrix effects. However, at the control test carried out at the end analysis, on the maximum standard solutions, there was found on a deflection in ICP + values, probably due to overheating torch.

For the same maximum acceptable deviation of 0.1% between the values obtained for the same indicator between two different laboratories, the correlation is 40.3% for lead and for cadmium of 52.42%.

ASSUMPTIONS, CONCLUSIONS

Atomic emission spectrometry with inductively coupled plasma (ICP) has some advantages over the flame atomic absorption or graphite furnace.

Firstly because of the possibility of detection multielemenatary has a very high productivity.

Secondly, compared with atomic absorption,where emission lamps are needed for each item separately and in which can be determined only one item of evidence, in atomic emission spectrometry sample, placed in an inductively coupled plasma, is the very source of emission, and, how each atomic species has it`s own well defined wavelengths emitting radiation, it can be easily identified using optical separation and detection systems.

Also, ICP in comparison to the atomic absorption it has a wide working field, and it can be measured in the same time and from the same sample, without dilution, concentrations of the order of mg / L and the hundreds of mg / L.

It is very important to determine the costs involved in using each of the two methods. Thus:

- for the two types of apparatus used to conduct tests a study has been made for the costs of acquisition and costs related to consumer devices

- according to technical data, AAS spectrometer cosumes fuel for the acetylene flame, at a flow 2l/min maximum, starting from the time used for determining the 165 indicators (33 samples for which were analyzed 5 metals) of approx. 180 min., 2L apparent as consumption of acetylene / determination,

- according to technical data, ICP spectrometer consumed to produce plasma and sample transport (also having the role of carrier gas) 7.5 1.6 L / min, starting from the time used to determine the same 165 indicators for about 180 min., Resulting a consumption of 6.37 L argon / determination, According to the market study for equipment and consumables, the costs are:

Spectrometria AAS		**Spectrometria ICP**	
Produs	**Cost/ unitate produs**	**Produs**	**Cost/ unitate produs**
Oxyacetylene flame AAS Spectrometer, double beam, lamps multicatod	15000-17000 €	ICP spectrometer, 130-770 nm spectral domain, the sequence	50000-60000 €
Lamp elements 5 user request / 3 years	600-1200 €		
Acetylene cylinder flamfotometrică 8 kg	17 €	Butelie argon spectral 5 mc	9,5 €
Consumer Cost Acetylene / indicator led	0,004 €	Cost consum argon/indicator	0,012 €

Prices come from the offers in 2008 of the three forms which sells equipment and consumables for qualitative and quantitative analysis and they are without VAT.

For both sample preparation methods for spectrometric analysis is made in the same way and that is why the costs of training do not affect cost effeciency benefit. Consumer costs for argon and acetylene were calculated starting from the prices and consumption previously determined.

According to the cost-benefit study and cost- required sensitivity study, it can be concluded that the flame atomic absorption spectrometry can be considered the suitable technique for determining heavy metals in soil and in vegetation as a basis of work of a monitoring implemented system at regional level. The method is ISO standardized (International Standards Organization) and also with the relevant national standards. For the determination of heavy metals in soil it is worked after the methodology of 11047/iulie SR ISO 1999 and for the heavy metals in edible vegetation, we use the methodology proposed by Order 1145/2005 - veterinary and sanitary standards for food safety, which requires maximum limits for certain contaminants present in food. Sampling and sample preparation is made according to SR ISO 11466/1999 for soil and STAS 5954/1986 for edible vegetation.

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STUDIA UNIVERSITATIS BABEŞ-BOLYAI, AMBIENTUM, LIV, 1-2, 2009

RADIOLOGICAL SURVEY OF THERMAL BATH IN IGAL-HUNGARY

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ABSTRACT. The radon and radium content of thermal waters is usually higher than that of surface waters. Consequently, the radon concentration in the air of thermal baths may increase, therefore the annual radiation dose of those taking part at the treatment and the workers may exceed the limit recommended by WHO. To find these data measurements have been carried out in Igal, in one of the most important medicinal and thermal baths in Hungary. The activity concentration of ^{222}Rn was measured in the hot and cold-water pools, and in the medicinal and drinking waters of the bath, and at several points in the air in the territory of the bath. The activity concentration of ^{226}Ra, and the gross alpha and gross beta activities were also identified in the sources. Radon activity concentration values resulted between 1.6 and 11.5 Bq/l, while the activity concentration of radium reached even 2.1 Bq/l, which leads to that if an adult is supposed to consume 1 litre of water daily, the resulting annual dose rate is 0.21 mSv. The activity concentration of radon in the air was below 200 Bq/m^3, and the dose rate originating from inhalation on workers varied between 0.34 and 0.7 mSv, while in case of visitors staying there meant an extra dose of 0.09-0.19 mSv/year only.

***Keywords**: radon, radium, thermal bath, Hungary*

INTRODUCTION

Nowadays, thermal baths are getting more and more popular for relieving different kinds of pain, in order to preserve health, and simply with the purpose of relaxation. Igal is a popular health-resort in Somogy County (Hungary), where the wide-scale use of balneotherapy is outstanding.

However, thermal waters may contain a significant amount of radio-isotopes (Baradács et al., 2001). This may mean radiation dose for the patients in a small degree, but in a significant degree primarily for those working there (Bender et al., 2005; Somlai et al., 2007).

During our work the ^{222}Rn concentration in the water of the fountains located in the area of the bath (hot water: No. 76, 58, 52, cold water: No. 1, and 2), that of the pools (two covered pools: thermal water pool – FGYM, and thermal water pool – FTM, and one open pool: thermal water pool – KTM), and that of the airspace of the bath were studied. ^{226}Ra, ^{222}Rn, and gross alpha and beta activity concentration of the water used for medication (fountain No. 76 – GYV) were measured. Based on the values measured the radiation doses of the workers and the bathing guests were estimated.

MATERIALS AND METHODS

Water sample analysis

^{222}Rn concentration measurement

Samples from the fountains and drinking water were taken 6 times, and from the pools 9 times. Radon concentration was determined applying the emanation method. Measurements were carried out using a gasifier type Pylon WG 1001, and a radon monitor type Pylon AB-5.

^{226}Ra concentration measurement

Samples from the water measured (GYV) were taken 5 times, ^{226}Ra activity concentration was determined using radon emanation method. Scintillation cells of a volume of 1 litre, and single-channel analyzer type NP-420P were used for the measurements.

Determination of the indoor radon concentration

The indoor concentration level of radon had been determined at 8 closed locations for 8 months with monthly change of CR-39 solid state nuclear track detector fixed in an NRPB case. After exposition the CR-39 track detectors had been etched by NaOH solution of 6.25 M, at a temperature of 90 ± 0.5 ^{0}C, for 2.5 hours. Detectors were evaluated using Virginia 99 software.

Estimation of the dose exposure

Radiation dose originating from thermal water consumption

The committed effective dose originating from radionuclide intake was determined using the following formula:

$$E = K \cdot G \cdot C \cdot \tau$$

where,

E: is the effective dose originating from intake of the radionuclide, (Sv)
G: is the water consumption, (litres/day)
K: is the dose coefficient of radium for oral intake, (Sv/Bq)
C: is the activity concentration of radium, (Bq/l)
τ: is the exposition time, (days)

Radiation dose originating from inhaling radon and progenies

Radiation dose originating from inhaling radon and progenies by workers and those taking a bath was calculated. Here, the average airspace radon activity concentration, the equilibrium factor of 0.4 given in literature, 2000 hours/year working hours of the workers, and 548 hours/year staying of those taking a bath (recommended bath-taking period is maximum 1.5 hours/day), and the dose coefficient $7.9 \cdot 10^{-9}$ Sv/Bqm^3h were taken into account. The radiation dose was calculated using the following formula:

$$E = c_{Rn} \cdot K \cdot f \cdot \tau$$

where,

E: is the effective dose (Sv)
c_{Rn}: is the activity concentration (Bq/m^3)
K: is the dose coefficient (Sv/Bqm^3h)
f: is the equilibrium factor
τ: is exposition time (h)

RESULT AND DISCUSSION

Radon activity concentration in the water samples

The monthly values of radon concentration for fountains are given in Figure 1, and for pools in Figure 2. The measured values show that the radon concentration of the water in the pools and in the fountains varied between 1.6 and 11.5 Bq/l. The radon concentration level of the cold-water fountains is higher due to the solubility of gases. Based on the radon concentration levels measured in the water of pools it can be stated that the values are low as compared to former measurements in the Balaton Upland, Hungary (Kovacs et al., 2003), therefore, radon escaping from the water of the pools cannot plays as significant radon source in the airspace of the bath.

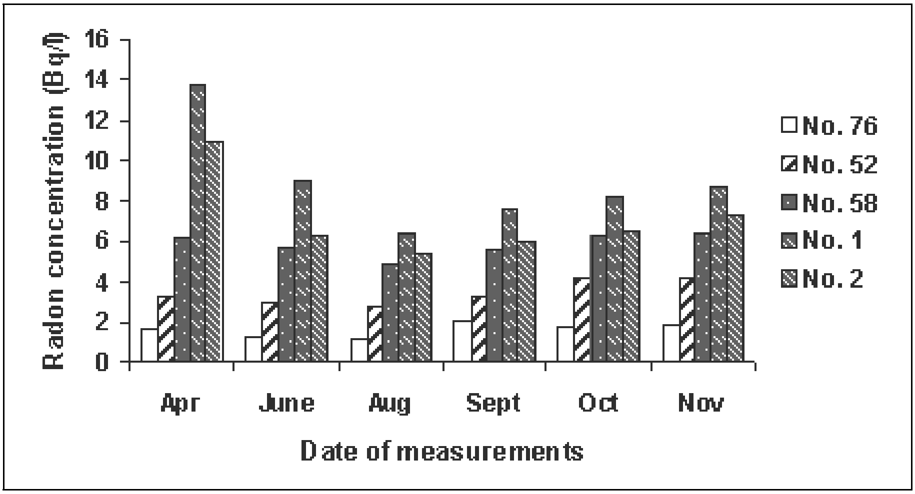

Fig. 1. *Radon concentration of fountain waters*

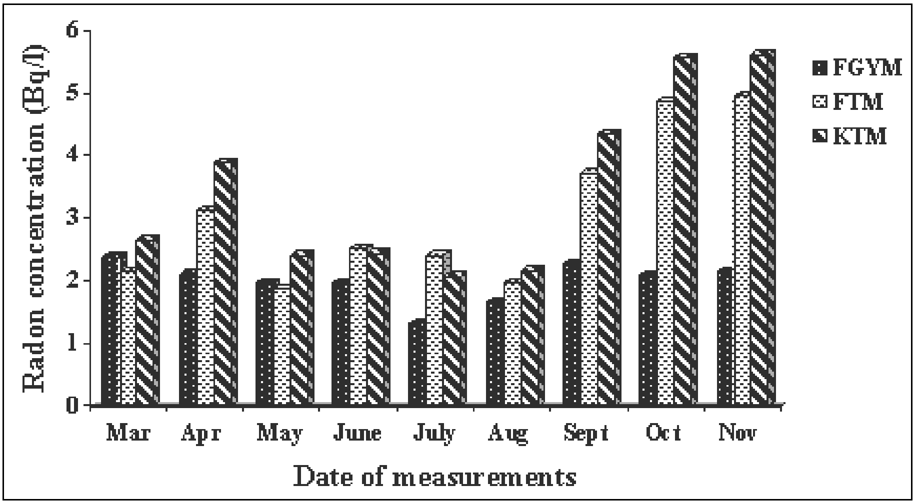

Fig. 2. *Radon concentration of pool waters*

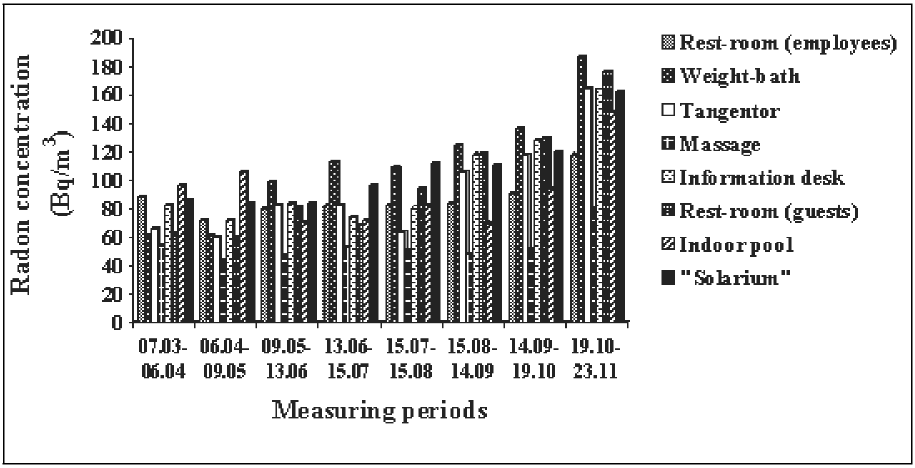

Fig. 3. *Monthly average radon concentration in the different places of the thermal bath in Igal*

Indoor radon concentration

The changes of monthly average radon activity concentration measured in the different airspaces of the thermal bath are shown in Figure 3. The graph shows that slightly higher radon concentration values were found during the autumn months. In case of Tangentor and the weight-bath the water used for medication is the mixture of water from fountain No. 52 and from the cold-water fountains. Since the radon concentration of the waters increased during the autumn months, we believe that this is also why higher radon activity concentration could be obtained in the airspace of the Tangentor and the weight-bath. On the ground of the results, it can be stated that radon activity concentration never reaches the strictest limit of 200 Bq/m^3 related to residential buildings at any of the measured points, and neither the limit value of 1000 Bq/m^3 related to workplaces.

Gross alpha and beta, and ^{226}Ra activity concentration of the thermal water

As mentioned before, the water of fountain No. 76 is also used for water-drinking during medication. Gross alpha and beta, and ^{226}Ra activity concentrations of the thermal water are shown in Figure 4.

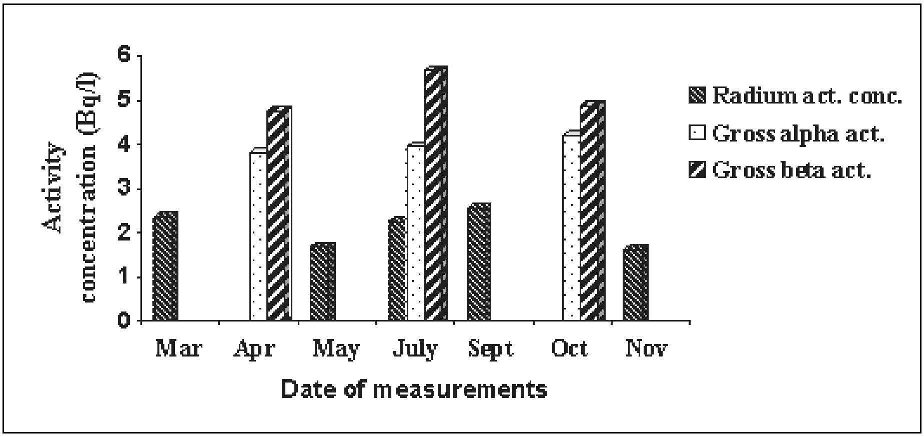

Fig. 4. *Gross alpha and beta, and ^{226}Ra activity of the thermal water*

It can be clearly seen in the Figure 4 that fountain No. 76 has high alpha and beta activity, and this is also confirmed by ^{226}Ra measurements. The water from fountain No. 76 used for drinking purpose exceeds 1 Bq/l in case of beta activity, and 0.5 Bq/l in case of alpha activity recommended by WHO (World Health Organization, 1993) concerning drinking waters.

Estimation of radiation dose exposure

The dose exposures due to radon in the indoor air concerning workers and bathing guests are given in Table 1.

It can be seen in the table that the annual committed effective dose concerning workers changes between 0.34 and 0.7 mSv. Daily visitors of the bath receive a committed effective dose between 0.09 and 0.19 mSv in the thermal bath annually.

Table 1.

Radiation dose exposure of workers and bathing guests

Location	workers (mSv/year)	guests (mSv/year)
Rest-room (employees)	0.55	-
Weight-bath	0.70	0.19
Tangentor	0.59	0.16
Massage	0.34	0.09
Information desk	0.63	0.17
Rest-room (guests)	0.62	0.17
Indoor pool	0.58	0.16
„Solarium”	0.67	0.18

Therefore, it can be stated that considerable radiation dose is neither received by those working there, nor by those wishing to heal there.

Since the thermal water is not only consumed by the group taking part at the medication, but also by the inhabitants in Igal. On the ground of our survey concerning drinking habits, a consumption of 1 litre per day was taken into account. According to the recommendation of BSS (Basic Safety Standard 12051., 2001) and WHO (World Health Organization, 1993) the dose conversion factor of radium due to ingestion is $2.8 \cdot 10^{-7}$ Sv/Bq, calculating using this value the value of the effective dose will be 0.21 mSv, which is not so significant comparing WHO reference level (0.1 mSv/year) (World Health Organization, 1993).

CONCLUSIONS

As a summary it can be stated that the radon concentration value of the waters is low (1.6-11.5 Bq/l), and the values were measured far below the 100-1000 Bq/l value recommended for mains waters by the EU, and the 100 Bq/l activity level recommended by WHO. Therefore, the radon-content of the thermal water used also for water-drinking will not cause significant extra dose for people consuming it. Due to the low values radon escaping from the water of the pools can neither be present as a significant source of radon in the airspace of the bath.

The radium concentration of the water used for drinking purpose is high (2.1 Bq/l). If the dose exposure originating from intake of radionuclide is ≤ 0.1 mSv/year, then it is allowed to consume. Based on the EU data, supposing a consumption of 2 l/day in case of adults, ^{226}Ra concentration of 0.49 Bq/l already exceeds the limit value 0.1 mSv/year (Kovacs et al., 2003). In case of water used of water-drinking the radium concentration level was 2.1 Bq/l, which is far above the limit value related to drinking water, although it is reasonable to take a consumption of only 1 litre into account in this case. The calculated value of the committed effective dose originating from swallowing is 0.21 mSv.

From the solid state nuclear track detector measurement results it can be established that the radon concentration level never exceeds at any of the measurement points the reference value of 1000 Bq/m^3 related to workplaces, set out by law, moreover, not even the strictest value of 200 Bq/m^3 related to residential buildings.

The radiation dose originating from inhaling radon and progenies was also determined for workers and those taking a bath. The results show that the annual committed effective dose on workers changes between 0.34 and 0.7 mSv. Regular visitors of the bath receive a committed effective dose between 0.09 and 0.19 mSv in the thermal bath annually. Therefore, it can be stated that neither those working there, nor those wishing to heal there receive considerable radiation dose.

ACKNOWLEDGMENT

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PARALLEL RADON AND THORON SURVEY AT SPECIAL UNDERGROUND CIRCUMSTANCES

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ABSTRACT. In this study a comparative integrating radon and thoron survey executed at underground workplaces are discussed.

Two types of solid state nuclear track detectors (Radopot and Raduet) including CR-39 were placed at four sites including a manganese mine, a bauxite mine, a show (tourist) cave and a hospital cave. Several numbers of detecting points were chosen at each site and 1-1 Raduet and Radopot detector were placed at each point. Both detector types contains two polycarbonate (CR-39) foil in different holders in order to determinate the radon as well as the thoron levels.

The detectors were changed in 30-60 days periods and the survey continued for a year.

The aims of this study. To gain information about the radon and thoron concentrations. To compare the performance of the two types of detectors and check their response in the special circumstances indicates by these underground places.

There was not considerable difference between the radon results provided by the two types of detectors. In the case of thoron the results are very variable and significant part of the detectors provides no data or unrealistic data.

The study suggests that both types of detectors are fit for the integrating radon measurement. The reason of the unreliability of the thoron measurement could be the high humidity (especially in the caves), the high aerosol concentration (especially in the mines) and the air change rate variation.

Keywords*: radon; underground workplaces; radiation dose; dose estimation*

INTRODUCTION

The decay product of radium (^{226}Ra), the radioactive noble gas radon, and its airborne progenies are considered to be the most important dose contributors due to natural radiation (UNSCEAR, 2000). Some studies showed that there is a not negligible correlation between indoor radon concentration and lung cancer risk even at relatively low exposure levels (below 200 Bq m^{-3}) (Darby et al., 2005; Krewski, 2005). Therefore, if the smoking considered being as an artificial agent, the radon is the leading naturally occurring cause of lung cancer. The International Commission on Radiological Protection (ICRP) provides guidance to regulatory authorities on the radon action levels in its publication of ICRP-65 suggesting that workers who are not regarded as being occupationally exposed to radiation should be treated in the same way as the general public. The suggested action level is between 500-1500 Bq m^{-3} (ICRP-65, 1993). The action level advised by the European Union (EU) accepting the recommendations of ICRP-65, is also the same (BSS, 1997). Many EU member countries established the same reference level for all types of workplaces.

In Hungary, the action level for workplaces is 1000 Bq m^{-3} average radon concentration over the working hours (Hungarian Regulation, 2000). This legislation, actually, was implemented in January 2003. Setting this action level an occupational exposure of 2000 hours per year and an equilibrium factor of 0.4 were considered. This level is in accordance with the ICRP-65 and the EU suggestion being the mid-value of their advised interval.

The probability of elevated radon concentration is considerably higher at underground workplaces than aboveground places therefore, radon concentration measurements advisable here.

For monitoring the average radon concentrations usually integrating detectors are used. The alpha track detectors are the most wildly used for large-scale and long-term surveys so as to obtain annual radon concentrations. It was find that some of alpha track detectors are sensitive to thoron (Tokonami, 2005). To get reliable data it is important to consider this effect and to chose detector types whose performance are not influenced in high extent by thoron.

Additionally, the thoron can have a role not just to disturb the radon measurements but it can present a not negligible dose contribution as well. Therefore the parallel radon-thoron measurements would help to improve the accuracy of dose estimations.

In this paper a one year long integrated radon and thoron measurements are described. Four typical underground workplaces were chosen using two types of radon-thoron discriminative detector.

MATERIALS AND METHODS

The survey was executed in four underground workplaces: a bauxite mine, a manganese mine a hospital cave and a tourist cave. 4-10 measurement points were chosen at each site where two types of detectors were placed side by side. The two types of detectors are: Radopot (Zhuo et al., 2002) and Raduet (Tokonami et al., 2005).

Both detectors have two separate diffusion chambers containing a CR-39 polycarbonate foil. One of the two chambers is constructed to get inside only the radon gas and the other one is the radon and thoron. Applying this set one can calculate the thoron radioactive concentration as well parallel with the radon. The Raduet is the remodeled Radopot. The Raduet is an up-to-date radon-thoron discriminative detector has been developed for conducting a large scale survey. Comparing with the previous detector (Radopot), some functional problems have been solved (Tokonami et al., 2005).

The detectors were changed in 30-60 days periods (approximately monthly) to make possible to gain information about the seasonal variations and the survey continued for a year (in 2007). The CR-39 polycarbonate foils were evaluated at National Institute of Radiological Sciences (NIRS).

RESULTS AND DISCUSSION

In the bauxite mine were 10 measuring points which reduced to 8 at the end of the survey because of some tunnel were closed during the investigation. Table 1 summarizes the radon concentrations measured in the bauxite mine. The "min." and "max." values mean the minimum and maximum levels showed by the 10 or 8 detectors. The results provided by the Radopots seem to be a little lower than the Raduets. According to the Raduets only in one month (April) exceeds slightly the average level the Hungarian limit (1000 Bq m^{-3}). But it needs to emphasize that this levels not represents the concentrations during the working hours. In the mine there is an effective ventilation system working only during the working hours. Therefore, the radon concentrations probably lower in these periods. There is no significant seasonal variation. In April and June the levels are slightly higher than other months. Because of the intensive differences in the working situations (close a tunnel, and open a new one) the airflow direction and intensity also can change significantly. This can influence the radon level at a measuring point.

Table 1.

Rn concentrations in the bauxite mine.

Month	Raduet [Bq m^{-3}]			Radopot [Bq m^{-3}]		
	average	min.	max.	average	min.	max.
February	226	52	778	246	53	1088
March	549	306	1449	545	332	1322
April	1108	118	3595	957	59	3110
May	322	120	664	201	43	498
June	238	123	473	105	6	201
July	926	174	1735	590	33	1292
August	578	244	1013	250	22	472
Sept.-Oct.	250	22	472	539	78	1801
November	529	175	791	234	42	375
Dec.- Jan.	442	157	820	215	60	347

Table 2 summarizes the radon concentrations measured in the manganese mine. Here were 10 measuring points. The "min." and "max." values mean the minimum and maximum levels showed by the 10 detectors. In this case the average radon concentrations exceed the Hungarian limit roughly in the half of the year. Also, the results provided by the Radopots seem to be a little lower than the Raduets. At the results of manganese mine can be observed marked seasonal differences, namely, during the summer months the radon levels are significantly higher. It is typical at underground places due to the air flow directions induced by the temperature and pressure differences.

