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CONTENTS – SOMMAIRE – CONTENIDO – CUPRINS

STUDIA UBB AMBIENTUM, LVI, 1, 2011, pp. 3-13

CONTRIBUTIONS TO THE DEVELOPMENT OF THE STRATEGIC NOISE MAP OF TRAFFIC FOR BAIA MARE CITY

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ABSTRACT. Noise pollution from traffic is a growing problem with the development of our society. To take effective measures to reduce the impact of this pollutant, it is necessary to know its distribution and magnitude in the area of interest, which is the role of noise maps. In this paper, is presented the method we used and the results obtained for the strategic noise map of traffic for Baia Mare city. In order to achieve the noise map we used specialized software and the calculation model that was applied is the French national method of calculation, NMPB Routes-96. As a result of the research was obtained the traffic noise map as well as the number of people exposed to different levels of sound intensity.

Key words*: traffic noise prediction, traffic noise maps, road traffic, noise pollution, CadnaA.*

INTRODUCTION

Knowing the traffic noise level is required to develop action plans in order to fix the problems caused by environmental noise. It is also necessary to know the areas most exposed to noise and the number of inhabitants affected by it (Farcas and Siverteen, 2009).

With the development of the city, will further increase the flow of cars and streets will be more crowded. Therefore future infrastructure development plans should take into account the noise aspect. New buildings will be designed to provide also protection against noise for those who will inhabit them (Bodin et al. 2009).

The uses of noise maps are numerous. They are the basic steps from which local governments build their ambient noise strategy. It is also a method for informing the population about the noise levels to which they are exposed. Once identified areas most at risk, you can find viable ways to reduce noise discomfort (Bontideanu, 2005).

Noise map preparation was based on a traffic study, conducted in 2006, for Baia Mare city. There was also used data about the location of buildings and traffic routes, demographic data, to be later estimated the number of people exposed to different noise levels. In order to determine the number of levels of the buildings were used satellite images and high-resolution ortho-photographs. The result was a 3D model of the city on which were represented using a color code, the different levels of noise.

PURPOSE AND PLACE OF STUDY

To quantify the magnitude of impact caused by road traffic in different parts of the city, was chosen as a solution to create a strategic noise map. This enables tracking of various intensities of sound from traffic, using a color code. Moreover, it is possible to estimate the number of inhabitants affected (Ciuca, 2005).

The research was conducted in the municipality of Baia Mare. Analysis from the point of view of traffic noise has been treated separately for each district, excepting Ferneziu and Firiza. The reason for which they were not analyzed is the lack of data on road traffic and other data such as demographics and computer representation of housing.

Baia Mare, Maramureș county residence, is an important urban center in northwestern Romania. City area is 23,471 ha.

The city road network is generally well developed, with broad streets in new areas, densely populated. In contrast, in the historic center and the districts of north and north east, the network has limited resources to carry out road traffic.

WORK METHOD

For the calculation of noise, levels and making the map of Baia Mare it was used dedicated software: CadnaA version 4.0, developed by German company DataKustik GmbH (CadnaA, www.datakustik.com).

As a calculation model was used French method for calculating road traffic noise: NMPB-Routes 96 and XPS 31-133 French standard.

In order to mathematically model the traffic and noise resulting from it, the city was divided into areas, located between major streets. The reason for this division is so in order to organize and work in stages, but especially for technical reasons (Covaciu et al. 2004). Modeling noise in terms of computer calculation is a long and complex process (Karakula, 2007).

Computer modeling is performed in emission points in a grid (grid) cell with 10 m and at a height of 2 m; the area mapped and specified in the noise map is representing the interpolation of noise indicators. For better accuracy of the result, the 5 m value was chosen for the grid cell.

Obtaining information

Strategic noise maps are made for specified areas. The starting point in order to achieve the noise map is a digitized model of these areas.

In the implementation of the project, we had digital models for road network and for all buildings in the studied area.

It was necessary, then, the use of data about the traffic on every street in hand and the number of residents in the buildings (EnviroConsult, 2007).

The noise prediction model calculates Leq (level of noise) in decibels (dB). The Leq is calculated over a period (normally 24 hours).

$$L_{eq} = 10log\left[\frac{1}{N}\cdot\sum_{i=1}^{N}10^{\frac{L_{eqi}}{10}}\right]$$

where: **N** is the number of elementary periods, Leqi is the short Leq corresponding, expressed in dB.

In this project, we chose the following glimpse of time: The day has 16 hours, and night is 8 hours long, for all noise sources analyzed. Their slots are 23.00 to 07.00 and 07.00 to 23.00, local time.

