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STUDIA UNIVERSITATIS BABEŞ-BOLYAI, AMBIENTUM, LIII, 1-2, 2008

Professor Dr. Iustinian Petrescu

In memoriam

It is not difficult to remember Professor Petrescu how he was about 25-30 years ago. He was a mature and dynamic dark-haired man, focused on using each moment for improving his teaching activity, for searching for a scientific paper in the library, for adding some more lines to a book or for making further steps in his research. In the classroom, he used to animate his students through his passionate lectures on the geological stages achieved by our planet Earth, the theoretical concepts being complemented with his own interpretations or genuine descriptions and observations resulted from his own experience. During the short breaks in-between the classes, his clear and convincing voice could be heard along the halls of the faculty, engaged in friendly discussions with his colleagues. It can be assumed that the greatest satisfaction resulted from his scientific research work – he used to spend countless hours looking into the microscope at pollen grains carefully separated from drill core samples or from bulk samples in the field.

– Look, this is a walnut looking much better than in the books! A pine, a fir, an exotic oak... this is how with a restless enthusiasm he reconstructed, based on the minute pollen grains, the forests that millions or tens of millions of years ago were moving with the winds on the present day areas of Oltenia, Sălaj, Jiului Valley etc. His overwhelming enthusiasm has generated a massive interest in this scientific topic in his students, each of them hoping to feel the joy of understanding the mysteries of the lost geological worlds. Besides the generous and unconditioned initiative that has characterised Professor Petrescu, this was the basis for the foundation of a geological school. More than that, this construction was oriented not only to his own scientific field of interest, but towards any of the study directions that were in need at the department in Cluj and that could contribute to its consolidation. His activity has overlapped with very tensioned historical moments, when the existence of a school of geology in Cluj was questioned. Due to the abnegation of Professor Petrescu, supported by a few other colleagues, this school has survived and it is still active, being a continuous source of high-quality science and experts in the field. The Geological Research Group that was founded by Professor Petrescu in the '80 has represented an ingenious and efficient solution for the foreseeable human resources crisis in the Geology Department. Some of the members of this research group currently form the core of the present-day teaching staff.

Professor Petrescu had genuine wisdom and diplomatic abilities that helped him solve current issues and elegantly anticipate potential - smaller or bigger – conflicts that could have represent a threat for the community's cohesion. These attributes were substantially used during his office as a Dean, first of the Faculty of Biology, Geography and Geology, and later of the Faculty of Environmental Science.

The scientific activity of Professor Petrescu represents an inspiration for the younger researchers, in spite of the more evolved analytical facilities that were not available 30 or 40 years ago. His more than 150 research papers have been published in well-known national and international specialized journals. He published more than 20 books, some of them being new contributions for the Romanian science. It is worthy to mention the books *Plante fosile (Fossil plants), Palinologie (Palynology), Geologia zăcămintelor de cărbuni (Geology of the coal ore deposits), Macro şi microflora oligocenă de la Corneşti-Aghireş (Oligocene macro and microfauna from Corneşti-Aghireş)* – the latter being written in collaboration with academician Răzvan Givulescu, another famous researcher of the fossil flora who also passed away not long ago. In the same time, Professor Petrescu was interested in promoting geology to a wider audience; he published several volumes addressed to the general public, such as: *Algeria – drumuri şi popasuri (Algeria – roads and sojourns), Coloşi printre vieţuitoarele străvechi (Giants among the extinct animals), Pământul – o biografie geologică (Planet Earth – a geological biography)* .

Unfortunately, Professor Petrescu departed us much too early, at an age when he could still work on his numerous unfinished projects. He was struck by a merciless illness which he hardly tried to confront for almost two years. Being always an optimist, he did not stop planning the future, as if each day would have been endless, as if our lives would be infinite.

Let us keep his memory alive, let us respectfully continue his work and thus take forward the ideals he believed in during his whole life.

CĂLIN BACIU

A teacher, a researcher of excellence, a distinctive personality

We have recently lost, prematurely, one of the great personalities of the Cluj Geology School. It is still hard to believe that Professor Petrescu is not among us anymore, when we think that he was an example of restless action and initiative.

From the beginning of his teaching career, Professor Petrescu was proving a great potential. The elder professors were referring to him with admiration and, sometimes, with a touch of envy. And this was not without good reason: he got his PhD title before many of his elder colleagues, in a field that was not traditional in Cluj - paleobotany, a field of research that he subsequently developed *via* remarkable studies of paleodendrology and palynology. The outstanding results he achieved in these topics led to his wide recognition on both national and international scales. However, he did not restrict his activities to high-quality sciences; as a genuine teacher - through his followers, he has created a school especially focusing on palynology. He was always active and interested in new perspectives, preoccupied by the fate of the institution which he had served. It is hard to imagine the Cluj geology after the '80 in the absence of Professor Petrescu… In those times, when the trend was to cancel the institutional geology teaching in Cluj and to preserve it only in Bucharest, Professor Petrescu had focused his energy for saving the destiny of the school of geology in Cluj; the institutional, but especially his personal efforts finally led to a successful result. In the same period, when some members of the staff figured that they were unique in the landscape of geological teaching in Cluj and when opening new positions in the department seemed to be phantasmagoric, Professor Petrescu, with his unique vision on the future had founded the Geological Research Group that gathered the most remarkable geology graduates of those years, later transformed into the core of the new teaching staff starting with 1990.

Once again, at the beginning of the new millennium, Professor Petrescu was the one who could sense the pulse of the future. He had the idea, he acted, he fought for, and finally he managed to found the Faculty for Environmental Science, which he headed in its first four years of existence, giving the impulse for its future evolution. In a moment when we were expecting new initiatives, new achievements and new remarkable scientific results, his trajectory has been ceased by a force that could not be defeated by either wish, perseverance, or will. We have all hoped, until the last moment, that he would be the winner, and that we could benefit of his active presence for many years to come. Unfortunately, this did not happen... His disappearance is an infinite loss for the geology of Cluj and of Romania, for society in general – of which active member he always was, and for his family that represented to Professor Petrescu a priority in the same measure as his profession. We will preserve him in our memory as the exquisite professor and researcher, the active and innovative person, the special man that many times has offered a helpful hand to so many others. We will always regret that his fate was unfair and took him too early from among us, and that we could not witness and benefit of his resourceful creativity for many coming years.

IOAN I. BUCUR

STUDIA UNIVERSITATIS BABEŞ-BOLYAI, AMBIENTUM, LIII, 1-2, 2008

MATHEMATICAL MODEL FOR ESTIMATING WIND ENERGY POTENTIAL

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ABSTRACT. Mathematical Model for Estimating Wind Energy Potential. The wind speed and the air density have temporal and spatial stochastic variability and the wind energy potential is directly proportional to the air density and the third power of the wind speed averaged a suitable time period. It is the main purpose of this paper to derive the most general wind energy potential formulation by considering simultaneously the temporal variability both in the wind speed and air density. The correction factor is derived explicitly in terms of the cross – correlation and the coefficients of variation. The application of the methodology is performed for wind speed measurements at Sfantu Gheorghe (Danube Delta) meteorological station.

Key words: *correlation coefficient, correction factor, stochastic variables, wind energy potential*

INTRODUCTION

For determining the wind potential value, several meteorological parameters should be analyzed: wind speed, air density, air temperature, atmospheric pressure etc. Knowing that wind speed and air density are stochastic variables it means that wind energetic potential is also a stochastic measure.

TOOLS AND METHODS

Kinetic energy of air masses is presented mainly by the density of the energy flux and it reflects the energy quantity that crosses normal surface unit on the wind direction in a time unit. So, energy flux density that is a unit force from dimensional point of view, for the normal surface to the wind direction, can be presented with the relation (Bandoc, 2005):

$$P_U = \frac{\rho U^3}{2}, \qquad (1)$$

where ρ is the air density [kg/m³], and U is the wind speed [m/s].

Density of the energy flux of the wind presents large variations in time and in space. For a specific surface, time mean written with < P_U >$_{t\ of}$ the energy flux density in a time interval *T*, large enough defines the wind potential of that specific surface:

$$\varepsilon = \langle P_u \rangle_t = \lim_{T \to \infty} \frac{1}{T} \int_0^T P_u(t) dt \tag{2}$$

Sometimes *wind potential* is also used for the annual mean energy that crosses the normal surface unit on the wind direction:

$$E = \int_0^T P_u(t) dt \, , \tag{3}$$

With *T* = 1 year and 1 year = 8760 hours, expressed as [kWh/m^2]. A proportion relation exists between these two defined measures:

$$E = T \cdot \varepsilon \, . \tag{4}$$

Based on the analyses of the data base from different stations placed at different altitudes, a super estimation of the wind energy with approximate 30% appears, due to air density (Reed, 1979). Thus, we propose introduction of a correction factor in wind energy estimation. Correction factor for air density depends on the altitude where the analysed surface is placed and on the annual variation of air temperature (Celik, 2003)

$$P_U(E) = \frac{1}{2} E\left(\rho U^3\right), \tag{5}$$

simple correlation coefficient is defined as a ratio between co variation between ρ if U^3 and multiply of the standard deviation of ρ and U^3:

$$r = \frac{\text{cov}\left(\rho, U^3\right)}{S_\rho S_{U^3}} \, . \tag{6}$$

where S_ρ is standard deviation of air density and $S_U{}^3$ is standard deviation for cubic value of wind speed.

It is well-known that covariance for two random variables is a measure of the simultaneous variation of these variables (Dodge, 1993) and in the present case:

$$\text{cov}\left(\rho, U^3\right) = E\left[\left(\rho - E[\rho]\right)\left(U^3 - E\left[U^3\right]\right)\right] \tag{7}$$

where $E[\rho]$ is mathematic expectation of variable ρ defined as average of random variable values ρ moderated with probabilities of appearance of these values:

$$E[\rho]=\sum_{i=1}^{n}\rho_i\, p(\rho_i) \tag{8}$$

where $E[U^3]$ is mathematic expectation of variable U^3 defined as average of random variable values U^3 moderated with probabilities of appearance of these values:

$$E\left[U^3\right]=\sum_{i=1}^{n}U^3 p\left(U^3\right) \tag{9}$$

By replacing the covariance cov(ρ, U^3) from relation (6) and (7) it results:

$$E\left(\rho U^3\right)=E(\rho)E\left(U^3\right)+rS_{\rho}S_{U^3} \tag{10}$$

and it is introduced in relation (5) the following relation obtaining:

$$P_U(E)=\frac{1}{2}\left[E(\rho)E\left(U^3\right)+rS_{\rho}S_{U^3}\right] \tag{11}$$

This formula is used for simple approximations of the wind potential.

Correlation coefficient is a measure of the linear intensity of two random variables and it takes values from domain [-1…1]. In case the coefficient value is 0, than equation (11) becomes:

$$P_U(E)=\frac{1}{2}E(\rho)E\left(U^3\right) \tag{12}$$

and this situation is valuable in case of missing and linear relation between the two variables.

In case density of the atmospheric air is constant, it results:

$$P_U(E)=\frac{1}{2}\rho E\left(U^3\right) \tag{13}$$

Practically the correlation coefficient variance between the cubic wind speed and the air density is situated between value -1 (perfect situation of reverse proportionality) and value +1 (perfect linear relation).

In case the wind speed is correlated with air density, a negative value for correlation coefficient is obtained and, in this case, relation (11) becomes:

$$P_U(E) = \frac{1}{2}E(\rho)E(U^3)\left[1 - r\frac{S_\rho S_{U^3}}{E(\rho)E(U^3)}\right] \quad (14)$$

where the term in front of the square bracket is named correction factor and it is noted with α, is un-dimensional. Equation (14) becomes:

$$\alpha = 1 - r\frac{S_\rho S_{U^3}}{E(\rho)E(U^3)} \quad (15)$$

Equation (15) can also be written considering variation coefficient C, defined as a ratio between standard deviation and arithmetic average of the value row. In this case the variation coefficient is calculated for the air density C_ρ and for the cubic wind speed C_U^3. Equation (15) can be also written as:

$$\alpha = 1 - C_\rho C_{U^3} \quad (16)$$

In case lower values of variation coefficient are obtained, correction factor is practically unimportant and in case variation coefficient values are high, the correction factor has a significant high level.

RESULTS

In the present article, the studied station is Sfantu Gheorghe (Danube Delta), where daily measures for an entire year have been made for the following variables: air temperature T[^{0}C](fig. 1), wind speed U[m/s] (fig. 2), atmospheric pressure P[mb] (fig. 3), and basing on these values daily variations of air density ρ[kg/m^3] (fig. 4) have been determined.

The mean wind speed value is 4,2615 m/s for the analysed period.

According to the relations presented above, statistic indicators for Sfantu Gheorghe Station have been calculated and are necessary for determining the correlation coefficient and correction factor used for evaluating the wind potential.

Using statistical calculations, a value of 0,0394 of air density has been obtained as well as variation coefficient for wind speed with the value of 0,51051. The value of correlation coefficient between air density and wind speed is – 0,204.

With these values, finally the correction factor has been determined for wind energetic potential for Sfantu Gheorghe Station and its values is 0,99623.

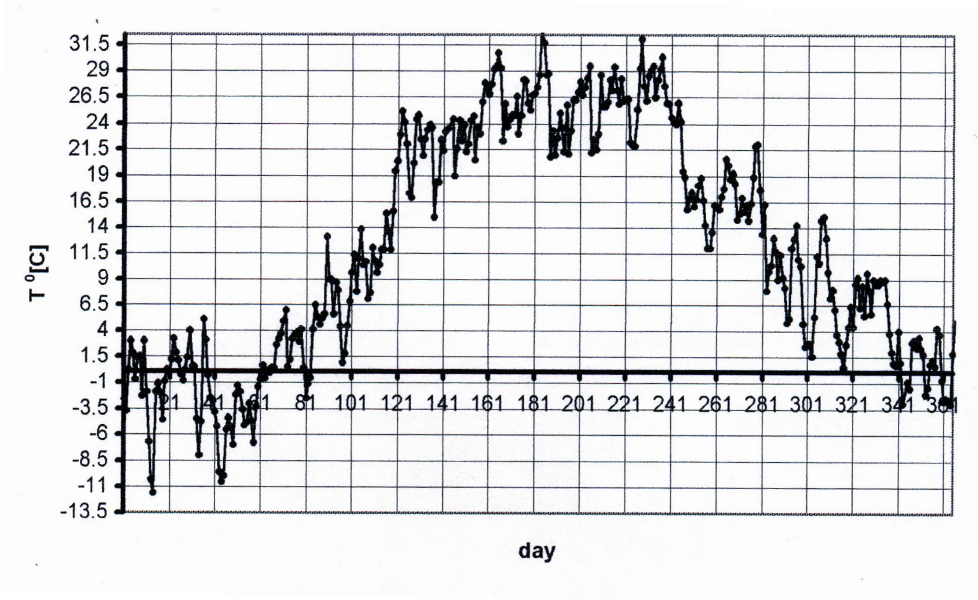

Fig. 1. *Daily air temperature variation T[°C] at Sfantu Gheorghe Station (Danube Delta)*

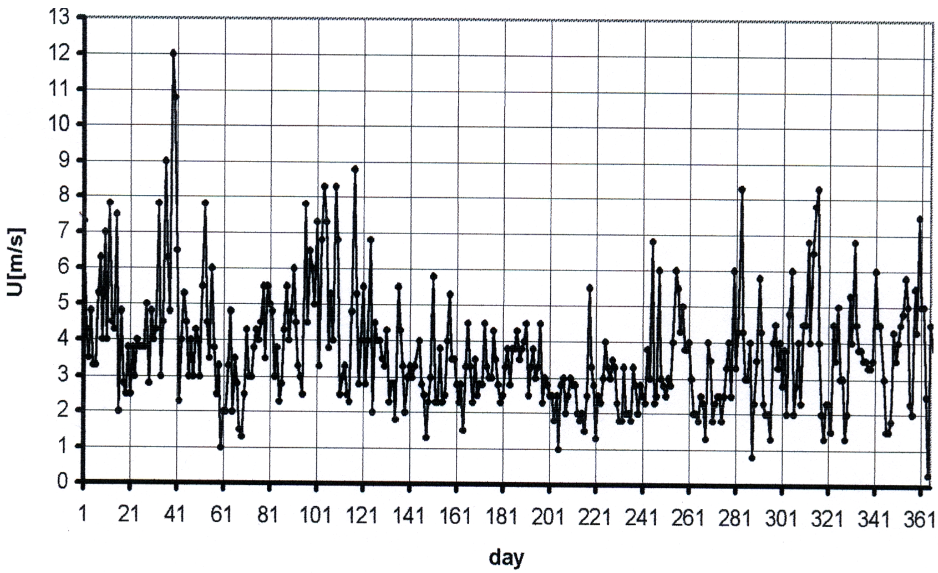

Fig. 2. *Daily wind speed variation U[m/s] at Sfantu Gheorghe Station (Danube Delta)*

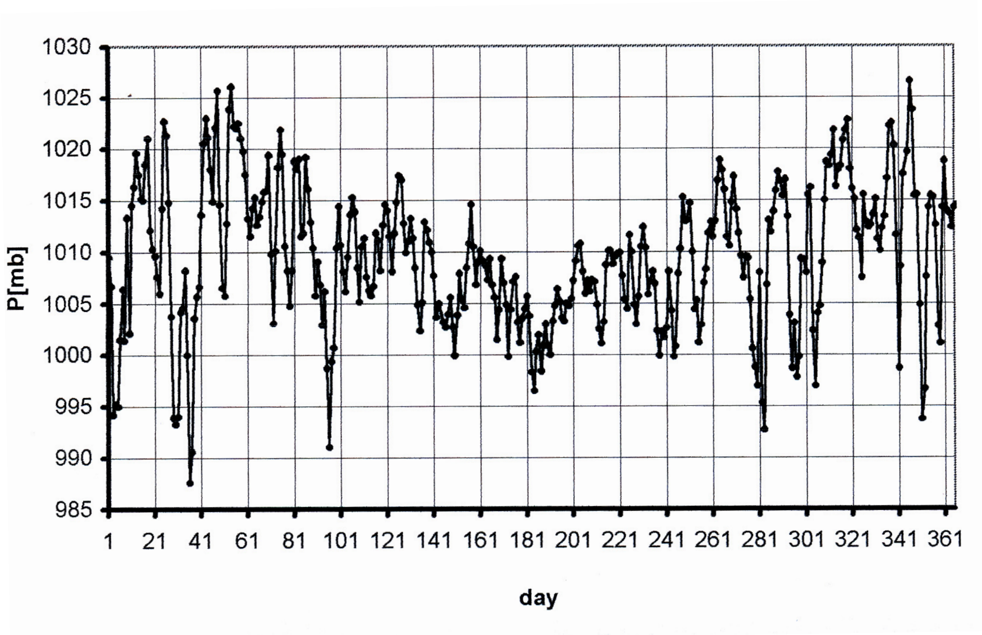

Fig. 3. *Daily atmospheric pressure variation P[mb] at Sfantu Gheorghe Station (Danube Delta)*

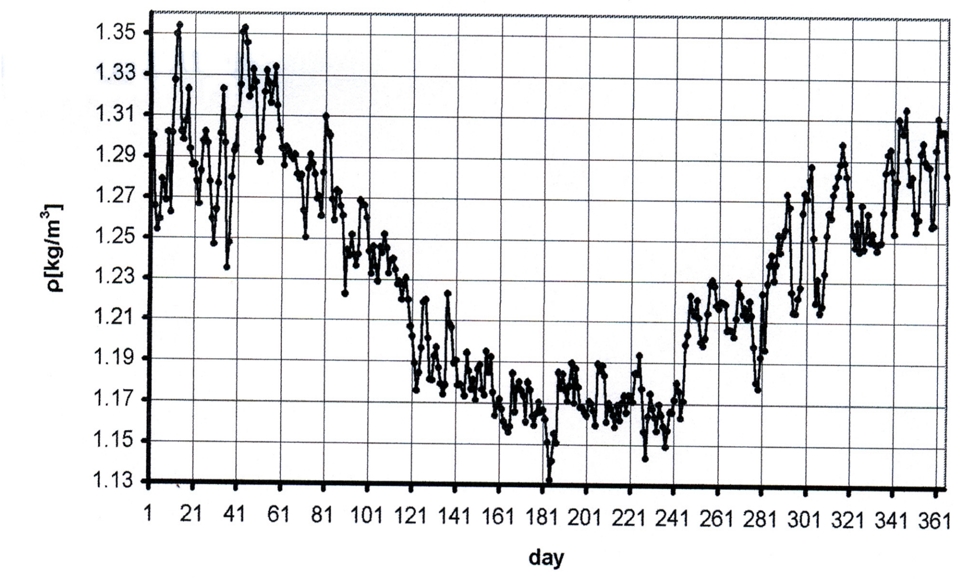

Fig. 4. *Daily air density variation $\rho[kg/m^3]$ at Sfantu Gheorghe Station (Danube Delta)*

CONCLUSIONS

In classic models where correlation between atmospheric air density and wind speed variation is not considered, energetic wind potential is calculated using simplifying hypothesis of constant air density.

The present mathematic model considers stochastic variation of both specific parameters; the calculation relation for mean wind energy is a function of variation coefficients of air density, wind speed and correlation coefficients between them.

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STUDIA UNIVERSITATIS BABEŞ-BOLYAI, AMBIENTUM, LIII, 1-2, 2008

THE FIRST RADIO-METRICAL ESTIMATES OF THE RED LAKE'S SEDIMENTATION RATE

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ABSTRACT. The First Radio-Metrical Estimates of the Red Lake's Sedimentation Rate. This work presents the first estimates of the Red lake's sedimentation rate. The determination of the sediment accumulation rate was estimated by using two well-known methods of recent sediment dating the Pb-210 and the Cs-137 method. Both methods are based on using gamma emission radio nuclides. The Pb-210 and Cs-137 concentration in the sediment were measured by using a gamma spectrometer with a Hp-Ge detector, GMX type. Then has been found activities between 40 – 110 Bq/kg for Pb-210 and 8-697 Bq/kg for Cs-137. Using the CRS methods for the calculation of sedimentation rate, we obtained a 0.5 cm /year value.

Keywords: *Pb-210, Cs-137, radioisotopes, dating methods, sedimentation rate*

INTRODUCTION

In 1837 in the metamorfico-mezozoic zone of the Oriental Carpathians happened a relatively rare phenomenon, the slope sliding of the Ghylcos Mountain blocked the Bicaz River and formed a natural barrage lake which received the Red name later.

The barrage resisted to the vertical and regressive erosion of the water pressure and to the static water pressure also and that's why the lake had remained for 167 years.

The lakes formed by natural barrage of the valley have often a short life, because the formed barrage erodes or are quickly silted. The Red Lake is a special case, because the accumulated water's volume after the valley's barrage was significant and the geology and consistency of the barrage did not allow the quick erosion of this. We don't have to forget that the barrage, even natural, constituted a damage for the natural dynamic of that side.

The sedimentation is a consequence of the reestablishing tendency of this equilibrium. In the case of the Red Lake there is the high sedimentation rate, which is highly influenced by men made activities.

In the process of the phenomenon's analyze we have to consider that because of the formation of the Red Lake, it is considered like an accumulation lake regarding the sedimentation. (Hewitt W. Jeter, 2000)

One of the most important recent sedimentation dating method is the Pb-210 method, which is the natural radionuclide result from U-238 series. In many cases, the method turned out to be accurate, especially in stable environment with constant sedimentation rate where the calculation model is well defined. The method also provides accurate results for non-uniform sedimentation (where the sedimentation rate is not constant), the difficulty is the finding of an appropriate sedimentation model. We have two simple models, which are called the CSR and CIC model (Appleby & Oldfield, 1992, Robbins, 1978).

The disequilibrium between the Pb-210 and the nuclear parent isotope, Ra-226, appears because of the intermediate radionuclide Rn-222. One part of the radon, resulted from Ra-226 from soil, ends up in the atmosphere where it's disintegrated in short life radio nuclides and followed by Pb-210. This end up on the surface of the soil or in the lakes, wet and dry deposition. (Wilkening, M. H., W.E Clements & D. Stanley,1975)

The lead which falls directly in the lake is transported by the water column and deposited to the bottom of the lake together with the sediment.

The second choice for dating the lake sediments is the artificial radio nuclides. The two sources of this is the nuclear weapon test between 1953-1963 and the accident of Chernobyl atomic plant power station from 1986.

The radionuclides which were deposited and are present nowadays in Sr-90, Cs-137, Pu-239-240-241.

In northern hemisphere the deposition reaches a significant level until 1954 and grew rapidly later.

In 1958 it was noticed a drop and it was followed by an increase because of the restarting of the testing.

After the 1963's agreement there was a fall, and at the beginning of the 70's there has been noticed a small increase because of the states which did not sign the agreement.

The Chernobyl accident from 26th April 1986 injected a lot of artificial radio nuclides in the atmosphere, this process continued until May, 1986. The principal radio nuclides were I-131, Cs-137, Cs-134. The deposition were at the thousands of km from the accident's place, in the northern hemisphere, these depositions are estimated to 10^{12}Bq compared to $4{,}3\text{x}10^{12}$ Bq which was provided from nuclear testing.

The radio nuclides' distribution was non-uniform and greatly controlled by winds and rains. In some parts of northern Europe (Scandinavia, Great Britain) and central Europe the deposition from the first days of Cs -137was higher than the total depositions was provided by nuclear weapon.

MATERIALS AND METHODS

Excess of Pb-210 is given by radioactive disintegration law, and the total lead is the sum of the two sources:

$$C_{Pb} = C_{Pb}(0)e^{-\lambda t} + C_{Ra}(1 - e^{-\lambda t})$$

(where λ is the disintegration constant of Pb-210). This equation can be used at dating sedimentation.

In the lakes where the erosion process from catchments area and residence time in water column are constant, the result is a constant sedimentation rate.

It can be supposed that each sediment layer would have the same quantity of sediment atmospheric Pb-210 activity (excess Pb-210) in the sedimentation moment.

So the sediment from a certain m depth (dry deposition in g/cm^2) will be of the age:

$$t = \frac{m}{r}$$

where r is sedimentation rate (g/cm^2) and (atmospheric) Pb-210 activity will vary with the depth after:

$$C_{(m)} = C(0)e^{-\lambda m / r}$$

where λ is the constant for Pb-210 (0,03114 year^{-1}) and

$$C(0) = P' / r$$

is the atmospheric Pb-210 activity in the superior part of sediment core. When it's represented in logarithmical scale the activity for Pb-210visa depth gives a linear profile.

The sedimentation rate average r can be determined from the graphic.(P.G. Appleby 2000)

The measures were made using a multichannel ORTEC Digidartt spectrometer with a HpGe detector, with a 1.92 keV resolution with 1.33 MeV line Co-60 and the relative efficiency of 34.2%. The lead shielding of the detector with 40 cm diameter, with 8cm wall, inside the lead shielding is a Cu layer of 3 mm. the shielding is very important especially in the case of environmental samples where the sample activity isn't bigger than the background activity. The used geometry was of "sarpagan" type, a cylindrical box with small dimensions. The minimal time of acquisition was of 24 hours. The activity concentration of lead 210 is determined using 46.5 keV peak with relative intensity of 4% and the Cs-137 from 661 peak. (P.A. Tanner, S.M. Pan, K.N.Yu 2000)

Ra-226 is determined using the radon peaks after a month of storage, when it reaches the equilibrium between Ra and Rn progeny. The detection limit is calculated using the formula below: (J. Uyttenhove, 2003)

$$MDA(E_{46}) = \frac{A_m}{\varepsilon_{46} \cdot f \cdot t_m}\left(\sqrt{2bR_{46}B_{46} + A_m^2 / 4} + A_m / 2\right)$$

where Am = 5 for an error of 20%

ε - detector efficiency

f – relativ intensity of peak 46 keV

tm- measuring time (s)

b- fittation factor =2

R- energy resolution of 46keV peak (channel)
B- background (impuls on channels)
For Pb-210 this value are 12 Bq/kg.

RESULTS AND DISCUSSION

For the Pb-210 concentration is sediment layers the values from table 1 were obtained. From the table we can see “the problem of the first layer”, which means that resulting from the collection of the samples the biggest problem is to maintain the first layer in the initial form.

Many times there are losses of material from the sediment’s first layer.

Table 1

Pb-210 activity of each sediment layer

Activity of Pb-210 on each sediemnt layer (Bq/kg)					
Nuclides	5	15	25	35	45
Pb-210	67±11	110±19	60±10	41±7	57±10
Ra-226	53±8	54±8	49±7	45±7	67±10
Cs-137	205±33	679±100	9±1	8±1	3±0.5
Th-232	57±7	30±3	50±7	40±5	67±9
K-40	757±63	509±42	715±58	1641±134	860±70

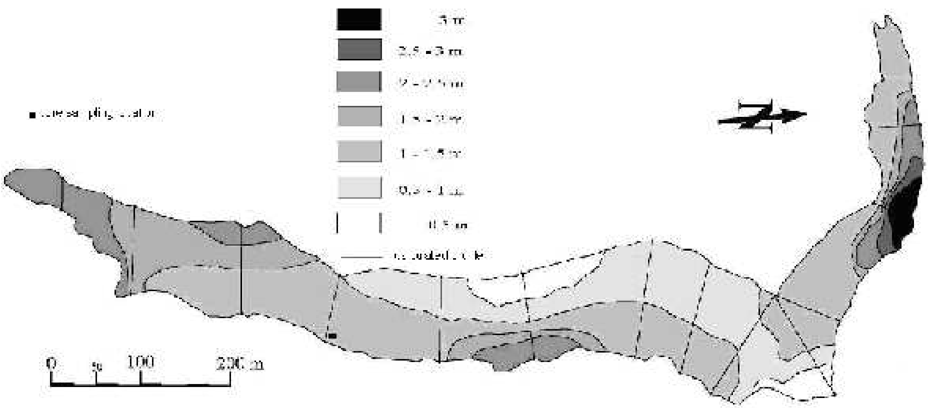

Fig. 1. *Sediment core location*

In figure 1 it is shown the place where the sediment sample was taken from, the column which was divided in 5 layers of 8-10 cm each.

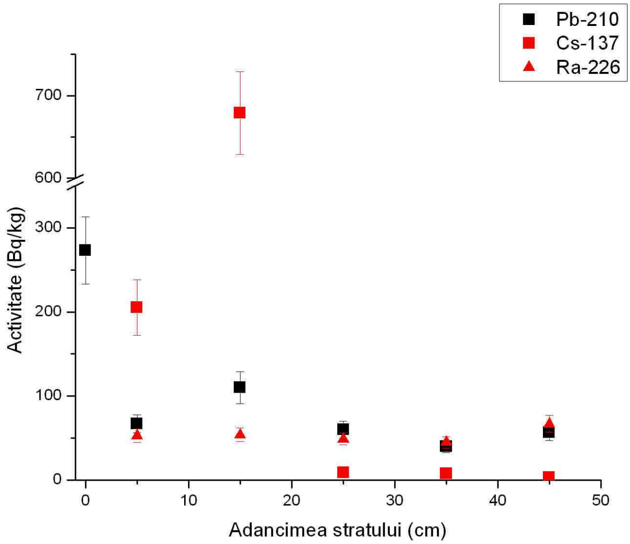

Fig. 2. *Obtained radionuclide concentration in each layer*

The obtained activities and graphic representation can be seen in Table 1.

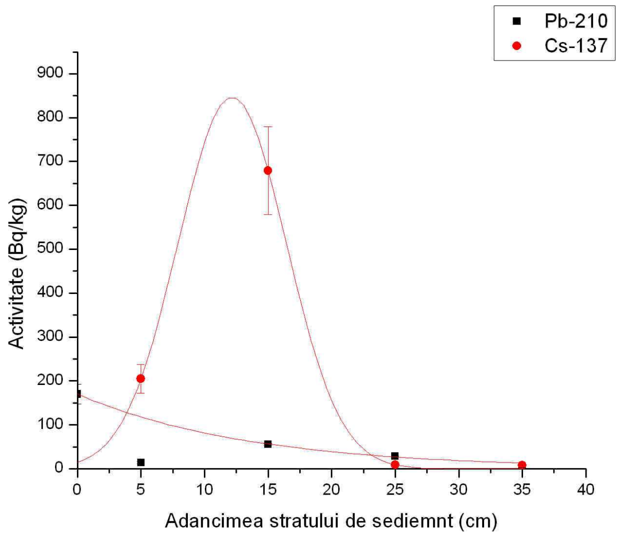

Fig. 3. *Distribution of radionuclid concentration*

For Pb-210 and Cs-137 concentrations we used two mathematical fittings and we obtained the graphic from figure 3. from the fittings we made and from the mathematical model the sedimentation rate was calculated and it gave 0,5 cm/year.

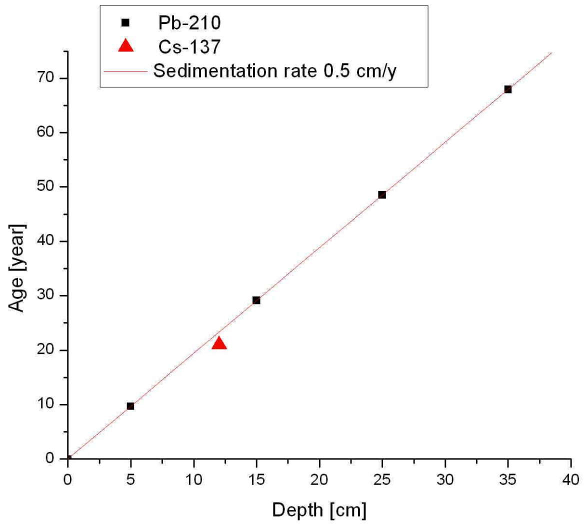

Fig. 4. *Sedimentation rate*

The results for the sediment layer's age obtained from Pb-210 were compared to the ages resulted from Cs-137, and that can be seen in figure 4.

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THE EFFECTS OF HEAVY METALS ON CHEMICAL EQUILIBRIUMS FROM ANTROPIC SOILS

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ABSTRACT. The Effects of Heavy Metals on Chemical Equilibriums from Antropic Soils. The study of heavy metals distribution and migration in antropic soils represent a priority problem of environmental geochemistry, both due to high toxicity of these metals and due to major perturbations induced by these metals at biologic and minerals systems level, from soils. Ours studies have follows the effects of heavy metals on: (***i***) stability of organic compounds with essential role in biogeochemical processes; (***ii***) essential mineral equilibriums for the re-adaptation capacity of soils (clay minerals, carbonates, etc.), (***iii***) acid-basic and redox equilibriums; (***iv***) inter-phases distribution equilibriums of microelements. In generally, the heavy metals determined a relative strong and fast destabilization of chemical equilibriums from soils, the intensity of these effects and their extinction aria being dependent by nature and heavy metals content, and by re-adaptation capacity of antropic soils, respectively. The heavy metals accumulation (ex. Cd, Pb, Cr, Hg) in soil solution determined a perturbation of acid-basic and redox equilibriums, which is usual correlated with a sever perturbation of mineral and organic components stability, from soil. These variations of physic-chemical conditions increase the accumulation probability of Cd, Pb, Hg and Cr, as species with high toxic potential and determined a major perturbation of inter-phases distribution equilibriums of microelements from soil. In this direction, ours studies have evidenced that the existence of some important perturbations of Zn, Cu and Ni distribution, due to the Cd and Hg accumulation, of Ca, Mg and alkaline metals due to the Pb accumulation, and of Fe(II) and Fe(III) equilibrium due to the Cr accumulation.

Keywords: *heavy metals, antrosoils, chemical equilibrium*

INTRODUCTION

From antropic soils (*ss. Antrosoluri*) [7, 8], as frequency and intensity, the most exposed to pollution are technosoils and hortic antrosoils (the soils from glass houses and solariums) [3, 15]. The study of distribution and migration of heavy metals in soils represent an important problem of environmental geochemistry, both due to high toxicity of these metals and due to major perturbations which can be generated at biological and minerals systems level from soils [1, 9, 13]. But, the pollution of antropic soils with heavy metals has a particular character, because these types of soils present sever modifications of lithology and chemical-mineralogical characteristics. In consequence, the inter-phases distribution and the mobility of heavy metals in antropic soils are conditioned by a relative high number of factors which, many times, have atypical values and variations. These make that the realization of quantitative estimations and establish of some explicit correlations, to be extremely difficult to due [3, 4, 10].

In the most times, in antropic soils the effects of pollution with heavy metals are most fast and more exaggerate manifested than in other soils types, due to their higher vulnerability. In these cases, the heavy metals determined a relative strong and fast destabilization of chemical equilibriums from antrosoils, the intensity of these effects and their expansion area being dependent by the type and the content of heavy metals, and by the re-adaptation capacity of antropic soils, respectively [1, 10, 15]. The heavy metals accumulation (ex. Cd, Pb, Cr) in soil solution determined a perturbation of acid-basic and redox equilibriums, which is usual correlated with a sever perturbation of mineral and organic components stability, from soil. The variations of physic-chemical conditions increase the accumulation probability of Cd, Pb and Cr as species with high toxic potential and determined a significant perturbation of inter-phases distribution equilibriums of microelements from soil [3, 4, 6]. Ours studies have evidenced the existence of some important perturbations of Zn, Cu and Ni distribution due to Cd accumulation, of Ca, Mg and alkaline metals due to Pb accumulation and of equilibrium between Fe(III) and Fe(II) due to Cr accumulation.

MATERIALS AND METHODS

The experimental studies have been performed on 14 antropic soil samples (s.s technosoil) from industrial zone of Iaşi city, from a perimeter situated on Țuțora Bvd (drawing by a distance of 3.2 km in SE direction, from a deep of 0-20 cm, in 2005 September-October period). The localization of soil samples from studied perimeter, the experimental strategy used for chemical-mineralogical analysis and the primary results of analysis have been reported in several previous papers [3, 4, 6]. In table 1 are summarized the chemical-mineralogical characteristics of studied antrosoils, and in table 2 are given the total and differential contents of determined Cd, Pb and Cr.

Table 1.

The physic-chemical characteristics of studied antrosoil samples

Observation	Minim	Maxim	Average
G.s.[(1)], g/cm^3	1.2677	1.5572	1.4383
pH(KCl)[(2)]	5.28	8.30	6.67
E_h[(3)], Volts	0.109	0.640	0.348
E.C[(4)], μS/cm	1.95	14.56	7.62
C.T.S.C[(5)]; mechiv.g / 100 g dry soil	6.77	33.26	17.91
$X_{CO_3^{2-}}$ [(6)]	0.0473	0.4806	0.2582
-log[$SiO_{2(aq)}$][(7)]	2.78	4.76	3.42
-log[K_{mobile}][(8)]	2.70	4.59	3.61

Observation	Minim	Maxim	Average
$-\log[Fe_{(aq)}]^{(9)}$	5.75	12.17	7.86
Clay minerals; % (w/w)	7.94	54.19	29.91
Carbonates; % (w/w)	0.65	8.32	2.60
Iron oxides and oxi-hydroxides; % (w/w)	0.59	3.53	1.80
Humus, % (w/w)	0.56	9.15	5.31

(1)Specific weight – determined by picnometric method. (2)Determined in KCl. (3)Redox potential. (4)(5)Total cationic exchange capacity. (6)Molar fraction of levigable carbonate (in aqueous extract). (7) Total extractable silica (in solution of 0.5 M NaOH), moli/kg. (8)Extracted in 1.0 N ammonia acetate, at pH = 7; µg/g. (9)Extracted with 0.3 M sodium citrate solution (buffered with sodium bicarbonate, pH = 7.3) + sodium dithionite, mol/kg .

The fix and mobile forms differentiation, and the speciation forms differentiation of heavy metals in antrosoils was done on the basis of results obtained by application of solid-liquid sequential extraction procedure. In function of extractability (levigability) in some extractants (solvents or aqueous solutions) and in agreement with the existent conventions was estimated and the relative association way of heavy metals with mineral and organic components of antrosoil [3, 5, 9]. The heavy metals effects on equilibrium from studied antrosoils have been estimated in the limits of thermodynamic and kinetics models, usual used in such studies [2, 12, 14, 15].

RESULTS AND DISCUSSION

The heavy metals can influence the chemical equilibriums from antropic soils in two main ways: (***i***) directly – by effective intervention in equilibriums evolution; in this case the effects have a relative high selectivity degree, and the intensity and action time depend both, on the total concentration of heavy metal and of his speciation forms which assist to equilibrium, and on the competition degree manifested by other equilibriums and / or ionic species; (***ii***) indirectly - by modification of physic-chemical properties of environment (pH, redox potential, ionic straight, etc.); in this case, the effects have a low selectivity degree and are mainly dependent by the physic-chemical characteristics of heavy metals and his total concentration. In case of antrosoils, the heavy metals effects are simultaneous manifested by both ways, thus from experimental point of view the individual contribution of the two mechanisms is difficult to differentiated.

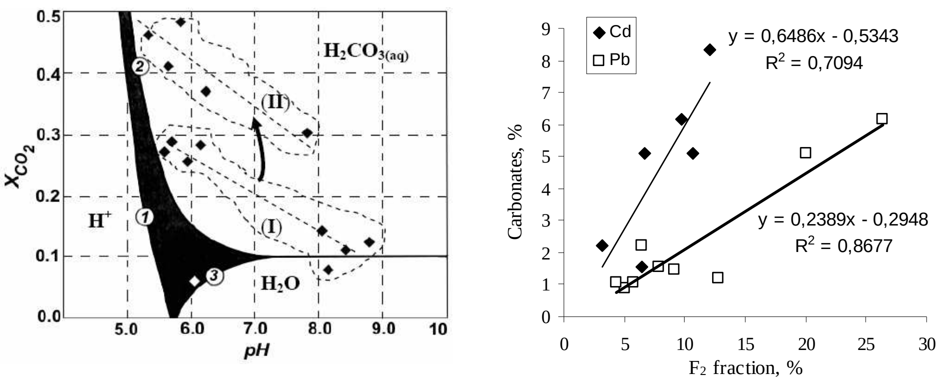
In agreement with the mineralogy, chemistry and geochemistry of studies soil samples, Cd, Pb and Cr have exclusive antropic origin, predominant accumulative tendencies, and their presence in soil is relative recent. This determined an atypical distribution of the three heavy metals, and association ways less characteristics of these with the mineral and organic components of antropic soils. Under these conditions, both the correlations between soils components and the correlations between these and total and differential contents of heavy metals, have an abnormal character. In consequence, the establish of some characteristic paragenesis and mineral associations is very difficult, and the correlations between mineral and organic components of antropic soils and the contents of heavy metals have a particular character and apparent geochemical significations.

Table 2.

The variation limits of Cd, Pb and Cr in studied antropic soils [3, 6]

Observation	Total; µg/g	F.1, %	F.2, %	F.3, %	F.4, %	F.5, %
Cadmium						
Minim	0.09	19.20	3.19	3.97	30.16	2.62
Maxim	1.36	55.75	12.07	12.58	59.22	5.61
Average	0.43	36.40	3.48	8.08	48.21	1.97
Lead						
Minim	25.83	13.71	4.33	2.19	25.93	1.86
Maxim	186.73	58.27	26.35	5.73	61.27	5.14
Average	89.71	36.97	12.07	2.29	45.11	2.97
Chrome						
	Total content; µg/g		Cr(III)		Cr(VI)	
			µg/g	%*	µg/g	%*
Minim	11.16		10.71	85.48	0.44	3.78
Maxim	129.35		124.33	96.22	8.39	14.52
Average	60.32		56.76	93.56	3.55	6.43

F.1 – easy exchanged cations (extraction with 0.1 M $NaNO_3$), F.2 – cations bonded on carbonates (extraction with 1.0 M CH_3-COONa, pH = 5, CH_3-COOH), F.3 – cations bonded by Fe and / or Mn oxides (extraction with 0.07 M $NH_2OH.HCl$, 4.5 M CH_3-COOH), F.4 – cations bonded by organic mater (extraction with 0.02 N HNO_3 and 30 % H_2O_2, 3 M CH_3-$COONH_4$ and 3.5 M HNO_3), F.5 – residual fraction (fix, dissolving with $HClO_4$ and HF). *% from total content.



(a) (b)

Fig. 1. (**a**) *The possible mechanisms of calcite dissolving in antropic soils in function of pH and* P_{CO_2} *(estimated from [CO_3^{2-}] solubilized, at 25°C) [11]. Lines (1), (2) and (3) delimited the domains in which [H^+], [H_2O] and [$H_2CO_{3(aq)}$] control the kinetics of calcite dissolving processes. On diagram are demarked the evolution tendency of global calcite dissolving processes at increasing of Cd and Pb concentration from studied antropic soils: (I) calcite dissolving is control by pH, (II) calcite dissolving is control by [$H_2CO_{3(aq)}$].* (**b**) *The correlations between the weights (% from total content) of Cd and Pb F2 fractions (bonded on carbonates minerals) and total carbonates content from antropic soil samples.*

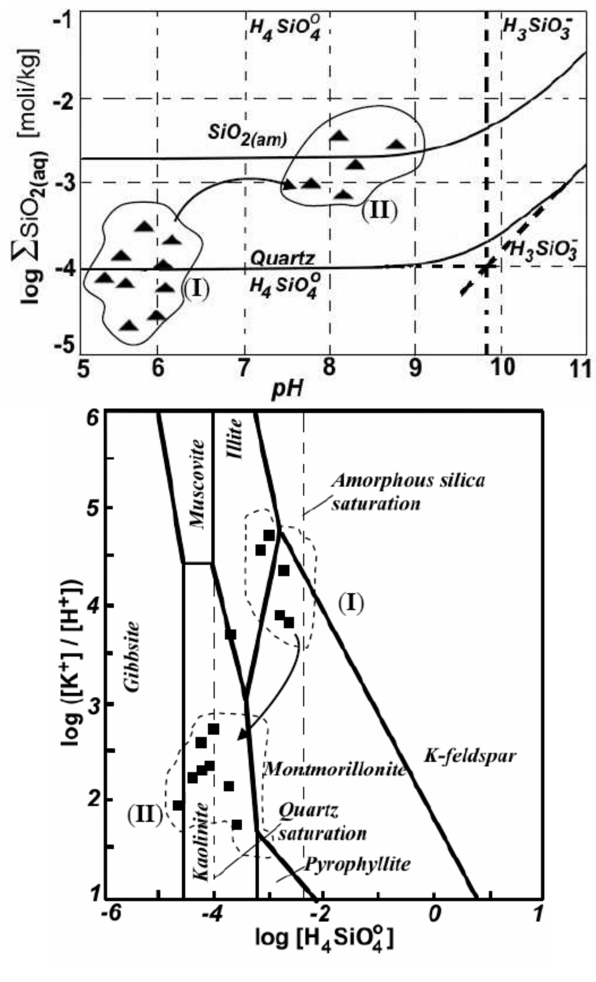
The our results have evidenced that the effects of heavy metals (Cd, Pb, Cr) on chemical equilibriums from antropic soils consist in: (***i***) directly or indirectly destabilization of some mineral and organic components of antrosoils; (***ii***) the inter-phases distribution modification of micro- and macro-elements; (***iii***) the modification of normal association way of micro- and macro-elements with mineral and organic components [3, 4, 6]. The study of correlations between total and differential contents of Cd, Pb and Cr and physic-chemical characteristics of soils (pH, redox potential, ionic straight, electrical conductibility), and mineralogical composition respectively, correlated with direct experimental investigations (microscopic studies, X-ray diffraction, IR and Raman spectrometry) [3, 4, 6] have evidenced that the heavy metals effects on chemical equilibriums from antropic soils are manifested predominantly by direct mechanism (significant perturbation of physic-chemical conditions).

In concordance with the relative association tendencies of Cd, Pb and Cr with mineral and organic components of antropic soils, the complexation processes at mineral/ solution interface, the ionic exchange and the adsorption processes determined fast local variations of pH, which has as result an accentuated destabilization, mainly of amorphous mineral phases (carbonates – figure 1, silica – figure 2.a, clay minerals – figure 2.b, iron oxides and oxi-hydroxides – figure 3).

In conditions of antropic soils, the carbonates destabilization is realized in two steps: (***i***) in first step, the global kinetics of levigation processes is control by pH ($w_3 = k_3[H_2O] = k_1[H^+] + k_2[H_2CO_{3(aq)}]$; w – reaction rate; k – rate constant) – at low concentrations of heavy metals in soils, (***ii***) in the second step, the global kinetics is control by [$H_2CO_{3(aq)}$] ($w_2 = k_2.[H_2CO_{3(aq)}] = k_1[H^+] + k_3[H_2O]$) – at higher concentrations of heavy metals (in conditions of rapid accumulation of these) – figure 1.a. This hypothesis is sustained both, by direct experimental studies realized on carbonates phases separated from antropic soil samples [3, 4, 6], and by the positive correlations between the weight (% from total content) of Cd and Pb F2 fractions (bonded on carbonates minerals) and the carbonates content from studied antropic soil samples (figure 1. b). Between those three heavy metals, the chrome has the most powerful destabilization on carbonates, follow by Cd, the effects of these being stronger at lower concentrations and in conditions of rapid accumulation. The destabilized effect of Pb on carbonates is more lower, in comparison with Cd and Cr, probable due to the inhibition of dissolving processes, by co-precipitation (as basic carbonate) at interface, and possible due to the stability effect on calcite structure induced by isomorphs substitution $Pb^{2+} \leftrightarrow Ca^{2+}$

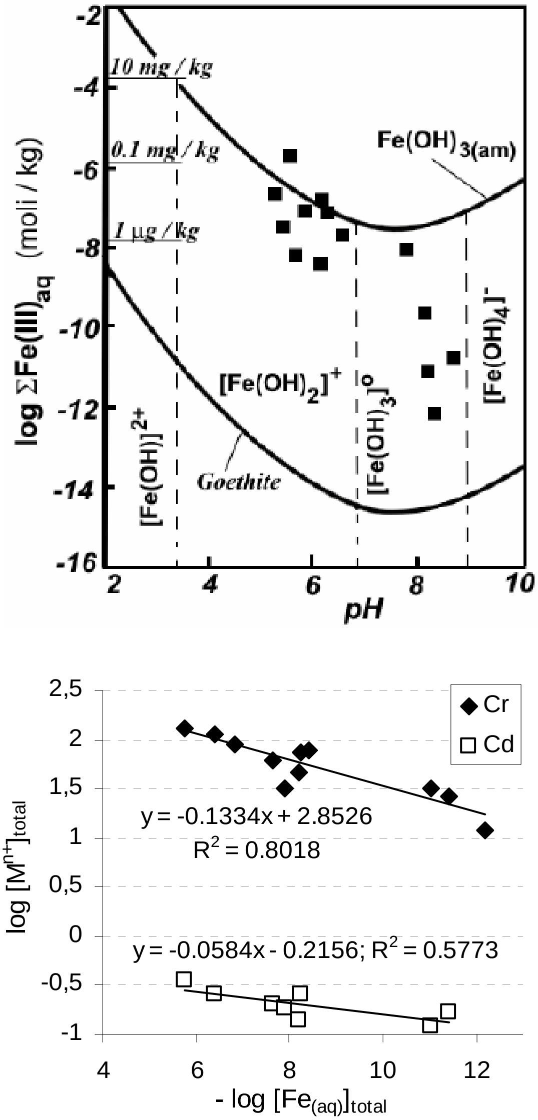
In conditions of antropic soils, the destabilization of silicates and amorphous aluminosilicates minerals is manifested by more accentuated levigation of silica and iron. Was observed that, at low concentrations of Cd, Pb and Cr (in condition of rapid accumulation), the amorphous silica dissolving is realized more fast and more accentuated, than at higher concentrations of heavy metals (figure 2.a). In case of amorphous clay minerals, the ionic exchange processes determined a strong and fast levigation of alkaline metals from soil solution, followed by a significant levigation of Si, Al and Fe. These have as effect the destabilization of equilibrium between ilite, smectite and kaolinite (equilibriums which are control by [K^+], $SiO_{2(aq)}$ and pH – figure 2.b), the dominant evolution tendency of these equilibriums being: illite $\rightarrow$

smectite → kaolinite, concomitant with increasing of heavy metals concentration. From considered heavy metals, Cr and Cd have the stronger effects on equilibriums between amorphous clay minerals.



(a) (b)

Figure 2. ***(a)*** *The quartz and amorphous silica solubility in function of pH, at 25°C [11]. On diagram is demarked the evolution tendency (estimated on the basis of total dissolved silica – extractable in 0.5 M NaOH solution) of amorphous aluminosilicates phases (amorphous silica, amorphous clay minerals and organic-minerals compounds) at increasing of heavy metals concentration (Cd, Pb, Cr) in antropic soil samples.* ***(b)*** *The equilibrium diagram between clay minerals in function of total extractable silica concentration, mobile potassium concentration and pH, at 25°C [11]. On diagram is indicated the evolution tendency of equilibriums between clay minerals in conditions of studied antropic soil, at increasing of heavy metals concentration (Cd, Pb, Cr).*



(a) (b)

Figure 3. ***(a)*** *The solubility of amorphous iron oxides and oxi-hydroxides ($Fe(OH)_3$ and goethite: α-FeO(OH)], estimated by total extractable Fe quantity (with solution of 0.3 M sodium citrate + sodium bicarbonate + sodium dithionite, pH = 7.3) in function of pH, at 25^oC [11].* ***(b)*** *The correlations between the total extractable Fe concentration and the Cd and Cr total concentrations.*

The destabilization of equilibriums between amorphous iron oxides and oxi-hydroxides is manifested by Fe levigation, follow by a rapid deposit of this as colloidal associations with clay minerals and humus, and as clay-ironhumic complexes, respectively. From considered heavy metals, the chrome has an extremely strong effect on iron oxides equilibriums whiles Cd and Pb destabilized more less these compounds (figure 3). In antropic soils, the equilibrium between Cr(III) and Cr(VI) is more mobile and more sensitive at variations of physic-chemical factors, than in other types of soils [6, 9]. Ours studies have evidenced the existence of some positive correlations between Cr(III) and Fe(II), Cr(VI) and Fe(III) respectively, which indicate a stronger reciprocal influence between Cr(III) –Cr(VI) and Fe(II)-Fe(III) equilibriums, than is mentioned in literature.

CONCLUSIONS

The effects of heavy metals (Cd, Pb, Cr) on chemical equilibriums from antropic soils consist in: direct or indirect destabilization of some mineral and organic antrosoils components; the modification of micro- and macro-elements inter-phases distribution; the modification of normal association way of micro- and macro-elements with mineral and organic components. These effects are predominant manifested by indirect mechanism (by significant perturbation of physic-chemical conditions).

In agreement with relative associations tendencies of Cd, Pb and Cr with mineral and organic components of antropic soils, the complexations processes at mineral / solution interface, the ionic exchange and the adsorption processes determined rapid local variations of pH, which has as result an accentuated destabilization, main of amorphous mineral phases (carbonates, silica, clay minerals, iron oxides and oxi-hydroxides).

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GLYCEROL DERIVATIZATION THROUGH ACETYLATION AND CARBONATATION FOR THE PRODUCTION OF ECOLOGIC DIESEL-LIKE ADDITIVES

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ABSTRACT. Glycerol Derivatization through Acetylation and Carbonatation for the Production of Ecologic Diesel-Like Additives. This study describes the glycerol derivatization in a process with two consecutive reactions: acetylation with butyraldehyde and hydroxyacetals carbonatation, with the production of glycerol acetal carbonates with dioxane and dioxolane structures. We aim to obtain the highest possible yield by the investigation of characteristic parameters that are specific for each reaction.

Keywords*: glycerol, acetylation, carbonatation, dioxane structure, dioxolane structure biofuel, transesterification*.

1. **INTRODUCTION**

The development of renewable nonpolluting energy sources is one of the main objectives of world's energetically policy which, in durable development context, has the purpose to increase the safety in energy feed, environment protection and the commercial development of variable energetic technologies. Renewable energies don't generate polluting emissions and have advantages for global environment and for combating local pollution. Last decades researches have shown that vegetable oil is a viable alternative to petroleum origin fuels.

From the existing methods of vegetable oils valorification as diesel-type fuels, a special interest has the utilization of fatty acids monoalkylesters (Abraham et al. (2004), Chintoanu et al. (2003)). The main reaction for the production of fatty acids monoalkylesters through vegetable oil transesterification is the following:

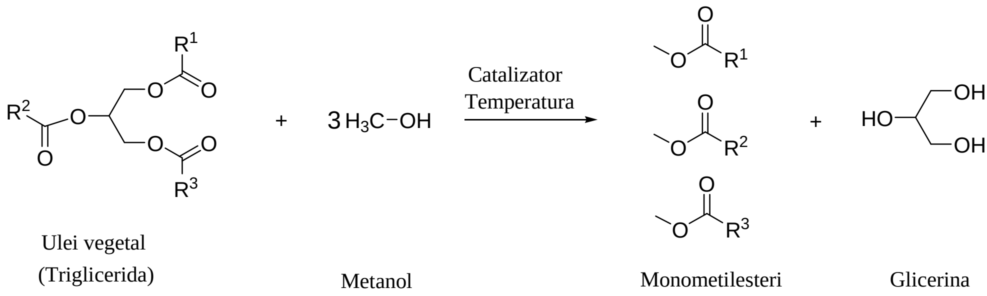

Fig. 1. *The production of fatty acids monoalkylesters through transesterification with methanol of vegetable oils*

There are many ways to use glycerin resulted in the biodiesel production process through triacylglycerol transesterification, in an efficient way. We only remind the food and cosmetics industry that uses glycerin as raw material for producing acrolein, an unsaturated aldehyde that is the basic compound for the production of several compounds with multiple utilizations.

Glycerin derivatizations for the production of diesel additive has been less studied untill now and the interest was to elaborate a technology for glycerin derivatization to obtain such compounds.

The hydrophobization of glycerin was studied based on a tandem reaction – acetylation with butyraldehyde – the carbonatation of free hydroxyl functional group of acetals with diethyl carbonate in the presence of sodium hydride. The general equation of glycerin derivatization is presented in fig. 2:

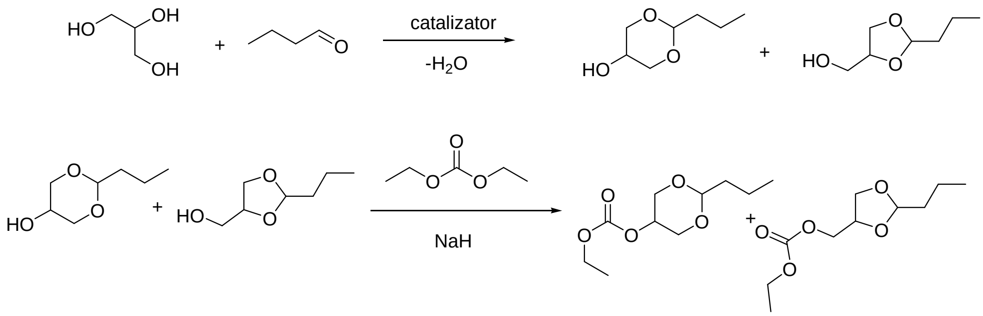

Fig. 2. *Glycerol acetal carbonates synthesis (biodiesel additive)*

2. MATERIALS AND METHODS

Glycerin, diethyl carbonate, butyraldehyde are purchased from Merck and were used without supplementary purification. The solvents were distillated and the sodium hydride was purchased from Fluka. ^{1}H- and ^{13}C-NMR spectra were registered with a Varian Gemini 300 spectrophotometer operated at 300, respective 75 MHz. All the spectra were registered in deuterated chloroform solution and the chemical displacements are measured in ppm on ∂ scale towards TMS as internal standard. For registering IR spectra it was used a FT-IR Nicolet 205 apparatus in CCl_4 solution. The gas-chromatograph (carrier gas H_2: detecting element FID) and an Astec B-PM chiral column that has a dimethylated β-cyclodextrine mobile phase.

Thin layer chromatography was performed on Merck layer of Kieselgel 60 F_{254} on alumina support. The spots were visualized by treating chromatography layers with ethanolic solution 5% of phosphomolibdenic acid. The preparative chromatography separation was made through vacuum chromatography [10] on Kieselgel 60 (0.063-0.200 mm) Merck.

3. RESULTS AND DISCUSSIONS

3.1 Parameters that influence the acetylation

To obtain a high efficiency, respective to develop an economical technology, the following parameters were tested: the catalyst type, raw material ratio, the existence of a co-solvent, the temperature of the reaction mass, the water formed during the reaction.

- **the catalyst type**: acids were proven to be better catalysts than bases: from all tested acids (mineral, organic, ion exchange) strong ion exchange acids proved to be most efficient catalysts.
- **raw material ratio:** the best glycerin-butyraldehyde molar ratio is 1:1.
- **the presence of a co-solvent:** 15 organic solvents were tested and benzene was the most appropriate one.
- **the temperature of the reaction mass:** the increase of the temperature lead to the decrease of the reaction temperature
- **the water formed during the reaction**: has to be continuously removed during the reaction through azeotrope distillation.

3.2 Parameters that influence the carbonatation reaction

In order to decrease the volatility of the hydroxyl functional groups of hydroxyacetals, these were further derivatised. It was chosen to transform them with a cheap reagent, diethyl carbonate. A high efficiency was followed through investigating the parameters that influence this reaction:

- **the catalyst type:** the most appropriate was sodium hydride, that through molecular hydrogen elimination passes every alcoholic group in alkoxides.
- **the reagent's effect** didn't show to be important in the reaction and so it was chosen a reaction in lack of organic solvent
- **temperature**: the reaction was made at an ambient temperature of 150^0C
- **the ratio between reagents:** the diethyl carbonate excess is imposed by the reversibility of the transcarbonatation reaction.

The global efficiency in acetal carbonates mixture is 79%.

A structural analysis, of hydroxyacetals and also of acetal carbonates shows that during the reaction compounds with five (dioxolanes) and six (dioxanes) atoms. Furthermore dioxanes have two geometrical isomers and dioxolanes admit the development of four diastereomers (Eliel and Wilen, 1994; Kirby and Wothers, 2001; Gromachevskaya et al. (2004)). The stereoisomeric composition of carbonated acetals is imposed by the stereoisomeric composition of hydroxyacetals. To control this stereochemical composition of acetals, a gas-chromatography method was developed to separate these stereoisomers. This was accomplished using an Astec B-PM chiral column, which has a mobile phase that allows quantity estimation. The chromatogram of stereoisomeric mixture is presented in fig. 3:

Some aspects regarding the stereochemical and structural composure of intermediate and reaction products were checked and confirmed with ^{1}H- and ^{13}C-NMR spectrometry. Because ^{1}H- and ^{13}C-NMR spectra are very complex, the protons and carbons signals can't be totally attributed.

For a better and a total attribution it would be necessary the register of COSY HMBC and HMQC bidimensional spectra. ^{1}H- and ^{13}C-NMR simple spectra are enough to confirm acetals structure respective the forming of acetal carbonates as final products.

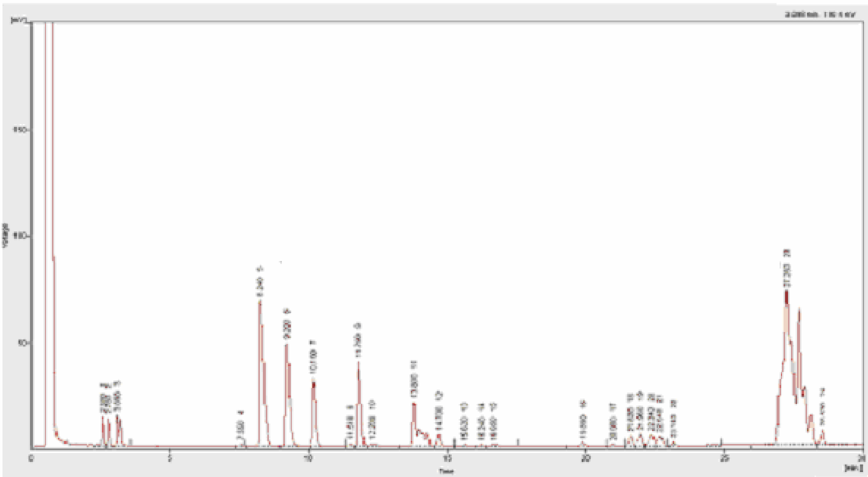

Fig. 3. *Stereoisomeric analyses of reaction products on an Astec B-PM chiral column*

The comparison of the ^{13}C-NMR spectra of hydroxyacetals and acetal carbonates mixture shows the appearance of a carbonyl group in the mixture's final spectrum through the presence of two signals at 171.1 and 171.3 ppm that are characteristics for carbon and these signals are not present in the hydroxyacetals spectrum.

The transformation of hydroxyacetals in acetal carbonates was confirmed with the help of IR spectrometry. Analyzing the hydroxyacetals mixture spectrum it can be observed a high intensity at 3400 cm^{-1} that is specific to alcoholic functional groups (fig.4). Analyzing fig.5 it can be observed an intense signal at 1740cm^{-1} specific to ester and alkyl carbonate groups. Comparing these spectra, a total transformation of hydroxyacetals in acetal carbonates is confirmed.

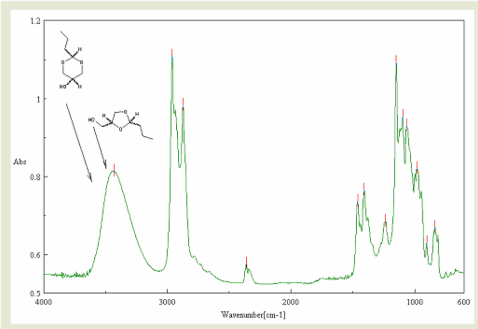

Fig. 4. *IR spectrum of hydroxyacetals mixture*

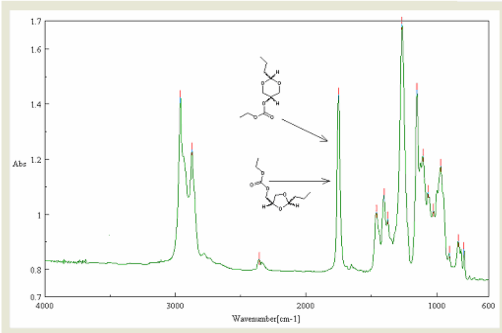

Fig. 5. *IR spectrum of acetal carbonates mixture*

4. CONCLUSIONS

The synthesis of acetal carbonates, that are of dioxane and dioxolane type, was studied to use the obtained glycerin from biodiesel production process through transesterification of triacylglycerols with methanol. The glycerin hydrophobization was made in a process with two consecutive reactions.

The first reaction is the glycerin transformation in dioxane and dioxolane hydroxyacetals with the help of butyraldehyde.

Hydroxyacetals are low volatile, so volatility was increased through the ethyl carbonatation of the alcoholic function.

It was taken into account the process optimization through investigation of the characteristic parameters for each reaction: catalyst type, co-solvent type, molar ratio of reactions, the adding reagents type, the reaction temperature and the influence of secondary products (water resulted from the acetylation reaction.

The obtained carbonates mixture composure was gas-chromatographic investigated using a chiral column. The intermediate and final product structure was confirmed with ^{1}H-,^{13}C-NMR and IR spectrometry.

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STUDIA UNIVERSITATIS BABEŞ-BOLYAI, AMBIENTUM, LIII, 1-2, 2008

DIFFERENCE IN HUMAN SENSITIVITY STARTING WITH ZERO MAGNETIC FIELD

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ABSTRACT. Difference in human sensitivity starting with zero magnetic field. A standard of exposure are based on studies that provide information on the health effects of electromagnetic field (EMF) and is very important in limiting of human EMF exposure. In very low electromagnetic fields the evidence for a causal relationship is limited, because does not allow a scientifically procedure for risk assessment. The exposure in such fields looking an excess of childhood leukemia, but only the epidemiological evidences are not enough in establishing of safety exposure margin. In this article are presented the exposure effects in zero magnetic fields, (ZMF), respectively, the lowest exposure for an electromagnetic field. The inducted genotoxic damage at lymphocytes level was different for disease patients, comparing with healthy donors, which means differences of exposure sensitivity starting with ZMF.

Keyword: *very low electromagnetic fields exposure, zero magnetic field, threshold levels, human sensitivities.*

INTRODUCTION

The International Agency for Research on Cancer (IARC) has concluded that magnetic fields are “possibly carcinogenic” to humans. This is based on pooled data from studies of children exposed to consistently high level residential magnetic fields showing an increased risk of childhood acute lymphoblastic leukemia. The few studies examining brain cancer and residential EMF exposure in adults have found no consistent evidence of an association.

The control of health risks from the exposure to any physical, chemical or biological agent is informed by a scientific, ideally quantitative, assessment of potential effects at given exposure levels (risk assessment).

Exposure-response assessment is the process of quantitatively characterizing the relationship between the exposure received and the occurrence of an effect. For most types of possible adverse effects (i.e. neurological, behavioral, immunological, reproductive or developmental effects), it is generally considered that there is an EMF exposure level below which adverse effects will not occur (i.e. a threshold). However, for other effects such as cancer, there may not be a threshold.

The ICNIRP concept of limits does not include such real “safety” factors. Such thresholds usually show a distribution of sensitivity within populations (of cells and of people), and so the induction of an effect will vary over this range within the population.

This article try to establish if is presented a difference in human’s lymphocytes sensitivities using an effect biomarker (comet assay), in the absence of a threshold level, when the cells cultures ageing in vitro, in Helmholtz coil system. The zero magnetic field exposure means the lowest exposure in order of very low electromagnetic field.

MATERIAL AND METHODS

The zero magnetic field could be the ideal exposure for very low electro-magnetic field, better said the lowest exposure. The natural magnetic field, mainly the static component of the geomagnetic field was compensated with a Helmholtz coils system, mounted on a wooden frame of 1.2 m in diameter, (picture 1).

The power supply of the coil was set to optimize the magnetic field induction within the coil to the lowest average value possible. The reduction factor of the natural magnetic field was ~ 100. We tried to reduce as much as possible any magnetic perturbations by removing any iron objects or electrical power supply from the close proximity of the coil and by placing it on the ground floor at a height of about 1.5 m, on a wooden frame. The controls were placed in the same room at a 2 m distance from the magnetic field of compensating system.

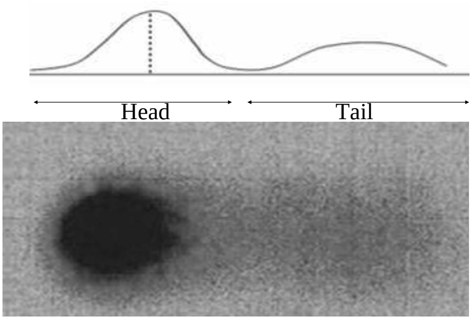
Picture 1. *Helmholtz Coil System*

The inducted DNA damages in zero magnetic field (samples) was studied for 3 healthy donors and 3 diseases patients (bronchitis), comparatively with the control exposed in normal geomagnetic field. DNA damage has been detected in lymphocytes cultures ageing in vitro in the Helmholtz coil system.

The working protocol used to detect DNA damage was in accord with ITRC: THE SCGE/ COMET ASSAY PROTOCOL modified after Brie and all, (1).

Evaluation of DNA damage

The overall structure resembles a comet with a circular head corresponding to the undamaged DNA that remains in the cavity and a tail of damaged DNA, picture 2.



Picture 2. *The overall structure of the "comet".*

Visual and computerized image analyses of DNA damage were carried out based on perceived comet tail length migration and relative proportion of DNA in the comet tail, picture 2. Etidium Bromide - stained nucleoids were examined at 40X objective with a Axioplan, Zeiss epifluorescence microscope, at 460 nm.

Individual comet images were captured for digitization with a CCD camera attached to the microscope. One hundred randomly selected non overlapping cells on each control or sample slide after 24, 48, 72 hours were scored visually as belonging to one of five predefined classes according to tail intensity and given a value of 0, 1, 2, 3 or 4 from undamaged 0 to maximally damaged 4.

RESULTS

Levels of DNA damage were assessed and quantified by visual and computer image analysis.

A point of interest to note is that levels of DNA damage vary considerably between different exposure conditions: control and very low magnetic field. Kinetics study of inducted genotoxic effects was done on lymphocytes cultures after 24 hours, 48 hours, and 72 exposure hours.

Total damage score (SL) meaning the summing over all grades are increased with the exposure "dose" in very low ELMF (hours of in vitro cells culture ageing), figure 1.