Table 2.

Rn concentrations in the manganese mine.

Month	Raduet [Bq m^{-3}]			Radopot [Bq m^{-3}]		
	average	min.	max.	average	min.	max.
December	638	91	1792	481	51	1285
January	562	135	1907	500	119	1640
February	689	138	2231	549	84	1745
March	807	285	1844	694	254	1511
April	1451	1174	2338	1204	777	1995
May	2231	1787	2975	1693	1444	2488
June	2187	1736	2746	1770	1414	2517
July	1986	1498	3813	911	347	1541
August	1813	1355	228	1304	349	1869
Sept.-Oct.	1114	694	1599	706	423	1036
November	553	179	984	193	50	336

Table 3 summarizes the radon concentrations measured in the hospital cave. Here were 4 measuring points. The min. and max. values means the minimum and maximum levels showed by the 4 detectors. In this case the average radon concentrations exceed the Hungarian limit almost in the all year. Also, the results provided by the Radopots seem to be a little lower than the Raduets. In the hospital cave there is no ventilation system therefore the seasonal differences are very sharp. Even during the summer months the radon levels seems to be too high for precise detection by the used detectors.

Table 3.

Rn concentrations in the hospital cave.

Month	Raduet [Bq m^{-3}]			Radopot [Bq m^{-3}]		
	average	min.	max.	average	min.	max.
December	362	248	583	236	154	355
January	994	1260	887	825	663	1026
February	2621	2092	2911	2004	1649	2283
March	1599	1133	1926	1373	729	1650
April	2226	1503	3008	2384	1234	3946
May	5174	4889	5577	4246	4075	4426
June	>~8000			>~7000		
July	>~8000			>~6000		
August	>~8000			>~5000		
Sept.-Oct.	938	917	976	585	559	611
November	1160	798	1731	416	320	535

Table 4 summarizes the radon concentrations measured in the tourist cave. Here were also 4 measuring points. The “min.” and “max.” values mean the minimum and maximum levels showed by the 4 detectors. In this case the average radon concentrations exceed the Hungarian limit in the all year. The results provided by the Radopots seem to be a little lower than the Raduets. In the tourist cave the seasonal differences are not too sharp. Here also was experienced that during the summer months the radon levels seems to be too high for precise detection by the used detectors. Maybe the sharp seasonal variation is present here also but the detectors not worked properly due to the extreme high humidity and the too high level of radon.

Table 4.

Rn concentrations in the hospital cave.

Month	Raduet [Bq m^{-3}]			Radopot [Bq m^{-3}]		
	average	min.	max.	average	min.	max.
December	7258	6652	8095	6206	5628	6784
January	8778	8698	8859	-	-	-
February	7481	6041	9143	6339	6031	6648
March	4434	833	6418	3845	653	5398
April	2831			1785		
May	>~9000	2044		>~8000	1661	
June	>~9000	3566		>~8000	3609	
July	>~10000			>~8000	2573	
August	>~8000			>~7000		
Sept.-Oct.	>~6000	1501		2787	983	3871
November	>~8000	614		2104	205	4027

The data presented here are not considered to be a base for dose calculation of the workers in the above mentioned underground workplaces.

In the cases of the mines during the working-hours strong artificial ventilation are present. This results a significantly different radon concentrations during these periods than the all-day average as our former continuous measurements showed (Kavasi et al., 2006).

In the caves the workers spent restricted time underground which can taken into consideration when one calculates the doses. To gain reliable data for dose assumption personal dosimetry is needed.

In the cases of the two mines the data comes from the personal dosimeters (not presented here) show that the annual dose significantly lower than the doses resulted using the data comes from the detectors placed in the mine. Consequently, the workers not get higher dose than the legislation suggests.

In the hospital cave and the tourist cave the radon concentration is high. Considering the legislation one cannot work here 2000 hours per year without exceeding the dose limit. (The patients and the tourists usually spend too little time in the caves to consider any reason of dose hazard.) The workers are monitored using personal dosimeters and there is a planned timetable ensuring that they not exceed the occupational dose limit.

The performance of the two detector types are compared shown in the Figure 1. For this comparison the average values were used from the Tables 1-4. It can be seen that the Radopot detectors measure a slightly lower levels than the Raduet ones. The differences are higher at higher radon concentrations.

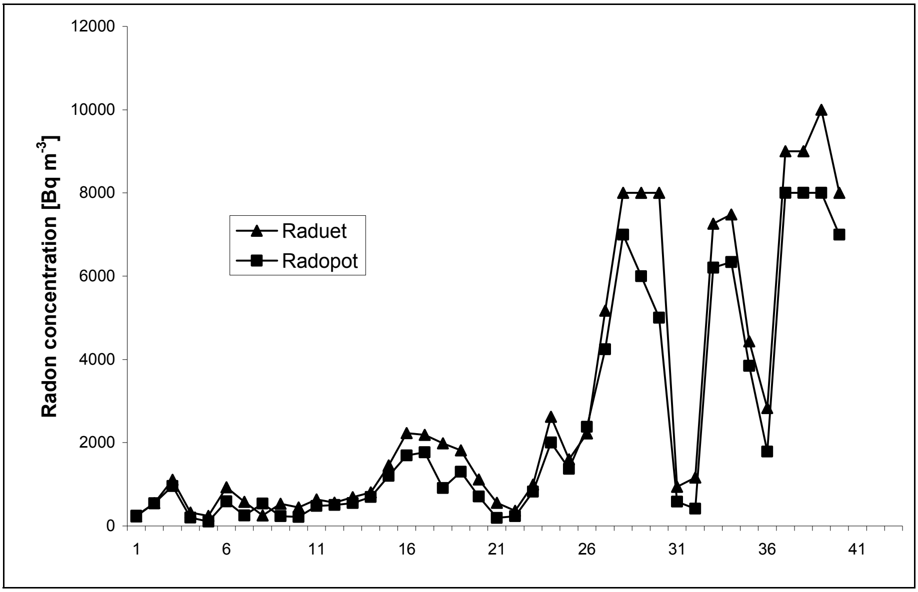

Fig. 1. *The radon concentrations measured by the two detector types.*

Measuring the radon it should be consider the thoron influence. The thoron can modify the results depending on the detector characteristics. Other hand the thoron itself can be a significant dose contributor. Therefore parallel with the radon measurements thoron measurements also were executed. Both used detector type have a part aimed for thoron detection. Evaluating the data unfortunately the thoron results seems to be very hectic and unusable. Almost half of the thoron detectors have shown no results both the Radopots and the Raduets. The detectors which presented data were in high inconsistency with each other, other words the Raduets and Radopots showed very different values. This probably can be due to the high humidity and in the mines the high aerosol concentration. Also, the ventilation can influence significantly the performance of thoron detectors.

In case of the both used detector type he container developed to detect the radon has a little sensitivity for thoron (Tokonami et al., 2008). Consequently the data gained for radon probably little influenced by thoron. However, the information of thoron would help the more precise dose estimation.

CONCLUSIONS

In this study integrated radon and thoron concentrations were measured at underground workplaces including two mines and two caves. The two main aims were: 1) To gain information about the radon and thoron concentrations at the chosen places including the seasonal variations. 2) To compare the performance of the two types of detectors and check their response in the special circumstances indicates by these underground places.

Concerning the first point the radon concentrations were found to be as the expected ones at the given underground places and were similar to our former measurements. In the bauxite mine the radon concentrations are not too high due to the ventilation system working in the working hours. In the manganese mine the measured values are higher especially in the summer period. Considering that during the working hours the radon levels are considerably lower not likely that the dose contribution of the workers exceeds the limit. More precise data can be gained using by personal dosimeters. In the two caves the radon concentrations are as high as one can expect these kinds of underground places. The variation in the concentration is typical (summer higher than winter). Because in the caves there is no artificial ventilation system the values are considerably higher than the mines. It could be expected that if one spent 2000 working hours here he or she can get dose contribution exceeding the occupational limit. Actually, the workers spent restricted time in the caves and they are under the personal dosimetry.

The detectors were constructed to measure thoron as well parallel with the radon. In the case of thoron the results are very variable and significant part of the detectors provides no data or unrealistic data. Unfortunately these data are seems to be uninformative.

Concerning the second point there was only a little difference (<10%) between the radon results provided by the two types of detectors. In the case of thoron the two detector types showed high inconsistency.

The study suggests that both types of detectors are fit for the integrating radon measurement at these special circumstances but it cannot be stated the same for the thoron measurement. The reason of the unreliability of the thoron measurement could be the high humidity (especially in the caves), the high aerosol concentration (especially in the mines) and the intensive ventilation and air change rate variation. To find the reasons needs further study.

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PRIVATE INSURANCE IN THE CONTEXT OF RISKS RELATED MINING INDUCED HAZARDS IN ROMANIA

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ABSTRACT. Any damage assessment is made in order to ensure adequate compensation to the affected persons. Currently in Romania, insurance companies have minor involvement in preventing and reducing the impacts of natural and technological hazards, including those related with mining operations. Under present circumstances the only financial resources for mitigating damages caused by natural disasters are funds from State budget and external credits. Commonly these funds are insufficient to cover the damages of natural disasters; hence, increased use of insurance is needed to indemnify disasters victims. To encourage disaster insurance, the insurance companies should be able to more accurately set their insurance premiums depending on the estimated risk for each property. This risk information should be compiled in Geographical Information System (GIS) maps based on multiple disaster risk evaluation methodology. The priorities targeted by this paper are: a). Expanding the use of natural and technological risks analysis including mining related disasters by private companies; b). Encouraging the use of private insurance companies services; c). Implementing vulnerability and risk methodology for GIS hazard mapping in Romania, including mining facilities. The present paper identifies major advantages of a better involvement of insurance companies at the local level in Romania based on a standard risk identification and quantification methodology. Since damages produced by a natural disaster can not be fully covered by State funds a better use of insurance will indemnify disaster victims. Insurance companies can more efficiently estimate their insurances premiums for every property and facility, using risk maps based on the multi-disaster risk evaluation methodology.

Key words*: risk, vulnerability, evaluation methodology, mining facility, insurance, GIS risk maps*

INTRODUCTION

The insurance companies are unwilling to insure goods and properties located in natural disaster-prone areas, vulnerable to different kind of natural or man-made disasters (table no. 1). The only financial resources for minimizing the damages caused by the natural disasters are the funds allocated by the State budget and external credits.

Table 1

The natural disaster more frequently in Romania

Disaster	Floods-drought	Land-slides	Storms	Earth-quakes	Forest Fires	Contami-nated Lands	Industrial Install-ations	Transport of Dangerous Goods
Severity	high risk	high risk	high risk	high risk	medium risk	medium risk	medium risk	medium risk

Legend:
high risk
medium risk

In Romania the hazards which produced the greater human losses and material damages, are as it follows: floods, earthquakes, landslides and storms.

History of the most catastrophic disaster of Romania, in the recent history are presented in the table no. 2.

Table 2

The most important damages ever recorded due to natural disasters in Romania

Year/data	Type of disaster-feature	Human life	Injured	Homeless	Affected	Damages (mil USD)
4 March 1977	Earthquake – 7.5 Richter scale magnitude	1641	11300	175000	386300	2000
May 1970	Flood	215			238755	1000
July 1975	Flood	60			1000000	750
11-12 July1999	Landslide (mudflow)	13				
April-September 2005	Flood	78			30800	1958
April-May 2006	Danube river Flood	1		16350		225
July 2008	Floods due a retrograde cyclone	5			27000	830

OBJECTIVES

In Romania there is a true need in supporting the local authorities in promoting a sustainable development in environmental factors management and land use development and planning. In this action, a good informational system projection and implementation for natural and technological disasters are of main importance for local authorities, environmental protection agencies and water management systems. The cartography of risk areas for damaged areas inventory, will help to organize the local development, to promote projects for local protection of the population and economical objectives, and will update the actual risk evaluation of the existent vulnerable areas (fig. no. 1). The tight connection between Romanian experts in the different fields of activities according to the different hazards, natural and technological, will led to innovative aspects in the field of disaster mitigation and protection, in order to create sustainable development of local communities.

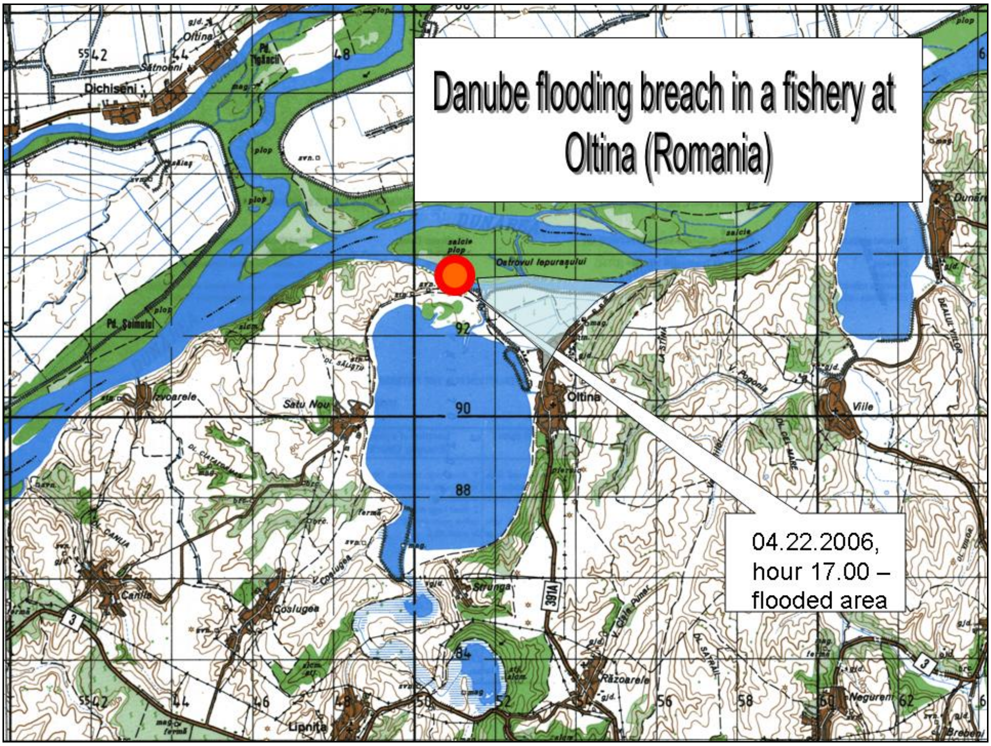

Fig. 1. *At present time the available maps used in case of disasters in Romania missed the areas prone to natural disasters in the inhabited areas. (example: the case of the Danube River flooding)*

Presently, in Romania are a limited number of fully agreed methodologies for drawing up the hazard maps. There were elaborated just in the field of floods, earthquakes and landslides. Even for these fields, the methodologies have a limited range of appliance, and the results are not often represented on the same map, being used differentiated on each type of disaster.

According to the generally accepted definition, Risk equals the product of Probability and Vulnerability:

Risk = Probability x Vulnerability

While the probability of generating a disaster is generally known, the assessment of the consequences is difficult and involves numerous unknown elements. A special attention will thus be given to the “vulnerability assessment".

In this regard, a comparison, at national level, between the natural hazards which could inherently affect the population and the surrounding environment (e.g. floods, earthquakes, land slides, frost-defrost conditions) is highly recommended. Such an approach could lead to establishing priorities in terms of specific measures and needs, which the authorities involved in the natural or technological risks management must address. An improved management of the areas affected by natural and man-made disasters, will allow an accurate analyze for taking decisions, assuring an improved activity of prevention, mitigation and restoration of the areas affected by disasters, increasing the safety of the public and the confidence in the safety measures taken by the public administration.

Methods

Developing a common methodology for evaluation and mapping the risk posed by the natural and technological hazards, to be implemented under a pilot project at the county level in order to elaborate vulnerability and risk maps, using a dedicated GIS for storage and information dissemination to decision makers at various levels. The newly implemented methodology for estimation of the vulnerability and risk that threatened the different forms of property, will better establish the responsibilities and the rules of land use development and planning of the territory, as illustrated in Fig no. 2.

Main results

The main advantages of this project are the following:

-The implemented methodology for estimation of the vulnerability and risk that threatened the different forms of property will better establish the responsibilities of the administrative bodies and will help the future decisions related to land use and planning of the territory.

-The newly implemented system of risk mapping provides the stakeholders and the insurance companies a unique source of information to assist their decisions: the GIS risk map from the county or local public administration.

-The tight connection between Romanian experts in different hazards, natural and technological, will led to innovative aspects in the field of disaster mitigation and protection.

-The stringent problem of indemnifying the people or institutions affected by natural and anthropogenic disasters will be solved through the implication of the insurance companies.

- Delimitation of the areas prone to natural risks, using GIS maps, also for prevention and attenuation of the effects, which are produced by the destructive natural phenomenon and to the risk posed by the technological hazards, will assure the safety of the public.

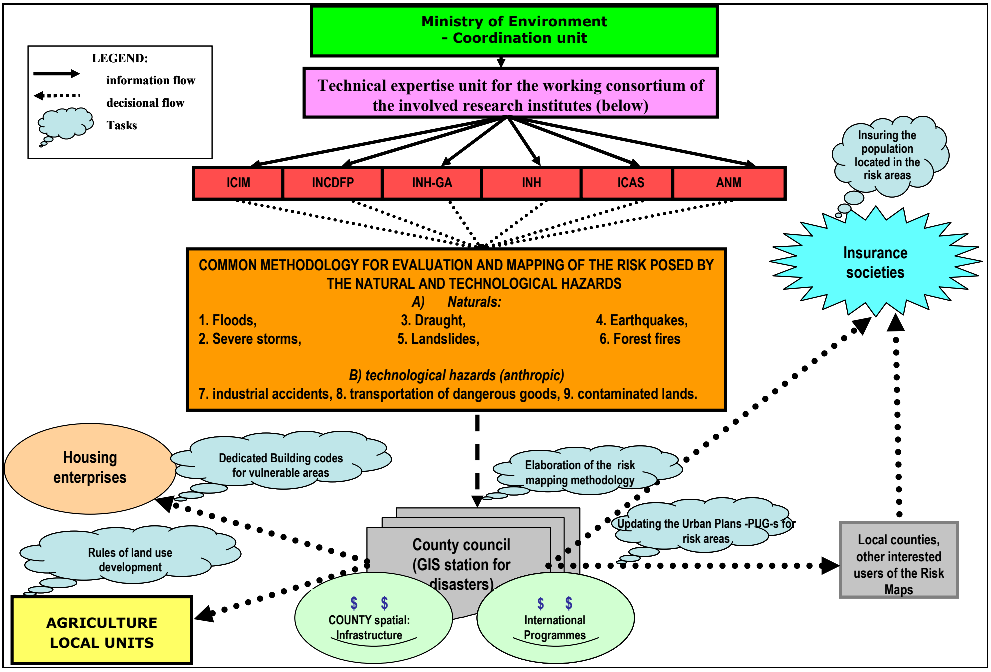

Fig. 2. *Hazard mapping project scheme at the county level, involving the private insurance companies based on the risk maps, using GIS for the vulnerable areas at natural and technological hazards*

It is also mentioned that the NATECH (technological disasters due to natural hazards) type hazards can be presented using GIS technique. This type of disaster has not been constantly assessed in Romania so far.

Even the multiple risk term has been only recently implemented in Romania.

Case study example

For example, the case study of a recent NATECH event, the overflowed tailing dam upstream an inhabited village, in 2006, should involve the use of GIS risk maps for a better evaluation of the consequences over the populations and environment in case of a possible future recurrence of the dangerous phenomena, presented as it follows.

Tarnicioara tailing dam nearby the Calimani National Park, became a NATECH risk zone due to severe rainfall during 27.06-02.07.06. Heavy rainfall led to torrential flows on the slopes surrounding the dam from the north-east of the country, which formed a temporary lake on the top of the hydro technical construction, threatening almost 5000 people located nearly 3 km downstream, in the village of Ostra (Fig. no. 3). It has to be specified that Tarnicioara tailing dam belongs to the mining company SC Minbucovina, Preparation unit Tarnita, and was decommissioned since 2001.

Since decommissioning, the tailing dam has a significant impact over the quality of environment, because the heavy metal concentrations from the soil sampled annually from the downstream area of the tailing dam, which are exceeding the thresholds for heavy metals, regarding Cu, Zn, Pb and As, mostly 30 cm below the surface. Therefore an imminent collapse of the dam could significantly worsened the environmental conditions, because of the presence of the heavy metals, well known as for the mutagenic, theratogenic and carcinogenic effects over the whole food chain, including human and biota.

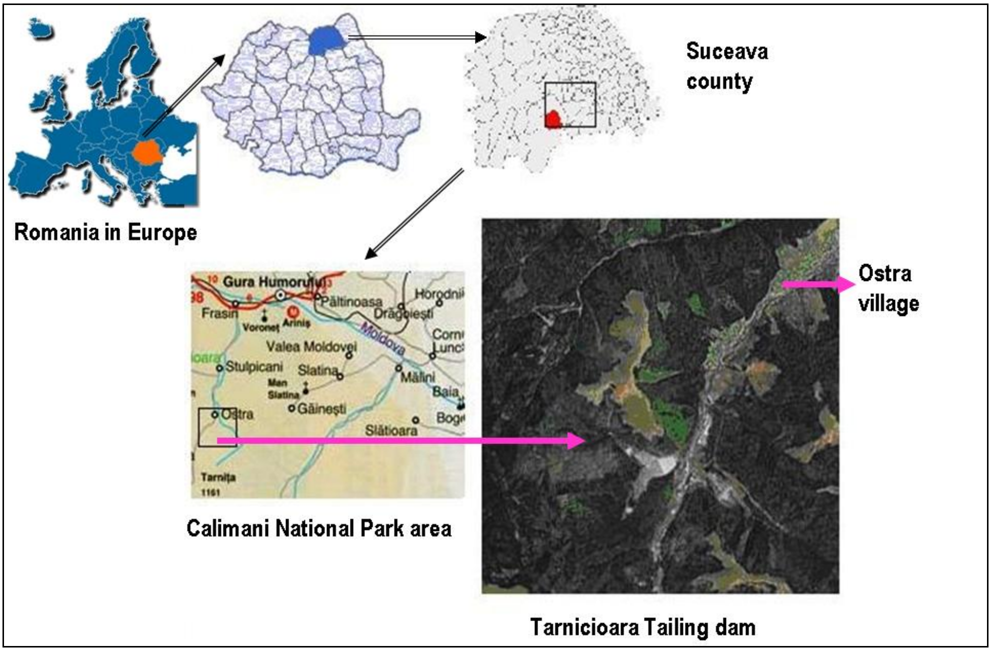

Fig. 3. *Localization of the Tarnicioara tailing dam, upstream of Ostra village*

As a result of the heavy rainfall in the area of Tarnicioara tailing dam, due to the accumulation of the excess water from the nearby creek, was created on the top of the tailing dam a reservoir of 12 m water deep (fig. no. 4). Because of the strong gusts of wind accompanying the heavy rain storm, large waves started to battered the tailing dam crest, being in danger to overflow and to flood the downstream village, Ostra, location of many turistical pensions.

The torrential flows on the slopes of the upstream water course, Scaldatori creek, normally diverted on a escaping tunnel, overflowed the discharge tunnel due to the clogging with debris and branches, up to 2,5 m thickness of sediment. The inflow of the Scaldatori creek reached almost 2200 l/s (aprox. 7920 cm/h).

Fig. 4. *Temporary lake formed in the top of the tailing dam endangering the downstream inhabitants and tourists located in Ostra village (detail of the diverting tunnel of the creek from the upstream area of the tailing dam, partially blocked with debris, and the operative measures of the emergency teams on a boat, for mitigation of the flood effects)*

Prevention measures

In the frame of the global activity of preparedness against the disasters, represented also about the events caused by the mining activities, a significant contribution was given through the activities undertaken by National Emergency system (fig. no. 5), which at the national level accomplish the following measures:

– Assure the organisation, supervision and control of the instruction activity of the population;

– Propose the allocation of technical and financial resources for assurance of the civil protection activity in optimum conditions;

– Were undertaken scientific researches, and designed instructions plans and researches themes in the field of civil protection activity.