In the present situation, we have:

$$L_{zi} = 10\cdot\frac{\lg 1}{24}\left(16\cdot 10^{\frac{L_{day}}{10}} + 8\cdot 10^{\frac{L_{night+10}}{10}}\right)$$

Shall be taken into account a representative year in terms of noise emission and an average year in terms of weather conditions.

Entering input data

In order to make the noise map is necessary to conduct 3D model of the city. This is based on a series of information:

- topographic data:
  - GIS terrain model;
  - GIS model of infrastructure: roads, railways, buildings;
  - Height of buildings.
- Additional data necessary for the calculation:
  - Data describing road infrastructure;

- Traffic Information: traffic on the road-road;
- Weather data;
- Demographics: number of inhabitants in buildings;
- Isolation.

The following data are needed to calculate the noise emissions of traffic on main roads and roads within an urbane area:

- The amount of traffic;
- Traffic speed;
- The gradient of the road;
- Traffic fluctuation;
- Percentage of heavy vehicles;
- Road surface;
- Meteorological data.

Traffic magnitude was obtained from a traffic study provided by the municipality, from which, the values for the main streets were taken.

For the class 1, 2 and 3 roads (highest traffic) traffic values from the study were used, while for the other streets were given the following default values:

Table 1. *Traffic values depending on the road type*

The following values of traffic flow are used:		
Road type	Number of vehicles/time period	
	day	night
Residential roads	350	50
Connecting roads (roads linking residential and main roads)	700	100
Small main roads	1400	200
Big main roads	Data from traffic study	

Vehicle speed was chosen as being equal to the legal limit for each stretch of road, respectively, predominant 50 km / h. Road gradient was considered equal to zero. Traffic fluctuation was considered pulsating for all roads within the city due to frequent changes in the flow of traffic (due to congestion, traffic lights, pedestrian crossings, etc.). Since no data on the number of heavy vehicles was available, we considered them as 20% of the total number of vehicles. It was taken into account the tread surface, which may differ depending on each street.

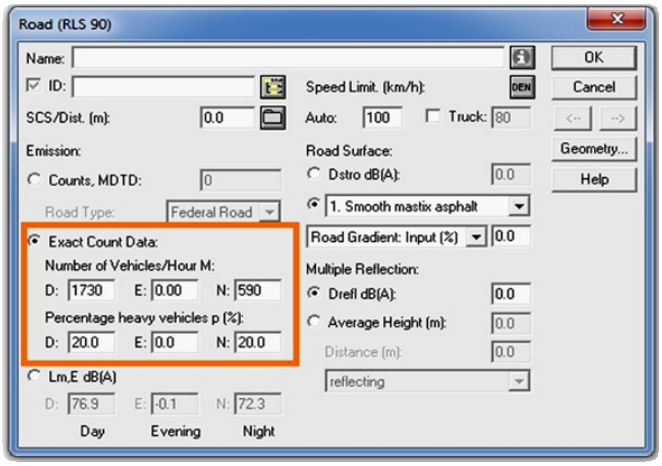

Fig. 1. *Entering traffic values.*

Calculation of number of residents in each building

Next, building assessment was made from the point of view of noise exposure on the facade of buildings. To obtain that the calculation of population density was made. No information was available on the number of residents in each separate building; therefore, the calculation of the number of residents was conducted using information about a specific area population, relative to the type of buildings and according to the number of floors and their surface. The following formula was used:

$$N = \frac{f}{40} \cdot \frac{h}{3}$$

where,
N – Number of residents in de building;
f – Surface of building;
h – Building height.

After this step, it was obtained the number of people exposed to noise at different sound intensity levels with an interval of 5 dB, as required in HG 321/2005.

RESULTS

3D Modeling

In the mathematical modeling of traffic and implicit the noise resulting from it, the study area was divided, a division area is framed by large streets. The reason of this division is so in order to organize and work in stages, but mostly for technical reasons. Modeling noise in terms of computer calculation is a lengthy and complex.