In figure 1, could be observed the genotoxic effect of ZMF, only for healthy donors, especially after 48-58 exposure hours, when lymphocytes ageing in vitro at 17 ^{0}C.

This effect was not observed for the disease lymphocytes cultures exposed in ZMF.

But, a great difference in the cells sensitivity was observed between healthy, respectively disease patients, in inducted of DNA damage.

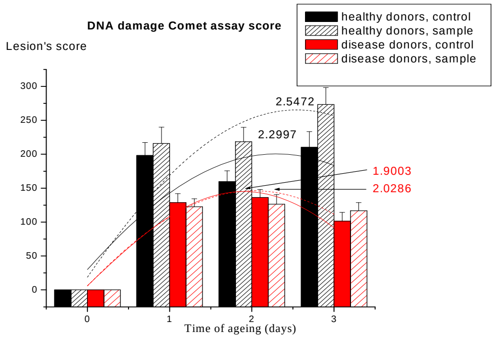


Fig. 1. *In vitro dose–response plots to very low electromagnetic field for lymphocytes cells culture quantified by SL (total damage score).*

Quantification of exposure in very low electromagnetic field exposure using tail factor showing an increase of DNA in the tail more accelerate for exposed sample, than control, the relevant aspects for healthy donors, figure 2. The relative percent of DNA in the tail are significantly increased for sample, when the genotoxicity was quantified by tail factor, DNA damaged.

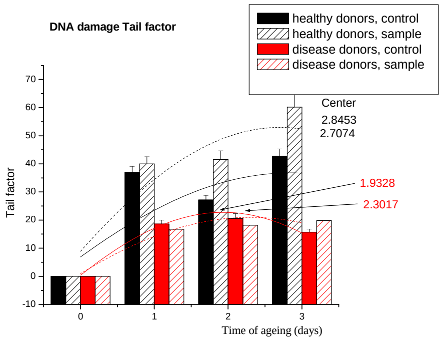


Fig. 2. *In vitro dose–response plots to very low electromagnetic field for lymphocytes cells culture quantified by tail factor, DNA damaged.*

DISCUSSION

Scoring for DNA damage- score lesion (SL) represent the sum of relative units (UR), means the product between cells number finding in a special stadium and the number of comet class, [1].

SL (UR) =A0 + B1 + C2 + D3 + E4, where A, B, C, D, E, = number of cells in 0, 1, 2, 3, and 4 stadium.

A total damage score for each slide was derived by multiplying the number of cells assigned to each grade of damage by the numeric value of the grade and summing over all grades (giving a maximum possible score of 400, corresponding to 100 cells at grade 4). Tail factor (TF) represents a quantification parameter over 500 of studied cells, meaning the relative percent of DNA in tail.

$TF(\%) = (A\ F_A + B\ F_B + C\ F_C + D\ F_D + E\ F_E)/500$, where F_A, F_B, F_C, F_D, F_E, is the relative percent of DNA in tail.

The comet assay represents an effect biomarker, used in evaluation of DNA damage induction for human lymphocytes culture exposed in vitro, especially to ionizing radiation. It isn't a specific test, but in our condition could be very good for study of genotoxicity.

When threshold exposure level must be established, very important are to take into account the individual sensitivity in accord with genetics, sex, illness, s.a. So, the illness could be a reason of observed different sensitivity in zero magnetic fields.

Usually, the cellular sensitivity (chromosome aberrations and cell death) are discussed after the therapy with ionizing radiation, when the genomic instability is associated with increased susceptibility in the defects induction and high cancer risk, [2].

Several studies have been carried out to determine the genotoxic potential of non ionizing radiation, [3-10]. For example, Yokus has concluded that EMFs can induce oxidative DNA damage and lipid peroxidation. The extent of DNA damage and level of lipid peroxidation depends on exposure time. The observed exposure time dependence may have important health implications, as long-term EEMF exposure may cause cumulative oxidative DNA damage, [4]. The genotoxicity was also investigated to Fatigoni and co-workers. They concluded that a 1-mT 50-Hz MF is genotoxic in the Trad-MN bioassay, and this assay may be suitable for detecting genotoxicity of ELF MFs under field conditions, [5].

In accord with our study, [11], the very low electromagnetic field from Helmholtz coil system induces an increase of relaxed areas of DNA with increase of comet tail and head.

Many other remarks about people sensitivity exposed to electromagnetic fields was done to Norbert Leitgeb, [12]. So, the investigation of interpersonal variations of sensitivities to electric currents among the general population leads to three conclusions. On the one hand, they show that there is a gender- related difference with women being considerably more sensitive compared with men. On the other hand, children do not exhibit increased sensitivities exceeding those of women. Also, the reduction factors as chosen by ICNIRP to account for biological uncertainties do not leave space for an additional “safety margin” to prevent from adverse effects in case of additional contributions of electromagnetic fields from mobile sources or due to unintended overload conditions, [12].

CONCLUSION

We consider the exposure in ZMF the lowest exposure in a very low electromagnetic field and should be a good point for studies about dose-effect relationship.

In this study was presented a different lymphocytes sensitivity to inducted DNA damage between healthy and disease donors for zero magnetic field exposure.

Knowing the action mechanism of very low electromagnetic field is also, very important to be discussed in relation with different sensitivities between exposed groups.

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STUDIA UNIVERSITATIS BABEŞ-BOLYAI, AMBIENTUM, LIII, 1-2, 2008

LONG-TERM VARIABILITY IN PRECIPITATIONS IN CLUJ-NAPOCA

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ABSTRACT. Long-Term Variability in Precipitations in Cluj-Napoca. The main goal of this study is the analysis of long-term precipitations variability in Cluj-Napoca. The analysis is based on time series of climatic data from Cluj-Napoca weather station with a series of 100 year (1907 - 2006). The non-parametric tests to determine temporal trends in climatic data sets are used. The evolution of the observed parameter was complemented by the analysis of the secular trend. The definition of extreme precipitation events is based on the Standardized Precipitation Index (SPI). The period for calculating the SPI values was 48 months. The parametric analysis of long-term drought and wet events proves that the greatest part of the major and medium intensity events are associated with the same periods of pluvial deficit or excess.

Keywords*:* *precipitations, variability, trend, Standardized Precipitation Index (SPI), Cluj-Napoca*

1. INTRODUCTION

The study represents a small part in the general context of the present climate changes, identified in larger or smaller spatial scales. The main goal of this work is to analyze the long-term variability in precipitations amounts in Cluj-Napoca Weather Station. Thus, long-term trends were determined together with wet and dry events identified using 48-months Standard Precipitations Index (SPI). Statistical analyses made are based on the climatic datasets recorded at Cluj-Napoca Weather Stations of the National Meteorological Administration Network (table 1). Monthly, seasonal and annual precipitations data were analyzed for 100 years (1901-2000 to identify wet/dry events and 1907-2006 to identify secular trends). Data sets were provided by National Weather Administration or they were identified in international electronic data basis [8,9]

Table 1.

Geographical position of Cluj-Napoca Weather Station

Weather station	Height	Latitude	Longitude
Cluj-Napoca	410 m	46°47' N	23°34' E

2. METHODS

Precipitations datasets for the period 1901-2000 were processed using SPI method. Wet and dry events were defined according to 48-month SPI (table 2).

The Standardized Precipitation Index was proposed in 1993 by T. McKee, N. Doesken and J. Kleist, from Colorado State University, U.S.A. and it is an index based on the probability of precipitation for any time scale.

In Romania, the method was already successfully used for other studies on precipitations (Croitoru, 2006, Holobâcă & Croitoru, 2000, Holobâcă et al., 2008).

Technically, the SPI is the number of standard deviations that the observed value would deviate from the long-term mean, for a normally distributed random variable.

Worldwide, SPI is nowadays used because it explicitly expresses the fact that it is possible to simultaneously experience wet conditions on one or more time scales, and dry conditions at other time scales, often a difficult concept to convey in simple terms to decision-makers. Due to the fact that a separate SPI value is calculated for different time scales covering the last 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 15, 18, 24, 30, 36, 48, 60, and 72 months, according to user necessities, and ending on the last day of the latest month, the index is considered one of the most flexible in this field.

The 48-months SPI compares the precipitations for that period with the same 48-months period over the historical record. Otherwise, the computed value corresponding to a specific month take into account precipitations amounts of the 47 previous months also. This ensured the inertia of evolution for the SPI values against the short-term variations of the amount of precipitations *(*Edgard, 2007).

Table 2.

Criteria for identification the intensity of dry and wet event (after McKee et al., 1993)

SPI values	Feature
+ 2.0 or above	Extremely wet
+1.99 ... +1.50	Very wet
+1.49 ... +1.00	Moderately wet
+0.99 ... -0.99	Near normal
-1.00 ... -1.49	Moderately dry
-1.50 ... -1.99	Very dry
-2.0 or below	Extremely dry

The method proposed by McKee et al. (1993) has the advantage of ensuring the identification of quantitative parameters of the drought and wet events. A drought event is defined as a period in which the SPI is constantly negative and the SPI index is less than or equal to -1.0. A wet event implies a series of positive SPI values with a maximum intensity above +1.0. The parameters used for the calculations are: the beginning, the end, the duration, the maximum intensity and the magnitude of the event (Croioru, 2006).

The duration of an event is calculated as the difference between the moment of its beginning and that of its ending.

The magnitude of the event is the cumulative measure of the intensity of the sequences of pluvial deficit and excess and is defined as the sum of the SPI values that correspond to the sequences of negative or positive values:

$$\mathbf{M = -}\left(\sum_{j}^{x} SPIi\right);$$

where :

- M – magnitude;
- j – first month of the wet/dry event;
- x – last month of the wet/dry event;
- SPI_i – SPI values of *jx* sequences calculated over a period of *i* months.

Maximum intensity is considered the highest/lowest SPI values in the wet/dry event.

The monthly average intensity was calculated as magnitude divided with the duration (in months) of each event.

In order to identify the existence of possible trends in the temporal evolution of precipitations amounts, the monthly, seasonal and annual datasets were checked with statistical significance tests. Non-parametric trend tests were preferred, as they do not imply a pre-existing distribution of data sequences (e.g., a normal one). Thus, in order to determine the presence of significant monotonous trends (whether ascending or descending), the Mann-Kendall test was used. To approximate the moment of the beginning and of the end of a statistically significant trend and/or a climatic change, the Mann-Kendall sequential test was used (Mann, 1945, Kendall, 1975). The statistical values of these tests make it possible to accept or to reject the null hypothesis I_0 for different thresholds of statistical significance. The bilateral variant of the tests was used for the 95% significance threshold.

Mann-Kendall tests usually are used in the environmental sciences because they are simple, robust and take into consideration the lacks of data and the values situated below the detection limit in the analyzed datasets.

The distance-weighted least squares method was also used to identify trends in the datasets because the method fits a curve to the data by using the following procedure: a polynomial (second-order) regression is calculated for each value on the *X* variable scale to determine the corresponding *Y* value so that the influence of the individual data points on the regression decreases with their distance from the particular *X* value.

3. RESULTS

The use of 48 months-SPI allows to emphasize, for Cluj-Napoca, 10 wet/dry events with main characteristics presented in table 3.

Table 3.

Wet/dry event parameters in Cluj-Napoca (1901-2000)

jx	j	x	d	Im	M	I_I
-	1916 IX	1920 VII	46	1	28	+0.61
+	1920 VIII	1923 IX	38	-1	25	-0.66
-	1923 X	1926 VI	32	-1	25	-0.78
+	1932 VI	1937 IV	59	1	39	+0.66
+	1938 IV	1943 IX	69	2	85	+1.23
-	1943 XI	1969 VI	307	-1	272	-0.89
+	1969 VIII	1974 IV	59	1	59	+1.00
-	1976 IV	1980 V	49	-1	34	-0.69
-	1983 VII	1997 VI	167	-1	140	-0.84
+	1997 VII	2000 XII	42	1	31	+0.73

Legend:
+: wet event;
–: dry event;
j: first month of the event;
x: last month of the event;
d: length of the event (months);
Im: maximum intensity of SPI during the event;
M: magnitude of the event;
I_I: monthly average intensity.

One can see that considering the length and magnitude parameters, the most important events were the dry ones. Thus, period November 1943 – June 1967 cumulated 307 months (25 years and 7 months), and the period July 1983 – June 1997 cumulated a total of 167 months (13 years and 11 months). The two highest magnitude values (272 and respectively, 140) are also characteristics to the same two events. The maximum intensity of –1.00 was specific to both events.

The longest wet event occurred between April 1938 and September 1943 and it cumulated „only" 69 months (5 years and 9 months). The magnitude of 85 and the maximum intensity of +2.00 are associated to the same wet event. Thus, is confirmed that, in the analyzed location, wet events are shorter but more intense than dry events.

Values resulted after applying the Mann-Kendall test for the statistical series of 100 years, in Cluj-Napoca, are presented in table 4.

Table 4.

Results of Mann-Kendall test, with statistical significance level equal or grater than 0.1 (Cluj-Napoca, 1907-2006)

Month	Trend value	Season	Trend value	Annual	Trend value
I	-0.32	Winter	0.57	Annual	-0.31
II	-0.58	Spring	-0.23		
III	0.17	Summer	-0.38		
IV	-0.19	Autumn	-0.40		
V	-1.00				
VI	0.05				
VII	0.19				

Month	Trend value	Season	Trend value	Annual	Trend value
VIII	-0.80				
IX	0.40				
X	-1.30				
XI	0.26				
XII	1.41				

Trends found in precipitations amounts, both in annual and seasonal or monthly scales are not statistically significant. The 0.1 significance level for which the values in table 5 are calculated for, is to high that the trends be considered real.

Consequently, one can consider that, in Cluj-Napoca, in the last 100 years no trends in the precipitation amounts are recorded. The lowest trend value is associated to June, with 0.05 mm/year (0.5 mm/decade), while the highest values are calculated for October (-1.30 mm/year, respectively -13.0 mm/decade) for descending trends, and December for ascending trends (1.41 mm/year, respectively 14.1 mm/decade). Taking into account that both months are characterized, as average values, by very low monthly amounts of precipitation, if the trends were considered statistically significant, they would be very important.

Annual precipitations trends identified by using the lowest quarters method and the distance-weighted least squares method are presented in figure 1.

The Mann-Kendall sequential test was used to identify changes in the trends (the beginning and the end of an climate change) and indicates that there were no such changes in the last 100 years, in Cluj-Napoca (figure 2).

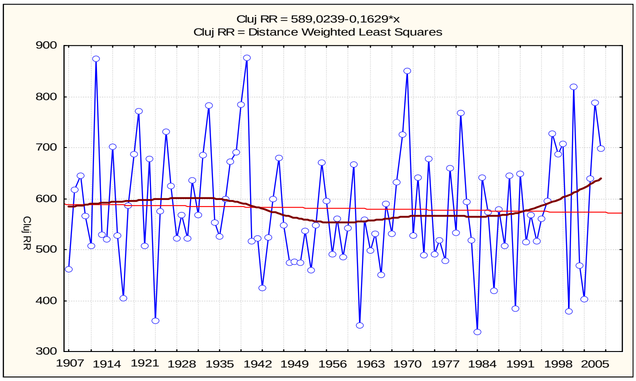

Fig. 1. *Trend of annual precipitations amounts identified by using lowest quarters and the distance-weighted least squares methods, Cluj-Napoca (1907-2006)(the straight line in the chart is the linear trend calculated by using the lowest quarters method and the smooth line represents the polynomial trend calculated by using the distance-weighted least squares method)*

CONCLUSIONS

Time series analyses of annual, seasonal and monthly precipitations amounts recorded in Cluj-Napoca allows emphasize few important conclusions:

a. using 48-months SPI method, ten wet/dry events were identified during XXth century;

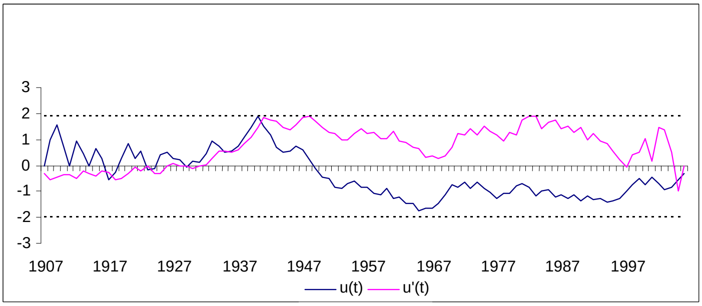

Fig. 2. *Mann-Kendal sequential test applied to Cluj-Napoca annual precipitation values (1907-2006): u(t) – direct series; u'(t) – retrograde series*

b. dry events are longer and with a higher magnitude than wet events, while wet events are more intense than dry events;

c. identified trends are not statistically significant either for annual values or seasonal/monthly values;

d. descending trends are common both for annual and for seasonal/monthly values with 0.1 significance level (considered not statistically significant).

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CAN PRESENT ROMANIAN AGRICULTURE BE USED AS A GUIDE TO THE SWEDISH AGRICULTURAL HISTORY?

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ABSTRACT. Can Present Romanian Agriculture be Used as a Guide to the Swedish Agricultural History? Agriculture in the Romanian mountains is still run in a traditional way, compared to most European countries. Most probably, there are large resemblances between the present agriculture in Romania and past agriculture in countries more penetrated by modernization. The aim of this paper is to se if Romania can be used as a reference for research on pre-industrial agriculture in Sweden. The comparison shows large resemblances concerning the fundamental agricultural system. Similar techniques are utilized in the use of grassland (hay meadows and pastures) for feeding livestock summer and winter. Also the land ownership for different land use types is comparable. However, farms are smaller and villages much larger in Romania compared to Sweden. There are also differences in some details concerning the use of grassland, arable fields and forest.

Keywords: *agriculture, history, Sweden, Romania.*

A COMPARISON BETWEEN PRE INDUSTRIAL SWEDISH AGRICULTURE AND PRESENT AGRICULTURE IN THE ROMANIAN MOUNTAINS

INTRODUCTION

Coming to the Romanian Carpathians and Apuseni mountains is for a Swedish agricultural historian like a travel through time. Walking in the landscape and talking to peasants gives images of how grasslands may have looked like and how they were used in the past in Sweden. The country may offer possibilities to study, in situ, the agricultural system that researchers are trying to unravel through historical maps and documents. In order not to jump into fast conclusions it is necessary to compare the present agriculture of Romania and what is known about the pre-industrial Swedish agriculture. The aim of the comparison is to clarify some of the prerequisites for using Romania as a reference to find out more about Swedish agriculture in the past.

BACKGROUND

Swedish agricultural history

Already with the first agriculture during the Neolithic, livestock was introduced in Sweden. Cows, sheep, goats and pigs came first and horses slightly later. The agriculture consisted of small fields that were cultivated only for a couple of years.

New areas were cleared and burned every year causing ambulating arable fields. Livestock were not stalled but were kept grazing outdoors during the winters (Welinder et al, 1998).

During the Iron Age, agriculture went through a complete reorganization and the land was divided into infields and outland. This new agricultural system basically persisted until the late 19th century. The phrase "Meadow is the mother of arable fields" refers to the significance of grasslands in the system. The hay meadows produced winter fodder for the livestock. The size and productivity of hay meadows decided the number of livestock that could be kept during winter and thereby the amount of manure that could be spread on arable fields. During the summer, the animals were grazing in the outland or in small enclosures. In south Sweden the outland was situated close to the village centre enabling the animals to return to the farm every evening. In the north, grazing had to be found further away from the villages why livestock was kept in summer farms for several summer months. There the milk was processed into cheese and butter by the woman herders. All over Sweden, livestock has been herded with the purpose to lead the animals to good grazing spots, protect them against predatory animals and thieves and to protect meadows and arable fields against hungry grazers. Fences has partially had the same function in stopping livestock from entering grounds that carried growing crops and leading livestock to different enclosures during the summer (Welinder et al 1998, Kardell 2006).

Despite the fact that the agricultural system has persisted, changes occurred within the framework of the system. Periods of increasing population were followed by expansion of the agriculture (16th century, 18th century onwards) while periods of population decrease were associated with land abandonment (1350-1500, 17th century). Every expansion was associated with new technique and shift in the balance of arable land, hay meadows and pastures.

During the second half of the 19th century another agricultural system was introduced including crop rotation, animal breeding and chemical fertilizers. The introduction of the crop rotation system enabled fodder production on arable land why the use of natural hay meadows and outland grazing decreased. When fertilizers came arable production was possible with without having livestock. In the 20th century the production on arable land and forest was disconnected for the first time in history. Earlier the outland and infield were essential parts of the same system.

Romanian agricultural history

Romania has been well known as the granary of the Ottoman Empire and the country continued to export cereals also after the independence 1878. The exporting farms only made out 2.5 per cent of the total number of farms, but these managed as much as 40 per cent of the land (Evans, 1924).

The Romanian agriculture has gone through several land reforms. The aims of the reforms of 1864 (in the old kingdom) and 1848 (in the Hungarian provinces) were to even out the land ownership, decrease the polarisation to create a larger number of self sustained farm units. But the distributed allotments were too small to be self subsistent which lead to exchange of land between land owners and polarisation once more. Between 1864 and 1905 the number of landless people in the old kingdom increased from 60 000 to 300 000. This polarisation eventually lead to another land reform through two laws in 1918 and 1921. The aim was again to split large farm units and offer land to smallholders. But also the second land reform failed. Only two thirds of the entitled person actually received land, and those who did were given too small units to be self subsistent. This resulted in decreased production, partly due to the fact that land was unmanaged in the time lags of the transition of land. But the reform also resulted in political calmness among farmers. 1941, more than half of the farms in Romania were smaller than 3 hectares, only 10 per cent of the farmers land that exceeded 10 hectares (Nilsson, 2002).

During the communist time (1948-1989), and primarily during the 1960´s, arable land and the ownership of livestock was collectivised into larger units again. The collectivisation primarily concerned the plains and in smaller extent the mountainous areas. At the same time, the state was building up the industries of Romania. The proportion of the population involved in farming decreased as a result from the demand of work power in industries (Romania, Working document may 1998).

After the revolution of 1989 yet another agricultural reform followed. Land under collectivization was returned to people, either the same persons or relatives to the persons that had been owners before the land was put under joint management. Not only the same number of hectares was returned, but exactly the same pieces of land were given back. Another result from the revolution was that the industries became uncertain sources of income, why many found it better to return to agriculture to be able to make a living. In many respects, the agriculture returned to the level before the communist time. Decades of large-scale production were wiped out and replaced by small self subsistent family farms. In cases when people tried to coordinate agriculture in collective farms they usually failed since people were now suspicious to cooperation. Many agricultural buildings were destroyed after the revolution and the machines were still owned by the state, out of reach from private farmers (Lange 2004, Swain & Vince 2001).

Present Romanian agriculture

Parts of the plains of Transylvania and Banat are today cultivated with relatively modern methods like large monocultures worked with tractor power, improved with fertilizers. In the plains of Moldova and Wallachia horse power is still dominating. The use of fertilizers is also common in Wallachia (Rey et al, 2006). The division of land in small parcels with different land owners is still dominating in large parts of the plains. In most communes more than half the population are working with agriculture. In the regions with many horses the agriculture is more labour-intensive, i.e. there is a higher number of persons (active in the agriculture) per hectare arable land (Rey et al, 2006).

In the whole Carpathians and Apuseni mountains, grassland dominates the open land (Rey et al, 2006). More than 81 per cent of the agricultural land in the mountains consists of pastures and hay meadows, traditionally used. The typical farm is a self subsistent family farm, cultivating very small plots of arable land with maize, beans, potatoes and different vegetables. The most important part of the agriculture is animal husbandry, dependent on large areas of grassland. Hay meadows are managed by hand with scythe and rake to collect hay for the winter demand. Pastures can be either close to or distant from the village, where the animals are attended by herdsmen through out the summer.

People in the Romanian mountains are usually also dependent on income from the forest. The process of returning the forest from the state to private owners is still going on. The forest in the hand of the state may not be used by the villagers, unless each outtake of trees is paid for. There is also wooded land, old pasture land that has become covered with forest or bushes during years of extensive or no management. This type of forest usually belongs to the village and the trees may be cut down in order to regain the pasture land. Since 1989 large areas has been deforested (Surd & Petrescu, 2007). This counts both for state and private forest and village owned pasture-forest. Deforestation creates new grassland, generally used for grazing.

Since the turn of the millennium the number of people active in agriculture has declined drastically, but the total rural population shows a smaller decline (Rey et al, 2006). This can be explained by the large numbers of people from the rural areas that are working abroad, primarily in Italy and Spain, to compensate for income from closed industries or mines or just to enable an improved standard of living in Romania.

THE COMPARISON

In this paper I will compare the agricultural condition, primarily in the mountainous parts, in Romania with the Swedish pre-industrial agriculture (during the 18th and 19th centuries as far as 1850). The focus will be on the use of grasslands and less attention will be paid to cultivation of arable fields (including fruit- and wine-growing) and forests. However the two latter land use types will sometimes be included since these are a part of the same agricultural system and can not be completely separated from grassland use. The comparison includes aspects of 1) production direction of the agriculture, 2) the basic agricultural system 3) size of farms and villages and 4) the ownership of land.

Production direction

In Sweden and Romania the direction of agriculture follows to a large extent topography. Plains usually have soils suitable for cultivation but limited forest resources, why arable production is dominating. The agriculture in upland areas, on the other hand, are dominated by livestock husbandry and milk production since there are smaller areas for cultivation but abundant land for grazing. All agriculture can not be classified to be either plains or upland agriculture as I have done here to simplify. In reality there are a number of agricultural production strategies that does not fit in any of these descriptions.

In Sweden, the plains are concentrated to the south and central parts of the country, mainly within the counties Skåne, Östergötland, Västergötland, Södermanland, Närke and Uppland. The whole of Norrland in (the north) and Småland (in the south) are the largest upland areas. In Romania the plains are situated south of the Carpathian crescent (large parts of Wallachia), east of the Carpathians (eastern Moldova), in the western country (Banat and Crişana) and the Transylvanian plateau (inside the Carpathian crescent). The upland, (mountainous) areas are made out of the Carpathians and Apuseni Mountains (Măhăra et al, 2006). In a national perspective Romania has a larger proportion of plains compared to Sweden. The mountains of Romania, that still holds a traditional agriculture, can roughly be said to correspond with the Swedish uplands.

The production direction is also visible in the composition of livestock. Traditionally, farms in Swedish plains has had a larger proportion of working animals (horses and oxen for working in the fields) and pigs, while upland regions had a larger proportion of cows, sheep and in some places goats (Myrdal & Söderberg 2002, Dahlström 2006). In Romania the same pattern can be seen. Horses, tractors and pigs are more abundant in the plains. Cattle are concentrated to mountainous areas. Milk production is particularly important in west Suceava and Maramureş but also in some plain regions like Cluj, Arad and Vrancea. Sheep are common all over the country but less abundant in Wallachia (Rey et al 2006).

The basic agricultural system and elements within the system

In the Swedish agricultural system of pre-industrial times the land was divided after the dominating way of using the land, into gardens, arable fields, hay meadow, enclosed pastures and outland (Fig 1). In the *garden* there was both place for houses and smaller cultivations. *The arable fields* were used for cultivation of human food, first mainly rye and barley. During the 17th century wheat, oats and root vegetables like potato became more common. The winter fodder for animals was collected from *hay meadows*. Grass and herbs was cut with a scythe during July and August (Fig 2). The hay was dried on the ground or on drying-racks before being transported to the barns for winter storage. Branches were also cut from trees (pollarding) in order to use the dried leaves for winter fodder (Fig 3). Another way to collect the leaves was to cut the trees close to the ground (coppicing) (Fig 4). Coppicing was used when the primary aim was to get fire wood and was common in some parts of Sweden. Gardens, arable fields and hay meadows together made out the *infields*.

PLATE I

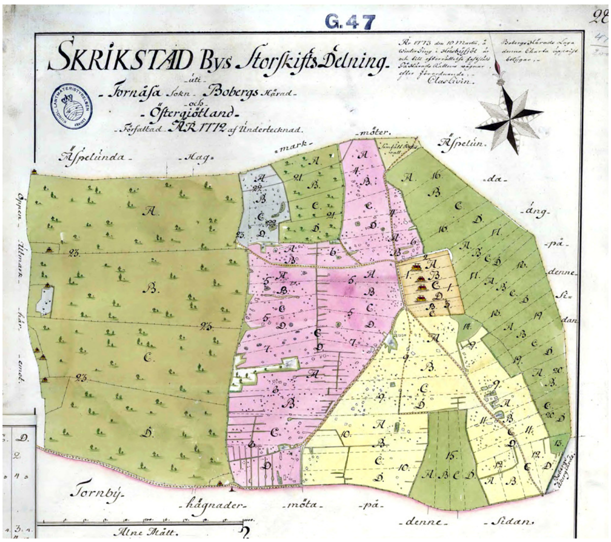

Fig. 1*. Swedish cadastral map from 1730, showing the outline of land use. In the center-right is the village consisting of four farms. Arable fields are surrounding the village in the north, west and south (in yellow and grey). The main hay meadow is in the east (green). Outland pasture is in the far west (brownish green). Source: Archive of the national land survey of Sweden, Gävle D23-12:2*

Fig. 2. *Mowing of a hay meadow in the village Dămuc (Neamț, Romania). Photo: Anna Dahlström, September 2007*.

PLATE II

Fig. 3. *Pollarded trees in the hay meadow of the national park Garphyttan. Photo: Anna Dahlström, June 2007*.

Fig. 4. *Coppiced trees in Maramureş, Romania. Photo: Anna Dahlström, August 2005.*

PLATE III

Fig. 5. *Open and wooded pasture in Fornåsa village, Sweden. Photo: Anna Dahlström, June 2006.*

In the *enclosed pastures* the livestock grazed during the summer. These were situated in the boundaries between infields and the *outland,* the latter was used for grazing but without being enclosed with fences. The location of former outlands corresponds well with forested land today but historically the outland was not always forested. Indeed, the outland was where the largest supply of trees were to be found but the outland could be everything from completely open to covered with rather dense forest, however not as dense as the forests of today (Fig 5). In large parts of *Norrland* (the northern two thirds of Sweden) we also had summer farms, *fäbodar*. Places where people and livestock lived during the summer months to utilize fodder resources at some distance from the village. The summer farm can actually be characterized as outland, used in a specific way since people and livestock lived there and processed milk from cows, sheep and goats.

The use of arable fields, hay meadows and pastures/outland was not as simple as described above. In practice all land use types were used both for cultivation, grazing and collecting of winter fodder. Except from producing human food, the arable fields were used for grazing after the harvest or, for fallow land, during the whole summer. The straw made up an important part of the winter fodder. Hay meadows were used for grazing after the mowing was finished. Parts of the hay meadows were sometimes tilled into temporary fields where cereals or other crops could be cultivated. The use of outland was not restricted to grazing and forestry. Leaves were collected for winter fodder and temporary arable fields were created through burn-beating.

Agriculture in the mountainous parts of Romania is still conducted within the same agricultural system as in pre-industrial Sweden. There is a similar division of land into infields and outland. The houses are situated in gardens where vegetables are cultivated. Arable fields are situated close to the gardens. The main crops in the plains are maize, beans, wheat and in the mountains, potatoes. Adjacent to arable fields are hay meadows for the collecting of winter fodder (Fig 2). The pastures are situated further away, either bordering to the meadows or further away as summer farms *stână* (Fig 6). There are large similarities between both countries since they share the basic agricultural system. There are, however, differences or possible differences in the use of grasslands that I want to emphasize.

Fig. 6. *The summer farm at Vârtop (Alba, Romania). Photo: Anna Dahlström, June 2007.*

There are also deviations from the basic system regions in Romanian mountains like in west Suceava where the cultivation of arable fields practically has ceased. Instead, milk production is central and except for small gardens and occasional potato-fields there are only hay meadows, pastures and forest. Strictly speaking this is no longer the same agricultural system as described above since a central feature of the system is the use of manure on arable fields.

Hay meadows

The use of temporary arable fields, *lindor*, in Swedish hay meadows are known to have covered large areas in Norrland (Larsson, 2005). They also occurred in south Sweden but abundance of temporary fields is still unknown. In Romania, the use of temporary fields is extensive at least in Apuseni Mountains. A few years of cultivation is followed by several years of grass, used for winter fodder. As a result, arable fields are ambulating in the meadows. For several years it is clear to see the plots of previous cultivations and the sequence of cultivation. This methods probably improves both fields and hay meadows. Hay meadow gains from the added manure from the years of cultivation, resulting in higher hay production. Temporary fields probably suffer less from insects and fungii that may negatively affect cultivations. If the years of cultivation in one plot becomes more frequent it is rather the case of a crop rotation system, especially if the fodder crops (grass, clover or other leguminous herbs) are sown. This type of cultivation is olso present in the mountainous areas of Romania, for example in Maramureş, and really represents element of the agricultural system that in Sweden followed after 1850.

The hay in Romania is generally stored inside the meadow in haystacks. These are built in a way that preserves the hay from rain and snow. Only the outer layer is affected and the stacks can remain for several years. In Sweden, there were no hay stacks but hay was stored indoors in hay barns. Hay barns are actually used also in parts of Romania, like in the eastern Carpathians. Drying hay on drying racks, like in Sweden, is very common in the north-eastern highlands of Carpathians.

The most productive hay meadows in Romania are mowed twice every summer. These are usually situated close to the village and may have been improved with fertilizers, ploughing and cultivation. Through Swedish historical sources hay meadows are only known to have been mowed once in the summer.

The Swedish hay meadows seem generally to have been grazed in late summer, starting a couple of weeks after finished mowing. In Romania this is not the case everywhere. There are both meadows that are used for late summer grazing and meadows that are only used for cutting hay. Nevertheless it can not be excluded that some Swedish hay meadows escaped from grazing, although this has probably not been searched for in the historical sources.

Romanian farmers seem to generally have abandoned the habit of using leaves for winterfodder, but it still occurrs, and is probably more common in bad hay-years.

Pastures, summer farms and forest

The Swedish summer farms were not restricted to only grazing and milk-handling. Hay meadows were common in association with the summer farms and sometimes there were also small cultivated plots. In Romania I have only seen summer farms used for grazing and handling of milk, all hay meadows seem to be situated close to the village. The herding in Sweden was always conducted by woman or children. This differs from the usual European herding system where the herdsmen were and still in Romania are adult men.

Another possible difference is that the forests in Romania often are spatially separated from the pastures. That counts at lest for the state owned forests. Forests on previous pasture land are, as mentioned, being brought back to pastures and are during the process used both as forest and pastures. There are also areas where wooded land and grassland (both hay meadows and pastures) are intermingled into a mosaic of glades and denser groups of trees (Fig 7). In Sweden the outland contained both pastures and forests, but whether these were separated to different areas within the outland has not been possible to read out from the historical sources.

PLATE IV

Fig. 7. *Grassland mixed with wooded areas in the village Niştoreşti (Vrancea, Romania). Photo. Anna Dahlström, September 2007.*

The use of Romanian forests is today restricted to logging and at some places grazing. The Swedish forest (outland) was also used for leaf-fodder collection, burn-beating, charcoal burning and potash production. Multiple uses of forest like the one in pre-industrial Sweden probably creates a tree-and bush-layer that is more open and varied than in forests used for logging only. The Swedish outland was also more clearly a part of the agricultural system through its multiple functions, than the Romanian forest. Theoretically is it possible to run a Romanian mountain farm without owing a forest if the farmers have other pastures and can get hold of wood when needed. Practically, however, the forest is probably necessary since agriculture primarily provides food, not money, while the forest may give monetary income to the household.

Size of farms and villages

The farming units are usually smaller in Romania than in Swedish farms. This concerns both the acreage of the land and the number of livestock. In 19th century Sweden farms in two parishes in the southern uplands (Småland and Östergötland) had 1-3 horses, about 12-19 cattle and 8-16 sheep (Dahlström, 2006). In the uplands of Norrland the farms had on an average 8 cows and a single horse (Gadd, 2000). In the village Botiza (Maramureş) and five villages in the commune Vizantea-Livezi (Vrancea) each farm have on an average 1 cow, 4 sheep and much less than one horse (Agricultrual statistics from the communes of Botiza and Vizantea-Livezi).

The land is more difficult to compare since the registration differs between the countries. Usually common pastures and summer farms are not included in the statistics. The Swedish farms in the two parishes had between 4 and 39 hectares of arable fields, 9-17 hectares of hay meadow and 34-120 hectares of pasture. In Romania the arable fields amounted to 0.5 hectares (Botiza) and 1.5 hectares (Vizantea-Livezi). Hay meadows were between 1 and 2 hectares and pastures less than one hectare (common lands not included).

If the comparison is extended to the village-level the opposite relationship stands out. The Romanian villages are usually large, like the typical central European village. The village of Botiza consists of nearly 900 households. The five villages in the commune Vizantea-Livezi of nearly 1100 households, that is about 200 per village. In most mountainous areas the villages are long and stretched at the bottom of a valley in connection to a river. In the plateau of the Apuseni Mountains the villages are smaller and more spread in the landscape, concentrated to water sources (Onac et al, 2007). The Swedish villages are smaller than the typical Romanian village, more like in the Apuseni Mountains, on an average 2 households in Kristberg and 10 in Alseda.

Ownership of land

The ownership of land has had different meanings in different times in the Swedish history. Before the land reforms in 18th and 19th centuries it did nor make a big difference for the Swedish farmer whether he owned the land or not. The important thing was to have the right to manage the land. Non until the mid 19th century it became important to be able to sell land, and therefore to be the single owner (Ågren, 1992). In Sweden, the arable fields were privately owned early in history. Every farm owned and cultivated their strips of land, but the timing of cultivation and the chosen crop were decided by the village community since fields belonging to the different farmers were situated in the same enclosure and the grazing of the field was common. The hay meadows were also privately owned, but were jointly managed. Instead of dividing the meadow land, the dried hay was divided after mowing according to the ownership situation. The pastures could either be privately or commonly owned. Privately owned pastures became more general during the 19th century and were often fenced in smaller enclosures. Common land more often consisted of unfenced large outlands. The grazing in common pastures was regulated according to the share in the village community. The same goes more or less for pastures at summer farms with the difference that people from one village could have the right to grazing resources at different summer farms and several villages could share one summer farm.

Also in Romania the arable fields are privately owned and cultivated. This is also true for hay meadows, which is different from the Swedish situation. The only commonly owned and used land is pastureland, both close to the villages and at summer farms.

SUMMARY AND CONCLUSIONS

The existence of resemblances between the Swedish pre industrial agriculture and the present agriculture of mountainous Romania was a starting point for this paper and for my interest in Romania, as an agricultural historian. What I have done in this paper is to compare the fundamental agricultural systems and point out some details within the system that is known through literature or observed in field studies. But, it must be noted that there are gaps of knowledge concerning both countries that, when filled, may somewhat alter the picture presented here. More knowledge is needed about the details about the management of grassland, for example the use of fire or the management regimes.

The agriculture of Romanian mountains can primarily be compared with the Swedish uplands. The basic system shows large similarities with the pre-industrial Swedish system. Extensive hay meadows are managed with similar techniques as in Sweden, with scythes, and rakes. Trees are still pollarded for wood (and leaves). At least in some areas temporary arable fields are present in hay meadows. The situation of land ownership is similar. Arable fields and hay meadow are privately owned, while pastures are usually commonly owned by the village.

One difference is the small farm units and large villages in Romania compared to Sweden. The cultivated crops are also different. Concerning hay meadows, the storage of hay differs. In Sweden the hay were kept in barns during the winter, in Romania in the characteristic hay stacks (although barns are also present). In Sweden, the hay harvest was usually followed by grazing. In Romania this is not always the case. Instead some meadows are mown twice. However, this difference may also be due to lack of sources that may show possible cases of non-grazing of Swedish hay meadows. Another lack of knowledge is the abundance and frequency of temporary arable fields in south Sweden. In Romania I have primarily seen it in use in the Apuseni Mountains, but there are field traces in the landscape that indicate that it may have been present also in other areas. In many places, crop rotation systems are in use, which can be seen as a development of the temporary field system or a transition to another agricultural system. The pastures are probably used similarly in the both countries, however a spatial separation of pastures and forest is more common in Romania than in pre-industrial Sweden.

To sum up, the comparison has shown large resemblances between the present agriculture in Romania and the pre-industrial agriculture of Sweden. This is encouraging for Swedish researchers that are interested in using Romania as a reference land for Swedish land use history. There are gaps of knowledge about Swedish land use history that is difficult to fill through archival studies only. Parallel studies in Romania will enable new insights about Swedish management regimes. This, together with to large extent a shared species pool, gives good precondition for Swedish grassland biologists to learn more about grassland management and its significance for biodiversity, that in Romania can be studied in a landscape perspective including a large variety of management regimes.

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STUDIA UNIVERSITATIS BABEŞ-BOLYAI, AMBIENTUM, LIII, 1-2, 2008

SPATIAL DISTRIBUTION AND MOBILITY OF THE HEAVY METALS IN SOILS FROM BAIA MARE AREA

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ABSTRACT. Spatial Distribution and Mobility of the Heavy Metals in Soils from Baia Mare Area. In Baia Mare area there have been studied the control factors of the spatial distribution and mobility within soil profile for Pb, Cu, Zn, Cd in various type of soils, eutricambosol, luvosol, aluviosol. Lead concentration is higher (1429 - 6563 ppm) in Romplumb areal compared to the Cuprom areal (909 - 995 ppm) and is associated with the rich in humus horizon, in pH acid condition, with high values of the cation exchange capacity. The mobility of the Pb within the soil profile is slow or inexistent. Copper presents the concentrations between 90 - 199 ppm in organo-mineral horizons in Cuprom areal. Cadmium in the A horizons of the soil profiles presents the highest concentrations in Romplumb areal (5.74 - 19.43 ppm) followed by the ones in Cuprom areal (1.20-9.44 ppm). For Cd is specific the mobility within the soil profiles with an increase of the content in the intermediate horizons up to 50 ppm in Romplumb areal and with the maintenance of the values that exceed the maximum allowable limit in the areal (Cuprom). The Zn pollution is excessive in Romplumb areal (377 - 3296 ppm) and moderate in Cuprom areal (536 - 252 ppm). Using the loading/pollution index, calculated for the 0 - 10 cm and 10 - 50 cm depth, the spatial distribution and mobility of the heavy metals maps have been made. This has been done by using GIS, ArcView technology.

Keywords: *heavy metals, loading/pollution index, spatial distribution, GIS technology*

1. INTRODUCTION

The soils from Baia Mare area, situated in the influence area of the two Romplumb and Cuprom metallurgical plants occupy representative areals for the urban area, forest and agricultural fields. The accumulation of the analysed toxic metals, Pb, Zn, Cd, Cu, in the soils of the two areals, is today recognized as being a semnificative problem, representing a major risk both for the human health and for the ecology systems, being felt at over 1m depth. This owes to the fact that heavy metals are not biodegradable, having the tendency of accumulation and persistence in soils, (Kabata-Pendias and Dudka, 1991). The presence of heavy metals in excess, in soils, reduce plants growth, (Jjemba, 2005). Pollution with heavy metals in adjacent soils of the industrial sources, affects the microorganisms activity of soil, (Wang, et al. 2007). The C:N report, is generally high for the organo-minerals horizons from the soils profiles of the two areals, from 10,8 to 25,7 in Romplumb areal and from 12,2 to 22,1 in Cuprom areal. These suggest limitation of the biological activity of nitrogen fixation, the cause being the increased concentration of heavy metals, according to the studies by Khan and Scullion (2002). The numerous researches that have been realized in the Baia Mare area, indicate a multiple pollution with heavy metals (Pb, Cd, Cu, Zn), (Răuță, et al., 1997, Lăcătuşu, et al., 1994).

2. MATERIALS AND METHODS

The soils of the two areals Romplumb and Cuprom have been studied within the soil profiles. Soil profiles location criteria have been: the distance from the pollution source, the position related with the direction of dominante winds and soil types that are representative for each areal. The sampling points have been localized with Global Position System (GPS). The soils samples were taken from each pedogenetic horizon. The spatial and vertical distribution (in soils profiles) of heavy metals concentration, specific to each soil type, is different in accordance with the metal and the specific processes of migration, in relation with the physical-chemical properties of soils. Variation of the spatial distribution with the depth of anlaysed heavy metals Pb, Zn, Cu, Cd, has been achieved on the basis of the loading/pollution index, after the proposed method by Lăcătuşu (1995).

The graphic representation has been achieved using the GIS, Arc View technology, at two depth of sampling, specific to soil profiles, depth of 0-10 cm and of 10-50 cm. The soil level 0-10 cm correspond, generally, in every profiles with A pedogenetic horizon, and the second level, of 10 to 50 cm correspond to horizons of type B, and eluvial layer E (luvosols case). The spatial distribution has been achieved in a separate way in the two areals, having in view their homogeneity under the aspect of soil type, of physical-chemical properties of soils, the distance toward the sources of pollution.

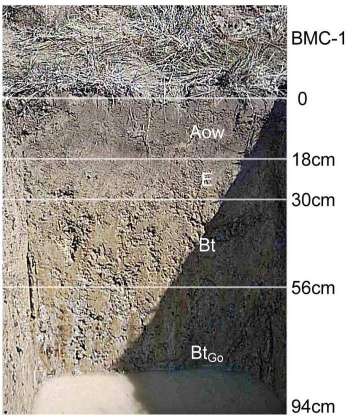

Fig. 1. *BMC-1 Luvosol (LV).*

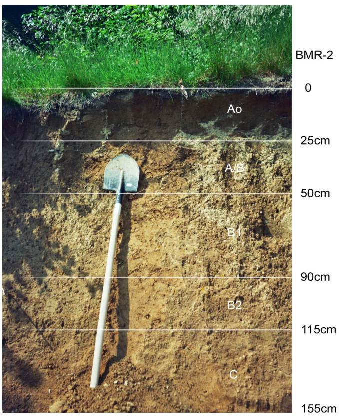

Fig. 2. *BMR-2 Eutricambosol (EC).*

2.1. Soil types

The main soil types from the studied areals are represented by: luvosol, eutricambosol, aluviosol, stagnosol, separated after Florea and Munteanu (2003).

Luvosols are the most frequent soils in the Cuprom areal. Clay are present in significant amounts in these soils. The parental material is represented by marls. The processes of eluviation/illuviation are very intensely within the soil profile. The soil profile is well differentiated: Aow-E-Bt_{Go}-C, (Fig. 1).

Eutricambosols are specific to Romplumb areal, they appear on limited surfaces at the junction of Firiza valley with Săsar and on Firiza valley. The relief on which they have formed, is represented by terraces with a good drainage. The soil profile is simple: Ao-A/B-Bv-C, (Fig. 2).

Aluviosols develop along Săsar River. The A horizon of these soils have a 20 cm thickness, and is disposed directly over the alluvial deposits of Săsar River, represented by: gravel deposits and coarse-grained sand. Between horizon A and C there can be delimited a horizon of transition A/C with thickness of 10 to 15 cm.

2.2. Physical-chemical properties of soils

Physical-chemical properties of soils of the two areals have been determined on the basis of the samples of the soil collected from the pedogenetic horizons of soil profiles. It have been taken into consideration the texture determination that influences the contamination level with heavy metals by the weight of clay fraction. The clay content is variable, being 31.4% in Romplumb areal and 28.4% in Cuprom areal. The texture class of the soil studied is represented by clay loam, silty clay loam and silt loam. As regards the chemical properties of soils, there have been analysed: the pH, humus content, the cation exchange capacity which influences the concentration of heavy metals at certain horizons. The obtained results from the analysis of agrochemical properties demonstrated the low content of nutritive elements: N, P, K.

The pH's values for the soils from Baia Mare area corresponds with the strong acid reaction state, (4.25 Romplumb areal and 4.20 Cuprom areal). After the humus content, the studied soil samples are included in the category of low contents for Cuprom areal, 1.20% and in category of high contents for Romplumb areal, 3.90%. The cation exchange capacity of soil samples from studied areas is moderated (18.29 me/100gsoil) for luvosols (Cuprom areal) and high (29.63 me/100gsoil) for eutricambosols in Romplumb areal. In the two areals, the humus content being so low, it is possible that clay fractions to be the main means of retention of heavy metals, (Griffin et al., 1997) together with Fe and Mn oxides, (McKenzie 1980).

3. RESULTS AND DISCUSSIONS

3.1. *Heavy metals in soil profiles and relation with chemical properties*

Lead presents excessive concentrations, associated with the horizons rich in humus, (Fig. 3), with acid pH conditions, and with high values of the cation exchange capacity, (Fig. 4).

Copper presents concentrations between 90 - 199 ppm in the organo-minerals horizons of soil profiles from Cuprom areal. Within soil profiles, the Cu concentrations are low under the normal values of 20ppm. Cadmium, in horizons A of soil profiles, presents the highest concentrations in Romplumb areal of 5.74 to 19.43ppm, followed by those of Cuprom areal (1.20 to 9.44ppm).

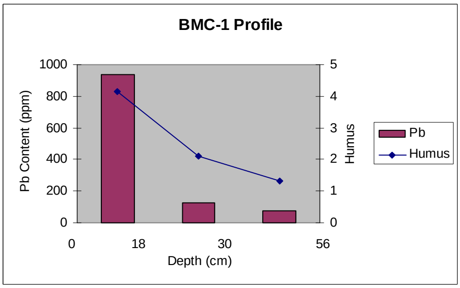

Fig. 3. *Variation of Pb content and humus in Cuprom areal.*

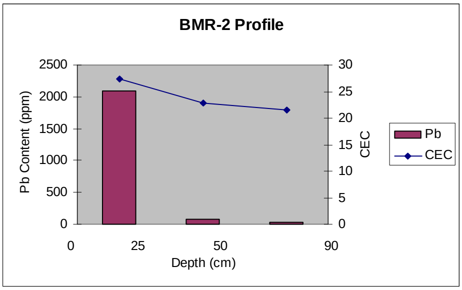

Fig.4. *Variation of Pb content and cation exchange capacity in Romplumb area.*

For cadmium, it can be seen a mobility on soil profile. The content of Cd increase in intermediate horizons up till 50ppm (Romplumb) with value maintenance that excel the specific values of maximum allowable limit, after (Kloke 1980), in (Cuprom) areal. High concentrations of cadmium from intermediate horizons of soil profiles from Romplumb areal, correlate with lower values of the cation exchange capacity and with higher values of the pH, (Fig. 5).

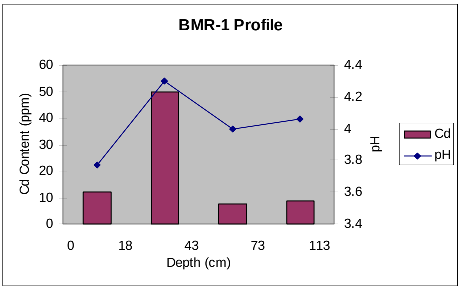

Fig. 5. *Variation of Cd content and Ph in Romplumb areal.*

Zinc migration on soil profile, with maximum concentrations or variables at intermediate and inferior horizons level, compared with those two from superficial horizon level is the combined effect of behavior of this metal under the aspect of higher mobility, and of alkaline low reaction of soils.

3.2. Spatial and vertical distribution of loading/pollution index of soils

To emphasize the level of soil pollution, caused by the activities that take place in the two metallurgical plants: S.C Romplumb S.A and S.C. Cuprom S.A., there had been realized maps of loading/pollution index. The maps represents maths pattern making of the values of loading/pollution index and they are obtained with the GIS program help by the intercalation of the obtained values for soil profiles, achieved in the two areas.

Calculation of loading/pollution index has been done in accordance with the method of establishment of pollution level of soils, suggested by Lăcătuşu (1995). This method consists in establishing the level of loading or pollution of a soil with a certain heavy metal, on the basis of calculation formulae taken form the Holland system. So, the loading/pollution index represents the rapport between the content determined in soil sample for heavy metal (Pb, Zn, Cu, and Cd) and the reference value obtained with the formula from holland normative specific to "level A" of soil loading. The reference values for the four analysed heavy metals, there have been calculated on the basis of formulae that has as variables the content of organic matter and clay size fraction <0.002mm of soil samples. So, the reference value for each metal is calculated with the following relations: 50+C+OM – for Pb; 50+1.5 (2C+OM) – for Zn; 15+0.6 (C+OM) for Cu; 0.4+0.007 (C+3OM) – for Cd; (C – clay content; OM – organic matter content). Making a rapport of metal content from chemical analysis at reference values, there are obtained the values specific to the loading/pollution index. The subunitary values of this index characterize the soil loading field and superunitary index values – the pollution field, (Lăcătuşu, 1995). The two fields have been divided in range of values that define a very low, slight, moderate, severe, very severe loading and slight, moderate, severe, very severe and excessive pollution.

On the basis of the loading/pollution index calculated for the four metals at the two depths of sampling, 0-10cm and 10-50 cm, there has been realized the maps of spatial and vertical distribution. The values of index have been multiplied with 100 in order to be compatible with the program of maps design.

For Cuprom areal, the maximum values in the surface layer, are registered in the east areal (in conditions of dominant wind from west). In the depth of the soil profile keep the same distribution, with a low migration from E to W, due to eluvial processes (at level of E horizon specific to luvosols from this area). For Pb, in Cuprom areal, at both depths prevails pollution with a low differentiation between the two depths from to very severe and excessive pollution in the first 10 cm to moderate to slight pollution up till 50 cm. This situation confirm Pb association with rich organic matter horizon of soil profiles.

For Zn, at depth of 10 cm, prevails slight pollution to moderate pollution with transitions at deph of 50 cm from slight pollution to very severe loading. By verifying the spatial distribution of Zn at 0 to 10 cm depth, it has been seen the separation of the two fields of moderate pollution to very severe loading on NW-SE direction, which corresponds with the prevail direction of winds and air currents.

For Cu, in the upper part of the soil profiles, prevails the field specific to pollution with transition from slight pollution to very severe pollution on North-West/South-East direction, (Fig. 6).

Cadmium, both on surface and in deepness, covers the field of slight pollution to very severe pollution. Distribution representations at the two depths, suggest Cd mobility with depth through individuallization of an areal specific to a very severe loading field at 50 cm depth, (Fig. 7).

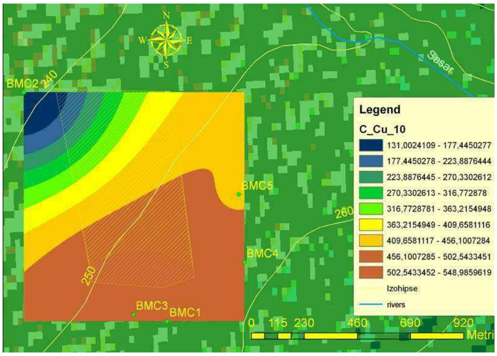

Fig. 6*. Spatial distribution of Cu in Cuprom areal at 0-10 cm depth.*

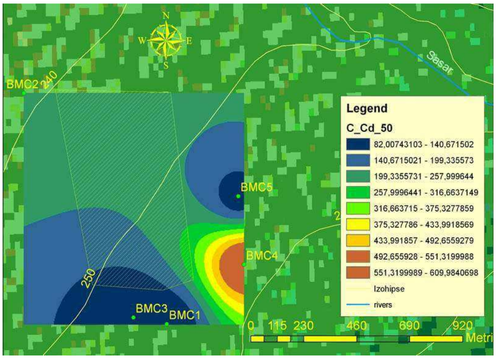

Fig. 7. *Spatial distribution of Cd in Cuprom areal at 10-50 cm depth.*

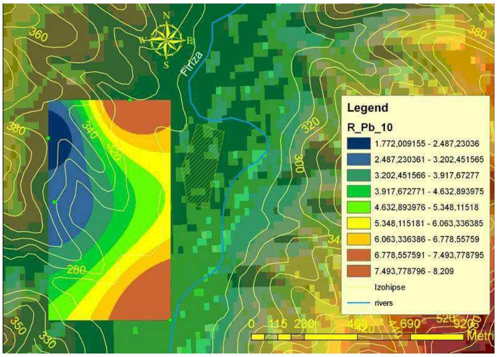

Fig. 8*. Spatial distribution of Pb in Romplumb areal at 0-10 cm depth.*

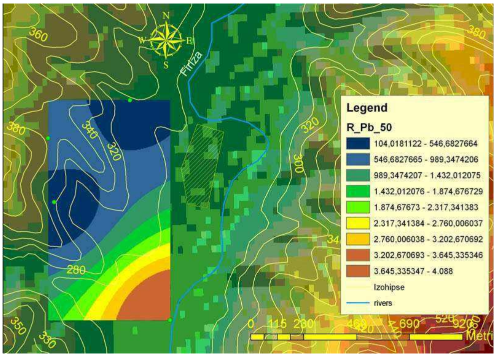

Fig. 9*. Spatial distribution of Pb in Romplumb areal at 10-50 cm depth.*

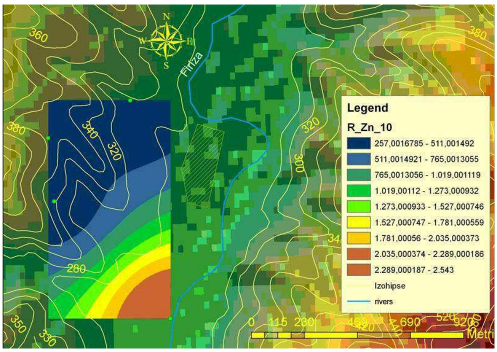

Fig. 10. *Spatial distribution of Zn in Romplumb areal at 0-10cm depth.*

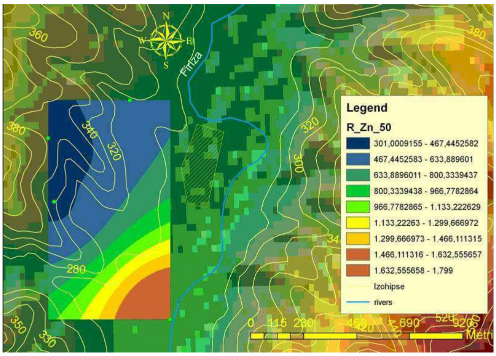

Fig. 11. *Spatial distribution of Zn in Romplumb areal at 10-50cm depth.*

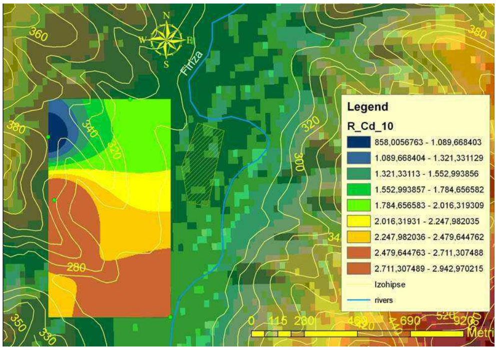

Fig. 12. *Spatial distribution of Cd in Romplumb areal at 0-10cm depth.*

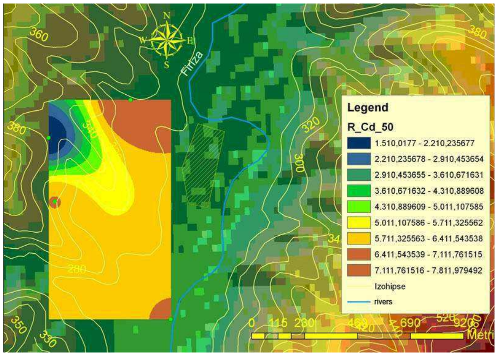

Fig. 13. *Spatial distribution of Cd in Romplumb areal at 0-50cm depth.*

For Romplumb areal, the most representative for the excessive pollution field is Pb at depth level of 0 to 10 cm (Fig. 8). At depth of 50 cm prevails slight pollution level (Fig. 9).

Zinc from Romplumb areal covers the slight pollution field to excessive pollution for both depths, (Fig. 10, Fig. 11). Cadmium covers the excessive pollution field at both depths of representation (Fig. 12, Fig. 13). It can be also seen the extension in area at both depths.

After the Cu examination, it is remarked a limited areal, specific to the very severe pollution field, at 0-10 cm depth, which is in relation with the accumulation in the parental material, specific to the alluvial area of Firiza valley.

4. CONCLUSIONS

Spatial distribution and mobility of heavy metals Pb, Zn, Cd, Cu in the soil profiles of Baia Mare area, was controlled by variable factors from the soil surface (pollution sources, atmospheric currents direction) or on the soil profile (soil type, pH, humus content, cation exchange capacity). The studied soils of the two areals present chemical properties that through specific mechanisms influence concentration and migration sense of heavy metals.

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STUDIA UNIVERSITATIS BABEŞ-BOLYAI, AMBIENTUM, LIII, 1-2, 2008

THE HEAVY METALS POLLUTION AND THE ADVERSE EFFECTS ON HUMAN HEALTH

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ABSTRACT. The Heavy Metals Pollution and the Adverse Effects on Human Health. The present paper presents some aspects impact of metals on environment and human health. The studied area is Copsa Mica, which alongside Baia Mare and Zlatna are known as the representative areas for nonferrous metallurgy in Romania. There are presented concentration data about 13 metals (including heavy metals) in the dump and on the premises of SOMETRA SA measured with X-ray fluorescence technique, and also about the biomarkers of exposure and effect upon children exposed to lead.

Keywords: *heavy metals, nonferrous metallurgy, lead, biomarkers*

INTRODUCTION

Urbanization is most often associated with an economic, productive, development that can lead to major benefit for the health and environment.

In some countries, Romania is included, the lack of an adequate infrastructure and services for controlling the pollution, environmental and health related problems, all lead to the situation in which costs related to water supply, health services, hygiene, garbage collection both for domestic and for industrial source are much higher and, in fact transferred in ht environment and health budget. Recently, an increase in the people's awareness was noticed regarding the risk of exposures from the physical and chemical agents from the environment that can harm the health of the people exposed [Gurzau E.S., Cucu M., 1997; Gurzau E.S.et al., 1997].

The level of pollution in Copsa Mica is one of the major environmental problem and risk for the health of the population in Romania. [Gurzau E.S.et al.,1997, Gurzau E.S. et al., 2002].

It is well known that in some concentrations, most of the metals are essential to life, but in excess, those same metals could be dangerous. Similarly, the prolonged exposure to high concentrations of heavy metals can affect people's health and can have severe effects in the long term. The heavy metals that pose greatest risk to health are lead (Pb), arsenic (As), cadmium (Cd) and mercury (Hg). Heavy metals were largely used in industry starting the XIXth century, thus being present in the environment nowadays. Sources of heavy metals include: emissions from industries that use solid fuels, especially charcoals, smelters and other industries (Pb, Cd and As), incinerators (Hg and Cd), mining lucrative facilities, pesticides industries and wood preservatives (As and Cr), fertilizers for soils (Cd for example can be found in phosphate based fertilizers), old house water supply systems (Pb) and old house paintings (Pb) [CDC's National Exposure Report, 2001, ATSDR. Toxicological Profile for Lead (Update), *Agency for Toxic Substances and Disease Registry*, Atlanta, GA. 1999, EPA Integrated Risk Information System. Lead and compounds (inorganic), *National Center for Environmental Assessment,* Washington, DC.].

The heavy metals can appear in the environment because of natural processes. As an example, in some parts of the USA, natural sediment of As suffered geological processes and as a result, the underground water layer was contaminated with the potential risk for contaminating also the drinking water supply [CDC's National Exposure Report, 2001].

Once released in the environment, the heavy metals have the potential to remain in the environment for decades or even centuries thus elevating the risk for human exposure. People are potentially at risk for intoxication throughout contact with contaminated soils and industrial discards or contaminated food. Food sources such as vegetables, cereals, fruits, fish and shell-fish could be contaminated with heavy metals from soil and water.

The present paper deals with just a small part of an much larger study conducted by the Environmental Health Center in Copsa Mica with the specified goal of evaluating the risk of exposure to high heavy metals concentrations. This paper is a summary of the aspects linked to the heavy metals concentration in the dump area inside Sometra Copsa Mica factory, the lab method used for the evaluation of the distribution of those heavy metals and some health related data in a selected population group with high susceptibility to lead poisoning.

METHODS

Soil samples were taken from the 30 cm depth of the dump inside the "SC SOMETRA SA" and from drilling inside the perimeter of the same factory in April-May 2004 time interval.The samples were collected in polyethylene bags, free of metals. The samples were labeled, sealed and transported to the lab were they were processed for X ray fluorescence technique (K-X-ray Fluorescence 720 SL, made by Niton in 2002).

The data entry was done using Microsoft Excel 5.0. Database was then imported in Stata 5.0 using Stata-Transfer module. The statistical analysis was performed using Stata 5.0. summary descriptive statistics and more advanced techniques were performed. Central tendency measurements (mean and median, frequency), measures of the variability of the data (interval, minim, maxim values, percentiles, standard deviation, variance, Skewness and Kurtosis coefficients).

A sample of 43 children age between 4 and 6 exposed to lead was studied. Exposure biomarkers (blood lead level) and effect markers (weight height status) were measured. Blood lead level was measured using anode stripped volt metric techniques using Lead Care System. The measures of both exposure and effect biomarkers were then compared and then the results were compared using statistical techniques.

RESULTS

Twelve metals were analyze (Pb, Zn, Cu, Cd, Sn, Mn, As, Cr, Hg, Mb, Ni, Se) in soil samples and sediments collected from the sterile dump and within the SC SMOETRA SA perimeter.

A total of 60 soil and sediment samples were collected. 8 out of them (13.33%) were collected from the dump area of the SC SOMETRA SA, 31 samples (51.67%) were collected from smelter from a 30 cm depth, 16 samples were collected from drilling within the SC SOMETRA SA perimeter and 5 samples (8.33%) were collected from sediment collected within the CS SOMETRA SA perimeter.

Analysis of the distribution of the mean concentration of heavy metals in soil collected from the dump, showed, with the few exception of some metals (Sn – mean concentration 293.8 ppm, threshold limit 300 ppm, Cr – mean concentration 0 ppm, threshold limit 600 ppm, Hg–mean concentration 0 ppm, threshold limit 10 ppm, Mo–mean concentration 30.8 ppm, threshold limit 40 ppm, Ni–mean concentration 0 ppm, threshold limit 500 ppm, Se–mean concentration 18.5 ppm, threshold limit 20 ppm) values over the intervention thresholds.

On the premises, in soil samples collected from the 30 cm depths, with the exception of Sn (283.2 ppm measured value and 300 ppm threshold limit), Mn (1950.2 ppm measured value and 4000 ppm threshold limit), Cr (44.8 ppm measured value and 600 ppm threshold limit) and Mo (1.7 ppm measured value and 40 ppm threshold limit) the concentrations of all other heavy metals exceeded the intervention threshold.

From the data on the distribution of heavy metals in soil, depending on the sampling site, we could conclude that, overall, the highest mean concentration of the heavy metals in soil were measured on the premises of the factory with the exception of Cd, Sn, Mn, Mo.

The comparative analysis using t test for mean concentrations of heavy metals in soil in different sampling sites, confirmed that, in general, the heavy metals concentrations were higher on the premises than in the dump area with the exception of few heavy metals (Cd, Sn, Mn, Mo) but the differences were not statistical significant for any of the metals. On the other hand, the difference in concentration in Mn and Mo between the dump and the premises was statistical significant (the dump Mn concentration – 6794.39 as opposed to the premises concentration – 1950.24 ppm and the dump Mo concentration of 30.82 ppm as opposed to the premises concentration) ($p=0.05$ for Mn mean concentration comparison and $p=0.000$ for Mo mean concentration comparison).

The comparative statistical analysis using t test for means of heavy metals concentrations in soil samples collected on the premises, from different depths, revealed the fact that, in general, the concentrations of heavy metals in soil decreased with the increase of depth, the differences were statistical significant for Pb (p=0.01), Zn (p=0.003), Sn (p=0.01), As (p=0.008) and Ni (p=0.03). The following heavy metals were exceptions: Cu – concentration 9346.5 versus 7892.75, Cr – concentration 53.7 versus 44.82, Hg – concentration 585.2 versus 349.29, Se – concentration 36.85 versus 20.22 and Mn – concentration 21451.03 versus 1950.24, but the observed differences is not statistical significant in all cases except Mn (p=0.02).

The comparative statistical analysis using t test for means of heavy metals concentrations in soil and sediment at the premises of the factory indicated the fact that the concentrations of heavy metals were higher in soil as compared to the sediment with one exception, Mn (2109.92 in the sediment as opposed with the concentration of 1950.24 in soil) but the difference is not statistical significant.

X ray fluorescence technique (quite new for Romania and new for the rest of the world) allows samples readings using 2 radioactive sources (Cd109 and Americiu 240) and generates X ray spectrum for the analyzed samples. The reading takes about 120 seconds to complete, with a sensitivity of 1 sigma (0.001 ppm) and accuracy of 99.99% [Method 6200 – Field Portable X-Ray Fluorescence Spectrometry For The Determination Of Elemental Concentration In Soil And Sediments, Sackett D., Martin K., 1998, Stephen S., 1997, Lead Dust Clearance Levels Guaranteed On-Site, 1999, Stephen S., 1997].

Evaluation of the children exposure to lead from the area in vicinity with SOMETRA SA through lead blood level measurements using Lead Care System showed an average of 39 µg/dL with a standard deviation of 15 µg/dL, the minimum measured value being 19µg/dL, and in one case the value exceeded 65 µg/dL. Statistical comparison performed on the lead blood levels by gender revealed that the average for boys (40.22 µg/dL) is higher than for girls (36.61 µg/dL) but the difference is not statistical significant.

The results of the comparison between blood lead level average values recorded in children living at different distances of the potential lead exposure source were not highlighted as statistically significant differences.

Investigating the weight and height for children age between 4 and 14 years from Copsa Mica area showed that the average weight and height decrease with the increase of the lead blood level (the decrease being statistical significant). The results of the advanced statistical analysis indicated the loss of the statistical significance of the correlation between the lead blood levels and the weight/height indicators after statistically controlling for errors factors identified in the previous steps.

The heavy metals may affect severely the human health including slowing growth and development of the organism, cancer appearance, serious sickening of internal organs, sickening of the nervous system and in extreme cases may cause even death. Exposure to some metals, as Hg and Pb may also lead to development of a condition in which the immunitary system of a person attacks his/her own cells. The result of this phenomenon are diseases of the joints (rheumatoid arthritis), diseases of the kidneys, circulatory system or nervous system. [CDC's National Exposure Report, 2001, ATSDR. Toxicological Profile for Lead, 1999].

The heavy metals represent a major risk for the development of the human embryo, for new-born and children. Some metals, such as Pb and Hg penetrate easily the placenta and may affect the brain [CDC's National Exposure Report, 2001]. Exposure during childhood to some metals may cause learning difficulties, may affect memory and the nervous system and even lead to behavioural deviations such as increasing agressivity and hiperactivity. In case of exposure to high levels of heavy metals they may affect the brain irreversibly. Children may accumulate via food ingestion higher doses of heavy metals because they consume a greater quantity of food than the adults, related to their own weight. The children also absorb much easier heavy metals via the intestinal tract than the adults [Lead Dust Clearance Levels Guaranteed On-Site, 1999, Stephen S., 1997].

A growth in the level of pollution with Pb especially in urban areas is observed in countries in course of development, and the children are the most affected by this pollution in proportion of up to 90% as shown by recent studies performed in China, Bangladesh, Africa [CDC's National Exposure Report, 2001, EPA Integrated Risk Information System. Lead and compounds (inorganic), *National Center for Environmental Assessment*]. Both local industries and gases generated as a result of using fuels with additives based on Pb are in these cases responsible for the pollution with Pb.

Children have a greater susceptibility to sickening as a result of lead poisoning because it affects the development of the nervous system. Children absorb and retain a greater quantity of Pb than adults related to their own weight and moreover most of the Pb ingested in the child's organism it remains in his/her body. Antenatal exposure was associated with a series of effects upon the child such as: premature birth, low weight at birth, immunity decrease and hipersensibility, diminution of the learning and memorizing capacity, intelligence level decrease, slowing the growth process, problems in kidney functioning, agressive behaviour. These effects may persist even after the child grows. [ATSDR. Toxicological Profile for Lead, 1999, EPA Integrated Risk Information System. Lead and compounds (inorganic), *National Center for Environmental Assessment*]

Pb is one of the few chemical elements for which effects upon health may be related directly to the measured blood lead level. Measuring the blood lead concentration is the preffered method for Pb exposure evaluation and its effcets upon health because reflects both the Pb quantity recently ingested and the one accumulated in other tissues, both in children and adults. The measured blood lead concentration for children is considered as being elevated if it is higher or equal to 10 µg/dL. Recent studies performed in the U.S. EPA showed that effects upon the central nervous system and upon development in children may appear starting from a concentration level of 2,5 µg/dL [CDC's National Exposure Report, 2001].