It is well known that the impact of the mining activities over the environmental factors lead to modifications of hydro-geological conditions, drainage works, deviation of water bodies, abandoning works without environmental reconstruction, and modifications of the infrastructure from a technical and social point of view. Reduction of agricultural and forestry activity by occupying the surfaces intended for the waste dumps construction and the impact over the natural heritage is significant in the mountainous areas. The impact over the soil and vegetation could be severe, because of the loss of stability of a waste dump if appropriate in-situ remediation measures aren't established.

Because of the risk posed by the temporary water reservoir from the top of Tarnicioara dam, resulted from the heavy rainfall during 27.06. - 02.07.2006, the intervention team tried to clean up by debris the diverting tunnel of the inflow creek, but renounced due to the imminent risk of the collapsing the roof tunnel due to water pressure, because the sudden de-clogging by the debris. The collapse risk could have been produced in the exact point where in 2001 was produced a suffosion and endangered the tailing dam stability.

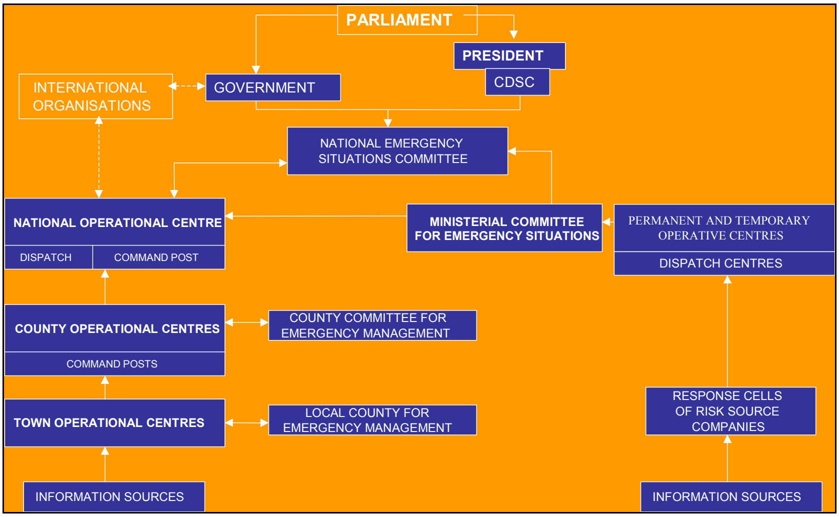

Fig. 5. *Romanian National Emergency system*

Response action and related lessons learnt

Were put in place 6 special pumps of ANIF (National Agency for Land Reclamation) used normally for flood control in irrigation systems, with a discharge over 1100 cm/h, and a higher capacity pump was brought (1600 mc/h) from a coal mining, specialized for removal of increased water levels (fig. no. 6). Also three additional pipes were installed upstream of the diverting gallery, in order to diminish the inflow in the tailing dam, working at their entire discharging capacity, until the flooding phenomena was diminished.

Fig. 6. *Mitigation measures in order to evacuate the excess water from the top of the Tarnicioara tailing dam*

A combined team o specialists from Suceava Water Management System (county branch of "Romanian Waters" National Agency), Inspectorate of the county emergency system and Tarnita preparation unit took action at the dam for few weeks, until the normal flow within diverting tunnel was completely restored.

Lessons learnt:

- Implementation of the Aquis communautaire (the entire body of EU laws) is necessary, especially in the acceding or candidate countries, for integration in the Communitarian structures, and has profound implications at all social-economical levels. A particular aspect of this relates to the safety aspects of existent industry processes. One of the most sensitive industrial activities is mining, especially in countries like Spain, Turkey, and Romania, where gold mines exist.
- Appropriate risk assessment and management is required to assure safe exploitation and operation of mine waste tailings dams, which can contain environmentally dangerous substances. The implementation of the Seveso II Directive, recently amended, regarding the prevention of major accidents involving dangerous substances, induces supplementary uncertainties due to the lack of risk assessment and inventory data at the European level, for tailings dams that may contain potentially dangerous substances.
- The quantification of risk associated with tailings dams and industrial waste deposits requires the use of a unified system of categorisation, for better correlation of the characteristics of varied sites and their potential hazards. Managing such risks requires that the obligations of dam owners and operators be defined so that they can be operated safely and so that adequate measures can be taken to reduce the risks of an accident. The nature of required controls will vary, based on the degree of potential risk and their potential environmental impact. A useful tool for dam owners would be the use of a common methodology based on quantification of the risk components, using a standardised system of criteria, indices, and notes (Mara S. et. al).
- Romania experiences a wide range of temperatures between warm and cold seasons, with a lower evaporation rate than other countries with similar extractive industries, such as Australia, Spain, and Turkey (Mediterranean Region), that are more arid and therefore do not have the same problems that Romanian operations have with the deposition of the sterile materials in settling ponds.
- Proper monitoring systems must be in place to assess structural performance, allowing accurate risk analysis and assessment of the operating functions for the tailing disposal facilities for the mining.

CONCLUSIONS

The most relevant ways in which the insurance societies can be involved in the reduction of the risk, are the promotion of working safety norms and by relocation of some economical and social activities in the low risk areas, through the assurance prime differentiated by risk classes.

To be encouraged to extend their activity to the insurance at disasters, the specialized companies should be able to estimate their insurance primes depending on the estimated risk for every property and facility.

The stringent problem of indemnifying the people or institutions affected by natural and anthropogenic disasters will be solved through an active implication of the insurance companies, supported by the tight connection with the Romanian experts in different hazards, natural and technological.

The public consultation will be realized more efficiently by GIS maps for hazards from the county level, as a result of the information visualization regarding the new development for industrial facilities with increased risk for major accidents.

The result of the further projects using GIS hazard maps will make increase the responsibilities of the decisional factors involved in the territorial planning, for establishing the efficient programs for population protection, including development programs taking into account the existing risk from the concerned area and will lead to promoting common projects at the level of the whole country.

The advantages of using GIS methodology for developing county-wide vulnerability and risk maps for various hazards (natural disasters such as: floods, severe storms, earthquakes, landslides, forest fires and technological disasters such as: industrial accidents, transportation of dangerous goods, contaminated lands, including those by mining activity) request a pilot project of a county with a currently implemented GIS system in its public administration. A follow up project is to be implemented, for multi-disaster risk maps of the entire country, including all mining perimeters. These newly implemented risk maps assist the stakeholders and insurance companies to evaluate the total disaster insurance needs from a single source of information.

Promoting a private insurance mechanism in order to cover the most part of the indemnity in case of disaster for the potentially affected people or institutions in Romania will lead to:

- Extending the interest of private companies for natural and technological disasters at the county level.
- Encouraging juridical and physical persons potentially affected by disasters to use private insurance company's services.

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STUDY OF SOME CLAY MINERALS USED IN ELECTRODE MAKING WITH APPLICATION IN ENVIRONMENT CHEMISTRY

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ABSTRACT. It was prepared few benthonite rocks from Valea Chioarului. Different granulation of montmorillonite compound was separated and studied by TEM microscopy, X ray diffraction, thermo differential analysis and FTIR spectroscopy. Cyclic voltammograms for the carbon paste electrode doped with clay in the presence of Cd^{2+} and Pb^{2+} on the synthetic solution was registered. The calibration curves registered for Pb^{2+} and Cd^{2+} using square wave voltammetry on the film composite electrode containing PEI and clay indicate that the electrodes are sensible and present a good linearity in the domain of low concentrations (10ppb-50ppb).

***Key words**: clay minerals, modified electrode*

INTRODUCTION

The impact of pollutants on the environment requires new modified elelectrodes for the detection of the heavy metals. Inorganic materials like zeoliths, hybrid, based on silica and clay took attention on electrochemists because of the modifying properties.

The ion exchange capacity and large specific surface of clay are excellent behaviors for modified carbon paste and films electrodes. The term clay refer to the collective of numerous sedimentary rocks, like benthonite, which is studied in present work.

The electrode is a heterogeneous complex constituted by solid conducting, semi conducting or insulated particles, and aqueous phase induced by clay and analyzed medium. The mass and charge transfer phenomena in these structure are very complicated. Rigorous characterization need for the clay because appear a variety of structure and composition, which depend of collecting place. For this reasons the behaviors of clay modified electrodes depend on the nature and proportion of clay and of course the preparation methods used. This work studied the benthonite from Valea Chioarului,Maramures.

The most important feature of benthonite is the proportion of montmorillonite. The name montmorillonite define the clay mineral with theoretical formula $Al_2(Si_4O_{10})(OH)_2$ which contain a relatively large amount of water molecules between sheets.

The crystalline structure involves a single elementary cell composed from two tetrahedral $[SiO_4]^{4-}$ sheet disposed in hexagonal rings, coupled by octahedral $[AlO_6]^{3-}$ sheet. The tetrahedral peaks are oriented inside of elementary cell, the oxygen ions placed in this peaks coupling the octahedral sheet from the middle of cell. The tetrahedral sheets are symmetrical face of octahedral sheets and oxygen ions of tetrahedral sheet are placed in the face of identical neiborouhs sheet. A week bond and cleavage result between sheets.

Frequently the Si^{4+} ions from tetrahedral sheet are substituted by Al^{3+} and Al^{3+} ions from octahedral sheet by Mg^{2+}, Fe^{2+}, Fe^{3+}, Zn^{2+} ions. It result an excess of negative charges, which create a possibility of cations absorption inside of elementary cell. Usually the cations, which are involved in ions exchange at surface of clay particles, are Ca^{2+}, Mg^{2+}, H^+, Na^+, etc. The forces which stabilized the cations are week and due this fact their can be easy substituted. This quality of benthonite from cationic clay class are commonly meet in terrestrial crust. Long time ago these clay was used in ceramic but it exist application in pharmacy, cosmetics, electrotehnics, catalyse, adsorbents, ions exchange and recently in electrochemistry.

MATERIALS AND METHODS

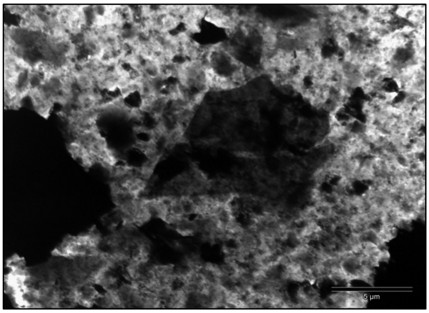
The benthonite from Valea Chioarului has washed by decantation resulting homogenous products reach in active montmorilonite compound. It was realized a comparative study on different samples with different size granulation on the levigable part containing active component. Separation on different granulation were make after literature procedure [Tanner C.G. et al, 1947; Jackson M.L. et al, 1949], by sedimentation, centrifugation and ultracentrifugation in accord with Stokes law. Samples, ‹ 50µm (2), ‹ 20µm (2-1), ‹ 2µm (2-4) and ‹ 0.2 µm (2-7) it was obtained. Chemical composition, ionic exchange capacity, size and shape of particles, was investigated by transmission electron microscopy (TEM), FTIR spectroscopy, X diffraction techniques and thermal analysis. Finally, after incorporation in electrode surfaces the clays was tested from electrochemical point of view. The following apparatus was used in the investigations:JEM1010 TEM, SHIMADZU XRD N 6000 difractometer, Thermo FINNINGAM Q Surf 9600, MOM 1500D thermal analyzer, Brucker FTIR, AUTOLAB PGSTAT 100 potentiostat.

RESULTS AND DISCUSSIONS

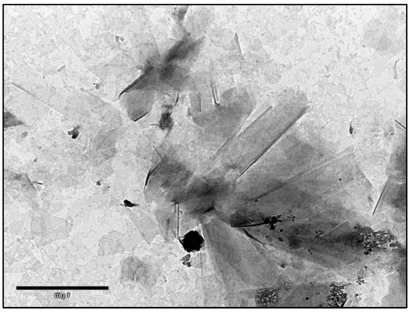
TEM recording of benthonite representative samples (fig.1) show an irregular, diffuse, transparent or translucent image (especially on the borders). The identified montmorillonite structures present fine lamellar sheet with nanometer dimensions.

By X ray, diffraction it was determined the reticular distances and intensity of characteristic reflexions of minerals, which compose the benthonite. The fraction with granulation ‹ 50 µm (sample 2) (fig.2a) indicate a reach content in montmorillonite (characteristic reflexsions at 12.61 Å, 4.47 Å, 4.08 Å, 3.11 Å, 2.49 Å), fact confirmed by the positions of maxima of diffraction in accord with literature [Emmett F., 1980]. In low proportions, we find other minerals like quartz, feldspat and muscovite.

Comparing the difractogram of sample 2 (fig.2a) with those of sample 2-7 (fig.2b) result that after separation the contents of montmorillonite increase (see the maxima of peak at 6.823 deg., respectively 6.943 deg.).The shift of peak denotes the superior stability of elementary cell for sample 2-7 in comparison with those of sample 2.



sample 2-1



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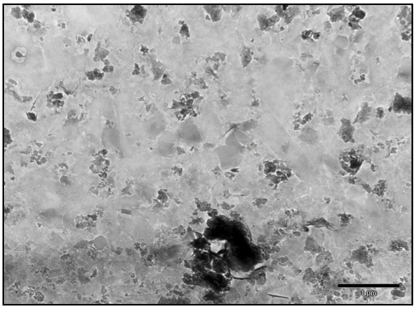
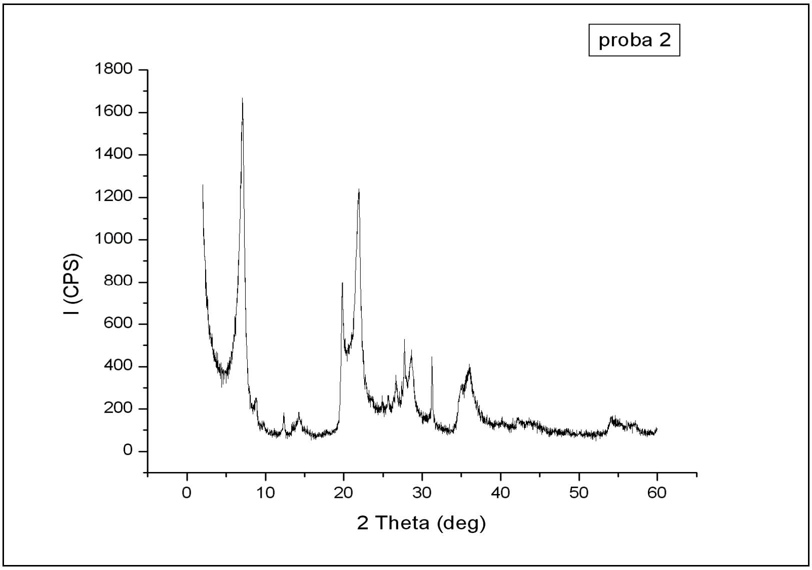


sample 2-7

Fig. 1. *Transmission electron microscopy recording of clay with different dimensions*



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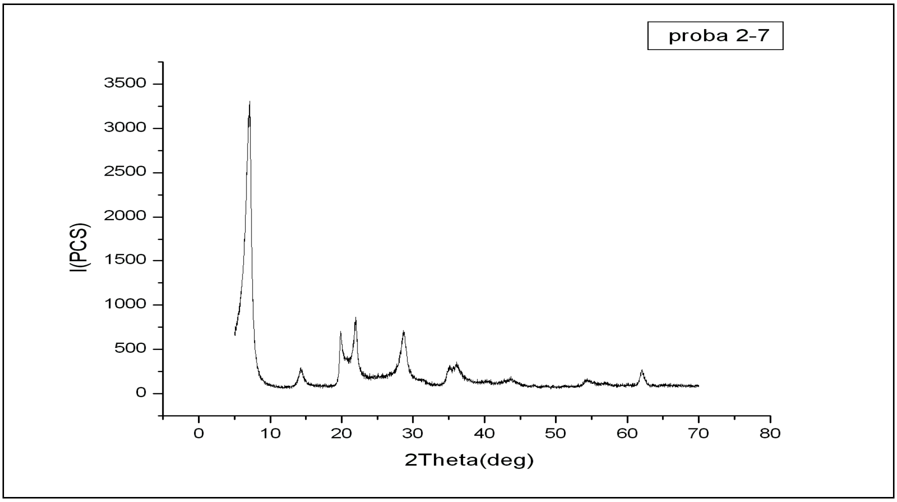

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Fig. 2. *X ray diffraction spectra of benthonite samples*

From calculus it result that a medium dimensions for montmorillonite crystallite (plane 001), in the case of 2-7 sample is 9.190nm.

Comparing our thermo differential analysis (fig.3) with literature data [Lucas J. et all, 1965; Tudor D.N., 1972] result a good superposition of DTA characteristics curves of montmorillonite.

First pronouncing endothermic effect appears between 60^o and 250^o, followed by a substantial mass lost due to adsorption water. Dehydratation is a reversible processes if the temperature remain under 250^{o}C and in this mode, the mineral can adsorb again the water, which can be eliminate in the new heating process.

The second endothermic effect appears between 600^o and 750^o followed by a mass lost due to the oxydril group's elimination. Finally, the third endothermic effect appears at 880^o quickly followed at 900^o by an exothermic effect due to the structural modification in the benthonite minerals.

By substitution of compensatory ions with NH^{4+} ions and quantitative analysis it was established the ionic exchange capacity. In the case of Valea Chioarului benthonite the value is 78.03 mE/100g.

Because of aggregation effect, which appear in dry process of fine granulation prepared benthonite, it was, determined the specific surface on the probe with less than 50μ granulation. The obtained value is 190.86 m^2/g.

From literature, data [Gilard P.,1980; Stoicovici E. et all, 1977] and our chemical analysis (see table 1) result that the benthonite rocks presents a large contents of SiO_2 and Al_2O_3 and an important water content. Variable and reduced quantities of MgO, CaO, K_2O, Na_2O, Fe_2O_3, TiO_2 appear in the samples. The divalent elements Mg and Fe are the substituents of Al in the octahedral configuration. The alkaline elements and Mg are fixed by adsorption between the structured layers.

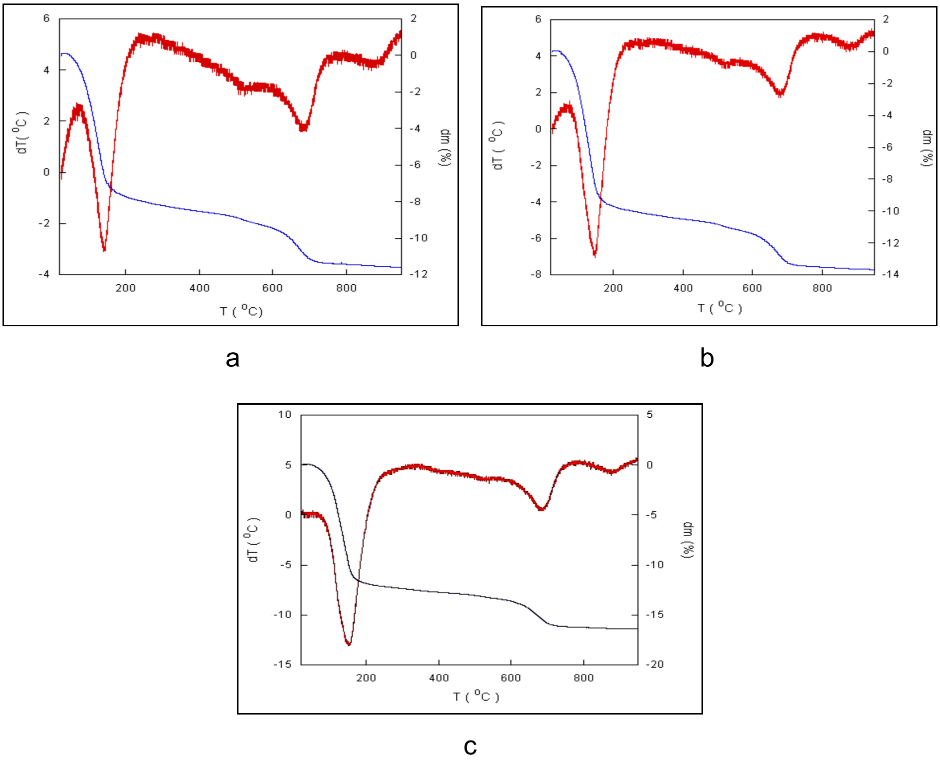


Fig. 3. *Thermo differential analysis recording of 2 (a), 2-1(b) and 2-7(c) samples*

Table 1.

Oxides contents (%) in the benthonite samples

Benthonite samples	SiO_2 %	TiO_2 %	Al_2O_3 %	Fe_2O_3 %	CaO %	MgO %	Na_2O %	K_2O %	C.L.* %
2	70,31	0,27	14,64	1,60	0,80	3,92	1,80	0,45	5,63
2-1	66,00	O,18	14,89	1,43	0,60	2,08	1,70	0,40	12,00
2-7	59,82	0,25	16,14	1,67	0,70	3,92	1,75	0,25	15,50

* lost in calcination process at 1000°C

The FTIR spectra on sample 2-7 (fig.4) revealed the characteristics groups of montmorillonite: 3446 cm^{-1} band, assigned to the water interlayer with specific shoulder at 3625 cm^{-1}, 1000-1200 cm^{-1} band assigned to the stretching vibrations of SiO_2 and respectively 520 cm^{-1} band assigned to Si-O-Al group [Socrates G. 2001].

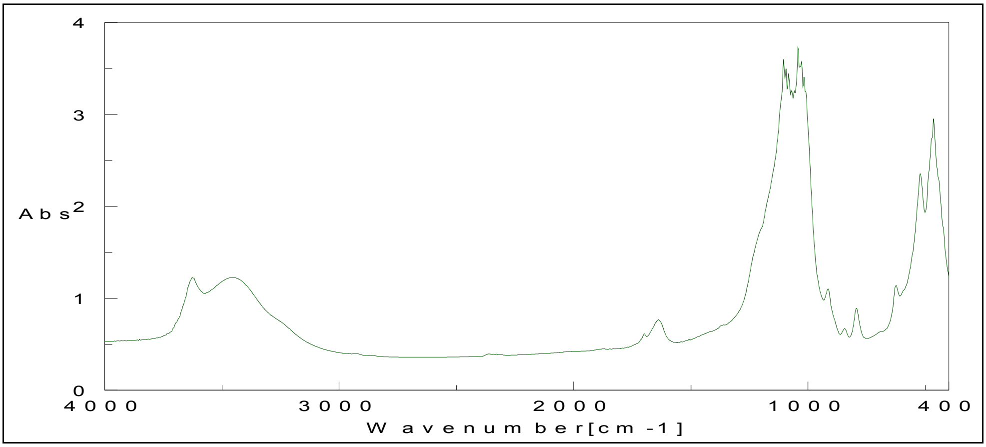
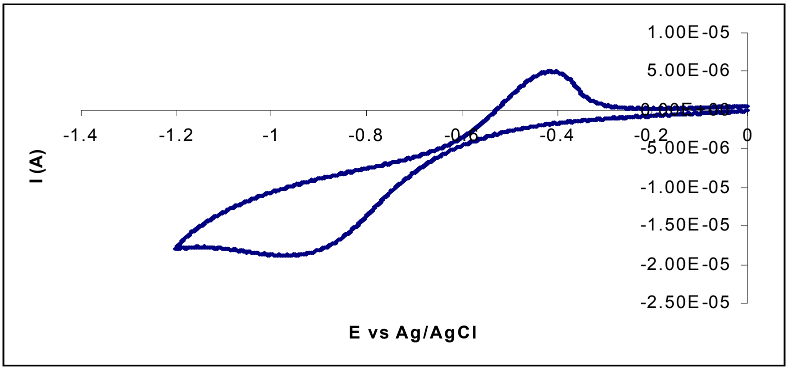


Fig. 4. *FTIR spectra of 2-7 sample*

For the electrochemical determination, carbon paste electrodes (CPE) were used as working electrodes. The CPE were modified with various amounts of clays (1-10%) and were prepared with Merck graphite powder (95-99%) in solid paraffin. Another configuration of the caly modified electrodes were prepared as follow: 5 mg of polyethylene imine (PEI) with 125 µL of ethanol and 120 µL of distilled water were mixed for 15 minutes with a vortex, 6,5 µL of nanoporous clay gel was added and mix again for 15 minutes. Equal amounts (20 µL) of this mixture were deposited on the surface of a glassy carbon electrode. Two solution containing clay with particle diameter < 20 µm and < 0.2 µm were employed. The modified electrodes were dried for 4 hours at 4^{o} C.

Figure 5 presents the cyclic voltammetry obtained on a CPE electrode modified with 5 % clay in 0.1 m HCl as supporting electrolyte in the presence of 10^{-3} M solution of Pb^{2+} (a) and 10^{-3} M solution of Cd^{2+} (b).