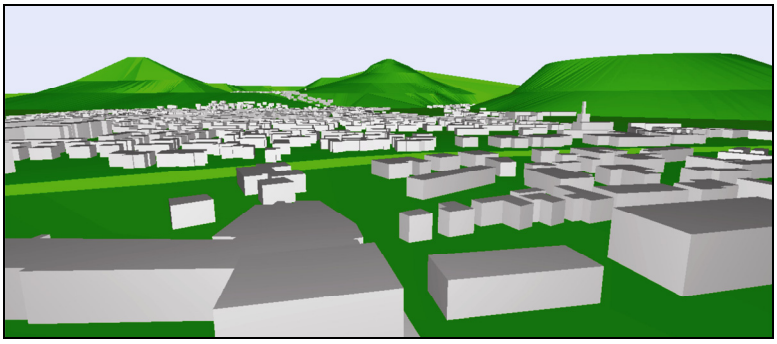

Fig. 2. *Example of the 3D model used.*

After entering, the input data follows the 3D Model of Baia Mare. In most of the city, the terrain has been considered as flat. Only on the north side of town, the terrain height was modeled because of the significant difference in ground level.

The Săsar river corridor that runs through the city from east to west was also represented. From the values on the position of buildings can be made and three-dimensional model for them, assigning values to the height of buildings. Because we did not have GIS data available about buildings (location and height), for the strategic noise map in Baia Mare, each individual building was digitally constructed.

In the absence of precise data about height of the buildings it was done according to the Guide MMGA 678/2006 (Ordinul MMGA 678/2006) high-resolution ortho-pho-tographs at suitable scale were used (1:1000) in order to find out the number of levels of each building (for blocks of flats). Considering the average height of a floor has a value of 3 meters, total height was determined for each block of flats. Regarding the houses due to high complexity of determining the height for each one, it was chosen the same height for all buildings respectively 5 meters.

Noise map

In order to be represented on the noise map, the different sound intensity levels are represented by a color code.

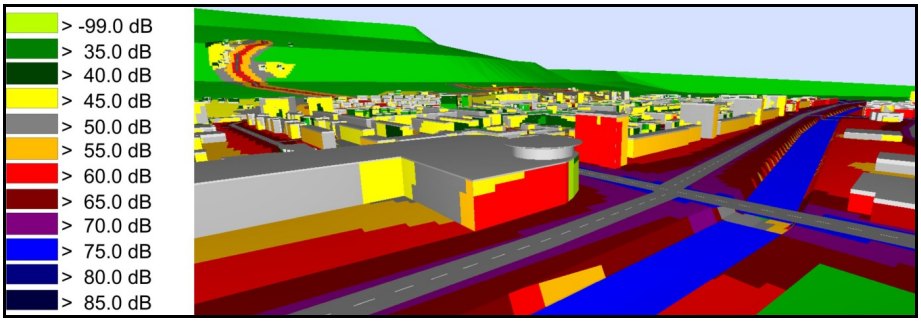

Fig. 3. *Noise values representation at ground level and building facade (3D model)*

Next, we made the building assessment regarding the noise exposure on the facade. For this, the population density calculation was made. No information was available on the number of residents in each building separately. After this step it was obtained the number of people exposed to noise at different sound intensity levels with an interval of 5 dB (decibels). Is very important to know the number of people affected in order to take a measures, to limit the impact of traffic noise, such as restricting the heavy vehicles in some areas, or using sound barriers, like trees for example.