CONCLUSION

1. Distribution of the concentration of metals in soil in accordance with the sampling points reflect the fact that with the exception of cadmium, tin, manganese

and molybdenum for which the concentrations in soil were more elevated at the level of the waste dump of SC SOMETRA SA the highest average values of the concentrations of metals in soil were recorded in the premises of SC SOMETRA SA.

2. The difference between the two locations in terms of concentrations of heavy metals in soil is not statistically significant related to any on the metals, nevertheless in case of manganese and molybdenum the difference of concentration between the waste dump and the premises (their concentration being higher in the waste dump - 6794.39 ppm compared to 1950.24 ppm in the premises in case of manganese and respectively 30.82 ppm compared to 1.7 ppm in the premises in case of molybdenum) being statistically significant (in case of manganese p=0.057 and in case of molybdenum p=0.000).

3. The comparative statistical analysis using the t statistic test of average values of concentrations of metals in soil collected from the premises from different depths indicate the fact that generally the concentrations of metals in soil decrease with the increase of depth excepting copper, chrome, mercury, selenium and manganese.

4. The comparative statistical analysis using the t statistic test of average values of concentrations of metals in soil and sediment in the premises indicate the fact that metals are in concentrations statistically significant higher in soil than in the sediment excepting manganese (2109.92 in sediment compared to 1950.24 in soil) but the difference is not statistically significant.

5. The factors to be taken into consideration regarding evaluation of predictible effects in public health are the following: distribution of exposure of population (groups at risk), realtionship exposure-response (variation of response, susceptibile groups), risk cummulation (geographic cummulation of risk factors).

It is requred to research more on the relations between the environment and deseases and this can only be done by working in teams. It is a continuum process that must be improved at the national level with the main goal of more precise understanding of the measures and policies that need to be implemented in the vast domain of the environmental health. There are three asptects that need to be considered:

- Integration of the environment and health fields into macroeconomic policies
- Cost benefit analysis
- Primary care for the environmental health.

The latest two ideeas mentioned above will assure a better understanding of the problems related to the inclusion of the environemntal health field in the investment decisions and programs and their implementation. One aspect requires an atentive and correct abordation: the identification and the evaluation of the risk areas for health and the environment that exist in romania, followed by the proposal of adequate programs for reducing and controling the risk sources.

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RELATION BETWEEN FORESTS AND SETTLEMENTS IN THE CATCHMENT AREA OF THE RIVER FEERNIC

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ABSTRACT. Relation between Forests and Settlements in the Catchment Area of the River Feernic. The extension of the forests in the area of the catchment area of the Feernic had become less and less due to the development of settlements and expanding of agricultural areas. We have studied this process in three periods of time. Near ecological changes, the economic and social effects of landscape modifying features had strengthened. In the 20th century parallel with deforestation, sedimentary processes accelerated, causing prompt elevation of channel floor in the Feernic and its tributaries. These processes, such as slope evolution, soil erosion, sedimentation, floodplain alluviation had accelerated owing to the social activities, such as deforestation, wrong agricultural works, etc. They created state of emergency because of natural disasters: danger of inundation, strengthen of torrents, periodical aridity in drier monthes in the western part of the region and degradation of infrastructure.

Keywords: *deforestation, forest-land extension*

INTRODUCTION

In the foreground of the volcanic plateau in the southwestern part of Călimani-Gurghiu-Harghita mountain chains microregions can be found, joined to different catchment areas. Feernic microregion is situated in the catchment area of the Feernic river. Its area includes the above mentioned volcanic plateau's southwestern part, the hilly regions of the river Târnava Mare and the pediment between the Olt and Mureş rivers. This microregion has an area of 200 km², which is traversed by the 33 km long Feernic river in the direction of northeast-southwest. It is the most important right-hand side tributary of the river Târnava Mare. The river Feernic springs from the brim of the volcanic plateau, at 901 m height. It goes through the Lupeni microbasin, then the Simoneşti-Cobăteşti-basins and its water flows into the Târnava Mare at 395 m height in the eastern part of the town Cristuru-Secuiesc. Firtuş (1062m), the highest peak of the region, is situated in the north. The interfluves go through at 700-1000 m heigh. The surfaces of the studied areas are covered mostly by Pannonian sediments. Sarmatian deposits can be found on the surface only at the mouth of the river Feernic. The formation and evoluation of relief was determined by spatial diversification of neogen deposits and geomorphic activity of the rivers. The valley slopes were denuded quickly due to configurations of the terrain and variations of climate. The horizontal dissection had been 1,3 km/km², the perpendicular dissection had also reached 150-200 km/km². The watercourses of the region had strong denudation and accumulation activities. The morphodynamical processes of valley slopes are the following: erosion due to the veil-like flow of rainwater, fluvial erosion and different forms of slope mass movements. The mean anual temperature is around 7,6°C near the mouth of the river Feernic and it is 7,2-7,4°C on the volcanic plateau. Going uphill the temperature is decreasing. The amount of rainfall depends on the altitude above sea level: about 600 mm in lower relief and above 900 mm on the volcanic plateau.

The catchment area of the river Feernic is a historical-etnograpical region. The southwestern- and central part of the catchment area of the Feernic, with its 14 settlements belong to Simoneşti community (administrative centre of the commune) from 1968. The northeastern part, with its 8 settlements and Sâncel, which is a scattered settlement, belong to Lupeni community (commune).

VEGETATION OF THE CATCHMENT AREA OF THE FEERNIC

The volcanic plateau, the drainage divide surfaces and slopes joined to them are covered by forests.

Beeck-trees (Fagus silvatica), spruce (Pinea excelsa) and mixed forests can be found in the western part of the volcanic plateau (the northern and northeastern part of the studied area). Around Calonda -peak in the volcanic plateau there are sessile oaks (Quercus petraea), spruces (Pinea excelsa) and fir trees (Abies alba).

In the slopes, joined to the volcanic plateau and in the lower interfluves there had been sessile oak-forests in olden times. But most of these places were deforested till nowdays.

Most of the catchment area is covered by pastures. Semiarid (mezo-xerofil) and mezofil plants are characteristic in higher hills and in the shelving areas, which has cooler and wetter microclimate.

In the southern and southwestern slopes semiarid mezoxerofil and xerofil plants are indigenous.

Over 700-800 m, with rising of the ground, the characteristic species of highlands and mountainous pastures can be found.

There are pastures, where different hidrofil species were indigenous, such as sedge (Carex), reed (Phragmites communis) due to the permanent wetter microclimate. This climate is characteristic in basins, in surfaces with little slope angles, in river-heads, which spring from valles slopes, and in lover part of volcanic plateau.

EVALUATION OF FOREST-LAND EXTENSION

In the catchment area of the Feernic today's settlement system had already been established till 1567. Most of the villages are situated in valley bottons, in lower surfaces.

The natural vegetation, the forests receded in direction of interfluves and volcanic plateau step by step, parallel with evaluation and expanding of settlement system.

Evaluation of forest-land extension is summarized and illustrated by ourselves in three periods of time according to our surveying on the 1st and 2nd Austrian military maps and statistical data (Fig. 1.).

We can observe significant differences in the extension of forests on the maps made between 1769-1773. In the lower slopes and the valley-bottoms of the river Feernic and its tributaries there were few forests even in the 18th century. Today's administrative area of Simoneşti community had fewer forest-land extent than the higher situated northeastern part of the catchment area of the river Feernic, belonging to Lupeni community.

The spatial development of settlements, the agricultural utilization of the areas resulted to forest-land lessening.

In 1894 the administrative area of today's Simoneşti was covered by forests in 28,9% and the administrative area of Lupeni in 37,6%. In 1992 the third period of time, which were studied by ourselves, the ratio of forest extension had diminished to 24,3% in the administrative area of Simoneşti and 33,7% in the administrative area of Lupeni.

Table 1.

Evaluation of forest-land extension in the catchment area of the Feernic river

	1764 %	**1894 %**	**1992 % - ha**	**Total area – ha**
The administrativa area of Simoneşti	46,4	28,9	24,3 3164	11829
The administrativa area of Lupeni	55,5	37,6	32,7 4427	13127

We have calculated data of 1764 and 1894 according to our surveying, made on the maps of the age and the data of 1992 are official statistical facts and figures.

LANDSCAPE MODIFYING EFFECTS OF DEFORESTATION

About 70% of the catchment area of the Feernic had been utilized in agriculture: 32% plough-land, 15% pasture, 17%grassland, 6% orchard. The inhabited areas, roads occupy only 4% of the region.

In agricultural areas the cultivated plants are determinant. They were originated from far away and were evolved and produced by people. In half of the agricultural areas cultivated plants are produced, such as: potatoes, sugar beet, fodder-plants, vegetables and cereals. In 1970's a lot of orchards were introduced in significant areas. Only a small number of species had remained from natural vegetation in the studied area.

Near cultivated plants there can be found some species of the potential flora and some harmful species are also present. They got in this region together with cultivated plants. These plants with homogenous composition are poor in species and connected to particular places. Except arborescent vegetation the extent and place of agricultural plants' areas had changed from time to time.

The diminishing of the areas covered by forests is continuing even today. This process led to the change of ecological features, soil erosion and acceleration of landslide.

The effects of economic and ownership change in the last ten years had influenced land use significantly. The wrong use of agricultural works accelerated the soil erosion. We have counted the value of the soil erosion according to MOȚOC M.'s formula. In the valleys of the Feernic and its tributaries the erosion was 6-7 ton/hectare/year (2nd table). In the catchment area of the Feernic the soil erosion touched around 5000 hectares.

Table 2.

The values of soil erosion in the catchment area of the Feernic

Place of surveying	The value of soil erosion Ton/ha/year	Erosion lessing possibilities
Western valley-slope of the Şoaş	8,048	Thickset cutivated plants (5-5,5 ton/hectare/years)
North-eastern valley-slope of Lețchert	9,472	Thickset cutivated plants (5,7-6,2 t/ha/years)
Northern valley-slope of the Feernic in Simoneşti	7,231	Strip of grass cultivated (2,5-3 t/ha/years)
Eastern valley-slope of Bucatariei-creek's upper course	15,378	Embankment
Eastern valley-slope of Bucatariei-creek's lower course	6,412	Strip of grass cultivated (2,5-3 t/ha/years)
Southern valley-slope of Feernic in Mihăileni	16,785	Embankment
Eastern valley-slope of Salom-creek in Bențid	6,649	Thickset cutivated plants (4-4,5 ton/ha/years)
Western valley-slope of Gada-creek in Păltiniş	6,742	Thickset cutivated plants (4-4,5 ton/ha/years)
Southeastern part valley-slope of Feernic in Mihăileni	8,127	Strip of grass cultivated (3-3,5 t/ha/years)

* In the parantheses it can be found the attainable values of soil erosion in case of using the recommended erosion lessing possibilities.

The eroded soil has become coherent alluvium and it is deposited on the smaller slope of river bed. This channel (3rd table) is the thickest in the southern part of Simoneşti on the large slope angles of valley sides: 12,3 m^3/hectare/year. These valley slopes are without forests.

In the western part of the region it is 3-5 m^3/hectare/year and 0,4 m^3/hectare/year is in the center and in the eastern part of the catchment area of the Feernic (ÚJVÁRI J.-MAKFALVI Z. 1986).

Owing to deforestation the modified environmental processes had nagative influences on society and economy. The worsening channels of communication and infrastructure, dwindling of economic possibilities delayed the development of settlements. These processes are reflected in the evoluation of population number (4th table VARGA E. Á. 1998), in demographical changes of villages, situated in disadvantageous natural, social and economic environment and difficult to access.

Table 3.

Transport of alluvial deposits in the catchment area of the Feernic

The name of the creek	Catchement area ha	Total firm deposits m³/year	Unit of firm deposits m³/ha/year
Alba-creek between the spring and Turdeni	103,7	81,6	0,79
Alba-creek	907,5	490,0	0,54
Nicoleni-creek	385,1	258,0	0,70
Baladi-creek	230,6	104,6	0,45
Baladi-creek between the spring and Medişoru Mare	179,9	127,0	0,71
Bencior-creek	147,0	1813,0	12,30
Chedea Mare-creek	205,7	845,0	4,11
Chedea Mică-creek	261,8	1382,0	5,28
Chedea-creek	769,6	1488,0	1,93
Şoaş-creek	760,0	2442,0	3,21

Table 4.

Changing of population number in the catchment area of the Feernic

	1786	1850	1890	1900	1900	1910	1920	1930	1941	1956	1966	1977	1992
Comuna Simonesti	3685	5486	5697	5644	5839	5827	5514	5606	6168	5611	5066	4474	3903
Benţid	195	193	294	319	341	346	299	363	374	328	308	290	190
Cădaciu Mare	267	285	420	386	403	421	374	407	388	378	234	202	159
Cădaciu Mic										115	112	88	84
Cehețel	228	401	420	404	400	429	425	444	467	420	361	281	200
Chedea Mare	113	203	226	183	189	202	182	159	195	177	152	72	29
Chedea Mică	162	176	193	202	197	217	166	174	228	222	215	118	64
Cobăteşti	224	375	498	491	497	530	490	485	521	595	469	444	404
Medişoru Mare	324	586	705	659	664	640	579	562	597	433	409	260	181
Mihăileni	381	491	373	423	458	458	424	418	505	471	462	472	453
Nicoleni	105	133	164	168	195	159	165	169	162	144	127	101	83
Rugăneşti	456	806	674	679	742	669	667	741	841	737	709	647	667
Simoneşti	599	807	877	902	882	915	954	1004	1087	1022	945	1072	1071
Tărceşti	239	374	318	351	342	379	287	339	401	352	270	217	200
Turdeni	392	538	535	477	529	462	502	341	402	332	293	210	118
Comuna Lupeni	2506	3762	4040	4265	4545	4804	4458	4804	5072	5068	4810	4876	4513
Bisericani	400	561	500	589	623	594	545	580	661	658	672	714	632
Bulgăreni	157	237	303	342	374	439	439	401	466	379	354	356	270
Firtuşu	226	343	314	316	307	348	294	301	331	319	274	236	210
Lupeni	597	1051	1120	1133	1204	1327	1282	1358	1432	1550	1482	1796	1871
Morăreni	495	655	705	721	794	771	692	780	751	757	719	724	733
Păltiniş	308	541	628	596	661	582	637	744	786	535	522	535	430
Păuleni	323	374	470	568	582	576	569	640	645	715	515	318	238
Satu Mic										179	120	124	95
Sâncel										119	152	73	34

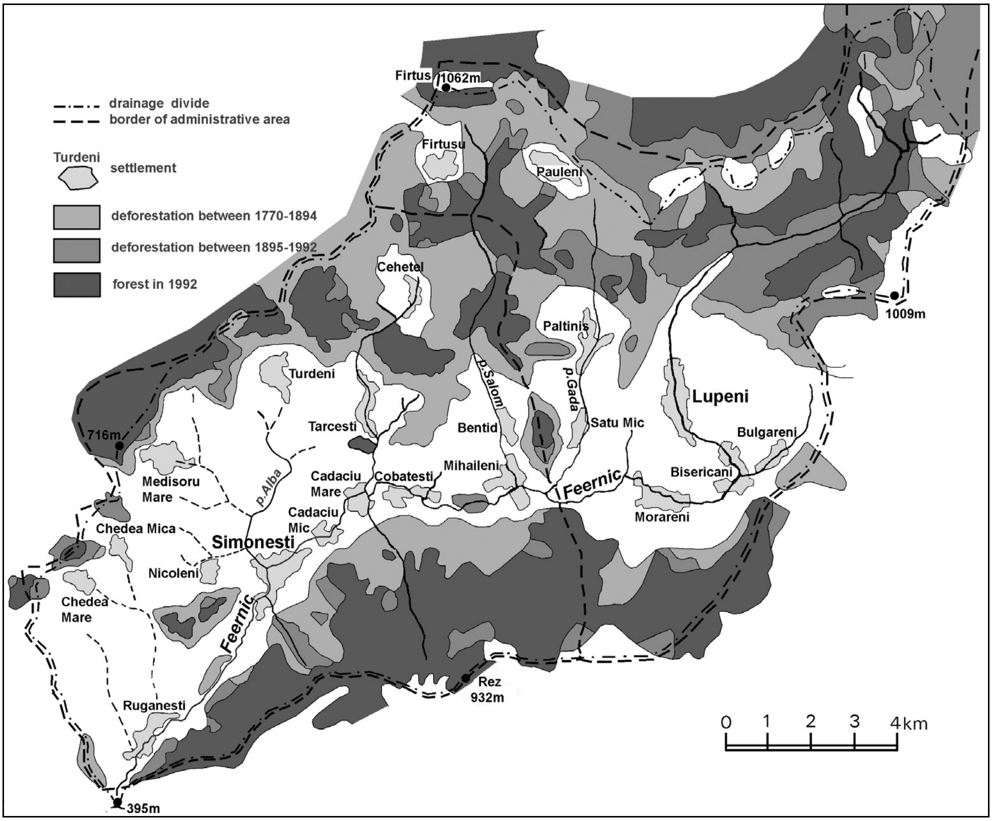

Fig. 1. *Changing of forest land extention in the catchment area of the river Feernic*

The negative effects of human activities could be felt in economic recession: degradation of soil quality and its productivity decrease. Parallel with these processes, geoecological components and relations between them had strengthened. Processes caused by them had been modified, changed and declined.

Studying these features: relations between geoecological components, knowledge and analysis of processes evoked by them, we can explore the reasons of these changes and afford possibility to lessen and eliminate the negative effects.

The disadvantageous natural features strenghten the specific economic and social processes. Nowdays the catchment area of the Feernic is characterized by firm agricultural character, low productivity, few forests, aging and decreasing population.

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URBAN AEROSOL POLLUTION. STUDY CASE: CLUJ-NAPOCA, ROMANIA

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ABSTRACT. Urban Aerosol Pollution. Study Case: Cluj-Napoca, Romania. Aerosols, suspended particles, can be classified by their size, composition and sources. Urban aerosols are created by the industrial and traffic emissions nearby human agglomerations. The importance of studding these aerosols is to be understood because of the effects they cause: weather mechanism and climate change, as well as the effects on health that include asthma, lung cancer, cardiovascular issues, and premature death. European Commission has set limits for the concentration of aerosol particles, limits that can be found in directives 1999/30/EC and 96/62/EC. In Cluj-Napoca, the monitoring of aerosols started in 1995 and the results show that the limit of average concentrations is only exceeded near the source regions such as intense traffic and industrial sites. By analyzing industrial emissions and traffic density relative to atmospheric conditions and terrain highs, combined with the effects of green squares – parks, a risk map of air quality was developed. Modern and efficient methods for aerosol monitoring are LIDAR (Light Detection and Ranging) and DOAS (Differential Optical Absorption Spectroscopy) measurements combined with MAP3D atmospheric modeling. Industrial Depollution techniques are separated in two categories: dry and wet solutions.

Keywords*: air quality, aerosols, dust, suspended particles, traffic pollution, LIDAR*

INTRODUCTION

The urban aerosol domain (and not just urban aerosol, but all kind of aerosols) is one of the challenges of today's science according to the following facts:

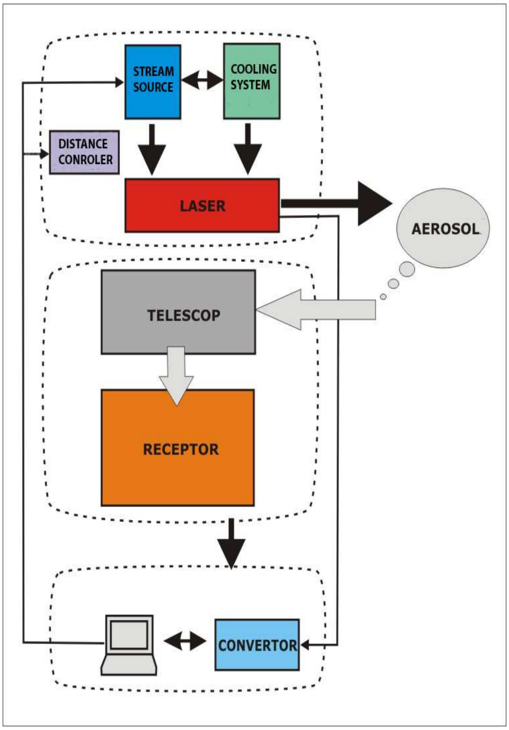
- ✓ The chemical complexity of the aerosols needs a deep study about the composition and the sources of these particles. Secondary aerosols are produced by the reaction and condensation of certain gases, or by cold vapor condensation.
- ✓ There is a great uncertainty about the dimension and composition of the particles that are responsible for human health.
- ✓ The cost of particle emission reduction is very expensive.
- ✓ The disposal of aerosol in the air is a critical factor that influences the manner in which the particle reaches the respiratory system.
- ✓ The chemical composition of aerosols is a critical factor that makes possible not only the influence over the human health, but also over the global warming [1-6].

In the period 1995-2000, the level of atmospheric impurification with suspended particles and sedimentary particles in Romanian cities has grown [7-11]. Generally, these levels of impurification (with sedimentary and suspended particles) are related [12].

SEDIMENTARY AND SUSPENDED PARTICLES OF CLUJ-NAPOCA

For the determination of suspended particles, using the gravimetric method, we used filters (which were dried out and weight). Using this method, we can only find out the weight of the dust, and then estimate the presence of these particles only at a low lever over the ground (a few meters).

For an efficient, modern measuring method, we propose a 3D investigation of the atmosphere using opto-electonical teledetection techniques (based on laser rays), complementary to the standard-classical ground monitoring techniques. This method is based on the interaction between the light rays with the atmospheric pollutants (gases and particles), interaction that creates a signal that can be interpreted and analyzed. The analysis leads to the identification of both concentration and chemical species, based on the micro-physic and optical proprieties of the particles, in a vertical profile. This can be used for a study over the dynamic of the boundary layer, a study that finds importance in the dispersion of the atmospheric pollutants [13].



In the year 2000, an European Network of Aerosol Research with LIDAR (EARLINET) was established. Romania is part of this network. Both **DOAS** technique (Differential Optical Absorption Spectroscopy) as well as **LIDAR** technique (Light Detection and Ranging) are based on the interaction of light rays with the pollutants in the atmosphere (gases and particles), interaction followed by an optical signal that will be analyzed. For the measurement of tropospheric aerosols, a special LIDAR type is used: RAMAN. The obtained data can be then visualized and analyzed with an extension of ARCGIS software called LP360. The accuracy of such system is 6 inch. The technical specifications that must be taken under consideration at this gear, besides the maximum detection distance, are: the wavelength of the laser rays, fervency, speed (in seconds), the telescope optical proprieties (focal distance, mirror diameter etc.), voltage and UV filter.

About the sedimentary particles, there were noticed extended values over the maximum limits (17,00 **g/mp/month**) almost every month during 2004-2005, especially in the Mining Institute area.

Suspended particles are only measured in A.P.M. Cluj area.

In 2004, the average concentration of suspended particles was higher in January, then, after slight decrees, beginning from the middle of February and until the middle of March, there was an ascension which did not reach the values from the beginning of January. Next, it comes a decrees until the minimal value of the year in the middle summer (middle of July). From August until October, the values grow again, then, until the end of the year, they drop. The conclusion is that in summer the values of these particles are lower, a fact that might be caused by the rainfall in this time of the year.

In 2005, the average concentration of suspended particles confirms the conclusions from the previous year: in the summer, the values are less high than in other seasons. Anyway, the values are higher compared to the year 2004. The maximum is measured in November. Sedimentary particles have been measured in the following sites:

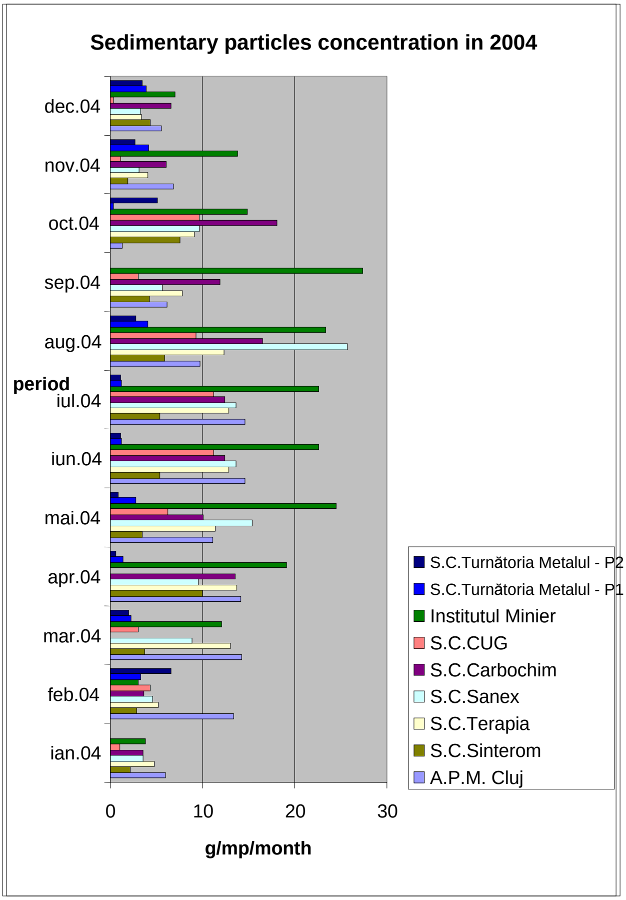
A.P.M. Cluj	S.C. Sinterom	S.C. Terapia	S.C. Sanex	Mining Institute	S.C. CUG	Turnătoria Metalul	S.C. Carbochim

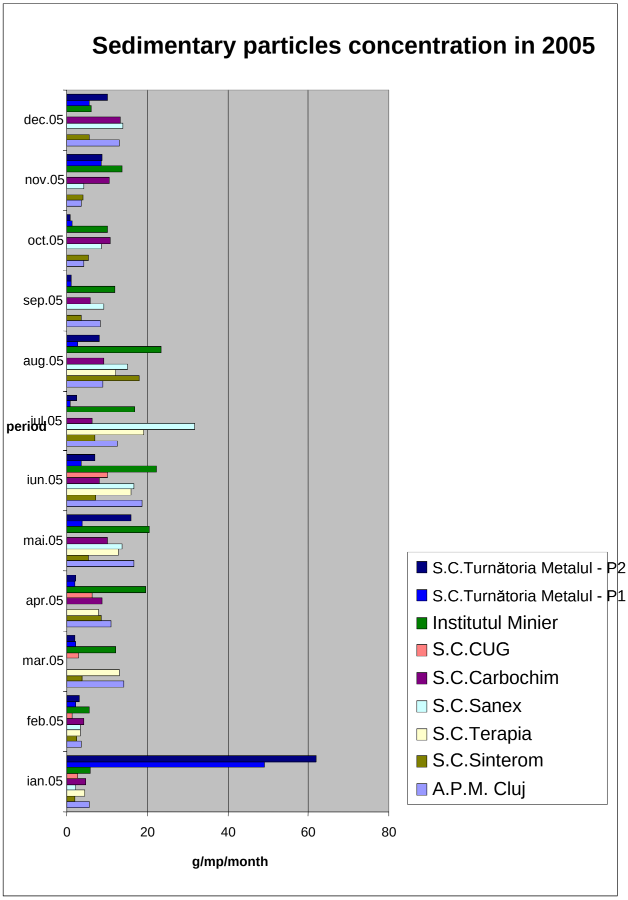
The biggest concentrations of aerosol particles, coming both from industry and construction sites, as well as from traffic, are noticed during autumn. It would be expected to find a maximum during summer, but, because in summer the traffic is not so intense (human activities are interrupted by vacations), the pollutant particles accumulate over the ground and will only play a more active role in the atmosphere in autumn.

In winter and spring, because of the snow fall and snow melting, the particles do not reach large quantities in the atmospheric suspensions. Of great importance in the annual variation of suspended particles, is the number of days with atmospheric rain phenomena.

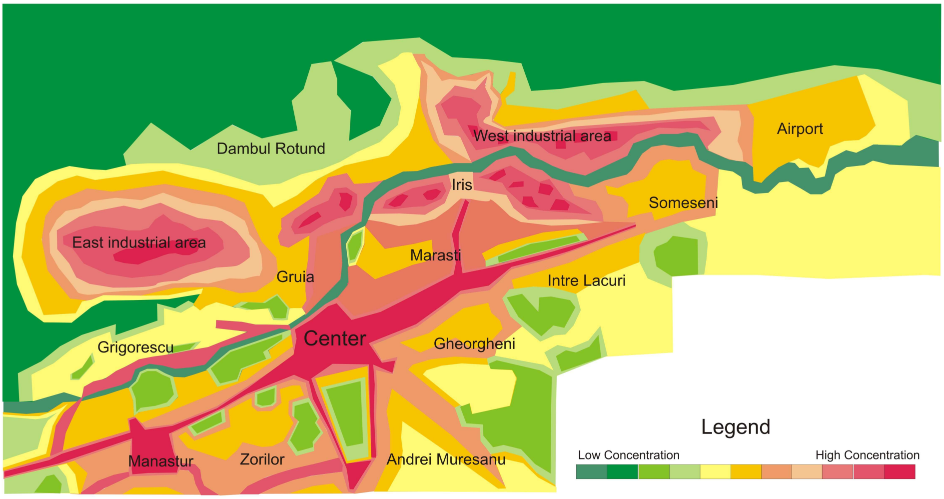
Lead particles have two maximum concentration levels during the day: in the time of driving to work (morning) and in the time of returning home (evening).

The grow of the average concentration of lead from 2004 to 2005, despite the actions taken to use more lead-free fuel, can be explained thru the grow of the cars number, the intensification of traffic. But, in 2006, the use of lead-based fuel became out of law, so a drop of lead concentration in the intense traffic areas is expected. This drop will not be sudden: the lead accumulated in the sedimentary particles will continue to be present in the next 2-3 years also.





In the industrial sites, the measurements of lead concentration revealed two minimal concentrations in the middle of May and August. Even if in January the suspended particles concentration is high, the lead concentration is at the bottom. The maximum lead concentration is measured in middle of April. In the year 2005, for the lead from suspended particles, we can observe again more low points during the year: April-May and July-August respectively, as well as reduced concentrations in January. In December, however, unlike previous year, there is a significant drop. A fact is that compared to the levels in 2004, the levels measured in 2005 are higher, proving an intensification of heavy metals pollution from suspended particles.



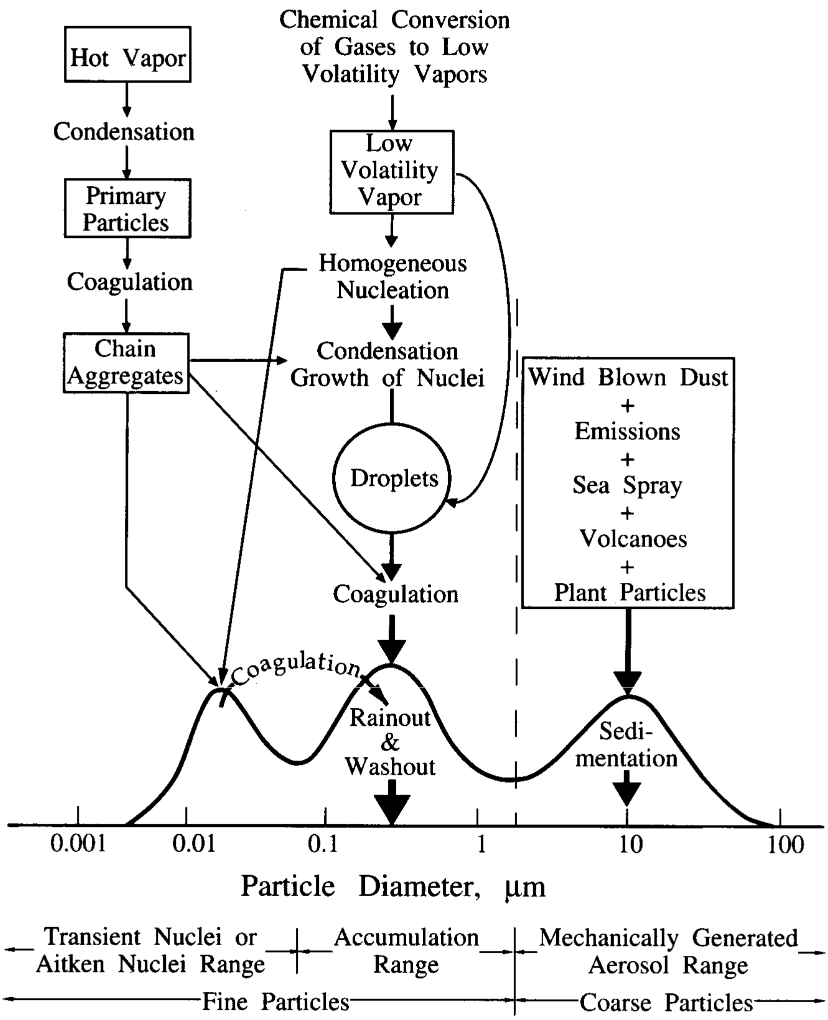
Aerosol Concentration Distribution Map over Cluj-Napoca City

By analyzing the map of dust distribution, we can notice a strong connection between the source of pollution, the transport network and the predominant wind direction. Regarding the climate, the predominant NV wind current transports the industrial particles from the East industrial site to the Mărăşti and Iris city areas, avoiding the center and the west part of the city, while the transport of particles from the West industrial site to the center is blocked by the Hoia hill filled with forest trees. However, the region of Cluj-Napoca is characterized by atmospheric stability and inversion phenomena that will determine a concentration and maintenance of these particles near the sources [14].

Dust deposition is conditioned not just by the existence or the lack of green surfaces (parks) and wet surfaces (lakes, rivers), the distance from the pollution sources, microclimate and relief, but also by the extremely variable weather conditions over short periods. This is why a graphical representation of the particle density over the urban area is hard to shape. In industrial areas, as observed during 2004-2005, particles emissions are not constant, a factor which also makes difficult to generalize a map. Anyway, we can observe a higher density of dust over the intense traffic routes, in industrial areas and most of all, in construction areas, and, lower concentrations in residential areas and large green fields like parks. Unfortunately, by comparing the surface of green spaces with the number of citizens in Cluj-Napoca, a city with over 100.000 citizens, an indice of 9,3mp/citizen results, which is a lot lower than the normal value: around 24mp/citizen.

The town's thermal island makes the temperature to be higher over the city than in the surrounding areas. In the condition of normal temperature layers, the temperature differences reach the highest values (up to +5 ℃) around midday, when the Somes bay is warmer than higher altitudes. In the condition of temperature inversion, the biggest differences appear during the night, and, most of all, during morning, when the temperature is lower in the bay than at higher altitudes. This phenomena makes possible the high concentration of aerosols over the bay (where the city is located), with forming of urban smog.

So, by adding to the equation the variable time, we could create a 4-D model of urban aerosol distribution: on one side we can visualize the 3-D scatter of particles with the help of optoelectronic system LIDAR, and on the other side, we can visualize and analyze the modifications of concentrations and correlate this with the emissions and atmospheric conditions. The importance of such model evolves into a better understanding of the necessary solutions for the establishment of residential areas with low impact over our health, as well as the establishment of the areas and of the ideal measures needed to reduce the pollution created by urban aerosols.



CONCLUSIONS

The urban air quality is a real problem no matter if we speak about a strongly industrialized city or a non-industrialized city. The intense traffic from the big cities, combined with the thermal island created by the location of the city and the urban structures, lead to the formation of secondary urban aerosols (more dangerous than primary aerosols) and contamination of sedimentary particles which we carry we us even inside the apartments. The lack of green surfaces adds to the maintenance of a high concentration of dust and harmful particles in the air.

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EL YACIMIENTO IOCG MANTO VERDE, III-A REGIÓN DE ATACAMA, CHILE. GEOLOGÍA, PRODUCCIÓN MINERA Y PROTECCIÓN DEL MEDIO AMBIENTE

IOAN FILIP

Compañía Minera Carmen Bajo-Chile

ABSTRACT. The Manto Verde IOGC Ore Deposit, Atacama 3rd Region, Chile. Geology, Mineral Production and Environmental Management. The main objective of the present paper is to present a system of mineral production by environmental sound processes. One of the main challenges for the important mineral producers in the world is the environmental protection and workers safety and health. Manto Verde deposit belongs to the IOGC category (iron oxide-copper-gold), a relatively recently described group of ore deposits, among which the most famous are Olympic Dam – Australia, and Candelaria – Chile. Manto Verde is a middle-sized and middle-grade Cu deposit with a low content of Au. There are several environmental actions that the mining company implemented, in order to comply with the environmental protection regulations:

- diminishing the surfaces covered by the ore stocks during the primary processing;
- diminishing the infiltration of liquid contaminants by installing impermeable liners;
- diminishing the air pollution by moistening the ore during the crushing operations,

SO_2 capture and sulfuric acid production.

Keywords: *IOGC ore deposits, environmentally sound mining, contaminants, air pollution*

DATOS SOBRE LOS YACIMIENTOS IOCG

Como yacimiento, Manto Verde pertenece a la clase IOCG (iron oxide-copper-gold) de yacimientos minerales, o sea oxidos de fierro con cobre y oro.

A pesar de qué en el mundo se conocían algunos yacimientos de este tipo, como clase de yacimientos fueron definidos por Muray Hintzmann en 1990, después del descubrimiento de los yacimientos Olympic Dam en Australia y Candelaria en Chile.

A diferencia de los yacimientos de magnetit-apatit, los cuales tienen, por lo general, el mismo estílo de mineralización, los yacimientos IOCG son mucho más variados, tanto genéticamente como morfológicamente.

Estudiando los yacimientos de los Andes Centrales de Chile y Peru, Silitoe R 2003, los clasifica en:

A - Yacimientos pequeños y medianos con menos de 20 millones toneladas de reservas:

- vetas de: -cuarzo, magnetita +Cu +Au;
- especularita+Cu +Au;
- chimeneas de brecha con Fe +Cu +Au;
- skarn calcico con Fe +Cu +Au.

B - Yacimientos compuestos de gran tamaño, con reservas de más de 20 millones toneladas.

En presente, los principales yacimientos conocidos en el mundo son:

Yacimiento	Pais	millones t	%Cu	g/t Au	%U
Olympic Dam	Australia	2600	1,20	0,5	0,06
Ernest Henry	Australia	166	1,10	0,5	
Salabo	Brazilia	1200	0,86	0,5	
Sossego	Brazilia	355	1,10	0,3	
Cristalino	Brazilia	800	1,30	0,3	
Alemao	Brazilia	170	1,50	0,8	
Candelaria	Chile	470	0,95	0,2	
Mantos Verde*	Chile	250* <400	0,75 0,52	 0,11	
Mantos Blanco	Chile	500	0,98		
Distrito Punta del Cobre	Chile	>120	1,50	0,6	
Mina Justa	Peru	600	0,59		
Raul Condestable	Peru	<50	1-2,5	0,5	

*minerales oxidados de cobre y van, como edad desde el Archaico y Proterozoico en Australia y Brasil, hasta el Cretácico en Chile y Peru.

Las principales características de estos yacimientos son:

- contienen inmensos volumenes de reservas (desde cienes hasta miles de millones de toneladas) con minerales de fierro (magnetit, hematit) e importantes contenidos en cobre y oro y subordinados en Ag, Mo, U, Co, P, Tierras Raras;
- están ubicados en los arcos magmáticos intracontinentales o de marjen continental, metamorfoseados en facies de esquistos verdes, amfibolíticos, u afectados por el metamorfísmo térmico y metasomático de contacto, generado por intrusiones batolíticos;
- tienen relación estrecha con los sistemas de fracturas crustales al márgen de los sistemas intrusivas batolíticas;

La asociación de minerales en las alteraciones asociadas, está formada por: albit, feldespato potásico, biotit, sericit, clorit, carbonatos (calcit, ankerit), cuarzo, amfiboles, turmalina, apatit.

La ubicación del Yacimiento Manto Verde desde el punto de vista geográfico, tectónico y geológico regional

Geográficamente el yacimiento Manto Verde está ubicado en el Distrito Cuprífero Los Pozos, en la Cordillera de la Costa Chilena, aproximadamente a 400 km sur de Antofagasta y a 100 km norte del Copiapo, en la Tercera Región de Atacama, Chile.

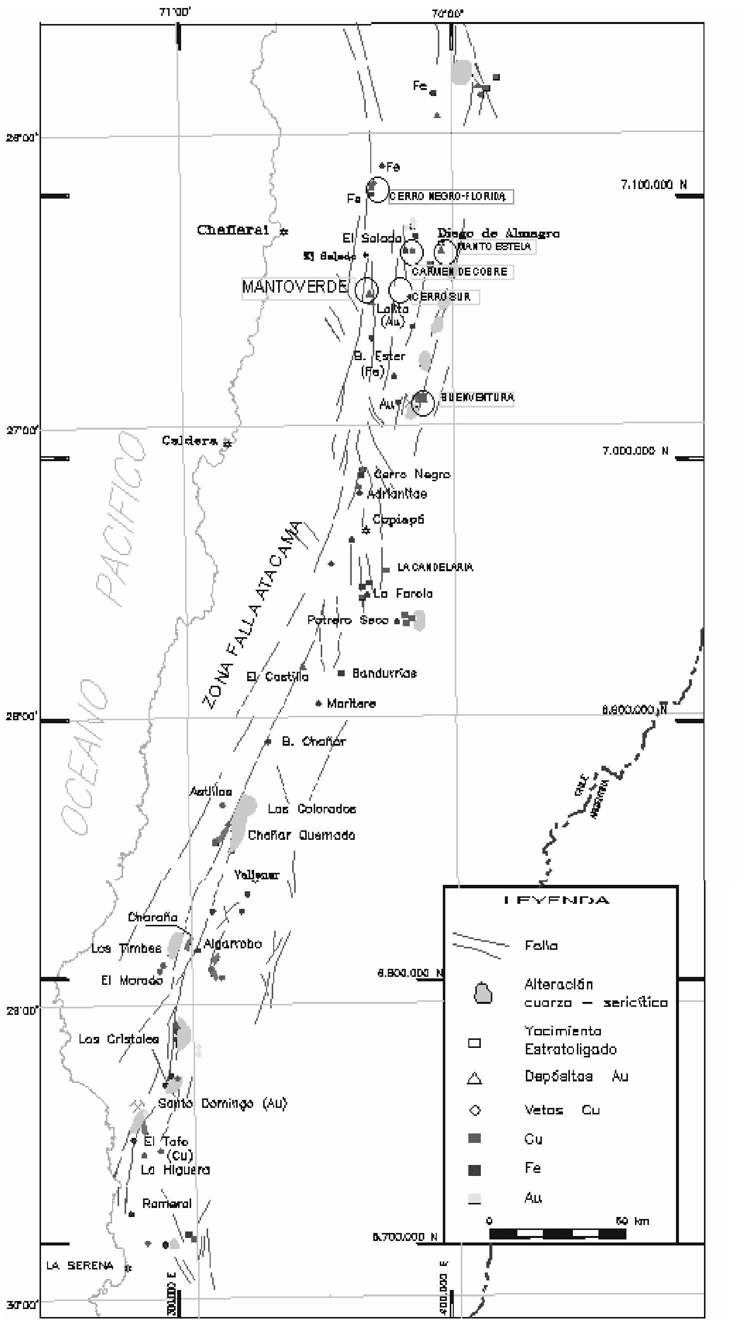

Fig. 1. *Ubicación geográfica y tectónica*

Desde el punto de vista tectónico, el Distrito Los Pozos y el yacimiento Manto Verde están ubicados en la zona de las Fallas Atacama (ZFA) asociada a la subducción, representando un sistema de fallas paralelas asociado al arco magmatico Jurasico Sup-Cretacico Inf, con rumbo general N-S, qué se extiende por más de 1000 km, a lo largo de la costa chilena. La zona de las Fallas Atacama (ZFA) está interpretada como un sistema de desplazamiento senestral, dessarollado sobre la litosfera continental, asociada á la subducción oblicua entre las placas oceánica y continental.

El Distrito Manto Verde está ubicado en el segmento El Salado de ZFA, representado por 4 fallas importantes con rumbo general N-S denominadas desde el oeste hacia el este: la Falla W, la Falla Central, la Falla Manto Verde y la Falla E.

Geológicamente el distrito está compuesto por flujos de lavas, brechas y conglomerados volcánicos, cloritizados, pertenecientes á la Formación de edad La Negra.

GEOLOGÍA DEL YACIMIENTO

Las mineralizaciones de Cu-Au del distrito, están ubicadas en cuerpos de brechas tectónicas, brechas tabulares y stockwork con calcita-especularita (Manto Verde), columnas de brechas (Manto Ruso) brechas tectonicas, cuerpos de brechas irregulares y stockwork de magnetit (Franko) y stockwork de specularit (Montecristo). Asociadas con las fallas del sistema ZFA, han sido emplazadas en una fase de extensión, que ha generado fallas normales y de desplazamiento horizontal, formando 4 cuerpos con una longitud total de 12 km y un ancho de 1500 m.

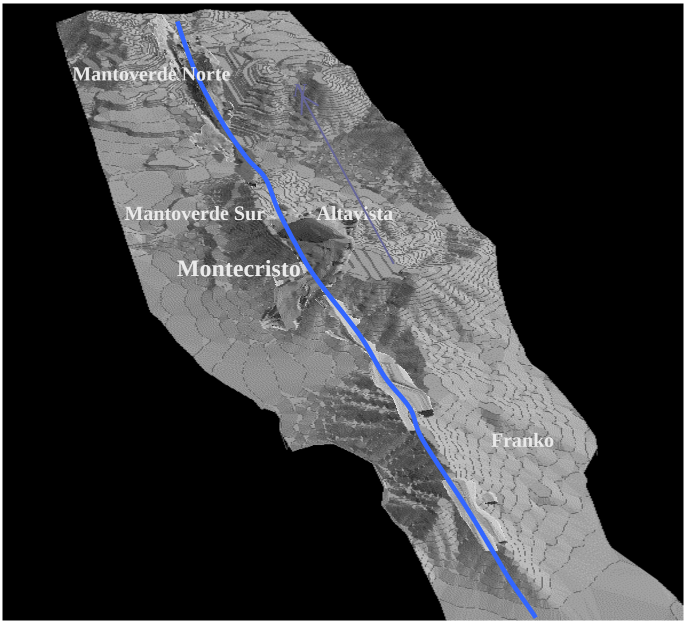

Fig. 2. *Distribución y relación Especial de los cuerpos con la traza de la falla Manto Verde*

Las alteraciones principales del sector, asociadas a los cuerpos de mineral están representadas en el área por: cloritización, alteraciones potasicas (biotit+feldespato potasico), silicificación, y sericitización en trés eventos de alteración:

- la cloritización masíva de las lavas;
- metamorfismo potasico con vetilleo de ortoza y biotitización masíva;
- alteración hidrotermal con cuarzo, clorita, sericita.

La mineralización de Cu-Au se ha depositado en dos etapas:

- depositación de especularita, magnetita, calcopirita, pirita;
- depositación de calcita, calcopirita.

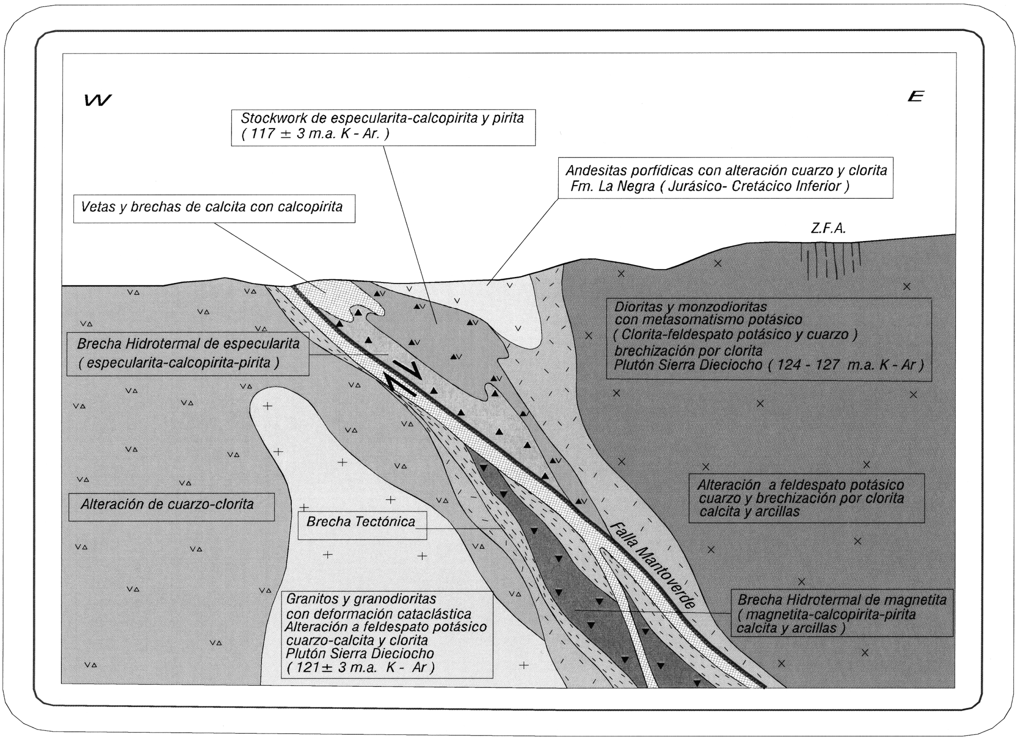

Fig. 3. *Modélo Genético de la Mineralización, Litología - Mineralización – Alteración*

En gran parte el yacimiento se oxidó. En el área oxidada la mineralización está reprezentada por: crisocola, brochantita, algo de malaquita y atacamita y mucha limonita. La mineralización primaria está representada por calcopirita, pirita subordinado pirrotina y bornita. La calcopirita y la pirita están asociadas con la specularita, magnetita, clorita o con la biotita-feldespato potasico.

La edad radiometrica K-Ar de la sericita indica 117-121 millones de años.

EXPLOTACIÓN Y PROCESAMIENTO DE MINERALES

Momentáneamente la mina Manto Verde explota minerales oxidados de cobre en tres rajos abiertos denominados Manto Verde Norte, Manto Verde Sur y Manto Ruso.

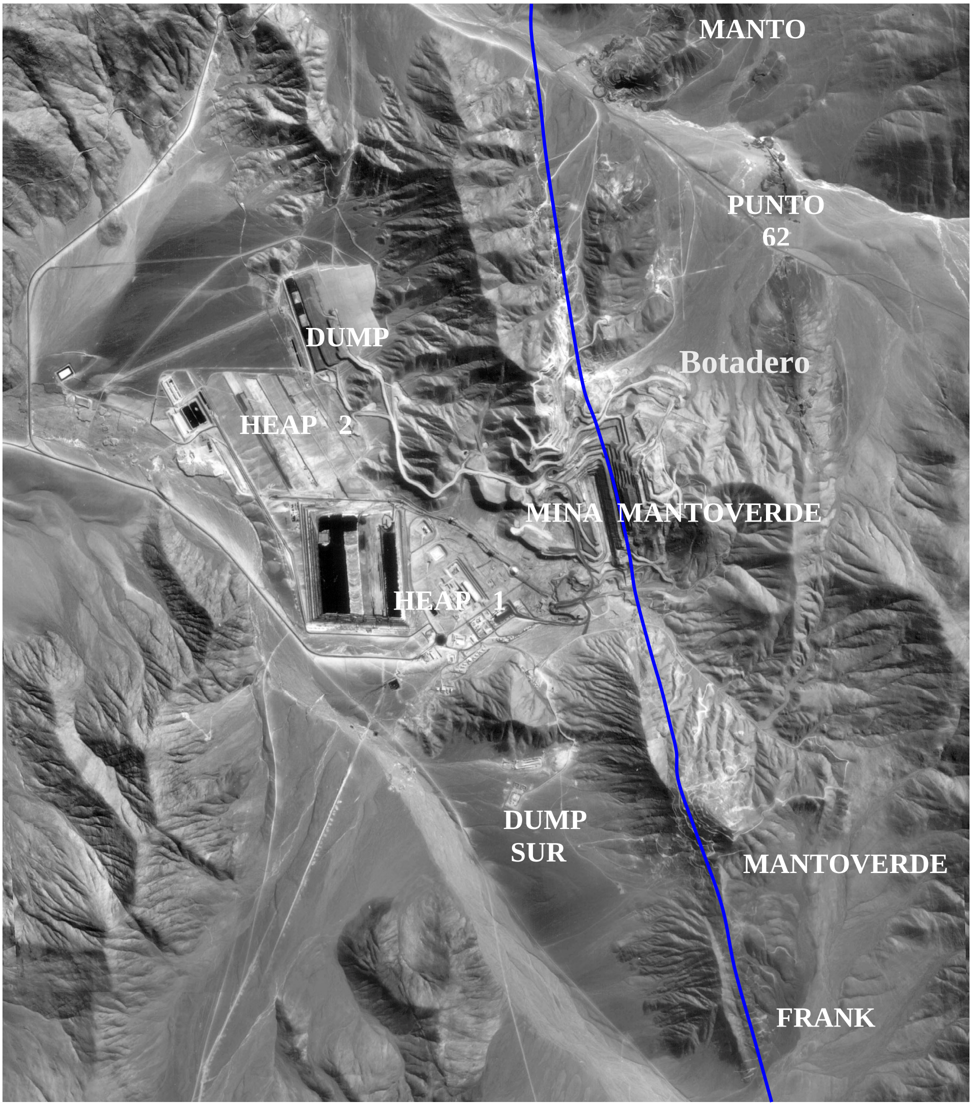

Fig. 4. *Fotografía aérea de las Instalaciones*

Después de la tronadura en los bancos del rajo, el mineral está transportado en grandes camiones (350 t) al sistema de chancado dónde está achicado, a menos de media pulgada y después depositado en pilas de lixiviación.

Fig. 5. *Equipos de perforación*

Fig. 6. *Equipos de Cargo*

El procesamiento del mineral oxidado se realiza mediante un proceso hidrometalúrgico denominado extracción por solvente y electrodepositación (SX/EW).

Durante el primer paso, la lixiviación se inicia riegando la pila de mineral con una solución diluida de ácido sulfurico y agua. El liquido percola en la pila disolviendo los minerales de cobre, produciendo un liquido con contenido de cobre, denominado “solución de lixiviación cargada” (PLS). La solucion PLS fluye hacía un depósito de recollección y después entra en una planta de extracción por solvente, donde se mezcla con un diluyente para así poder extraer electrolíticamente el cobre.

La solución pobre en cobre, denominada “solucion refinada” se carga de vuelta con acido sulfurico y se recicla completando así el circuito.

LA PROTECCIÓN DEL MEDIO AMBIENTE

Al revés de los procesos de flotación con la recuperación del cobre por fundición y refinación electrolítica, que producen en los hornos gases nocivos, que tienen como efectos las lluvias acidas, la extracción del cobre por la lixiviación del mineral oxidado y electroobtención es un proceso limpio y no contaminante. Preocupándose de la protección continua del medio ambiente la Divizión Manto Verde de la compañía Minera Anglo Americana, ha tomado también otras medidas preventivas :

- en el proceso de lixiviación, para no inutilizar grandes terrenos, ha inventado en premiera mundial la lixiviacion en pilas sobrepuestas;

- antes de iniciar una pila de lixiviacion, el terreno se impermebiliza con una capa de arcilla y después se recubre con una lona de polietilena pesada;

Para no contaminar el aire con polvo:

- las instalaciones de chancado están cubiertas, despresurizadas y utiladas con un sistema de humectación del mineral;

- los caminos de tierra están construidos por una mezcla de arcilla, agua y bishofit (MgCl) que después de asecarse se endurece y por la higroscopicidad en la noche o por el riego, humedece el camino, impidiendo el levantamiento del polvo.

Para evitar la contaminación del aire con dióxido de asufre, gas que provoca las lluvias ácidas, el Gobierno de Chile obligó las fundiciones a construir plantas de ácido sulfúrico. Así, el ácido producido, en vez de ser neutralizado durante procesos costosos está utilizado para extraer, en un proceso limpio, uno de los metales más utilizados por la industria mundial.

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STUDIA UNIVERSITATIS BABEŞ-BOLYAI, AMBIENTUM, LIII, 1-2, 2008

CLOSURE OF THE GYÖGYÖSOROSZI BASE METAL MINE IN HUNGARY

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ABSTRACT. Closure of the Gyögyösoroszi Base Metal Mine in Hungary. The Gyöngyösoroszi lead-zinc mine was once a 150,000 tonne/year underground facility. The combined historic production since 1952 until its suspension was 3,6 M tonnes of low-grade vein type Pb-Zn ore. The mining stopped in 1986, and provisional mine-water treatment facilities have controlled its ARD-producing mine water before entering into the natural drainage. Several surface installations – like the 2,1 million tonnes tailing pond – remained unprotected and impose considerable environmental hazard. Recent efforts aiming to reduce or eliminate these hazards and finding a cost-effective long-term solution are summarized. The mine water geochemistry and treatment methods, the present status of the tailing material is shown.

Keywords: *Hungary, Gyögyösoroszi, metal mine*

GEOGRAPHICAL SETTING

The Gyöngyösoroszi underground base metal mine is found 100 km E from Budapest, in the Matra Mountains, near Gyöngyös town. The Matra Mountains is one of the most popular protected resort areas in NE-Hungary, with peaks exceeding 900 m a.s.l. The Gyöngyösoroszi mine lies in the upper reaches of the valley of the Toka-creek, which runs southwards, passes through Gyöngyösoroszi and Gyöngyös towns before it enters into the Zagyva river. This setting of the mine makes its environmental impact a very sensitive issue for many local stakeholders.

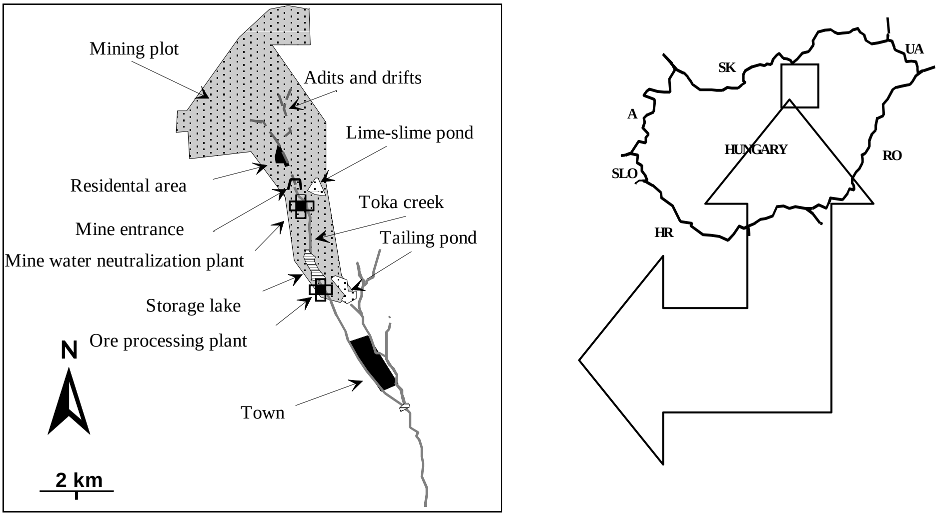

Fig. 1. *Location map of the Gyöngyösoroszi mine and its facilities*

GEOLOGY AND MINING HISTORY

The earliest records about mining go back to the 18th century. The area was explored by adits and shafts since the 1930s by several private companies, and opened as a state-owned mining company. It was once the largest of its type in Hungary, it operated between 1952 and 1986. The underground mine levels situated between +656 m and +100 m levels, i.e. in 550 m vertical span. The adit level to the surface (mine entrance) is at +400 m. (Kun 1998).

The Matra Mountains is built up from young sedimentary and volcanic rocks, andesites, less dacites and rhyolites, related pyroclastic rocks of Miocene age, 18-13 m.y. The mine sits in the center of a collapsed volcanic caldera. The ore bodies are in swarms of mesothermal and epithermal veins. 16 ore veins are known in the area, five of them were mined during the life of the operations. The veins fill dilatational fractures and fault zones in the volcanics. The immediate host rocks of the veins are slightly altered andesite and andesite-dacite tuff volcanics.

The mine produced low-grade Pb-Zn ore (cca Pb+Zn 4 % grade), in amount of 100-150 Kt of ore annually. The total ore production of the mine was 3,6 M tonnes, with 33 kt Pb, 102 kt Zn contained metal. The production was continuously subsidized by the state to meet the high extraction and treatment costs.

Two principal ore types were mined. The dominant one was from calcite-quartz-sulphide veins; the other type was from pyrite-rich breccia veins. Sphalerite, galena, chalcopyrite, bornite were the dominant sulphide minerals. The main mining method was shrinkage stoping and upward slicing with backfilling. These methods has left the underground stopes partially filled with broken ore waste, which present significant technical problem in sealing the underground mine voids. The abandoned stopes and drifts are now partially open, inaccessible, and unstable, the partial loose backfilling provides a continuous feed for ongoing ARD processes (Fig 1.). The total volume of the mine openings is 1.4 M m^3.

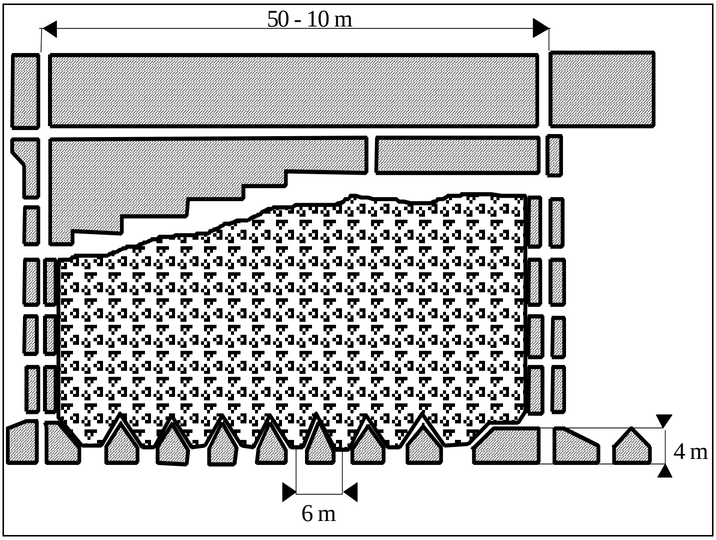

Fig. 2. *Shrinkage stopes – main mining method*

The 500 tonnes per day processing plant was built in 1952, three km downstream from the main entrance of the mine. Its 3 m^3/min water consumption was served from a 300,000 m^3 storage lake in the Toka valley, next to the plant. The ores were treated by traditional crushing – grinding – flotation circuits. In a period heavy-media separation was also used prior to the flotation process. The ore concentrates were exported to Bulgarian smelters. The tailings were deposited in the Szarazvolgy tailing pond, one km East from the processing plant. The total volume of the tailings exceeds 2.1 M m^3. Some 200,000 m^3 of tailing was accidentally discharged into the Toka creek during the early years of the mine, which appears now as contamination on the Toka creek floodplains.

PROVISIONAL MINE CLOSURE AND MINE-WATER NEUTRALIZATION

In 1985 the ore production was suspended. The water pumping was stopped in 1986, and the entrances of the mines (except for the one which ensures the drainage) plugged in 1988. Adequate waterproof closure was not possible since the mine collects the water infiltration from a 22 sq.km catchment area. Three underground dams were built with the aim of separating the mine water of the northern ARD producing mine sections (V1, V2 dikes), and controlling the release of the main southern orebodies (V3 dike). With this arrangement, it was thought to eliminate the acid mine water problem and provide a cost-efficient walk-away situation. Soon the V2 dam failed, and the mixing of the two types of mine water has made the need for mine water treatment perpetual.

The acid mine drainage produced by the effluent mine waters of Gyöngyösoroszi was recognized in 1957. The first measures aiming to reduce this effect were implemented only in 1971, first with aeration of the effluent water, then testing different technologies and additives. During production the untreated mine water has had pH 2 values. Since 1979, the mine water has been treated with lime addition. A treatment plant was then installed at the drainage point where the mine water reached the surface in order to prevent the development of ARD. From 1982 an automatic equipment was installed, which added lime to the outcoming mine water in function of its actual acidity to adjust its pH to 7,5-8, The resulting heavy-metal contaminated lime sludge was deposited in a nearby storage pond.

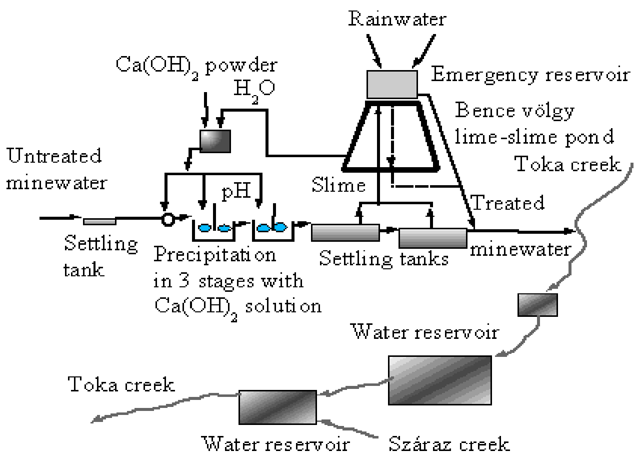

Fig. 3. *Mine water neutralization circuit at Gyöngyösoroszi*

In 1987 still pH 1,0-3,8 values were recorded in the untreated mine water, for which mainly the pyrite-rich breccia ores were responsible. After suspension of ore production the mine water quality has gradually improved. The results from 1997 showed that the even the untreated mine water chemistry has shown significant improvement, as well as the neutralization plant ensured effective precipitation of the dissolved heavy metals.

Table 1.

Chemistry of treated and untreated mine water 1997

Sample-site nr	*1*	*2*	*3*
No of samples	3	3	4
Fe mg/l	81	0,07	<0,1
Mn mg/l	5,4	2,4	0,15

Sample-site nr	*1*	*2*	*3*
Zn mg/l	17,5	0,13	0,073
Cu µg/l	<1,5	<1,5	1,9
Pb µg/l	<25	<25	<25
As µg /l	236	2,9	1,5
pH	5,99	8,25	8,04

1 untreated minewater
2 treated minewater at discharge point to natural drainage
3 irrigation pond at the Toka creek 10 km from the neutralization plant
Source: Ódor et al 1998.

During the 1997-2002 period the heavy metal content of the mine water was further decreased, although in case of Fe, Zn it is still considerably higher than the authorized target values for effluents into natural drainage.

Table 2.

Average composition of treated mine water 1997-2002(Source: Bőhm et al, 2004)

mg/l	*measured*	*target values*
Fe	59	10
Mn	5	2
Zn	17	1
Cu	0.03	0.5
Cd	<0.02	0.005
Pb	<0.05	0.05
Ni	<0.03	0.5
Cr	<0.04	0.2

The precipitates are in the form of lime hydroxide, which contains heavy metal hydroxides, hydrocarbonates. The volume of the lime sludge storage pond is 300,000 m^3; the present stored volume of the lime sludge is approximately 150,000 m^3. According to chemical tests the weak acid soluble heavy metal content of the lime precipitate is significantly higher than the target values, thus the deposited heavy metal rich lime sludge has been considered as hazardous waste.

The total heavy metal content of the lime sludge along with the target values B (threshold value for contamination) and C (threshold value for intervention):

Table 3.

Heavy metal content of the lime sludge precipitates in mg/kg (Source Bőhm et al, 2004)

Year	*1999*	*2003*	*Target B*	*Target C*
Element				
Zn	42900	29000	200	2000

Year	*1999*	*2003*	*Target B*	*Target C*
Pb	223	146	100	600
Cd	68	102	1	10
Fe	148000			
Mn	85			
As	963		10	60

WASTE DUMPS AND TAILINGS

During the ore production 2,1 million tones of flotation tailing have been deposited in the Szarazvolgy tailing pond. Later it has been covered by clayey soil, which was taken from a nearby development site. In certain periods other industrial waste (galvanization mud) was also deposited on this site illegally, now their harmful effects are combined (Ódor et al 1998). Several small historic waste dumps are also found on the wider mining zone. They also continuously release heavy metal contamination. The table below shows the calculated contents (from the historic chemical composition data of the deposited tailing) and the measured contents from the recent sampling. Significant differences can be observed in the zinc contents.

Table 4.

Heavy metal content of the flotation tailing (Source Bőhm et al 2004)

mg/kg	*calculated*	*measured*
As		325
Cd		17
Cu	500	536
Pb	1000	1212
Zn	6000	2898
Au	0.47	
Ag	3	

The tailing pond has got no sealing towards its base neither it has protective cover to prevent oxidation. According to waste and soil sampling data, the effluents contain significant heavy metal contamination in both dissolved and suspended solid form. The acid-base-accounting tests of the tailings have revealed significant acid producing potential of the tailing material. Microscopic and microprobe investigations on samples from auger holes in the fine tailings have revealed, that the sulphide material is only slightly oxidized and have a long term potential to produce acids from the tailings. This has been confirmed by preliminary acid base accounting tests. (Madai and Vass, 2004).

To determine the possible environmental impact of the flotation tailings, ABA (Acid Base Accounting) Test Procedure was carried out. Static Net Acid Generation (NAG) Procedure was used to determine the AP (Acid Producing Capacity), and EPA (Sobek) Method was applied to measure the NP (Neutralization Potential) of the tailings. To assess the environmental hazard of this matter we calculated the NPR (Neutralization Potential Ratio) values, which is the ratio between the NP and the AP values. If this value is strongly positive, the material has high neutralization capacity, near 1 or smaller values indicate acid generation capacity. Three different portions of the tailing impoundment were sampled: (1) the present surface area, (2) the intact inner parts of the impoundment and (3) the bottom part, close to the base of the tailings.

Table 5.

Results of the acid-base-accounting tests

Sampled locationl	*NPR values*	*Classification*
surface area	14.63	Not ARD generating
inner parts	1.93	Possible ARD generating
bottom part	3.58	Not potentially ARD generating

The classification was proposed by Price et al. (1995).

The material may present environmental hazard, since the present construction of the tailing facility does not stop oxidation neither prevents seepage. Under the thin oxidized layer the pyrite, galena, sphalerite remained intact according to mineralogical investigations.

SEARCH FOR PERMANENT SOLUTION

The treatment costs amount approximately 300,000-500,000 USD per year. This has triggered several attempts to find a cheaper way of safe closure of the underground and surface facilities of the mine.

Three major concerns were outlined in connection with the final closure of the Gyöngyösoroszi mine:

- mine water – reduction of volume and heavy metal content
- treatment and safe disposal of the deposited heavy metal loaded lime slime
- rehabilitation of contaminated surface areas, waste dumps, tailing ponds etc.

Jambrich et al (1994) have prepared a review of the mine and processing plant complex. They found, that the mine drains almost the total intake precipitation of the catchments area.

Bőhm et al (2004) has concluded from the composition of the effluent mine water that ARD producing pyrite-rich breccia ore mine section provides about 40 % of the total water output. The objective is to separate and control the two types of mine water sources, and possibly reduce or eliminate the contribution of the pyrite rich breccia zones to the drainage. Both plans opposed to seal the mine drainage stating that the renewed surface discharge points, springs would release heavy metal contamination in uncontrolled way and coined the continuing controlled lower-point discharge and water treatment.

In 1998 the Hungarian Geological Institute and the USGS has carried out surface sampling programmes to check the floodplain contamination against the natural background values along the Toka valley (Odor et al 1998). It was found, that former historic malfunctions of the processing plant and tailing management have caused significant heavy metal contamination on the flood-plains of the Toka, and the effect can be detected more than 10 km beyond the mine-site. This is due to the transported fine solids and not to the dissolved heavy metals since the attenuation of the dissolved heavy metals downstream of the mine is rapid (Odor et al 1998).

It was also recorded that the natural background and the anomaly threshold values for several base metals, like lead, zinc, are originally high, while other contaminants – As, Cu, Cd – remain at or near the national average value.

Table 6.