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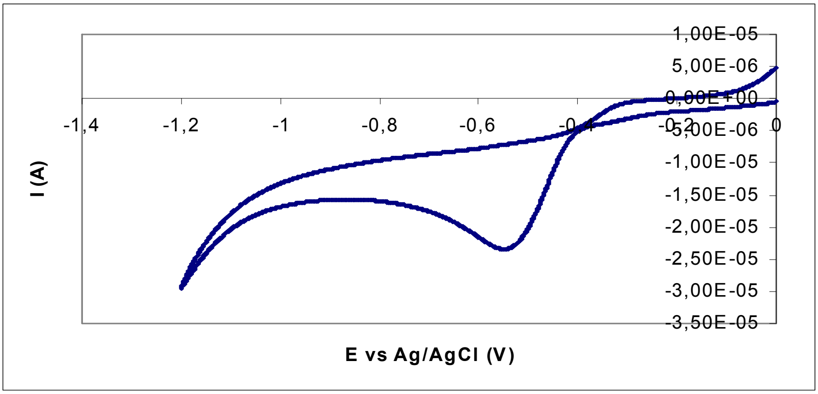
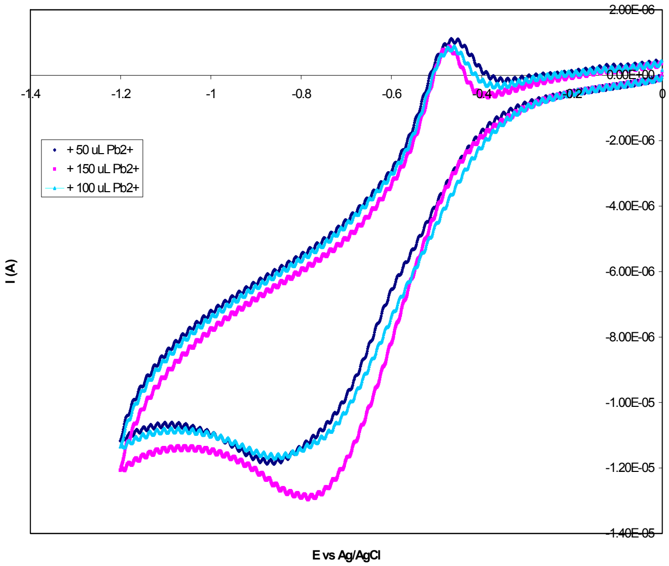


b

Fig. 5. *Cyclic voltammograms obtained on CPE electrodes doped with 10% clay in the presence of 0.1 M HCl as supporting electrolyte: a- in the presence of a 10-3 M solution containing Pb^{2+} and b. in the presence of 10^{-3} M solution containing Cd^{2+} both accumulated on the surface of the electrode; reference electrode Ag/AgCl, counter electrode glassy carbon, v = 100 mV s^{-1}.*

Standard additions of a stock solution of 1 ppm Pb^{2+} and Cd^{2+} cause an increase in the reduction current that could be observed for each addition of cation solution (fig. 6).



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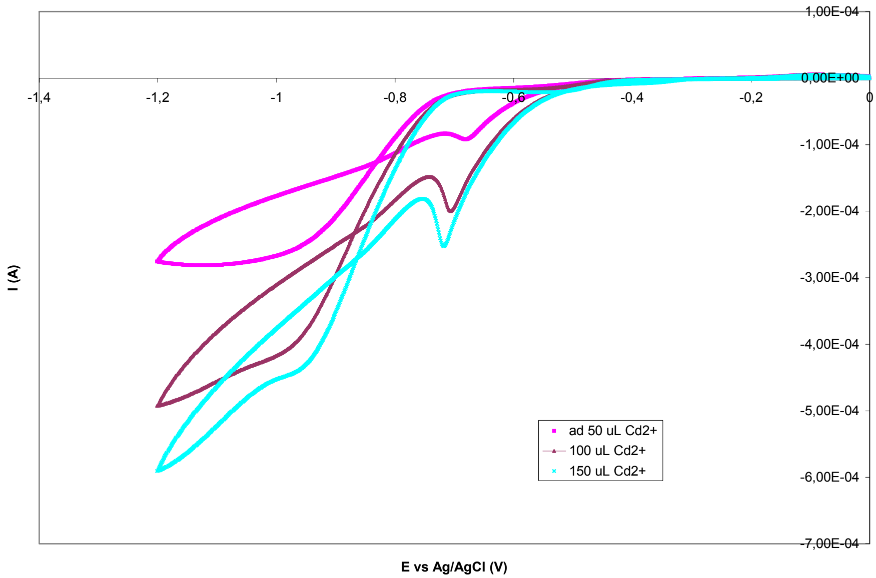

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Fig. 6. *Cyclic voltammograms obtained on the GC/PEI-clay thin film electrode in the presence of a- standard additions of a solution of 1 ppm Pb^{2+}, b- standard additions of a solution of 1 ppm Cd_2^{+}, reference electrode Ag/AgCl, counter electrode glassy carbon, v = 100 mV s^{-1}.*

The calibration plots for the two mentioned cations obtained from square wawe voltametry data are presented in figure 7.

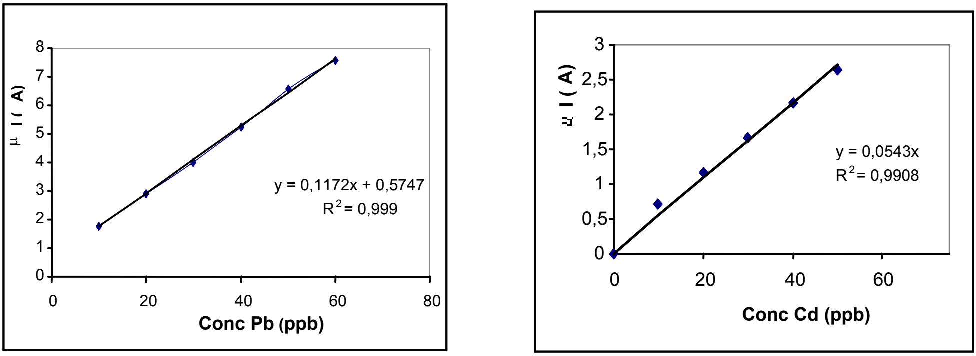

Fig. 7. *Calibration plots for the Pb^{2+} and Cd^{2+} obtained on the GC/PEI-clay thin film electrodes*

It can be noticed that the detection of heavy metals traces is possible on the modified electrodes with different amounts of clay.

CONCLUSIONS

From the analysis of the determinations made on the bentonite samples results that the procedure followed for the elevation of the clay properties has been achieved with direct consequences on the particles dimensions, specific surface, increasing the quantity of the montmorillonit and the crystallinity. New composite electrodes were elaborated using the autochthon clay completely characterised. The two electrodes configurations (carbon paste doped with clays and glassy carbon modified by a thin film of polyethyleneimine and clay) present a good capacity of adsorption and a good sensitivity towards the investigated heavy metals cations (lead and cadmium).

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STUDIA UNIVERSITATIS BABEŞ-BOLYAI, AMBIENTUM, LIV, 1-2, 2009

NO_2 DETERMINATION FROM AMBIENT AIR IN URBAN MEDIUM BY UV-VIS SPECTROMETRY AND CHEMILUMINESCENCE METHODS

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ABSTRACT. The study presents the results of NO_2 determination from ambient air, in urban medium from Cluj county, obtained by two methods: by UV-VIS Spectrometry and Chemiluminescence.

The measurements have been efectuated with a portable prelevator of gazes poluttants and with the automatic stations of air quality monitoring.

***Key word**: Imissions, Ambient air, Spectrometry UV-VIS, Chemiluminescence*

1. INTRODUCTION

This article presents the results of the measurements of NO_2 imissions from ambient air, in urban medium from Cluj county, obtained by two methods: by UV-VIS Spectrometry and Chemiluminescence.

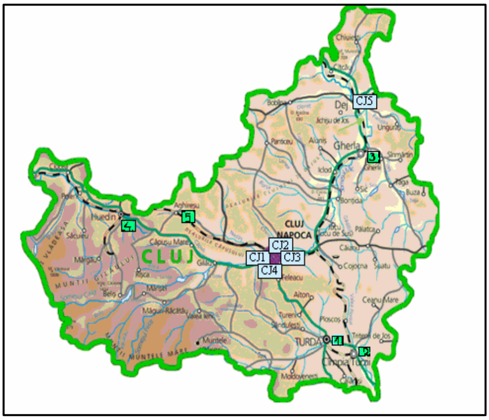
For NO_2 imissions determination, have been efectuated measurements, during 30 min, with a portable prelevator of gazes poluttants and the results have been compared, by UV-VIS Spectrometry method, with the results obtained by Chemiluminescence method, which stayed to base of the continues measurements, realised with automatic stations of air quality monitoring.

The sampling has been efectuated in Ian-Jun 2009, and the locations for determinate the concentrations of NO_2, were the 7 urban zone from Cluj county: Cluj-Napoca, Turda, Câmpia-Turzii, Gherla, Dej, Huedin and Aghireş.

2. INFORMATIONS ABOUT THE POINTS OF PRELEVATION AND OF DETERMINATION METHODS

2.1. THE POSITION OF THE PRELEVATION POINTS

In fig 2.1. are presented the position of the prelevation points for determination of NO_2 imissions from Cluj county. In 1, 2, 3, 4 and 5 points have been efectuated measurements, during 30 min, with portable prelevator of gazes poluttants, and in CJ1, CJ2, CJ3, CJ4 and CJ5 points, the determinations were realised with automatic stations of air quality monitoring.



CJ1-Aurel Vlaicu Str, Cluj-Napoca
CJ2-Constanța Str, Cluj-Napoca
CJ3-1 Decembrie Str, Cluj-Napoca
CJ4-Dâmbovița Str, Cluj-Napoca
CJ5-21 Decembrie Str, Dej
1-Turda-centre
2-Câmpia-Turzii-centre
3-Gherla-centre
4-Huedin-centre
5-Aghireş-centre

Fig. 2.1. *The position of the prelevation points in Cluj county*

2.2. DETERMINATION METHODS

2.2.1. The determination of the NO_2 concentration from ambient air with UV-VIS Spectrometry

2.2.1.1. The sampling

- The establishment of the points of prelevation: The measurements have been efectuated in 5 urban zones from Cluj county: Turda, Câmpia-Turzii, Gherla, Huedin and Aghireş, traffic – centre.
- The necessary number of prelevations: mounthly prelevations.
- The recipients of prelevation: recipients of plastic with one lid which is automatic sealing when it's closed.
- The transport of the samples: in isotherm boxes, by autolaborator.
- The prelevation during time: 30 minutes.
- The samples have been prelevation by absorption an air volume, with 0,3 l air/min debit, in 30 min during time, in a NO_2 barbotation solution, with a portable prelevator **DESAGA GS 312 (**fig. 2.2.1.1). [1]

Fig. 2.2.1.1. *Portable prelevator DESAGA GS 312*

2.2.1.2. NO_2 determination

♦ **The usedfull reagents**: The NO_2 absorbant solution – 5.0 g sulphanilic acid dissolves in aproximatly 600 ml distilled water. For dissolvation, the solution can be heated easily at 50-60°C temperature. After the cooling, it's added 50 ml acethic glacial acid, 10 ml acetone, 0,05 g N-1-naphtilendiamin clorhidrated and it's completed with distillated water until the 1.000 ml. The obtained solution is constant few months, if is keeped at cold and dark. [2]

♦ The mode of work: In the absorption vessels are added 40.0 ml absorbent solution. The content of the absorption vessel is introduced in a graduated balloon of 50 ml and is completed at sign with distillated water. The sample is homogenizing, and after 30 minutes is measure the extinction at LOVIBOND spectrometer, (fig 2.2.1.2.) at the wave length of 550 nm, compared with the absorbant solution like control sample.

♦ **Calculate**: *NO2 (mg/m³) = C/V* [1]

where:

C = concentration in mg NO_2 from air sample prelevate

V = air volume, m^3

Fig. 2.2.1.2. *UV-VIS PC SPECORD LOVIBOND Spectrofotometer*

2.2.2. The determination of the NO_2 concentration from ambient air with Chemiluminescence

The **continue** determination of NO_2 from air it based on the chemiluminescence principle. Chemiluminescence it based on the reaction of the NO_X with the O_3.

The determination of NO_2 it realised in a chemiluminescence analizor where the air is prelevate through a filter, to evite the contamination of the transportor gaz system, in a special to optic components of the analizor. The air is alimentated with a constant debit in the reaction room of the analizor. The prelevate air is introduced through a convertor where NO_2 is reduce at NO.

The emissive radiation (chemiluminescence) is proportional with the number of the molecules of NO_2 in the detection volume and is proportional with NO_2 concentration. The emissive radiation is filtrated through a selectiv optic filter and transformated in a electric signal by a photomultiplicator tube or a photodiode.

Chemiluminescence is the light emission during a chimical reaction. During a reaction in gaseous phase of NO with O_3 is produced a radiation with proportional intensity with NO concentration, when the molecules's electrones excitated by NO_2 are reviving at form with low energy. **[3]**

This chemiluminescence method is based of reactions (1) and (2):

$$NO + O_3 \rightarrow NO_2^* + O_2 \quad (1)$$

$$NO_2^* \rightarrow NO_2 + hv \quad (2)$$

NO_2 excitated (NO_2^*) emites radiation in IR region closed (600 nm - 3000 nm) with a maximum at aproximatly 1200 nm. For determination NO_2, NO_2 present in prelevate air is transformated in NO in a convertor after the reaction (3):

$$NO_2 \xrightarrow{\text{convertor (catalizator)}} NO \quad (3)$$

The NO_2 concentration is direct measured in volume units/volum. The final result for the report is in µg/m^3 using the standard factors of conversion, which for NO_2, at 20°C and at 101,3 kPa are:

1 µg NO_2/m^3 = 0,523 nmol/mol NO_2
1 nmol/mol NO_2 = 1,912 µg NO_2/m^3

Fig. 2.2.2. *The traffic monitoring station Aurel Vlaicu street, Cluj-Napoca*

In fig. 2.2.2. is representated a traffic monitoring station of air quality, which is established on Aurel Vlaicu street, in Cluj-Napoca, with which have been efectuated the continue measurements of the NO_2 imissions, from atmosphere.

3. RESULTS AND DISCUSSIONS

The results of the NO_2 concentration measured in january 2009, in 5 urban points from Cluj county, were situated under the maxim concentration admised, 0,3 mg/m^{3,} (STAS 12574/87 air from protected zones) (table 3.1. and fig. 3.1.).

In January 2009, at the traffic station on the Aurel Vlaicu street, from Cluj-Napoca, have been registered values of NO_2 daily average concentrations contented between 17,89 µg/m^3 and 67,81 µg/m^3 (fig. 3.2.)

Table 3.1.

NO_2 concentrations, UV-VIS Spectrometry -30 min samples, January 2009, Cluj county

Date	Zone	Point of prelevation	NO_2 (mg/m^3)	
			The measure value	**C.M.A.**
13.01.2009	Turda	Turda-centre	0,0350	**0,300**
13.01.2009	Câmpia-Turzii	Câmpia Turzii-centre	0,0760	
15.01.2009	Gherla	Gherla-centre	0,0100	
22.01.2009	Huedin	Huedin-centre	0,0100	
22.01.2009	Aghireş	Aghireş-centre	0,0100	

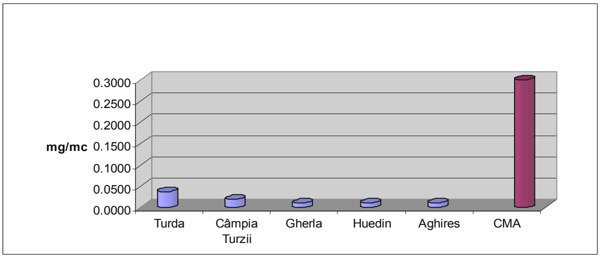


Fig. 3.1. *NO_2 determination - UV-VIS Spectrometry -30 min samples, January 2009, Cluj county*

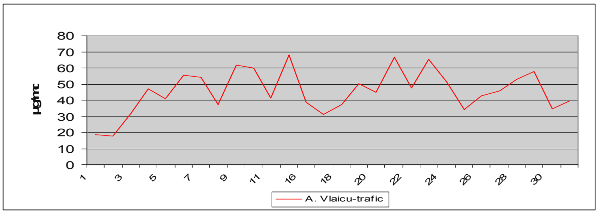


Fig. 3.2. *NO_2 daily average concentrations - Chemiluminescence, Aurel Vlaicu street, January 2009, Cluj-Napoca*

In April 2009, the results of the NO_2 concentrations, in atmosphere, at the samples of short during time, 30 min. have been registered values under the maxim admise concentration 0,3 mg/mc in all of that 5 points of prelevation: Turda, Câmpia-Turzii, Gherla, Huedin şi Aghireş, (fig. 3.3.).

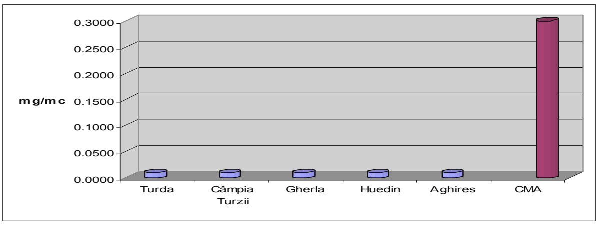


Fig. 3.3. *NO_2 determination - UV-VIS Spectrometry-30 min samples, April 2009, Cluj county*

According to fig 3.4. almost hourly concentrations values for NO_2, in April 2009, were situated under limit value, 200 µg/mc, corresponding to Order 592-2002. It has been registered a hourly minimum concentration - 0,0099 µg/mc and a hourly maximum concentration 209,37 µg/mc.

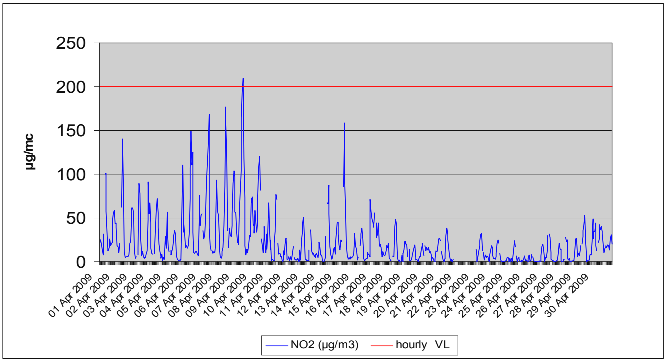


Fig. 3.4. *NO_2 determination, hourly concentrations, Chemiluminescence, Dâmbovița street, Cluj-Napoca, April 2009*

In April-June 2009, the NO_2 imissions concentrations, have been situated under the admise maximum concentration, in all of the prelevation points. (Table 3.2. and fig. 3.5.).

Table 3.2.

NO_2 concentrations, UV-VIS Spectrometry, 30 min, April-June 2009, Cluj county

Zone	**Point of prelevation**	**April NO_2 (mg/m^3)**	**May NO_2 (mg/m^3)**	**June NO_2 (mg/m^3)**	**C.M.A**
Turda	Turda-centre	0,01	0,0870	0,0140	**0,300**
Câmpia-Turzii	Câmpia Turzii-centre	0,01	0,0124	0,0170	
Gherla	Gherla-centre	0,01	0,0100	0,0060	
Huedin	Huedin-centre	0,01	0,0100	0,0012	
Aghireş	Aghireş-centre	0,01	0,0100	0,0010	

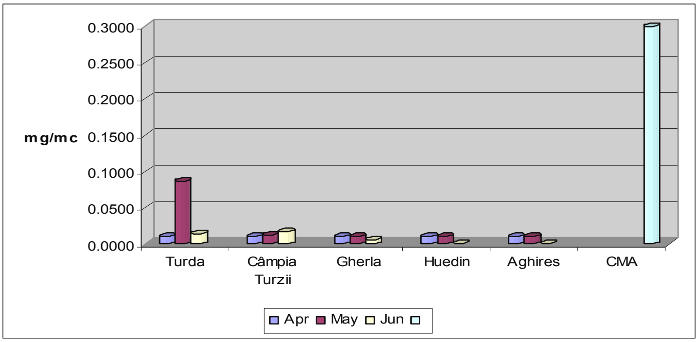


Fig. 3.5. *NO_2 determination - UV-VIS Spectrometry -30 min samples, April-June 2009, Cluj county*

At the industrial automatic monitoring station of the air quality, situated on Dambovita street, from Cluj-Napoca, for NO_2 indicator have been registered values of the hourly concentrations contented between 0,0099 µg/mc and 209,37 µg/mc. Just in April 2009 have been registered some overtakings of limit values, 200 µg/mc (fig. 3.6.).

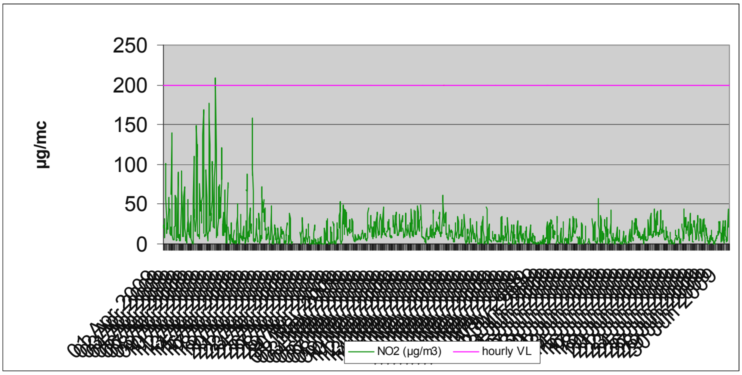


Fig. 3.6. *NO_2 determination, hourly concentrations, Chemiluminescence, Dâmbovița street, Cluj-Napoca, April-June 2009*

According to table 3.3. and fig. 3.7. the values monthly average concentrations for NO_2, in April-June 2009 have been situated between 11,70055 µg/mc, value which has been registered at the industrial station situated on Dambovita street, in June 2009 and 62,40863333 µg/mc, concentration registered at suburban station, amplasated in Grigorescu, in April 2009.

Table 3.3.

NO_2 Concentrations, monthly averages, Chemiluminescence, April-June 2009

Point of prelevation	**Apr 2009**	**May 2009**	**June 2009**
Aurel Vlaicu street	61,31341379	28,4101	28,6622
Grigorescu	62,40863333	21,7071	17,9591
Dambovita street	23,24907143	13,75745	11,70055
Dej	37,53304545	-	14,67117

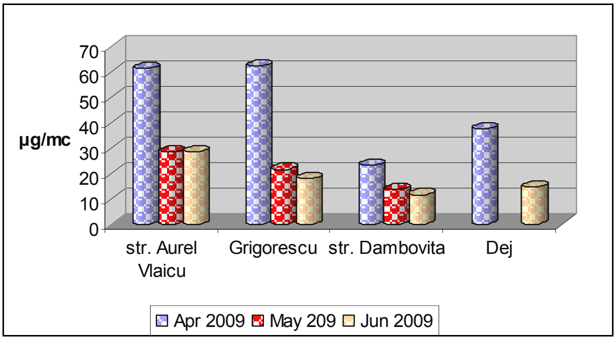


Fig. 3.7. *NO_2 Concentrations, monthly averages, Chemiluminescence, April-June 2009*

4. CONCLUSIONS

NO_2 determination from atmosphere, in urban medium from Cluj county, have been realized by two methods: by UV-VIS Spectrometry and Chemiluminescence.

By both methods of determination, UV-VIS Spectrometry and Chemiluminescence, NO_2 imissions concentrations have been registered values under admise maxim concentrations.

In January 2009, to the trafic station on Aurel Vlaicu street, from Cluj-Napoca, have been obtained values of NO_2 daily average concentrations contented between 17,89 µg/m^3 and 67,81 µg/m^3.

At the industrial automatic monitoring station of the air quality, situated on Dambovita street, from Cluj-Napoca, for NO_2 indicator have been registered values of the hourly concentrations contented between 0,0099 µg/mc and 209,37 µg/mc. Just in April 2009 have been registered some overtakings of limit values, 200 µg/mc.

In Apr-June 2009, monthly average concentrations for NO_2 have been situated between 11,70055 µg/mc, value which has been registered at the industrial station situated on Dambovita street, in June 2009 and 62,40863333 µg/mc, concentration registered at suburban station, amplasated in Grigorescu, in April 2009.