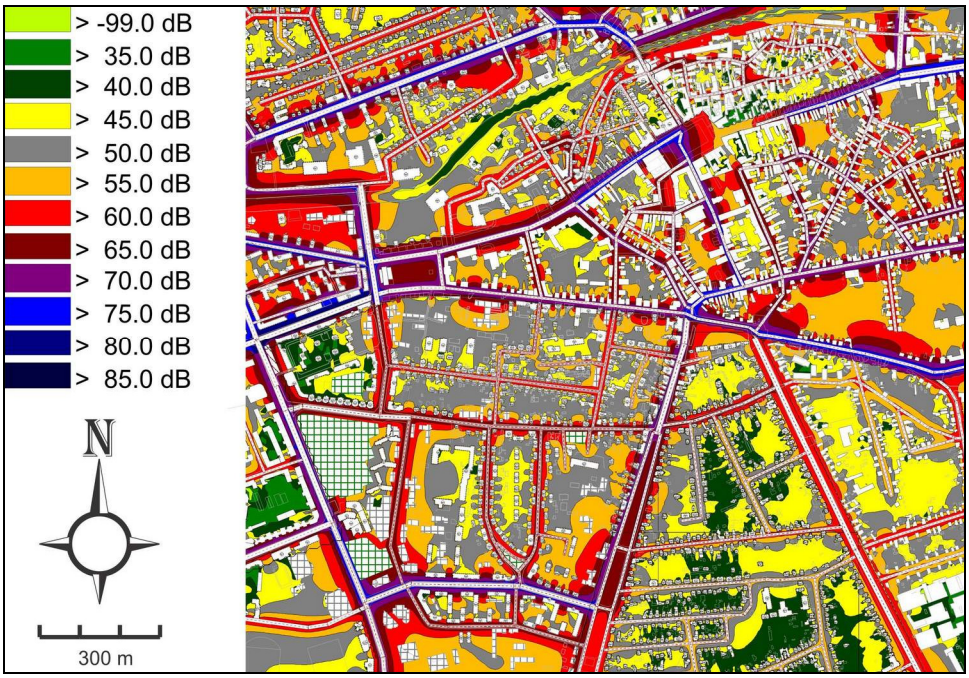

Fig. 4. *Noise map resulted for city center (L_{day})*

Following the completion of the noise map, it may be observed on the main arteries net high noise levels (represented whit colors from red to purple and blue). By comparison, in the residential areas, where low noise levels are seen in the nuances of ocher, yellow and even green. One can see that in many areas, although not very large at distances from a high traffic street, behind the buildings the noise level is much lower than at facade oriented towards the street. This is the screening effect that any sound barrier makes, buildings included. The higher the building, the more obvious this effect is. The figure below illustrates very well this phenomenon. The red and brown areas are the position of emission points, in our case, the roads.

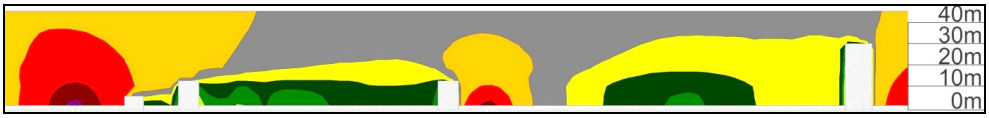

Fig. 5. *Vertical propagation of noise.*

Moreover, the analysis of vertical sections has shown that in many cases, at the upper floors of buildings, we have higher sound level values than at the lower levels of the same building. That being so well represented the spatial distribution of sound. Map analysis of noise map for the night period can take the same observations as for the diurnal period, the difference being that the noise levels are much lower, due to lower traffic values.

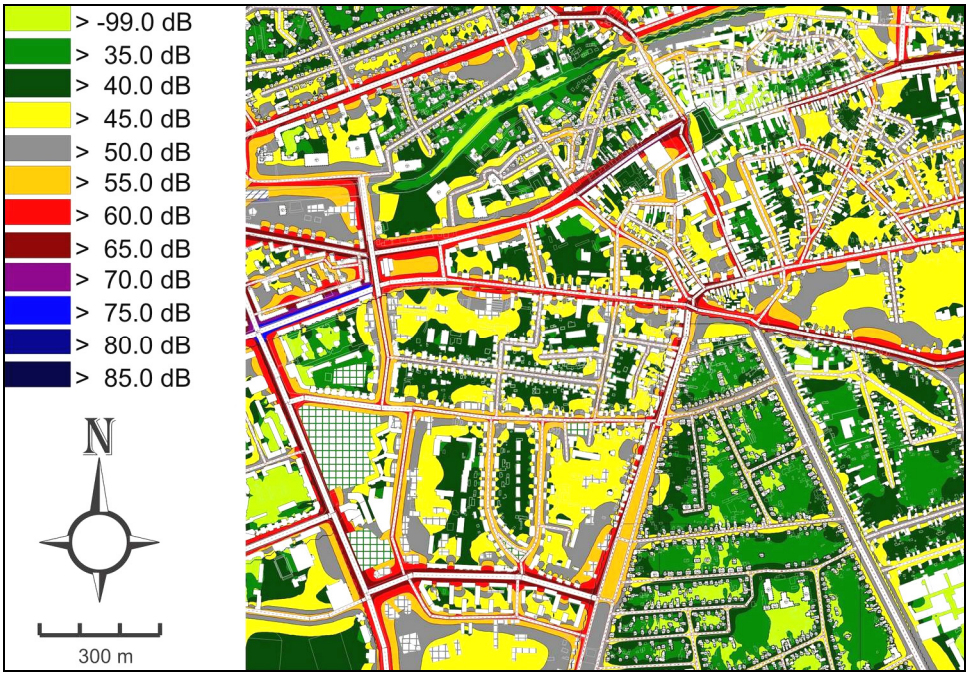

Fig. 6. *Noise map resulted for city center (L_{night})*

CONCLUSIONS

Following the completion of the noise map, and after assessing the population, values have been obtained, which represents the number of people estimated to be exposed to different noise levels.

City population is estimated at a total of 136 900 inhabitants in 2008.