Natural background and anomalies of certain heavy metals in stream sediments

Values are in mg/kg	*1*	*2*	*3*	*4*
No of samples	196	in total 104		
As	7,5	5,7	25	163
Cd	<0,5	<1	1	47
Cu	18,4	14	34	153
Pb	13,7	18,5	60	288
Zn	58	65	100	12200

1 National average, stream sediments
2 Average, Matra Mountains
3 Anomaly threshold, Matra Mts
4 Maximum values, Matra Mountains
Source: Ódor et al 1998

In a joint Hungarian-Swedish research program the bio-availability of trace metal content of effluent waters using diffusion gradients in thin films was studied (Fredriksson 2002). A resin collector was used to collect dissolved heavy metals from the effluent waters, with integration during 10 days sampling period.

Table 7.

Bio-available heavy metal content of effluents of Gyöngyösoroszi mine

µg/l	*Cd*	*Co*	*Cu*	*Fe*	*Mn*	*Ni*	*Pb*	*Zn*
1	7,92	18,3	0,26	38600	3900	6,79	1,58	11700
2	0,11	3,34	0,25	366	1425	1,79	0,11	146
3	0,49	1,3	0,32	122	382	1,25	0,28	135

µg/l	*Cd*	*Co*	*Cu*	*Fe*	*Mn*	*Ni*	*Pb*	*Zn*
4	0,27	0,46	0,46	275	292	0,62	0,46	73
5	0,08	0,35	0,25	64	578	0,64	0,46	59

Sampling sites *1 Untreated minewater*
2 Discharge point, remediation plant
3 1000 m downstream from point 2
4 3000 m downstream from point 2
5 5500 m downstream from point 2
Source: Fredriksson (2002)

It was concluded, that the remediation plant effectively reduces the heavy metal load of the mine water, while natural attenuation helps to reduce the dissolved heavy metals to acceptable levels within 5 km from the discharge point.

In 2002, an international effort resulted in a detailed airborne surveying and complementary field sampling campaign as part of the HIGHSENS program to investigate the environmental impact of mining around Gyöngyösoroszi. A spectral library was developed, goethite and jarosite was suitably discriminated in the surface sediments along the Toka valley (Kardevan et al 2003). The widespread distribution of jarosite may indicate the oxidation of sulphides escaped from the flotation plant or tailing pond during the previous historical spills. The widespread distribution of jarosite may indicate the oxidation of sulphides escaped from the flotation plant or tailing pond during the previous historical spills. Both minerals undergoing a dissolution or recrystallisation may release the absorbed heavy metals (Jambor et al. 2000.). The transformation gives rise to increased proton and sulfate activities in connected surface waters (Bigham and Nordstrom 2000).

The samples taken from the accumulated sediments in the natural drainage downstream of the tailing pond indicate a continuous leakage. The samples from a shallow auger hole show a continuous contamination in accordance with the mining sequence. The contaminants corresponding the epithermal ores (As, Hg), which were extracted in the early years of the mine life, decrease with time (upward in the drill section). The elements characteristic to the deeper mine level ores (Pb, Zn, Cd, Cu, Ni, Co) increase with time (i.e. decreasing downward in the drill section).

Table 8.

Chemistry of drillhole samples at the discharge point of the tailing pond

Interval	*As*	*Ba*	*Cd*	*Co*	*Cr*	*Cu*	*Hg*	*Mn*	*Ni*	*Pb*	*Sn*	*Zn*
0,0-0,5	63	218	3	16	43	78	1	1074	9	216	1	658
0,5-1,0	41	270	0	21	41	23	1	1286	12	51	2	90
1,0-1,5	43	177	0	7	33	15	4	699	4	19	2	42
1,5-2,0	65	148	0	4	34	14	5	350	0	31	3	20
2,0-2,5	74	148	0	5	32	19	7	327	0	37	2	23
2,5-3,0	121	183	0	8	30	15	5	172		14	2	21

Source: Otvos (unpublished 2004) *Values are in mg/kg*

FEASIBILITY STUDY OF FINAL CLOSURE

In 2002 it was decided to search for less expensive, preferably walk-away solution of the mine-water treatment and the integral assessment of all aspects of a permanent mine closure along with the rehabilitation of both the surface and subsurface environment.

The following main points were considered:

- permitting – EIA, environmental permits, technical plan permits
- continuation of drainage of the mine through the present discharge point at a lower water flow-rate
- rehabilitation of the Toka-creek to Gyöngyös town, 12 km
- insulation of the main ARD producing areas (stopes with pyrite-rich breccia ores)
- neutralization and safe deposition of the heavy metal loaded lime-slime
- removing all smaller waste dumps to the Szarazvolgy tailing pond and seal this one new tailing – waste rock site.

To establish design parameters the hydrogeology of the mine and surrounding areas were first studied in details to determine the major paths of mine-water flow, and the proportion of possible influence of the different ore types to the quality of the effluent mine-water. The results have shown that there is only a limited communication between major groups of abandoned stopes, and certain areas above the level of present discharge point possibly store appreciable amounts of stagnant mine-water. A drillhole was sunk into the main haulage level of the pyrite rich breccia zone ore stopes to determine hydraulic properties of the underground voids and connecting drifts.

Several options were tested and investigated for the backfilling of ARD producing stopes and drifts. About 100,000 m^3 voids have to be backfilled. The mine-area and the possible intake point underlie a residential zone, which makes the selection of technologies a difficult issue.

The owner of the mine property is the Mecsekerc RT, a 100% state-owned environmental company. The costs will be covered from the national budget. The final cost estimate is expected to be finalized after the completion of the feasibility study, i.e. end of 2005. The preliminary works for the mine closure amount cca 1,5 million USD, the final costs of the closure - rehabilitation- reclamation works estimated to 300 million US dollars.

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The Mecsekerc RT has authorized the publication of the unpublished research information. Otvos es Tsa KFT has provided unpublished geochemical data.

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DIAGNOSIS OF RISK FOR FLOODS OF THE CITY OF HOLGUÍN - CUBA

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ABSTRACT. Diagnosis of Risk for Floods of the City of Holguín – Cuba. The city of Holguín, located to the northeast of the Island of Cuba, was founded and April 4 1720 for the Spanish Captain García Holguín, of who takes the name. The parents founders chose the place for the beauty of the valley formed by the rivers, calls in that time Fernando and Isabel - in honor to the kings from Spain -, well-known today Jigue and Marañón like they called them in a principle the aboriginal ones. Presently, the city occupies an area of 51 km2, with a near population to the 280 thousand inhabitants. Located before in the valley of the rivers mentioned the city is exposed in a periodic way to the floods caused by intense rains that bring harnessed big material losses, contamination of the means and a negative impact in the community. The present work has as objective to evaluate the exposed area qualitatively to this phenomenon meteorological end, so that the authorities they can take efficient measures with view to minimize the damages and to assure a sustainable local development.

Keywords: *Cuba, Holguín, flood risks*.

INTRODUCTION

The City of Holguín, located on the northeast of the Island of Cuba, was founded in April 4 of 1720, in the cluster that outside of the Spanish Captain García Holguín, of who takes the name.

According to José A. García Castañeda, in “The municipality holguinera. Their creation and their development up to 1799”, pag 101 and Jacobo de la Pezuela “Geographical, statistical and historical dictionary of the island of Cuba”, T- 3, pag 403 - 404; the rhythm of the population's growth during the colonial stage was slow, until the Guerra the 95, when the politics of the rural population's concentration was applied in the cities on the part of the Spanish authorities. In the republican stage was also slow, being invigorated in the last years of this period. In 1959 with the Revolution in the power an unusual movement is reached (in 1971 - 131 765 inhabitants) that increases starting from 1976 with the New Division Politician Office worker when Holguín becomes the capital of the equal county it names, what brought harnessed new industrial and residence investments and registers a demographic increment that to the closing of the year 2006 belonged to 280 000 people that covers an area of 51,0 km^2 that embraces 13 Popular Councils.

According to Formless Geociudad preliminary version Holguín 2005, pag 13-15-16-85, the city is located on the geographical area of the group of heights of

Maniabón, in a valley with altitudes between 100-150 m on the half level of the sea (s.n.m.m.), surrounded by elevations among those that stand out the Hill The Guillenes, Hill de la Cruz (Cerro Bayado), Hill El Frayle, exceeding 300 m heights and other smaller ones as: The Fornet, Ramón Quintana and The Caguayo.

From the geologic point of view Holguín is characterized by an ophiolite melange, represented by the complex ultramafic and gabbroid, constituted by peridotite and amphibole gabbros (monomictic melange).

The hydrographic network involves the rivers Jigüe and Marañón that form the River Holguín and the streams Milagritos and The Güillenes. These rivers are of little flow and they are born in the elevations that surround the city. The natural drainage of the city is divided of the Hill Los Filtros, in alone 20% to the stream The Lirios and of there to the river Yabazón to the north and in 80% in the rivers Jigue, Marañón toward the south to the river Holguín and of there to the basin of the Cauto, one of the main aquifers of the oriental region and of the country. The whole socioeconomic development of the city that is framed fundamentally inside the limits of this rivers, needed the construction of three preys (Prey Gibara, Cacoyuguín and Guirabo) that contribute 31 million cubic meters of water/year for the supply, of those which approximately 24 millions become in residual liquids that sink to the natural glide.

For the before exposed and for the recurrent character of the precipitations, with a behavior of little aqueousness and others of a lot of aqueousness, it causes that at the present time, in the city of Holguín, register with precipitations on 100 mm product to hurricanes, tropical depressions, local storms or other severe meteorological phenomena that happen generally in the months of May to October, overflows of these rivers, in certain places of the city, with material losses, contamination of the environment and the population's dissatisfaction, being the example more representative of it the entrance of the Hospital "Vladimir I. Lenin" where the traffic is interrupted toward this installation of health.

Keeping in mind that the total protection before the natural phenomena is not viable and that at the present time, it is impossible to predict with accuracy the magnitude of the future changes, taking in consideration El Niño's phenomenon, the climatic variability and the climatic change, the administration of risks becomes a mitigation instrument in front of possible catastrophes and it shows the objective necessity to characterize the basin Holguín and it allows from a scientific optics the qualitative evaluation from the exposed areas to the risk, proposing recommendations that allow to the authorities to take more sensitive and more intelligent measures for a sustainable local human development.

DEVELOPMENT

Characterization of the hydrographic basin of the rivers Jigue and Marañón

River Jigue Nac X = 248 800 Y = 557 700
Give X = 246 950 Y = 560 980

This river is nurtured of three streams that are born to the foot of the Hill of the Frayle, with course in southeast address, to the same one they go incorporating several streams until arriving to the Street Mariana de la Torre, it goes by the driver to a side of the Hospital Lenin, it crosses the Streets Carbó, Mendieta, Victoria, until the intersection of the Streets Frexes and Rastro, continuing in parallel to the Street Maceo to the Station of Railroad incorporating to the river Marañón to the foot of the street 31 and 8 in the Allotment Pueblo Nuevo.

River Marañón, Nac X = 250 500 Y = 559 700
Give X = 243 300 Y = 559 500

In their beginning runs from west to east, toward the south to the foot of the Street 28 in the Allotment Alcides Pino, continues in south address crossing the Highway from Gibara to some 40 m of the Street Line, skirting the Allotment Luz and the Allotment Vista Alegre until uniting for the left with the stream The Guillenes, in the intersection of the Street Martí and Marañón in the Allotment Vista Alegre, this same address continues crossing the city for the east skirting the Allotment Pueblo Nuevo, crossing from behind of the Station of Railroad where is united by the right the river Jigue, waters below unite with the stream Milagrito for the left following the south course until uniting with the river name Holguín which unites to the Cuenca of the Cauto river.

DENOMINATION	U/M	CANT
Area of the basin (Ac)	km^2	13
Longitude of the river (Lr)	km	6,4
Slope of the river (to Go)	%/0	9,0
Slope of the basin (Ic)	%/0	79
Longitude of the hillsides (Lc)	m	515
Half height of the basin (Hm3)	m	160
Sumatoria of all the currents (to Go)	km	14
Half rain (Po)	mm	1 200
Glide sheet (Me)	mm	231
Half glide (Wo)	Hm^3	3,03
Half expense (Qo)	m^3/s	0,096
Glide module (M)	$l/s/km^2$	7,38
Glide volume for the probability of 75% (W75%)	Hm^3	1,56
Glide volume for the probability of 95% (W95%)	Hm^3	0,64
Expense of probability of 1%	m^3/s	170
Glide volume for the probability of 1% (W1%)	Hm^3	4,32
Expense of probability of 5%	m^3/s	94
Glide volume for the probability of 5% (W5%)	Hm^3	2,63
Expense of probability of 10%	m^3/s	73
Glide volume for the probability of 10% (W10%)	Hm^3	2,16

The annual half sheet for Holguín is of 1 200 mm with an uniform distribution in the area that causes the natural glide of these rivers and streams to what sink 24 millions m^3 of residual liquids, domestic, of services and industrial. According to Formless Geociudad preliminary version Holguín 2005, pag 69-76-77-78, the spill of residual waters toward the roads and streams takes place because the sewer system nets serve alone to the population's 31% while 69 remaining% pours the direct waste to the river or they use for its evacuation graves (~ 17 450) and latrines (~ 20 000), not appropriate for the city, in those that frequent overflows take place due to the high cycles of cleaning, being at the moment to 198 days, the pour of the gray waters that cannot spill in these deposits goes toward the gutters of drainage of the streets and of there to the rivers.

Also the obsolete system of pluvial drainage of the city that was built at the beginning of the years 60, for the center and some allotments in a partial way benefits alone to the population's 18%, situation that has stayed until the present time, for not having been executed new investments in the nets, the system constituted by main collectors and secondary nets being where frequent obstructs takes place for the maintenance lack and repair and for this the spill of residual waters toward the roads and nearer streams. In the rest of the allotments the pluvial drainage is carried out for the gutters of the lateral ones of the roads, which are slippery toward the net of natural superficial drainage, being affected the quick evacuation of the waters, for the lack of urbanization of these areas, where the biggest percent in the roads is of earth. Him before exposed ago when taking place intense rains the volume of water it is bigger than the bed and consequently happen the floods, to this it is added: i. narrowing and obstruction of the natural bed for the construction of housings and facilities in the riverbanks and in occasions in the same bed of these rivers (2 131.00 illegal houses); ii. the population's little environmental culture harnessed to the insufficient collection of solid waste that favors the pour of these in the rivers; iii. the deforestation of the riverbanks; iv. the financing lack for the maintenance of dikes, bridges and sewers.

To know the areas of the city more affected by the floods took like base the organizational structure of the city that understands 13 Popular Council, Formless Geociudad preliminary version Holguín 2005, pag 26, represented by a President of Council that respond to the Assembly of the Municipal Popular Power, what facilitates the urban gobernabilidad when knowing the problems better from the base, and to possess legal force so that the entities of national, provincial or local subordination, are due to the environment where they are located and cooperate in all the aspects that are necessary in favor of the local development. The carried out works allowed to determine that the floods affect 4,4% of the population of the following Popular Council.

Not	**Council Popular**	**Habitants'quantity**	**Inundables areas**
1	Alcides Pino	30 558	Margins of the river Marañón and the stream The Guillenes.
2	Vista Alegre	34 090	From the bridge give the Highway of Gibara in the Allotment Luz for the whole Street Marañón in the intersection with the Streets Sol, Colón, Prado, Cuba, Garayalde, Agramonte, Arias, Aguilera, Frexes and Martí and Allotment Sanfield to the south of the Factory of Tobacco.

Not	Council Popular	Habitants'quantity	Inundables areas
4	Pueblo Nuevo	39 643	Margins of the stream Milagrito from Street Carralero until Street Real.
8	Lenin	35 220	Area of the Hospital Lenin and of the Driver.
9	Center North City	27 478	Streets Cuba, Garayalde, Arias, Aguilera until Frexes and from Mendieta, Dositeo, Aguilera, Victoria and Carbó.
10	Center South City	28 000	Street Gral Vázquez and Angel Guerra% Pepe Torrez and José A. Cardet.

The most recent flood suffered by the city happened in the month of July of last year 2006 when rains of 105 mm/2h were reported that left a balance of 5 thousand flooded houses, 7 damaged partially, 2 total collapses, 5 damaged bridges in a partial way and 7 destroyed totally, contamination of the means and the population's dissatisfaction.

The whole flow of residual that arrives to these rivers without previous treatment they are confident to the car-purifying capacity of the waters of the rivers Jigue and Marañón, both tributaries of the river Holguín that has like final destination the basin of the Cauto river, what has borne to such negative impacts as:

- destruction of the biodiversity.
- emanation of bad scents.
- proliferation of vectors of diverse illnesses.
- impoverishment of the urban landscape.
- stimulation of the indiscipline environmental citizen.
- loss of prestige of the city.
- contribution to the contamination of the Cuenca of the Cauto (60%).

CONCLUSIONS

1. The rain sheet bigger than 100 mm causes the floods.
2. The deficiencies in the reparation of the residual waters (domestic, of services and industrial) makes that the same ones spill directly in the rivers increasing their natural flow.
3. The affected Popular Council are Alcides Pino, Cheerful View, I Populate New, Lenin, Center North City and Center South City

GENERAL RECOMMENDATIONS

Necessity of a restoring politics.
Reforestation of the riverbanks of the whole basin.

Increase of the capacity of the river (derivation channels, dredged, you work of it enlarges).

To clean obstruction the drainages and hoppers of the sewer system.

To maintain free of brashes and other waste the riverbanks.

To prohibit the shepherding of animals in the riverbanks.

To prohibit the connection of corrals to the sewer system net or direct to the river.

The population's understanding.

To make be worth the regulations established urbanisticas. (to avoid the construction of new housings in the flood planes).

To give appropriate maintenance to dikes, bridges and sewers.

To complete the sewer system nets (31%) and pluvial drainage (18%).

To build treatment Plant of residual.

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ROMANIAN FARMING IN THE EUROPEAN UNION

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ABSTRACT. Romanian Farming in the European Union. In Romania the agricultural sector should not be ignored if the goal is to give the population better living standards and increase the country's competitiveness in the world, but that is precisely what has happened in the past. Most Romanian farms are unable to compete on the European market, or even access it, and that is one reason for a rise in subsistence farming. Both the government of Romania and the European Union are now trying to change the situation through increasing the size of the farms and encouraging alterations in current methods of working, and that meets strong resistance from the population. Much resistance has cultural roots and is strongly encapsulated in habits, weak institutions or distrust and it increases the dependence on subsistence farming. Romania has the potential of becoming one of the best European deliverers of agricultural products, but that will demand drastic changes.

Keywords: *agriculture, farming, European Union, Romania.*

HOW DOES THE ROMANIAN MEMBERSHIP OF THE EUROPEAN UNION AFFECT AGRICULTURE IN THE COUNTRY?

Agriculture forms much of Romania's cultural heritage and it strongly influences all parts of the country, but the current structure is under pressure from both the European Union and the local government. Fundamental changes are needed and these will have dramatic effects on the entire Romanian civilization. The membership of the union brings hopes, demands, fears and changes to the country in general, but even more so to its agricultural sector. The discussion in this paper is focused on Romania from the first of January 2007 and is based on interviews with people living in the country and on written materials. The result is a complicated picture of an agricultural situation in rapid transformation and of small farmers in trouble.

This text is based on material that will be used in an upcoming Masters Thesis for the Political Science Department at the Stockholm University. A broad outline of what is said below was presented in a speech at the *Romanian language, culture and civilization* conference held on the Swedish island of Marstrand on 18-20 May 2007. Romanian agriculture was a success story at least until the 1930's (Hagman. 2005:29. Mihai, Gheorghe), but a strong focus on industrial expansion during the communist era made the sector fall behind without much direct help from the industry. Decades of governmental ignorance towards agriculture has brought food supply crises and lowered the standards of living in Romania (Nilsson, 1998). In June 1995 Romania applied for membership of the European Union

(Sveriges Riksdag, 2006) and at that time it was clear that fundamental reforms of the agricultural sector where needed if the application was to be accepted. Large sums of money where sent from the union to Romania to make such reforms possible and the country became a member on 1 January 2007.

Of the entire European Union of 2007 Romania has about 4,7% of the population, 5,5% of the surface area, adds 1,4% of the combined EU-Gross Domestic Product (GDP) and has over 30 % of all farmers. The Romanian agricultural sector adds almost 6 times the EU average to the country's GDP and is estimated to employ around 43 % of the population (Pop Daniel, European Commission 2002:6. Abrudean, Mircea. Mihai, Gheroghe). Changes in the estimated amount of farmers are interesting because in 1938 the Romanian workforce had 76,7 % farmers and that figure went down to 29,8 % in 1980 and from there to the current level of over 40 %. Some 47 % of the Romanians live in rural areas and these parts are characterized by a high rate of un- or underemployment, subsistence agriculture, poverty as well as low levels of education and health services (Bleahu. 2004:21, Firici and Thomsen. 1999:3. Bota, Dorin. Beac, Aurel.) and they are also dominated by an elderly population. It has been estimated that 5,6 million people work in the rural areas and that at least 4,1 million of those are involved with agriculture, but also that few receive a salary for that work. There is roughly 1% wage earners in the same areas and 98% of all farms are privately run (Bleahu, 2004:22). The cost for food is locally over three times the average of the 15 oldest EU members (EU-15) implying a comparatively costly and populous agricultural situation. The share of food expenditures in total income in 1997 was 17,4% for EU-15, 14 % for the US and 36 % for Central and Eastern European countries (Hubbard, 2007:133). Romanians spent between 53-69% of their incomes on food in 2003 (World Bank. 2005:10).

Well over a third (European Commission. 2002:6) of Romania's roughly 22,3 million inhabitants (CIA. 2007) are dependent on domestic agriculture. The sum of their production adds up to somewhere between 11,4 % (European Commission. 2002:6) and 20 % (MDP. 2004:16) of the country's GDP and the entire sector is valued at around five billion Euros. In the EU-15 the average GDP contribution from agriculture is 2 % from around 3-4 % of any population.

In the communist era land was often taken from private owners and then considered state property. It was common for farmers to have to work in farming collectives with state demands on production quantities (Pop, Daniel. The milkfarmer in Deva). With the fall of communism some 4,2 million rural beneficiaries received ownership and use rights of land in a transfer from the government (World Bank. 2005:XIX). At that time no family got more than ten hectares of land and the transfer also led to conflicting claims. Now at least 85 % (Hagman, 2005:29) of all land is privatised but most farmers have access to plots smaller than one hectare and they are usually subsistence farmers (European Commission. 2002:8, Firici and Thomson. 199:3). 98 % of all farms are smaller than ten hectares, but the sizes of large farms still cause the average size of a Romanian farm to be 3,1 hectares (World Bank. 2005:XVIII, Hagman. 2005:29.). In 2005 it was estimated that 65 % of land in rural areas was owned by pensioners causing a threat of an increase in passive land ownership (World Bank. 2005:XIX). The small plots ensure a fragmented agricultural sector (Hubbard. 2007:138) and that is worsened by a situation where a lack of uniform land registers for the entire country make it difficult to know for sure who owns what piece of land (Pop, Daniel). In the EU on average 44 % of all land is used for agriculture and in Romania the same figure is 62 %. Forests cover 28,5 % to 33 % of the country (European Commission. 2002:6, MDP. 2004:16). Chemical pollution caused by the excessive use of some fertilizers and pesticides as well as emissions of heavy metals and hydro carbonates have decreased the productivity of the agricultural lands with 20-30% (MDP. 2004:16). Little access to irrigation and drainage systems has decreased productivity further and makes the agricultural sector largely dependent on weather conditions. Land in mountainous regions are not as affected by chemicals and are therefore considered ecologically sound and a high degree of afforestation also helps these areas. Populations of livestock have over the last few years shrunk dramatically as well as the quality of their available pasture lands. Incomes for small farmers in the Romanian mountains have gone down to such an extent that the degree of poverty is higher here than for any other rural mountain population in Europe (MDP. 2004:17). 45 % of the population was estimated to live below the poverty line of roughly one and a half euro a day in the year 2000 (Solic, 2007:9). Another 500,000 land owners are urban residents with other careers and with little or no interest in pursuing active farming (World Bank. 2005:XIX). It used to bring prestige and power to own land and that has led to a situation where very few want to let go of it, rent it or lease it to someone else (Pop, Daniel. The milkfarmer). The situation is further complicated by low levels of trust for one another (Pop, Daniel, Mihai, Gheorge, The milkfarmer). The forced cooperative methods from the past have triggered a counter reaction where few want to work together even if it is more economical to do so.

A Romanian farmer is usually old, poor, have access to a small plot of land and is seldom able to sell more than small quantities of what is produced. It is also unusual for farmers to have the possibility of selling anything to anyone far away. Infrastructure and means of transport often make moving products and people in Romania a time-consuming business. Farmers sources of income are often limited to farming and old age pensions (European Commission. 2002:8. Firici and Thompson. 1999:3. Abrudean, Mircea. Beac, Aurel). Small plots also ensure difficulties in accessing financial assistance from investors (Hubbard. 2007:138), and high age naturally decreases agricultural productivity. Half of those who became landowners or received land-use rights where in 2005 over 60 years old and about 40 % where pensioners. The amount of retired workers has increased further with a low retirement age, an ageing population and because the government decided to give many workers early retirement when communism collapsed. A decrease in pensions paid has increased the amount of subsistence farmers and their dependence on farming (Pop, Daniel), but every year high age also takes some of the dependents away (Mihai, Gheroghe).

When the government began its struggle to develop the country's industry it aimed at the export market and let the agricultural sector work with what it already had (Nilsson. 1998:28). Available technology is old and sets strict and low limits to what can be produced or sold (European Commission. 2002:21, Pop, Daniel, Mihai, Gheorge. Bota, Dorin. Beac, Aurel). Tractors are too expensive to buy for an average farmer and renting or leasing of machinery is seldom an available alternative. Farming in Romania is therefore labour intensive and slow compared to other European countries. The sector is to a large extent uncompetitive and farmers are forced into subsistence farming and living off of pensions (Mihai, Gheorghe. Pop, Daniel. Beac, Aurel).

Both agricultural labour and land productivity are low in Romania. Milk yields are lower than any other European country and only four EU-countries get less grain from the same amount of land. Work from an average Romanian agricultural worker was in 2002 worth 1600 Euros per year and the average for the entire European Union was at that time 22 600 Euros per worker and year. It is very difficult to compete with the average EU farmer when the Romanians start with only 7 % of their productivity (World Bank. 2005:6) and the matter is, from a governmental perspective, further complicated when very few have enough contacts with any market to be able to sell anything there. Export mostly consists of raw products (European Commission. 2002:21) of sometimes questioned quality. Quality as such does unfortunately not seem to motivate farmers as now as much as prices do (Pop, Daniel, The milk farmer), but one usually brings the other. Some products encounter unnecessary domestic problems with what quantity can be exported. Wheat has, for example, very few collecting silos and they use the uncommon solution of charging farmers for storing their production instead of the usual organisation where the silos buy the wheat. The smallest farmers can not afford to pay this rent and probably also have problems getting to the silos. Growth in the Romanian economy has still been good over the last few years but in 2005 it lost speed from 8,3 % in 2004 to 4 %. This was caused by a sharp decrease in the agricultural sector, less industrial output and the floodings in 2004 (Svenska Exportrådet i Bukarest. 2006). What the draught in 2007 will bring is yet to be seen.

Opinion polls in 2006 show that only around 31 % of the Romanians trust their government. That is said to be a continuation of a downward trend which shows a 2 % drop from similar polls two months earlier and this is frequently verified by Romanians (Pop, Daniel, The milk farmer, Mihai, Gheorge). The church and the army enjoy the highest levels of trust (Svenska Exportrådet. 2006:5, 21). Bureaucratic obstacles, an unpredictable legal- and tax environment, high transaction costs and corruption are all reported to hinder Foreign Direct Investments, FDI, in agriculture. Still 14-15 % of all FDI between 1991-97 went to the food industry (European Commission. 2002:21). Many Romanians believe that politicians and the government almost entirely aim at their own personal benefit even though they are elected to serve the country as a whole (The milk farmer, Beny). Some say it seems that the government forgot the population in their negotiations with the European Union and simply said yes to everything the union demanded. Such statements can be exemplified with the drastic measures taken to make it possible for the country to live up to EU standards. In 2001 the Romanian government decided that the smallest dairy farm eligible for economic support had to have 15 cows and that a grain farm had to be 110 hectares or larger. This bias for large farms effectively excluded almost all farmers from support and was aimed at forcing small farmers out of business even though 95 % of the milk is produced by non-registered household farms (Här behövs en källla). The World Bank has criticised the method of basing agricultural support on size rather than commercial activity and EU pressure forced the Romanian government to abandon the policy of 2001 already in 2002 (World Bank. 2005:XVII, 16-18). Many small Romanian farms have, at least between 2003 and 2005, not been taxed. Some are taxed only on their profits and at low levels, if the farms are registered as legal entities (World Bank. 2005:23, The milkfarmer). The harm of such changing and unpredictable policies are likely to be a problem for a long time to come. It brings distrust where trust is much needed.

A study ordered by the EU-delegation to Romania and made in June 2005 concluded that 56 % of all Romanians believed that the membership of the union would bring disadvantages in unemployment, higher prices, a worsening for the agricultural sector and a loss of national identity. The EU was also seen as a question of gaining democratic legitimacy as well as a source of social security and external financing for needed domestic reforms (Romanian Market Research Institute (IRSOP), Svenska Exportrådet i Bukarest. 2006:21). Romania now pays one billion Euros to the EU and it gets five billion back. Five billion is also what Romanians living abroad has sent back home. Such remittances have become an important part of the Romanian economy (Nienhuysen, Frank. Pop, Daniel). Comparisons with experiences in other EU member states indicate that there should be an increase in food prices in Romania after the accession and that this can lead to inflation (Pop, Daniel) and changes in food consumption (Firici and Thomson. 1999:1-2). The effects of a rise in food prices should in the short-term have more negative effects on those who are not involved with farming than other households (Hubbard. 2007:128) and the EU has long seen the comparatively high prices for food as problematic. An expected general increase in demand for food products in developing countries (European Commission. 2001:14) and the fact that expenditure for overall consumption has been low in the past in Romania (Nilsson. 1998:28) make the predicted increase a promising sign for the future. The number of cows is expected to decrease but the yield per cow should, on the other hand, increase when the restructuring of the agricultural sector takes effect and brings more productive methods (European Commission. 2001:14, 17, 57-58. Refers to FAPRI, OECD, USDA and FAO.). Growing populations, rising disposable incomes, urbanisation and altered dietary patterns lead to expectations for strong gains in milk, and even more so for cheese and butter, in countries outside of the OECD (European Commission. 2001:21-22). In the Deva area these changes are seen in a change from 450 cows to 85 over a period of just a few years, but a retained belief in possibilities in the dairy sector. Another village close to Deva used to have 700 cows but now only have around 150 animals (The milkfarmer in Deva). The fragmented agricultural sector in Romania makes many unable to access financial assistance offered by the EU (Hubbard. 2007:138). At least 0,3 hectares of land was required for aid from an EU point of view (World Bank. 2005:XIII), but such support also required local co-financing and that made the demands impossible for most Romanian farmers even if they happened to have enough land (Mihai, Gheorghe). Complicated administration and bureaucratic obstacles also made life more difficult for the smaller farms if they wanted to look for support. To better the situation local authorities need to show farmers how to fill out necessary forms and indicate where they can find and use information on possibilities (Abrudean, Mircea. Bota, Dorin and speech by Dorin Bota). To many the EU has become another government and also a source of increasing amounts of paperwork. It sometimes happens that the local government puts the blame on the EU for shortcomings (Pop, Daniel, Mihai, Gheorghe). That is not something that is likely to develop trust among the Romanians for the EU or the Romanian government. Aid primarily went to larger farms with a governmental and EU wish to get smaller ones to give up farming altogether. Some fear that these changes will lead to severe poverty among primarily older farmers (Hagman. 2005:29) and that most farmers will be unable to benefit from the new opportunities offered by the union (Scrieciu. Page 30). The Romanian struggle to adjust to the rules of the union continues and the belief in a promising future for Romania remains strong, but many are still concerned with how the economy is developing (Svenska Exportrådet i Bukarest. 2006).

CONCLUDING DISCUSSION

Both Romanian farmers and their lands are inefficient compared to their European counterparts. The inefficiency primarily comes from the high age of the workers and the old methods and machinery used. Better technology would improve the situation for them, but that requires access to resources that are currently out of reach for almost all who would need it. Most farmers consume what they produce and have little connection to the market. Farmers with such connections tend to sell raw products and that is also what is usually exported. Improvements in infrastructure would give more possibilities. Access to additional funding and economical support is strictly limited for all but very few farmers and more education is needed to increase the chances for the farmers to find and receive assistance. Renting equipment is uncommon and so is renting or leasing of land. Land is in itself a complicated issue because it used to be a source of power and wealth and is seen as something that is more difficulty to take away than other possessions, and much was taken away from individuals in communist times. Who owns what is, however, still often difficult to determine and would need better registration to be efficient. Much land in relatively small pieces was transferred from state possessions back to private hands after the fall of communism and this is now a source of inefficiency because owners seldom want to work together, rent, lease or sell their land to achieve economies of scale. They prefer to hold on to and work their land; if nothing else for personal safety. Such security is needed for the many old landowners who have difficulties in surviving on current pensions if they do not produce their own food, but it is also seen as a state wide problem of mentality where few want to cooperate and a situation where it is uncommon for individuals to easily develop trust for each other. Otherwise cooperation could be a way to improve the circumstances. One way around such a problem could be for the government to encourage renting or leasing of land to farmers, but that is at the moment not happening in Romania. Institutional frameworks and the pension system clearly need improvements. Government actions have hurt the trust of both the population and investors and it does not improve the situation when its policies only benefit very few while it at best ignores the rest. Many Romanians have the impression that the government and the EU are best for those who already have large farms or much money. Alternatives to subsistence farming are few for the elderly and it seems they are expected to solve the problem of the large farming population by simply dying away. Romania gradually looses its agricultural workforce when the old remain in the countryside and the young move to the city, but that may lead to a more stable economy even though farms are likely to grow in size. A land registry and predictable governmental policies would be a good start for attracting much needed foreign investments. Through that Romania should be able to afford more of the technology needed to raise and control the quality of raw products or process them more before they are exported and that way get more money. In the current situation some of the cultural heritage is kept even though it is often seen as threatened, but preserving the heritage too eagerly also ensures farmers a lot of work for gradually less remuneration. A more drastic way of expressing the same thing is to say that without money or useful land the small farmers will starve even if a pretty countryside is preserved. In my view it is desirable to keep both as intact as possible and that would require more cooperation, trust and maybe diversification. The potential for lucrative farming in Romania is immense, but the sector needs fundamental restructuring to be economically sound. It is a long road to walk but the new European Union control over how the changes are made seems to be a good help for the Romanian government when it finds a working method for more than just the larger farms. The EU may be just another government but it does bring much needed capital, critique, control and expertise.

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UTILIZATION FACILITIES OF BUILDING INDUSTRY BY-PRODUCTS (RED MUD) AND THEIR RADIOLOGICAL QUALIFICATION

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ABSTRACT. Utilization Facilities of Building Industry By-Products (Red Mud) and their Radiological Qualification. In this work, the radionuclide concentration of Hungarian bauxite was determined, the by-products resulting from its processing, that is red mud, and lime accumulating as the by-product of coal mining and some clay samples used in the production of brick.

Keywords: *red mud, ^{226}Ra concentration, building materials, emanation factor.*

INTRODUCTION

Nowadays the assessment and limitation of the population's radiation dose resulting from radionuclides of natural origin, is getting a more important role. Although the material of the building mostly screens outer radiation, the radionuclide concentration of the building material increases it. Therefore the gamma dose in the buildings is usually higher [1] – world average is 84 nGy^{-1} – than outdoors – 57 $nGyh^{-1}$.

the international and national orders recommend the radiological classification of building materials and the limitation of their utilization according to these.

At the same time significant researches [11, 7] are being carried out in the field of recycling by-products and waste materials resulting from industrial production. Some industrial by-products have already been used in several places as building materials and/or building material additives. In several countries bricks are made of fly ash the so-called phospho-gypsum resulting from the production of phosphoric fertilizer and has been used as building material. For example, coal slag has been built in the floor structure as filler insulating material in Hungary.

Mostly this does not present any radiological hazards but it can be significant in case of using materials, rocks with elevated NORM or TENORM content [9]. The use of industrial by-products as building materials and/or building material additives is widespread. Nowadays several researchers [3] are examining the facilities of using red mud resulting from bauxite proceeding as a building material additive (e.g. by the production of special cement or bricks).

Some researchers achieved favourable results in the examination of the mechanical and aesthetic properties of building ceramics (brick, tile) made of red mud mixed with clay in different quantities (0-50%) [6].

Several researchers studied the production of cement with the use of lime + red mud + fly ash, lime + red mud + bauxite or lime + red mud + bauxite + gypsum and experienced that cements made from lime + red mud + bauxite or lime + red mud + bauxite + gypsum exhibit strengths comparable or superior to ordinary Portland cement [8].

Previously intensive bauxite mining and alumina production was going on in Hungary. The resulting red mud was placed in storage basins. At the moment red mud storage basins can be found in the regions of 3 settlements on a total area of 700 hectares, approximately 45 million tons. Considering its building industry utilization these can be taken into calculation as additives to the production of special cements, bricks or tiles.

Besides the red mud storage basins, barren rocks with originally high $CaCO_3$-content exposed during coal mining can be found in large quantities. Due to the self-ignition of the rest of the coal this actually changed over to CaO and in this way lime could be used together with red mud for the production of special cement.

Radionuclides of natural origin can often be found accumulated due to the technological processes in the industrial by-products [10]. In the case of high radionuclide concentration, higher radon concentration, gamma dose and consequently significant population dose increase must be taken into consideration [4].

Therefore the different national and international recommendations have determined limits concerning the radionuclide concentration of building materials [13].

In this works, the radionuclide concentration of Hungarian bauxite was determined, the by-product resulting from its processing, that is red mud, and lime accumulating as the by-product of coal mining, and some clay samples used in the production of brick.

Taking the resulting radionuclide concentration values and mixing ratios that were found in the mentioned literature into consideration, the by-products were qualified from a radiological aspect. This was based on the activity concentration index (I) recommended by the EU.

At the same time besides index “I” a separate limit was determined concerning ^{226}Ra concentration in several countries (eg. Austria, Finland, Germany, Luxembourg) in order to avoid the building material becoming a significant radon source in the buildings [12]. Therefore radon emanation measurements were carried out with the red mud samples.

METHODS OF MEASUREMENTS AND CALCULATION

Sampling and sample preparations

In the case of bauxites, broken-down samples were examined in Hungarian bauxite mines (Csordakút, Fenyőfő, Halimba). A total of 46 bauxite samples were taken from the recovered bauxite dumps, which were slightly chopped. The red mud samples (a total of 58 pieces) originated from the deposits of two alumina plants (Ajka and Almásfüzitő). The samples were taken from the surface and different depths (100-200 cm) of the deposit. The barren rock, which are lime samples (a total of 30 pieces) were collected from the refuse dumps located in the vicinity of the town of Ajka.

Several clay samples used in the processing of bricks were also analyzed. The samples were dried first in air then on 105 ^{o}C until mass constancy. The dried samples were stored for 30 days in air-tight aluminium Marinelli beakers with a volume of 600 cm^3 to reach the radioactive equilibrium of ^{226}Ra with its progeny.

Gamma activity measurements

The concentrations of natural radionuclides were determined by high resolution gamma ray spectrometry, using an Eurisys EGNC 20-190-R n-type HPGe detector with an efficiency of 20% and an energy resolution of 1.8 keV at 1332.5 keV. The gamma spectra were recorded by a Tennelec PCA-MR 8192-channel analyser. The data collection time was 60000-80000 s. The system was calibrated using an standard certified by the Hungarian National Authority of Measures.

The ^{226}Ra concentrations were determined by measuring the activities of its decay products ^{214}Pb (295 and 352 keV) and ^{214}Bi (609 and 1120 keV) that were in secular equilibrium with ^{226}Ra following the 30-days storage. The activity of ^{40}K was measured by the 1461 keV gamma ray, the ^{232}Th by the 911 keV gamma ray of ^{228}Ac and the 2614 keV gamma ray of ^{208}Tl [5].

Characterization of samples for use as building elements

The radiological testing of the investigated material is based on the concentration of the consisting ^{226}Ra, ^{232}Th and ^{40}K. The value recommended by the European Union (and some other countries like Finland, Norway) for the activity concentration index[22, 29].

$$I = \frac{C_{Ra}}{300\ \ Bq\,kg^{-1}} + \frac{C_{Th}}{200\ \ Bq\ kg^{-1}} + \frac{C_{K}}{3000\ \ Bq\ kg^{-1}}$$

where:

-I is the activity concentration index

-C_x is the measured activity concentration of the radioisotope x (Bq kg^{-1}).

Values recommended by the EU were taken into consideration during the qualification (Table 1).

Table 1.

The activity concentration index ("I")

Dose criterion	0.3 mSv y^{-1}	1 mSv y^{-1}
Materials used in bulk amounts, e.g. concrete	I ≤ 0.5	I ≤ 1
Superficial and other materials with restricted use: tiles, boards, etc.	I ≤ 2	I ≤ 6

Dose criterion means the dose exceeding the annual dose measured outdoors, which is usually determined by the value 0.3 $mSvy^{-1}$ or 1 $mSvy^{-1}$ according to the recommendation. At the moment there is no limitation for this in Hungary.

The mentioned industrial by-products are mostly used as additives in the production of building material. This must also be taken into consideration by the qualification as the recommended limit values refer to the end-product.

The recommended mixing ratios of the different literatures in the production of building ceramics and special cements are shown in Figure 1a. and 1b.

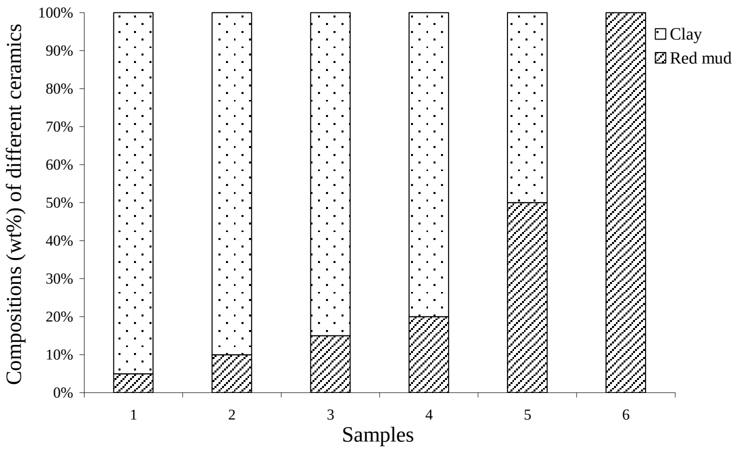

Fig. 1a. *Mixing ratios recommended in the production of building ceramics*

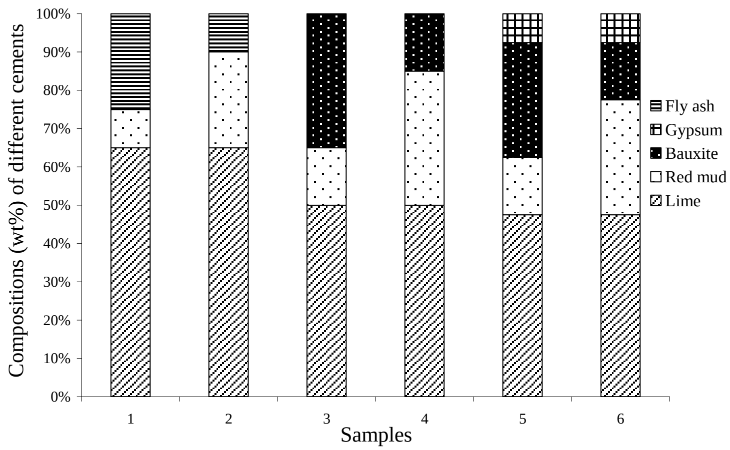

Fig. 1b. *Mixing ratios recommended in the production of special cements*

Determination of the emanation of the red mud

Following the gamma-spectrometry measurements the radon-emanation examinations were carried out on six pieces of red mud samples with different radon concentration, with 5-5 parallel per sample.

The red mud samples were dried and sieved on 105 ^{o}C until mass constancy. As more than 99% of the samples were within the range of 0.090-0.063 μm, measurements were only carried out with this fraction. 10g of the red mud was filled in a 50 cm^3 glass vial. The exact mass was measured after drying and the vial was sealed off. For the equilibrium of radium-radon it was left to stay for 30 days. Afterwards it was put in a metal dish called breaking cell with two faucets made by us and sealed airtight. The glass vial was broken with a shaking movement. The radon was flown from the breaking cell into a vacuumed $1dm^3$ Lucas cell with radon-free nitrogen gas (Figure 2.) through a filter preventing the inflow of dust particles and daughter elements stuck to them. The determination of the transmission efficiency was carried out on a slag sample with a high-emanation factor according to those described above. Here, the transfer was repeated with further two vacuumed Lucas cells and the total quantity of radon driven over to the 3 cells were considered to be 100%. The transmission efficiency examination was carried out five times and according to these the average was used for further calculations.

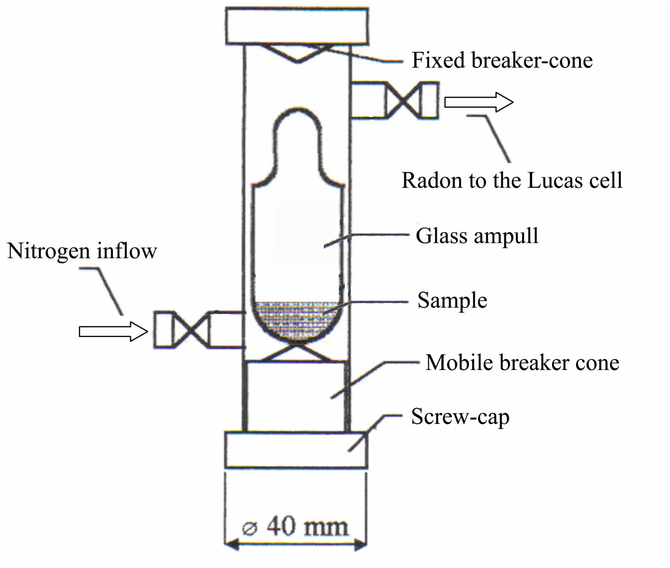

Fig. 2. Cross section of the breaking cell with the glass vial

To reach the equilibrium between radon and its daughter elements with a short half-life period, the Lucas cell was left to stay for 3 hours and then intensity was measured by connecting it to an EMI photoelectron multiplier for 2x2000 seconds.

Lucas cells were calibrated in a Genitron EV03209 calibration chamber using a PYLON RN 2000A radon emanation source (with ^{226}Ra activity: 105 ±0.4% kBq, radon emanation: 100%).

The activity of radon gas originating from the measured red mud was calculated according to the following relationship:

$$A_{Rn} = \frac{(B-H)}{\eta_t \cdot \eta \cdot_c S \cdot 3} \quad \text{where:}$$

A_{Rn}: activity of radon originating from the measured red mud (Bq)
B: gross intensity (cps)
H: background intensity (cps)
η_t: transmission (or transfer) efficiency
η_c: counter efficiency of the Lucas cell (cps Bq^{-1})
S: decay correction factor
„3": number of alpha particles following the radon decay in case of an equilibrium

The ^{226}Ra concentration of the given red mud sample was determined with an HPGe detector according to those described above. The emanation factor was calculated according to the following relationship.

$$\varepsilon = \frac{A_{Rn-222}}{A_{Ra-226}} \quad \text{where:}$$

A_{Rn-222}: is the activity of the ^{222}Rn generated in the glass vial from the measured red mud (Bq).

A_{Ra-226}: is the ^{226}Ra activity of the red mud measured in the glass vial (Bq).

RESULTS AND DISCUSSION

Radionuclides in the samples

Table 2. shows the ^{226}Ra, ^{232}Th and ^{40}K activity concentration, minimum and maximum and average values of bauxite, red mud lime and clay samples. The variation coefficients of the concentration measurements were between 3 and 10% depending on the radionuclides, activities, etc. The average values of lime and other gypsum literature values that were not examined by us are also indicated here.

Table 2.

^{226}Ra, ^{232}Th and ^{40}K average concentration of bauxite, red mud, lime and clay samples (minimum and maximum values).

Sample	Number of samples	Average radionuclide concentrations (min.-max.) (Bq kg^{-1})		
		^{226}Ra	^{232}Th	^{40}K
Bauxite	46	419 (132-791)	256 (118-472)	47 (10-82)
Red mud	58	347 (225-568)	283 (219-392)	48 (4.9-101)
Lime	30	1187 (358-2686)	33.4 (8.9-72.8)	185 (61-369)
Clay	7	39 (31.8-52.5)	59 (40.6-75.3)	688 (518-843)
Gypsum (world average)		10	10	80
Clay (world average)		50	50	670

Characterization of samples for use as building elements

The values of index I calculated from the radionuclide concentration of the given samples are shown in the following figure.

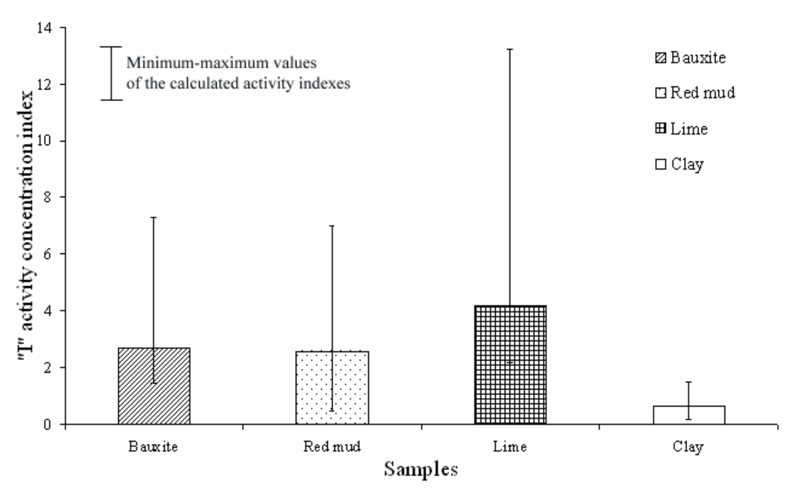

Fig. 3. *I values calculated from the activity concentrations of the examined samples*

Taking into consideration the dose recommended in the production of building ceramics and the measured average concentrations, the values of the activity index “I” were the results shown in Figure 4.

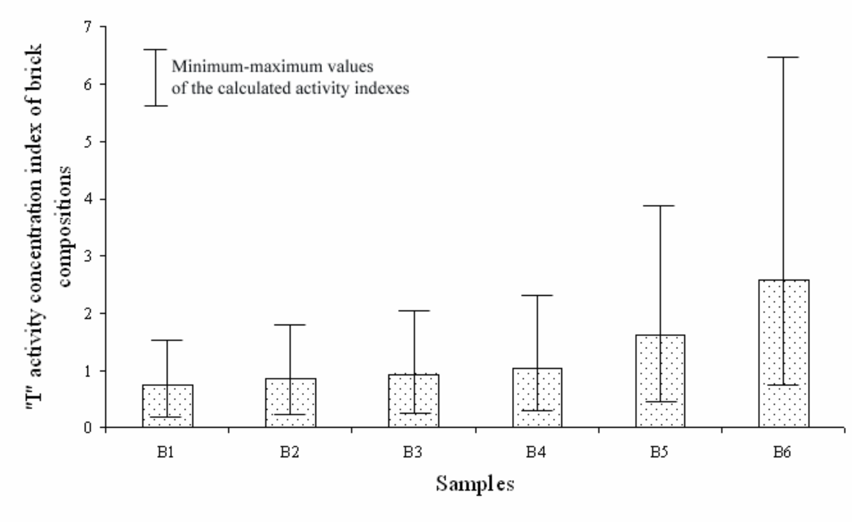

Fig. 4. *The "I" activity index values of brick compositions taking the activity concentrations measured by us into consideration*

According to the average values of the measured samples the activity indices "I" concerning cements are found in Figure 5.

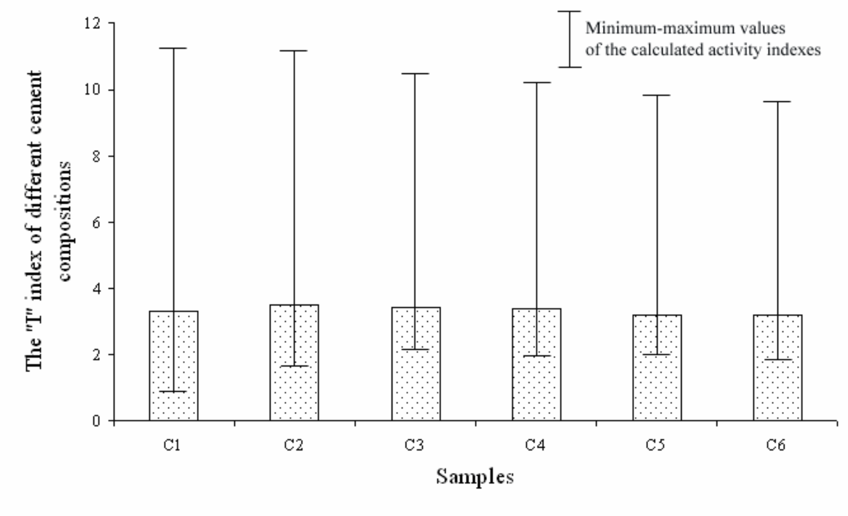

Fig. 5. *"I" activity index values of cement compositions*

As the ^{226}Ra activity concentration of lime originating from the coal barren rock is very high, it was examined how the values of "I" activity index change in the case of the use of lime with normal (that is corresponding to world average) radionuclide concentration (Figure 6.).

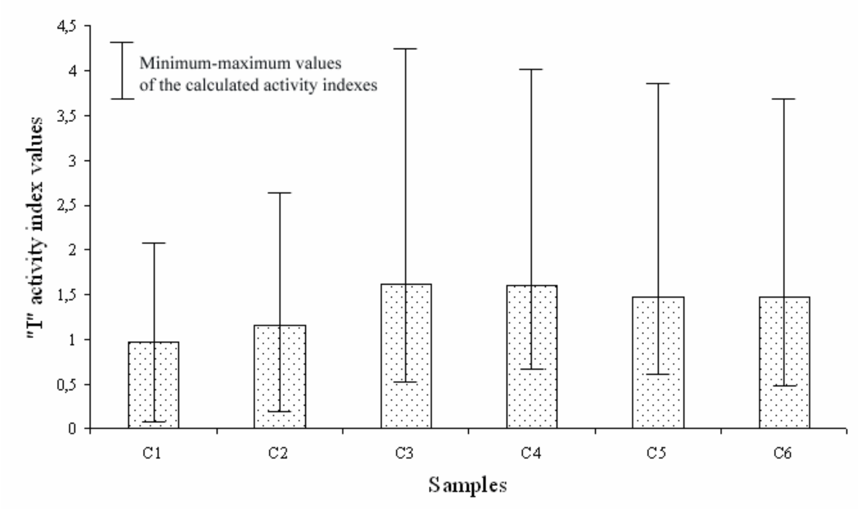

Fig. 6. *"I" activity index values of cement compositions calculated with the world average of gypsum and lime activity*

The use of these materials by road constructions planned near the disposal sites seems to be rather favourable as the radiological criteria of the usable materials are not so strict according to the international literature [2, 7, 9].

Emanation

The transmission efficiency's average result of the 5 measurement sequence was 99.7 (± 0.2 %) % in the first Lucas cell. Therefore afterwards radon was only transmitted to 1 cell from the breaking cell and a 99.7% transmission efficiency was used for calculation.

By the calculation of radon activity the efficiency characterizing the Lucas cell used for the actual measurement was calculated.

The emanation factor of the 6 pieces of red mud samples originating from different reservoirs was: 16.4 (14.5-18.6) ±12%.

CONCLUSIONS

According to the gamma spectrometry measurements it can generally be stated that the ^{232}Th and ^{226}Ra concentration measured in bauxite and red mud samples, significantly (5-7 times) exceeds the world average of radionuclide concentration of building materials (50-50 Bqkg^{-1}) but the concentration of ^{40}K has significantly stayed under (world average of ^{40}K 500 Bqkg^{-1}). The ^{232}Th and ^{40}K concentration of lime originating from coal barren rock is low but its ^{226}Ra concentration is very high. The ^{232}Th and ^{40}K activity concentration in the measured clay samples slightly exceeds the world average values measured in clays but it is not significant.

From a radiological point of view none of these materials – except for clay – can be used for building directly in great masses.

During brick production the 20% red mud composition ratio - considered to be optimal from a mechanical point of view- index “I” slightly exceeds the value $I \leq 1$ ($I=1.04$) therefore the usability is questionable. The condition $I \leq 1$ is only met in the case where the concentration of red mud is lower than 20%. A higher ratio of mixing is not recommended from a radiological aspect.

In the case of cements - used in relatively small amounts at building works-, the limits $I \leq 2$ and $I \leq 6$ must be met. From the aspect of average values only the recommendation valid for 1 mSv/y could be kept and this is true for all compositions. In the case where the lime does not originate from the coal barren rock with high ^{226}Ra-content is used as an additive, recommendation $I \leq 2$ equal to an overdose of 0.3 mSvy^{-1} is also met.

The radon emanation capability of red mud samples is high, therefore besides the gamma dose increase the radon concentration must also be accounted for. The radon emanation is supposed to vary on the course of the processing so studying it in the future is planned.

As a summary it can be stated that taking the average radionuclide content of red muds in Hungary into consideration these could be used in brick production in smaller quantities (e.g. as colouring agents), but it would be practicable to check all the products from a radiological point of view.

In the production of cement even lime originating from the high quantities of coal barren rocks found near red mud reservoirs could also be used for.

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SOURCE ZONE CHARACTERIZATION OF CHLORINATED SOLVENT CONTAMINATED SITES IN DEJ, ROMANIA

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ABSTRACT. Source Zone Characterization of Chlorinated Solvent Contaminated Sites in Dej, Romania. When we think of chlorine, we often related it to the salt used in food preparation, chloride in the oceans, chlorine gas from swimming pools, and gaseous chlorofluorocarbons that have close links to the depletion of stratospheric ozone. We rarely think of thousands of chlorinated hydrocarbons that exist in the natural systems, several of which are highly toxic to humans. These molecules tend to stay in the environment for a longer time, and threaten to contaminate aquatic and soil systems. There are also reported occurrences of bioaccumulation of anthropogenic chlorinated compounds in areas remote from human settlements, and such widespread distribution of organo-Chlorurated compounds is believed to be due to the high stability of man-made organohalogens and their long-range transport in the environment. The behavior and the ultimate fate of organo-Cl compounds in the environment are not well understood, and need a critical evaluation using the *in-situ* molecular techniques. Considerable amounts of organochlorine were detected in river water and soil samples during a 6 month study in Dej city region of Romania. They were identified using gas chromatographic - mass spectrometric (GC-MS) method. This paper demonstrates that static headspace GC-MS offers an alternative approach to this determination.

Keywords: *Volatile disinfection by-products, Trihalomethanes, Chlorine, Water Treatment Plant.*

INTRODUCTION

Many synthetic organic compounds that contain chlorine atoms (organochlorine compounds) were developed and used during the period of 1940-1980 for industrial applications. The widespread use of volatile chlorinated compounds like chloroform, trichloroethene and tetrachloroethene in industrial societies cause a large annual release of these compounds into the environment (1, 2). Due to their role as a source for halogen radicals involved in various catalytic atmospheric reaction cycles, including the regulation of the stratospheric and tropospheric ozone layers, these compounds also constitute a risk for drinking water resources (8) as they can be transported to the groundwater from contaminated field sites or even from atmospheric deposition (4,3,5). One characteristic of these compounds is their stability and persistence in the environment (12). The compounds were transported to rivers and streams by rainfall runoff and were incorporated into aquatic organisms and adsorbed to suspended sediment (6, 7, 9, 10, 11). Because of their stability and persistence in the environment and toxic effects on aquatic organisms and humans, organochlorine compound use decreased during the 1970's. Also because of the heavy use, persistent nature, and toxic effects, there is a need to understand the past and present occurrence of organochlorine compounds in the environment to help understand their effect on humans and aquatic organisms. Knowledge of the long-term occurrence of organochlorine compounds will help evaluate the effectiveness of environmental regulations controlling chemical use.

Identification and investigation of sources and sinks of volatile chlorinated compounds are of particular interest. Chlorinated solvents are organic compounds that are used in a variety of industrial, commercial, and domestic applications. Four of the most commonly used solvents are given focus here - methylene chloride, PCE, TCA, and TCE. Although relatively large quantities of these solvents are still used today, their production began declining as early as the 1970s in response to human-health and environmental concerns. Specifically, all four solvents have known human-health concerns, and methylene chloride and TCE are classified as probable carcinogenic. Most organochlorine compounds and trace elements are not highly water soluble; rather, they sorbed to sediments and accumulate along stream bottoms. Once contaminants reach the stream bottom, they can be ingested by benthic organisms and subsequently work their way through the aquatic food chain where they can bioaccumulate in animal tissue.

MATERIALS AND METHODS

Sampling: The sampling was made in different location on Somes River from Dej city. The water sample were take in duplicate, once he water was stored in 40 mL vials and closed with Teflon lined screw cap, preserved with sodium thiosulfate ($Na_2S_2O_3$) and keep refrigerated until analysis and in the second case the water sample were take in 1 liters bottles and kept at 4 ºC until the analysis. Soil samples were stabilized with methanol and kept at 4 ºC until the analysis.

Analysis: Soil and water sample was analyzed during six month. The quantitative and qualititative analyses of volatile halogenated hydrocarbons in the present review were achieved on Focus GC – quadupole DSQII MS (Thermo Electron Corporation, USA) using as column TR-5MS, 5% Phenyl (equiv) Polysilphenylene-siloxane (Thermo Finnegan, USA) with the following characteristics: 30 m x 53 mm, 3 μm film thickness, (Thermo Finnegan, USA). All analysis was performed using full scan mode.

RESULTS AND DISCUSSIONS

Beside the industrial sources of chlorinated compounds, natural sources may contribute significantly to the chlorocarbons in the environment.

Since chloroform has been identified as a carcinogenic compound for humans, and is present in enclosed environments and in our drinking water as result of treatment technology, it may be a cause for concern when high concentrations are discovered. Chloroform is a major contributor to natural gaseous chlorine. It was found to be emitted by several anthropogenic and natural sources including the terrestrial areas. However, the global anthropogenic flux of chloroform into the atmosphere is much too low to account for observed global background concentrations. Therefore, it is clear that natural sources also exist and must make major contributions to the total global sources. While chloroform alone may play a minor role in the global chlorine cycle, it may be worth considering more seriously when taken together with other naturally-produced chlorocarbons.

In analysis of the water sample and soil sample the main found organochlorine were chloroform, TCE and PCE (see table 1 and 2).

Table 1.

Chloroform, trichloroethene and tetrachloroethene concentration value (μg/l) during May – October 2007 from soil sample collected near from downstream of Somes River.

Month	Chloroform (μg/l)	Trichloroethylene (μg/l)	Tetrachloroethylene (μg/l)
May	57.92	36.09	27.66
June	66.29	33.26	54.37
July	79.5	52.1	76.28
August	86.22	44.68	69.45
September	74.92	43.95	35.82
October	43.95	29.41	39

Table 2.

Chloroform, trichloroethene and tetrachloroethene concentration value (μg/l) during May – October 2007 from raw water sample collected from exit from Dej city.

Month	Chloroform (μg/l)	Trichloroethylene (μg/l)	Tetrachloroethylene (μg/l)
May	22.14	25.09	18.26
June	15.92	28.71	34.08
July	28.34	18.44	42.08
August	19.05	37.09	44.51
September	11.53	28.69	27.63
October	14.02	19.48	20.49

Higher levels of these compounds were founded at down the river, close to exit from city.

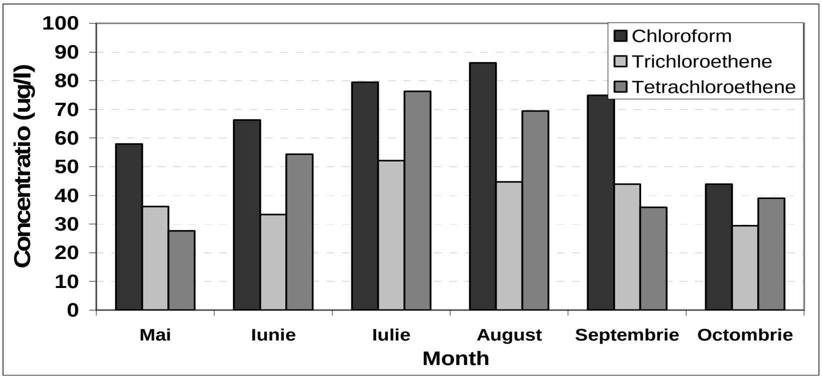

Figure 3. *Chloroform, trichloroethene and tetrachloroethene variation during May – October 2007 from soil samples (center of city).*

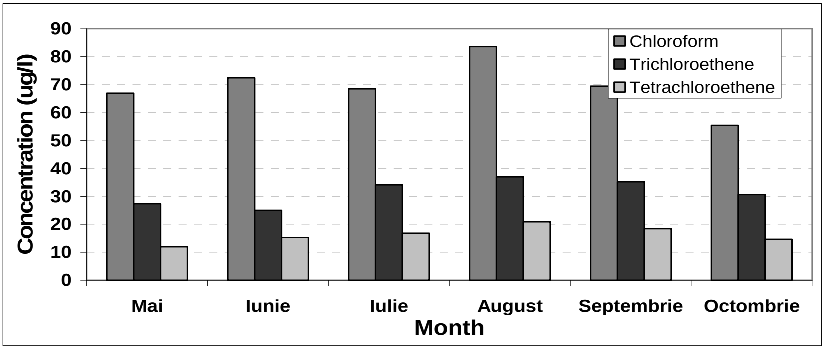

Figure 4. *Chloroform, trichloroethene and tetrachloroethene variation during May – October 2007 from surface water samples (exit from city).*

The formation and emission of chloroform by forest soil and observed large variation seen between sampling areas to the question of whether a seasonal variation exist (see figure 3 and 4). This may be expected if the production is biologically catalyzed.

CONCLUSIONS

The major identified organochlorine compounds in the water and soil sample was chloroform, trichloroethene and tetrachloroethene. The presented of TCE and PCE can be explained by human hand made pollution of the environmental especially in Dej city where in the environmental sample these compounds were measured in higher concentration.

That could be caused from the factory that releases the used water in the Somes River. Also they used in their work process substances like TCE and $CHCl_3$. But also the natural sources for chloroform exist and make a contribution to the global sources. While chloroform alone may play a minor role in the global chlorine cycle, it may play be worth considering more seriously when taken together with other naturally – produced chlorocarbons. During the different month it was observed a highly seasonally variability for that compounds. That can be explaining by the fact that when the temperature increases, reaction is faster between chlorine and natural organic matter present in the environment. In the winter months it is wait to be less concentration of these compounds because in some case ice cover protects surface of raw water and soil, and in that case the concentration of TCE, PCE and $CHCl_3$ found in nature due to their anthropogenic source are lower due to lower temperature and natural organic matter.

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STUDIA UNIVERSITATIS BABEŞ-BOLYAI, AMBIENTUM, LIII, 1-2, 2008

THE CO_2 ISOTOPIC SIGNATURES STUDY IN THE AREA OF CLUJ-NAPOCA

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ABSTRACT. The CO_2 Isotopic Signatures Study in the Area of Cluj-Napoca. The existing and potential feedbacks between terrestrial ecosystem processes and atmospheric CO2 concentrations remain one of the largest uncertainties in our understanding of the global carbon cycle. The isotopic composition of atmospheric CO2, contains information about the magnitude and distributions of sources and sinks of carbon. Biological and anthropogenic contributions to the CO2 mixing ratios are currently studied by using stable isotopes of carbon and oxygen. In this work, we identified the sources of the CO2 by Keeling plot method, which allows us to identify the sources of CO2 in the urban area of Cluj-Napoca.

Keywords*: stable isotopes, mass spectrometry, greenhouse gases, isotopic signature*

INTRODUCTION

Carbon dioxide has been called "the most important substance in the biosphere" *(Revelle, R.).* It makes life on Earth possible and warms our planet to the habitable conditions such that H_2O is in the liquid state. Carbon is the foundation of the world's major energy source, and as fossil fuels continue to be burned at an alarming rate of 30 trillion metric tons of CO_2 emitted per year, we have come to recognize the anthropogenic-induced global warming. The carbon cycle is a complex system of feedback mechanisms at many levels and has been the object of intense geological research. Stable isotopes have played a critical role in this research, constraining amounts and fluxes into and out of the various carbon reservoirs (*Sharp, Z.)*.

Carbon exist in oxidized, elemental and reduced forms. Oxidized forms include CO_2 and carbonates, elemental forms include graphite and diamond, and reduced forms include methane and organic matter. Other examples of each form exist as well. As in the case of almost all compounds, the heavy isotope ^{13}C is concentrated in more oxidized forms. The metabolic reduction of carbon (i.e., the formation of organic matter) is a non-equilibrium process in which ^{12}C is strongly partitioned into organic matter, leading to two major crustal reservoirs of carbon; a reduced low-$\delta^{13}C$ reservoir and an oxidized high- $\delta^{13}C$ reservoir. Assuming that most carbon in the surficial or crustal reservoir originated as volcanic CO_2 emissions, the massive biologically induced reduction of carbon over time led to a concomitant production of free oxygen (O_2 gas) critical to most life-forms on Earth today.

The carbon cycle is complex and has been studied at many scales. The mantle reservoir, which swamps all others in size, is unimportant in a consideration of changes in atmospheric CO_2 related to short-term anthropogenic contributions. Transfer to and from the mantle reservoir is simply to slow. Likewise, the abundance of CO_2 in the atmosphere is minuscule compared with the major reservoirs and can be ignored when one is concerned with the long-term carbon budget. However, the transfer of CO_2 between reservoirs can be accomplished via the atmosphere, making it an important flux between reservoirs. In addition to size, therefore, fluxes into and out of the different reservoirs are of critical importance.

As a first approximation, we can assume that the carbon cycle is a balanced, steady-state system. Fluxes into and out of each reservoir are more or less the same with the anthropogenic flux of fossil fuel CO_2 causing a minor, short-term imbalance. Although atmospheric CO_2 is small in amount, the fluxes involving it are immense, so that equilibrium between oceans and terrestrial organic carbon is maintained at a nearly steady state. There is a huge annual incorporation of CO_2 during plant respiration ($122x10^{15}$ g C/year) which is nearly balanced by the decomposition of plants and organic carbon in soil. The other large flux is between atmosphere and surface ocean, where CO_2 is transferred to dissolved bicarbonate and back again.(*Sharp, Z.)*.

MATERIALS AND METHODS

The air sampling was made in a particularly area of Cluj-Napoca ($46^0$78' N; $23^0$59' E). We collected the samples of air at different heights (0 m; 0.50 m; 1.25 m; 1.75 m; 2.1 m; 2.30 m) in flasks of 500 ml, that were evacuated previously. Air was pulled down into the flask, through a desiccant tube containing magnesium perchlorate using an EGM-4 Environmental Gas monitor for CO_2. Air was passed through the flask for approximately 5-10 min. before the flask to be closed. The flask was then returned to the laboratory for the extraction and purification of CO_2 from the sample air by cryogenic distillation by using a vacuum system, with two liquid nitrogen traps and finally transferred into a sample vial. Stable isotope carbon ratios were measured using the stable isotope mass spectrometer type Delta V Advantage using dual inlet method.