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STUDIA UNIVERSITATIS BABEŞ-BOLYAI, AMBIENTUM, LIV, 1-2, 2009

INVESTIGATION OF RADON AND THORON IN DWELLINGS NEARBY A CLOSED HUNGARIAN URANIUM MINE

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ABSTRACT. Radon (^{222}Rn) and thoron (^{220}Rn) integrated measurements were executed in a Hungarian a village, located in vicinity of an abandoned uranium mine. The applied passive radon and thoron monitor were the RADUET which based on CR-39. The investigated 43 houses were one storey buildings made of bricks. The rock under the village is gray-sandstone with 136 and 77 Bq kg^{-1} average uranium and thorium contents respectively. The detectors were mostly placed in the inhabited areas of the houses, such as bedrooms and living-rooms, at a height of 1-1.5 m close to the wall. The measurement periods were between December 2006 – May 2007 and May 2007 – February 2008. Annual averages of radon concentrations were calculated applying seasonal correction factors to the results of the two measurement periods. The results show that the radon concentrations in case of considerably part of the investigated dwellings seems to be significantly higher (data are under evaluation) than the Hungarian averages for ground-floor houses (152 Bq m^{-3}). The thoron concentrations in some case are also not negligible indicating that radon measurements which are sensitive to thoron can be misleading. Additionally, thoron also can be a contributor of extra dose.

***Keywords**: dwellings; uranium mine; radon; thoron*

INTRODUCTION

As it is known the radon (^{222}Rn) gas and its progenies are considered to be the major contributors to human exposure from natural radiation sources (UNSCEAR, 2000). Several surveys seem to have concluded that the radon in the living environment implies an increased health risk (Darby et al., 2005; Martinez et al., 2004; Denman et al., 2007). This is the reason why national authorities and international organizations issues guidelines concerning radon levels in homes.

Although radon has the main concern among the health physicists, the thoron also needs attention. Previous studies have shown that thoron (^{220}Rn) was find in a not negligible extent in traditional Japanese houses (Wichman et al., 2005; Mishara et al., 2004; Gargioni et al., 2003), in dwellings of Mexico City (Guo et al., 2001) and it has gained an important part in surveys in India (Tokonami et al., 2004) and China (Ma et al., 1997; Tokonami et al., 2001).

The presence of thoron can effects on the accurate radon measurement (Chung et al., 1998) and thoron itself might results radiation exposures comparable to those due to radon (Krewiski et al., 2005). The measurement of thoron usually more complicated than the radon measurements. Thoron concentrations is highly inhomogeneous with a strong dependence on the distance from the source (Doi, Kobayashi, 1994).

In this paper a radon survey executed in a Hungarian a village, located in vicinity of an abandoned uranium mine are described. Seasonal correction factors were applied to the lesser-than-one-year measurements in order to calculate the annual averages of radon concentrations.

Radon measurements executed earlier in this village showed higher levels here than the characteristic one for Hungarian villages (Toth, 1999). Our former investigations also indicated elevated radon levels in this village (Kavasi et al., 2007).

MEASUREMENTS AND METHODS

The applied passive alpha track etch detector were the RADUET. The RADUET is a twin detector containing a plastic container with CR-39 inside only for radon detection and an almost identical other container enhancing its air change for detecting both radon and thoron. The two parts of the twin detector are implanted in a cardboard holder which helps to keep the appropriate distances from the wall (95 mm between the wall and the center of the container). These detectors were developed in a collaboration of the National Institute of Radiological Sciences (NIRS), Japan and a Hungarian factory, RADOSYS. The detectors were sent to evaluate to NIRS.

The village chosen for this study was Kővágószőlős. It is located in the Mecsek Mountains in the south part of Hungary. There is an abandoned uranium mine in vicinity of the village. (Some tunnels are under the village.) The village has 1200 inhabitants; the investigated houses were one storey buildings made of bricks.

The rock under the village is gray-sandstone. The analysis of the drill cores taken from a depth of 1-2 m in the soil of the village showed that the average uranium and thorium contents were 136 and 77 Bq kg^{-1} respectively. These values exceed world averages (UNSCEAR, 2000) (33 and 45 Bq kg^{-1}).

The detectors were mostly placed in the inhabited areas of the houses, such as bedrooms and living-rooms, at a height of 1-1.5 m in a way that the cardboard holder situated close by the nearest wall for keeping the appropriate distance. (This could be important for the thoron measurement.)

The measurement periods were between December 2006 – May 2007 and May 2007 – February 2008. The number of the investigated dwellings was 43 but in 8 cases one of the detectors were lost or damaged therefore, only in 35 cases was information for both measurement periods.

Annual averages of radon concentrations were calculated applying seasonal correction factors to the results of the two measurement periods. Radon levels in the domestic built environment are assumed to vary systematically during the year, being generally higher in winter than summer. The seasonal correction factors comprise a series of numerical multipliers, which convert a 1-month or 3-month radon concentration measurement, commencing in any month of the year, to an effective annual mean radon concentration (Denman et al., 2007). In this case seasonal correction factors for 1-month exposures suggested by Woods et al (Woods et al., 2000). were used to calculate the appropriate factors to the measurement periods. Table 1 show the above mentioned seasonal correction factors for 1-month exposures suggested by Woods (Woods et al., 2000). These seasonal factors were normalized to 12 months. This means that the sum of the 12 monthly factors is 13.43. 12 divided by 13.43 resulted 0.8935. Each monthly factor was multiplied by this providing the "normalized" values for each month. As correction factors were applied the arithmetical mean of the normalized seasonal correction factors for 1-month exposures take into consideration the given months. Consequently, the multiplying factor for the measurement period of December – April was 0.71; the arithmetical mean of the five appropriate values from the Table 1 (0.70; 0.61; 0.64; 0.72; 0.89). Using the same method the applied multiplying factor for the period of May – February was calculated as 1.04. We are aware that these seasonal correction factors maybe not fit perfectly to our case; however the inaccuracy can be acceptable.

Table 1.

Seasonal correction factors for 1-month exposures (Woods et al., 2000) and the normalized values

Month	Correction factors	Normalized factors
January	0.68	0.61
February	0.72	0.64
March	0.81	0.72
April	1.00	0.89
May	1.18	1.05
June	1.39	1.24
July	2.00	1.79
August	1.65	1.47
September	1.30	1.16
October	1.04	0.93
November	0.88	0.79
December	0.78	0.70

RESULT AND DISCUSSION

The annual radon concentrations in the 35 dwellings calculated from the data come from the two measurement periods can be seen in Figure 1. The values come from the 10 months long measurements systematically higher than provided by the 5 months long ones. The reason can be partly the yearly variations and – maybe more probably – the inaccuracy of the applied correction method.

The average (arithmetical) radon concentrations in the two survey (10 month and the 5 months) are 700 (122-2195) and 458 (37-1445) Bq m^{-3} respectively.

The number of dwellings being above 200, 400, 600 and 1000 Bq m^{-3} can be seen in the Table 2.

Table 2.

The number of dwellings being above 200, 400, 600 and 1000 Bq m^{-3}.

Annual average Rn concentration (Bq m^{-3})	Number of dwellings (%) 10 months survey	5 months survey
>200	34 (97%)	29 (83%)
>400	26 (74%)	15 (43%)
>600	15 (43%)	7 (20%)
>1000	7 (20%)	3 (8.5%)

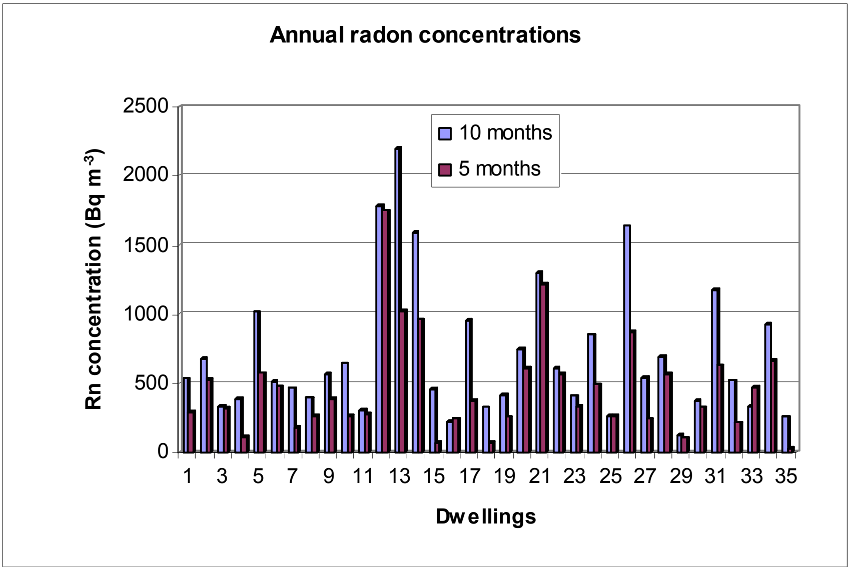

Fig. 1. *The annual radon concentrations in the 35 dwellings*

The results show that the radon concentrations in case of considerably part of the investigated dwellings seems to be significantly higher than the Hungarian averages for ground-floor houses (152 Bq·m^{-3}). The thresholds in the first column of Table 2. corresponds to different values advised by international and national guidelines. In Hungary at this moment there is no official limit for houses.

The results of the thoron measurements can be seen in the Figure 2.

The presence of thoron in some cases seemed to be not negligible. However, considerably part of the data provided by the detectors were unusable or unrealistic. The restricted number of results is not enough to be a basis of any statement. Because of the characteristic of the applied radon detector is not sensitive to thoron this results are not influenced the radon detection considerably.

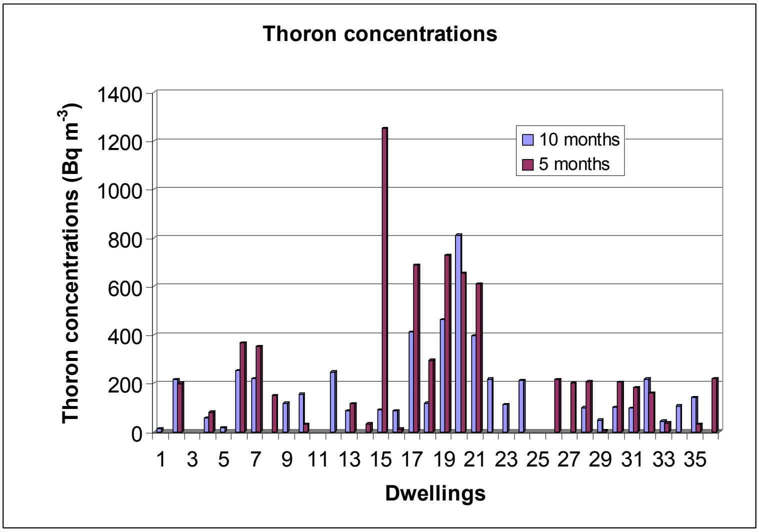

Fig. 2. *The measured thoron concentrations*

CONCLUSIONS

Integrated radon measurements were executed in a Hungarian a village, located in vicinity of an abandoned uranium mine. The applied detector was the RADUET which are constructed to measure thoron parallel with the radon. The detectors were placed in two periods a five and a ten months long. The number of the investigated dwellings was 43. Annual averages of radon concentrations were calculated applying seasonal correction factors. The results show that the radon concentrations in case of considerably part of the investigated dwellings seems to be significantly higher – with calculated yearly averages of 700 (122-2195) and 458 (37-1445) Bq m^{-3} according to the two surveys – than the Hungarian averages for ground-floor houses (152 Bq m^{-3}).

The thoron concentrations in some case are also not negligible indicating that radon measurements which are sensitive to thoron can be misleading.

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STUDIA UNIVERSITATIS BABEŞ-BOLYAI, AMBIENTUM, LIV, 1-2, 2009

CONSIDERATIONS RELATING TO MONITORING OF GREENHOUSE GAS EMISSIONS IN MARAMURES COUNTY

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ABSTRACT. The paper refers to issues related to evolution of greenhouse gas emissions in Maramures County, in the context of their monitoring as part of the National Inventory of Greenhouse Gas Emissions. These gases represented by carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), hydrofluorocarbons (HFC_s), perfluorocarbons (PFC_s) and sulfur hexafluoride (SF_6) constitute the leading cause of global warming and hydro-meteorological changes attracting the major concern of scientists around the world. The biggest impact generated by the human activities is due to CO_2 and NH_4 emissions which are responsible for increasing with 50% in GHG concentrations in the atmosphere. In Maramures County the largest GHG emissions result from industry and traffic. The most contribution in CO_2 equivalent is due to CO_2 emissions (52.4%) and NH_4 (45.5%). The monitoring of GHG emissions in Maramures County has been done using the CORINAIR methodology.

Romania is included in Annex B of the Kyoto Protocol and has committed to reduce the greenhouse gas emissions by 8% between 2008-2012, compared to1989.

The increasing by 0.74 ^{0}C of global average temperature in the last century and its gradual trend triggered a high interest in this area not only of scientific but also political viewpoint.

Key words: *greenhouse gases, climate changes, CO_2 equivalent, GWP*

INTRODUCTION

It is well known that the earth warming has been generated by natural causes but this phenomenon is emphasized by gases resulted from human activities (Coman, M., 2006). These gases are reaching a point at which they can adversely affect climate namely, by emission of large quantities of carbon dioxide and other greenhouse gases. It is known that CO_2 and other greenhouse gases, such as CH_4, absorb infrared radiation by which earth loses heat (Andrei, L., Dupleac, et.al., 2004). The levels of these gases have increased markedly since 1850 as nations have become industrialized and as forest lands and grasslands have been converted to agriculture [Manahan, S., 1999].

Romania is included in Annex B of the Kyoto Protocol and has committed to reduce the greenhouse gas emissions by 8% between 2008-2012, compared to 1989 (Law no. 3/2001) and the national GHG emissions inventory shows a decreasing of GHG emissions by 37% below the target set for Romania (Fig. 1).

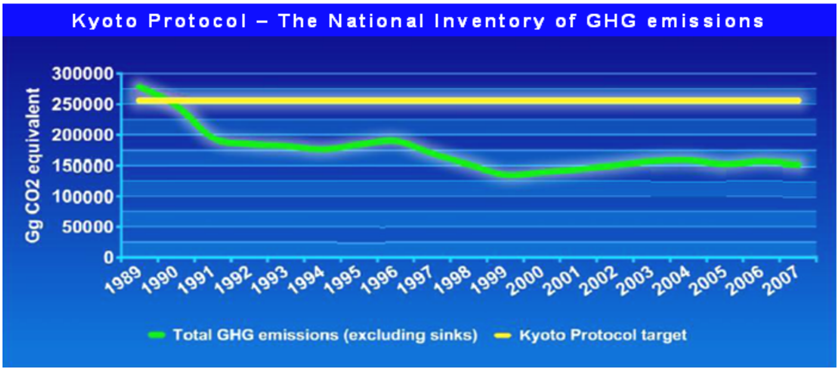

Fig. 1. *Evolution of national GHG emissions in relation to Kyoto Protocol target*
(Source: http://www.ramboll.ro/news/~/media/Files/RRO/Documents/1%20Hortensia%20Dumitriu%20ANPM.ashx)

GASES RESPONSIBLE FOR THE GREENHOUSE EFFECT

It is thought that CO_2 is responsible for about half of the atmospheric heat retained by trace gases. It is produced primarily by the burning of fossil fuels, and deforestation accopanied by burning and biodegradation of biomass.

Table 1.

The main greenhouse gases (Source: http://www.grida.no/publications/vg//climate/page/3060.aspx)

Nr. Crt.	Greenhouse gases	Chemical formula	Atmospheric lifetime (years)***	Anthropogenic sources	Global warming potential (GWP)*
1	Carbon-dioxide	CO_2	variable	- fossil fuel combustion - land use conversion - cement production	1
2	Methane	CH_4	12	- fossil fuels - rice paddles - waste dumps - livestock	21**
3	Nitrous oxide	N_2O	120	- fertilizer - industrial processes - combustion	310
4	CFC-12	CCl_2F_2	102	- liquid coolants	6200-7100****
5	HCFC-22	$CHClF_2$	12.1	- liquid coolants	1300-1400****
6	Perfluoromethane	CF_4	50000	- production of aluminium	6500
7	Sulphur hexa-fluoride	SF_6	3200	- dielectric fluid	23900

* GWP-for 100 year time horizon
** Includes indirect effects of tropospheric ozone production and stratospheric water vapour production
*** No single lifetime for CO_2 can be defined because of the different rates of uptake by different sink processes
**** Net global warming potential (including the indirect effect due to ozone depletion)

On a molecule-for-molecule basis, methane, CH_4, is 20-30 times more effective in trapping heat than CO_2. Other trace gases that contribute are chlorofluorocarbons and N_2O (table 1). The potential of such a gas to cause greenhouse warming may be expressed by a global warming potential (GWP) which is a function of both the infrared sorption characteristics and the lifetime of the gas [S. Manahan, 1999].

THE MECHANISM OF GREENHOUSE EFFECT PRODUCTION

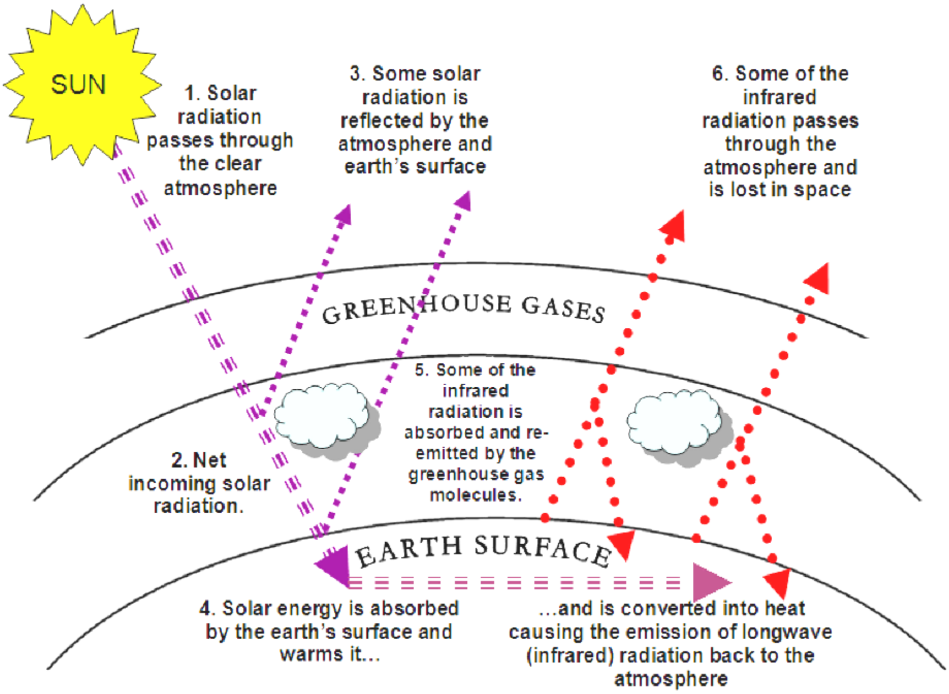

Fig. 2. *An overview of the greenhouse effect. (Modified scheme after http://www.grida.no/publications/vg/climate/page/3058.aspx)*

Solar energy is absorbed by the earth's surface, getting warm to the earth which emits infrared radiation. The greenhouse gases trap the infrared radiation leading to the atmosphere warming (Fig. 2).

Naturally occurring greenhouse gases include water vapour, carbon dioxide, ozone, methane and nitrous oxide, and together create a natural greenhouse effect but human activities are causing greenhouse gas levels in the atmosphere to increase.

THE MONITORED GREENHOUSE GASES IN MARAMURES COUNTY

In Maramures County the equivalent global potential calculated using the CORINAIR methodology is given below (Fig. 3).

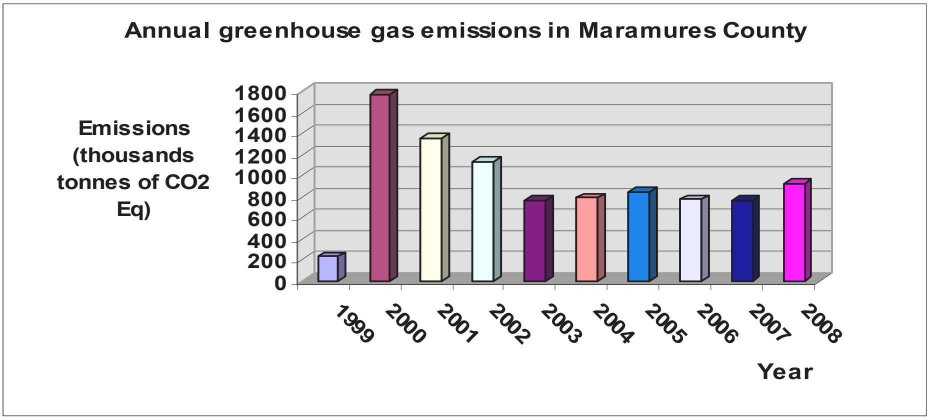

Fig. 3. *GHG emissions in Maramures County between 1999-2008 (Source: www.apmmm.ro)*

The largest share of the main greenhouse gases in Maramures County is owned by CO_2 followed by those of CH_4 and N_2O and the main generators are: industry, traffic, distribution of fuel (methane), agriculture, waste treatment and waste storage etc, (Fig. 4.5).

In accordance with the National inventory of emissions of greenhouse gases, developed under the national system for estimating anthropogenic emissions of greenhouse gas emissions from sources or detention by sinks of carbon dioxide, the situation on hydrofluorocarbons Maramures County, for the year 2008, is given by Fig. 6. 7. 8. 9. Many times the hydrofluorocarbons are comprised in freons which are symbolized with "R" followed by a number or a number and a letter. Freons are used in refrigerating and air conditioning sectors.

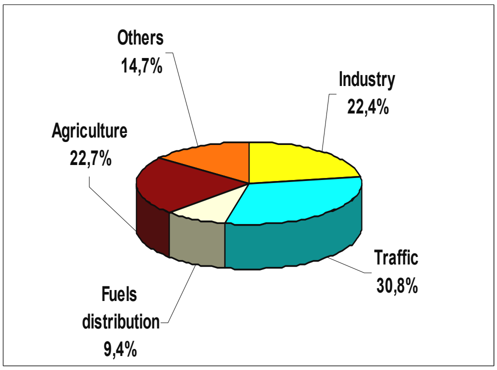

Fig. 4. *CO_2 equivalent share of activities sectors (Source: www.apmmm.ro)*

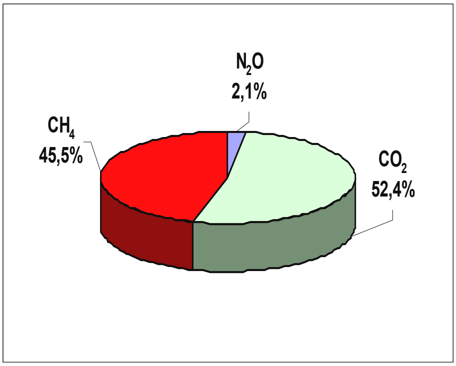

Fig. 5. *Major GHGs share expressed in $CO_{2\ eq.}$ (Source: www.apmmm.ro)*

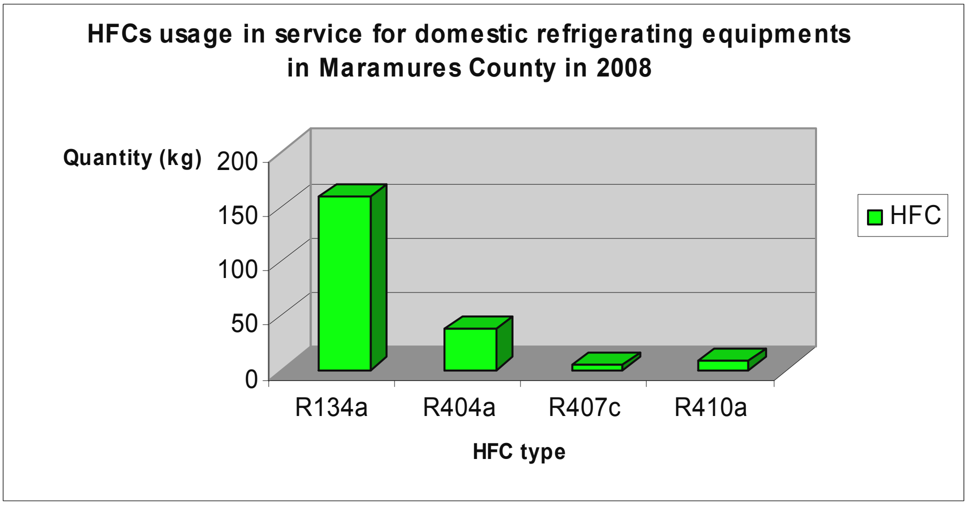

Fig. 6. *HFCs used for refilling of the domestic refrigerating equipments in Maramures County in 2008 (Source: www.apmmm.ro)*

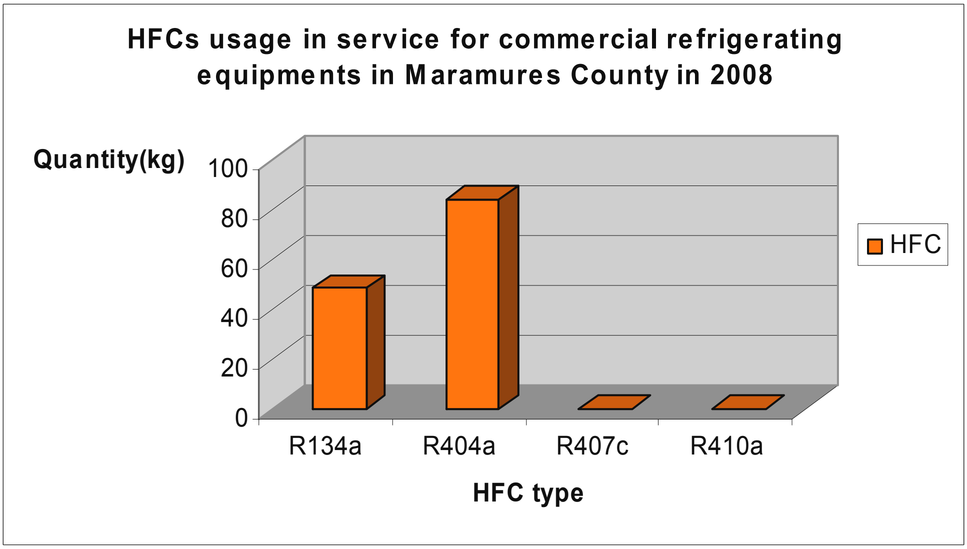

Fig. 7. *HFCs used for refilling commercial refrigerating equipments in Maramures County in 2008 (Source: www.apmmm.ro)*

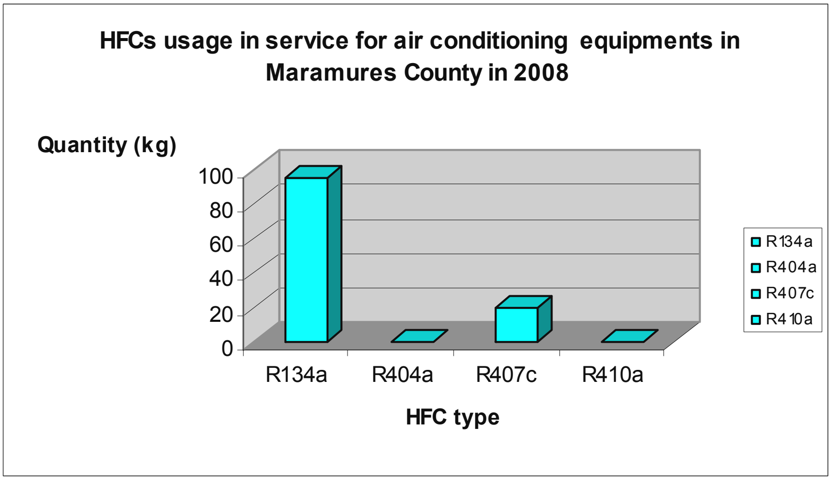

Fig. 8. *HFCs used for refilling of air conditioning equipments in Maramures County in 2008 (Source: www.apmmm.ro)*

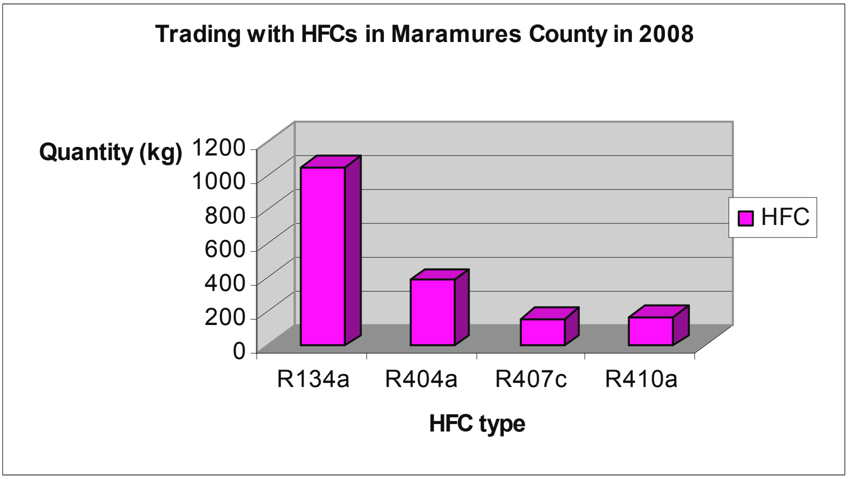

Fig. 9. *HFCs traded in Maramures County in 2008 (Source: www.apmmm.ro)*

POTENTIAL CLIMATE CHANGE IMPACTS

The climate changes are expected to be more pronounced for the next decades. Their impacts could have wide-ranging effects on the natural environment as well as on human societies and economies (table 2). In reality, the full impact could be more complicated because the impacts on one sector can affect other sectors, indirectly. In order to assess potential impacts, it is necessary to estimate the extent and magnitude of climate change, starting with local and national levels.

The potential climate change impacts could be on the categories given below.

Table 2.

Potential climate change impacts
(Source: http://www.grida.no/publications/vg/climate/page/3073.aspx):

Impact on…	♦ **HEALTH**	➢ Weather-related mortality ➢ Infectious diseases ➢ Air-quality respiratory illnesses
	♦ **AGRICULTURE**	➢ Crop yields ➢ Irrigation demands
	♦ **FOREST**	➢ Forest composition ➢ Geographic range of forest ➢ Forest health and productivity
	♦ **WATER RESOURCES**	➢ Water supply ➢ Water quality ➢ Competition for water
	♦ **COASTAL AREAS**	➢ Erosion of beaches ➢ Inundation of coastal lands ➢ Additional costs to protect coastal communities
	♦ **SPECIES AND NATURAL AREAS**	➢ Loss of habitat and species ➢ Cryosphere: diminishing glaciers

Other consequences could be expressed by: sea level rising, changes in amount and frequency of precipitations, drought occurence in unexpected areas, unusual meteorological events and appearance forms, so on.

These impacts can be better perceived in term of „sensitivity", „adaptability" and „vulnerability" of the studied system (fig.10). These features depend on the magnitude and the rate of climate change.

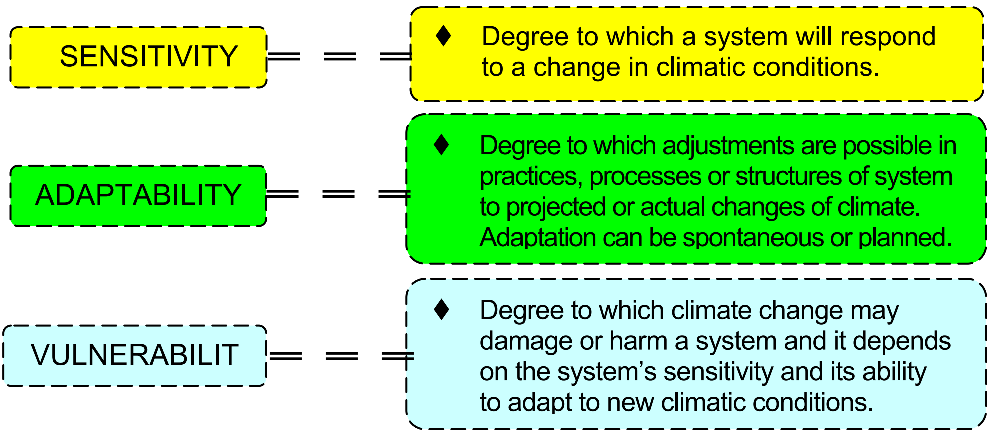

Fig. 10. *Characteristics of a subjected system to climate change*
(Source: http://www.grida.no/publications/vg/climate/page/3078.aspx)

POLITICAL AND STRATEGIC FRAMEWORK FOR THE REDUCTION OF GHG EMISSIONS

By the act of ratifying the Kyoto Protocol, adopted on December 11, 1997, Romania has assumed the responsibility for this Protocol requirements concerning the limiting the emissions of greenhouse gases in 2008-2012 by 8% from base year 1989. To achieve this commitment was developed in 2005, National Strategy on Climate Change which has established the measures of compliance with international obligations under United Nations Framework Convention on Climate Change (UNFCCC) and Kyoto Protocol plans action, obligations and priorities of our country on climate change (Law no.24/1984, Law no.3/2001).

Application of Directive 2003/87/EC (as amended by Directive 2009/29/CE) to set up a scheme of emissions trading of greenhouse gases transposed into Romanian legislation by GD. 780/2006, allows traders to participate in the trading of emissions allowances for greenhouse gas emissions through a national registry that are pursued the issue, holding, replacement, cancellation, retention and reporting of emissions units greenhouse, under Art. 7.4 Kyoto Protocol.

Also, the National Register ensures proper accounting records of electronic transactions for issuing, holding, transfer and cancellation of certificates of emission of greenhouse gases, including electronic operations with units of emission of greenhouse gases under the Protocol Kyoto. The flexible mechanism under the Kyoto Protocol applied in Maramures County is the “international trade emission allowances of greenhouse gases” and it is used by a single plant covered by Directive 2003/87/EC, which has got permit for emissions of greenhouse gases (Directive 2003/87/CE)

CONCLUSIONS

Emission trend of greenhouse gases in Maramures County is continuously monitored in a national inventory of emissions of greenhouse gases.

The last decade has shown a decrease in these emissions, the years 2000 and 2001 having the highest rates. This may be related to the restructuring of industry sector whose consequence was the close of the main pollution sources in this area.

As outlined in the graphical representation, the main generator of GHG is the traffic followed closely by agriculture and industry. Predominance of greenhouse gases is owned by CO_2 and CH_4. To these gases hydrofluorocarbons are added that are contained in the cooling agents used in the refrigeration service sector and air conditioning. From the graphic representations it can be seen that in Maramures County there are used only ecological freons which have a low contribution in greenhouse effect generation.

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*** Directive 2003/87/EC of the European Parliament and of the Council of 13 October 2003 establishing a scheme for greenhouse gas emission allowance trading within the Community and amending Council Directive 96/61/EC

*** Law no. 24/1994 to ratify the United Nations Framework Convention on Climate Change signed in Rio de Janeiro on June 5, 1992;

*** Law no. 3 / 2001 to ratify the Kyoto Protocol to the United Nations Framework Convention on Climate Change, adopted on December 11, 1997.

http://www.apmmm.ro

http://www.grida.no/publications/vg/climate/page/3058.aspx

http://www.grida.no/publications/vg/climate/page/3060.aspx

http://www.grida.no/publications/vg/climate/page/3073.aspx

http://www.grida.no/publications/vg/climate/page/3078.aspx

http://www.ramboll.ro/news/~/media/Files/RRO/Documents/1%20Hortensia%20Dumitriu%20ANPM.ashx

STUDIA UNIVERSITATIS BABEŞ-BOLYAI, AMBIENTUM, LIV, 1-2, 2009

RADON AND RADON EXPOSURE OF WORKERS IN HUNGARIAN SHOW CAVES

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ABSTRACT. Radon can accumulate in underground areas, such as in show caves. Therefore, workers, tourist guides may be exposed to significant radiation dose in most of the show caves. It is necessary to measure the radon concentration in order to estimate the exact radiation dose caused by radon. Usually the radon concentration of the caves shows significant seasonal fluctuation, therefore, in order to determine it, this study work involved nine show caves visitable for the public in Hungary, where monthly changes of radon concentration had been studied for one year. Despite the fact that all of the caves formed in karst rocks, the annual average radon concentration levels were rather differing (541-8287 $Bq \cdot m^{-3}$). We measured the monthly average radon concentration in working hours with personal radon detector too and estimated the dose of the tourist guides. The committed effective dose of workers calculated from the yearly average radon concentration of cave, supposing 2000 hour/year working time and 0,4 equilibrium factor, is 3.4 – 52.2 mSv/year, the real yearly effective dose of tourist guides in the studied show caves which was calculated based on personal dosimetry is 0.3 – 31.2 mSv/year.

***Keywords**: radon, show cave, radiation dose, dose estimation*

INTRODUCTION

More than half the natural radiation dose effecting people is caused by radon and its progenies (UNSCEAR, 2000). The carcinogenic effect of radon as a radioactive noble gas is well-known (Hornung et al., 1998; Archer et al., 1973) and some new epidemiological study shows strong correlation in case of low radon level too (Darby et al., 2006). Most of the international recommendations and legislation cover the maximum level of radon allowed at workplaces. The activity level recommended (ICRP, 1994) by the ICRP 65 for annual average radon concentration is 1000 $Bq \cdot m^{-3}$. Hungarian regulations (Hungarian Regulation, 2000) for workplaces set a radon concentration level of 1000 $Bq \cdot m^{-3}$ as an annual average activity level, which thus means an equilibrium factor of 0.4 and a 6.3 mSv/year radiation dose for 2000 working hours/year. If this limit is exceeded and it is not possible to decrease it, then such a workplace would be determined to be a hazardous radiation workplace. With these regulations, workers receive a maximum radiation dose of 100 mSv/5 year (that is an average of 20 mSv/year), and included is a limitation that the dose must not exceed 50 mSv within one year. Taking into consideration the ever constantly high radon concentration in the cave and the long hours spent there by workers, the limit of 20 mSv/year was taken as a reference value for the radiation dose limit.

The development of high radon concentration radon values can be expected in places where the radon source is ^{226}Ra and it occurs in high concentration in walls and building materials (Cothern, Smith, 1987; Somlai et al., 2005) surrounding enclosed air spaces. This is especially so if the degree of ventilation is low (Hakl et al., 1997; Perrier et al., 2004), as the emanated radon can easily accumulate. Almost all the latter conditions always exist in underground air spaces such as cellars, mines, and caves, so the quality of air in such workplaces should be given special attention.

In caves that are popular for tourists, those visiting the cave are exposed to radiation doses due to high radon concentrations for such short times that the effect is insignificant (Solomon et al., 1996; Gillmore et al., 2000;). However, for those working in the cave, the extra dose must in all cases be taken into consideration (Kobal et al., 1988; Duffy et al., 1996; Somlai et al., 2009; Field 2007; Bahtijari et al., 2008; Sainz et al., 2007).

As the radon concentration is affected by a lot of factors (season, period of the day, temperature, air pressure, air change, etc.) the determination of the average radon concentration is not a simple task to do. Several studies have been devoted to the seasonal, monthly and daily variations of radon concentration in dwellings (Harley, Terilli, 1990; Hamori et al., 2006) and offices (Hakl et al., 1997;Tokonami et al., 2003; Yu et al., 1998)

Because of the expense and the urgent need for knowing the results, year-long measurements might be not acceptable in many cases. In the Scandinavian countries the regulation requires that the average has to be determined from statistically sufficient measurements (Naturally Occurring Radioactivity in the Nordic Countries – Recommendations, 2000). Other authors suggest 1-3-month-long measurements for workplaces (Gregory, Scivyer, 1995).

In Hungary, nine caves are open for tourists almost throughout the year. (Besides, of course, very many caves are visitable, but they are not built out for visitors, therefore, they can only be entered after preliminary appointment, and wearing special equipment.) The above mentioned show caves attract numerous visitors every year. In some of the caves shorter radon measurements have already been carried out before (Szerbin, 1996; Hakl et al., 1997; Somlai et al., 2009), but a survey lasting for a whole year and concerning all show caves has only been carried out this time.

Therefore we measured the monthly average radon concentration for one year in Hungarian show caves, and the monthly average radon concentration in working hours with personal radon detector and estimated the dose of the tourist guides.

MATERIALS AND METHODS

Study area

In show caves at least 100 m long, located in Hungary and visitable for the public almost the whole year (1-8) the changes of the monthly average radon concentration levels have been measured for a year. In one case (Lake Cave in Tapolca – 8) measurements have been carried out for 4 years in order to study even annual fluctuation (Somlai et al., 2009). Markings and locations of the caves are shown in Figure 1.

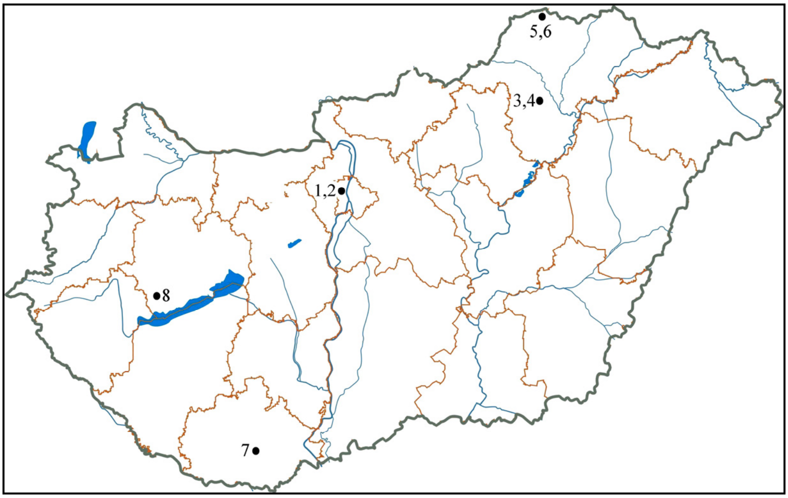

Fig. 1. *Show caves inspected in Hungary*

Each of the caves formed in karst rocks, but the age of the limestone, and the mechanism of cave forming are different. Most important characteristic data of each cave are summarized in Table 1.

Table 1.

Major characteristics of caves inspected

Mark	Cave	Mountains	Cave length (m) explored	Rock
1.	Szemlő-hegyi (Budapest)	Budai	2200	Travetine (aragonite precipitating)
2.	Pálvölgyi (Budapest)	Budai	19000	Eocene Limestone, Bryozoa Limestone
3.	Szent István (Lillafüred)	Bükk	1043	Middle and Upper Triassic Limestone
4.	Anna (Lillafüred)	Bükk	570	Travertine
5.	Baradla (Aggtelek)	Karstic Mtn. at Aggtelek		Middle Triassic Wetterstein and Steinalm (light-grey), Limestone
6.	Baradla (Jósvafő)	Karstic Mtn. at Aggtelek	25000	Gutenstein Limestone (black-dark grey)
7.	Abaligeti (Abaliget)	Mecsek	1380	Middle Triassic Anisian Limestone (dark grey)
8.	Tavasbarlang (Tapolca)	South Bakony	2500	Sarmatian Limestone

Previously, in some of the caves sampling (Szerbin, 1996) and radon concentration measurements with sampling had already been carried out. In case of large sized caves the radon concentration at different locations of the cave may greatly differ, which have been verified by previous measurements (Hakl et al., 1992). As Table 1 shows only a smaller section of the caves explored are visitable for the public. When selecting measurement points, detectors were placed at 1-2 points in these sections (taking previous measurement results into account), which defined the radon concentration of the territory visited by normal tourists and their guides, with acceptable accuracy.

Radon measurement

For the measurement of the integral radon concentration, CR-39 type TASTRAK nuclear track-etch detectors were used. The detectors were placed in holders that were made by the National Radiation Protection Board, U.K. and were placed in appropriate areas in the cave. Personal track etched detectors, using the above mentioned solid-state track detectors. The track detectors were required to be worn on their working clothes during working hours. After working hours the detectors were stored in a room in a controlled low radon level environment

After one month's exposure the detectors were etched in 6M NaOH solution at 80$\pm$0.5 ^{o}C for 2 hours. The track detectors were calibrated in an airtight radon chamber (an EV 03209, produced and calibrated by Genitron Instruments GmbH), employing a PYLON RN 2000A calibration standard source.

RESULTS

Radon concentration in the caves

Results measured in caves relatively close to each other (few km), and in the Aggtelek and Jósvafő section of the Baradla cave are shown on one joint figure.

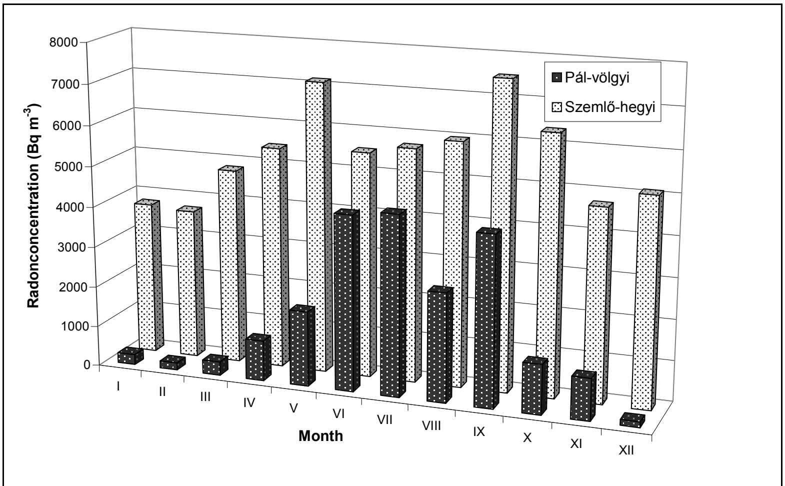

Fig. 2. *Monthly average radon concentration measure in caves Szemlőhegyi (1) and Pálvölgyi (2)*

As Figure 2 shows, cave Pálvölgyi acts as a typical piedmont cave. Radon concentration generated is low in winter months, while rather high in summer months, several thousand Bq·m^{-3}.

In case of Szemlő-hegyi cave the trend is similar, although radon concentration in the section inspected was high (3500-5000 Bq·m^{-3}) in winter months.

In case of Szent István and Anna caves values corresponding to piedmont caves with smaller anomalies were found, but radon concentration values here do not exceed the value 1600 Bq·m^{-3} even in summer months.

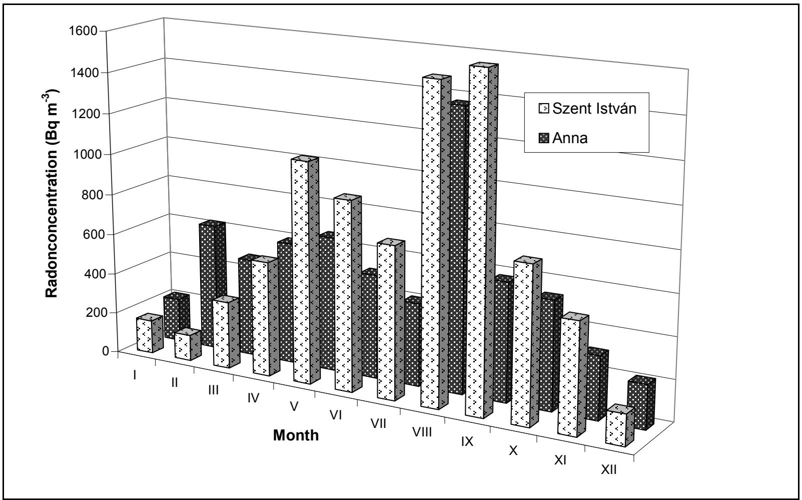

Fig. 3. *Monthly average radon concentration values measured in caves Szent István and Anna*

Concerning the Abaligeti cave, based on previous inspections, radon concentration was measured at two locations. One of the measurement locations was in an almost horizontal corridor, the other one in a big hall lying 18 m higher. Results gained are shown in Figure 4.

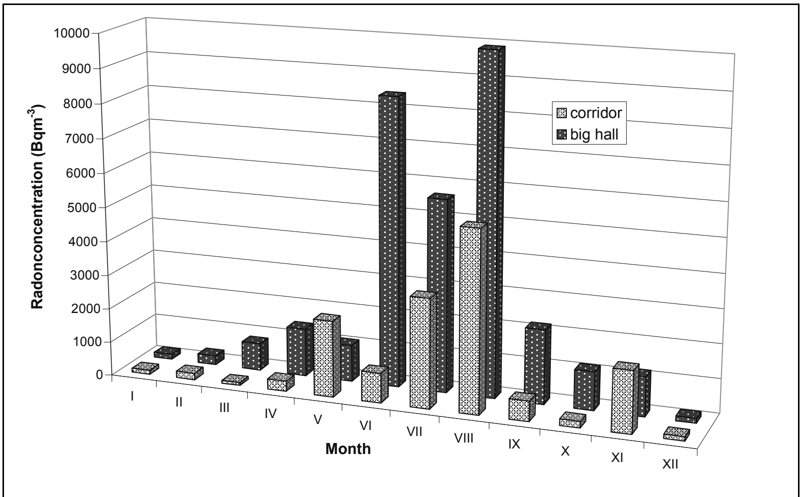

Fig. 4. *Radon concentration measured in the cave at Abaliget*

Figure 4 shows that the monthly average radon concentration significantly changes and during summer months it reached high values, especially in the big hall.