RESULTS AND DISCUSSION

Stable isotopes are a powerful research tool in environmental sciences and their use in ecosystem research is increasing. As the atmosphere integrates surface processes over space and time, CO_2 concentration measurements, provide constraints for regional scale sources and sinks of atmospheric CO_2 on time scale of months and longer (*D. E. Pataki et all).* Stables isotopes signatures of CO_2 along with CO_2 concentration measurements provide the basis for the "Keeling plots"

(*Keeling, C.D.*). This approach allows the identification of the isotopic composition and the contribution of ecosystem, or ecosystem components, to the exchange fluxes with the atmosphere (*Peter S. Bakwin et. all.).*

The equation used in the Keeling plot is derived from the basic assumption that the atmospheric concentration of a substance in an ecosystem reflects the combination of some background amount of the substance that is already present in the atmosphere and some amount of substance that is added or removed by sources or sinks in the ecosystem:

$$C_E=C_{bg}+C_s \tag{1}$$

where, C_E, C_{bg} and C_s are the concentrations of the substance in the ecosystem, in the atmosphere, and of the CO_2 that contributed by ecosystem sources, respectively. Isotopic mass balance can be expressed by a simple mass balance equation:

$$C_E\delta_E=C_{bg}\delta_{bg}+C_s\delta_s \tag{2}$$

where δ_E, δ_a and δ_s are the isotopic composition of the substance in the ecosystem, in the atmosphere, and of the sources respectively. Combining eqs. 1 and 2:

$$\delta_E=C_{bg}(\delta_{bg}-\delta_S)(1/C_E)+\delta_S \tag{3}$$

This is a linear relationship with a slope of $C_a(\delta_a - \delta_S)$ and an intercept at the δ_S value of the net source/sinks in the ecosystem. Even if the ecosystem source/sink is composed of several different sources/sinks, the Keeling-type plot can still be used as long as the relative contribution of each of these subcomponents remains fixed *(Yakir, L. and Sternberg S.L.).*

The carbon and oxygen isotope data are reported as δ values relative to VPDB, in units per mill (‰). The $\delta^{13}C$ is given as:

$$\delta\,^{13}C=[(^{13}C/^{12}C)_{sam}/\ (^{13}C/^{12}C)_{ref} - 1]*1000$$

and applies to $\delta\,^{18}O$ as well.

In this work we identified the sources of CO_2 in the urban area of Cluj-Napoca. The study was performed during a period of two month (August-September, 2007).The variations of CO_2 concentration C (CO_2) and its δ^{13} C value in collected air samples are summarized in Table 1.

Table 1.

Air samples collected in an area of Cluj-Napoca

Nr Crt.	**δ^{13} C**	**CO_2 concentration**	**$1/CO_2$**
1	-10.54	416	0.002403846
2	-11.453	427	0.00234192
3	-9.551	398	0.002512563
4	-9.851	395	0.002531646
5	-11.581	416	0.002403846
6	-11.299	416	0.002403846
7	-10.438	403	0.00248139
8	-10.974	412	0.002427184
9	-11.371	416	0.002403846

Nr Crt.	δ^{13} C	CO_2 concentration	$1/CO_2$
10	-10.682	404	0.002475248
11	-8.773	386	0.002590674
12	-8.901	387	0.002583979
13	-9.485	391	0.002557545
14	-8.383	385	0.002597403
15	-8.67	388	0.00257732

From the δ^{13}C values presented in Table 1 we can see that these values range between –11.581 ‰ and –8.383 ‰, depending on the time/date of sampling, height, and environmental factors.

Using these data we plotted the δ^{13}C values versus $1/CO_2$ and we obtained the Keeling plot. The intercept of this plot was found to be –41.35 ‰ (Fig. 1), which represents the isotopic signature of the source. This isotopic signature is composed by biogenic and anthropogenic source. Due to the fact that the sampling was performed in an urban area without vegetation, the biogenic source can be neglect in contrast with the anthropogenic sources. The isotopic signature of the source that we obtained is in a good agreement with the data reported in the literature (*Schimel et all, Broecher, W.S. and Pemg, T.H.)* for the anthropogenic sources (e.g. ≈ -40‰ for natural gas, - 30‰ for gasoline). From the isotopic fingerprint value we may conclude that in the studied area the anthropogenic source was mainly represented by CO_2 arising from natural gas rather than gasoline burn. This fact could be explained by taking into account the localization of the studied area.

The ~~high~~ R^2 value from the Keeling plot (R^2=0.911) show a small dispersion of the experimental points which means that the intercept value was not affected by experimental errors.

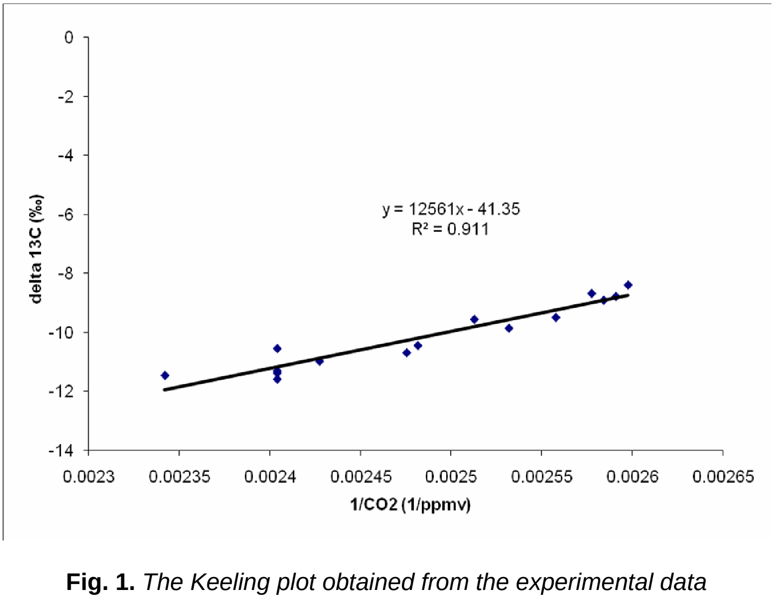

Fig. 1. *The Keeling plot obtained from the experimental data*

CONCLUSIONS

We collected air samples from different heights from an urban area to investigate the CO_2 emission at local carbon budget. By plotting $\delta^{13}C$ versus $1/CO_2$ we obtained the Keeling plot and thus we determined the isotopic signature of the source of CO_2. The value that we found suggests that the main contribution at CO_2 in the studied area is due to anthropogenic contribution. From the isotopic fingerprint value we may conclude that in the studied area the anthropogenic source was mainly represented by CO_2 arising from natural gas.

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STUDIA UNIVERSITATIS BABEŞ-BOLYAI, AMBIENTUM, LIII, 1-2, 2008

ACTUAL CLIMATIC CHANGES AND WHEAT PESTS IN CENTRAL TRANSYLVANIA

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ABSTRACT. Actual Climatic Changes and Wheat Pests in Central Transylvania. Elaborated in 1989-2006, at the Agricultural Research Station in Turda (The Romanian Academy of Agriculture and Forestry Sciences), in central Transylvania, the paper is a synthesis of the research on the plant protection and environmental applied domain of entomology and ecology.

The paper presents data on the pests and useful arthropod fauna, biological and agro-ecological aspects, experimental field trials for pest control and preventive measures, in order to achieve the integrated control system of the main species damaging wheat crops, to protect and use the natural reservoir of entomophagous in cereal agro-ecosystems.

The reason for this study has been the knowledge progress in the entomological research domain concerning the agricultural production safety by the development of the pest control technologies, the management of biological resources from agro-ecosystems, the increase and quality of the agricultural productions, in concordance with the concept of sustainable development, under the present climatic and agro-ecological changes.

Keywords: *wheat flies, cereal leaf beetle, aphids, leafhoppers, trips, predators.*

INTRODUCTION

The research regarding the populations dynamics, attack evolution and the control of wheat pests was carried out at Agricultural Research and Development Station Turda, in Central Transylvania, in the special conditions of 1989-2006 period. The paper presents the main wheat pests: Diptera, Homoptera, Thysanoptera, Coleoptera-Chrysomelidae, insecticides efficiency, cultural measures and entomophagous predators involved in the actual adequate strategy of integrated pests control, as part of agroecological technological system for sustainable development of wheat crop in Transylvania (Malschi and Mustea, 1992, Malschi, 1999, 2004, 2006, 2007).

Under the conditions of actual agro-ecological changes, yielded by climatic warming and dryness and new technological and economic conditions of zone agricultural exploitations, the original research was pointed aut the increasing attack of main wheat pests: wheat flies, leafhoppers, aphids, trips, bugs, cereal leaf beetle etc. and the oportunity of insecticide control.

MATERIAL AND METHODS

The data related to the composition of species, biology, evolution of the attack level and experimental control of wheat pests were obtained by researches performed in cereal agroecosystems and were statistically processed using correlation, variance analysis methods. The samplings were achieved by capturing insects pests and useful entomophagous predators, by means of pitfall soil traps, white adhesive sticky traps and 100 double sweep net catches. According to the natural agroentomocoenotic model, studies on prey compositions and feeding rate of predators were made in laboratory trials with pests.

RESULTS AND DISCUSIONS

Based on author's research studies at the Agricultural Research Station in Turda (The Romanian Academy of Agriculture and Forestry Sciences), in central Transylvania, in 1989-2006 period, the paper presents the agro-ecological study on the population dynamics and attack evolution of wheat pests entomofauna: Diptera, Homoptera, Thysanoptera, Coleoptera, Heteroptera etc., and biotechnological experiments on the adequate integrated pest control methods, including insecticides efficiency, cultural measures and entomophagous predators limiters, environmental protection, conservation and sustainable use of biodiversity, involved in the actual pests control strategy, as part of the technological system for sustainable development of cereal crops. The paper presents data on the pests and useful arthropod fauna, biological and agroecological aspects, experimental field trials for pest control and preventive measures, for the integrated control of the main species damaging wheat crops (Baniță et al.,1999, Baicu 1996, Bărbulescu 1997, Malschi and Mustea 1992, Wetzel 1995).

In the last years, the increase of pest density in some crops and some unexpected attacks (table 1) have been produced by specific zonal factors such as the continuous annual increase of biological reserve of pests, the increase of arid microclimate and the attack aggressions of pest, the decrease of the grain crops area, the exploitation farming system with incomplete or incorrect crop technologies of wheat crops in Central Transylvania (Malschi and Mustea, 1992, 1995).

The natural predators play an important role in decreasing the wheat pest abundance (Basedow 1990, Banița et al.1999, Malschi, Mustea, 1995, 1997, 1998, Malschi, 2003, Rupert, Molthan 1991, Wetzel, 1995, Welling 1990). The well-known systematic groups of enthomophagous predators: Aranea; Dermaptera; Thysanoptera (Aeolothripidae); Heteroptera (Nabidae etc.); Coleoptera (Carabidae, Cicindelidae, Staphylinidae, Sylphidae, Coccinellidae, Cantharidae, Malachiidae); Diptera (Syrphidae, Scatophagidae, Empididae etc.); Hymenoptera (Formicidae etc.); Neuroptera (Chrysopidae) were represented in the structure of arthropod fauna (table 2).

The spring months of the last years 2000–2006 (table 3), was characterized by an increased warming, heating and dryness periods, causing the increasing of pests abundance and damages on wheat crops, in Transylvania (Malschi 2000, 2001, 2004, 2005, 2006, 2007). It was remarked (tables 4 and 5) a reduction of species diversity and an increasing abundance of the species with a single generation by year: *Delia coarctata* Fallén 1794*, Opomyza florum* Fabricius, 1794*, Phorbia penicillifera* Jermy, 1952*, Oulema melanopus* Linnaeus, 1758*, Chaetocnema aridula* Gyllenhal, 1827*, Eurygaster maura* Linnaeus, 1758*, Aelia acuminate* Linnaeus 1758*, Haplothrips tritici* Kurdjumov, 1912*, Zabrus tenebrioides* Goeze, 1777, and of the other species of chloropids (*Oscinella frit* Linnaeus, 1758, *Oscinella pusilla* Meigen, 1830, *Elachiptera cornuta* Fallen, 1820, *Meromyza nigriventris* Macquart, 1835, *Chlorops pumilionis* Bjerkander, 1778, *Lasiosina cinctipes* Meigen, 1830), anthomyiids (*Phorbia securis* Tiensuu, 1936*, Delia platura* Meigen, *1826, Delia liturata* Meigen, *1838*), cecidomyiids (*Mayetiola destructor* Say, 1817), leafhoppers (*Psammotettix alienus* Dahlbom, 1850, *Macrosteles laevis* Ribaut, 1927, *Macrosteles sexnotatus* Fallen, 1806, *Javesella pellucida* Fabricius, 1794), aphids (*Schizaphis graminum* Rondani, 1847, *Macrosiphum (Sitobion) avenae* Fabricius, 1775, *Rhopalosiphum padi* Linnaeus, 1758, *Metopolophium dirhodum* Walker, 1849) etc., well favored by consecutive wheat crops and zone cereal ecosystems presence (tables 6 and 7).

The attack critical moments of the different species were registered with 3–4 weeks earlier and superposed. The insecticide treatments were imposed at the end of tillering phase in April and at the spike appearance phase, in middle of May.

Table 1.

Evolution of the attack potential of wheat pests, in 1989-2005, at ARDSTurda

Pests	**1989-1999 period**	**2000-2002 period**	**2003-2005 vegetation year**	**Economic density threshold/ vegetative stage**
Cereal flies-diptera : *Delia coarctata, Opomyza florum, Phorbia penicillifera, Phorbia securis, Oscinella frit, Meromyza nigriventris*	22 April	10 March-20 April	15-30 April	*Tillering*
	16 % plants 6 % tillers	26 % plants 11 % tillers	30 % plants 11 % tillers	5-10% plants
	10-28 May	4-10 May	12-22 May	*End of tillering*
	17 % plants 12% tillers 65 tillers/m^2	28 % plants 23 % tillers 186 tillers/m^2	66-87 % plants 62-72 % tillers 321 tillers/m^2	10-15 % plants
Cereal leaf beetle: *Oulema melanopus*	8-15 June	28 May-17 May	6-24 May	*Flag leaf-heading*
	265 larvae /m^2	317 larvae/m^2	13 adults/m^2 350 larvae/m^2	10 adults/m^2 250 larvae/m^2
Wheat thrips - adults : *Haplothrips tritici*	25 May	15-17 May	12-22 May	*Heading*
	6 adults/ear	12 adults/ear	12 adults/ear 20 adults/m^2	8 adults/ear 5 adults/m^2
Wheat thrips - larvae *Haplothrips tritici*	10-25 June	10-25 June	12 June	*Milky- ripening*
	13 larvae/ear	22 larvae/ear	11 larvae/ear	10-40 larvae /ear

Pests	**1989-1999 period**	**2000-2002 period**	**2003-2005 vegetation year**	**Economic density threshold/ vegetative stage**
Cereal bugs *Eurygaster maura, Aelia acuminata*	10-25 June	15-25 May	22 May-10 June	*Heading-ripening*
	1-2 adults/m^2 2-3 larvae/m^2	1-3 adults/m^2 3 ears/m^2	3-6 adults /m^2 4,4 % ears	3-4 adults/m^2 3-5 larvae/m^2
Aphides: *Sitobion avenae, Schizaphis graminum, Rhopalosiphum padi, Metopolophium dirhodum*	25 June	10-24 June	10 June	*Milky- ripening*
	12 aphides/ear	32 aphides/ear	1,3 aphides/ear	25 aphides/ear
			14.11. 2002	*2-3 leaves*
			4-6 aphides/pl. 80% plants	5 afide/plant
Cicadae: *Psammotettix aliaenus Javesella pellucida Macrosteles laevis ş.a.*	5-14 July	20 June-5 July	10 May-10 June	*Emergence*
	9,9 /m^2/10/ sweep net catches	2,5-5 cicadae /m^2/10 sweep net catches	7-10 cicadae/m^2	5 cicadae/m^2/10 sweep net catches
			14 Nov. 2002 6 cicadae/m^2	

Table 2.

Structure of enthomophagous predators in cereals agro-ecosistems, at ARDS Turda

1. Ord. Dermaptera	Fam. Forficulidae: *Forficula auricularia* L.
2. Ord. Heteroptera	Fam. Nabidae: *Nabis ferus* L. Fam. Anthocoridae: *Anthocoris nemorum* L. Fam Miridae: *Daraeocoris ruber* L.
3. Ord. Thysanoptera	Fam. Aeolothripidae: *Aeolothrips intermedius* Bagn.
4. Ord Coleoptera	Fam. Carabidae: *Poecilus cupreus L., Amara aenea De Geer., Pterostichus melanarius Ill., P. macer Marsh., Harpalus distinguendus Duft., H. rufipes De Geer., H. aeneus L., H.affinis Sch., Brachinus explodens Duft., Loricera pilicornis F., Platynus dorsalis Pont., Dolichus halensis Schall., Agonum muelleri Hbst., Carabus coriaceus L., Carabus nemoralis Mull.* Fam. Cicindelidae: *Cicindela campestris* L. Fam. Staphylinidae: *Tachyporus hypnorum L., Staphylinus sp.* Fam. Sylphidae: *Sylpha obscura L., Necrophorus vespillo L.* Fam. Cantharidae: *Cantharis fusca L.* Fam. Malachiidae: *Malachius bipustulatus L.*

	Fam. Coccinellidae:*Coccinella septempunctata L.,Propylaea quatuordecimpunctata L., Adalia bipunctata L., Anattis occellata L., Hippodamia tridecimpunctata L., Adonia variegata Goeze., Chilocorus bipustulatus L*.
5. Ord. Hymenoptera	Fam. Formicidae etc.
6. Ord. Planipennia	Fam. Chrysopidae: *Chrysopa carnea* Stephn.
7. Ord. Diptera	Fam. Empididae: *Platypalpus* sp. Fam. Dolichopodidae: *Medetera* sp. Fam. Scatophagidae: *Scatophaga stercoraria* L. Fam. Tachinidae: *Lydella* sp. Fam. Syrphidae: *Episyrphus balteatus Dg., Metasyrphus corollae Fabr*.

Table 3.

Average temperatures and sum of rainfall zone conditions by month,from March toSeptember by vegetation year, in1989-2006, and by normal annual conditions, at ARDSTurda

Average temperatures ^{o}C	Mar.	Apr.	Mai	Iun.	Iul.	Aug.	Sept.	Annual
2006	3.4	10.8	14.3	17.6	21.2	18.5	15.8	8.9
2005	1.5	9.8	15.7	17.2	19.7	19	16.1	9.0
2004	4.7	10.7	14	18.3	19.3	19.3	14.1	9,1
2003	2.4	8.4	19.5	21.1	20.3	21.9	15.9	9,4
2000-2002	6.0	11.2	16.9	18.4	20.5	20.4	14.3	9,76
1989-1999	4.3	9.8	14.7	18.3	19.9	19.8	14.5	9,09
Normala	3.9	9.4	14.5	17.4	18.5	18.5	15.0	8,6
Rainfall sum (mm)	**Mar.**	**Apr.**	**Mai**	**Iun.**	**Iul.**	**Aug.**	**Sept.**	**Annual**
2006	45.3	70.8	77.9	118.2	16.5	148.6	32.6	589,0
2005	33.3	81.5	54.9	95.4	131.6	180.8	62.4	798,5
2004	28.8	49.4	15.2	85	160.1	111.9	76.6	527,2
2003	13.9	17.9	26.6	21.9	151.3	1.3	28.3	406,9
2000-2002	26.1	30.6	46.8	65	77.2	37.5	66.5	442,7
1989-1999	14.1	44.1	60.5	102.8	58.4	53.6	44.8	487.1
Normala	24.2	48.2	71.3	75.7	70.8	55.5	34.5	509,2

Table 4.

Dynamics of cereal pests, in 2003-2005, ARDS Turda

Sampling data	21. 04.	06. 05.	12. 05.	22. 05.	26. 05.	30. 05.	10. 06.	12. 06.	18. 06.	29. 06.
Oulema melanopus		58	1	7		4	1		4	1
Chaetocnema aridula	2	78	5				10	19	3	5
Phorbia securis	25	11	2							
Oscinella frit	3	6	40	1	2	3	6		6	3
Elachiptera cornuta		2	8	1	1					
Meromyza nigriventris		25	68	1	1	2	3	1	5	6

Sampling data	**21. 04.**	**06. 05.**	**12. 05.**	**22. 05.**	**26. 05.**	**30. 05.**	**10. 06.**	**12. 06.**	**18. 06.**	**29. 06.**
Lasiosina cinctipes		46	8	1	1	2				
Opomyza florum							6	4	3	
Delia coarctata		4	4	1			6	8		3
Haplothrips tritici		14	160	200	140	180	32	66	37	10
Aphids			2	6	3	5	51	62	36	8
Cicades	4	44	68	7	2	5	46	27	68	33
Eurygaster, Aelia etc.		6	3	27	15	3	58	11	20	7

Table 5.

Dynamics of cereal useful entomophagous arthropod fauna, in 2003-2005, ARDS Turda

Sampling data	**21. 04.**	**06. 05.**	**12. 05.**	**22. 05.**	**26. 05.**	**30. 05.**	**10. 06.**	**12. 06.**	**18. 06.**	**29. 06.**
Aranea	3	37	29	16	3	7	58	32	16	15
Hymenoptera		15	6	3	3	6	9	2	1	2
Chrysopa carnea			2		2			2	2	
Aeolothrips intermedius			8		3	26			6	
Nabis ferus		7	1	8	2	4	55	31		
Coccinella 7- punctata		2	2	1	1	2	2	2		4
Propylaea 14-punctata		4	5							
Malachius bipustulatus			1	3	4	2	1		1	
Cantaris fusca			3			15				
Carabidae	13	17	2	2						
Platypalpus sp		2	3	2						
Thaumatomyia glabra		3			1	2	1			
Syrphidae				3	1	1				

Table 6.

Structure of cereal pests in 2003-2005, ARDS Turda

Cereal pest species	In winter wheat	In spring barley
Haplothrips tritici	35,1%	4,0%
Oulema melanopus	3,2%	80,1%
Chaetocnema	15,2%	1,7
aridula	5,1%	0,4%
Phylotreta sp.	13,7%	7,1%
Cereal flies	12,7%	6,1%
Cicades	7,2%	0,4%
Aphids	6,4%	0,1%
Cereal bugs	1,4%	0,1%
Other pests		

Table 7.

Structure of pest larvae in wheat tillers, in the spring:10-20.05.2003-2005, ARDS Turda

Species	consecutive wheat crop	wheat with bean precursory crop
Phorbia securis	38,0 %	19,7 %
Phorbia	26,0 %	12,5 %
penicillifera	12,0 %	4,2 %
Delia coarctata	4,0 %	4,2 %
Opomyza florum	4,0 %	9,0 %
Chloropidae	16,0 %	50,0 %
Chaetocnema aridula		

The paper point out the extension risk of wheat pests attack with an increasing potential, affecting the wheat crops yields and causing possible crops damages or carried at compromise of the specially sowing fields of consecutive wheat crop and of early sowing, in September and the importance of the elaboration of agro-ecological integrated control strategy (ICS). The attack reduction methods of the ICS are: **a) agro-technical methods:**_avoid early planting in the autumn to minimize the incidence of insect vectors and diptera species, destroy volunteer wheat, adequate fertility, use good seed quality, the weeds, main pests and diseases control, conservation and use of biological factors: tolerant varieties, entomophagous limiters; **b) application of selective insecticides,** with economic and ecological efficiency, at two different selective moments. Usual insecticides treatments (pirethroids, neonicotinoids, fipronil, acetamiprid, organo-phosphorics etc.) were tested and efficiently used, in the two different selective moments of application: 1 - on the control of wheat flies larvae *(Delia coarctata, Opomyza florum, Phorbia securis, Ph. penicillifera, Oscinella frit etc.)*, in April, at the end of tillering phase (13-33 DC stage), controlling other pests of wheat, too; 2 - on the wheat thrips (*Haplothrips tritici*) adults control during spike appearance phase in 45-59 DC stage, during May 15th-25th, the treatments being efficient in controlling all dangerous pests of wheat.

Laboratory tests and investigation regarding the role of the main species of predatory entomophagues as regulators of pest populations in cereal agro-ecosystems, demonstrated that various species feed preferentially on wheat flies, cereal aphids, trips, bugs, *Oulema* etc**.** (table 8). The results of laboratory feeding trials with cereal pests regarding feeding habits of predators, prey composition and feeding rate per day and individual presented the importance of dominant predatory species (Malschi, Mustea, 1995, Malschi Dana, 2003). *Coccinella septempunctata L. (Coccinellidae*) is able to eat eggs and larvae of *Oulema melanopus* L., larvae and pupae of diptera (*Opomyza florum* F., *Phorbia securis Tiensu*, *Delia coarctata* Fll.), eggs of *Eurygaster maura* L., larvae of *Haplothrips tritici* Kurdj., aphids (*Sitobion avenae* Fabr., *Rhopalosiphum padi* L.) etc., *Malachius bipustulatus* L.(*Malachiidae*) consumed larvae of *Oulema*, aphids, adults and larvae of *Haplothrips tritici*. *Cantharis fusca* L. (*Cantharidae*), was capable of destroyng *Oulema* eggs, aphids, adults of Haplothrips, larvae and pupae of diptera (*Opomyza*). *Episyrphus balteatus* Dg.(*Syrphidae*) consumed especially aphids and trips. *Chrysopa carnea Stephn. (Chrysopidae*) and *Nabis* spp. (*Nabidae*) could kill eggs and larvae of *Oulema*, aphids, trips, eggs of *Eurygaster* etc. *Sylpha obscura (Sylphidae)* consumed larvae and eggs of *Oulema*, eggs, larvae, pupae of diptera (*Phorbia*); *Tachyporus hypnorum* L., *Staphylinus* spp. (*Staphylinidae*) and *Poecilus cupreus* L., *Harpalus rufipes* De Geer, *Brachinus explodens* Duft., *Amara aenea* De Geer (*Carabidae*) consumed aphids, eggs of Eurygaster, eggs and larvae of *Oulema*, larvae and pupae of diptera etc.

Tabel 8.

Prey composition and feeding rate of main predators with cereal pests in laboratory trials

Entomophagous predators	1	2	3	4	5	6	7	8	9	10	11
Chrysopa carnea (larva)	10	5	10	40	30	50	10	3	1	2	-
Nabis ferus (adult)	8	5	-	42	60	25	-	3	4	3	4
Nabis ferus (larva)	-	-	-	30	25	17	-	-	-	-	-
Coccinella 7-punctata	10	3	-	35	50	25	16	5	7	5	7
Propylaea 14-punctata	7	3	-	20	40	25	-	-	2	-	-
Malachius bipustulatus	-	10	15	30	40	-	-	-	-	3	-
Cantharis fusca	6	-	15	-	40	-	-	2	-	4	-
Staphylinus spp.	10	-	-	-	30	15	-	1	-	4	4
Tachyporus hypnorum	8	-	-	-	-	25	-	1	-	1	-
Poecilus cupreus	9	6	-	-	60	50	10	5	10	5	7
Pseudophonus pubescens	8	9	-	-	60	50	10	1	-	2	1
Harpalus distinguendus	8	3	-	-	-	50	-	-	-	2	2
Harpalus aeneus	5	4	-	-	-	50	-	-	2	4	2
Amara aenea	9	5	-	-	-	50	10	-	-	8	-
Brachinus explodens	-	5	-	-	25	30	-	-	-	-	-
Sylpha obscura	14	3	-	-	-	-	10	1	4	2	4
Episyrphus balteatus	-	-	10	-	25	-	-	-	-	-	-

1-Oulema melanopus eggs and 2-larvae, 3-Haplothrips tritici adults and 4- larvae, 5- Sitobion avenae, 6. Rhopalosiphum padi, 7- Eurygaster maura (eggs), 8- Opomyza florum larvae and 9- pupae, 10-Phorbia securis larvae, 11-pupae.

Diptera pest species. The increase of damages produced by diptera larvae was registered in zonal cereal crops, intensely affected by climatic unfavorable conditions and by the exploitation agro-ecosystems. The recorded diptera species are present in their geographical area and possess a high biological reserve (Malschi and Mustea 1992, Malschi 1997, 1998, 1999, 2006). The early sowing of crops in September provokes the dangerous autumn attack of *Oscinella frit* L., *Mayetiola destructor* Say and *Phorbia securis* Tiensuu. The biological potential and the early spring attack of *Delia coarctata* Fall. and *Opomyza florum* F. increase very much when the emergence of wheat takes place in October. But, the late emergence of crops in November determined the preferential attack of *Phorbia penicillifera* Jermy and *Ph. securis* in the spring and the development of populations. The most important attack of diptera took place at the beginning of spring. The experimental results suggest the following preventive control measures: late sowing data (in the first half of October); zonal adequate agrotechnological measures for wheat crops, ensuring a good development of plants and for a productive compensatory tillering effect of attacked plants; cultivation of wheat varieties with high compensatory capacity after the diptera attack (consisting in 70-80% at Transylvania, Turda 95, Arieşan, Apulum varieties). The grain yield losses for every attacked plant were registered at: the level of 0.92-1.47 g/plant for *Delia coarctata*; 0.57-1.22 g for *Opomyza florum*, in April and 0.93-1.27 g for *Phorbia securis*, in May. This means: 516; 397 and 478 kg/ha average grain yield losses, under optimum zonal wheat crop conditions, with a density of 450 wheat plants/m^2 and 10% attacked plants.

Preventive seed and field treatments with insecticides have only a partial efficiency (50-75% larval mortality) because of the life cycle of different species and the feeding behavior of larvae within wheat tillers. Special chemical control should be related to the economic damage threshold, the insecticides biological efficiency, the side-effect of insecticides on the useful entomophagous fauna, especially predators (Carabidae, Staphylinidae, Sylphidae, Coccinellidae, Nabidae, Aranea etc.) involved in diptera pest population levels. The results of field tests concerning the side - effects of insecticides showed the slightly harmful toxicity on the auxiliary entomophagous predators, in the early spring applications of insecticides.

The optimal moment of spring treatment application is at the first larval stage of *Opomyza florum* and *Delia coarctata* and at the adult flying of *Phorbia* species, simultaneously. The biological effect of applied insecticides was significantly on the increasing wheat yields with 7-21 % when dimethoate, chlorpyriphos-etil, chlorpyriphos-metil, bensultap, fipronil, acetamiprid, lufenuron, thiachloprid, thiametoxam, different complex insecticides as fenitrotion with esfenvalerat; oxidemeton metil with betaciflutrin were used (Table 9 and 10).

Cereal leaf beetles (*Oulema melanopus* L.). In the last years the biological reserve and the attack potential of the cereal leaf beetle have exceeded the economic damaging threshold, being higher than 10 adults/m^2 and 250 larvae/m^2 (Malschi 2000, 2005). The increase of pest density and attack in certain crops was due especially to the arid microclimate in early spring and in May-June period which caused the increase of the attack aggressions of adults and larvae for the establishment of their favorable nourishment conditions.

The pest larvae damaging potential is reduced by the predators activity and by climate conditions as abundant rains and low temperatures, which are unfavorable for the eggs and larvae of the pest first age. Chemical control is recommended after the limitative activity of the natural factors has been developed, at the massive apparition of the first age larvae and it is applied in the attack areas identified. The insecticide control of *Oulema* had more than 85% efficiency.

Table 9.

Efficiency of seed insecticides for wheat diptera pest control, in 2001-2006, A.R.D.S. Turda

Varianta	Doza p.c./t	Efficiency (%)	Kg/ha (%)
COSMOS 250 FS *(fipronil)*	2,5 l	40	115
YUNTA 246 FS *(imidacloprid)*	2,0 l	44	111
CRUISER 350 ST*(thiametoxam)*	1,5 l	19	116
CRUISER 350 ST	3,0 l	25	117
TEFLUTHRIN 300	0,17 l	47	107
TEFLUTHRIN 300	0,33 l	42	112
TONIC *(tefluthrin 200)*	0,5 l	42	109
TONIC	1,0 l	35	108
Check (163 larvae/m^2)	-		100 (3964 kg/ha)

Table 10.

Efficiency of insecticides for wheat diptera-larvae-pest control, in April, 2000-2002, A.R.D.S. Turda

Insecticides	Product and dose/ha	Efficiency %	Grain yield		
			Kg/ ha	%	Differ.
Bensultap	Victenon 50 WP (400 g)	43	4635	106.7	291*
Fipronil	Regent 200 SC (90 ml)	45	4778	110.0	434***
Acetamiprid	Mospilan 20 SP (100 g)	56	4778	110.0	434***
Thiacloprid	Calypso 480 EC (100 ml)	29	4735	109.0	391**
Thiametoxam	Actara 25 WG (60 g)	45	4661	107.3	317**
Lufenuron	Match 050 EC (300 ml)	58	4844	111.5	500***
Oxidemeton metil-betaciflutrin	Enduro 258 EC (1000 ml)	41	4722	108.7	378***
Fenitrotion-fenvalerat	Alpha-Combi (500 ml)	47	4865	112.0	521***
Clorpirifos-etil	Pyrinex 25EC (3500 ml)	50	4952	114.0	608***
Clorpirifos metil	Reldan 40 EC (1250 ml)	44	5039	116.0	695***
Dimetoat	Dimezil 40 EC (2000 ml)	47	5256	121.0	912***
Check (186 larvae/m^2)		-	4343	100.0	-
F=5.1* (3.05); LSD 5% - 225 kg; LSD 1% - 303 kg; LSD 0.1% - 404 kg					

The laboratory tests have established the importance of the auxiliary entomophagous predator species (*Chrysopa carnea* Stephn, *Nabis ferus* L., *Coccinella septempunctata* L., *Propylaea quatuordecimpunctata* L., *Malachius bipustulatus* L., *Cantharis fusca* L., *Tachyporus hypnorum* L., *Aleochara bilineata* Gyll., *Poecilus cupreus*

L., *Pterostichus mellanarius* Ill., *Pseudophonus pubescens* De Geer., *Harpalus distinguendus* L., *H. aeneus* L., *Amara aenea* De Geer., *Brachinus explodens* Duft., *Sylpha obscura* L.), involved in pest natural biological control, pointing out the active predatory species which have a high predatory capacity, eating between 5 and 39 eggs/ day/individual and between 3 and 40 larvae of *Oulema*/day/ individual predator.

Wheat trips (*Haplothrips tritici* Kurdj.) is an important pest, the adults and larvae causing damages by feeding on wheat ears (Baniță 1999, Malschi 2001, 2005). Larvae cause the greatest damage at the end of June and beginning of July. In the last years the increase of *H. tritici* populations at average values of 12.5-22.0 larvae/ear has been favoured by the agro-ecological conditions especially by warming microclimate and by constant wheat cultivation in the zone.

One of the most important factors for limitation of pest development is represented by the activity of natural entomophagous predators which destroy the trips adults, eggs and larvae. At the beginning of spike appearance, the economic damaging threshold (EDT) of 5 adults/m^2 (or 5 adults/10 sweeps with net catches) is surpassed, but in the next vegetation stages, at the kernel formation and ripening, the EDT values of 8 adults/ear or 10-40 larves/ear are no more attained, due to predators activity. The maximum activity of predators involved in natural limitation of wheat thrips is attained at flowering and milky stage, in half of June. The studies on the destructive ability of predators against wheat thrips *H. tritici* their individual pray ratio/day in laboratory feeding trials have demonstrated that 10-15 adults of thrips/day/individual of *Chrysopa, Episyrphus, Malachius* or *Cantharis* have been destroyed and also 10-42 thrips larvae per day and per individual of *Chrysopa* and *Epishyrphus* and adults and larvae of *Nabis* and *Coccinella* of *Propylaea, Malachius, Pseudophonus pubescens.*

Some insecticides efficiency in the larvae control and the influence on wheat yield were tested in the period of 15-25 May 2001-2002, at heading-spike appearance phase (in 45-59 DC stage) (Table 11) in order to protect and use the beneficial predators peak activity, too The treatments with adequate insecticides: chlorpirifos-metil, dimetoat, deltametrin, tiacloprid, thiametoxam, acetamiprid, fipronil, bensultap, fenitrotion-fenvalerat, oxidemetonmetil-betaciflutrin, chlorpirifos - cipermetrin etc. provided statistically significant grain yields amounting to 10 to 23 % and high thrips control efficiency to 70 on 90%.

Tabel 11.

Effect of insecticides treatment on wheat thrips (Haplothrips tritici Kurdj.) control at heading- spikes appearance phase, in 45-59 DC stage, at May, 15-25 period, 2001-2002,ARDS Turda.

Product and dose/ha	Efficiency %	Grain yield		
		Kg/ha	%	Difference
Check (9,2 larve/spic)	-	5081	100	-
Mospilan 20 SP 100 g	44	5887	116	806*
Alpha-Combi 25,26EC 500ml	78	5657	111	576
Victenon 50 WP 500 g	66	5657	111	576
Actara 25 WP 60 g	57	5696	112	615

Calypso 450 SC	100 ml	62	5555	109	474
Nurelle D	400 ml	68	5788	114	707*
Reldan 40 EC	1250 ml	70	5946	117	865*
Regent 200 SC	90 ml	72	6330	124	1249***
Average			5805	114	724
DL p 5%-641, DL p1%-883, DL p 0,1 %-1216					

Homoptera (Aphidina, Cicadina). The main Homoptera species: *Schizaphis graminum* Rond., *Macrosiphum avenae* Fabr., *Rhopalosiphum padi* L., *Metopolophium dirhodum* Walk. (Aphididae) and *Psammotettix alienus* Dahlb., *Macrosteles laevis* Rib., *M. sexnotatus* Fall. (Cicadellidae), *Javesella pellucida* Fabr. (Delphacidae) were find out with an important populations abundance (Malschi and Mustea 1992, Malschi, Perju, 1999, Malschi and all. 2006). Because of agro-ecoclimatic conditions and because of the predator activity the populations level is limited at an average of 12-32 aphides/ear (in June) and only 5-10 cicades/m^2 or /10 sweep net catches (in July). These levels can overpass the economic density thresholds in some favorable years for the development of aphids and cicades.

In laboratory feeding trials with *M. avenae* and *R. padi*, the achieved daily feeding rate by individual predator species were studied, as follows: for *Nabis ferus* L., adult (60 aphids) and for *Nabis* larvae (17 and 25 aphids/day/individual), for *Chrysopa carnea* Stephn.(30 aphids), for *Episyrphus balteatus* Dg. (25 aphids), *Coccinella septempunctata* L. (25-50 aphides), *Propylaea quatuordecimpunctata* L. (25-40 aphides), *Cantharis fusca* L. (40 aphids), *Tachyporus hypnorum* L. (25 aphids), *Poecilus cupreus* L. (60 aphides), *Harpalus rufipes* De Geer. *(Pseudophonus pubescens* Műll.) (50-60 aphids), *H. distinguendus* Duft. and *H. aeneus* L. (50 aphids) and for *Brachibus explodens* Duft. (25-30 aphids).

CONCLUSIONS

Under the conditions of actual agro-ecological changes, yielded by climatic warming and dryness and new technological and economic conditions of zone agricultural exploitations, the original research has pointed out the increasing attack of main wheat pests: wheat flies, leafhoppers, aphids, trips, bugs, cereal leaf beetle etc., and the opportunity of insecticide control.

The spring months of the last years have been characterized by increasing warming, heating and dryness periods, causing the increase of pests abundance and damages on wheat crops, in Transylvania. A decrease in species diversity has been noticed together with an increasing abundance of the species with a single generation by year: *Delia coarctata* Fall., *Opomyza florum* F., *Phorbia penicillifera* Jermy, *Oulema melanopus* L., *Chaetocnema aridula* Gyll., *Eurygaster maura* L., *Aelia acuminata* L., *Haplothrips tritici* Kurdj., *Zabrus tenebrioides* Goeze, and of the other species of chloropids, anthomyiids, cecidomyiids flies, leafhoppers, aphids etc., well favored by consecutive wheat crops and by zone cereal ecosystems presence. The attack critical moments of the different species were recorded 3–4 weeks earlier and superposed. The insecticide treatments were imposed during the spring phase, in April and during the spike appearance phase, in mid May.

The paper points out the extension risk of wheat pests attack with an increasing potential, affecting the wheat crops yields and causing possible crop damages or leading to the compromise especially of the sown fields of consecutive wheat crop and of early sowing in September, and the importance of the elaboration of agro-ecological integrated control strategy (ICS).

The attack diminishing methods of the ICS are: - agro-technical methods: avoid early planting in the autumn to minimize the incidence of insect vectors and diptera species, destroy volunteer wheat, adequate fertility, use good seed quality, the weeds, main pests and diseases control, conservation and use of biological factors: tolerant varieties, entomophagous limiters; - application of selective insecticides, with economic and ecological efficiency, at two different selective moments. Integrated pests control strategy is an important section of agrotechnological system for wheat crops sustainable development. High insecticides efficiency and the achieved increasing yield rates of 7-24 % have been the experimental results recommending an adequate technological system and modern insecticides pest control strategy.

The natural predators play an important role in decreasing the wheat pest abundance. The well-known systematic groups of enthomophagous predators: Aranea; Dermaptera; Thysanoptera (Aeolothripidae); Heteroptera (Nabidae etc.); Coleoptera (Carabidae, Cicindelidae, Staphylinidae, Sylphidae, Coccinellidae, Cantharidae, Malachiidae); Diptera (Syrphidae, Scatophagidae, Empididae etc.); Hymenoptera (Formicidae etc.); Neuroptera (Chrysopidae) were represented in the structure of arthropod fauna. Laboratory tests and investigation regarding the role of the main species of predatory entomophagues as regulators of pest populations in cereal agro-ecosystems, has proved that various species feed preferentially on wheat flies, cereal aphids, trips, bugs, *Oulema* etc.

Cereals agroecosystem of central Transylvania are rich in beneficial entomophagous arthropod fauna. In open field area agroecosystems, it was necessary to apply the insecticide treatments. The abundance and the quality of activity of entomophagous populations were higher in the system of field crops with protective forest belts, favorable for the development of entomophagous arthropod fauna and for a real natural entomocenotic equilibrium and a natural biological control of important zone pests, like *Oulema melanopus* L., flies, aphides, cicades, thrips etc. has been achieved.

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NANOMATERIALS AND NANOPARTICLES, HEALTH AND ENVIRONMENTAL RISKS

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ABSTRACT. Nanomaterials and Nanoparticles, Health and Environmental Risks. Numerous examples of modern technologies and many latest research areas in use today are based on nanomaterials and nanoparticles. At the same time, it is accepted that their applications may raise new safety challenges for the reason that many materials properties may change radically at small length scales primarily due to the increased surface to volume ratio. The increased development and use of nanoparticles in industries could lead to increased exposure, which may possibly have a strong influence upon the human health and the environment. The biological behaviour of nanoparticles is induced by the chemical composition and for this reason the human exposure to airborne nanoparticles within workplaces and laboratories along with the environment contact with these materials should be permanently controlled in order to prevent bioaccumulation.

Keywords: *nanoparticles, nanomaterials, human exposure, environmental effects*

1. INTRODUCTION

Several natural sources of nanocomponents such as minerals (iron oxides, and silicates) or microorganisms (bacteria, algae) are able to generate nanoscale dispersions of nanosized-particles. Natural colloids such as emulsions or foams and as well smokes and fogs are commonly meet within environment (Tina, 2003). Nanoparticle behavior changes with size and therefore by reducing their dimensions into the nanometer scale, the behavior is similar to vapors and gases. (Aitken, 2004) The difference between particles in nanoscale and microscale range is that for microparticles the inertial and gravitational forces govern, while for nanoparticles, gravitational and diffusion forces are important. (Aitken, 2004) The influence of the size to particle diffusion, agglomeration and deposition is important for developing new strategies which involves exposure and control. (Aitken, 2004)

Many research activities were carried out on nanoparticles made of organic and inorganic materials to acquire stable aqueous dispersions, emulsions and powders, by means of chemical bonding (Katharina, 2004), nanodroplets growing (Katharina, 2004) and electrostatic interactions between oppositely charged surfactants and polymers (Shlomo, 2004). Usually nanostructures differ structurally and in how their atoms and molecules are ordered. The most used configurations in nanotechnology and as well the fundamental structures includes nanoparticles (Aitken, 2004) with various shapes which can be experimentally controlled and created atom by atom, nanocrystals (Aitken, 2004) which contain highly ordered particles and as well nanolayers (Aitken, 2004), nanowires (Aitken, 2004) and nanotubes (Aitken, 2004) with variations in composition (Golberg, 2002) and notable mechanical properties (Baughman, 2002) which can lead to a large variety of applications (Tina, 2003; Aitken, 2004; Service, 1998)

1.1. Technological and commercial applications of nanomaterials

As the technology advances, new properties are observed for different materials having nano- and microdimensions (Feynman, 1991; Ball, 2001), which leads to a large variety of commercial applications (Salata, 2004). A very large diversity of nanoparticles (Katharina, 2004), are successfully used today in distinctive applications (Nano-business Alliance, 2003; Luther, 2004; UK Royal Academy of Engineering report, 2004; Anon, 2003; UK report, 2004; Nemmar et al., 2001; Xiang et al., 2003) in chemical industries (surface coatings, special components for car tires), (Peter and Oleg, 2004), as components in cosmetic products (sunscreens, toothpastes), (Peter and Oleg, 2004) and biotechnological industries (biomaterials, sanitary equipments), (Peter and Oleg, 2004) and as well in various medical applications (markers in biological imaging, gene vector (Xiang et al., 2003), cell signaling (Brown et al., 2004) and even food industry (improved food products), (Shlomo, 2004; Peter and Oleg, 2004).

Nanoparticles are often used as efficient components in sunscreen lotions, ensuring the skin protection against UV light and sunburns by getting deep through the skin layers. (Lademann et al., 1999) Moreover nanostructured materials are largely used today in modern technologies for fabricating microelectronics from biopolymers (Williams, et al., 2002; Wybourne et al., 1999) and to replace toxic materials which were used in some industrial applications (Socolof et al., 2001) due to a higher selectivity for some chemical reaction products (Tina and Wel–Xianzhang, 2003; Samorjai and Mc.Crea, 2001). Nanosized particles were also used for decorating pottery since ancient times and lately during middle ages and renaissance they were often exploited due to their metallic reflections, iridescent properties and the capability of applying them as films onto transparent surfaces for preventing oxidation. (Michael, 2003) At the present time, the most recent conservation and the restoration techniques of antiquities, art objects and old wall paintings, are based too on nanotechnology and nanoparticles because of their optical effects, enhanced reactivity and mechanical properties. (Piero and Rodorico, 2006) Materials containing nanoparticles commonly present a high resistance, strength, density and hardness. These characteristics offer them efficiency against chemical and physical degradation caused by unfavorable weather conditions, pollutants influences and other environmental conditions. (Piero and Rodorico, 2006)

In medicine, nanoparticles were successfully used as mediators (Alyaudtin et al., 2001; Pulfer, 1999; Schroeder, 1998; Kreuter, 2001) and loaded to drugs, for constructing new drug deliveries systems (Peter and Oleg, 2004) which can be released inside cells. This system is successfully used in medicine for delivering genes and proteins and also for protecting proteins and the DNA for being degraded. (Abraham, 2004) Moreover magnetic nanoparticles with iron oxide magnetic cores may offer a new approach to selectively treat cancer by heating cancer tissue from within at the cellular level (Robert, 2007). Another option for tumor targeting with nanoparticles is based mainly on attaching the molecules which can recognize cancer cells to the external surface of nanoparticles and then connecting them with the molecules or with the receptors situated onto the surface of tumor cells. (David, 2006) By introducing the nanoparticles with the attached ligand onto the surface into the circulatory system, the antitumoral drugs can penetrate tumor cells more easily, thus increasing the treatment efficiency. (David, 2006)

Nanoparticles have been also proved to be useful in several environmental treatment and remediation processes and as well in pollution prevention activities (Lynn G, Christine C, 2005) due to their capacity of supporting the alteration and transformation of the pollutant material in less harmful components (Zhang, 1998; Elliot and Zhang, 2001; Ponder et al., 2000; Diallo et al., 1999; Wei-xian, 2003) and also for vitalizing the microbial growth (Lynn G, Christine C, 2005). These materials offer a significant assistance for the transformation and detoxification of several frequent environmental pollutants (heavy metals, organic solvents and pesticides). (Wei-xian, 2003) Some techniques used for the remediation of contaminated land, involves the movement of particles through the soil. The advantages of these techniques results from their ability to be taken up and degraded by soil organisms. (HM Government, 2005)

1.2. The influence of nanoparticles and nanomaterials upon the environment

The study of the particle formation and aggregation is important for understanding the influence such particles can have to the environment. On the other hand nanomaterials may present a severe health risk to many living organisms, due to their size, which is similar or smaller than biological constituents of the organism or than some viruses or other irritants (Lynn G, Christine C, 2005). The harmful effects occur from the nature of the nanomaterials and from the reactivity, due to their small size and large surface area which makes them more reactive with the cellular matter. (Gorman, 2002) The physical-chemical properties of the particles and the characteristics of the final products which enclose nanomaterials in combination with the fabrication techniques used during the technological process may also generate harmful effects. A significant challenge for environmental studies consists of removing and recovering the nanoparticles from the environment and consequently transforming, reusing or degrading them into environmentally safe products and adjusting their pollution potential. Nevertheless the toxicity of recent engineered nanomaterials is almost unknown (Lynn G, Christine C, 2005).

2. THE HUMAN AND ENVIRONMENTAL EXPOSURE TO NANOPARTICLES

Human and environmental exposure is conditioned primary by the source of the nanoparticles such as workplace (engineering and laboratory activities), deliberate and unintentional environmental releases (industrial or domestic waste streams), direct application from consumer (cosmetics) or medical products (drugs, treatments, therapeutic devices), then secondly by the pathway that it takes from the source to humans and the environment, and last by its behavior during transport. (HM Government, 2005) The personnel may be exposed to particles within workplace during the fabrication process or by handling materials which contains nanoparticles. By releasing into environment production wastes which may contain nanomaterials or during disposal process or recycling, the inhabitants may also be affected. (William, 2006) The nanoparticle distribution within the environment can possibly lead to new by-products, undesired components or wastes that also could generate hazards. (William, 2006)

To evaluate the risk and for managing the environmental impact of the nanoparticles, it is essential to understand the nature and the level of human and environmental exposure and to establish the most significant issues which can provide helpful information on where a potential risk may take place (HM Government, 2005).

2.1. The pathways followed by nanoparticles

It is known that nanomaterials can enter the human body through several ports, by accidental or involuntary contact during production, or most frequently through the lungs from where a rapid translocation may occur through the blood stream to other vital organs (Nemmar et al., 2001; Xiang et al., 2003). Nanoparticles may take different pathways from the original source to get to the human receptor and as well to the environment, through the air, soil and water (figure 1). Nevertheless there are not completely known all behaviors of these particles during passing through these pathways, but it is important to identify how they interact with various substances which can be found in nature in water and soil such as organic compounds and how they interact with other pollutants (HM Government, 2005).

Humans are exposed both directly and indirectly to nanoparticles, most commonly during medical applications, by swallowing and inhaling medical products, by drugs injection, by exposing to medical devices or by implanting medical devices and also by using consumer products applied directly to the skin, such as cosmetics (HM Government, 2005). However, the physical-chemical properties of the nanoparticulate materials used within deliberate and direct exposure may be different from those that will result in unintentional exposure, due their behavior inside the human body (HM Government, 2005).

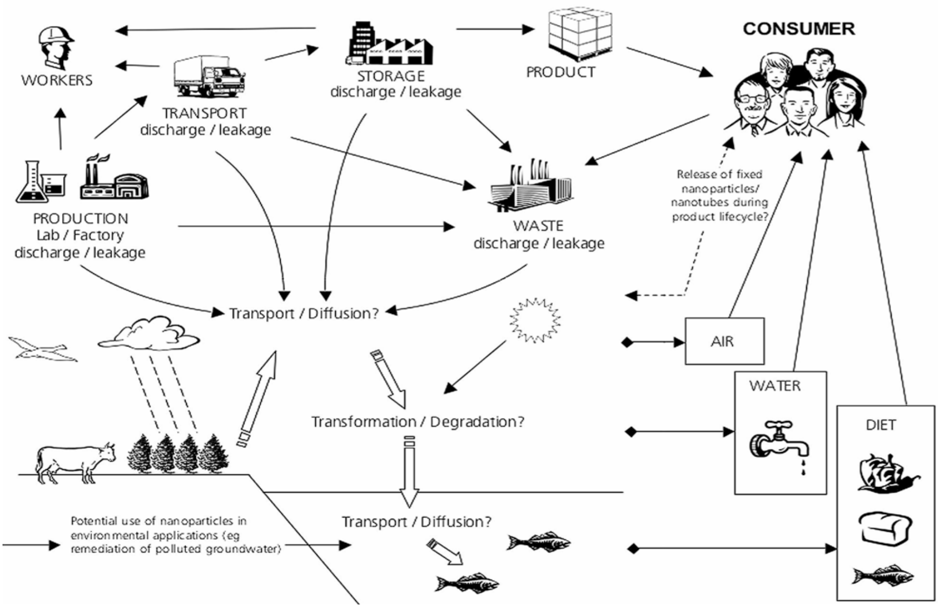

Figure 1. *Possible exposure routes for current and future applications of nanomaterials (UK Royal Society and Royal Academy of Engineering, 2004)*

2.2. Human and environmental exposure through air, water and soil

The atmosphere is a direct path for human and environment exposure to various types of nanoparticles. The most affected human categories are those who produce or use nanoparticles within working places or research laboratories, while the exposure of the general population is expected to be very small and mostly to non-engineered nanoparticles (combustion products), (HM Government, 2005). To minimize the exposure within the workplace, various control and exposure reduction devices for both aerial and dermal exposure have been lately developed and successfully implemented (HM Government, 2005). However the human exposure through air and through skin as well has been insufficiently studied at the moment. Accordingly it is necessary to develop technologies which may easily enable a precise work-related and environmental measurement of the nanoparticle exposure through air and may offer a good understanding of nanoparticle behavior in air.

Little is known about the water as a potential source of exposure to nanoparticles and about their behavior in aquatic environment, but it is assumed that this could be a major route of human exposure. Several techniques (HM Government, 2005) have been also improved in order to change the concentrations, the chemical and physical properties of the nanoparticles in water which occurs from natural sources. For engineered nanoparticles, the applicability of these methods is yet not fully developed.

The exposure to nanoparticles within soils may result from intentional releases (soil and water discharges produced from remediation technologies), from agricultural uses (fertilizers) and from potential accidental releases (by means of air, water or from sewage sludge applied to soil) and strongly depends on the chemical and physical properties of the soil (HM Government, 2005).

2.3. Human health and safety hazards

The main concern today among researchers is to study and to understand the hazards which nanoparticles may have on human health. The most important entry routes for nanoparticles to human body and how they are circulated and distributed to organs are schematically shown in figure 2.

By elucidating the entry mechanisms and distribution methods, it is possible to identify which organs may be affected or not and also to estimate the acceptable exposure doses to particles, their toxic effects and the body reaction after the exposure. Inside the body, nanoparticles when compared to larger particles of the same material are capable to cause organs inflammation, generally due to the oxidative stress which is associated with the degradation process of the genetic material (DNA), (HM Government, 2005). Until now only few studies have been made for investigating the possibility of nanoparticle adsorption through the lung, skin and gut, and consequently for the evaluation of their toxicity. Several research studies were made to detect the localization of nanoparticles within cells and the transport mechanisms of the nanoparticles between and within the cells and across cell membrane (HM Government, 2005). Experimental data indicates that the size, the shape and the composition of the nanoparticles are important factors which have a strong influence on their toxic effect (HM Government, 2005). Also nanoparticles which contain different functional groups are more damaging than those with unmodified surface, causing some severe tissue and organ inflammations (HM Government, 2005). Therefore the surface modification is a key factor for toxicity and the hazard potential of these materials.

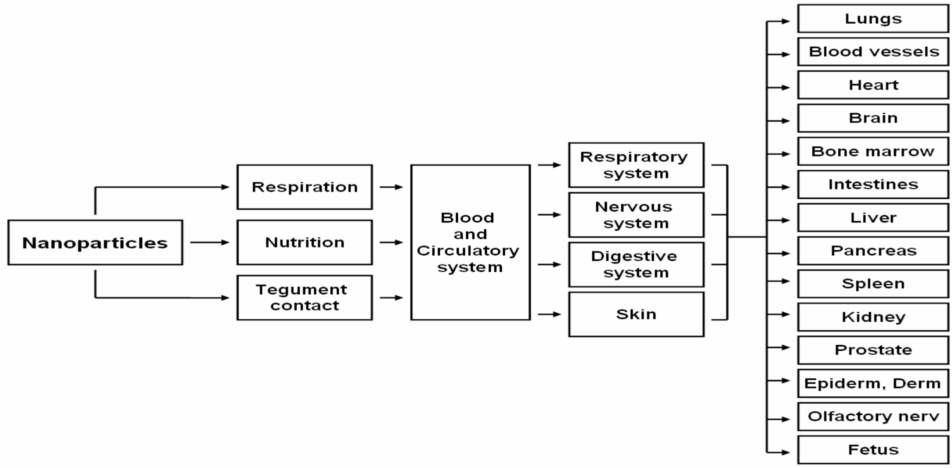

Figure 2. *The distribution of nanoparticles inside human body (Source, Government research report, Department for Environment, Food and Rural Affairs, 2005)*

2.4. Human exposure to nanosized particles

Among the entire possible exposure routes, inhalation is identified to be the most common and the major route of exposure to nanoparticles. Also ingestion and dermal exposures have to be considered while working with nanomaterials during manufacturing, disposal, transport or usage in various applications. Nevertheless, little is known about the direct (for example through medical procedures) or indirect (due to the environment contamination) exposure levels (Günter et al., 2005). Few data can be found in literature with reference to the pathogenic effects generated by nanoparticles in the case of exposure within the workplace and within the environment, predominantly to ultra fine combustion products (HM Government, 2005). After entering the body through inhalation, they generate inflammatory reactions within lungs, due to the transport into, through and between tissue layers inside lung (HM Government, 2005). Moreover, they can transfer to the blood stream and affect the cardiovascular system, furthermore being possible to travel to the brain (HM Government, 2005). It also has been reported in the literature, the translocation of inhaled nanoparticles through the olfactory nerves (Oberdorster et al., 2002). The smaller the particles, the deeper they travel within the lung and as a result of accumulation they cause the lung inflammation. The severity of the harmful effects depends mainly of the quantity of inhaled material, the lung load (Moolgavkar et al., 2001) and the properties of the material itself. It has been found that the shape of the particles plays an important role. Nanofibers can penetrate deeper inside the lung structures (Lippmann, 1990; Moore et al., 2001; Oberdorster, 2000; Oberdorster, 2001; Oberdorster, 2002; Warheit et al., 2001) and for preventing the exposure of the personnel to ultrafine particles or other harmful airborne nanomaterials within workplaces, some protective measures has to be taken. By using filtration systems for airborne particles, personal protective equipments and other electronically devices designed for controlling nanoparticles and the air quality (ventilation systems, fume hoods), several inconveniences may be eliminated.

At the moment the level to which nanoparticles are able to penetrate the skin and cause toxicity is also not fully understood. However, using them in consumer products leads to the exposure of the skin which is also an important gateway for entering inside the human body (HM Government, 2005). The penetration of the skin barrier is size-dependent, so the nanoparticles are capable to enter more deeply into the skin than other larger particles (Peter and Oleg, 2004). Moreover, particulate materials which can dissolve or break into smaller parts can enter the skin reaching deeper layers, thus being very hard or impossible to predict their behavior. A large variety of artificial made fibers and as well mineral fibers are widely used due to their multiple industrial applications. While in contact with the skin, they may provoke a severe mechanical irritation (dermatitis) and also allergies (Peter and Oleg, 2004). Experimental studies have shown that the number of microparticles in the skin decreased with the depth (Jalon, 2001) and the particles which penetrate the skin normally are removed through the lymphatic system (Blundell et al., 1989; Corachan, 1998).

Nanoparticles may also cross the gut barrier under normal conditions, but there are no sufficient amounts of research data sufficient to conclude if they are able to determine a strong adversely effects inside human body, affecting the gut, bone marrow and other organs (spleen, liver, heart and the placenta/fetus) after exposure (HM Government, 2005). It has been suggested that the genetic predisposition in combination with the environmental factors may have an influence over the immune responses (Lomer et al., 2002). On the other hand there is much information related to the relationship between human health and exposure to particles within workplaces and environment. Many of them confirm an increasing of cancer mortality (lung cancer) and respiratory diseases following work-related exposure to nanoparticles (asbestos and other nanaofibers) (HM Government, 2005). The ingestion exposure to nanoparticles is believed to result mainly from the contact between contaminated food and the digestive system which primary comes from hand-to-mouth contact more often within the workplace. There are several data available in literature which refers to particles translocation mechanisms and intestinal absorption (Florence and Hussain, 2001; Hussain et al., 2001; Jani et al, 1990) which confer precise information necessary to predict the behavior of some particles within the intestines.

The toxicity of nanoparticles is closely related to particle sizes and dimensions and as well to the properties of the surface area (HM Government, 2005). To evaluate the hazard of nanoparticles, several toxicological, physico-chemical properties and characteristics (size, shape, durability, composition and surface reactivity) must be considered.

2.5. Environmental exposure to nanosized particles

Today many efforts are made for preserving the quality of air, soil and water resources and for preventing pollution by detecting and eliminating the contaminants (Lynn G, Christine C, 2005). By identifying the potential sources of release to the environment and their behavior (agglomeration, mobility within soils), helpful information can be collected to identify which segment of environment is most exposed at risk. The toxic effects of the nanoparticles to the environment it is still under research and up till now only few reliable data are available (HM Government, 2005). A detailed examination of the fabrication techniques used today in modern industries and scientific fields which involves nanotechnology is also needed. Within the environment nanoparticles may badly influence various living species which can be found in soils and ground waters (starting from micro-organisms and plants, to invertebrates, fish and mammals), affecting as well individuals and large populations. For that reason it is believed that they posses a serious hazard potential to all ecosystems, generating a severe impact onto the environment. The environmental impact depends on the physical-chemical properties, the material behavior, particles habitation time within the environment and their environmental (short and long-term) toxicity, and persistence within the organisms (bioaccumulation potential), (HM Government, 2005).

The effects of the nanoparticles upon ground waters and soils

Nanoparticles can also be used for groundwater and contaminated land remediation processes, for sewage treatment procedures and also for identifying microorganisms in soils and groundwater, due to their properties of showing toxicity to bacteria. New ground remediation technologies are based today on these characteristics (HM Government, 2005). Several data are available from studies made on toxicity of fullerenes to aquatic species (fishes, invertebrates and microorganisms). Nevertheless at the moment there is only a partial understanding of the mechanisms performed at the cellular level (HM Government, 2005). New research activities are carried out for studying the contaminants effect (engineered and non-engineered nanoparticles) at low doses for longer time periods together with the evaluation of the combined effects of nanomaterials and other contaminants (metals, organics), and their influence on the human health and to the environment (HM Government, 2005).

The ignition and explosion potential of the nanoparticles

For nanoparticles which may ignite, explode or cause fire when exposed to air (metal nanoparticles which oxidize easily) due to the formation of a flammable dust, a detailed understanding of their physical-chemical properties is crucial. This comes first from their large specific surface and second because they have enhanced electrostatic charging and could possibly acts as a source of ignition, when dispersed in air. Additionally, the energy required to ignite the particles is a function of particle diameter (HM Government, 2005).

2.6. The risk assessment and the environmental detection and analysis

Due to an insufficient amount of toxicology data concerning nanoparticles, a reliable risk assessment is very difficult to achieve. Further researches are also needed for newly developed nanomaterials in order to identify the potential hazards and for developing an accurate database for the purpose of risk assessment. Pollution detection can be completed by using several types of sensors (chemical and electrical sensors (Kong, 2000), nanotube sensors (Kong, 2000), and boron-doped silicon nanowires (Cui et al., 2001) which are capable of detecting contaminants at the molecular level (Lynn G, Christine C, 2005). Most of the available data about the exposure to nanoparticles comes from studies of combustion product particles in urban environments and from studies of the possible effects generated by inhalation and ingestion of non-engineered nanoparticles (HM Government, 2005). Given that nanomaterials are potentially toxic, risks caused by molecular manufacturing or advanced nanotechnology techniques can be grouped into health and environmental threats, with the consequent impact on society (Hunt and Metha, 2006; Xia and Whitesides, 1998). Nowadays the environmental detection of nanoparticles and the analysis of their influences are situated at an early stage (William, 2006). New analytical methods and detection techniques may be required for nanoparticle detection and sampling within the environment.

CONCLUSIONS

Certain properties and behaviors of nanomaterials could conceivably contribute to the overall environmental risk, although the mechanisms by which nanomaterials could be toxic, based on their chemical and physical characteristics, is not yet fully understood. More people working in industries which are using nanoparticulate materials are affected by particle exposure and for that reason a better perception of the hazards need to be acquired. Numerous studies are focused as well on the optimization and development of several technologies which enables the measurement of exposure to nanoparticles in soil and water and their behavior and interactions with and within the environment (HM Government, 2005). When evaluating the hazards and risks potential to human health, factors such as particle shape, size, chemistry, composition, surface characteristics and doses should be taken into consideration for determining the toxic potential of the particles. The possible risk generated by nanoparticles to the living organisms depends also on several important factors, such as the physico-chemical characteristics of exposure sources, the exposure magnitude, the properties of the nanoparticles, their toxicity, the persistence inside living organisms, their behavior within the environment, and the bioaccumulation potential through the food chain (HM Government, 2005). Nanoparticulate materials can affect the human body on different levels by entering in several ways directly or indirectly and reaching various depths, depending on the size and surface properties, therefore increasing the risk of internal organ diseases (Peter and Oleg, 2004). Currently only few limited information are available related to the adverse effects after the exposure to ultra fine powders, dust and fine particles, during handling, transport and disposal process. (Aitken and Creely, 2004, 2) By combining all these research data significant information can be obtained and subsequently used to predict the biological activity and the adverse effects of the nanoparticles to human body and to the environment.

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PIPING RISK ASSESSMENT

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ABSTRACT. Piping Risk Assessment. The paper reviews the aspects of piping risk assessment with special attention to the application of the layer of protection analysis framework (LOPA). This method is defined as a semi-quantitative method based on a system of protection layers that includes simplified approaches to characterize the consequences and estimate the frequencies for risk determinations of the particular accident scenario. Such a use for piping is called classical LOPA approach (pLOPA). Due to numbers of uncertainties concerning required failure frequency rate of the protection layers, that work explores of the application of fuzzy logic which typically can deal with uncertainty and imprecision, and it is an efficient tool for problems where lack of knowledge occurs. Such approach is called fuzzy LOPA (fpLOPA). Both approaches will be illustrated by the case study for the segment of long pipeline transporting flammable product.

Keywords*: pipelines, risk assessment, layer of protection, fuzzy logic*

1. INTRODUCTION

Pipelines are generally recognized to be most safe and most economical way of transporting hazardous substances in comparison with other method of transport (CULLEN, 1996, de WOLF, 2002). This is the reason why there is considerable interest in many European countries concerning transport of hazardous liquid materials using transmission pipelines system. The EU pipeline networks for oil products amounts to approximately 31000 km and other dangerous substances, e.g. ethylene, propylene, chlorine, ammonia about 10,000 km, whereas gas pipelines networks exceeds 110000 km. It is predicted that the transport of oil and chemical products are to increased by 50 % in next 5 years. Much wider use of pipelines exists in USA where there are about 2.2 million miles of pipeline, of which about 157,000 miles carry crude oil and petroleum products.

It is widely recognized that pipelines posses “major accident hazard “potential. The existing data shows that pipeline accidents, while less frequent than those of ‘Seveso’ establishments, are at least as serious in their consequences [1,2,3]. A closer analysis of major pipeline accidents shows that environmental damage is mostly related to oil spills, whereas health damage is mostly related to gas releases.

Pipelines safety is based on different regulations. In USA this issue is controlled by the Pipeline Integrity Management Rule [4] and other related regulations like OSHA Process Safety Management (PSM) [5] and EPA Risk Management Program - RMP [6]. Standard API 1160 [7] also was developed to help operators comply with the New Federal Rule on Pipeline Integrity Management in High Consequence Areas. In all these regulations risk management and assessment are clearly required. The method use for the risk assessment may be varied from simplified qualitative one to fully quantitative method with assessment of risk indexes. No matter the method used the risk assessment may essentially help to verify the design credibility and other important safety management issues.

Pipelines in most European Union countries are not subjected to risk assessment and are not included within the scope of Seveso Directive 96/82/EC because of some inherent differences in fixed chemical installations, e.g. the vast majority of pipelines are buried underground or under water and they are not controlled by the operator being exposed to the third party activity, recognized as a dominant cause of pipeline failures. However, in some countries e.g. in the UK, there are some separate regulations [8]. The issue on risk assessment is also important for land use planning aspects where the risk of harm to people in the vicinity of major hazards must be taken into account.

The paper reviews the aspects of piping risk assessment with special attention to the application of the layer of protection analysis framework (LOPA). This method is defined as a semi-quantitative method based on a system of protection layers that includes simplified approaches to characterize the consequences and estimate the frequencies for risk determinations of the particular accident scenario. Such a use for piping is called classical LOPA approach (pLOPA). Due to numbers of uncertainties concerning required failure frequency rate of the protection layers, that work explores of the application of fuzzy logic which typically can deal with uncertainty and imprecision, and it is an efficient tool for problems where lack of knowledge occurs. Such approach is called fuzzy LOPA (fpLOPA). Both approaches will be illustrated by the case study for the segment of long pipeline transporting flammable product.

2. MAJOR HAZARD FOR PIPELINES

2.1. Pipeline General

Pipeline are used for the transportation of substances from producers to the range of consumers, e.g. water supply in a modern city, crude oil from oil wells to tank farms for storage or to refineries for processing, gasoline from refineries to distribution storage farms and some piping system are utilized to carry liquids, chemicals, mixtures, gases, vapors, and solids from one location to another. The natural gas transportation and distribution lines convey natural gas from the source and storage tank to points of utilization, such as power plants, industrial facilities, and commercial and residential communities. The utilization of that way of transport is very wide and continuously increasing.

Main liquid transmission lines are buried underground and may go through different location including in majority rural, industrial, residential and commercial areas. Also they may cross different areas including water bodies, railways and motorway tracks and other sensitive ecological systems. The routing may affects the location of release incidents, size of the release as well as a frequency rate.

Pipeline apart from typical pipe, flanges, fittings, valves elements etc. contain also as a integral part a pumps station, and an appropriate control system being in that way quite complex system. There are different classification of piping according to their function, according to type of transporting medium and the operating parameters. Especially, there is usual industry practice to classify the piping in accordance with the pressure temperature rating system used for classifying flanges. The most of standards requirements are cover by the piping standards are covered by the ASME B31 and B36 series in USA; BS8010 in UK.

The primary hazard for safe transportation of hazardous substances arises from the pipeline failure taken as a loss of tightness and release of the transportation medium to the environment. Such a release can contribute to safety concern and/or to environmental issues. This is a typical risk assessment problem to be considered in that work.

2.2. Pipeline risk factors

Pipelines represent a linear risk source connected with different types of the hazards. There are numbers of factor which contribute for a risk analysis that involves a variables connected with the pipeline itself and its location relative to sensitive receptors. Most of them may be gather in the following groups:

1. Design and construction elements
2. Operational conditions
3. Maintenance and inspection practices (corrosion, cathodic protection)
4. Third party prevention
5. Proximity of sensitive receptors
6. Protection and mitigation means

In terms of risk assessment those groups of the different variables may affect particular components of risk, that is the probability and / or severity of the consequences of the releases. The design and maintenance practices usually affect the probability of pipeline failure whereas operational conditions, existing protection means as well as proximity of the pipeline to sensitive receptors, meteorological conditions, and local terrain, topography and land use affect the severity of consequences.

It is only illusion to assess the frequency failure rate for particular pipeline based on the application of the typical reliability models, although such models may be formed and helpful to some extend. Uncertainties and lack of the frequency rate associated with basic events can effectively to exclude such an opportunity. However more reliable data can be obtained from historical review of the pipelines accidents and appropriate statistical analysis. The research report of HSE UK [9] provided numbers of data necessary for pipeline risk assessment. Fig 1 presents the causes of pipeline failure and provides rough contribution of each cause.

According to many different European and USA sources a third party interference, classified in group of external events, like farming, drilling, bulldozing etc., is recognized as a dominant cause of pipeline failure.

The further data of referenced HSE Report provide the piping failure frequency rate separately for each failure type, size of the hole and pipe wall thickness. Some of these data are presented in Table 1. The HSE data provides the effects of the depth of the cover, pipeline age and detection and shut down times. These data were used for the case study presented in chapter 7.