Radon concentration has been measured at two locations in Baradla cave for one year. One of them characterizes the short section belonging to the entrance at Aggtelek, while the other one the section belonging to the entrance at Jósvafő.

At further two locations (located on the routes of longer tours) measurements could only be carried out for a half year due to reconstruction works there. Values measured are shown in Figure 5.

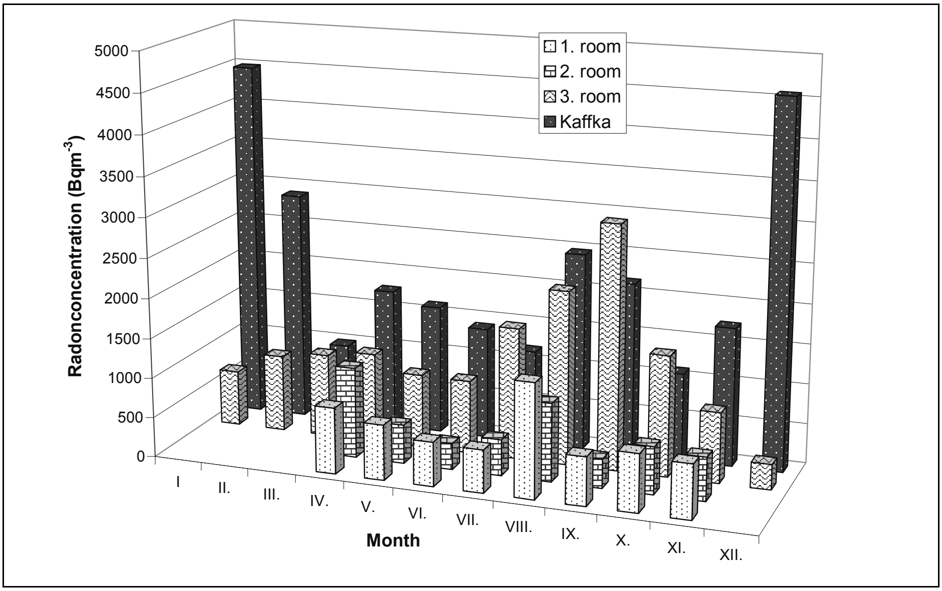

Fig. 5. *Radon concentration measured in Baradla cave*

It can be seen that the values measured in the Kaffka-room typical of the section at Jósvafő are higher (annual average was ~ 2000 Bq·m^{-3}) than the values measured in the sections belonging to the Aggtelek part (where the average radon concentration was ~ 1000 Bq·m^{-3}). Special attention should be given to the changes of the values measured in the Kaffka-room. Here, the highest values were measured in the colder, winter months, which shows airing different of piedmont caves.

The results of the measurements having been carried out through four years in the Tavasbarlang (Lake Cave) in Tapolca are shown in Figure 6. As the figure shows, high differences (even nine times) were found especially in colder winter months of the different years. The average of the four years (min-max values) was 8287 (6411-9726) Bq m^{-3}, that is the average values of the different years differ by maximum 22% from the average of the four years.

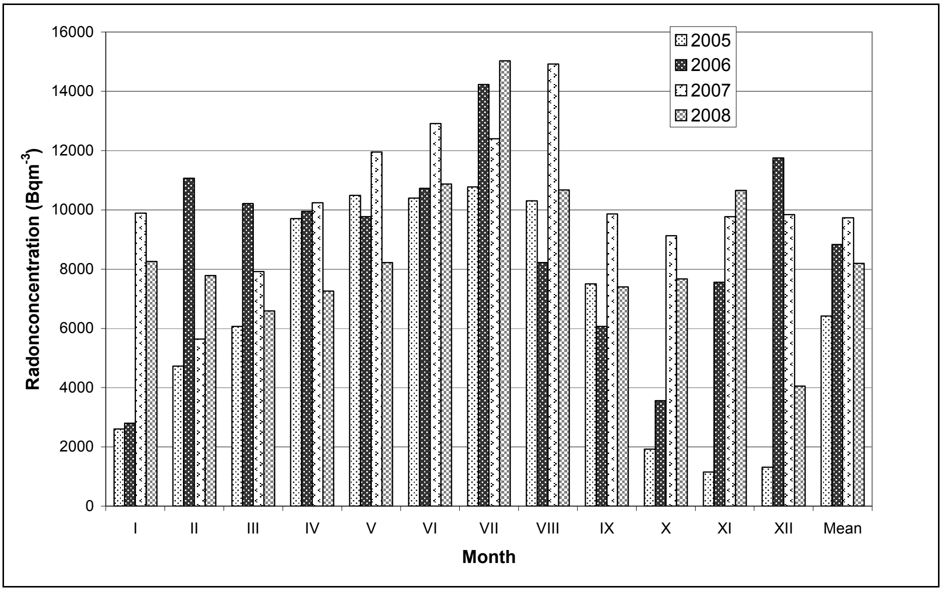

Fig. 6. *Monthly changes of radon concentration in the Tavasbarlang (Lake Cave) in Tapolca between 2005 and 2008*

In table 2 there are the monthly minimum, maximum and yearly average values of radon activity in the studied show caves

Table 2.

The monthly minimum, maximum and yearly average values of radon activity in the studied show caves

Cave	Radonconcentration (Bq m^{-3}) Min - Max	Average
Pálvölgyi	141-4434	1801
Szemlőhegyi	3697-7520	5484
Szent István	128-1600	708
Anna	214-1369	541
Aggtelek	316-3051	1270
Jósvafő	986-4568	2193
Abaliget corridor	121-5312	1253
Abaliget big hall	143-9896	2689
Tapolca Tavasbarlang*	5884-13107	8287

Consequently, in caves where the expected changes of radon concentrations with the seasons are considerable, 12-months-long measurements are strongly recommended.

The theoretical yearly effective dose of tourist guides (estimated from yearly average radon concentration of cave, and 2000 working hour/year) are in the Figure 7.

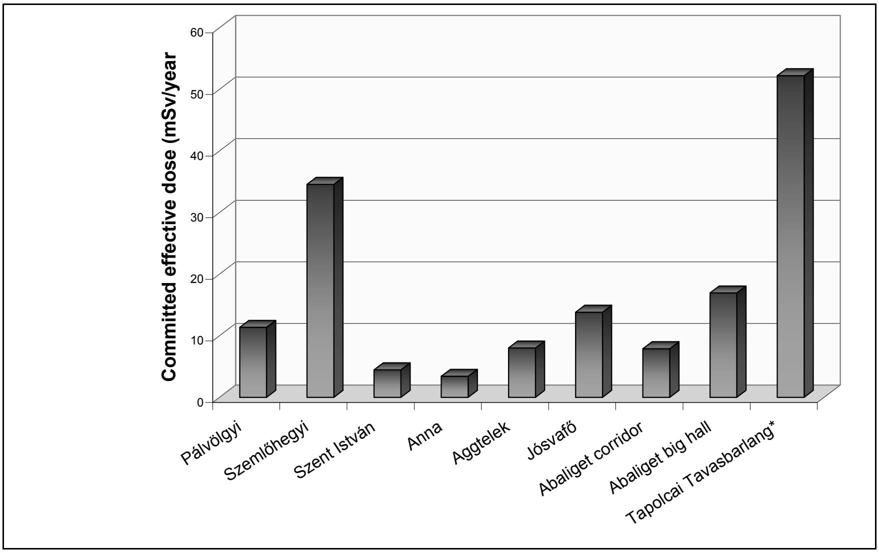

Fig. 7. *Yearly committed effective dose of tourist guides (estimated from yearly average radon concentration of cave and 2000 hour/year)*

The real yearly effective doses of tourist guides in the studied show caves which were calculated based on personal dosimetry are in Figure 8.

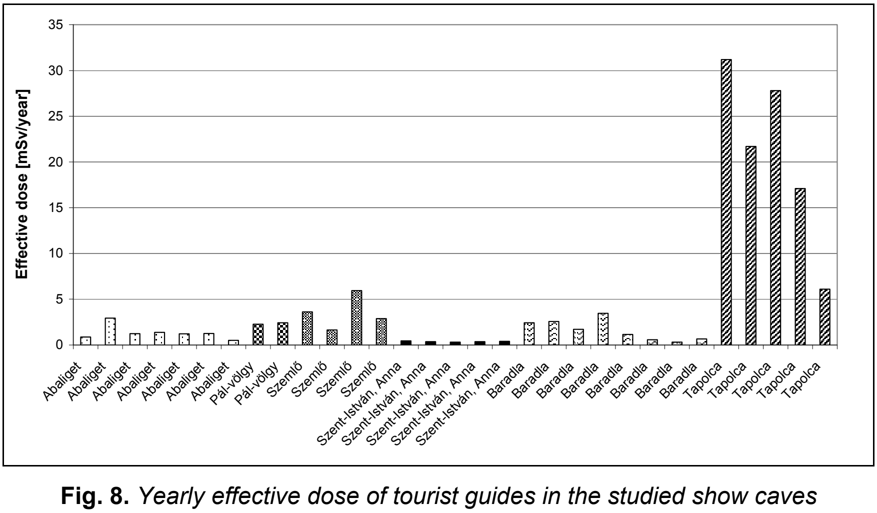

Fig. 8. *Yearly effective dose of tourist guides in the studied show caves (estimated from personal dosimetry)*

In the Tapoca cave the doses were high, so here we measure the dose of workers continuously.

CONCLUSIONS

Based on the measurements it can be stated that the radon concentration in the nine show caves in Hungary visitable for the public almost throughout the whole year show seasonal changes. It can be stated that the one-three months long measurement period in case of caves recommended in certain literature, usually cannot be used when defining the radon concentration level of workplaces. Based on this, it can be declared that reliable results can only be gained in case of 12 months-long measurement periods.

Despite the fact that each of the caves are of karstic origin, the annual radon concentration average levels greatly differ (541 – 8287 $Bq{\cdot}m^{-3}$).

The committed effective dose of workers calculated from the yearly average radon concentration of cave, supposing 2000 hour/year working time and 0.4 equilibrium factor, is 3.4 – 52.2 mSv/year, the real yearly effective dose of tourist guides in the studied show caves which was calculated based on personal dosimetry is 0.3 – 31.2 mSv/year.

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THE RELATIONSHIP BETWEEN SOLAR ACTIVITY AND THE ANNUAL PRECIPITATION IN THE CLUJ-NAPOCA AREA, ROMANIA

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ABSTRACT. Solar radiation is the driving force for the hydrological cycle. However, there are an insufficient number of measurements of solar radiation for many practical problems. In this paper, we examine the relationship between solar activity and the annual precipitation in the Cluj-Napoca area. The results indicate that annual rainfall is closely related to the variation of number of sunspots and less of variation of global solar radiation, and that solar activity probably plays an important role in influencing the precipitation on land. To estimate the global solar radiation from sunshine hours, it is used the Angstrom-Prescott equation. Also, the proposed research here describes the fact that a solar beam can penetrate the atmosphere more easily when there is no rain and it is attenuated when precipitation intensity is higher.

Keywords. *Sunspot numbers; global solar radiation; precipitation; Angström–Prescott equation; t-test statistics; correlation.*

INTRODUCTION

Many studies of different fields of astronomy, space physics, climate and weather, and hydrology, have shown that there is a correlation between solar activity and disaster climate and weather. Many forms of solar activity, such as flares, solar radiation bursts and solar wind, can cause radiation enhancement and plasma movement. All these affect global climatological changes directly or indirectly (Herman et al., 1978). It has been known for some time that there is a statistical relation between solar activity as expressed, for instance, by the sunspot number, and the precipitation on the land on the Earth's surface. Much scientific effort has been exercised in trying to understand how much influence the Sun exerts on Earth's precipitation. According to Guo et al. (1992), super floods may more easily occur in the years of maximum solar activity because the increase of energy from the Sun will cause an enhancement in the thermo-mechanical function of the Earth's atmosphere. However, in an activity minimum year super floods are also easier to occur because of the spontaneous magnetostriction effect. Another study of Verschuren et al. (2000) presented a decade-scale reconstruction of rainfall and drought series in equatorial east Africa over the past 1100 years. According to their analyses, the "Little Ice Age" (≈AD 1270–1850) was interrupted by three prolonged dry periods, 1390–1420, 1560–1625 and 1760–1840, and that these dry periods were all broadly coeval with phases of high solar radiation, while the intervening periods of increased moisture were coeval with phases of low solar radiation. Also, Starkel (2002), who investigated the change in the frequency of extreme events as an indicator of climatic change in the Holocene, attributed the above-average rainfall during the Little Ice Age to solar influence.

The development of many solar energy devices and for estimates of their performances requires an accurate knowledge of solar radiation distribution at a particular geographical location. Unfortunately, solar radiation measurements are not easily available for many developing countries for not being able to afford the measurement equipment and techniques involved. Global solar radiation is measured only at a limited number of sites in the world, while sunshine duration is measured in many stations. Therefore, it has been the most widely available factor for solar radiation estimations (Şen, 2001). So, where no radiation measurements exist, using global solar radiation estimations calculated from sunshine duration data is recommended. Furthermore, it is known that sunshine duration measurement is easier than global radiation measurement. It is, therefore, likely that the accuracy of sunshine duration measurement is higher than that of global solar radiation (Yorukoglu and Celik, 2005).

Solar radiation is infrequently measured at most engineering sites because it requires sensitive solar radiation sensors which are difficult to maintain (e.g. frequent de-dusting). Many researchers have used different techniques for its estimation, e.g. Iziomon and Mayer (2002) categorized the solar radiation models as cloud based and sunshine based models. Hammer et al. (2003) used the HELIOSTAT method to derive surface solar irradiance from satellite images while Kandirmaz et al. (2004) used the Metoestat Wefax type visible image (C3D) data for the solar radiation mapping of Turkey. Samani et al. (2007) derived a procedure for the estimation of the daily net radiation using canopy temperature, albedo, short wave radiation and air temperature whereas Polo et al. (2006) recommended a new filtering technique for solar radiation ground data by generating models for solar irradiance estimation using geostationary satellite data.

Cluj-Napoca, belonging to Cluj County of Romania, is located in the north-west of Transylvania, in a region surrounded by hills, more exactly in the valley of the Someşul Mic River. The climate of the city is on the whole acceptable: warm summers alternate sometimes with cold winters, and the rainfall is not great. The temperature and precipitation characteristics of Cluj-Napoca city are reported in Table 1. For analyzed period (1987-2008), the annual mean temperature is 9.0°C and the amount of annual precipitation is 526.8 mm/year. The mean monthly temperature is high (20.1°C) in July while January witnesses a low (-2.7°C). In contrast, the average amount of monthly precipitation is high (81.9 mm/year) in August and low in March (22.0 mm/year).

The global solar radiation characteristics of this town are also shown in Table 1. The annual mean value of global solar radiation over Cluj-Napoca for the period 1987 to 2008 is 148.059 W/m^2. Like temperature, it is observed that the amount of global radiation is high during the summer time and low in spring. The biggest value of mean monthly global solar radiation is in June (258.615 W/m2), but also July is very close to this value. Similarly, the lowest value of global radiation is in December (38.705 W/m2) as it is the winter season. The high mean monthly global radiation in June could be attributed to higher long day because during the June solstice, locations in the Northern Hemisphere experience their longest day as compared to that of July.

In this paper, we will mainly check the variation of annual precipitation in the Cluj-Napoca area, and compare it with the solar activity. Also, we will use one of the most widely known methods for estimating solar radiation from sunshine hours namely the Angstrom-Prescott equation.

Table 1.

Monthly and seasonal temperature, precipitation and global solar radiation means (1987-2008).

Month	T_{mean} (°C)	Precipitation (mm)	SD[a] (mm)	CV[a] (%)	Global solar radiation (W/m^2)	SD[b] (W/m^2)	CV[b] (%)
January	-2.7	27.6	30.2	911.8	47.085	5.026	25.3
February	-0.7	26.9	48.0	2306.2	81.613	8.707	75.8
March	4.1	22.0	22.0	484.2	128.105	13.829	191.2
April	9.8	37.6	31.6	995.9	182.866	16.067	258.2
May	14.9	57.8	68.5	4699.0	235.194	18.073	326.6
June	18.1	73.6	71.2	5065.2	258.615	22.733	516.8
July	20.1	80.8	68.9	4747.7	256.996	18.260	333.4
August	19.4	81.9	92.8	8605.5	225.396	19.715	388.7
September	14.4	34.9	20.8	432.2	156.856	17.348	301.0
October	9.3	25.1	23.1	532.1	105.246	11.207	125.6
November	3.1	23.3	26.4	695.3	60.027	18.308	335.2
December	-1.6	35.4	65.5	4291.8	38.705	4.819	23.2
Annual	**9.0**	**526.8**	**252.0**	**63481.8**	**148.059**	**5.754**	**33.1**
Spring	9.6	117.3	83.8	7020.9	182.055	10.452	109.3
Summer	19.2	236.3	146.6	21494.4	247.003	10.676	114.0
Autumn	8.9	83.2	54.2	2937.8	107.376	9.372	87.8
Winter	-1.8	87.7	132.8	17647.5	55.675	3.865	14.9

[a, b] SD and CV are computed for annual mean precipitation and global solar radiation.

DATA AND METHODS

The analysis is based on data collected at Cluj-Napoca, Romania (latitude: 46°47'N; longitude: 23°34'E; altitude: 414m) for a 22-year period (January 1987 – December 2008).

Global solar radiation data were calculated from the monthly sunshine hours and were taken from the Monthly Climatic Data for the World (MCDW). The annual relative sunspot numbers for the same period are taken from Solar Geophysical Data (SGD) of National Oceanic and Atmospheric Administration (NOAA) and National Geophysical Data Center (NGDC) of USA. Annual precipitation data were taken from National Climatic Data Center/Climate Date Online (NCDC/CDO).

For the sunspot numbers, global solar radiation and precipitation dataset, the annual time series were computed using EViews (3.0) software (statistical software). Linear regressions of each of the time series of these three variables (sunspot numbers, radiation and precipitation) at the used station over the period 1987-2008 were calculated in order to detect trends. Also, we used PAST (PAlaeontological STatistics) program to find some correlation between two datasets. We obtained the 95% correlation coefficients and the values for probability (uncorr) which means the columns (the two variables) are *not* correlated.

There are different statistical methods considering trend analysis (Haan, 1977; Bobee and Ashkar, 1991; Salas, 1992). Student's t-test is a common method for trend analysis of climatic parameters (e.g., Chattopadhyay and Hulme, 1997) and this one was used to evaluate the significance of the trend. On other words, the Student's t-test was used to determine whether the slope of the fitted trend model was significantly different from zero. The trend was deemed statistically significant where the significance level reached 95% or greater. A linear trend line was added to the series to simplify the trend. Temporal changes in the annual values were tested with t-test to confirm the significance of the observed trend. The used method in this paper for the dependent t-test is the Least Squares.

To estimate *H* from sunshine records, Angstrom's model required measurements of global radiation on completely clear days (H_{cl}). The modified version of the Angstrom's correlation has been the most convenient and widely used correlation for estimating the global radiation (Prescott, 1940). This modified Angström equation is known as the Angström–Prescott equation (Martinez-Lazono et al., 1984; Gueymard et al., 1995), which is given as

$$\frac{H}{H_0} = \left(a + b\,\frac{n}{N}\right) \tag{1}$$

where H and H_0 are, respectively, the global solar or shortwave radiation (MJ m^{-1} day^{-1}) and the extraterrestrial solar radiation on a horizontal surface (MJ m^{-2} day^{-1}); n and N are, respectively, the real sunshine duration (h) and the day's length (h); n/N is relative sunshine duration; a and b are empirically determined regression constants, where a is the intersection of the line (constant) expressing the fraction of H_0 reaching the Earth on cloud-covered days when n = 0, b is the coefficient of regression, and $a + b$ = a fraction of H_0 reaching the Earth on clear-sky days, when n = N.

Based on many measurements made at various locations on the Earth and published by more than one author, Allen et al. (1998) recommended the values of $a = 0.25$ and $b = 0.50$ in estimating global solar radiation (H), when there is available data on sunshine duration and direct measurements on H are missing. However, these values have a relatively high degree of variation on the Earth and their more precise knowledge in zones of geographic, agricultural, or hydrological interest is the permanent purpose of scientists who could lead to an improvement in global solar radiation evaluation and its derivative indicators.

RESULTS

In this study, we investigated sunspot numbers, global solar radiation and precipitation trends and possible influence of solar activity on the precipitation in the Cluj-Napoca area, Romania. Results are presented as the annual time series and statistical test application in Tables 2-3, respectively.

1. Trends of the variables (sunspot numbers, radiation and precipitation)

Table 2 shows the trends, linear equations, and their significance tested by t-test of the sunspot numbers (SN), annual average global radiation (H) and precipitation (P) at the weather station in Cluj-Napoca for 1987–2008.

Table 2.

Trends of the annual SN, GSR and P at the Cluj-Napoca station (1987-2008). Linear equations and their significance tested by t-test.

	Trend[a]	**Linear equation**	**Calculated *t***[b]
Sunspot numbers (SN)	-	y = 103.481 – 3.5649x	-2.3494*
Global solar radiation (H)	+	y = 144.190 + 0.3684x	2.0444
Precipitation (P)	+	y = 469.591 + 5.4527x	0.6347

[a] - Denotes decreasing trend, + denotes positive trend.
[b] *Significant at 0.05 level.

The time variation of the original sunspot numbers for the period 1987 to 2008 shows a decreasing trend, which is statistically significant at the 0.05 level (Table 2). The graphic of annual sunspot numbers along with their linear trend is presented in Fig. 1.

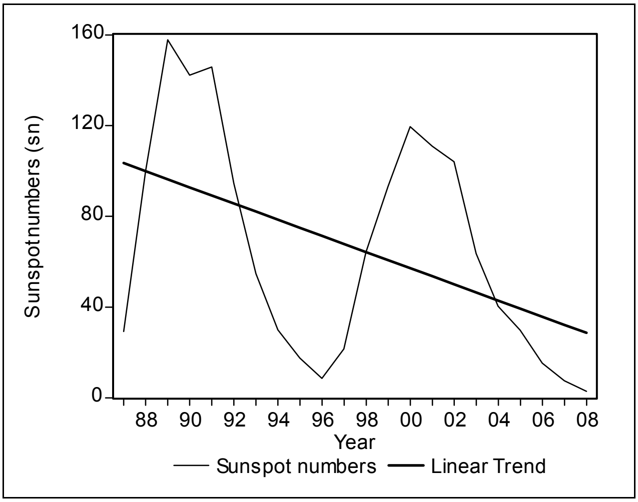

Fig. 1. - *Annual sunspot number trend for the period 1987 to 2008*

The *H* at Cluj-Napoca station from 1987 to 2008 shows an increasing trend, but is not statistically significant (Table 2). The mean annual global solar radiation along with trend line during the period 1987-2008 is presented in Fig. 2.

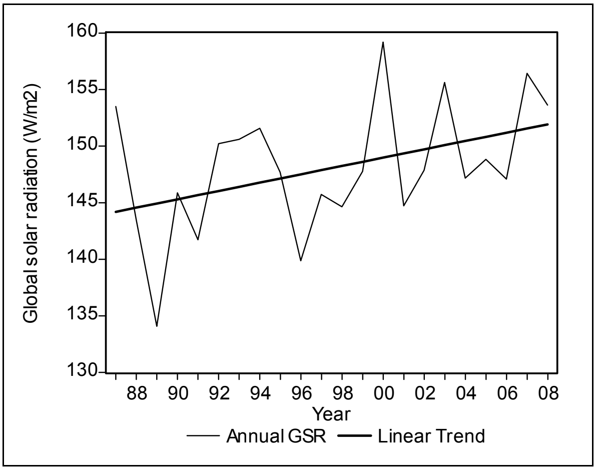

Fig. 2. *Annual global solar radiation trend at Cluj-Napoca (1987-2008)*

The time series of precipitation at Cluj-Napoca station from 1987 to 2008 also show an increasing trend, but not statistically significant. The mean annual precipitation along with trend line during the period 1987-2008 is presented in Fig. 3.