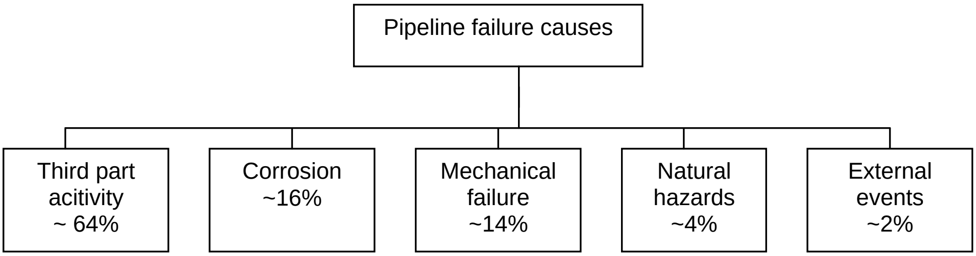

Fig. 1. *Causes of pipeline failure*

Table 1.

Proposed failure frequency for gasoline pipelines 5 to 10 mm wall thickness.

Failure frequency for gasoline pipelines 5 to10 mm					
Failure type	Failure rate/ 1000 km-year				Per\cent
	Leak	Hole	Rupture	Total	%
Mechanical failure	0.07	0.056	0.017	0.143	34.2
Operational error	0.023	0.018	0.006	0.047	11.2
Corrosion	0.042	0.033	0.01	0.085	20.2
Natural hazard	0.006	0.005	0.002	0.013	3.1
External impact	0.064	0.051	0.016	0.132	31.3
Total	**0.206**	**0.164**	**0.051**	**0.42**	**100**
%	49	39	12	---	100

The examination of the consequences must consider the hazardous properties of the transported material as well as a size of release, e.g. for flammable liquids like gasoline the most important are the following: probabilities of ignition, pool formation, spray releases and ability to migrate to water bodies or sewers. Fig. 2 presents possible outcome consequences after release of gasoline from pipeline.

As can be seen there are various type of the outcome consequences which may lead to human losses or environmental damages; first of all a jet fire for leakages releases and pool fire or flash fire for rupture type of the releases. Environmental damages depend on the location of the sensitive area in relation to release. It may affects the water bodies, ground as well as bring about some infrastructure losses.

Having an appropriate probability data for the releases phenomena (e.g. using statistical historical data presented in Table 1 and failure frequency of the indicated safety function in event tree based also on historical data [9]) the frequency of the particular outcome frequency can be assessed.

Failure event	Jet release	Ignition	Liquid pool	Ignition	Migration to sewage systems	Spillage to water systems (rivers, drainages)	Late ignition	Consequences

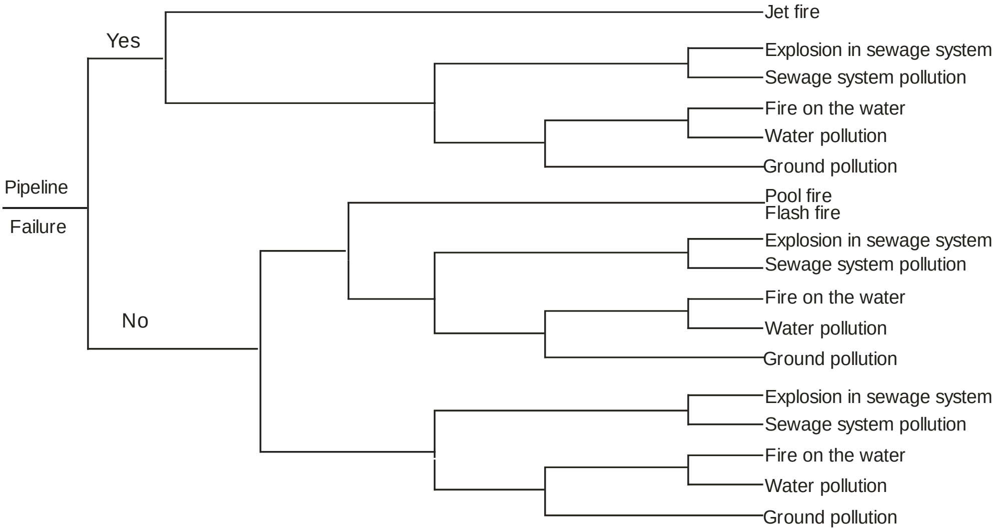

Fig. 2. *Event tree for release of the flammable liquid for pipeline*

The severity of the consequences depends on the size of release and type of the substance as well depends on some conditional events (e.g. ignition) and presence of sensitive receptors. The size of release will be mainly affected by detection and shut down times. Historical data shows that a large releases (like rupture) may be quite fast detected (in about 5 - 10 minutes) and turn down by operator whereas the small leaks are discovered mainly by third party, often after long time (even from 3600 hours and 4500 hours). The typical data on release time presents Table 2. These parameters will affect mainly the severity of consequences.

Table 2.

Estimation of detection and shutdown times

Size of release	Detection time [min]	Shut down time [min]
Leak	1000- 10000	1000-100000
Hole	10-1000	100-10000
Rupture	1-10 min	1-100

The only examination of whole technical and control systems of particular pipelines may provide more detailed data on release time needed for calculation of the severity of the consequences.

3. RISK ASSESSMENT FOR PIPING

Risk assessment methods in either or pipelines industries are based on a classical definition of risk in form as:

Risk = f (event likelihood and severity of event consequences)

The consequences of the various potential accident scenarios may then be combined with their frequencies in order to calculate the overall risk index.

As in process industries three basic classes of risk analysis methods may be selected: qualitative (QlRA), semi-quantitative and quantitative methods (QRA). Pipeline operators use all methods for different decisions concerning compliance with the standards, maintenance issues (setting inspection and testing interval) and a selection of safeguards.

3.1. Qualitative methods

Qualitative methods may focus only on assessment of the compliance with the approved standards and other code of practice, e.g. with [API RP 1129 [10]. The other way may focus only on relative consequences or assess the probability and consequence in relative terms, such as high, medium and low. Qualitative approaches combining probability and consequences often use numerical scoring methods to generate a relative risk ranking of pipeline segments along a pipeline route. The factors are mathematically combined, usually by addition, to yield a numerical score value for each predefined segment length of pipeline. In that way, segments can be ranked and grouped according to relative risk. Fig. 3 presents the structure of such a risk assessment method [11].

3.2. Semi- quantitative method

The semi-quantitative methods may assess risk by means of quantitatively determined category of event probability and severity of consequences and subsequently category of risk using in majority cases a risk matrix. The most applicable method in that group is the Layer of Protection Analysis (LOPA) [12, 13] which will describe later in details.

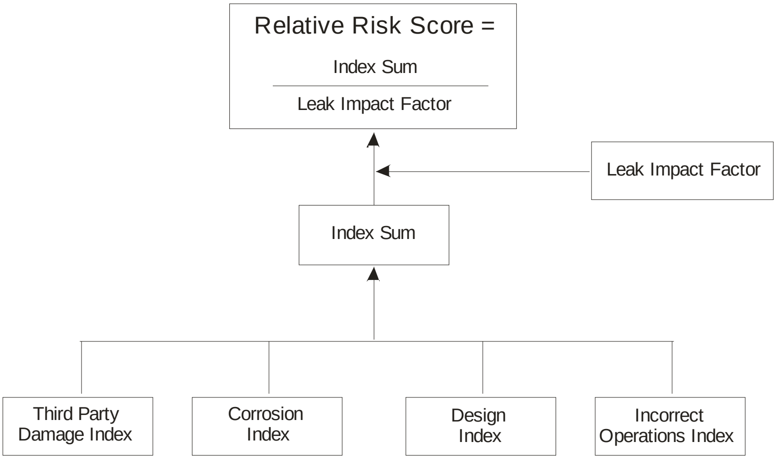

Fig. *3.* *Structure of relative risk assessment tool*

3.3. Quantitative method

Quantitative or probabilistic methods (QRA) are also used in the pipelines industry. These include the same fault tree and event tree methods applied in the process industries. In addition to probabilistic estimates based on historical data for a leak or spill, there are specialized methods for predicting the effects of known anomalies or defects, such as corrosion areas, or cracks, on the likelihood of failure within a specified time span. Such methods are used in setting re-inspection and testing intervals based on known conditions.

Quantitative Risk Assessment (QRA) methodology, which is based on assessment of the probability of accidents and its severity of consequences, uses the risk indexes (individual and societal) to project the overall risk. This is similar approach as classical major hazard risk assessment as routinely applied to most types of chemical or process plants in many European countries, e.g. Holland, UK, Italy, Hungary, and Slovenia. Some studies using that method was also published for pipelines [2, 14]. Above research demonstrated that the risks from gasoline pipeline are generally, of order $1x10^{-6}$ /year depending on the type of convening material and operating pressure. However QRA is perceived by industry as over complex task, requiring vast amount of work frequently based on uncertain data. It also requires numbers of input data concerning reliability characteristic of the pipelines elements as well as specialized programs to perform the consequences analysis.

4. LAYER OF PROTECTION ANALYSIS FOR PIPING SYSTEM (PLOPA)

LOPA was developed as a result of requirements concerning reliability of the safety instrumented system (SIS) to be applied in process industry [12]. Layer of protection analysis (LOPA) is a simplified risk assessment used to identify safeguards to meet the risk acceptance criteria. Safeguards form a multilayer system of protection acting in a specified sequence. The details of the classical layer of protection usually used for the process industry and those used for the long-distance piping system presents the Table 2.

Each layer of protection is a barrier to prevent undesired impact events from reaching people, the environment, or equipment that could be injured or damaged. The reliability of a barrier is often expressed in terms of the Probability of Failure on Demand (PFD), focusing on random faults. This is the probability that the barrier will not perform its intended function when challenged by an initiating event. LOPA assumes that accident scenario is represented by one typical pair of events: cause – consequence and it takes place as a result of failure of independent protection layer (IPL) which forms a multilayer system which are not able to cope with the unwanted initiating event and its further developments.

The calculation of the outcome frequency rate of particular scenario consequences (F) is based on event tree analysis which is presented in Fig. 4 [12]. The Outcome Frequency (F) of the consequences exceeding is estimated by multiplying the frequency of the initiating event by the product of the PFDs for the applicable IPLs.

Although LOPA appears to have a number of advantages, however there are also some disadvantages, mostly connected with limited availability and uncertainty of the failure rate of all safeguards systems and first of all with the assumption that severity of consequences remains constant with the activity of independent protection layers (IPLs). These problems were taken into account in the fuzzy Layer of Protection Analysis (fLOPA) [20].

Table *2.*

Layer of protection for piping system

Protection function	Type of classical layer of protection	The main goal	Type of layers of protection for piping system
Prevention -	Process design and construction	To provide physical containment of the piping system	Compliance with codes and standards for design, materials, fabrication, erection, test, and inspection of piping system
	Basic Process Safety System - BPCS	To monitoring process variables that allow the deviation to be detected and corrected before operating limits are exceeded	Classical process controls (flow, pressure, temperature)
	Process Alarms	To provide an appropriate alarms when process deviations occur	Optical, sound and other types of alarms
	Operator intervention	To react on process deviation and process alarms	Procedures, training, knowledge level etc.
	Pipeline Integrity Management	To provide necessary organizational barrier	Set of risk management elements including PHA, MOC, audits, Corrosion Mangm. Program etc.
	Security system	To prevent external event (third party) from affecting the piping process	Helicopter, mobile groups, risk communication and “one-call” system

Protection	Critical alarms and action of operators	To detect and inform operator or provide necessary automatic action by SIS	Operator/control system or alarm management
	Safety Instrumented System (SIS)	To provide automatic corrective action if operational deviation exceed critical safe limits	Shutdown or ESD to maintain the containment integrity
	Physical Protection	To protect the equipment against overloads	Double shell protection during passage under the roads and rail tracks or additional load in water bodies
Mitigation	Detection and/or isolation of releases	To shut down a release as quickly as possible	Leak detection and fast isolation valves
	Emergency planning and response	To mitigate of releases.	Emergency response procedures and resources

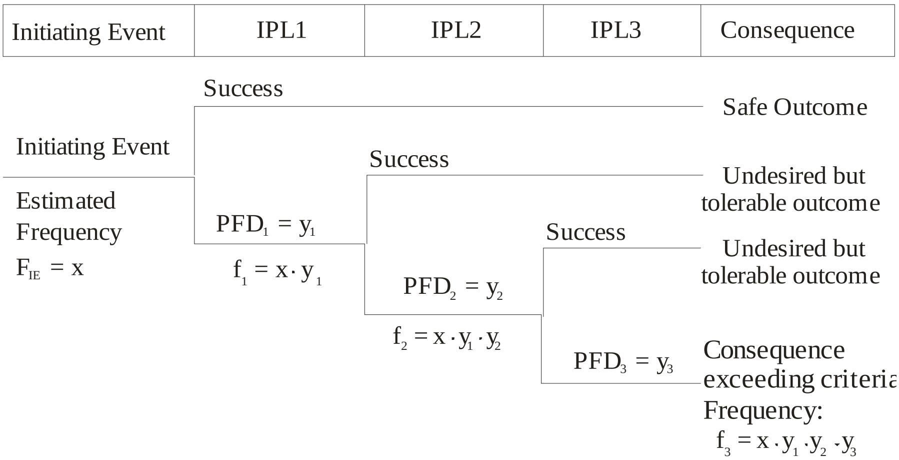

Fig. 4. *LOPA event tree for calculation of outcome frequency of the accident scenario*

5. FUZZY LAYER OF PROTECTION ANALYSIS (FLOPA)

Process industry, including piping, is very complex using variety of different technologies and a large number of apparatus and equipment where particularly a process piping system is very crucial. Such a complex system requires good scientific and engineering knowledge on variety of different issues. The more complex system the less precise information is available [15]. Although this knowledge is rapidly developed there is still much lacking and uncertain information, implicit in the variables, models and subjectivity, especially in the area of a very rare event like major accident hazards. Lack of knowledge may be decreased by the application of fuzzy logic [16] as it was confirmed in numbers of publications [13,17]. Fuzzy logic can work with uncertainty and imprecision and can solve problems where there are no sharp boundaries (or problem definitions).

It especially refers to the input data exploited in the Layer of Protection Analysis. In fuzzy approach fLOPA these data are presented in terms of fuzzy sets defined on the universe of discourse X and each variable may belong to particular fuzzy set with a varying degree of membership in particular set A. This degree of belongingness represents a membership function $\mu_A(x)$, has value 0, representing non-membership, to 1, representing total membership. A special fuzzy set is a fuzzy number that is commonly defined by the points at which the membership function is equal to 0, 1 and 0.

Contrary to the classical LOPA, fLOPA presents a new approach to risk assessment based on two assumptions [13]:

1. different functioning of the layer of protection,
2. application of fuzzy logic.

The first assumption refers to the structure of layers of protection and their different functions in terms of the risk assessment. The two risk components are taken into account in different ways. We assumed that the outcome frequency of particular accident scenario F is only affected by prevention and protection functions, whereas the severity of consequences, S, is affected by protection and mitigation functions. This concept is shown in Fig. 5.

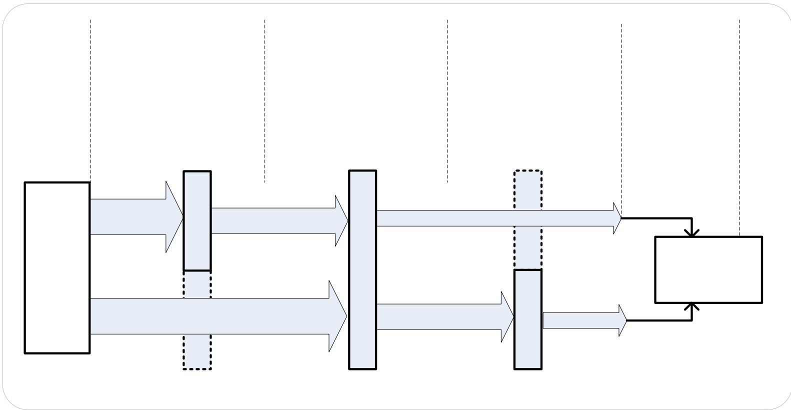

Fig. 5. *Function of layers of protection in fLOPA*

(F_{IE}, frequency of initiating event, F – outcome frequency of particular scenario, PFD – probability of failure on demand of IPLs, S_0 – unmitigated severity of consequences, SRI – severity reduction index, S – mitigated severity of consequences)

In the second assumption all linguistic variables (F, S and R) are expressed by fuzzy sets defined for the range or for its universe of discourse.

The overall fuzzy Layer of Protection Analysis calculation model (fLOPA) is presented in Fig. 6.

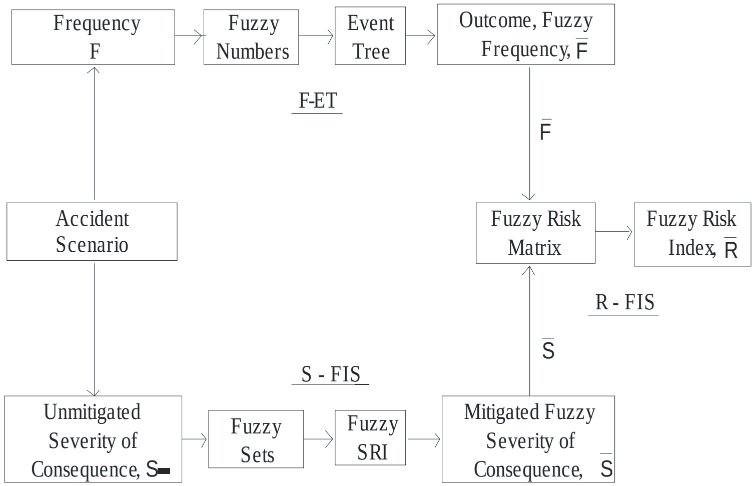

Fig. 6. *Structure of fLOPA*

The fLOPA starts from the identified incident scenario represented by one pair of events: initiating event (IE) and particular outcome consequence. This is obtainable by the application of any Process Hazard Analysis method, especially HAZOP. The model applies three main sub-systems: the two parallel that is Fuzzy Event Tree (F-ET) which calculates the fuzzy frequency of an incident scenario and the Severity Fuzzy Inference System (S-FIS) for the estimation of the severity of consequence for the incident scenario. Both systems provide inputs for the third sub-system, that is the Risk Fuzzy Inference System (R-FIS), comprising the fuzzy risk matrix. As a result of use of an appropriate fuzzy arithmetic and reasoning, the final crisp risk index is obtained, which is used for further decision-making in risk management processes.

This structure is extended to the piping system and the method is called pfLOPA.

6. FUZZY PIPING RISK ASSESSMENT (FPLOPA)

6.1. Fuzzy piping frequency rate failure assessment

Fig. 7 shows the event tree used for piping fuzzy failure frequency rate assessment. As can be seen, the number of input variables was limited to the really most representative basic components of a piping incident scenario including: initiating release event (A), and reactions of the safety functions like automatic shut down system (B), occurrence of ignition (C) and possible action of the environmental protection system (D).

Release event	Automatic shut down system	Ignition occurs	Environmental protection system	Consequence	Sequence of events
A	B	C	D		

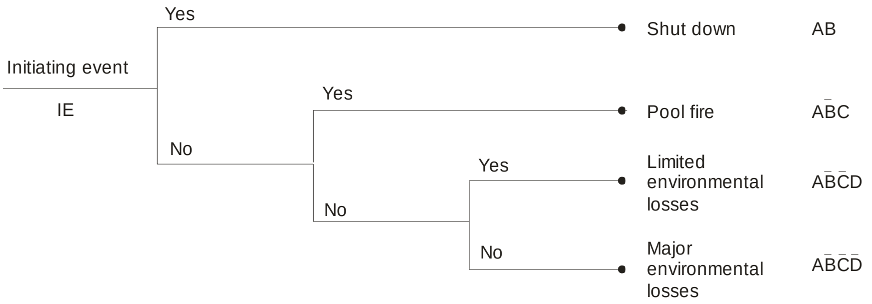

Fig. 7. *Event tree for piping*

According to the assumption for each input variable (A, B, C, D) an appropriate frequency data were identified and they were replaced by the fuzzy sets expressed in terms of fuzzy numbers. Further calculation of the outcome frequency for particular range of consequences is based on:

$$\overline{F} = \overline{F_{IE}} \otimes \prod_{1}^{n} (\overline{PFD_i}) \tag{1}$$

Where: $\bar{F}$ is the fuzzy output frequency failure rate,

$\bar{F}_{IE}$ is the fuzzy frequency rate of the release,

$\overline{PFD_i}$ is the probability failure on demand for the i-th safety function.

6.2. Severity of outcome consequences

The outcome severity of consequence assessment is based on possible size of the release from piping which depends on the volume of piping sector, type of failure, material characteristic and reaction of safety systems which are in place. The Severity-Fuzzy Inference System (S-FIS) is used for this purpose. It involves the design of the membership function that assigns linguistic values to the linguistic variables (size of release and type of hazard connected with a particular substance) and subsequently the application of the design fuzzy rules IF-THAN to describe fuzzy category of severity of the consequences [19].

According to the fLOPA model the category of severity of consequences, S, decreases due to realization of the safety function fulfilled mainly by the mitigation layer. The effect of that change depends on performance of the mitigation layer of protection. For that purpose the Severity Reduction Index (SRI) has been employed by the following:

$$S = (S_0 - SRI) \qquad (2)$$

where: S_0 – unmitigated severity of consequence category, SRI – severity reduction index.

The index SRI employs two elements characterizing the performance of mitigation layer of protection, that is the effectiveness E and time of the response TR. The SRI takes values from 0 (no reduction of the severity category), 1 (reduction by 1 category) and 2, being the maximum reduction index. Data concerning the E and TR incorporated into the analysis are based on the generic knowledge of data available in industry for particular mitigation layer of protection; however they may vary from one technical system to another. More details are given in our previous work [13].

6.3. Risk Fuzzy Inference System – (R-FIS)

R-FIS employs a risk matrix to assess risk index. As it is known, risk matrix presents the relations between frequency rates, severity of the consequences and risk index for certain accident scenario and it can rank process risk index that is typically identified through one of the PHA methods.

Fuzzy risk matrix development requires an application of the Fuzzy Logic System (FLS), which is shown in Fig. 8.

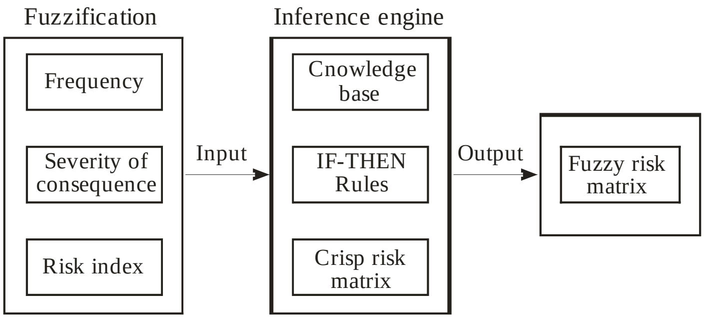

Fig. 8. *Fuzzy logic system (FLS) for development of fuzzy risk matrix*

Fuzzification maps of the input crisp inputs into fuzzy sets for each linguistic variable (frequency, severity and risk index. Inference engine of the FLS maps input fuzzy sets, by means of a set of rules, into fuzzy output sets. It handles the way in which rules are combined. This set of rules is generated from engineering knowledge by means of the collection of IF-THEN statements. The set of 35 knowledge rules (e.g. <**IF** Frequency is "LOW" and Severity of Consequence is "HIGH" **THEN** Risk Index is "TNA">) was applied using the classical risk matrix consisting of 7 categories of the frequency, 5 categories of the severity and 4 categories of the risk. The fuzzy risk matrix applied in this study is shown in Fig. 9.

More details on the construction of fuzzy risk matrix are provided in our previous work [18].

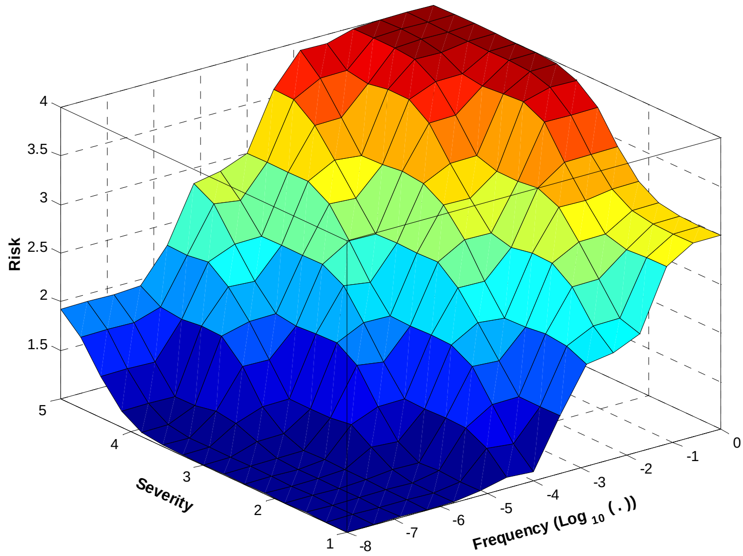

Fig. 9. *Fuzzy risk surface*

The fuzzy output frequency rate, $\bar{F}$ and fuzzy category of severity of consequence, $\bar{S}$ are deffuzified by the centroid method [17] and using the fuzzy risk matrix, a fuzzy risk index is determined. Finally, a crisp value of risk may be obtained.

7. CASE STUDY

7.1. Pipeline description

The fpLOPA was performed for the gasoline pipelines located in central part of Poland. The total pipeline length is about 212 km, inner diameter 400 mm and rated pressure 6.3 MPa. The analysis was performed for one section 20 km long located close to a township. Figure 10 shows a diagram of this section of the pipeline with appropriate process safety systems. The pipeline was designed according to the best available technique (BAT) and it complies with all necessary pipeline standards (Pipeline Integrity Management Rule – IMP Rule -49 CFR Part 195). It was confirmed by the pipelines integrity analysis which includes four different subjects (third party activity, corrosion, design parameters and operational errors).

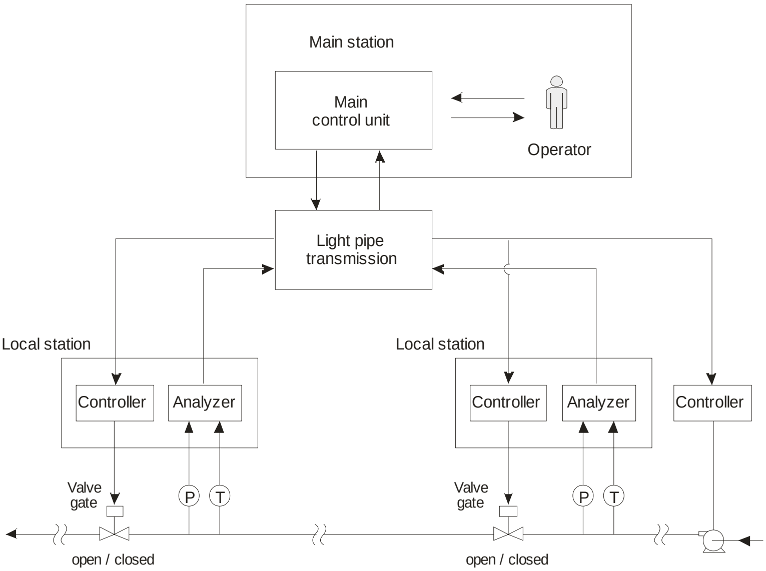

Fig. 10. *Diagram of pipeline section*

In view of a possible release of the transported material, the layers of protection system take action. First of all, the main safety function fulfils the process control monitoring system. Arising pressure impulse after conversion of signal into digital one is tele-transmitted from a release point to the main station where an operator takes an appropriate decision. If a release is considered, then the operator may automatically close the transferring pump and both isolation gate valves on the threatened section of the pipe. This safety function realizes an automatic shut-down system. The time of release depends on the size of release, operating parameters, as well the length of the pipe section. The outcome consequences depend on conditional events, location of the release point, and vulnerability of the environment as well as the performance of the emergency response system. As can be seen from Fig 8, there are three outcome events leading to unwanted consequences. Our attention is focused on major hazards outcomes, i.e. pool fire and major environmental losses.

7.2. Development of input data for fpLOPA

The input data assumed for the case study can be described as a generic data based on available databases as well as on expert opinion. Generally, these data may not be quite precise but they were used for illustration of the presented methodology and they may be specific for this study only. The input data for the F–ET analysis are presented in Table 3. All these inputs undergo fuzzification by assigning an appropriate fuzzy number to each variable. Subsequently, the calculation of fuzzy frequency of outcome event $\overline{F}$ using the event tree presented in Fig. 7 was performed.

Table 4 presents input data necessary for the S-FIS. Size of release was determined based on the possible amount of liquid released as well as on the assumption of the time of release. This time consists of two components: pumping time to shut-down and after that the drainage phase time. Data representing these times for different pipe failure causes were taken from the experience. As can be seen, the time of release is the shortest for pipe rupture but leak may go unnoticed through a long time (buried pipe).

Table 3.

Failure frequency rate input data

No	Failure or conditional event	Overall frequency rate [1/1000 km.year]	Probability of failure on demand, PFD	References
1	Failure cause			[1,2]
	Leak (4 mm)	0.206	-	
	Hole (40mm)	0.164	-	
	Rupture (400mm)	0.051	-	
2	Automatic shut down system	-	10^{-2}	[4,6]
3	Ignition			[1.,2]
	Leak (4 mm)	-	0.0124	
	Hole (40mm)	-	0.062	
	Rupture (400mm)	-	0.062	
4	Environmental protection system	-	0.5	Expert opinion

The effectiveness (E) and time of response (TR) of the mitigation by the community response which allows calculating Severity Reduction Index (SRI) were selected arbitrarily. In comparison to the F-ET system, the design of the fuzzy sets for two variable involved (initial category of consequences –S_0, Severity of Reduction Index (SRI) was based on the Gaussian type of membership function. A similar design of fuzzy sets comprises the risk level. The details are provided in our previous works [19].

Table 4.

Severity of consequences input data used for the Severity-Fuzzy Inference System (S-FIS)

No	Failure cause	Size of release	Category of severity	Time of release [min]		Community response	
		kg	S_0	Pressure phase	Drainage phase	E [%]	TR [min]
1	Leak	50000	5	>300	120	50	300
2	Hole	20000	5	5	120	50	10
3	Rupture	200000	5	3	to empty	40	10

7.3. Results

Table 5 presents six outcome results based on the F-ET, S-FIS and R-FIS systems. For comparison, there are also the crisp value of the risk index R, estimated on the basis of the classical LOPA and risk matrix approach. As can be seen, the fuzzy risk index $\overline{R}$ is different than the classical risk index. For some calculations, especially No. 5 and 6 the differences reach from 20% to 30%. The contribution of each membership function (A, TA, TNA and NA) to the total value of risk index $\overline{R}$ is also shown which enables an optimal and more reliable selection of layers of protection. There is no possibility to receive such conclusions from the classical LOPA calculation results.

Table 5.

Fuzzy Risk Index

No.	Type of initiating event	$\overline{F}$ [a] ×10^4	$\overline{F}$ [b] ×10^6	$\overline{S}$	R	$\overline{R}$	% μ A	% μ TA	% μ TNA	% μ NA	Risk index	Causes
1	Leak	0.16	0.32	5.00	2	1.88	15.3	84.1	0.6	0	TA	Pool fire
2	Hole	0.64	1.28	4.55	2	2.18	0.4	78.2	21.5	0	TA	
3	Rupture	0.20	0.40	4.82	2	1.79	25.2	73.8	1	0	TA	
4	Leak	12.0	24.0	5.00	3	2.90	0	13.2	86.6	0.2	TNA	Major environment losses
5	Hole	9.22	18.4	4.55	3	2.55	0.2	45.2	54.5	0	TNA	
6	Rupture	2.87	5.74	4.82	2	2.76	0	27	73	0	TA	

[a] per 1000 km and year; [b] for 20 km long pipe per year

8. CONCLUSIONS

1. The review of pipeline publications has shown that the existence of 'pipelines legislation' in other industrialized parts of the world, such as the United States, contributes to better knowledge about major accidents and their consequences. As a general principle governing environmental policy, the prevention principle should be respected, i.e. to take prevention measures based on risk assessment rather than to react only after an accident has happened**.**

2. Long distance pipelines recognized to be most safe and most economical way of transporting hazardous substances in comparison with other method of transport,

3. Layer of protection analysis with the use of fuzzy logic can be successfully applied for piping risk assessment. Results of the final output data on risk index are more precisely determined in comparison to the classical LOPA results. It may enable

a better assessment of the incident scenario risk and appropriate assessment of safety assurance.

4. The highest part of unacceptable risk level (TNA) was received for the scenarios with a release from leak and hole causing environmental losses. It indicates the importance of a more reliable monitoring system for possibly small releases.

5. The extension of the received results for the other piping establishments should confirm input data used for calculation.

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STUDIA UNIVERSITATIS BABEŞ-BOLYAI, AMBIENTUM, LIII, 1-2, 2008

DIGESTION METHODS FOR HEAVY METALS ANALYSIS IN ANIMAL ORIGINATED FOOD PRODUCTS

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ABSTRACT. Digestion Methods for Heavy Metals Analysis in Animal Originated Food Products. This paper presents the comparison between two mineralization methods of some food product samples (dairy products): 1. acid digestion in open system with thermal heating; 2. microwave acid digestion in closed system, under controlled pressure. The analytical determination was realised with an atomic absorption spectrometer with flame and graphite furnace.

There were marked out the advantages of the microwave digestion: analysis short time, minimal contamination of the sample, necessity of small quantities of the sample and reagents, minimal residual generation and the maintenance traceability of the results.

Keywords***:*** *wet digestion, microwaves, atomic absorption spectrometry*

INTRODUCTION

The development of the industrial processes lead to an increase concentration of heavy metals in the environment, determining the accumulation in human organism through the food chains. This fact determined the need to measure the concentration of this pollutants, for population exposure and health risk assessment. Generally, the analytical procedures for heavy metals determinations in aliments suppose two phases: mineralization (digestion) and the analysis. The last one lasts a few minutes (hundreds), the digestion lasts a couple of hours. Frequently, the digestion requires a prolonged heating of the sample with concentrated acids.

The mineralization method has to determine the decomposition the sample matrix, so that the analytical compound is completely soluble and is compatible with the chosen analytical method. This makes the mineralization method more efficient.

The sample preparation represents the critical phase in the heavy metals determination analysis in organic samples. The sample treatment suppose the moist or dry mineralization of the sample, in opened or closed systems, using thermal, ultrasonic or radiation (infra-red, ultraviolet and microwaves) energy. After the solubilization of the sample, the quantitative determination is made, using different analytical techniques: atomic absorption spectrometry, atomic emission spectrometry and mass spectrometry.

A particular signification for the human health is represented by the chemical contamination of food. The increased concern about this pollution is determined by the enlarging process of contamination and its augmentation.

The metallic contaminants, especially heavy metals, attract the attention of sanitary organs due to their negative biologically repercussion (Mănescu, 1985).

The analysis of organic samples to determine heavy metals imply the sample's total or partial dissolution prior to instrumental analysis. Only few methods admit the direct sample's admission in analytical instrument, without previous preparation: X-ray fluorescence (XRF), instrumental neutron activation analysis (INAA), thermogravimetry, spectrography. In these methods, the absence of calibration techniques represents the main issue. On the other side, the sample preparation allows the separation and/or preconcentration of analytes and also, the use of several quantification methods, as: gravimetry, volumetry, spectrometry, chromatography (De Oliveira, 2003).

Sample preparation involves digestion, extraction of analytes before the analysis, this step being time consuming, necessitating approximately 61% from total analysis time, and could introduce 30% of total error of analysis (Revesz and Hasty, 1987).

The common approach for samples digestion, in order to determine heavy metals content, imply sample dissolution in concentrated acids, at high temperature, to obtain soluble analytes (Lagha et al. (1999)).

Wet digestion

For the wet digestion of the organic samples, it is used oxidation agents in order to determine the heavy metals contents, usually concentrated acids, like nitric acid, hydrochloric acid, sulphuric acid, perchloric acid or a mixture of them. In the case of sample decomposition in open vessels, the acid's boiling point controls the maximum temperature that can be used to avoid the loss of volatile elements. The wet digestion procedures can be performed using several energies: thermal, ultrasound, radiant (infrared, ultraviolet, microwaves) (Kingston and Jassie, 1986).

Wet digestion with thermal energy

Sample decomposition in closed vessels can be performed using for heating hot plate, Bunsen heater, digestion block, oven. The main disadvantages are: time consuming analysis (hours), large amounts of consumed reagents, near-by contamination, preconcentration of reagent impurities, constant sample surveillance (McCarthy and Ellis, 1991).

Microwave wet digestion

Microwave radiation (2450 Mz, 12,2 cm) interaction with the sample and the reagents leads to the ions migration and dipoles rotation, leading to rapid heating of reaction mixture. The digestions occurring in closed vessels allow high temperatures reaching, accelerating digestion process. The advantages of this methods are: short sample decomposition time (minutes), direct heating of samples and reagents, minimum contamination and volatile elements avoidance (Gilman and Grooms, 1988).

The objective of this study was to determine the heavy metals content (Pb, Cu, Zn) in some food products by atomic absorption spectrometry after sample digestion. We compared two digestion methods:

- classical acid digestion in open vessel with thermal heating on a hot plate (conventional method), and
- microwave acid digestion in closed vessels.

EXPERIMENTAL

To determine heavy metals (Pb, Cu, Zn), we have analyzed the food products (cheese) shown in Table 1.

Table 1.

Cheese sample analysed for heavy metals determination

Cow Feta, produced in Baia Mare	sample 1
Cow Feta, produced in Cluj-Napoca	sample 2
Sheep Feta, produced in Baia Mare	sample 3
Sheep Feta, produced in Cluj-Napoca	sample 4
Processed cheese produced in Sighisoara	sample 5
Processed cheese produced in Brasov	sample 6
Processed cheese produced in Satu-Mare	sample 7
Processed cheese produced in Harghita	sample 8

Cheese samples have been collected from food stores and then acid digested through two methods, and then the quantification was performed by absorption atomic spectrometry.

Instruments used in the methods:

- Electric hot plate, with power adjustable;
- Microwave digestor, OI Analytical, with 12 PTFE vessels, capacity 60 ml, and controlled and steps programmable pressure;
- Atomic absorption spectrometer, SpectrAA220 VARIAN, with air-acetylene flame and graphite furnace GTA 110, fully automatised, double beam, background correction with deuterium lamp electronically modulated.

For microwave digestion we used a closed-vessel laboratory microwave system equipped with temperature and pressure regulation with the maximum high pressure (200 psi) control. The challenges of the study was to determine the low analyte content of the samples and the relatively severe spectral interferences arising from the biological matrix subjected to this direct wet dissolution procedures.

The reagents used for the calibration curves were high purity quality. Used standard solutions were from Merck-Germany acquisitioned. Their concentration was 1000 mg/l. Work standard solutions were prepared from stock solutions, diluting them with double distilled water. Calibration solutions were automatically performed by autosampler, for the graphite furnace analyses.

Samples solutions were analyzed by flame atomic absorption spectrometry for the Cu, Zn determinations, and by electrothermal atomization atomic absorption spectrometry for Pb determinations.

Graphite furnace operating parameters for Pb determination are written in the instrument book, and also in the instrument's computer soft.

The used length waves were: Pb 217.0 nm, Cu 324.8 nm, Zn 213.8 nm.

Classical acid digestion. Method description

Organic matter from sample is decomposed by heating with nitric acid, then with a mixture of sulphuric acid and nitric acid, and in the end with hydrogen peroxide.

Cheese products samples were grinded in a mortar with pestle to obtain a homogenized composition. 10 g were weighed, with 0.001 g accuracy, and were introduced in a conical flask. 10 ml double distilled water and 10 ml concentrated nitric acid (65%) were added to the sample and then stirred for dispersion. The samples were left over the night and then were heated on a hot plate. First, the heating was slowly to slight boiling, the samples were fluid and the volumes were reduced to 15-30 ml. Then, 10 ml nitric acid were added and the samples were heated more intensely, avoiding liquid evaporation and sample carbonization. After the flask cooling, 5 ml nitric acid and 5 ml concentrated sulphuric acid (1.84 density) were added to the sample, heating first moderately and then intensely boiling to eliminate water excess. The nitric acid treatment was repeated 3-5 times, till the liquid was brown-yellowish coloured. Then, 3 ml hydrogen peroxide 30% were added and the sample was heated slowly to start the oxidation and then more intensely. After the total cooling of sample, there were added 15 ml water, heating again till white vapours of sulphur trioxide appeared. The water adding was repeated twice.

After the flask cooling, the sample solution was discarded in a 50 ml volumetric flask and filled with double distilled water. The blank sample was prepared following the same procedure (STAS 10542/1-86).

Microwave digestion. Method description

0.5 g (0.0001 g accurately weighed) homogenized sample, 8 ml nitric acid 65% and 2 ml hydrogen peroxide 30% were added in the digestion vessel. The mixture was slowly stirred and left for 20 minutes before closing the vessel. The vessels were closed, sealed and put in the microwave digestion oven. The temperature program consisted of 3 steps, as shown in Table 2.

The maximum amount (0.5 g) of food sample to be efficiently digested is limited by the maximum working pressure of 13.8 bar (or 200 psi) allowed in the closed-vessel microwave digestion system.

The presence of H_2O_2 helped to maintain a higher temperature under the pressure limit and reduced the carbon content in digestates (Wu et al. (1997)).

Table 2.

Heating program

Step	**1**	**2**	**3**
T ℃	200	200	100
Power, %	70	70	40
Time, min.	35	20	10

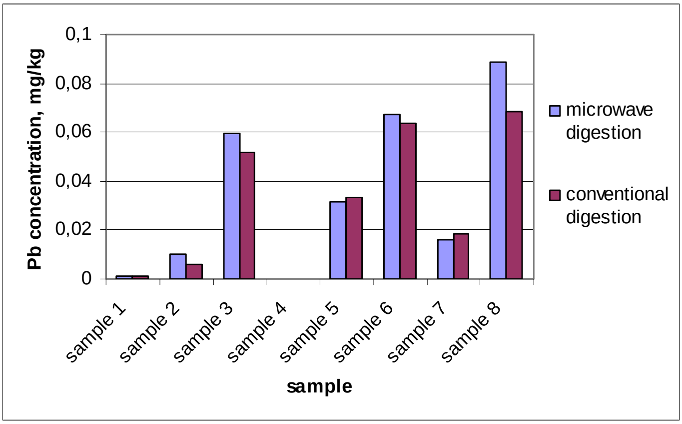
Before opening carefully the vessels in a fume board, we waited 20 minutes to avoid foaming and to allowed vessels to cool at room temperature, according to Berghof Products, Germany, Application report. The obtained sample solution was clear, light yellowish coloured.

After the complete sample digestion, the solution was filtered in a 25 ml volumetric flask and filled with double distilled water. Similarly, a blank sample was prepared.

In the graphite furnace, the automatic autosampler injected 20 µl of digested sample. The results were calculating by interpolating the calibration curves and then, is divided to weighed mass of sample.

RESULTS AND DISCUTION

The obtained results (Pb, Cu, Zn concentration) after two digestion methods are shown, comparatively, in Figure 1.



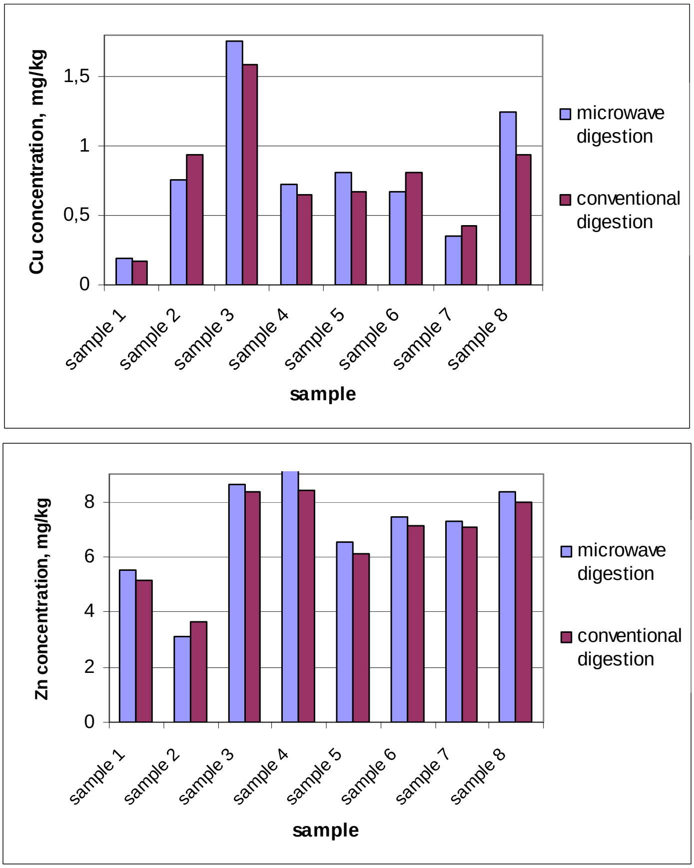


Fig. 1. *Heavy metals (Pb, Cu, Zn) concentrations after two digestion methods, comparatively*

The obtained results showed that:

Lead: the determined metals concentrations were with 5-40% higher after microwave digestion than after conventional method, although, the values are higher for samples 5 and 7 after conventional digestion (with 5%, and 12% respectively);

Copper: the determined metals concentrations were with 9-25% higher after microwave digestion than after classical digestion, although, the values are higher for samples 2, 6 and 7 after conventional digestion (with 20%, 17% and 18% respectively);

Zinc: the obtained concentrations were with 3-19% higher after microwave digestion of all food samples, except for sample 2 (Zn value was higher after classical method with 15%);

An explanation for these results could be that during microwave digestion the temperature and pressure are higher than during classical method, resulting in higher destruction of organic matter. Due to that fact, the most concentrations of

Pb, Cu, Zn and are higher than those obtained after acid digestion in open vessels and thermal heating.

CONCLUSIONS

In the last years, the microwave digestion has significantly drawn attention, due to the simplicity of sample treatment, and shortness of analysis time, comparing to classical acid digestion techniques.

Microwave digestion has also other obvious advantages:

- reduced amount of sample used in analysis;
- reduced amount of acids used for digestion;
- microwave energy is rapidly absorbed by the food components: proteins, fats, carbohydrates;
- reduced amounts of reagents has lead to reduced analysis price and minimized the risk of strong acids use;
- reduced sample contamination from the environment;
- it is not necessary the constant surveillance of sample like during the hot plate digestion;
- reduced acid fumes analyst’s exposure;
- reduced glass materials used for digestion;
- used Teflon vessels could be reused and their cleaning procedure is easy and rapid;
- reduced equipment’s corrosion;
- reduced amount of residues obtained after the analysis;
- possibility of fully automated process;
- increased process safety.

Overall, the microwave digestion method is simple, rapid and suitable for the analysis of trace elements in biologic matrices for food or environmental assessment risks.

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STUDIA UNIVERSITATIS BABEŞ-BOLYAI, AMBIENTUM, LIII, 1-2, 2008

MONITORING OF VOLATILE ORGANIC COMPOUNDS (VOC's) EMISSIONS IN A FURNITURE FACTORY

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ABSTRACT. Monitoring of volatile organic compounds (VOC's) emissions in a furniture factory. The aim of this study was to assess the levels of some organic compounds used as solvents for varnish paints in the emissions of a furniture factory. Their concentrations as well as the total organic carbon in these emissions were calculated. The highest concentrations were found fof n-butyl acetate and xylene. The levels of total organic carbon varied between 39.8 and 124.1 mg/m^3 air. Gas chromatography was usd as analytical method for the monitoring of VOC's emissions.

Keywords: *VOC's, emissions, gas chromatography*

INTRODUCTION

ManyVOC's are frequently used as solvents for varnish paints and adhesives. The composition of such solvent mixtures varies from a factory to another depending on the varnish paint used. Sometime, even in the same factory fluctuation from day to day or even in the same day. The VOC's encountered in solvent mixtures appertain to various classes of substances: hydrocarbons (aliphatic and aromatic), ketones, esters, alcohols etc.

Due to their high volatility as well asto the method of varnishing, VOC's are present in the working atmosphere. In order to protect the worker health, various methods of removing VOC's vapor or aerosols are used. Most frequently the contaminated air is exhausted and VOC's will pollute the atmosphere.

The objective of this study was to assess the levels of some organic compounds used as solvents for varnish paints in the emissions of a furniture factory where the compressed air pulverization of varnish is used.

MATERIAL AND METHODS

Sampling

Sampling was done in four different seasons of 2007 by collecting VOC's in tubes with activated charcoal using personal air sampling pumps. Every time 3 sampling were done for each exhauster chimney. VOC's emissions were assessed for 7 exhauster chimnies.

Analysis of VOC's

VOC's concentrations were determinated by gas chromatography, using a Hewlett-Packard 4890 D gas chromatograph equipped with flame ionization (FID) detector. A number of 84 samples have been analysed after the desorption of VOCS's in carbon disulphide.

Separation swere done on a capillary column BP-5 (30 m x 0.32 mm) with a carrier gas flow rate of 2 ml/min .The temperature programme was: 50 ^{o}C (2min), 7 ^{o}C/min to 125 ^{o}C. Injector and detector temperatures were 175 ^{o}C.

Identification was performed oh the retention time basis, using standard mixtures. Quantitation was done by the external standard method

Using the described method, we had in view the identification and quantitation of the following VOC': aceetone, methyl ethyl ketone, ethyl acetate, n-butyl acetate, ethyl alcohol, n-butyl alcohol, benzene, toluene and xylene.

The levels of the total organic carbon in the emissions were calculated from the individual concentrations of each VOC (average value of the 3 samplings).

RESULTS AND DISCUSSION

Acetone, methyl ethyl ketone, ethyl acetate, n-butyl acetate, toluene and xylene were present nearly in all the samples excepting two cases were according with the results a mixture of only acetone and methyl ethyl cetone was used as varnish paint solvent.

The highest concentrations were found for n-buthyl acetate and xylene. Their concentrations varied between 9.5 and 48.4 mg/m^3 air, respectively between 3.2 and 67.1 mg/m^3 air. The average values of VOC's concentrations in the investigated emissions are presented in Tables 1-4.

Table 1.

VOC's concentrations (average of the 3 samplings), sampling in 03.16.2007

Sampling point	VOC's concentration (mg/m^3 air)								
	Acetone	Methyl ethyl ketone	Ethyl acetate	n-Butyl acetate	Ethyl alcohol	n-Butyl alcohol	Benzene	Toluene	Xylene
Chimney 6	65.5	2.2	-	-	-	-	-	-	-
Chimney 7	2.7	12.0	8.8	13.5	-	-	-	3.9	22.3
Chimney 12	14.0	14.3	8.2	10.0	-	-	-	5.5	16.9
Chimney 13	65.5	2.2	-	-	-	-	-	-	-
Chimney 15	6.2	10.5	6.5	12.5	-	-	-	3.9	23.1
Chimney 16	9.9	11.5	10.6	17.3	-	-	-	5.1	23.9
Chimney 17	3.9	10.8	8.1	13.4	-	-	-	9.7	22.0

Table 2.

VOC's concentrations (average values of the 3 samplings) in emissions, sampling in 05.31.2007

Sampling point	VOC's concentration (mg/m^3 air)								
	Acetone	Methyl ethyl ketone	Ethyl acetate	n-Butyl acetate	Ethyl alcohol	n-Butyl alcohol	Benzene	Toluene	Xylene
Chimney 6	-	7.9	13.8	11.0	-	-	-	5.3	43.1
Chimney 7	2.8	6.4	-	31.8	-	-	-	8.4	41.1
Chimney 12	0.8	1.0	6.0	27.8	-	-	-	7.7	47.7
Chimney 13	0.3	6.5	15.7	25.7	-	-	-	13.5	28.4
Chimney 15	2.3	2.4	11.0	36.7	-	-	-	15.9	21.6
Chimney 16	3.1	-	3.1	38.4	-	-	-	21.1	22.0
Chimney 17	18.6	0.4	15.9	37.0	2.5	7.3	-	3.4	16.3

Table 3.

VOC's concentrations (average values of the 3 samplings) in emissions, sampling in 09.26.2007

Sampling point	VOC's concentration (mg/m^3 air)								
	Acetone	Methyl ethyl ketone	Ethyl acetate	n-Butyl acetate	Ethyl alcohol	n-Butyl alcohol	Benzene	Toluene	Xylene
Chimney 6	1.1	3.6	12.7	11.1	-	-	-	6.6	57.7
Chimney 7	10.0	-	-	9.5	-	-	-	4.4	28.2
Chimney 12	27.5	-	12.7	17.5	-	-	-	19.5	25.1
Chimney 13	10.7	-	3.7	12.5	-	-	-	7.5	18.4
Chimney 15	2.4	24.7	18.1	33.2	-	-	-	22.4	63.4
Chimney 16	16.2	15.0	14.9	29.5	-	-	-	8.3	49.2
Chimney 17	47.0	-	0.4	11.6	-	-	-	2.2	9.5

Table 4.

VOC's concentrations (average values of the 3 samplings) in emissions, sampling in 12.07.2007

Sampling point	VOC's concentration (mg/m^3 air)								
	Acetone	Methyl ethyl ketone	Ethyl acetate	n-Butyl acetate	Ethyl alcohol	n-Butyl alcohol	Benzene	Toluene	Xylene
Chimney 6	2.0.	2.3	4.2	21.7	-	-	-	10.9	51.8
Chimney 7	4.8	10.6	-	15.6	-	-	-	7.5	47.2
Chimney 12	38.3	11.6	-	19.8	-	-	-	5.9	34.5
Chimney 13	15.7	2.1	-	23.0	-	-	-	6.2	45.1
Chimney 15	2.1	4.6	5.2	46.4	-	-	-	22.9	63.4
Chimney 16	3.0	2.9	5.7	48.4	-	-	-	16.6	67.1
Chimney 17	80.4	6.3	-	1.9	-	-	-	2.5	3.2

The levels of the total organic carbon in the emissions varied between 39.8 and 124.1 mg/m^3 air and are presented in Table 5. Values exceeding the maximum allowable level (75 mg/m^3 air) were found in 2 out of the 28 measurements (7.1 %).

Table 5.

Values of the total organic carbon in the emissions

Sampling point	Total organic carbon concentration (mg/m^3 air)			
	03.16.2007	05.31.2007	09.26.2007	12.07.2007
Chimney 6	59.9	63.5	74.9	59.9
Chimney 7	46.6	70.7	41.6	46.6
Chimney 12	49.2	71.9	73.1	49.2
Chimney 13	42.2	67.1	39.8	42.2
Chimney 15	46.5	65.9	124.1	46.5
Chimney 16	56.6	66.6	98.5	56.6
Chimney 17	51.0	67.3	47.0	51.0

It must be specified that these are average values and that if this parameter would be calculated for each individual sampling, much more values exceeding the maximum allowable level will be find. Fluctuations of VOC's concentrations in the emissions of the same chimney exist not only from a season to another but even in mthe same day. It is due, probably, to some inherent interruptions in the painting activity as well as to the filters capacity to keep the VOC's (Filters with activated charcoal are installed on each chimney in order to diminish VOC's emissions).

CONCLUSIONS

Due to the inherent fluctuations of the VOC's emissions in the factory investigated, monitoring has to be done periodically, especially when short time samplings are performed. This monitoring is also useful for assessing the efficiency of the equippments used to diminish the pollution.

The determination of individual compounds in emissions is very important because VOC's have different toxicities and the level of total organic carbon alone cannot reflect the real effect of the VOC's on the environment.

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STUDIA UNIVERSITATIS BABEŞ-BOLYAI, AMBIENTUM, LIII, 1-2, 2008

SAMPLING AND IDENTIFICATION OF VOLATILE AND PARTICULATE AIR CONTAMINANTS ON HEAVY TRAFFIC ROAD

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ABSTRACT. Sampling and Identification of Volatile and Particulate Air Contaminants on Heavy Traffic Road. This work presents a case study carried along a busy, heavily circulated road in an important N-W town of Romania. The objective was to assess the impact of heavy road traffic on the air quality on adjacent streets. A simple method was used for the collection of volatiles from air, in charcoal filled tubes. The analytes were desorbed in an organic solvent, then separated on a capillary column. The concentration of volatile organic atmospheric contaminants mainly originating from the exhaust gas of internal combustion engines, were determined by using GC/MS quantitative analysis methods. Particulate matter concentrations in the air along the monitored street, were determined in 9 sampling sites, using a portable detector provide with proper sensors, and applying the short duration standard methodology. The results showed that the air quality suffers from exposure to particulate matter and to engine exhaust gases.

Keywords: *atmospheric pollution, engine exhaust gases, particulate matter*

INTRODUCTION

Air quality assessment and monitoring address the concentrations assessment procedures, setting regulations, improving the air quality indicators, control and monitoring. As outlined in a European Economic Area Briefing of 2006, Europe is the most densely populated and urbanized continent: 75 % of population already live in urban zones, and more than ¼ of the continent surface is affected by urban use. Estimates foresee that by the year 2020, this percent will increase to 80, and even 90 % in certain countries. Action is needed to provide green and clean zones in urban areas, improve the economic and ecologic performance of urban centres and disseminate good practice examples.

Urban transportation, though heavily impacting on the environment, is vital to the whole antropic activity associated to metropolitan areas. The main air contaminants due to road traffic exposure are: exhaust gases from internal combustion vehicles, unburned volatiles from petrol fuels, namely BTEX (benzene, toluene, ethyl-benzene and xylenes), dust, and noise (Hedlund et al., 2004, Ilacqua et al., 2007).

Wide concern related to atmospheric concentration of volatile organic compounds VOCs and particulate matter, combined with increasingly strict regulations of air quality monitoring, both outdoors and indoors (Ilacqua et al., 2007) are all due to the impact that these compounds have on the environment and on human health. Exhaust gas, unburned volatiles and dust are the main air contaminants due to road traffic exposure. They contribute to photochemical smog and tropospheric ozone formation (Finlayson-Pitts et al., 1997, Hassoun et al., 1999) they are eye and respiratory irritants (Kim et al., 2002), and may have hepatotoxic (Chen et al., 2002), nefrotoxic and neurotoxic effects (Lehman et al., 2002). Of the volatiles, benzene is one of the most monitored air pollutant in areas with intense road vehicle transportation. Recent studies (Tubaro et al., 2003) showed that under sunlight, benzene and toluene react with oxygen to form phenol and thus additionally contribute to the air quality degradation in industrial and urban areas with busy traffic. Furthermore, elevated atmospheric levels of particulate matter PM_{10} are associated with a systemic response that contributes to the pathogenesis of cardiovascular and respiratory morbidity and mortality (Van Eeden et al., 2001, Samet et al., 2000).

Analysis protocols and monitoring methodology of dust and volatile air contaminants are subject to research and improvement in terms of specificity, accuracy, detection limit, and rapidity (Mc Clenny et al. 2002, Blanchard et al. 2003, Drake et al., 2007).

EXPERIMENTAL

Identification of the volatile analytes

The experimental determinations in this study were carried out in three stages. Initial sampling was done by using a syringe provided with solid phase microextraction SPME fiber with 100 µm film of polydimethyl-siloxane PDMS non-polar coating. The SPME needle was exposed for 15 minutes to the exhaust gas pipe of an internal combustion engine, of a local car model Dacia that uses lead-free gasoline, a model often encountered on Romanian roads. The SPME fiber was then capped and isolated, for subsequent laboratory analysis, being introduced in the GC injector (at 200 ^oC). The analytes adsorbed on the SPME fiber were identified, being separated (Fig. 1) on a DB-5 (30 m x 0,5 mm x 0,25 µm) capillary column, using a temperature program: 50 ^oC (5 min isothermal) to 150 ^oC @ 10 ^oC/min.

Air samples collection on site

In a second stage, a case study was carried out along a busy road in the centre of the city. For quantitative analysis of the identified analytes, volatiles from the street air were collected in glass tubes filled with active charcoal, using a portable, battery operated air pump, with an air flow set at 200 ml/min. Sampling time was of 30 minutes, for each of the samples labeled $\mathbf{V_{1-6}}$. The collection sites were as follows: $\mathbf{V_1}$ **-** in a park zone, on top of Cetatuia hill, where no cars were passing during the sampling time; $\mathbf{V_2}$ **-** at 1 m distance from the exhaust pipe end, with the engine running at rest; **V_3 -** in the car cabin, with the engine running at rest; **V_4** – on Baritiu street, near the Magyar Opera House,**V_5** – on Baritiu street, at half way from its ends, close to the TUC-N building, and **V_6** at the crossing of Baritiu street with M. Viteazu Square and King Ferdinand street. The collection sites for volatiles are indicated on the map in figure 2.

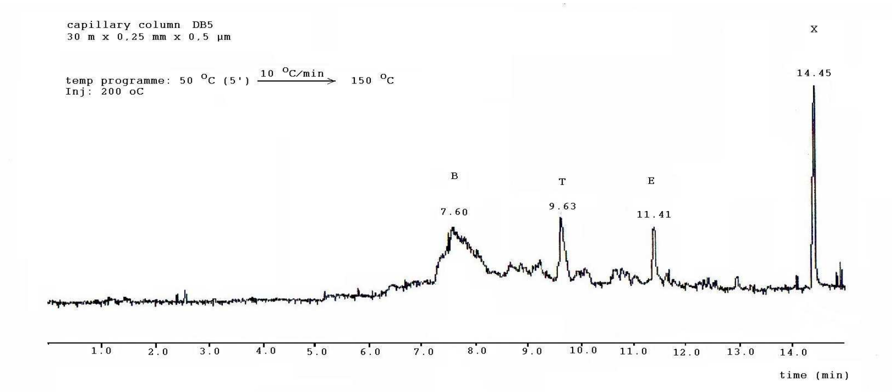

Fig. 1. *Analytes (BTEX) collected on the SPME fiber, and separated on the DB-5 capillary column*

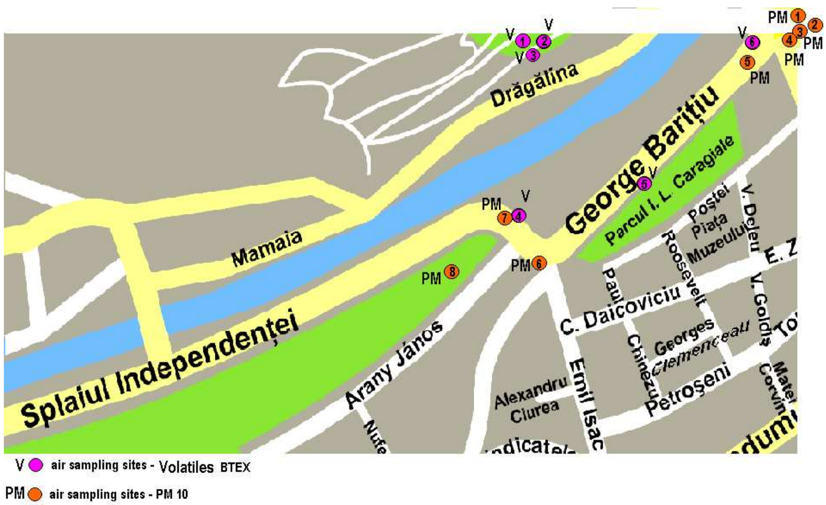

Fig. 2. *Sampling sites for volatiles (**V: 1-6)** and for particle matter PM_{10} (**PM: 1-6**) from street air*

Desorption, GC separation and GC/MS quantitative determination of analytes

The analytes were then desorbed in 0,5 mL solvent (DCM- dichloromethane) under ultrasonic agitation (2 min), and a constant amount of internal standard (bromo-benzene) was added, having identical concentrations in each sample. Then 1 µL of the supernatant was injected in the GC/MS device: a VARIAN STAR 3400 gas chromatograph coupled with a CX-SATURN 3 mass spectrometer. The compounds were separated on a DB-1 (30 m x 0,25 mm x 0,25 µm) capillary column, with carrier gas He (1 mL/min), and a temperature program T: 35 ^{o}C (5 min isothermal) then to 150 ^{o}C @ 5 ^{o}C/min and then to 250 ^{o}C @ 15 ^{o}C/min. The injector temperature was set at 250 ^{o}C, with initial 15” in splitless mode, then 1:16 splitting ratio.

Identification and quantitation of BTEX (benzene, toluene, ethyl-benzene and xylenes) from the air samples was done in the SIM-GC/MS mode, based on monitoring certain selected ions from each compound mass spectrum and from the mass spectrum of the internal standard bromobenzne. Calibration graphs were plotted for each compound targeted, and a quantitative method was developed, that was applied in this case study.

Particulate matter determinations

In the third and final stage of the experimental case study, particulate matter PM_{10} determinations were carried out using an air sampler for PM_{10} Zambelli model EGO BASIC, prec. ±2%, with a pump flow of 4 L/min and 30 min sampling time. Dust collection was done on sites marked PM 1-8, in figure 2, along Baritiu street and in vicinity areas, adjacent to busy roads. Sample masses were determined with a precision balance SHIMADZU, series AUX-120, with internal standard calibration.

RESULTS AND DISCUSSION

Figure 1 shows the separation on the DB-5 capillary column of the 4 volatile analytes identified as *benzene*, *toluene, ethyl-benzene and xylenes* (BTEX), found in the sample collected on the PDMS coated SPME fiber, next to the exhaust pipe end.

The total chromatograms obtained from the “clean” air sample (V-1), from the cabin interior (V-3) and from the street air sample collected close to the Magyar Opera House (V-4) are shown in figure 3. The analytes and internal standard are well separated on the capillary column DB-1, with the average elution times 2,5’ (B), 4,5’ (T), 7,7’ (E), 8,1’ (p, m-X), 8,8’ (o-X), and 9,8’ (internal standard).

Table 1 presents the compounds molecular masses and the masses of the ions selected from the mass spectra, for the quantitative SIM-GC/MS analysis.

Table 1.

Compounds analyzed, molecular masses, and masses of the selected ions for the SIM-GC/MS quantitative analysis of volatile air contaminants: benzene (B), toluene (T), ethyl-benzene (E), xylenes (X, o-, m-, p-), IS (BB- bromobenzene)

Compound	Molecular mass (amu)	Selected ions for quantitative analysis m/z (Da)
B	78	78
T	92	91, 92
E	106	91, 105, 106
p-, m- X	106	91, 105, 106
o-X	106	91, 105, 106
BB (IS)	156	77, 156, 158

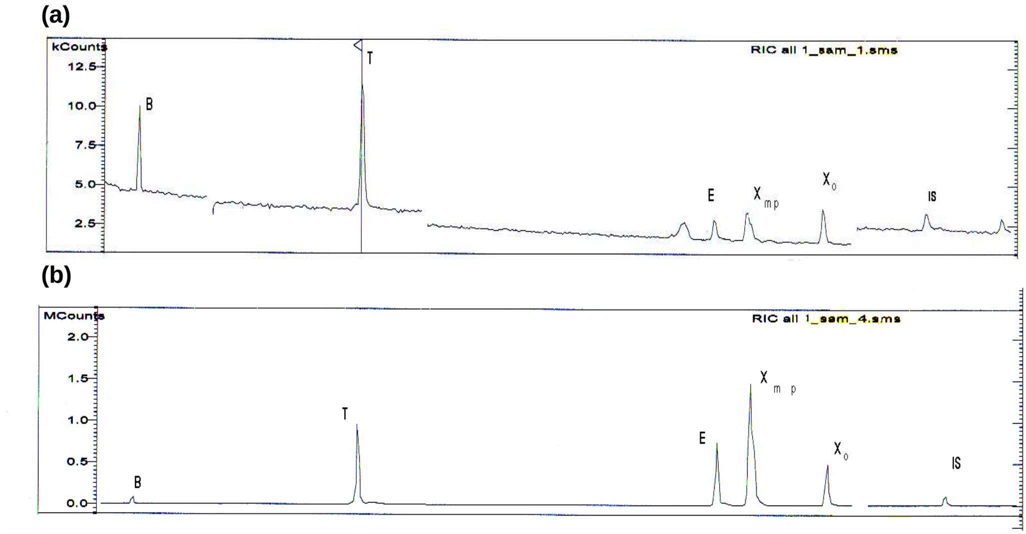

Fig. 3. *SIM-GC/MS chromatogram of separation of analytes and internal standard (bromobenzene, BB) on the DB-1 capillary column (30 m x 0,25 mm x 0,25 µm), in samples:* ***V-1*** *(a), and* ***V-2*** *(b).*

Quantitation was done by calculating the ratios of the total analyte peak areas to the internal standard selected peaks area, and comparing to the calibration graphs of the SIM-GC/MS response, that were plotted for solutions of known concentrations of BTEX.

Table 2 presents the values found for the BTEX concentrations in street air, in the 6 sampling sites.

Table 2.

BTEX concentrations found in street air

Sample nr.	Sampling site	Benzene (µg/m^3)	Toluene (µg/m^3)	Ethyl-benzene (µg/m^3)	Xylenes (µg/m^3)
V_1	Green area, on top of hill	40	77	13	18
V_2	1 m from exhaust pipe end	48	162	147	563
V_3	Car cabin, engine on	42	135	130	243
V_4	M. Opera	256	192	154	323
V_5	Baritiu str., nr 25	130	187	162	562
V_6	Baritiu/Ferdinand/M. Viteazu	103	187	162	580

Particulate matter determinations in the street air were made in the sampling sites marked with **PM 1-8** in the map of figure 1. The measurements were carried out in the time interval 15:00-20:00, with intense road traffic on Baritiu street and in the adjacent zones. Values obtained for the dust concentrations found in the monitored sites are shown in Table 3.

Table 3.

Air concentrations of PM_{10}, found in the air of sampling sites

Sampling site	**PM_{10}** concentration (μg/m^3)
PM- 1- M. Viteazu Square; "Napolact"	83
PM- 2 – M. Viteazu Square – bus stop	83
PM- 3 – Park, near M. Viteazu statue	20
PM- 4 – crossing: Baritiu str/King Ferdinand str	125
PM- 5 – pedestrian lane – Baritiu street	250
PM- 6 – crossing str. E. Isac- str G. Baritiu	160
PM- 7 – pedestrian lane – M. Opera House	108
PM- 8 – in Central Park (50 m from the boundary)	7,5

As may be observed in table 1, the values found for the air concentrations of VOCs (namely BTEX) especially from exhaust gas of internal combustion engines, are very high, even in a green area expected to have "clean air". Along the busy road sector: G. Baritiu street, between M. Viteazu Square, King Ferdinand str, and Magyar Opera House, the heavy traffic, typical for that street and for long time intervals, daytime and night time, explains the great values obtained for the volatiles determined. Also, in the days of measurements, special meteorological conditions were favouring the mixture of pollutants and migration by wind flows in areas remote from road traffic. Cold winter afternoons, with short but intense wind pales, low clouds and temperature inversions - favoured high concentrations of air contaminants in a large and busy town situated between hills.

Concerning the concentrations found for PM-10, except for the site located deep in the Central Park (PM-8), the other samples showed increased values. Relatively smaller dust concentrations were found in the air in the small park near M. Viteazu statue (PM-3), and also, some acceptable values were found on each side of "one way" roads, adjacent to this small green zone (PM-1 and PM-2).

On the contrary, at the street crossings, and along busy roads with double ways traffic, on 2 lanes are the cause of very high PM-10 concentrations, at sites (PM-4-8).

The air quality documents in force at present (STAS 12 547-87) specify that the maximum allowed air concentration of dust is 50 μg/m^3 in residential areas, and 150 μg/m^3 in industrial zones. The Baritiu street supports a consistent quota of the routine traffic connecting highly populated districts of the town. All the zones monitored in the present case study support an intense vehicle traffic, heavy trucks, public transport vehicles and automobiles, therefore they have a functional role, and thus may be assimilated to an "industrial" area. Yet, the streets monitored are also adjacent to buildings with dwellings, offices, educational activity, commerce. The green areas are zones for leisure and recreation, expected to have clean air. As they are situated in the vicinity of busy roads, the air quality is poor on the frontier of the Central Park and in the small green areas in Mihai Viteazu Square. Busy traffic, in the absence of a ring-road for preventing heavy trucks from crossing the whole town, produces considerable atmospheric contamination and noise pollution along the streets examined in the present case study.

CONCLUSIONS

The present case study confirmed that busy roads with heavy traffic seriously impact on the urban environment, contributing to the degradation of air quality, being contaminated with relatively high concentrations of volatiles from internal combustion engines, and with dust, associated to the road transportation activity. Small areas with vegetation and roads with one way traffic contribute to diminishing the air contamination with dust. Volatiles though, are easily mixed in the atmospheric gas and high concentrations may accumulate even in areas remote from busy roads, and expected to be clean.