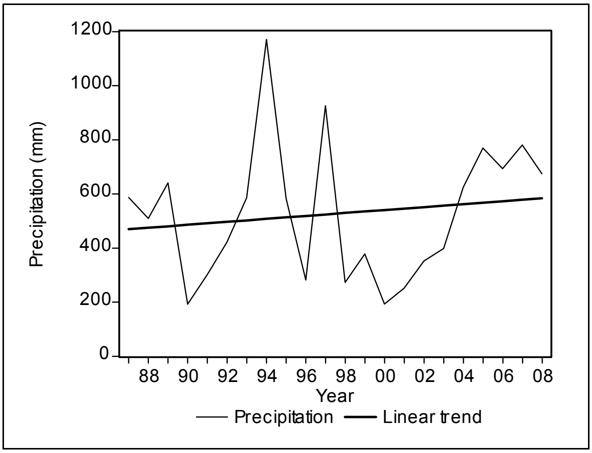

Fig. 3. *Annual mean precipitation trend at Cluj-Napoca (1987-2008).*

2. Correlation Analysis

The correlation between two variables reflects the degree to which the variables are related. The correlation used in this paper is the Pearson Product Moment Correlation (called Pearson's correlation for short). When measured in a population the Pearson Product Moment correlation is designated by the Greek letter rho (ρ). When computed in a sample, it is designated by the letter "r" and is sometimes called "Pearson's r." Pearson's correlation reflects the degree of linear relationship between two variables. It ranges from +1 to -1. The p (uncorrelation) means probability (p) that the columns (the two variables) are *not* correlated.

The results of the correlation for analyzed variables (SN & Prec. and GSR & Prec.) are shown in Table 3. In the first case, the value of Pearson's correlation is -0.58. A correlation of -0.58 means that there is a negative linear relationship between sunspot numbers & precipitation and the probability (p) that the two variables are correlated is very strong. The scatterplot shown in Fig. 4 depicts such a strong negative relationship. It is a negative relationship because high scores on the X-axis (SN) are associated with low scores on the Y-axis (Prec.).

Table 3.

Linear correlation r between SN & Annual Precipitation and GSR & Annual Prec. in the Cluj-Napoca area

	Correlation coefficients	Confidence interval	p (uncorrelation)
SN & Prec.	-0.58*	95%	0.0045
GSR & Prec.	0.14**	95%	0.532

* Strong negative relationship (high correlation); ** Insignificant positive relationship (low correlation).

In the second case, the value of Pearson's correlation is 0.14. Such a correlation of +0.14 means that there is a positive linear relationship between global solar radiation & precipitation, but probability (p) that the two variables aren't correlated is very true.

The scatterplot shown in Fig. 5 depicts such a relationship. It is a positive relationship because high scores on the X-axis (GSR) are associated with high scores on the Y-axis (Prec.).

The scatterplots between Prec. & SN (see Fig.4) and Prec & GSR (see Fig.5) together with the regression line (solid) and the 95% confidence lines (dotted) show a clear difference in the slope of the regression line; this is negative for prec. & sunspot numbers and positive for prec. & GSR. However, there are a more number of years outside of the 95% confidence lines, especially in the case of prec. & GSR. From Table 3 we find that the observed correlation coefficient between original SN and precipitation series is over the 99% significance level.

This suggests that there is probably a direct solar activity influence on the annual precipitation in the Cluj-Napoca area and that the periods of precipitation arise from solar activity. At least, solar activity possibly accounts for a portion of the influence.

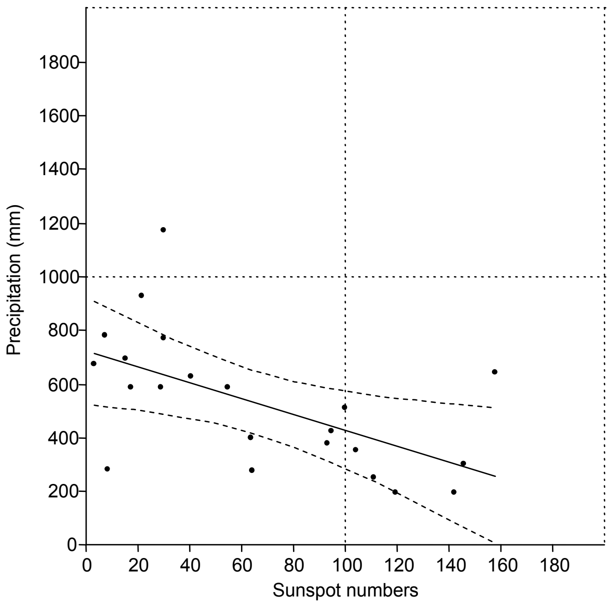

Fig. 4. *Scatterplots between precipitation and sunspot numbers with the regression line (solid) and the 95% confidence lines (dotted).*

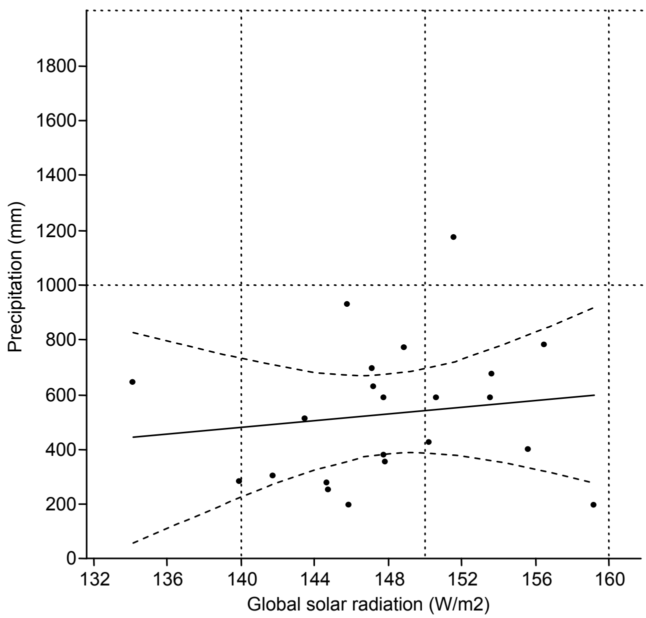

Fig. 5. *Scatterplots between precipitation and global solar radiation with the regression line (solid) and the 95% confidence lines (dotted).*

Variations of solar activity reaching the Earth are thought to influence precipitation, but it is still hard to understand how the periodic variation of solar activity influences the variation of the precipitation on land, and the extent of this influence on timescales of millennia to decades still remains unclear. It is significant that further investigations and detailed studies on the physical mechanism of solar activity can probably improve the medium-term and long-term prediction of annual precipitation in the area. Solar activity prediction is being paid more attentions and the prediction methods are being improved (Wang et al. 2002).

It was observed that the higher the precipitation intensity, the higher is the attenuation of the solar beam and consequently lower the fraction of (H_0) reaching the ground surface. It has been demonstrated that precipitation intensities clearly influence the solar beam attenuation through the atmosphere. It was found that for minimum precipitation intensities of 0 mm $hour^{-1}$ (no rain) and <0.2 mm^{-1} resulted in the mean percentage of extraterrestrial radiation reaching ground to be of the order of 44% and 33% respectively, which was reduced to 0.11 for precipitation intensity greater than 2.0 mm^{-1} thus clearly showing that the higher the precipitation intensity, the lesser is the percentage of extraterrestrial radiation received on the ground (Shamim et al., 2008).

CONCLUSIONS

The present analysis suggests that the relationship between the precipitation and sunspot numbers and global solar radiation is dependent on solar activity, being negative, but significant for SN and not significant or even positive for GSR.

Our result strongly supports the view that the variability of solar activity can effect the annual precipitation in the Cluj-Napoca area, although the physical mechanism of such influence remains still unclear. Also, precipitation intensities influence the solar beam attenuation through the atmosphere. Further studies in the future may help us to understand the mechanism that links solar activity with annual precipitation.

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NOISE POLLUTION – A PROBLEM OF THE BIG CITIES. CASE STUDY

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ABSTRACT. The problem of urban traffic noise pollution is universal and in the past few decades it has grown to the point that it has become a major concern. Sound is an important part of everyday life, but when sound becomes noise, we like to know that there are regulations protecting us from its detrimental effects. Noise regulation includes statutes relating to sound transmission established by national, provincial and municipal levels of government. Sounds are created when a vibrating source causes waves of acoustic energy to travel through a medium. The sound pressure waves move out from the vibrating source and become weaker the further they travel. Noise pollution can be defined as unwanted noise that disrupts, distracts, or detracts from regular functioning. Road traffic is probably one of the most serious type of noise pollution. It has become a serious problem now because of inadequate urban planning in the past. The main building houses were built on roads without buffer zones or adequate soundproofing. The problem has been compounded by increases in traffic volumes more rapidly than the expectations of the early urban planners. This paper presents a study of traffic noise pollution in Cluj-Napoca town. Equivalent noise levels were measured in four different districts. Measured values were compared with Romanian legislation allowed limits. The objective of the present study is to give answers and solutions to the influence of the noise pollutions factors on the environment

***Key words**: environmental noise, noise pollution, equivalent noise levels, admissible values*

OBJECTIVES

Noise contributes greatly to diminishing citizens' quality of life. Exposure of people to noise levels above 65 dB (A) can cause severe health problems. In urban areas road traffic is the main source of noise, accounting for about 80 % of total noise pollution.

In June 2002, DIRECTIVE 2002/49/EC of the European Parliament and of the Council relating to the assessment and management of environmental noise entered into force. The environmental noise directive (END) aims to establish a common approach, and thereby prevent or reduce the harmful effects of environmental noise. This aim is to be achieved using a bundle of measures:

- introducing harmonized noise indicators;
- harmonizing the calculation methods for determining noise levels;
- harmonizing the procedures used to create noise maps and action plans for noise reduction;
- providing information to the public on the environmental impact of noise (Guidelines for road traffic noise abatement, 2003).

During the last decade, in the urban area of Cluj-Napoca town, the noise pollution problem increased substantially.

High noise levels are determined by a number of factors, including:

- increasing population and public works, particularly it leads to increasing urbanization and urban consolidation;
- increasing volumes of road traffic, flight traffic, railway traffic.

These are considered main environmental sources of noise pollution and they can represent a series of disturbance factors with important effects on human health.

An analysis of the noise pollution recorded values in main crossing roads and avenues with intense traffic in Cluj-Napoca is the main objective of this paper.

1. METHODS

The method used for determination of the urban noise level according to STAS 6161/3-82, is the method of equivalent noise level determination, L_{eq}, which represents the actual acoustical energy present in a fluctuating sound over the observation period.

The L_{eq} is the hypothetical equivalent steady sound level containing all of the acoustical energy in an actual time-varying sound sample over a given time period (Cavanaugh J. W., Wilkes J., 1999).

In STAS 10009-1988 are established the admissible limits of the equivalent noise level in urban areas. The admissible limits for exterior noise level on streets are given in Table 1.

1.1. Measurement points

The measuring points for the noise traffic level were settled in four districts:

1. Grigorescu District – Crossing point Fantanele St. with Miraslau St.
2. Manastur District – Calea Floresti
3. Marasti District – Traffic circle
4. Mihai Viteazu Plaza – Baritiu St.

For all four measurement points, intense traffic period was selected (hour schedule 13:00 – 18:00).

1.2. Equipment

Equivalent noise level was determined with a son meter (portable analyzer) Brüel & Kjaer type PULSE 3560B and with a type 4189 microphone unit. The microphone was located on the sidewalk at the edge of the roadway traffic lane. The height of the microphone was 1.30 m from the pavement level. The instrumentation and calibration of equipment were performed in accordance with the manufacturer's recommended procedure.

L_{eq} measured values of traffic noise represent the average of all measurements in each district. Measured values were confronted with local legislation allowed limits, and the measurement points were classified as “acoustically polluted or unpolluted”.

2. MAIN RESULTS

The equivalent noise levels obtained in all four points of measurement are presented in figure 1. The maximum measured values, 76.3 dB, were recorded in Mihai Viteazu Plaza – Baritiu St., due to the intense and heavy road traffic within the area and to the vibration from trams. At this noise levels many of the activities are adversely affected by noise from traffic.

In all measurement points the values of the noise pollution were over the maximum allowed limit.

The sound pressure measured values are presented in figure 2. At medium and high frequencies the values were over the admissible noise curve limits.

3. CONCLUSIONS

Measuring noise level is a necessary step towards the reduction of noise in the city. The source of most outdoor noise is transportation systems, including motor vehicle noise, aircraft noise and rail noise.

Findings of this research had shown that the traffic noise levels in Cluj-Napoca urban area is high enough to adversely affect the activities and productivities of its residents.

Poor urban planning may give rise to noise pollution to a critical dimension. On many existing roads, traffic has increased well beyond expectations.

All major cities in developing nations are over populated; a continuous migration from rural to urban areas is in the process, there are a lack of proper city planning and practically no control strategies for reducing the level of noise from various sources (Al-Mutairi N. et al., 2009).

A permanent educational campaign on noise, its causes, effects and solutions, involving school and mass media should be developed.

Noise level produced by different sources can be reduced by following these measures:

- Space in urban environments is limited, so a combination of distance, structures and vegetation is useful for reducing noise level (maximizing the distance from the sound source is always the first step - most loud sounds will dissipate over extended distances, including green spaces within inhabited areas).
- Traffic management measures (speed reduction and traffic calming measures can provide reduction in traffic noise, reducing percentage of heavy goods vehicles, introducing of low-noise buses and trams).
- Road surface design measures (productions of low-noise road surfaces like porous road surfaces which offer properties of reducing both the generation and propagation of tyre noise).
- Development of special insulation for buildings against environmental noise (implementation of wall materials having required sound transmission loss values and sound-proof windows).

- Performing noise maps measures (according to HG 321/14.04.2005, in all urban agglomerations with over 250,000 inhabitants and roads with over 6,000,000 vehicles/year, beginning with 2006 such noise maps must exist).
- Noise reduction measures are also needed in the rail and air traffic sectors.

REFERENCES

Al-Mutairi N., Al-Rukaibi F., Koushki P., 2009, Measurements and Model Calibration of Urban Traffic Noise Pollution, p. 613

Cavanaugh J. W., Wilkes J., 1999, Architectural acoustic. Principles and practice, p. 13

Guidelines for road traffic noise abatement, 2003, p. 9

STAS 10009–1988 – Acustica urbană p. 213

STAS 6161/3 – 1982 – Determinarea nivelului de zgomot în localitătile urbane

STAS 10144/1– 80 – Caracteristici ale arterelor de circulație din localitățile urbane şi rurale – Prescripții de proiectare

ARTWORK

Table 1

Admissible limits of the noise level

No. crt.	Street type (cf. STAS 10144/1 - 80)	Level of equivalent noise L_{ech} * dB(A)	The value of noise curve, C_z, dB **	Level of rush Noise L_{10} dB (A)
1	Street of IV technical category, of local serving	60	55	70
2	Street of III technical category, of collection	65	60	75
3	Street of II technical category, of bind	70	65	80
4	Street of I technical category, magisterial	75…85***	70…80***	85…95***

* The equivalent noise level is calculated (different for the day and night periods) according to STAS 6161/1-79.

** The evaluation through noise curves C_z is used only in case of some noises with pronounced stationary character.

*** At magisterial projection to adopt the necessary measures for equivalent levels obtained (real measured) most near to minimum values from the table, without to past the maximum values (STAS 10009, 1988).

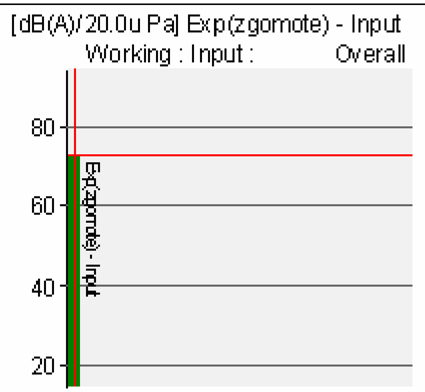
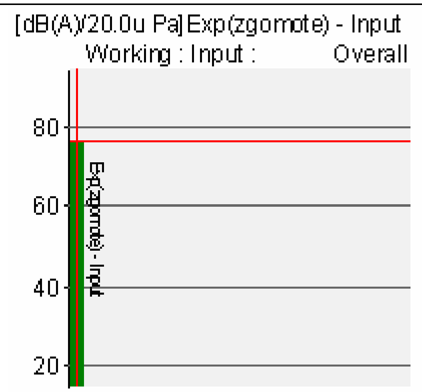
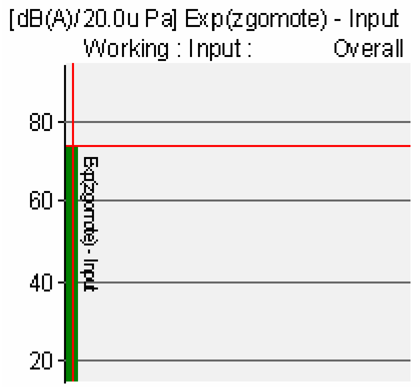
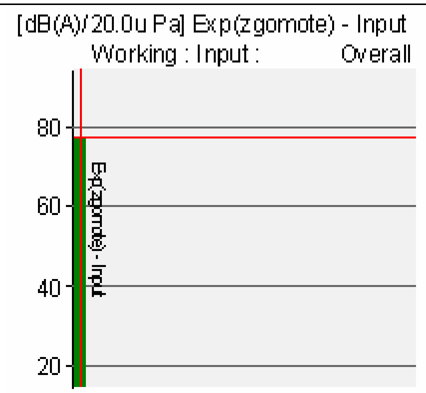
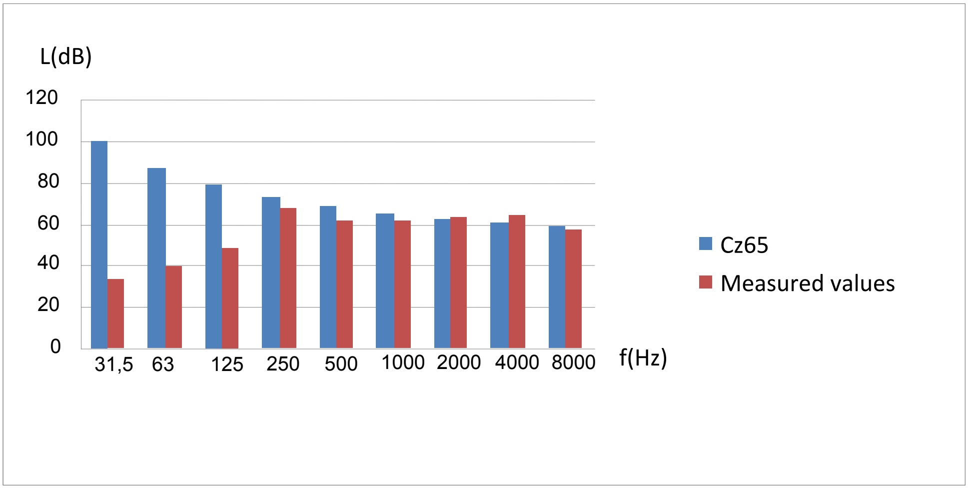
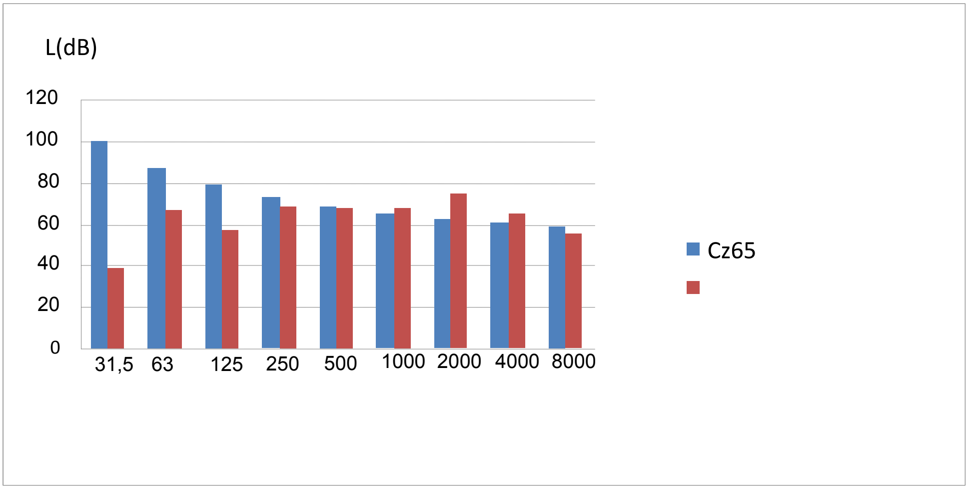
GRIGORESCU DISTRICT	MĂNĂŞTUR DISTRICT
	
L_{eq} = 72.9 dB(A)	L_{eq} = 75.4 dB(A)
MĂRĂŞTI DISTRICT	MIHAI VITEAZU PLAZA
	
L_{eq} = 74.1 dB(A)	L_{eq} = 76.3dB(A)

Fig. 1. *Equivalent noise levels*

GRIGORESCU DISTRICT

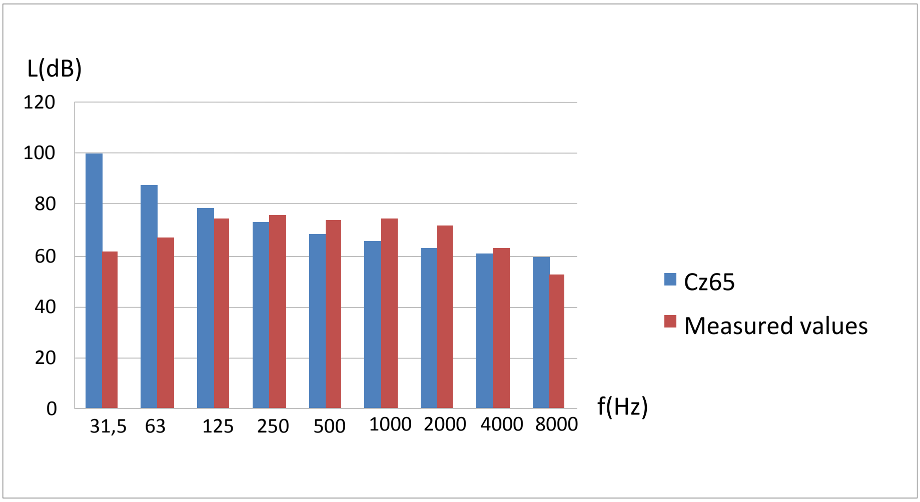


MĂRĂŞTI DISTRICT



Sound pressure levels

MĂNĂŞTUR DISTRICT



MIHAI VITEAZU PLAZA

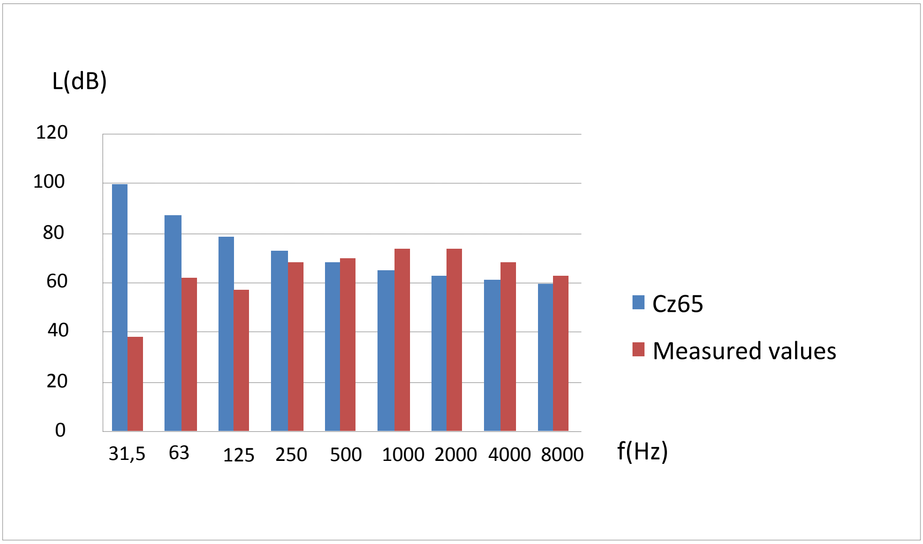


Fig. 2. *Sound pressure levels*

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King C., Park, A., 2007, *Advanced environmental monitoring* (**2nd** ed.), John Wiley & Sons, Inc. New York, 682 p., New York.

Meng X. G., Korfiatis G. P., Christodoulatos C., Bang S., 2005, Treatment of arsenic in Bangladesh well water using a household coprecipitation and filtration system. *Water Res.*, **35**, pp. 2805-2810.

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