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THE ANTHROPOGENIC ENERGETICALLY BALANCE SHEET OF TIRASPOL TOWN

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ABSTRACT. The Anthropogenic Energetically Balance Sheet of Tiraspol Town. The notion „life's quality" changes its content commensurate writh the development of the human society, directly proportional to the requirements of increasing satisfaction of the man's necessities. This lead to an increasing global offerts for energetic substances, obtained through the exploitation of the underground deposits. In the burning process, big quantities of energy are being released in the environment. The energy cumulated in the underground deposits among the geological ages, in an relatively short geological time, is being released in the environment. The basic element of an ecosystem is the energetic balance. In this paper we analize the energetic balance of the town Tiraspol, Moldova Republic.

Keywords: *energetic balance, environment protection, pollution*

CONCEPTIONS

The urban ecosystem is an open system in which the human activity takes place. It can't develop without the anthropic influence [2].

The same processes take place in the urban ecosystem as in the natural ecosystems:

- energy consumption and substance circuit subordonated to the social interests;
- the evolution of the urban ecosystem has both objective and subjective feature: it depends on the social-human relations, political, historical and cultural factors;
- the urban ecosystems influence the natural ecosystems prevailing the negative feature;
- the natural ecosystems influence the chemical and physical processes in all the spheres of the geographical cover: atmosphere, lithosphere, hydrosphere, biosphere.

The notion „life's quality" changes its content commensurate writh the development of the human society, directly proportional to the requirements of increasing satisfaction of the man's necessities. During the last century the reduction of the environmental quality was determined by the volume of the polluting substances emanation in liquid, solid and gaseous state especially from the big industrial centres. The improvement measures of the ecological situation in the spheres of the geographical cover had the purpose to reduce their volume. The environmental protection became a sphere of activity where the investigation of the branches of the many fundamental sciences are intercalated. In the Republic of Moldova maximum shares of emanations of the polluting substances in the environment were obtained in the second half of the twentieth century.

From all the towns Tiraspol highlighted itself through the volume of emanations where often there were negative phenomena in the atmosphere such as: „smog", „greenhouse effect", „inversions of temperature", „acid rains". (fig. 1)

Today the technical and scientific, social and economic succeses have declined the axis of the direction of ecological activity towards the quality of emanations and their individual effect over the components of the geographical cover. The energetics becomes one of the cardinal problems of the mankind. The increasing requirements of „social comfort" led to the appearance of the offers of carrying substances of energy obtained through the valorization of the underground stocks. Enormous volumes of energy are emanated after their burning, „released" from the state of preservation in the environment. The accumulated energy into the underground stores for ages is released in the environment in a geological relative short time.

The energy sources of the all processes in the geographical cover are the following: the solar radiation, the internal energy of the earth, the force of gravity, the cosmic energy, the chemical energy (it is shown predominantly in the oxidation and reduction processes), the biogen energy of the industry (with the trend of doubling every 14-15 years [2]. The interaction process between the society and environment obtains a remarkable aspect through the multiple manifestation of the antropogenic elements – the urban systems, hydrotechnical objects, means of transport etc.

The anthropic ecosystems don't possess any capacities of development: in the case when the changes were planned and implemented in nature by the man are not supported artificially the ecosystem of an anthropic origin does not regenerate and also it does not presserve. The base element in any system is the balance sheet. In this article it is analysed the energetical balance sheet of Tiraspol town, the Republic of Moldova.

Tiraspol is situated at latitude 46º50' North on the plain of the Black Sea, at average altitude of 50 *m*. There are two different geomorphological units in the limits of the town – the waterside and the old terrace of the Nistru river.

The yearly balance sheet of the solar radiation consists of 53,2 $kkal/cm^2$. About a half from the value of this index belongs to the summer months. The radiation balance sheet has negative values during the winter months. The medium temperature of the hottest month is 22º*C* and of the coldest one is - -3,6º*C*. The annual medium temperature is +9,6º*C*. Following the diurnal evolution of the temperatures in more points of observation during a year in the limits of Tiraspol it determined that they are higher than the temperatures of the observation center in medium with 2,1º*C* from its outside. In spring and autumn, the differences of temperatures are less expressed.

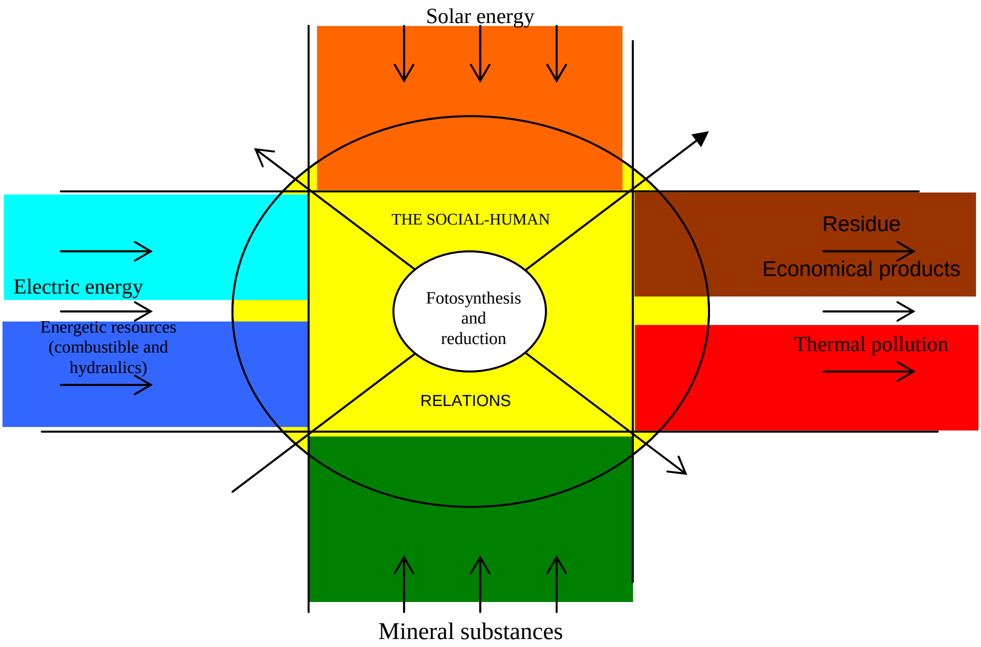
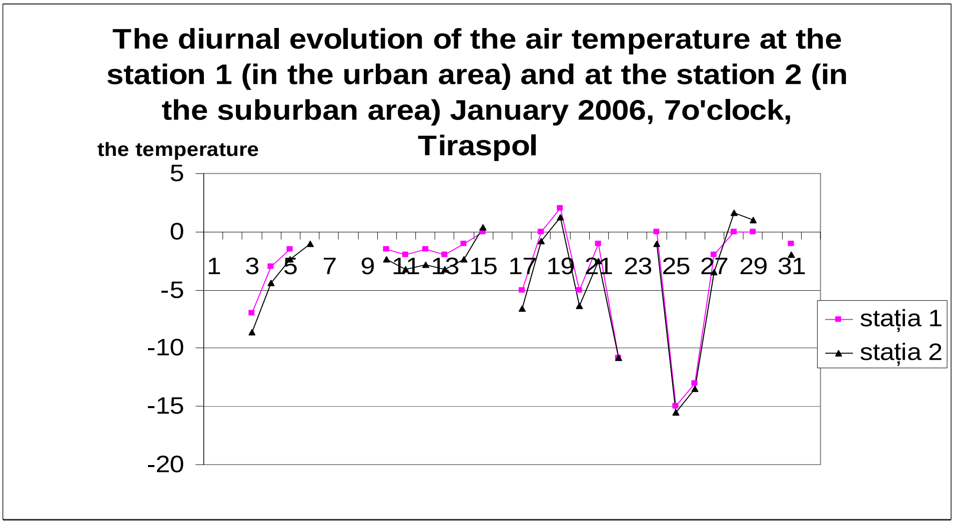


Fig. 1. *The energy and substance movements in the urban ecosystem*

Table 1.



In order to maintain the tempo of life, annual Tiraspol receives energetic resources: natural gaz, electric energy, fuels in liquid state (petrol, diesel oil, kerosine), coal. The biggest quantities from these resources are used during the cold period of the year.

Table 2.

The annual consumption of the natural gaz in Tiraspol town (2006)

month	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	year
mln.m³	34	31	25	9	5,5	5	4,7	5,1	5,8	10,5	24	28	187,6
in %	18,2	16,5	13,3	4,8	2,9	2,7	2,5	2,7	3,1	5,6	12,8	15	100

The biggest part from the volume of natural gaz in the town is spent in the cold period of the year – 142 *mln. m.c*. (75,6%) which is used in order to heat the houses. Annual at its burning it is produced a quantity of energy equal with $37{,}2\cdot10^9$kkal and during the cold period of the year – $28{,}14\cdot10^9$ kkal.

And other energetic substances are imported into the town in order to maintain the economic base, such as: petrol, diesel oil, gaz for the jet engines, coal.

Table 3.

The caloric values of the power resources imported in Tiraspol, 2006 year

Power resources	The quantity m^3, tons, *kW/h*	Energetic value, kkal
Natural gas (methane), mln m^3	187	$1775{,}2217 \cdot 10^9$
Petrol	275	$3{,}02 \cdot 10^9$
Diesel oil	635	$6{,}365 \cdot 10^9$
Kerosene	1	$0{,}01 \cdot 10^9$
Coal	15645	$108{,}283 \cdot 10^9$
Electric energy (thousands *kW/h*)	377 775	$0{,}4397 \cdot 10^9$
Total		$1893{,}3394 \cdot 10^9$

The electric energy also participate to the formation of the energetic balance sheet of Tiraspol urban ecosystem. In 2006 there were consumed 377815 *thousand kW/h*, from which 62860 *thousand kW/h* were consumed by people in communal purposes and 314955 *thousand kW/h* by economical agents. The surface of the town is 5423 *ha*. Ascribing the quantity of „released” energy in its limits, we obtain the supplement of energy of an anthropic origin to a unit of surface which provokes the rise of temperatures comparated to the extra-urban temperatures:

$$\frac{18933{,}394 \cdot 10^8 kkal}{5423 \cdot 10^8 cm} = 3{,}5 kkal/cm^2 \ .$$

CONCLUSIONS

The obtained investigations and results can be used to:

- the ecological estimate of the towns;
- the determination of the urban type and statute according to the nature of the imported and used substances in the limits of the town (industrial, cultural, balneal etc.)
- the determination of the urban role (of the urban agglomeration) in the formation of the ecological conditions in the limits of the physical and geographical regions, continents, subcontinents and geographical cover.

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LE GISEMENT DE LIGNITE DE LA VALLÉE DE LUPOIȚA, DÉP. DE GORJ – ASPECTS ÉCONOMIQUES ET JURIDIQUES

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ABSTRACT. Le gisement de lignite de la Vallée de Lupoița, dép. de Gorj – aspects économiques et juridiques. The exploitation of the lignite deposit from Lupoita Valley is made in a quarry situated in Catunele settlement, Dolj County. Due to the small impact of the surface stripping and to the high demand in energetic coal in the area, the exploitation is profitable, the profitability rate being superior to the interest practiced by the banks.

Keywords: *lignite, quarry exploitation, technological flux, profitability rate*

DONNÉES GÉNÉRALES

Le périmètre d'exploitation de la Vallée de Lupoița est situé dans le département de Gorj, dans la Colline de Lupoița, sur l'interfluve séparant la Vallée de Lupoița de la Vallée de Ip, à la limite de l'ancien périmètre minier souterrain de Lupoaia, sur le territoire de la commune de Cătunele. Il est délimité au nord par la Vallée de Ip, au sud par la Vallée de la Vache, à l'ouest par le périmètre minier souterrain de Lupoaia et à l'est par le canal régularisé du ruisseau Lupoița.

Du point de vue géomorphologique, la zone est disposée dans le secteur nord-ouest du Piémont gétique représenté par les Collines de Jiu.

Le gisement de lignite qui va faire l'objet de l'exploitation est un charbon énergétique et se présente sous la forme d'un strate à faible inclinaison.

Il est cantonné dans les formations daciques situées à la limite du champ minier de Lupoaia. Le strate de lignite est continu, il se développe sur une superficie considérable, à partir de la cote + (240-245)m., ce qui représente la cote de l'afleurement.

La recouvertement stérile augmente de l'est vers l'ouest et du nord vers le sud, de 0 m. de l'afleurement à 21 m. et 24-26 m dans les forages.

Le gisement est monoclinal, avec des inclinaisons de 2°-3°, qui augmentent vers les zones d'afleurement. La direction générale de cette structure monoclinale est de NE-SO, avec des descentes vers SE.

Le facteur le plus important dans l'exploitation efficiente des ressources énergétiques est l'épaisseur du paquet de roches. Dans le périmètre analysé, l'épaisseur maximale des roches stériles peut atteindre 50 m.

L'influence des roches de recouvrement est caractérisée le plus fidèlement par l'indicateur „rapport de découvrement"; cet indicateur s'exprime en $m.^3$ de stérile/tone et il montre combien de mètres cubes de stérile doivent être excavés pour obtenir une tone d' utile.

Fig. 1. *Le périmètre de la Vallée de Lupoița-amplacement dans le region*

Dans le cas du périmètre de la Vallée de Lupoița, cet indicateur se situe environ la valeur de 4,0-4,5 m.³/t.

LA PROFONDEUR MAXIMALE D'EXPLOITATION

Le périmètre d'exploitation se trouve sur le versant sud de la colline, ce qui conduit à ce que l'exploitation soit pratiquée en grande partie à des cotes supérieures à la demi-tranchée d'ouverture. Le strate afleure aux environs de la cote 240 m., étant recouvert jusqu'à la cote 290 m. On va d'abord excaver des roches stériles, et ensuite exploiter toujours par excavation sous la cote +232 m.; pratiquement, la profondeur de l'exploitation sera au maximum de 10 m.

Le facteur le plus important dans l'exploitation efficiente des ressources énergétiques est l'épaisseur du paquet de roches de la couche supérieure du strate d'utile. Dans le périmètre analysé, l'épaisseur maximale des roches peut atteindre 50 m.

L'influence des roches de recouvrement est caractérisée le plus fidèlement par l'indicateur „rapport de découvrement"; cet indicateur s'exprime en m.³ de stérile/tone et il montre combien de mètres cubes de stérile doivent être excavés pour obtenir une tone d' utile.

Dans le cas du périmètre de la Vallée de Lupoița, cet indicateur se situe environ la valeur de 4,0-4,5 m.³/t. Le recouvrement maximal est de 5/1 dans la zone ouest du périmètre.

CONDITIONS TECHNIQUES ET ÉCONOMIQUES D'EXPLOITATION ET DE VALORISATION

L'expoitation des ressources de lignite par l'application des technologies classiques est conditionnée en général par les facteurs suivants:

- l'épaisseur, l'inclinaison, l'étendue et la structure des strates,
- la nature et les propriétés physiques et mécaniques des charbons et des roches environnantes,

- la structure de toute la colonne lithique et la corrélation des paquets de roches,
- les conditions hydrogéologiques du gisement.

TRAVAUX MINIERS D'OUVERTURE

L'ouverture des carrières est influencée par la configuration morphologique du terrain, par la superficie du périmètre et par les propriétés physiques et mécaniques des roches.

La position du strate, compte tenu de la morphologie du terrain, permet l'ouverture de la carrière par une demi-tranchée ayant le point d'attaque emplacé dans la proximité du chemin de parcelle qui ouvrait l'accès aux propriétés particulières.

Sur le fond de la demi-tranchée sera aménagé le chemin technologique pour le transport du stérile et de l'utile.

La demi-tranchée va ouvrir toutes les marches de stérile, et pour l'exploitation de l'utile, après l'exécution des travaux préparatifs, on devra exécuter une tranchée dans le charbon.

Pour la première année, les travaux vont avoir les caractéristiques suivantes:

- Longueur du chemin: 120 m.
- Largeur du chemin: 8 m.
- Pente du tronçon d'accès: 10%
- Pente générale: 12,5%
- Angle des talus latéraux: 65°
- Volume de roche extraite pour l'exécution des demi-tranchées: 2500 m³

La longueur totale des chemins d'accès sera: 1 400 m.

Le volume de roche extraite pour l'exécution des tranchées: 8 000 m³

Le volume des travaux d'ouverture: 1,05 m. de chemin/1000 m³ de production extraite et 5,85 m³ de travaux miniers d'ouverture / 1000 m³ de travaux miniers d'exploitation.

Les principaux éléments techniques et géométriques des travaux d'ouverture sont:

Type de travail d'ouverture: **demi-tranchée intérieure groupée commune-simple-définitive,** réalisée à l'intérieur du périmètre, pour une durée de fonctionnement égale à la durée de la carrière et qui va desservir plusieurs gradins d'utile et de stérile, celle-ci étant empruntée tant par les moyens de transport chargés que par les vides.

Le point d'emplacement des demi-tranchées d'ouverture est conditionné par la possibilité d'emplacement ultérieur des haldes de stérile, ainsi que par l'organisation de surface. Les travaux d'ouverture étant exécutés dans le périmètre, ils ne nécessitent pas de travaux d'excavation supplémentaires.

TRAVAUX D'EXCAVATION DU STÉRILE

Le gisement présente un recouvrement stérile constitué par des argiles et des argiles sablonneuses.

La tranchée de préparation qui sera creusée selon la méthode d'excavation combinée avec le transport auto, va avoir la base relativement horizontale, avec une faible inclinaison vers les travaux de traitement des eaux.

Les roches stériles seront extraites à l'aide des outillages classiques (excavateurs à pelle), en gradins descendants, d'une hauteur maximale de 15 m., aux retraits qui auront la largeur égale au rayon d'action du bras de l'outillage utilisé.

Sur la verticale, les roches de recouvrement seront divisées en couches et gradins, le premier gradin étant situé à la cote 280 m., le deuxième à la cote 265 m., et le troisième à la cote 250 m. À partir de la cote 250 m. vers le bas, on va excaver en fonction de la position et de l'épaisseur du strate de charbon, soit par un seul gradin divisé en deux sous-gradins (l'un pour le stérile, l'autre pour l'utile), soit par deux gradins indépendants, l'un pour le stérile jusqu'aurecouvrement (toit) du strate, l'autre pour l'utile.

Les fronts de préparation proprement-dite seront précédés par des travaux de récupération du sol fertile.

TRAVAUX D'EXPLOITATION

L'extraction des roches utiles se fera par des méthodes et technologies classiques qui supposent la taille des roches à l'aide des excavateurs à pelle, puis le transport et le dépôt à la halde de stérile par des camions à benne basculante.

Les données géométriques des gradins ont été déterminées en tenant compte des propriétés physiques et mécaniques des roches, de la dotation technique de la société engagée pour les travaux, de la capacité de production escomptée. En fonction de tous ces éléments, les travaux d'exploitation seront caractérisés par les paramètres suivants:

Taille mécanique:

- ✓ La hauteur des gradins varie de 3 m. à 15 m.;
- ✓ L'angle du talus de travail, de 45÷75m.;
- ✓ Les bermes des gradins en cours de travail auront des hauteurs variant entre 15÷30m.;
- ✓ L'angle du talus général sera variable en fonction du nombre de gradins, de 19° à 35° (la berme de sécurité va avoi r au moins la hauteur du gradin supérieur);
- ✓ La distance minime (de sécurité) entre l'outillage et le bord supérieur du talus d'un gradin inférieur= 4m. (à établir après avoir exécuté le contrôle de la stabilité);
- ✓ Les bermes sur lesquelles on exécute le transport devront avoir des largeurs de 12÷15m. pour assurer la circulation dans les deux sens.

PERTES D'EXPLOITATION ET DILUTIONS

Le mode de présentation du lignite dans le gisement, sous la forme d'un strate avec des intercalations de stérile, crée la possibilité de diluer la production et de l'altérer par l'apport rajouté de roches stériles.

Une autre forme de dilution supposerait le risque d'englober certaines quantité de roches du recouvrement et d'autres couches de fond. La marge des roches stériles comme apport au volume de la production est estimée à 5%-7% du total de la production.

Les pertes des ressources exploitables se retrouveront dans les talus définitifs en marge de la carrière.

Sur les réserves estimées, on pourra perdre environ 8% de l'épaisseur du strate, perte due en particulier aux technologies d'exploitation, puisqu'une partie de cette épaisseur du strate sera exploitée en même temps que l'extraction des roches de recouvrement, tandis que l'autre partie sera abandonnée au fond de la carrière.

ANALYSE DU RISQUE

La technologie d'extraction consacrée, la viabilité économique de la valorisation du lignite extrait, l'existence d'un marché relativement stable pour les produits finis, la souplesse et la capacité technologique de s'adapter aux exigences du marché, tout cela fait que l'activité de valorisation des produits qui vont être obtenus soit une entreprise profitable, soustenable financièrement dans des conditions de marché variées.

La marge de risque, mineure dans le cas de ce gisement de lignite, est en étroite relation avec la dynamique de l'économie dans son enemble.

Les méthodes utilisées pour quantifier le risque de l'investissement:

Parmi les méthodes proposées pour estimer le risque des investissements dans la sphère des productions, rappelons:

- L'analyse des probabilités; les principaux indicateurs dont on opère sont: le taux de rentabilité, la variation des flux des liquidités;
- La méthode de l'arbre de décision, qui est appliquée pour la prise des décisions d'investir;
- La méthode de la correction des indicateurs du projet d'investissement, ce qui représente une forme simple d'estimation du risque qui consiste dans la correction de certaines variables prises en calcul ou la correction directe des résultats obtenus par les calculs.

Dans notre cas, les correcteurs les mieux conseillés sont:

- L'analyse de la sensibilité (qui va attirer la modification des frais d'investissement);
- L'écourtement de la durée du projet ou le dévancement du début de l'exécution de l'investissement;
- La diminution de la valeur résiduelle de l'investissement;
- La majoration du taux d'actualisation par le taux de risque.

La méthode des points critiques consiste à déterminer certains paramètres-limite du projet d'investissement qui désignent le seuil entre la zone d'efficience et celle d'inefficience.

Les indicateurs les plus utilisés sont: la durée d'amortissement de l'investissement et le taux interne de rentabilité, le revenu net actualisé.

L'activité à la carrière de la Vallée de Lupoița a un taux interne de rentabilité supérieur au niveau des intérêts pratiqués par les banques.

La valeur nette actualisée calculée comme différence entre la production –marchandise et le total des frais (les frais de production plus l'investissement): **VNA =46,65** pour un taux d'actualisation i=10%:

L'indicateur coût/bénéfice est P/C=1,02>1 pour un taux de 10%.

Si nous tenons compte que l'amortissement sera réinvesti, alors la VNA calculée comme différence entre la production-marchandise plus l'amortissement et le tout des frais (frais de production plus l'investissement), cela va nous donner un taux interne de rentabilité de 30%, très bon pour ce secteur d'activité économique.

Le temps de récupération (d'amortissement) de l'investissement: environ 4,5 ans.

T= investissement/profit=15,5 ans.

ASPECTS JURIDIQUES

L'exploitation du lignite est réalisée en conformité avec la Loi des Mines n°85/2003, l'arrêté gouvernemental HG n°639/1998, l es Normes d'application de la Loi des Mines, l'Ordre n°93/1998, l'Ordre du prési dent de l'A.N.R.M. concernant l'approbation des instructions techniques en vue de l'application unitaire de la Loi des Mines, et les

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TEXTILE INDUSTRY: ENVIRONMENTAL IMPACTS AND WASTEWATER TREATMENT METHODS

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ABSTRACT. Textile Industry: Environmental Impacts and Wastewater Treatment Methods. Effluents containing textile dyes discharged by dye manufacturing and textile wet processing industries present significant environmental problems. With the worldwide growth in fiber consumption, the use of dyes and their discharge is likely to continue to rise. Modern textile dyes are chemically stable and resistant to degradation by sunlight, water, soap, bleach, and perspiration. They are difficult to degrade in textile wastewaters under the aerobic conditions that prevail in biological treatment plants. Dyes in wastewater create aesthetic problems and limit the possible uses of the water. Moreover, they reduce the efficacy of microbiological wastewater treatment because of their possible toxicity towards microorganisms. Dyes absorb and scatter the sunlight essential for the algae growth. The products of dye degradation can be mutagenic, carcinogenic, or teratogenic and cause long-term health concerns. In view with the above effects, biological, physical, and chemical treatment methods for textile wastewater are discussed herein.

Keywords: *textile industry, environmental impacts, textile dyes degradation, wastewater treatment methods*

INTRODUCTION

Effluents containing textile dyes discharged by dye manufacturing and textile wet processing industries present significant environmental problems. In 1978, 9,000 tons (2%) of the 450,000 tons of dyes produced worldwide was discharged in effluents from textile dyeing industries [26]. The total amount of dyes discharged was about 50,000 tons [26]. With the worldwide growth in fiber consumption, the use of dyes and their discharge is likely to continue to rise. Modern textile dyes are chemically stable and resistant to degradation by sunlight, water, soap, bleach, and perspiration [25]. They are difficult to degrade in textile wastewaters under the aerobic conditions that prevail in biological treatment plants [6,7]. Dyes in wastewater create aesthetic problems, limit the possible uses of the water, and reduce the efficacy of microbiological wastewater treatment because they may be toxic to microorganisms [10]. Dyes absorb and scatter the sunlight essential for the algae growth. The products of dye degradation can be mutagenic, carcinogenic, or teratogenic [11] and can cause long-term health concerns [2]. Azo dyes that incorporate the –N=N– moiety account for up to 70% of all textile dyestuffs produced [25].

The degradation of organic dyes has therefore attracted much attention. New technologies for wastewater decolorization are especially needed. Modern chemical methods include TiO_2-mediated photodegradation [12,14] Fenton systems [22] and soluble transition metal catalysts in combination with various oxidizing agents [15,9]. Several research groups have studied the catalyzed decolorization of dyes by H_2O_2 [23]. Tosik and Wiktorowski have reported on the decolorization by ozone and H_2O_2 with Fenton reagent [21]. Ozone degrades practically all dyes, reacting rapidly with both C–N and N=N bonds. The H_2O_2 reactions are slow at lower temperatures and require higher catalyst and H_2O_2 doses. Segal *et al*. have studied the oxidation of Pinacyanol chloride by H_2O_2 in the presence of several catalysts in aqueous alkaline solution at room temperature [17]. The catalysts known as octahedral molecular sieves are the most active when doped with Fe^{III}, Cr^{III}, and Co^{II}. Fourteen different catalysts have been compared. The deepest bleaching (65%) was accomplished in a matter of 30 min.

We have long been interested in developing green methodologies for decomposing pollutants in effluent streams and have synthesized highly active catalysts, called Fe-TAML activators (Fe^{III} complexes of *T*etra*A*mido *M*acrocyclic *L*igands, **1,** Figure 1), that exhibit the capacity to marshal hydrogen peroxide to destroy pollutants in various effluent streams [5,18] Fe^{III}-TAML activators and their degradation products tested to date appear not to present toxicity concerns [18]. Here we describe the beginnings of a detailed investigation of the use of Fe-TAML catalysts for the oxidative degradation of Orange II ([4-[(2-hydroxynaphtyl)azo]benzenesulfonic acid], sodium salt) by H_2O_2 and organic peroxides. In aqueous solution, Orange II predominately exists as a keto tautomer (Figure 2) [1].

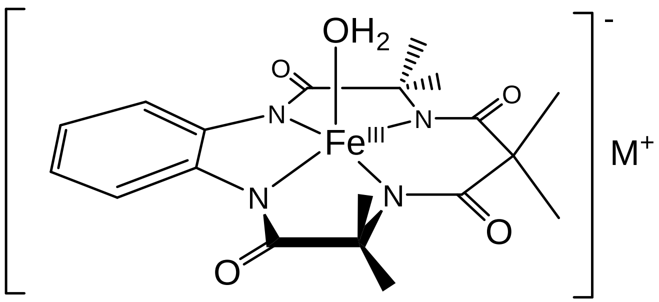

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Fig. 1. *Fe^{III}-TAML activators*.

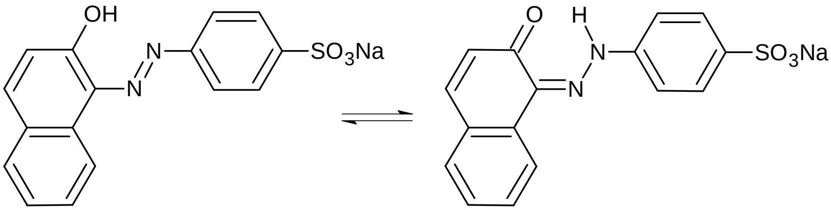


Fig. 2. *Orange II*

The reactivity of Fe-TAML activators is comparable to that of H_2O_2-activating enzymes. Therefore, it has been of interest to evaluate the relative catalytic features of Fe^{III}-TAML activators and enzymes in oxidation of the dye. Reports on the horseradish peroxidase-catalyzed oxidation of Orange II are conflicting. According to Stiborová *et al.* horseradish peroxidase does not catalyze the oxidation of Orange II by H_2O_2 at pH 4.7–8.4 [19] Morita *et al.* and Zhu *et al.* claim that this oxidation occurs [24]. Stoddart *et al.* have reported that microsomal cytochrome P450 readily catalyzes the oxidation of Orange II with a maximum activity observed at pH 7 [20]. Chivukula and coworkers have described the lignin peroxidase-catalyzed oxidation of Orange II into 1,2-naphthoquinone and 4-sulfophenyl hydroperoxide [3] López *et al.* have reported that manganese peroxidase also degrades the dye and have identified the degradation products by ^{1}H NMR and electrospray ionization-ion trap mass spectrometry [27].

UV-VIS STUDIES

Electronic spectroscopy is a rational technique for monitoring the oxidation of Orange II. The dye has an intense absorption band with a maximum at 485 nm in water. Hydrogen peroxide itself oxidizes Orange II very slowly. Fe^{III}-TAML activators increase the rate immensely; the spectral changes observed during **1**-catalyzed oxidation of Orange II are presented in Figure 3. The major oxidation trend is a gradual decrease in the maximum intensity at 485 nm. The collapse of the 485 nm chromophore is due to the lost conjugation in the dye leading to colorless oxidation products. The Inset to Figure 3 shows that absorbance at 350 nm first increases and then decreases. The catalytic degradation performed at $[H_2O_2] = 3.3\times10^{-4}$ M and [**1**] = 2×10^{-7} M (pH 9-11, 25 °C) is usually complete within 10-30 min. Control experiments with Fe^{III}-TAML activators in the absence of H_2O_2, or with H_2O_2 in the absence of the catalyst, or with the catalase enzyme from *Aspergillus niger* in the presence of H_2O_2, all indicated no degradation of Orange II under these experimental conditions.

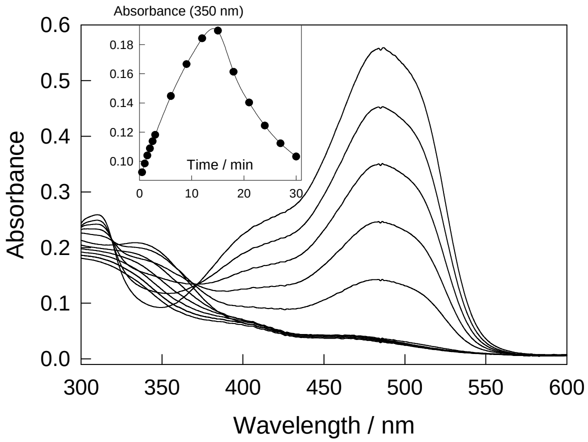


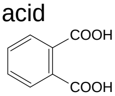
Fig. 3. *Spectral changes that accompany the catalytic oxidation of Orange II by H_2O_2 in the presence of **1**. Conditions: [**1**] 2.6×10^{-7} M, [Orange II] 2.7×10^{-5} M, [H_2O_2] 4.4×10^{-4} M, pH 9 (0.01 M phosphate), 25 °C; spectra recorded with 3 min interval.* ***Inset*** *shows changes of absorbance at 350 nm with time; see text for details.*

IDENTIFICATION OF DEGRADATION PRODUCTS OF ORANGE II

The formation of small organic acids and inorganic ions as mineralization products was anticipated. Phthalic acid was quantified using GC-MS. Formic, glycolic, and oxalic acids were detected by ion-chromatography; the data is summarized in Table 1. These breakdown molecules, known as ultimate organic products during the aromatic ring-opening, are non-toxic and biodegradable. The mineralization products are nitrite, nitrate, sulfate, and CO_2 (Table 1). Nitrite and nitrate are produced from nitrogens of the azo group of Orange II. The ions NO_2^- and NO_3^- could not be reliably measured due to interference from carbonate (0.2 M). Sulfate originates from the sulfonyl group. The level of mineralization equals 35% from determining the total organic carbon.

Table 1.

*Mass balance (in %) after treatment of Orange II (10^{-4} M) by Fe^{III}-TAML ([**1a**] 2×10^{-7} M), H_2O_2 (10^{-2} M) at 25 °C, pH 10 (carbonate buffer).*

Product / Buffer	Phthalic acid 	Oxalic acid HO_2C-CO_2H	Glycolic acid $HOCH_2CO_2H$	Formic acid HCO_2H	NO_2^-	NO_3^-	SO_4^{2-}	CO + CO_2	**Total**
0.02 M	12.2	2.1	0.7	3.4	1	2.2	4.3	32	**57**
0.2 M	10.4	2.2	2.7	3.2	-	-	6.2	35	**61**

The data in Table 1 indicates that more than 61% of Orange II was degraded under these conditions yielding products shown in Table 1. There may be other products, which are difficult to detect by the techniques employed. Phthalic acid, the major degradation product, is stable under the experimental conditions. It is formed from the naphthalene ring of Orange II. The presence of phthalic acid was also confirmed by GC-MS analysis. A control test with the dye before the catalytic degradation shows no presence of this compound.

TOXICITY STUDIES

The toxicity of the solution has been evaluated before and after degradation. The data is shown in Figure 4. The degradation products are non-toxic. The initial toxicity of Orange II decreased after the treatment by a factor of *ca.* 3 (see Figure 4). Due to the protocol of the method [16], the value of mL of tested sample is a measure for toxicity. The larger this number the smaller is the toxicity. Zero points of immobilization of *Daphnia magna* in the control tubes were confirmed. A maximum toxicity of 20% was observed in both experiments. Zero mortality of *Dafnia magna* in the control tubes has been confirmed.

This result demonstrates that the Fe^{III}-TAML-catalyzed degradation of Orange II by H_2O_2 is safe and free from the formation of toxic oxidation products. It should be mentioned that other research groups studying peroxide catalysts employing Fenton chemistry would encounter major toxicity issues.

An intriguing (and perhaps general) mechanism for the decolorization of dyes by one-electron oxidizing agents has been proposed after studying Orange II bleaching by pulse radiolysis [4]. It involves diffusion-controlled disproportionation of two primary dye-radicals formed after the initial, rate-limiting electron transfer. The diffusion-controlled disproportionation affords a starting dye and the product of its 2-electron oxidation, which is further involved in a series of transformations. Early steps of this mechanism are shown in Scheme 1. This mechanism is useful for describing the results of catalysis by **1** assuming that the oxidized catalysts **1** generate the primary radical **3** shown in Scheme 3 in a pathway described by the rate constant k_{II}.

We did not detect 4-diazenylbenzosulfonate (**4**) and 1,2-naphthoquinone by HPLC under our catalytic conditions. The probable reason that the quinone was not detected is that under these conditions 1,2-naphthoquinone is rapidly oxidized into phthalic acid plus two additional products just by H_2O_2 without participation of **1**. 4-Diazenylbenzosulfonate should be unstable as well. A formation of 4-nitrobenzo- and 4-hydroxybenzosulfonate detected by HPLC could presumably result from the oxidation of 4-diazenylbenzosulfonate. Phthalic acid and 4-hydroxybenzosulfonate undergo the catalyzed oxidation by H_2O_2 giving a variety of small biodegradable, non-toxic organic products with substantial mineralization.

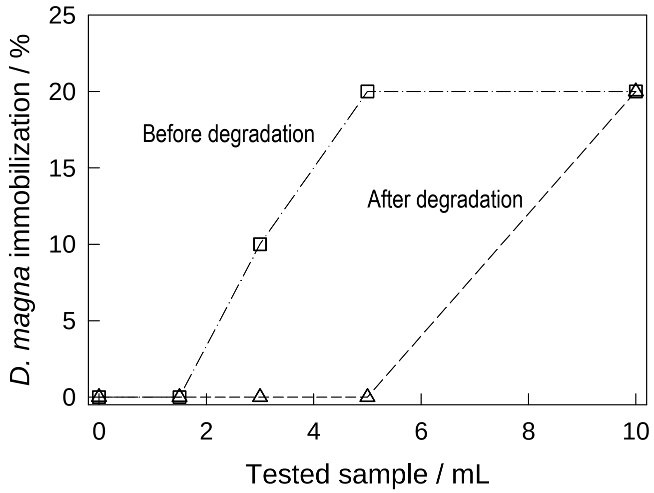
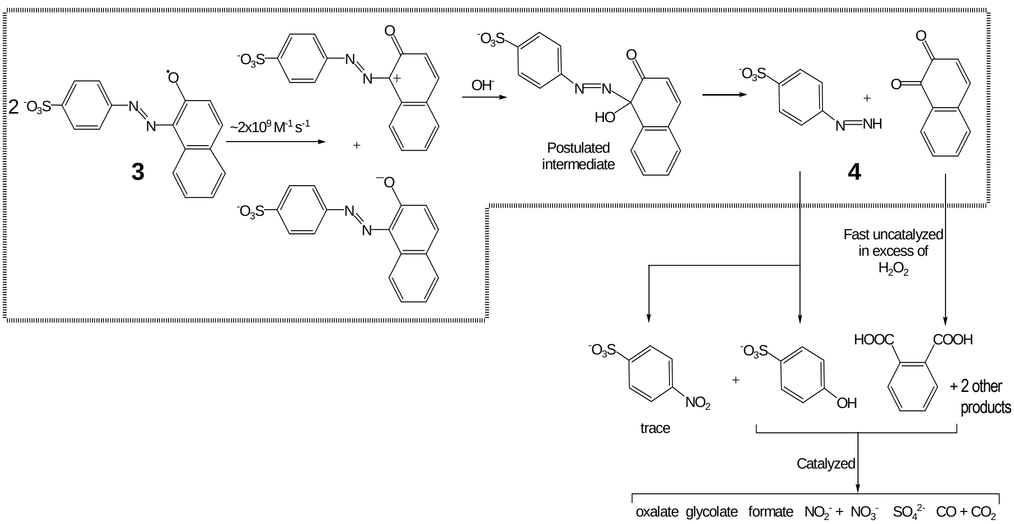


Fig. 4. *Effects of Orange II (Δ) and its degradation products (□) on immobilization of Daphnia magna. Conditions: [Orange II] 10^{-4} M, [**1**] 2×10^{-7} M, [H_2O_2] 10^{-2} M, 25 °C, pH 10 (0.02 M carbonate).*



Scheme 1. *Plausible scheme of **1**-catalyzed oxidative degradation of Orange II by peroxides. Steps in the dotted box were suggested previously.*[28]

CONCLUDING REMARKS

In conclusion, the Fe^{III}-TAML/H_2O_2 system efficiently degrades Orange II into small biodegradable and non-toxic organic products. Substantial mineralization has been observed. The oxidation occurs rapidly compared to biological and other chemical systems that have been previously studied. Furthermore, the ecotoxicological examination suggests that the described technique is an environmentally safe process. With current concerns regarding the treatment of the ever-increasing burden of synthetic chemicals in water, a green process for degrading water-borne pollutants is greatly needed; this is especially true for textile dyes. The Fe-TAML/H_2O_2 systems show considerable promise to provide such a technology.

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STUDIA UNIVERSITATIS BABEŞ-BOLYAI, AMBIENTUM, LIII, 1-2, 2008

TRIHALOMETHANES EVOLUTION IN DISTRIBUTION SYSTEM OF CLUJ-NAPOCA

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ABSTRACT. Trihalomethanes Evolution in Distribution System of Cluj-Napoca. Water suppliers that practice chlorine disinfections face conflicting objectives in providing adequate microbial protection while minimizing the formation of harmful chlorinated organic byproducts. Chlorine is a strong oxidant that reacts with the natural organic matter (NOM) present in all natural waters. Although chlorine is invaluable in the protection of public health the disinfection by products released after chlorination process present long-term health risk to water consumers. Such of disinfection byproducts are trihalomethanes (THMs). Trihalomethanes are a group of volatile organic compounds that can form when the chlorine used to disinfect drinking water reacts with naturally occurring organic matter (e.g., decaying leaves and vegetation). The preliminary results presented in this paper shown that the THMs levels from Gilau Water treatment Plants and Cluj-Napoca distribution system. The results have higher values in the summer period relative to other seasons.

Keywords: *Volatile disinfection by-products, Trihalomethanes, Chlorine, Water Treatment Plant.*

INTRODUCTION

Chlorination is the most widely used procedures in Water Treatment Plants (WTP) from Romania. The treatment procedures have been carried out since the dawn of the 20th century to eradicate and inactivate the pathogens from water. However many researches has shown that using chlorine as disinfection agent will leads to the formation of potential harmful by-products called disinfection by-products (DBPs). These DBPs are considered potentially carcinogenic to humans and more recently have been associated with adverse reproductive outcomes following exposure during pregnancy [Cantor and Lynch, 1988; Graves and Matanoski, 2002]. Trihalomethanes (THMs) is the result of reaction between chlorine and natural organic matter (NOM) present in all type of water, referred as precursor of THMs formation [Rook, 1976; Bellar and Lichtenberg, 1974]. Because of this unwanted effects of chlorination process USEPA and other Public Health and Environmental Protection Agencies from the world has promulgated legislation to limit the concentration of total THMs (TTHMs) in drinking water [USEPA, 1999a].

In Romania the regulation and monitoring of THM has became a current issue in connection with Romania's entry to the UE and the fulfillment of the required drinking water standards. In order to minimize cancer risk Romania has adopted the maximal permissible value fixed in the EU drinking water directive and has been adopted by the Romanian legislation in 2002, granting the water companies a transition time of 10 years to meet the requested standards and accepting in the first 5 years a TTHM value of 150 μg/L. In terms of monitoring, the Romanian water law stipulates a minimal number of samples per year depending on the magnitude of the treatment plant. The local health authority carries out the monitoring. Hence engineers are required to minimize the concentration of THMs in water in the distribution system.

MATERIALS AND METHODS

Sampling: Several water samples were collected from different sampling point of the Gilau Water Treatment Plant (WTP) and distribution system from Cluj-Napoca – located in Cluj jurisdiction. Gilau WTP has as water sources the Somesul Mic River basin and also Tarnita Storage Lake. All the samples were collected in every month of 2007. The sampling contains the following samples: i.) raw water, filtrated water, chlorinated water from exit reservoir – sampling points that are located in the WTP of Gilau; and ii.) Sapca Verde, Beer Factory, Chemistry Faculty, Environmental Faculty and Public Health Institute – sampling points that are located in the distribution system. Water samples were collected and stored in 40 mL vials and closed with Teflon lined screw cap and they were preserved with sodium thiosulfate ($Na_2S_2O_3$) at 4 °C until the analysis. All samples were measured between in 1 and 7 days after sampling.

THMs analysis: THMs were carried out by Thermo Finningan U.S. Trace GC Ultra gas chromatography with electron capture detector (GC-ECD) with TriPlus HS auto sampler. The analysis was made using headspace technique. 10 ml of sample was filled into 20 ml headspace vials and closed with Teflon lined screw cap. After that the samples were equilibrated in an oven at 60 °C for 45 minutes, 1 ml of the headspace was then injected into the GC (Cyanopropylphenyl Polysiloxane column, 30 m x 53 μm, 3 μm film thickness, Thermo Finnigan, USA). The column program was 35 °C (hold time 3 minutes), 15 °C/minutes to 200 °C (hold time 3 minutes). The inlet was set at 200 °C.

The standard stock solution containing 2000 μg/l of each Trihalomethanes from Restek (Bellefont, U.S.) was used. THM working standard solutions (100 mg/L, 4mg/L) were prepared through dilution of the stock solution in 10 ml Methanol. The calibration standards were made using that THM stock solution and the calibration were prepared for the range 0 – 100 μg/L in mineral water Izvorul Alb.

RESULTS AND DISCUSSIONS

During the THMs analysis the main founded THMs species detected in the water sample was the $CHCl_3$. The $CHCl_3$ concentration differed from month to month during the years. Usually higher $CHCl_3$ concentration was found in the wormer season, than in the winter season. In Gilau WTP and distribution system the highest $CHCl_3$ concentration was detected in August 2007 – 81.1 μg/L. The measurement shows that the $CHCl_3$ concentration increased in the distribution system. The chloroform concentration range in the WTP at the exit of reservoir sampling point was in the range 8 μg/L (March 2007) and18.75 μg/L (November 2007). That could be explain by the fact in the winter season in the water are present lower concentration of NOM than in summer season due to low temperature and light. From that reason less chlorine concentration are required for water disinfection process. During the measurements was observed also that the chloroform concentration increased with distance. Started from the exit of the reservoir from the WTP (considered 0 point) the chloroform concentration increased with 30 % at the entrance of the city (located at 18 km from the Gilau WTP) and in the city center (located at 25 – 30 km from the Gilau WTP) the chloroform concentration was double or almost much with three times. That shows the THMs concentration increased with distance – see table 1.

Table 1.

$CHCl_3$ concentration measured in 2006 – 2008 at the Gilau WTP and Cluj. *Obs: Ex.R. – represent exit of reservoir, En.C. – Entrance of city, Cen. – center of city.

$CHCl_3$ concentration (μg/L)			
	2007		
Month	Ex.R.	En.C.	Cen.
January	25.4	31.1	40.4
February	12.0	31.6	48.6
March	8.0	18.7	21.6
April	8.2	29.2	33.8
May	14.7	40.6	50.2
June	19.2	60.2	66.3
July	21.0	65.2	69.0
August	28.0	69.0	81.1
September	24.5	39.58	52.4
October	20.1	32.8	47.9
November	18.75	24.9	35.9
December	9.32	12.78	21.7

There are several factors what affect the formation of trihalomethanes. Previous studies have shown that the major factors that affect THM formation are chlorine dose and residual, concentration and nature of NOM (mainly humic substances), contact time, pH, temperature of water and the presence of inorganic ions like bromide. Higher THM concentrations are expected at higher levels of the above-mentioned parameters.

The main THM found in laboratory analysis of water sample collected from different sampling point from Cluj and Gherla was $CHCl_3$. In Gherla and Cluj distribution system was measured the highest chloroform concentration, that can be explain due to the fact that Ghela city take water also from Gilau WTP and is located after 40 km from water treatment plant and it is know that the concentration of THMs increase with distance due to chlorine consumption, see figure 1.

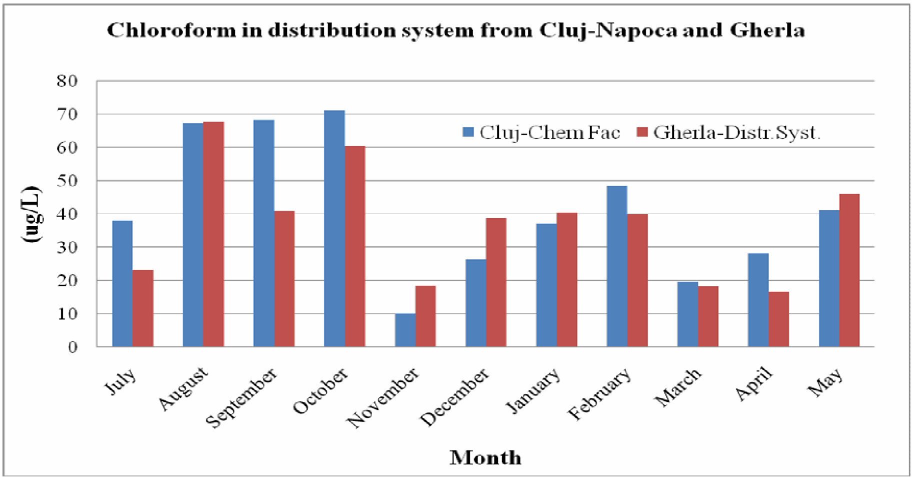

Figure 1. *Chloroform concentration (µg/l) in the distribution system from Cluj Napoca, located after 18 km from Water Treatment Plant (WTP) Gilau and from the distribution system from Gherla.*

Also it is known that as the chlorine dose increase, disinfections byproducts also increase (Figure 2.). When increase chlorine dose and residual, formation of trihalomethanes, in special the chloroform formation becomes greater. The THMs level rises with increasing chlorine dose. Anyway there are some disagreements regarding the quantitative relations between chlorine concentration and THM levels (or the rate of THM production). In much case was found a linear relationship between chlorine consumption and THM production, whit an order of reaction greater than or equal to unity but it is also possible that the order of reaction changes during the course of the reaction. In the water treatment plant from Gilau the water disinfection is obtained through addition of chlorine gas. The chlorine gas is regulated manually to achieve free chlorine at the exit of the reservoir (were the water arrives 15 minutes after chlorination) of 0.5 – 0.7 mg/l Cl_2 in winter and 0.7 – 0.9 mg/l Cl_2 in summer.

Also after a long period analysis was observed a strongly influence in THMs formation of the season variation, because when the temperature increases, reactions are faster and a higher chlorine dose is required, leading to higher formation of DBPs. Subsequently in summer months when the temperature increases the chloroform – the most praise THMs – formation also increase. In the winter season the THMs concentration are lower due to lower water temperature and NOM. In this condition the chlorine demand is lower, therefore, the chlorine dose required to maintain adequate residual in the distribution system is also less.

The studies conducted to examine the effect of residence time on disinfections byproducts formation have shown that longer reaction time increases the formation of THMs (Figure 1.). The water treatment plant Gilau is located about 16 km to west of city of Cluj, so once with distance the THMs concentration will decrease.

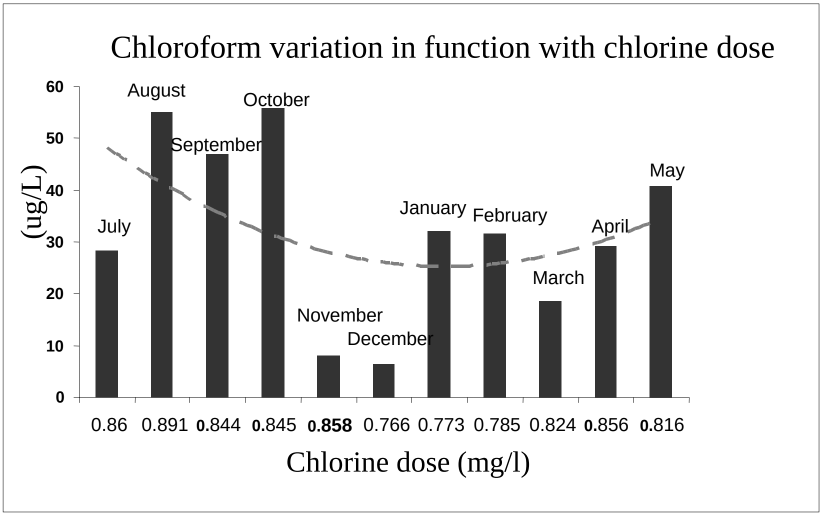

Figure 2. *Chloroform concentration measured in Sapca Verde sampling point in function with the chlorine dose what was added in the sampling day in the water treatment plant from Gilau.*

Other factor that has a strong influence on disinfections byproducts formation is the water pH. Is shown that the pH increase also the trihalomethanes formation increase. In the winter seasons when the pH decrees to 6.3, 6.6 and 6.8 in December, January respectively in February lowest concentration of chloroform was observed. When the pH increases, in special in the summer months also the chloroform concentration increases significantly.

CONCLUSIONS

This study examined the trihalomethanes formation and they concentration in different sampling point collected from different sampling points in Cluj-Napoca. Following conclusions were drawn based on the results of the measurements conducted with water samples of every month in 2007.

Chloroform was the most observed THM species after the chlorination of reservoir water during all studied months. Brominated compounds of trihalomethanes wasn't observed, just $CHCl_2Br$ but in very slow concentration. We can suppose for that reason, the bromine compounds in the raw water is very slow or almost inexistent.

The major factor that influences the trihalomethanes formation is the temperature that is clearly praise in chloroform concentration measured in different months of year. In the months like July, August, September and October when the temperature was highest (21 – 24 °C water temperature) also the chloroform concentration was high (66.3 – 81.1 μg/L) and when the water temperature wasn't high (2.8 – 3.7 °C) the chloroform concentration was between 21.7 – 40.4 μg/L. The major differences in temperature and pH value affect trihalomethanes potential formation (THMFP), with more volatile THM species being produced at the higher temperature and pH. Also we can concluded the season when the water matrix is change from the winter season to summer season also have a seriously influence on THMs formation.

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STUDIA UNIVERSITATIS BABEŞ-BOLYAI, AMBIENTUM, LIII, 1-2, 2008

THE CURRENT STATUS OF GEOTHERMAL DEVELOPMENT IN ROMANIA

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ABSTRACT. The Current Status of Geothermal Development in Romania. The exploration of the geothermal resources began in Romania in 1962, and over 200 wells have been drilled since than, proving the existence of low enthalpy geothermal resources with temperatures of 40-120^{0}C. The total installed capacity of the existing wells, for direct use, is about 480 MWt, for a reference temperature of 30^{0}C. At present only about 145 MWt are used from about 96 wells, which are producing hot water in the temperature range of 45-115℃. The proven geothermal reserves a re currently estimated at about 200 000 TJ for the next 20 years. Unfortunately the geothermal production in Romania is far below the demonstrated potential. The main obstacle for the geothermal development in Romania is the scarcity of domestic investment capital. In order to stimulate the interest of potential investors from developed countries, and to cope with the requirements of large international banks, an adequate legal and institutional framework has been created, adapted to a market-oriented economy.

Keywords: *geothermal energy, low enthalpy resources, direct use, Romania*

INTRODUCTION

Most of the European States have passed through a process of great transformations in the energetic field. This process was determined by the necessity of the rise in the safety standards of the consumers energy supply. Considering this requirement the renewable resources offers a valid solution, including that of environmental protection.

In recent years, energy efficiency and the exploitation of the renewable energy resources for electricity generation have gained an important role in defining Romania's development and economic policies. One of the renewable energy sources with great potential, which was exploited for more than 40 years in our country, is the geothermal energy.

The search for geothermal resources for energy purposes began in Romania in the early 1960's based on a detailed and well-funded geological program for hydrocarbon exploration. The first geothermal well was drilled in 1885 at Felix Spa, near Oradea. The well was 51 m deep, with a flow rate of 195 l/s and a temperature of

49^0C. This first well is still in operating. It was followed by the wells drilled at Căciulata (in 1893 - 37^0C), Oradea (in 1897 - 29^0C) and Timişoara (in 1902 - 31^0C).

Over 200 wells have been drilled, with depths between 800 m and 3500 m, proving the existence of low enthalpy geothermal resources with temperatures of 40 -120^0C. The drilling results have led to the identification of eight geothermal areas; six of them are situated in the Western part and two in the Southern part of the country. The proven geothermal reserves are currently estimated at about 200 000 TJ for the next 20 years.

THE GEOTHERMAL RESOURCES OF ROMANIA

The main geothermal systems discovered on the Romanian territory are located in porous, permeable formations such as sandstones and Pannonian siltstones (interbedded with clays and shales) specific for the Western Plain and the Senonian, specific for the Olt Valley. The geothermal systems are found also in the carbonate formation of Triassic age (in the basement of the Pannonian Basin), and of Malm-Aptian age (in the Moesian Platforms). [Cadere 1985].

The localization of these geothermal systems and some other perspective areas are presented in the figure 1.

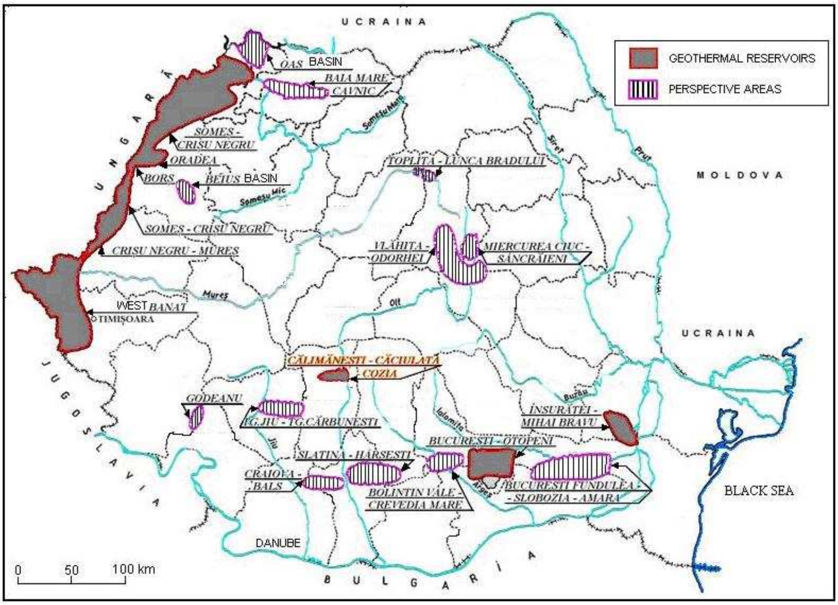

Fig. 1. *The Romanian Geothermal Resources Map.*
[after Cadere 1985]

The Pannonian geothermal aquifer is multilayered, confined and is located in the sandstones at the basement of the Upper Pannonian (late Neogene age) on an approximate area of 2500 km^2 along the Western border of Romania from Satu-Mare in the North to Timişoara and Jimbolia in the South. The aquifer is situated at the depth of 800 to 2,100 m. The main geothermal areas, from North to South, are: Satu-Mare, Tăşnad, Acâş, Marghita, Săcuieni, Salonta, Curtici, Lovrin, Tomnatic, Sânnicolau Mare, Jimbolia şi Timişoara.

The aquifer it was investigated using 80 geothermal wells, out of which 37 are currently in use. The thermal gradient is 45-55^{0}C/km, the water temperature at surface varies between 50-85^{0}C. These geothermal waters have a mineralization of 4-5 g/l, are sodium-bicarbonate-chloride type, most of the water show carbonate scaling. In many cases in these water are found important quantities of gases (mainly methane), which are separated from the geothermal water before utilization, by using specific technologies. The gas water ratio (GWR) varies between 0,8 to 2 Nm^3/m^3. The wells are produced manly artesian but also with downhole pumps. The energy equivalent gained from geothermal wells is about 19000 toe (tones of oil equivalent) at an installed capacity of 55 MWt. The exploitable heat reserves for the next 10 years are estimated to be over 1,2x10^{18} J with the existing wells. [Veliciu 2006]

The Oradea geothermal reservoir is located in the Triassic limestone and dolomites at depths of 2,200-3,200 m, on an area of about 75 km^2 and is exploited by 12 wells (11 production wells and one injection well) with a total flow rate of 140 l/s, the well head temperature of geothermal water is about 70-105^{0}C. The water from Oradea geothermal aquifer have a low mineralization (lower than 0.9-1.2 g/l), theses water are calcium-sulphate-bicarbonate type and there are no dissolved gases. The *Triassic aquifer of Oradea* is hydro-dynamically connected with the *Cretaceous aquifer Felix Spa*, and both are part of the natural circuit of water. The recharge area is in the Northern edge of the Pădurea Craiului Mountains and the Borod Basin. At present the total installed capacity is over 30 MWt, but changing the exploitation to down hole pumping and injection, by operating more 4 doublets, this capacity can be doubled. The Felix Spa reservoir is currently exploited by 6 wells, with depth between 50-450 m. The total flow rate available from these wells is 210 l/s. The geothermal water has a well head temperature of 36-48^{0}C.

The Borş geothermal reservoir is situated at about 6 km north-west to Oradea. The reservoir is located in the same fissured carbonate formations like the Oradea geothermal reservoir, but the Borş reservoir is a tectonic closed aquifer with a small surface area of 12 km^2. The water has a relatively high mineralization of 13 g/l with a high scaling potential. In these geothermal waters are important quantities of dissolved gases (70% CO_2 and 30% CH_4), the gas water ratio (GWR) is 5 Nm^3/m^3. The reservoir temperature is greater than 130^{0}C at the average depth of 2,500 m and the well head temperature is about 115^{0}C. The installed capacity is 15 MWt and annual energy savings are 3,000 toe. The artesian production of the wells can be maintained only by reinjecting the whole amount of extracted geothermal water. At present 5 wells function in Borş perimeter, 3 production wells with a total flow rate of 50 l/s and 2 other wells are used for the water reinjection. At present the Borş reservoir is closed because the greenhouse from Oradea (close to Borş) witch used the geothermal water from Borş were bankrupted.

The Beiuş geothermal reservoir is situated about 60 km south-east of Oradea. The reservoir is located in fissured Triassic calcite and dolomite 1870–2370 m deep. The first well has been drilled in 1996 down to 2,576 m. Because the aquifer has negative piezometric levels (-18,48 m) a line shaft pump was set in the well (in 1999), and now is producing geothermal water up to 45 l/s with 84℃ wellhead temperature, and a low mineralization of 0,46 g/l. A second well has been drilled in early 2004, also with a line shaft pump installed. At present, the geothermal water from the first well is used to supply district heating in town (5 substations in the flats area, a hospital, two schools, etc.). The second well is being connected to the system and will supply 5 more substations. The company having the exploitation concession for the Beiuş reservoir (Transgex S.A.) intends to drill one more production well and a reinjection well in the area, and connect the entire town to the geothermal district system.

The Ciumeghiu geothermal reservoir is also situated in the Western Plain, 50 km South to Oradea. The aquifer is located in Lower Pannonian age gritstone, at an average depth of 2,200 m. The geothermal water is produced in artesian discharge, having a wellhead temperature of 105□C and a mineralization of 5-6 g/l, with strong carbonate scaling prevented by chemical inhibition at the depth of 400 m. The GWR is 3 Nm^3/m^3 and the main dissolved gas is CH_4. In the past the reservoir was investigated by 4 wells, but only one was in use (with a capacity of 5 MW_t, of which 1 MW_t from the separated combustible gasses). Until recently just one well functioned, but it was closed because the greenhouse in the area, witch used the geothermal water, have been closed. [Rosca et al, 2005]

In the Southern part of Romania there are two important geothermal systems (the Otopeni and the Cozia-Călimăneşti geothermal reservoir) that were investigated and exploited since the ’60s. These systems represent 18% from the exploitable geothermal resources of the country. At present the geothermal energy equivalent gained from these systems is about 4500 toe.

The Otopeni geothermal reservoir is located north to Bucharest. The 12 wells that were drilled proved the existence of an important aquifer, located in fissurated limestone and dolomites. The aquifer, situated at a depth of 1900-2600 m, belongs to the Moesic Platform. The geothermal water has the temperature of 58-72^{0}C and a relatively low mineralization of 1.5-2.2 g/l, with a high content of H_2S (over 25 ppm). The production in carried out using downhole pumps, because the water level in the well is at 80 m below the surface. The total flow rate is 25-30 l/s. At present, there are only 3 wells in production (5 MWt), with annual savings of 1900 toe, and another 2 wells which are used for reinjection.

The Cozia-Călimăneşti geothermal reservoir (Olt Valley) is situated in fisurrated siltstones of Senonian age. The reservoir depth is 1900-2200 m and produces artesian geothermal water, with a flow rate of 20-25 l/s and well head temperature about 90-95^{0}C. The mineralization of water is 14 g/l and there is no scaling and the GWR is 2 Nm^3/m^3 (90% CH_4). The thermal potential that is possible to be achieved from the 3 wells is 18 MWt, but at present only 8 MWt are used. The energy equivalent gained in this way is 2500 toe/year.

THE UTILIZATION OF GEOTHERMAL ENERGY IN ROMANIA

From the theoretical perspective, considering her highest geothermal potential, Romania occupies a privileged place among the European countries, after Italy, Island, Hungary, France Turkey, etc. Romania, as many other Central and Eastern European Countries, has low enthalpy geothermal resources (with temperatures of

40-120^{0}C) suitable only for direct heat utilization. Unfortunately the geothermal production in Romania is far below the demonstrated potential.

As we mentioned before, in Romania in the early 1960's based on a detailed and well-funded geological program for hydrocarbon exploration, there have been drilled over 200 wells. The total thermal capacity of these wells is about 480 MWt, for a reference temperature of 25°C (respectively 320 MWt for a reference temperature of 30°C). At present are used only 96 wells with a total thermal capacity of 145 MWt (respectively 137 MWt, if the reference temperature is 30°C) corresponding to an annual energy use of 2,841 TJ/yr (see figure 2 and 3).

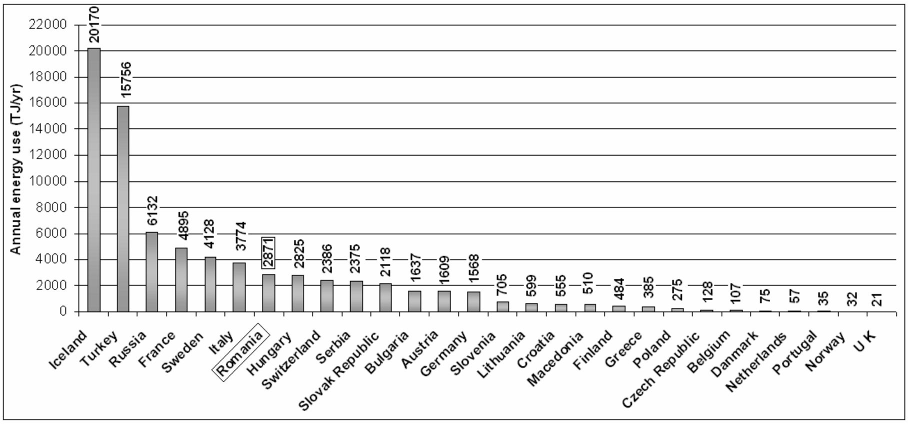

Fig. 2. *The annual heat generation (TJ/yr) for the direct use purposes of the existing geothermal wells from the European countries in 2000.*
[after Lund and Freeston 2001]

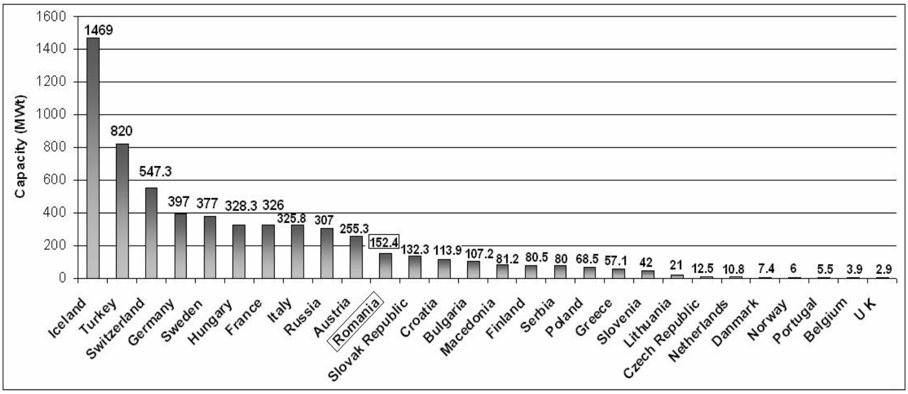

Fig. 3. *The total installed thermal capacity (MWt) of the existing wells in the European countries, for the direct utilization of geothermal energy in 2000.*
[after Lund and Freeston 2001]

These 96 wells are producing hot water in the temperature range of 45-115°C. More than 80% of these wells are artesian producers, 18 wells require anti-scaling chemical treatment, and six are reinjection wells. The wells are placed in 38 locations; most of them (85%) are situated in the Western Plain. About 40 wells are used for health and recreational bathing in 16 spas, which have a treatment capacity of over 850,000 people/year. Geothermal water is also used in 24 outdoor and 7 indoor pools.

At present, the geothermal resources are exploited by two geological research companies which have the exploration or exploitation concessions for some geothermal reservoirs located in different areas in the country. These two companies are Foradex S.A., located in Bucharest, which has the exploration/exploitation concessions for the geothermal reservoirs located in the southern side of Romania (Banat county, Olt Valley, and Bucharest regions) and Transgex S.A., located in Oradea, a drilling company privatised in 2000, which has the exploration/exploitation concessions for the geothermal reservoirs located in the western part of Romania (mainly Bihor county).

These two companies try to offer consumers an advantageous alternative for the thermal energy produced from fossil fuel. This alternative is a very good one especially for the environment; because it was proved that the geothermal energy use has minimal environmental impact. Beside this, there is another important aspect regarding the price of this type of energy. These two companies sell the energy at a lower price comparing with the price of the thermal energy produced from fossil fuel. For example in 2006 the price of thermal energy produced from geothermal water was 3.5 USD/MW_th, three times lower than the one asked by the National Electricity Corporation (RENEL) for the thermal energy produced by the fossil fuel fired co-generation power plants.

There should be mentioned and the activity of the University of Oradea which has a Geothermal Research Centre, an International Geothermal Training Centre, and the Faculty of Energy Engineering which offers undergraduate and graduate studies in renewable energies, specially geothermal one.

Before 1990, the entire geothermal research and development were supported by the State Budget, in so called “the centrally planned economy”. This is the reason why, until 1986-1987, the use of geothermal water and heat was free of any taxes, the experimental exploitation being considered as part of the geological and technological research. Because of these, the rural communities and the small urban areas had the opportunity to use not only a non pollutant source of energy but also o cheaper pone. The thermal energy was used especially for space heating and in some local small industry purposes such as timber drying, milk pasteurization, wild fruit mushroom drying. Another alternative was the cascade use of geothermal resources, even those resources with low flow rates available by artesian discharge.

During 1989 and 1999, with financing from the National Budget, 26 exploration-production geothermal wells were completed and tested. The wells were drilled to depths of 1,500-3,500 m; only two wells were dry holes and the rest have flow rates and temperatures of commercial interest, and after the feasibility study nine of them are currently in use for district heating.

From these 26 wells, 14 of them were drilled during 1995-1999, financed from the State Budget, within the framework of the national geological exploration program. Five wells were exploration wells, and were drilled in areas which haven’t been explored yet, and nine wells were drilled in areas where geothermal resources were already identified. During 1995-1999 the total investments in geothermal projects were 24 million USD, 12% less than the investment from 1990-1994 and 28% less than those from 1985-1989. [Veliciu, 1998]

During 2000-2004, four geothermal wells have been drilled in Romania with National financing. The wells were drilled to depths of 2,000-3,000 m, and they are producing geothermal water with 37-84℃ wellhea d temperatures, so they can be used in commercial interest.

In figure 4 is presented a summary of the evolution of the geothermal direct heat use in Romania, for the period of time between 1994 and 2004. [Panu 1995], [Rosca et al, 2005]

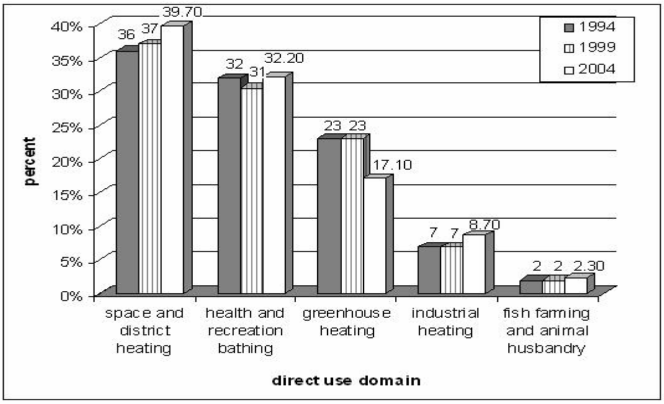

Fig. 4. *The evolution of the geothermal direct heat use in Romania since 1994 up to 2004. [after Panu 1995, Rosca e al.2005]*

It is important to notice that in Romania during the latest years the use of geothermal resources increased. In *1994* from the total thermal capacity of the existing wells, only 137 MWt were used with an annual energy use of about 2,753 TJ/yr compared to *1999* when were used 152 MWt with an average use of 2,870 TJ/yr; and in *2004* the total thermal capacity was 145 MWt corresponding to an annual energy use of 2,841 TJ/yr. This increase of geothermal energy use was the consequence of the technologically upgrading and the accomplishment of three new geothermal projects. [Antics and Roşca, 2003], [Roşca et al, 2005]

THE ROMANIAN GENERAL LEGISLATION FRAMEWORK RELATED TO THE GEOTHERMAL ENERGY

The mineral resources (including the geothermal ones) are owned by the State, their exploitation and exploration being regulated by the Mining Law issued in 1998.

The Governmental institutions with activities related to the geothermal resources are: the Romanian Geological Survey (exploration and resources information), the National Agency for Mineral Resources - A.N.M.R. (resource database, award of exploration and exploitation licenses) and the Ministry of Industry –D.G.R.M. (Energy Department).

The National Agency for Mineral Resources is the Governmental institution in charge of issuing exploration and exploitation permits (long term concession). Long-term licenses are awarded by the National Agency for Mineral Resources (NAMR) for either the exploration or the exploitation of mineral resources, including the geothermal ones.

At present, the Romanian legislation related to geothermal development is harmonized with European Union principles and supports renewable energies, among which the geothermal is specifically mentioned. There are several laws and regulations in force at present regarding investment in general, which may concern geothermal energy sources development by private producers:

- *Law No.14/1997*- for approving The Charter of Energy Treaty and the Proceedings to the Charter of Energy on the energy efficiency and environmental aspects, signed at Lisboan, on 17 December, 1994

- *Law No.99/2000* – for approving Governmental Emergency Ordinance No.29/1998 on establishing, organizing and functioning of Romanian Energy Regulatory Authority-ANRE

- *Law No.199/2000* – republished – on efficient usage of the energy

- *Law No.85/2003 – Mining Law*

- *Law 3/2001*, by which Romania ratified the Kyoto Protocol regarding the decreasing of the greenhouse gases

- *Law No.318/2003 – Electric Energy Law*

- *Governmental Decision No.443/2003* on *The Promotion of Electricity Production from Renewable Energy Sources*, which transpose the European Parliament and Council Directive 2001/77/EC

- *Governmental Decision No.1535/2003 on The National Strategy on Harnessing Renewable Energy Sources* takes an overall look at the potential of renewable sources in Romania and sets forth the main objectives to be reached by the country in the near future. In defining such objectives, the Romanian authorities acknowledged the proposals advanced at European level, including the strategic goal of achieving at EU level a 12% penetration of the renewable energy sources in the overall consumption of primary sources by the year 2010, as set forth in the Commission's 1997 White Paper for a Community Strategy and Action Plan on renewable sources of energy, as well as a 22.1% indicative share of electricity generated from renewable energy sources, in the overall Community electricity consumption by 2010, as set forth in Directive 2001/77/EC on the promotion of electricity produced from renewable energy sources in the internal electricity market. Romania has to increase the share of renewable energies in order to reach a level of 11% in 2010 and 11,2% in 2015.

- *Government Decision No. 163/2004* on *The National Strategy on Energy Efficiency,* sets forth the objectives Approved by the Romanian concerning energy efficiency for the period up to the year 2015. The main purpose of the strategy is to identify the possibilities and means to increase energy efficiency at all levels of the energy chain, by implementing specific programs in order to reach its ultimate goal: the increase of primary energy efficiency by 30% to 50% by the year 2015. Failure to implement a firm energy policy promoting energy efficiency would increase the primary energy consumption associated with the estimated evolution of the Gross Internal Product by 30% by the year 2015, which in turn would lead to a decrease of Romania's energy independence, evaluated in the year 2004 at 70%.

- *Governmental Decision No.1892/2004* – establishing a promotion system from renewable sources

CONCLUSIONS

There is no doubt that Romania has a great geothermal potential, but unfortunately the geothermal production in our country is far below the demonstrated potential.

The development of direct utilization of Romanian geothermal resources has been hindered considerably by the inevitable difficulties attending transition from a centrally planned to a free market economy, as well as by operational capabilities which in some cases have not kept up with the recent technological advances. As a result, current geothermal production falls far short of the country's considerable demonstrated potential. The main obstacle for the geothermal development in Romania is the scarcity of domestic investment capital. In order to stimulate the interest of potential investors from developed countries, and to comply with the requirements of large international banks, an adequate legal and institutional framework has been created, adapted to a market-oriented economy.

Despite these obstacles, it is important to notice that in Romania during the last ten years the use of geothermal resources increased, and there were completed successfully new geothermal projects.

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SIGNIFICANT ASPECTS REGARDING MINE CLOSURE AND ENVIRONMENTAL MANAGEMENT

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ABSTRACT. Significant Aspects Regarding Mine Closure and Environmental Management. The paper presents a literature synthesis regarding the mine closure policies from the environmental and sustainable development perspective. Mining operations in Romania and at international level present major significance from the environmental management point of view. An essential aspect to achieve sustainable development is the integration of the environmental management concepts in all the evolution stages of a mining exploitation, may it be on open-pit or underground mine, beginning with the geological exploration and the investment project to the post-closure actions, land rehabilitation and ecological reconstruction of the site.

Keywords*: mine closure, environmental risks, sustainable development, ecological rehabilitation.*

MINE CLOSURE: CONCEPTS AND TERMINOLOGY

In Romania, the mining activity is regulated by the Mining Law (no. 85/2003) and by the Governmental Decision regarding the approval of the mining law application norms. According to article 51 of this law, the exploitation of a deposit ceases under the following three situations:

a) depletion of the mineral resources;

b) impossibility to continue the exploitation activities due to natural (floods, falling of ground, landslides) or antropical (fires, gas explosions) causes whose effects cannot be removed by technical interventions, under economically efficient circumstances;

c) economical non-profitability of the exploitation.

In the specialty literature, there are used several terms to describe mine closure: decommissioning, ecological reconstruction, rehabilitation and post-closure.

Decommissioning refers to a transition period between the ceasing of the operations and the final closure (Mudder, Harvey, 1999).

Ecological reconstruction refers to the physical aspects of the land, slopes regarding or regularizations and revegetation.

The term **rehabilitation** supposes the recovery of the stable, productive, and self-sustained conditions of the lands affected by mining, taking into account the beneficial uses and the surrounding lands (Peck, 2005). Rehabilitation must thus take into account the possible uses of the site, as well as the changes of the hydraulic regime of the land. Often, the aspects related to the landscape should be taken into account.

Closure is a term used for that moment in time when the revegetation is complete, the excess solutions have been removed to the extent a passive management has been implemented and/or a monitoring program of the watertable was initiated (Mudder, Harvey, 1999).

Post – closure is a term used to designate the period following the closure and ecological reconstruction. If all the environmental impacts have been appropriately approached, the owner of the mine may “leave” the site. However, the monitoring will be necessary for a certain period of time, in order to guarantee the fact that the remedial works have been performed in a stable and safe manner. Under the conditions of an active management, there may be achieved the perpetual maintenance of a site, besides the post-closure monitoring. Under a passive management, periodical checks and monitoring will be performed.

These basic concepts and terms are applied to various types of mining operations at any site.

The objectives of mine closure include long term reduction of the environmental liabilities, assuring the compliance with the regulations and maintenance of the geotechnical stability, while developing the closure operations, as efficiently as possible from the point of view of the costs – in a manner to recover the safe and stable configuration of the land for post-mining uses.

Adequate planning of mine closure should begin from the feasibility, design and permitting phases and be permanently improved during the entire mine operation period. This approach has become a standard or it is used as a necessary practice. The lack of an appropriate and updated mine closure plan might have severe environmental and economic consequences. This closure plan should be consulted and updated permanently during the life cycle of a mining exploitation.

The concept of Life Cycle Management (LCM) refers to the integration and approach of all the phases of the mine life from the environmental management and sustainable development point of view (Figure 1).

In a report of Mining, Minerals and Sustainable Development, starting with April 2002 there are listed the phases of the final closure of a mine: (1) removal of the infrastructure, (2) implementation of the public safety measures, (3) delineation and revegetation (rehabilitation), (4) continuous maintenance of the structures on the site and monitoring of the environmental factors, (5) operation of the facilities on the site necessary for the reduction and prevention of long term environmental degradation prevention and mitigation and (6) completion of the company involvement within the economic and social sustainable programs of the community.

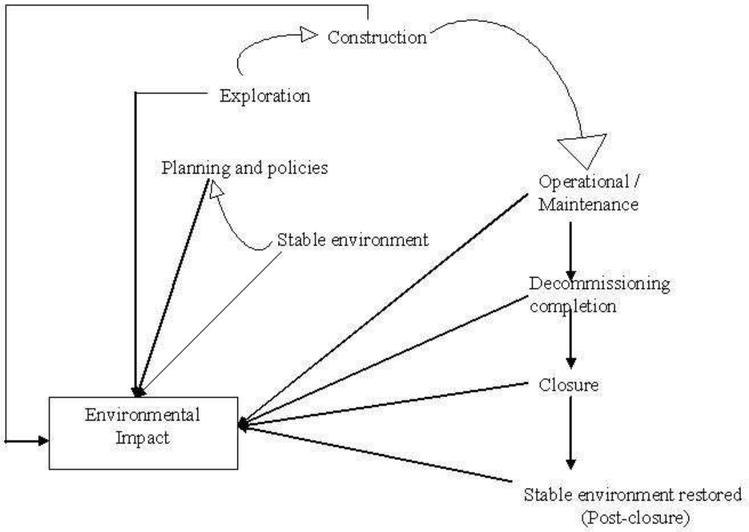

Fig. 1. *General Model of a Mine Life Cycle (Fourie, A., et al., 2006)*

Mine closure has as main objective the provision of long term stability of the geochemical and geotechnical conditions in the areas affected by mining, to protect the health of the population and to diminish and prevent additional environmental degradation (Nazari, 1999). The closure of mines is necessary when the operations are no longer viable and when the value of the goods is inferior to the expenses necessary for achieving the environmental objectives of mine closure. The purpose of ensuring the funds necessary for closure in an early stage is to reduce the risk that a mining company will not want or will not take when closing the exploitation due to the lack of funds allocated to closure. The general objective is to achieve a social, economical, and environmental sustainable development.

Mudder and Harvey (1999) have identified as objectives of mine closure: reduction of long term environmental obligations, achievement of a legislative compliance and maintenance of a geotechnical stability, during the most cost effective and rapid closure – in a manner that renders the safe and stable configuration of the land for future uses. Some of the key features taken into consideration during the decommissioning and closure of a mining exploitation include any underground works, tailings dams embankments, open pits, open tailings dumps and leaching pads.

Philip Peck (2005) focuses on *"mining for closure"*, which implies the integrated planning of the mining exploitation including a closure plan as part of the life cycle of a mining project. This closure plan should be designed in such way to ensure the public health and safety; in order to prevent the physical or chemical damage of the environmental resources; to ensure the long term sustainable development of the site; to reduce any socio-economic impact and to enhance the socio-economic benefits.

A rational approach of the aspects related to mine closure is necessary. The inheritance of an alarming level of pollution impedes the sustainability of the mining operations and that is why there are necessary some mine closure comprehensive systems. There should be taken major decisions, which implies the involvement of governments, of mining companies, of non-governmental organizations and civil communities. Focus should be on lessons learned from the experience of other countries which have efficient systems for mine closure.

PRESENTATION OF THE CURRENT STATE OF ROMANIAN MINING

The state of the mining industry has significantly changed during the last decades. From an industry which provided before 1989 the entire necessary of mineral resources of the national economy, nowadays it turned into an industrial branch mainly grant - aided. In this period there were applied some restructuring activities which resulted in several problems among which we mention:

- The economic regress in the mining regions affected by the restructuring process of this sector;
- exacerbation of the social problems;
- poverty exacerbation;
- inefficient and non-profitable operation of the mining companies.

At the end of 1989, in Romania there were 278 mines and quarries, there were 70 operational plants and processing facilities of which 30 were operating in the metalliferrous ores sector, 34 in the non-metalliferrous sector and 6 in the coal sector. There were 41 mining basins, located on the territory of 23 counties, covering approximately 17,500 ha of land (Fodor, 2005).

After 1990, Romania’s production capacity decreases, and the difficult exploitation conditions and high production costs led the Romanian state to the situation of supporting the mining industry by budgetary allocations and subsidies. Thus, the subsidies for the support of the mining activity have increased in the year 2000 from 2441 billion lei to 5451 billion lei in the year 2004 (Fodor, 2005).

Nowadays, according to the Strategy of the Mining Industry for the period 2007-2020, there are 65 mines and quarries where there are developed extraction activities and 22 plants where ores are processed (Figure 2). These activities are performed by 16 state capital companies and 363 private capital companies. The infrastructure and the technologies are generally in a visible physical wear state and degradation, which has serious consequences upon the environment, production, and employees.

Also, in the Strategy of the mining industry for the period 2007-2020, which comes as an update to the Strategy for the period 2004-2010 approved by Decision no. 615 of April 21, 2004, it results that the losses are higher than the subsidies, but the measures adopted during the period 2000-2005 have led to the decrease of the exploitation losses.

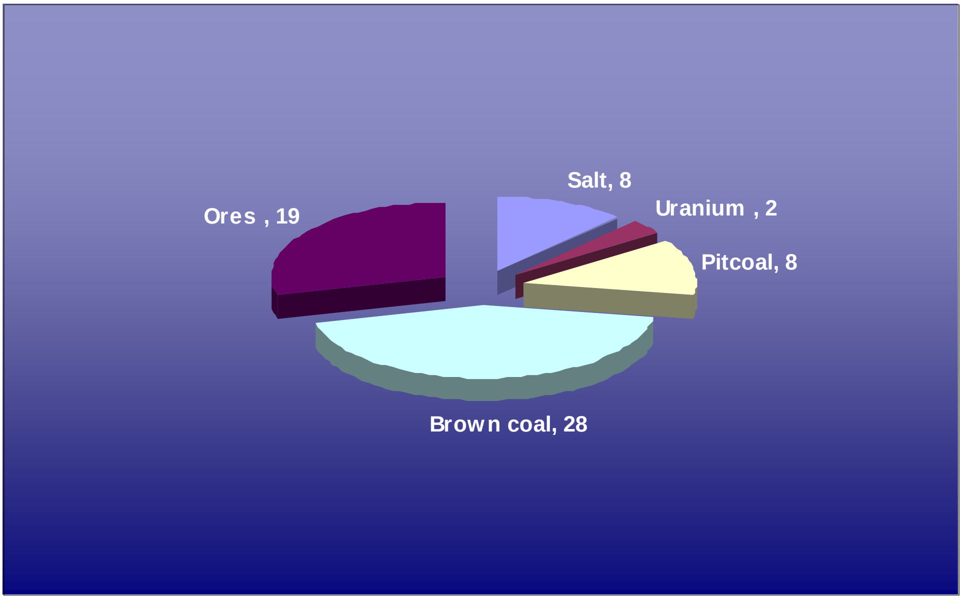

Fig. 2. *Distribution on categories of useful mineral substances of the 65 mines and quarries existing nowadays in Romania (Source: Strategy of the mining industry for the period 2007-2020)*

With Romania's adhesion to the EU it started the process of changing and completing the environmental legislation, of changing the technologies and the attitude regarding the mining activities and their impact upon the environment. There are yet many issues to be approached and taken into consideration. The difficulties in approaching the environmental problems are caused especially by the lack of knowledge and by the inability to assume the responsibilities for the damage of the environmental factors.

The restructuring of the mining industry initiated after the year 1990 pursued mainly the maintenance of the extraction activity only in the mining facilities with geological reserves and favorable geological conditions, which, by re-engineering and modernization actions, may exploit the useful mineral deposits under economically efficient conditions. Thus, due to their non-profitability, the Ministry of Economy and Finances has published the closure situation of 462 mining sites (mines and quarries) approved by governmental decisions. These sites are to be closed according to current legislation.

NATIONAL AND INTERNATIONAL MINE CLOSURE POLICIES

For the structuring of a mine closure policy, one should take into account several aspects. Among these, we mention the existence of a closure plan; update of the mine closure regulations; continuous search of better technological alternatives for the implementation of a closure plan; search of more economically efficient alternatives for the development of the mine closure process. The governments should take into consideration the interest and opinions of the civil society, especially of the mining communities directly affected by these activities. It is necessary to encourage the information exchange between countries, with special focus on the experiences of the countries which have developed and still develop well structured mine closure programs.

The specific mine closure standards and requirements should reflect the balance between costs and benefits, and the policies should be structured in such manner that encourages the mining companies to reach a specific standard or requirement at the lowest possible cost. The mine closure policies should be designed to offer financial incentives for the technological innovation of mine closure, in order to reduce the compliance costs.

Recently, the focus of management of mine closure environmental aspects was directed towards the idea of *mining for closure* (Philip Peck, 2005). Mine closure represents a series of activities beginning with the pre-planning and completes with the achievement of long term stability of the site and of a self-sustaining ecosystem.

The objective of the rehabilitation and mine closure plans is to encourage the recurrence of the mining sites to viable ecosystems, to the extent that these plans are appropriately financed, implemented, and monitored.

The management plan for mine closure and environmental rehabilitation takes into consideration mine activities associated to preparedness and planning of closure, measures for environmental rehabilitation during the non-operational periods and the post-closure period.

In the United States and Canada, the mining companies should submit a closure plan in the project phase, before they even receive the authorization to start the mining operations. The legislative framework of these two countries enables the companies to operate changes in the closure plan according to the evolution in time of the exploitation operations. In order to provide sufficient funds for the successful achievement of the closure plans, all the Canadian jurisdictions and most of the North-American ones ask the companies to provide some form of financial liability (IIED, 2002).

In Australia, ANZMEC – the Australian and New Zealand Minerals and Energy Council has elaborated in the year 2000 “The Strategic Framework for Mine Closure”, document containing a general set of concepts and principles to provide the framework for more specific guidelines developed by the industry and the government. This Strategic Framework focuses mainly on the environmental factors and highlights the need of “effective and efficient approach of financing the closure process which enables the rehabilitation of mines and of other proposed environmental objectives”. Also, he states that “the objective of mine closure is to prevent or reduce the long-term adverse environmental impact and to create a natural self-sustaining ecosystem or an alternative land use”.

In Romania, mine closure is performed according to the Mining Law no. 85/2003. Final or temporary closure of the exploitation activities is authorized by the competent authority (National Agency for Mineral Resources, NARM), based on the activity cessation plan. This is defined in the law as follows: “the complex of technical, economic, social and environmental documentations justifying the closure and containing the actions necessary for the provision of finance and effective achievement of the activity cessation measures" (art. 3, align. 25). Mine closure and environmental rehabilitation are the obligation of the exploitation license owner, on its own expense, except the mines or quarries shut down before the coming into force of the law 85/2003. These will be shut down of budgetary funds, by the competent ministry, by the specialty divisions, with the agreement of NARM.

The Government has launched a restructuring program of the mining industry and efforts are made to close the non-productive mines and to solve the environmental problems. This engagement is supported by the Mine Closure and Social Mitigation Project (MCSMP) initiated in 1999.

By the ministerial order no. 273/2001, the Mine Closure Manual was approved, which is a document including the framework norms regarding mine closure and the procedures for the conservation and closure of mines. This manual approaches all types of mines, except the salt and the uranium mines. The Annexes of this Manual include guidelines for the closure of the exploitation and the rehabilitation of the tailings dams and waste heaps.

Before 2006, the closure of 462 mines and quarries was approved by 9 Governmental decisions issued during the 1999 – 2006 period. According to these provisions, by the Governmental Decisions no. 926/2003 and 1846/2004 the closure of another 84 mines and quarries was approved, distinctly highlighting the expenses for the post-closure monitoring of the environmental factors. The expenses related to the conservation/closure operations and for the monitoring of the environmental factors are covered of the license owners' funds and of the budgetary allocations of the Ministry of Economy and Finances.

EUROPEAN LEGISLATION REGARDING THE MINING INDUSTRY

Like other industrial activities, the mining industry is regulated by the laws, norms, and standards of environmental protection, within all the development stages of its activities. The requirements regarding the mining industry and environmental protection are implemented by instruments such as: environmental legislation; planning and assessment legislation; environmental protection legislation; legislation regarding the occupational safety and health and many others.

In the European Union the extractive industry which generates among the largest quantities of industrial wastes has drawn the attention of the legislative bodies upon the need of adequate legislation (Hámor, 2004). Thus, the applicability of the environmental international directives started to be studied and efforts were made for a pan-European monitoring of this industry. Accent is placed on the sustainable development of this industry, in compliance with the sustainable development concept.

Rational extraction of mineral resources was one of the significant objectives of many international treaties and conventions. Among the first such agreements we mention the Treaty of Rome (1951) which stipulated among others, "the promotion of a policy to rationally use the natural resources and to avoid their irrational depletion". The Euratom Treaty (1957) established also specific provisions regarding the raw matter reserves. Later, in 1997, the Amsterdam Treaty was to implement a coherent policy regarding the environment by adopting the concept of *sustainable development* ("the prudent and rational use of natural resources").

The main document which approached the problem of sustainable mining was the communication of the European Commission "The Promotion of Sustainable Development in the EU Extractive Industry" (COM 2000, 265). Despite the limited purpose, this document offered a complex revision of the mining industry and emphasized the need of a balanced approach of the economic, social, and environmental aspects in view of sustainable development of this industrial branch. The communication provides the elaboration of an action plan materialized in a new communication of the Commission on "The safe operation of the mining activities: as a result of the mining accidents" (COM 2000, 664). This communication described the mining accidents from Aznalcollár and Baia Mare and provided a review of the communitarian environmental legislation, focusing on the safety of the tailings dams.

The European environmental legislation regulates the industrial activities by the EU Directives on wastes (the Council Directive 1999/31/EC, on landfills of wastes, the Council Directive 75/442/EEC amended by 91/156/EEC, 96/350/EC, entitled The Wastes Framework Directive), the water quality (The Waters Framework Directive 2000/60/EC) and air quality (96/62/EEC), the Nature Conservation Directives: the Birds Directive (79/409/EEC) and the habitats (92/43/EEC). The Directive on environmental impact assessment (85/337/EEC on the assessment of the effects of some public and private projects on the environment, amended by the Council Directive 97/11/EC) is applied upon the open pits and the sites whose perimeter exceeds 25 ha. Since 2006 there is also a Directive on mining wastes (Directive 2006/21/EC regarding the management of wastes resulting from the extractive industries). Article 13 of this Directive stipulates that "the mining operators elaborate appropriate waste management plans for the prevention of the generation, decrease of the quantity, treatment, recovery, and safe storage of mining wastes".

Another important European Directive is the Directive concerning the integrated prevention and pollution control (IPPC - 96/61/EC). The plants which produce non-ferrous metals of concentrated ores and secondary raw matters by metallurgical, chemical, or electrolytic processes, covering a small segment of the extractive industry are subjected to this directive. The activities approached by this directive should prevent and reduce the pollution by the use of BAT – Best Available Techniques. The Directive focuses on prevention, not on "end-pipe" treatment.

The Council Directive 96/82/EC (The Seveso II Directive) regarding the danger of major accidents involving dangerous substances was adopted as a result of the Convention concerning the Transboundary effects of the industrial accidents from Helsinki, 1992. This directive was amended by the Directive 2003/105/EC, extending its validity upon the mining industry, as a result of some major accidents among which the cyanide discharge from Baia Mare, into the Tisza River, in May 2000.

These are a few of the European acts regulating the mining industry and environmental protection. However, there are still many other aspects such as occupational safety and health, supply of mineral resources and development of the industry which are approached by the legislation. The legislative tools of the environmental acquis are diverse and act by the control upon: the emission sources by permitting some activities and material flows based on qualitative and quantitative criteria; the pollution paths by the regulation of the activity *per se* and of the affected receivers (humans, ecosystems) by administrative measures or by establishing some qualitative norms.

NATIONAL LEGISLATION REGARDING THE MINING INDUSTRY

The main law governing the development of the mining operation in Romania is the Mining Law no. 85/2003. This defines the terms used in the mining industry, establishes the rules of acquiring the prospecting permits, the exploration and exploitation licenses, the owner's rights and obligations, as well as the taxes, the mining dues and tariffs.

Chapter 7 of this law is intended for mine closure. Article 52 includes the documentation necessary for the cessation of the activity. Alignment (1) letter b) stipulates the compulsoriness of including the post-closure environmental factors monitoring program within the technical decommissioning program of conservation. In article, 53 align.(3) of this law there is also specified the way to finance the post-closure monitoring program, as the responsibility to pursue the obligations resulting from the activity cessation plan belongs to the competent authority (National Agency for Mineral Resources, NARM).

In the following chapters the law approaches the attributions of the competent authority, the responsibilities of the ministry and the sanctions applied in case of non-observing the provisions of the law.

The law includes also references to other laws which might be applicable, among which the Emergency Ordinance no. 195/2005, regarding the environmental protection.

Based on this law the Mine Closure Manual was elaborated, with the purpose to ensure a unitary framework of measures applicable within the closure process. In the Annexes of this Manual there are presented: the national and international regulations applicable for closure; the requirements regarding the data describing the initial conditions; the documents necessary for mine closure; quality monitoring and management; the social protection program; the decommissioning of other objectives and management of the dangerous materials and substances; a model for the mines and quarries monitoring plan; closure of the underground mining works and of the open pits; rehabilitation of the waste heaps and tailings dams; technical references used in editing the mine closure manual.

Other laws and governmental decisions applied to the mining industry are:

- Law No. 645 / 2002 for the approval of the OUG no. 34/2002 regarding the integrated pollution prevention, reduction, and control.
- OUG no. 244/2000 concerning the safety of dams.
- Ministry of Labor and Social protection, 1998 – Specific norms for labor protection applied to the exploitation of the ferrous, non-ferrous, rare, radioactive and non- metalliferrous ores.

- The governmental decision no. 678/1998 regarding the assessment and enforcement of the infringements related to fire prevention and extinction.
- HG no. 856/2002 regarding the approval of the wastes list including the dangerous wastes.
- HG 1470 / 2004 regarding the approval of the Waste Management National Strategy and of the Waste Management National Plan.
- HG 2406 of 21/12/2004 (published in the Official Gazette, Part I no. 32 of 11/01/2005) regarding the management of incapacitated vehicles
- Order of the minister of labor and social protection no. 838/1997 – Specific norms for labor protection regarding the storage, transport, and use of explosives materials.

Specific normative acts used in the elaboration of the *Mine Closure and Environmental Rehabilitation Plan* are the following:

- Mining Law no. 85/2003 – chapter VII;
- General Rules concerning the protection against the fire danger and the fire extinction, approved by Ministerial order O.M. 775/22.02.1998;
- Order of the minister of industry and resources no. 273/04.09.2001 for the approval of the Mine Closure Manual;
- Order of the minister of Economy and Commerce no. 172/2003 regarding the approval of the contract form for the execution of mine closure and environmental rehabilitation/conservation works

Annex 1 of the Mine Closure Manual widely presents the national and international regulations applicable to the mining industry and implicitly to the mine closure process.

The Romanian legislation is subjected to continuous changes, in view of adopting the communitarian acquis. Within the process of adopting and implementing the European legislation, there often occur inconsistencies as a result of the different terminologies used. These will be established by a combined and joint approach of the environmental impacts induced by the mining industry.

CONCLUSIONS

The development strategy of the mining sector promoted in Romania before 1990 was based on the concept of “economic self-sustainability” in ensuring the necessary of mineral raw matters. As a result, the mining companies have directed their efforts first towards increasing the production, without paying too much importance to the economic results and environmental effects.

In the next period, for the sustaining and restructuring of the mining sector, the state has spent significant amount of money, so that the development of the Romanian mineral resources basis represents, almost entirely, the result of mining policies and geological research efforts before 1990.

Subsequently, for the mining sector there was promoted a specific strategy which pursued the development of mining activities under environmental protection conditions, the provision of the support for the mitigation of some social problems caused by the closure of non-viable mines and rebirth of the economy in the damaged mining regions.

There are still many aspects which should be approached and taken into consideration. The difficulties in approaching the environmental problems are due mainly to the lack of knowledge and by the inability to take the responsibility for damaging the environmental factors.

Mainly, for the restructuring of the mining sector it is necessary to take some measures and elaborate some specific norms for the restructuring of the production capacities and improvement of the technological performances, reduction of activities and closure of non-viable mines, the privatization of the viable mines and of those which might become viable and the provision of the financial sources for their development and modernization, the development of the mining activities under environmental protection conditions by:

- making an inventory of previous environmental damages
- establishing the obligations of the mining operators
- promoting an European environmental management
- perfecting and completing the institutional and regulatory framework.

Based on those stated above, the main possible action directions in view of improving the economic efficiency at the level of the entire mining sector are the following: the improvement of the legislative and organizational framework for the development of the mining activities at national level by adapting the environmental legislation to that in the countries with a developed mining sector; the restructuring of the activities at the level of large mining companies by focusing on the exploitation of some ores; practice of modern management methods; geographical restriction of the mining activities (where possible), as well as directing the investment resources only towards the high potential deposits.

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AIR TEMPERATURE TRENDS IN CLUJ-NAPOCA (1978-2007)

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ABSTRACT. Air Temperature Trends in Cluj-Napoca (1978-2007). Cluj-Napoca has a moderate continental climate, characterized by hot dry summers and cold winters. The climate is influenced by the city's proximity to the Apuseni Mountains and some West-Atlantic influences that are present during winter and autumn. This paper investigates air temperature trends in Cluj-Napoca and the data set is represented by time series at Cluj-Napoca airport station. The period analyzed is 1978-2007 for all seasons. The short-term change in temperature has been evaluated by *t*-Test and linear trend. The analysis reveals significant increase in mean annual and mean maximum temperature and slight decrease in mean minimum temperature. This increase in temperature is more pronounced during the summer season, which could be ascribed to solar variations, natural climate change or urbanization of this town.

Keywords. *Urbanization, temperatures, t-test rank statistics, warming trend, significance levels*.

INTRODUCTION

Assessing the impacts of urbanization and land use change on mean surface temperature calculations is a challenging task. Several studies (Balling and Idso, 1989; Karl et al., 1988; Goodrich 1992) published in the last 15 years have attempted to assess the effects of urbanization on local and regional climate. A study by Jones et al. (1990) on urbanization and related temperature variation indicates that the impact of urbanization on the mean surface temperature would be no more than 0.05℃ per 100 years. This value appears to be too small when compared with the other studies (Fujibe, 1995; Hingane, 1996) using a similar technique. According to the study for Japan by Fujibe (1995) a rising trend of 2–5℃ per 100 years in minimum temperature has been observed at several large cities in Japan. While another study (Hingane, 1996) estimates rising trends of 0.84 and 1.39℃ per 100 years in the mean surface temperature calculated for Mumbai and Kolkata, respectively. Another study (Wibig and Glowicki, 2002) related to the variability of minimum and maximum temperature in Poland reveals that the strongest increase in minimum and maximum temperatures occurs in mid and late winter. However, beginning of winter and summer indicates decreasing tendencies.

Local temperature is one of the major climatic elements to record environmental changes brought about by industrialization and urbanization. In view of the importance of air temperature, it would be of interest to study the short-term variation of surface air temperature in Cluj-Napoca, which, during the last 30 years saw phenomenal rise in industrialization (during the 1970s to 1980s) and urbanization (at present).

Therefore, the objective of the present work is to investigate the annual and seasonal temperature trends over Cluj-Napoca. It is also of interest to find out whether the overall change in temperature is due to change in minimum or maximum temperature.

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 characteristics of Cluj-Napoca city are reported in Table 1, which indicates higher variability during spring, summer, and autumn season than during winter season. The mean monthly temperature is high (19.4°C) in July while January witnesses a low (-3.2°C). The mean maximum temperature is also high (25.5°C) in July because it is the summer season. Similarly, the mean minimum temperature is in January (-6.6°C) as it is the winter season.

Table 1.

Monthly and seasonal temperature means.

Month	**T_{max} (°C)**	**T_{min} (°C)**	**Mean temperature (°C)**	**SD (°C)**	CV (%)
January	0.4	-6.6	-3.2	2.5	6.4
February	3.0	-5.5	-1.5	2.9	8.5
March	9.7	-1.1	4.1	2.2	5.0
April	15.5	3.5	9.5	1.6	2.7
May	20.9	8.4	14.7	1.8	3.2
June	23.7	11.6	17.7	1.6	2.5
July	25.5	13.1	19.4	1.7	2.8
August	25.4	12.5	19.0	1.6	2.4
September	20.8	8.3	14.4	1.6	2.5
October	15.3	3.6	9.1	1.3	1.6
November	7.2	-1.0	2.8	2.1	4.4
December	1.9	-4.7	-1.5	2.0	4.0
Annual	**14.1**	**3.5**	**8.7**	**0.8**	**0.6**
Spring	15.4	3.6	9.4	1.2	1.5
Summer	24.9	12.4	18.7	1.3	1.6
Autumn	14.4	3.6	8.8	1.0	0.9
Winter	1.8	-5.6	-2.1	1.4	1.9

Note: SD and CV are computed for mean temperature.

DATA AND METHODOLOGY

All temperature data during the period 1978–2007 are taken from National Oceanic and Atmospheric Administration's Climate Prediction Center (NOAA's CPC).

We analyzed short-term temperature trends based on a homogenized series of temperature data in Cluj-Napoca at elevation of 410 m.a.s.l. for the last thirty years (1978–2007).

From the basic temperature data, mean maximum (T_{max}), mean minimum (T_{min}) and mean temperature, along with their standard deviation (SD) and coefficient of variation have been computed for each month and four seasons: spring, summer, autumn and winter, that are depicted in Table 1. December, January and February are considered for the analysis of winter temperature as these 3 months record lower temperatures (Table 1). While computing the mean for winter season December of the previous year is included. March, April and May represent the spring season. June, July and August are months with highest mean maximum temperatures and, therefore, represent the summer season. September to November months constitute the autumn season. These data were then subjected to a 7-year running mean to find the trends. A linear trend line was added to the series to simplify the trend. Temporal changes in the annual and seasonal values were also 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 and the formula for the dependent *t*-Test is:

$$t = \frac{\sum D}{\sqrt{\dfrac{n\sum D^2 - \left(\sum D\right)^2}{\mathrm{n - 1}}}},$$

where ***D*** is the difference between pairs of scores, $D = X_2 – X_1$. Notice that we subtract the score for the first X from the paired second X. This is probably so that when we are finding the difference between the pre-test and post-test, that we subtract the pre-test (X_1) from the post-test (X_2). The degree of freedom for the dependent *t*-Test is **df = n – 1** and n is the number pairs of subjects in the study.

To get the best results, all data were computed using a special program named EViews. As sample, I used the data range 1978 – 2007, that is 30 included observations.

RESULTS AND DISCUSSIONS

1. Annual temperature trends

The mean annual, T_{max} and T_{min} along with 7-year moving mean and trend line are presented in Fig.1. The mean annual temperature shows a significant short-term increasing trend, significant at 0.01 level (see Table 2). Similar features are also seen in annual T_{max} with slight differences in the relative dominance of warm and cool periods. The annual T_{min} temperature shows a slightly decreasing trend but not statistically significant (see Table 2), while T_{max} shows a warming trend, statistically significant at 0.01 level.

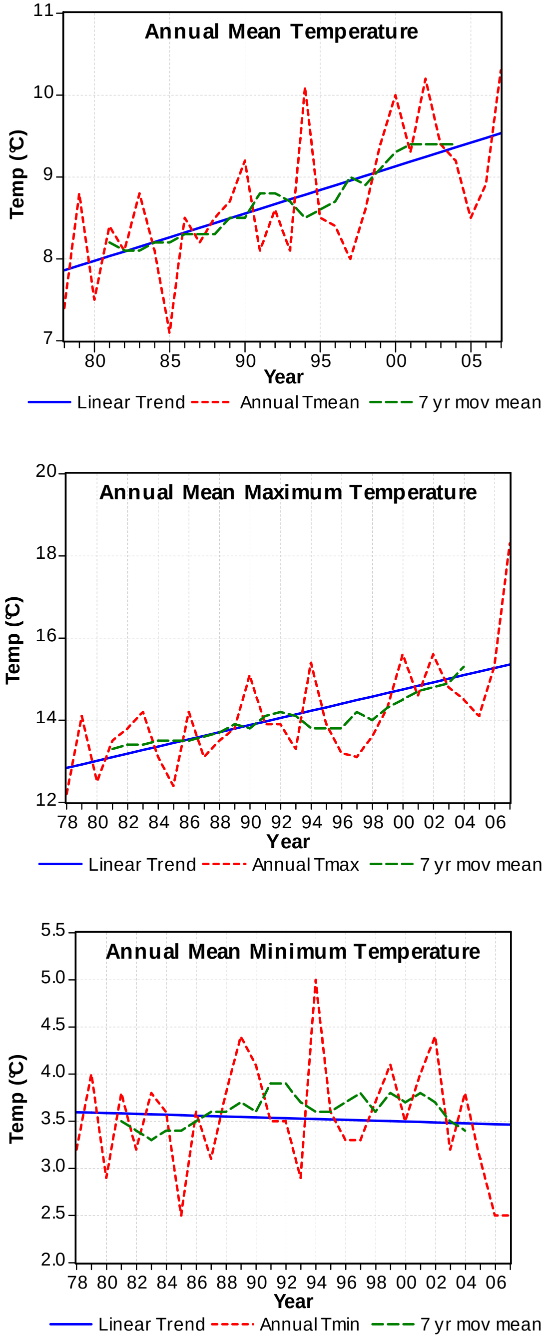

Fig. 1. *Annual temperature trends at Cluj-Napoca.*

Table 2.

Linear equations and their significance tested by t-Test.

Seasons	**Linear equation**	**Calculated *t***
Annual mean temperature	$y = 7.859 + 0.0577x$	4.3470**
Annual T_{min}	$y = 3.595 - 0.0045x$	-0.3612
Annual T_{max}	$y = 12.837 + 0.0868x$	4.3507**
Spring mean temperature	$y = 8.591 + 0.0583x$	2.4623*
Spring T_{min}	$y = 3.900 - 0.0184x$	-0.9689
Spring T_{max}	$y = 14.052 + 0.0878x$	2.5131*
Summer mean temperature	$y = 17.076 + 0.1089x$	6.1450**
Summer T_{min}	$y = 11.679 + 0.0499x$	3.8716**
Summer T_{max}	$y = 23.110 + 0.1188x$	5.9861**
Autumn mean temperature	$y = 8.387 + 0.0277x$	1.3820
Autumn T_{min}	$y = 4.429 - 0.0551x$	-2.0057
Autumn T_{max}	$y = 13.398 + 0.0711x$	2.6147*
Winter mean temperature	$y = -2.670 + 0.0404x$	1.4203
Winter T_{min}	$y = -5.681 - 0.0079x$	0.2549
Winter T_{max}	$y = 0.748 + 0.0707x$	2.0875*

*Significant at 0.05 level, **significant at 0.01 level.

2. Seasonal temperature trends

The mean temperature and the T_{max} and T_{min} for spring, summer, autumn and winter seasons during the period 1978–2007 are presented in Fig.2, 3, 4, and 5. The figures also gives 7-year moving average of the temperature.

2.1. Spring

The spring mean temperature and T_{max} show an increasing trend in spite of intermittent increases and decreases, while T_{min} indicates a decreasing trend. It is observed in Table 2 that only T_{min} is not statistically significant while mean temperature and T_{max} are significant at 0.01 level. The 7-year running mean indicates that spring mean temperature and T_{max} is increasing up, while minimum temperature is decreasing (Fig.2).

2.2. Summer

The summer mean temperature also shows an increasing trend, significant at 0.01 level. This increase is caused by significant rise in maximum and minimum temperature. The *t*-Test indicates that T_{mean}, T_{min} and T_{max} increases are significant at 0.01 level (Table 2). Therefore, it can be inferred that daytime temperatures in summer are significantly increasing (Fig.3). The 7-year running mean indicates that the temperature during summer has come up.

2.3. Autumn

Like spring season, the autumn mean temperature and T_{max} show an increasing trend in spite of intermittent increases and decreases, while T_{min} indicates a decreasing trend. Here, only T_{max} is statistically significant at 0.05 level, while T_{mean} and T_{min} are not. The 7-year running mean indicates that T_{max} is increasing up while minimum temperature is decreasing. Though the autumn mean temperature is not significant at any level it shows a slight increasing trend (Fig.4).

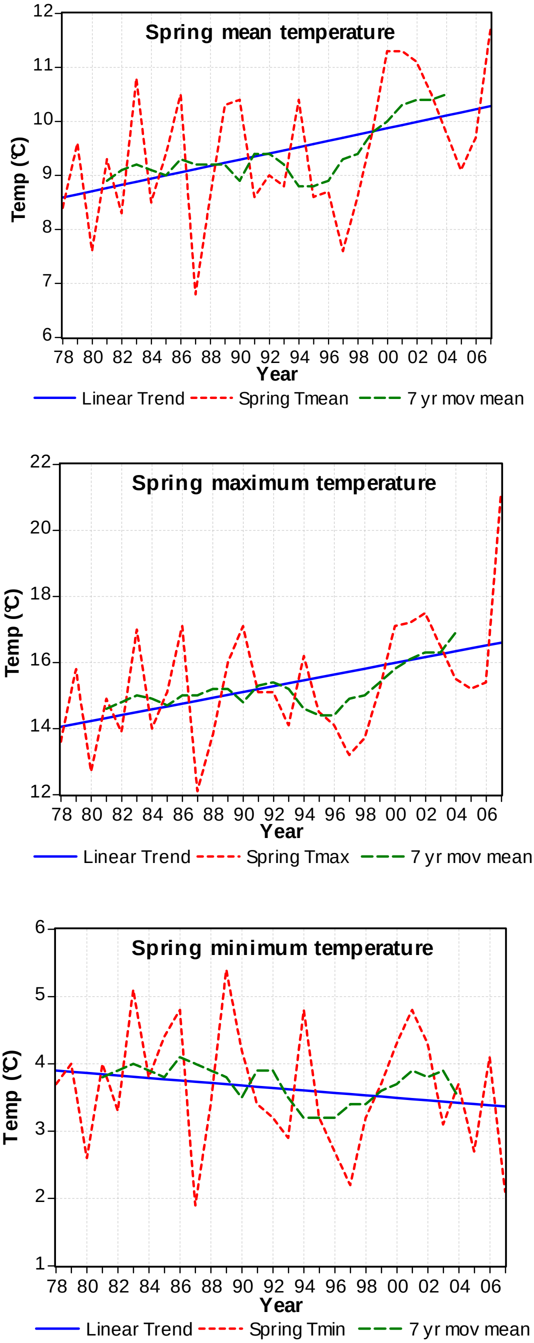

Fig. 2. *Temperature trends for spring at Cluj-Napoca.*

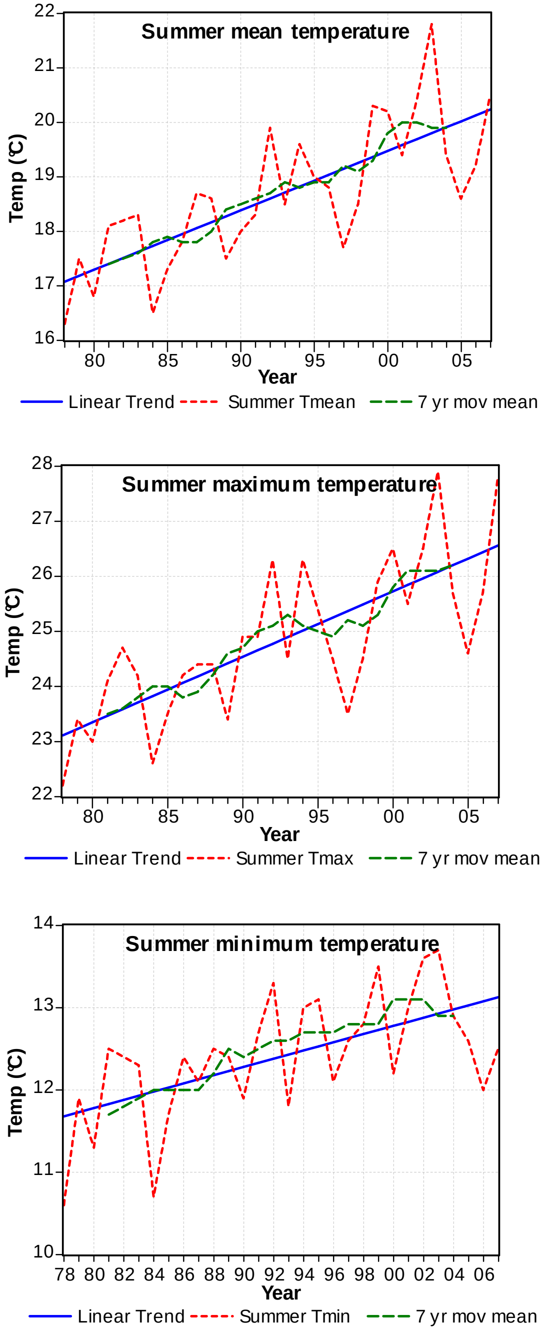

Fig. 3. *Temperature trends for summer at Cluj-Napoca.*

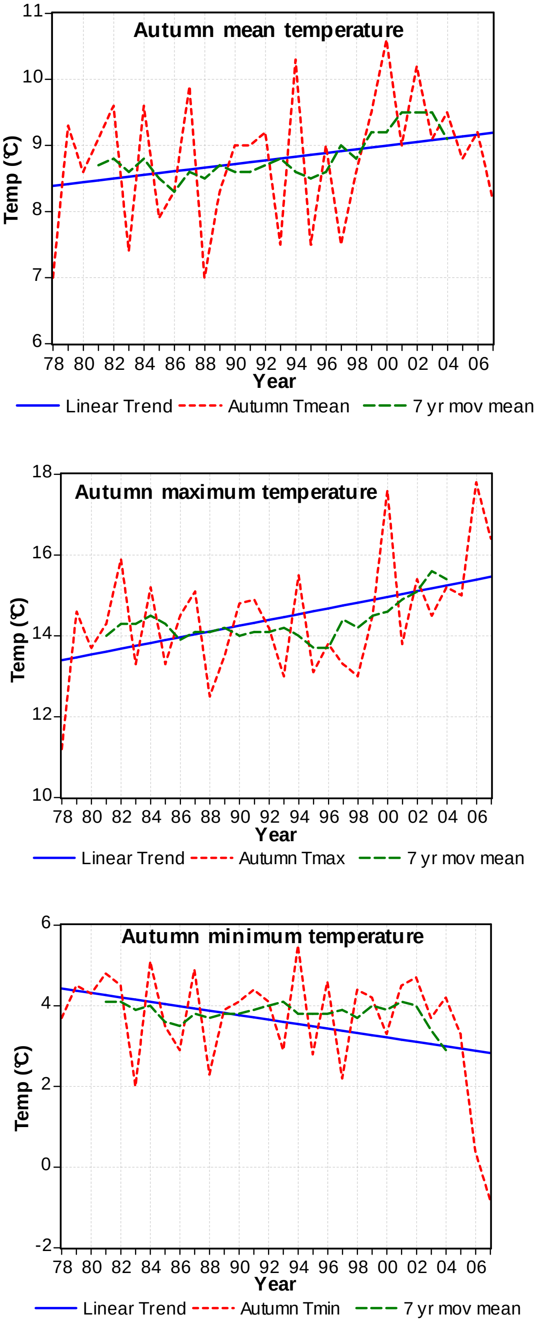

Fig. 4. *Temperature trends for autumn at Cluj-Napoca.*

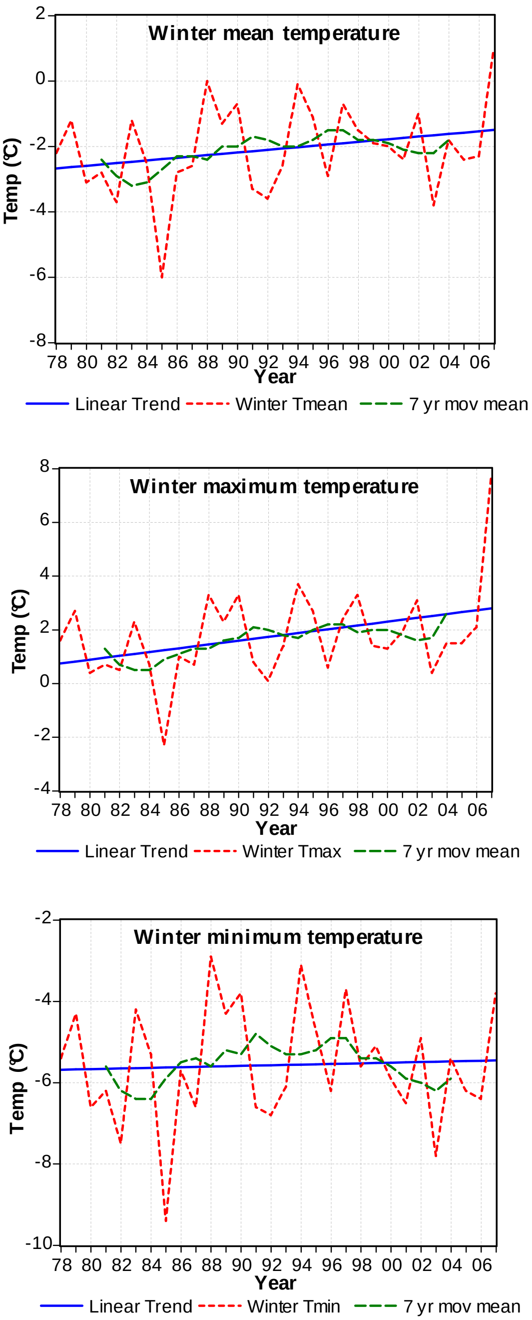

Fig. 5. *Temperature trends for winter at Cluj-Napoca.*

2.4. Winter

The winter mean temperature, T_{max} and T_{min} show a very slight increasing trend in spite of intermittent increases and decreases. However, it is observed in Table 2 that only T_{max} is statistically significant at 0.05 level while mean temperature and T_{min} are not. The 7-year running mean indicates that winter temperature is slight increasing up for mean temperature, T_{max} and T_{min} (Fig.5).

t-Test when applied (Table 2) indicates that annual mean temperature and T_{max}, summer mean temperature, T_{max} and T_{min} are significant at 0.01 level, while spring mean temperature and T_{max}, autumn T_{max} and winter T_{max} are significant at 0.05 level. Thus, all the trends are also well-supported statistically.

CONCLUSIONS

An important aspect of the present study is the significant warming trend in mean annual temperature and T_{max}, which is more predominant during summer season. The spring and autumn season also shows significant warming trend due to increase in T_{max}, but the main problem with these two seasons is that their T_{min} trends are decreasing. The winter season shows a slight increasing trend in T_{mean}, T_{max} and T_{min}, but there is only one statistically significant trend during this season, and this is winter T_{max}.

In the present study, temperature data during the period 1978–2007 have been studied. The result indicates significant increase in summer temperature at 0.01 level. This suggests that the last 30 years have witnessed a phenomenal epoch in temperature series, leading to an increasing trend from non-significant to significant. Contrary to this, the minimum temperatures (except summer and winter T_{min}) show a very slight cooling trend, but not significant at any level.

There is a need to know more about the possible dimensions of natural climatic variability. We are still a long way from understanding the complex interaction of many physical processes that determine the evolution of climate.

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THE IMPORTANCE OF SOME NON-TARGETTED CELLULAR EFFECTS IN ASSESSING THE LUNG CANCER RISK INDUCED BY RADON AND ITS PROGENY

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ABSTRACT. The Importance of Some Non-targetted Cellular Effects in Assessing the Lung Cancer Risk Induced by Radon and its Progeny. Until about two decades ago, there was a dogma in radiation sciences that biological effects appear only in case of direct irradiation of cells, when energy deposition occurs in the nucleus of the cell. Lately, a different approach than the deterministic relationship "hit-effect" model was adopted in radiobiology, in favor of some concepts regarding the responses at the cellular level. At low doses of exposure to ionizing radiation a number of delayed, non-targeted effects of cells not directly hit by radiation were reported. In this study, a mechanistic model was proposed, for estimating the lung cancer risk induced by direct and particularly indirect biological cellular effects that occurred after exposure to alpha particles. The objective of the present study was to explore the role of non-targeted cellular radiation effects on the shape of the dose-effect curve in the low dose region, i.e. to investigate whether mechanisms such as bystander effects and adaptive response will increase or decrease lung cancer risk shape at radon exposure levels characteristic of residential exposures.

Keywords: *non-targeted effects, lung cancer, risk, bystander, adaptive response*

INTRODUCTION

The interest in estimating the lung cancer risk induced by radon and its progeny has been increasing with time, especially in the last decades, because it was proved that besides acute exposures, the low residential exposures to ionizing radiation are also hazardous, being associated with elevated cancer risk, Kadhim et al., (2006). In the whole world, residential exposure to the short lived radioactive progeny of the chemically inert gas ^{222}Rn is responsible for about half of all non-medical exposures to ionizing radiation because radon concentrations can build up indoors (although outdoors radon concentrations are low), Darby et al., (2005). For example, it contributes about 49% to the annual average dose to the UK population, Kadhim et al., (2006). Analyses of case-control studies on residential radon and lung cancer risk, Darby et al., (2005), also conclude that collectively, great hazards from residential radon have been shown, particularly for smokers and recent ex-smokers, and indicate that residential radon is responsible for about 2% of all deaths from cancer in Europe. On the other hand, studies of exposed miners have consistently found associations between radon and lung cancer, Darby et al., (2005). Epidemiologic studies- reporting data on professional exposure reveal that the highest radon concentrations to which workers have been routinely exposed occur underground, particularly in uranium mines, Darby et al., (2005).

^{222}Rn occurs naturally from the decay of ^{238}U, which is ever-present in the earth's crust and thus air pollution by radon is ubiquitous, Darby et al., (2005). It has a half life of almost four days, allowing it to diffuse through soil and into the air before decaying by emission of an alpha particle into a series of short lived radioactive progeny. Two of these, polonium-218 and polonium-214, also decay by emitting densely ionizing high linear energy transfer (LET) alpha particles.

After being inhaled, radon itself is mostly exhaled immediately but its short lived progeny, however, which are solid, tend to deposit on the bronchial epithelium, thus exposing cells to alpha irradiation, Darby et al., (2005). Random alpha particle intersections of bronchial target cells during a given exposure period, selected from a Poisson distribution, were simulated in this study by an initiation-promotion mechanistic model formulated in terms of cellular hits. This model - quantifying the lung cancer risk induced by radon and its progeny as a function of cell hits (traversals) during direct exposure - will be further improved, considering also the non-targeted cellular effects such as bystander effects, genomic instability, induction of apoptosis and adaptive response, mechanisms occurring specifically at low-dose exposures. Analytical initiation and promotion functions were derived from presently available experimental *in vitro* data on oncogenic transformation and cellular survival, presently available. For the comparison of predicted lung cancer risks, expressed as functions of dose, with epidemiological data, reported as functions of WLM, a dose-exposure conversion factor of 5 mGy/ WLM was applied, Hofmann et al., (2006).

THE INITIATION-PROMOTION MODEL

The Initiation-Promotion (IP) model presented in this paper represents a simplified version of the State Vector Model (SVM) of radiation carcinogenesis, where lung cancer risk R(D) is expressed as the product of the initiation function I(D) and the promotion function P(D). In the State Vector Model (SVM) of radiation carcinogenesis, Crawford Brown and Hofmann, 1990, Hofmann et al., (2006), formulated in terms on an initiation-promotion model, it is assumed that a cell must pass through several stages until producing a fully developed tumor. While transition rates between these stages were obtained from experimental data as functions of dose rate, only fragmentary information on transition rates for single alpha particles is presently available. Thus a simplified Initiation-Promotion model, based on the SVM was developed which allows the simulation of single alpha particle effects. Within this model, it was assumed that oncogenic transformation is the primary initiation step, while stimulated mitosis by killing adjacent cells is interpreted as the necessary radiological promotion event. Initiation and promotion functions were derived from experimentally observed *in vitro* oncogenic transformation and survival data for C3H 10T1/2 mouse cells exposed to charged particles of varying LET, Bettega et al., (1992), Miller et al., (1995), and rat tracheal epithelial (RTE) cells irradiated with ^{241}Am alpha particles Kugel et al., (2002), Poncy et al., (2002). The LETs of the charged particles used in both experimental studies correspond to the LET spectrum of radon progeny alpha particles in bronchial epithelium, Hofmann et al., (2006). The transformation data, i.e. the transformation frequencies per surviving cell, were expressed by a linear-quadratic function of dose, ($\alpha D + \beta D^2$), and the corresponding survival data were fitted by an exponential function, exp(-γD), where the coefficients α, β were obtained by fitting the above experimental transformation and survival data, and γ represents the cell killing probability [3]. Thus initiation will be expressed by the initiation function I(D), representing the transformation frequency per exposed cell, TF(D):

$$I(D) = TF(D) = \left(\alpha \cdot D + \beta \cdot D^2\right) \cdot \exp(-\gamma \cdot D) \qquad (1)$$

Promotion is expressed as the probability that an initiated cell undergoes division-related fixation of the initiating damage under *in vivo* conditions due to stimulated mitosis:

$$P(D) = \lambda_1 + p \cdot \lambda_2 \cdot [1 - \exp(-\gamma \cdot D)] \qquad (2)$$

where λ_1 is the normal mitotic rate of lung cells, equivalent to a cycle time of 30 days, NRC, (1999), ($\lambda_1 = 1/\tau$), where τ is the cell cycle time, which may increase to λ_2, the rate of division under conditions of extensive tissue damage and cellular replacement, corresponding to a cycle time of approximately one day, and p denotes the probability that a progenitor cell will divide as a direct result of the inactivation of an epithelial target cell, Hofmann et al., (2006). It was assumed here that p = 1, i.e. each dead epithelial cell would force a stem cell to divide, Hofmann et al., (2006).

Studies on radiation-induced lung cancer suggested that in cases of protracted exposures the crucial quantity for cellular effects is the dose per cell cycle, Chadwick et al., (2003). Thus calculations in this study were made for cells with an average cell cycle time (τ) of 30 days NRC, (1999). While the number of cellular hits increases with the tissue or organ dose, the average dose received by the traversed cells remains constant until multiple alpha particle hits start playing a greater role. This observation questions the applicability of average doses for alpha radiations at the cellular level, where radiobiological effects originate, at sufficiently low doses and thus average dose will be replaced by the frequency of single and multiple alpha particle hits. Cellular alpha particle hits were assumed to be uniformly distributed throughout a defined exposure period reported in the epidemiological data used, Tomasek et al., (2008), and Hornung and Meinhardt, 1987. For a given average number of cellular hits ($\overline{H}$) per cell cycle during the total exposure period (T), equivalent to the average dose D, the actual number of single and multiple hits (P_n), delivering an average dose D_n to a traversed nucleus of a basal or secretory cell during the lifetime of these cells, were selected from a Poisson distribution is:

$$P_n = \frac{\overline{H}^n \cdot e^{-\overline{H}}}{n!} \qquad (3)$$

where $\overline{\mathrm{H}} = \frac{\mathrm{N_h}}{\mathrm{N_0}}$, $N_h = \frac{D}{\overline{\overline{D_c}}}$ is the number of hits, N_0 is the number of cell cycles in the exposure period considered (T), $N_0 = \frac{T}{\tau}$ and $\overline{D_c}$ is the mean cellular dose per hit.

Thus, lung cancer risk R(D) induced by direct exposure to radon and its progeny will be:

$$R(D) = C \cdot \sum_{i=1}^{n} TF(D_n) \cdot \{\lambda_1 + \lambda_2 \cdot p \cdot [1 - \exp(-\gamma \cdot D_n)]\} \cdot P_n \qquad (4)$$

where C is a constant scaling factor relating the lung cancer risk function R(D) to the epidemiological data, Hofmann et al., (2006).

For alpha particle irradiation, a linear relation between TF(D_n), the transformation frequency per exposed cell, and dose D was obtained from experimental *in vitro* data at low doses:

$$TF(D_n) = \alpha \cdot D_n \cdot \exp(-\gamma \cdot D_n) \qquad (5)$$

where $D_n = n \cdot \overline{D_c}$, α = 1, γ = 1.298 Gy^{-1}, Poncy et al., (2002), and $\overline{D_c}$ =0.33 Gy^{-1} for cells with nuclear diameter of 9 μm, and LET=130 keV/μm.

The model predictions were compared to the following epidemiological data: the Czech miner data reported by Tomasek et al., (2008), for the low exposure region and the Colorado Plateau uranium miner data reported by Hornung and Meinhardt, 1987, for the higher exposure region. Epidemiological data chosen for the above mentioned comparison were in agreement with the Committee of BEIR VI approach that also turned to analysis of epidemiological data as the basis for developing its risk models, NRC, (1999). The reason why both low and high exposure levels were analyzed in our studies - within the framework of the IP model - was that extrapolation from higher to lower radon exposures is influenced by the inverse dose-rate effect, likely to occur at exposure levels at which multiple particle traversals per cell may occur, NRC, (1999). As BEIR VI specifies, there was a need to assess risks of radon in homes on the basis of miner data corresponding to as low an exposure as possible, accounting for the diminution of the inverse exposure-rate effect with decreasing exposure NRC, (1999). Thus, the Czech miner data were selected to be the fundamental data in analyzing the lung cancer risk at low exposure levels, which makes the object of the present study.

To compare the predicted lung cancer risks, expressed as functions of dose, with epidemiological data, reported as functions of WLM, a dose-exposure conversion factor (CF) of 5 mGy/WLM was applied, Hofmann et al., (2006). For the same reason, all risk functions were normalized to a relative risk of 4.44 at 135 WLM (0.675 Gy) for the Czech miner data, and to a relative risk of 29 at 2600 WLM (13 Gy) for the Colorado miner data. This normalization was introduced because the primary goal of this study was to examine the shape of the dose-effect curve at low exposures and not the absolute number of lung cancer cases. Czech miner data, model predictions and the linear- no threshold hypothesis are plotted in Figure 1, indicating excellent agreement between the epidemiologically observed relative risk and the theoretically predicted risk.

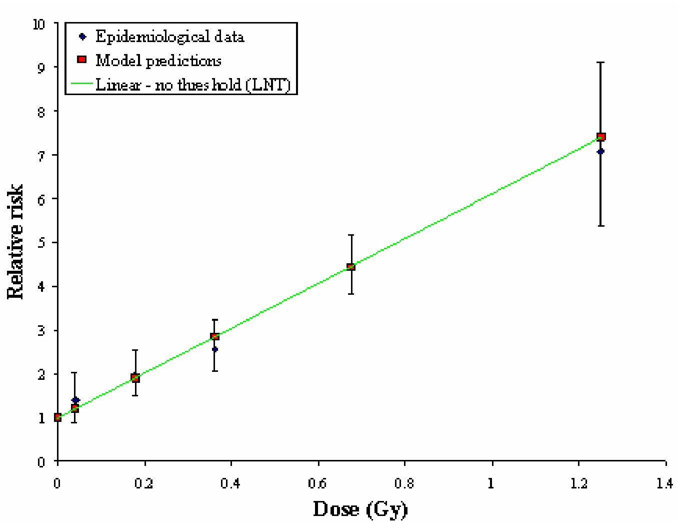

Fig. 1. *Model predictions compared to Czech miner and the linear-no threshold hypothesis*

NON-TARGETED EFFECTS AT LOW DOSES

The major adverse consequences of radiation exposures are attributed to DNA damage in irradiated cells that has not been correctly restored by metabolic repair processes, Coates et al., (2004). However, the dogma that genetic alterations are restricted to directly irradiated cells has been challenged by experimental observations in which untargeted effects also add important short and long-term contributions to the final outcome after radiation exposures, Coates et al., (2004). To investigate the shape of the lung cancer risk function at chronic, low level exposures in more detail, additional biological factors describing the tissue response and operating specifically at low doses were incorporated into the Initiation-Promotion (IP) model. The non-targeted mechanisms - modifying the initial direct response at the cellular level - examined in this study were: bystander mechanisms, and adaptive response, which are in a possible correlation. Both detrimental and protective bystander effects, Iyer and Lehnert, 2002 have been reported in literature, but the detrimental ones will be more thoroughly studied in this paper.

Bystander Mechanisms

A general definition for bystander effects refers to damage that occurs in cells that were not traversed by radiation, but were in the neighborhood of an irradiated cell, i.e. they were bystanders at the time of irradiation. Implicit in this definition is that the bystander cells were not hit by the radiation, but received signals from the irradiated cell through gap junction-mediated intercellular communication or by extracellular signalling molecules. Thus, a "detrimental" bystander effect amplifies the biological effectiveness of a given radiation dose by effectively increasing the number of cells that experience adverse effects over that directly exposed to the radiation, Brenner et al., (2001). In broad beam irradiations with low fluences of alpha particles, where not each cell is traversed by an alpha particle, an important contribution to the damage results from responses occurring in cells that were not actually traversed by an alpha particle, Sawant et al., (2001).

For alpha particles, Sawant et al., (2001), reported that the resulting transformation frequency when 10% of the C3H 10T1/2 cells were exposed to alpha particles was not less than in the case when all the cells on a dish were exposed to the same number of alpha particles. These data for transformation frequencies in mouse fibroblast cells were analyzed in terms of a microdosimetric bystander model, Fakir et al, (2007). At low dose exposures, where the average number of hits is less than 1, the bystander induced foci exceed the direct contribution by almost an order of magnitude, while for higher doses, when the average number of hits is greater than 2, the bystander effect is less efficient, Fakir et al, (2007). The ratios of the bystander-initiated transformations to the direct effect for a given average number of cellular hits were implemented into the IP model. Since the average number of hits calculated for the Czech miner data is less than 1, the bystander effect significantly increases the risk values. However, the average number of hits is so small that the shape of the dose-effect curve is hardly affected (Figure 2).

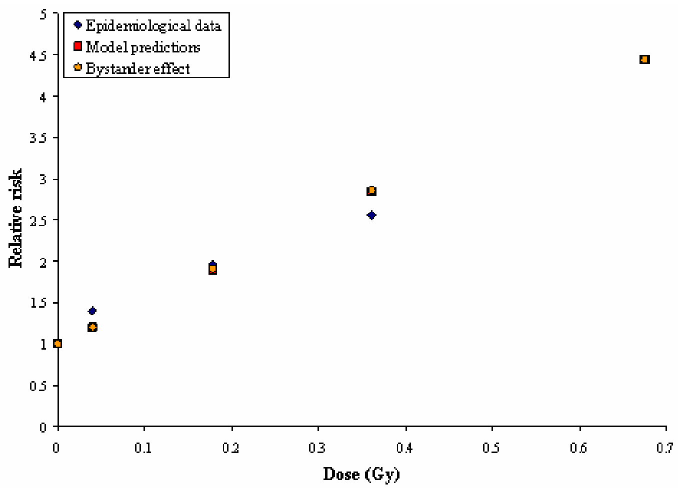

Fig. 2. *Illustration of bystander effect on the shape of lung cancer risk predictions*

The results obtained with our model for the average number of hits are consistent with the mechanistic, experimental and epidemiological considerations reported in BEIR VI, stating that low exposures, specific in most indoor exposures are characterized by an average number of hits (traversals) of much less than one per cell location, NRC, (1999).

The study of Brenner and Sachs, 2003, concluded that in the case of domestic radon exposures, the risk could be dominated by bystander effects. Their analysis states that a naive linear extrapolation of radon miner data to low doses, without accounting for dose rate/bystander effects, would result in an underestimation of domestic radon risks by about a factor of ~4. Compared to the number of *in vitro* studies on bystander effects, there are relatively few studies on bystander effects *in vivo*. While the existence of radiobiological bystander effects *in vitro* is well established, Hall and Hei, 2003, Prise et al., 2003, Mothersill and Seymour, 2001, the studies by Brooks et al., (1983) indicate that bystander effects can also occur *in vivo* in presumably non-irradiated tissue.

In contrast to the above discussed detrimental bystander effects, also "protective" bystander responses have been reported. For example, potentially damaged or sensitive cells may be removed by either apoptosis or by premature differentiation, Belyakov et al., (2006). The experiment of Iyer and Lehnert, 2002, on normal human lung fibroblasts ought to be mentioned, in this respect, concluding that direct exposure of cells to a low dose of ionizing radiation can induce a condition of enhanced radioresistance, i.e. a "radioadaptive" response. They observed that supernatants from cells exposed to a low dose of α particles contain growth-promoting activity, suggesting that this new bystander effect may be related to an increase in DNA repair and cell growth/cell cycle regulation.

Adaptive Response

Adaptive response is another natural defense mechanism of the organism against oncogenesis. It refers to the cells first exposed to low doses of low LET radiations, rendering cells resistant to a subsequent exposure of high or low LET radiations and thus reducing the detrimental effects of radiation, Sawant et al., (2001).

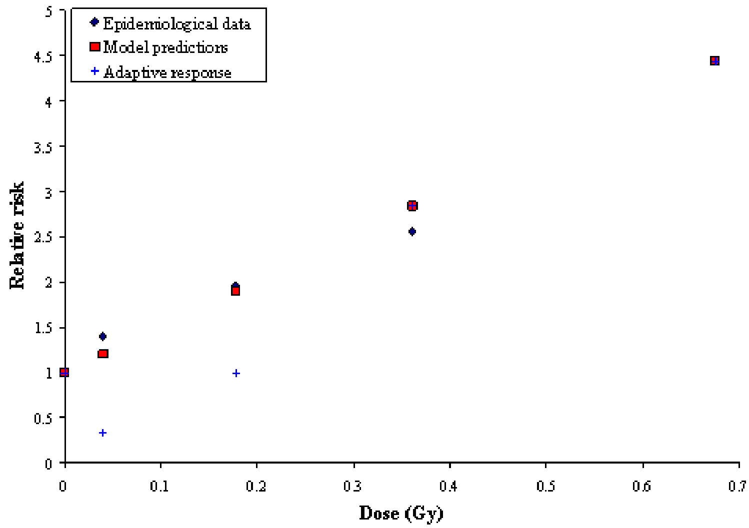

Fig. 3. *Illustration of the effect of adaptive response on lung cancer risk predictions*

The *in vitro* observations reported by Sawant et al., (2001) suggest that adaptive response resulting from irradiation with a low adaptive dose (2 cGy) of X rays can cancel out about half of the bystander effect on transformation frequencies produced by high LET particles. Other studies observed that, in plateau-phase, C3H 10T1/2 cells pre-exposed to chronic doses of 0.1 to 1.5 Gy low-dose rate γ-radiation before an acute 4 Gy challenge dose manifested adaptive response by enhanced DNA double-strand break repair capacities, thus being less susceptible to subsequent radiation-induced neoplastic transformation, Azzam et al., (1994). In the case of radon exposures, the required adaptive dose may be produced by either external gamma rays in mines or homes or by radon progeny alpha particles, Iyer and Lehnert, 2002. In the present analysis, experimental *in vitro* data for X-rays, Redpath et al., (2003), were used to simulate the dose dependence of the adaptive response mechanism, indicating that transformation frequencies exhibit a significant reduction at very low doses, until they rise again in a linear fashion at higher doses.

As can be seen in Figure 3, adaptive response significantly reduces lung cancer risk at low radon levels, exhibiting a sublinear response.

CONCLUSIONS

It is has been shown that non-targeted effects have a great impact on assessing the real lung cancer risk. An irradiated cell can send out signals and induce responses in cells whose nucleus were not hit by irradiation. This might result in genetic changes, including damage in non-irradiated cells. In general, non-targeted effects such as bystander effects in essence "amplify" the biological effectiveness of a given radiation dose, by effectively increasing the number of cells that experience effects over those directly exposed to radiation. On the contrary, adaptive response decreases the risk values, being considered defense mechanism against oncogenesis. While these observations are related to the absolute number of lung cancer cases, the results of the present calculations suggest that their effect on the shape of the dose-response relationship may be different. Indeed, adaptive response causes a substantial reduction of the risk at low doses, while detrimental bystander effects slightly increase the risk.

The indirect effects described in this study indicate that the target for the detrimental effects of radiation may be much greater than the precise volume irradiated, thus having important implications for human health. A model based both on direct and indirect cellular mechanisms for the assessment on lung cancer is the most appropriate and correct for making assumptions on the limits of indoor and occupational exposures. Still, there are a few significant limitations of the current modeling approach that have to be recognized: at present we do not know whether the relative magnitudes of these non-targeted effects observed *in vitro* are the same as *in vivo*, where cells are communicating with each other and to what extent these mechanisms will indeed affect lung cancer formation.

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