From the research we obtained the percentage of people living in quiet areas, were the sound levels do not exceed 45 decibels during daytime and 35 decibels during nighttime. The results are quite low, 11.5 for the day and 11.4 for the night.

According H.G. 321 of 2005, values representing estimates of the population exposed to noise figure are rounded to hundreds.

Table 2. *Number of inhabitants exposed to the different noise levels.*

Sound level (dB)	**Number of inhabitants**		**Number of inhabitants (amounted)**		**Percent from total (%)**	
	L_{day}	L_{night}	L_{day}	L_{night}	L_{day}	L_{night}
45 ← 50	8600	46600	8600	46600	**6.3**	**34.0**
50 ← 55	11700	27000	20300	73600	**8.5**	**19.7**
55 ← 60	25200	31700	45500	105300	**18.4**	**23.2**
60 ← 65	30900	12100	76400	117400	**22.6**	**8.8**
65 ← 70	32000	3500	108400	120900	**23.4**	**2.6**
70 ← 75	9700	400	118100	121300	**7.1**	**0.3**
>75	3100	0	121200	121300	**2.3**	**0.0**
Total	121200	121300	121200	121300	**88.5**	**88.6**

Considering the available inputs, is observed reaching the 70 dB for L_{day} or 60 dB for L_{night} on the street axis of several main roads, which have the most intense traffic flow. We consider that these streets have a significant impact on the population, from the aspect of traffic noise:

București	Mărgeanului
Closca	Motorului
Crisan	Piata Revoluției
Culturii	Reconstructiei
Decebal	Republicii
Electrolizei	Traian
Gheorghe Șincai	Unirii
Hortensiei	Vasile Alecsandri
Independentei	Vasile Lucaciu
Luminisului	Victoriei

The total number of people exposed to levels exceeding these limits is estimated to be 12,800 for daytime (07:00 – 23:00) and 16,000 people for the night (23:00 – 07:00).

According to the study conducted, it was obtained as a result that a large percentage of the population is exposed to a noise level higher than that established under the laws in force at the time of the research.

It should be noted that the values obtained refer to sound level at a distance of 1 m from the facade of the buildings, so the sound intensity felt in buildings can vary depending on the type of sound insulation of each building individually. It should also be taken into account the type of joinery used for the buildings windows.

With these considerations it is stated that for 49.5% of the population during the day, it is estimated an average noise level (up to the threshold value of 65 dB), and 32.8% at levels that exceed this value.

In the estimates for the overnight, we have 53.7% of the population exposed to noise levels of up to 55 dB and 34.9 percent of the population estimated to be exposed to levels between 55-75dB.

Regarding accuracy questions: using the prediction software only does not mean that the noise levels are accurate; they are based on predictions and mathematical models. In a further part of the research, this map should be calibrated by sound measurements in key locations of the city, in order to ensure the accuracy of the data provided.

Acknowledgments. Thanks are due to Mr. Vasile Barbul, city manager at Baia Mare town hall, who kindly provided the information required in this study.

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STUDIA UBB AMBIENTUM, LVI, 1, 2011, pp. 15-21

STUDIES ON PH AND POWER OF A MICROBIAL FUEL CELL

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ABSTRACT. The microbial fuel cell (MFC) is considered to be an unconventional device of electrical power generation through its ability to oxidize organic matter in a biodegradable manner and in an anaerobic way. The aim of the current paper was the monitoring of pH in three microbial fuel cells, in the anodic and cathodic chambers of the cells for an overall period of time of 190 days. At the same time power generation was monitored, being influenced by the feeding cycles of the MFCs. The majority of the fuel cells had a feeding period of 7 days at 10 ml of sodium acetate 1M. We could observe the increase in power when the anode chamber would receive a new dose of nutrient and also predict when the bacteria in the anode chamber consumed the sodium acetate by looking at the decrease in power values. Two of the anodic chambers were filled with active sludge in excess, while the remaining anodic chamber had digested concentrated sludge. The two types of sludge used in these cells came from the wastewater treatment plant from Someseni, Cluj Napoca. The three cells, named A1, A2, A3 were monitored. In our studies we used two types of solutions for the cathode chambers. Two of the MFCs, named A1 and A3, contained water with a pH of approximately 7, in which we added 1 % NaCl. The other MFC, A2 contained a type of algae *Synechocystis* that would be kept under artificial light for several hours every day.

Key words: *microbial fuel cell, pH, power generation*

INTRODUCTION

Microbial fuel cells have been first used in 1910, when professor Michael Cresse Potter introduced the first MFC using *Escherichia coli (E.coli)* and platinum metal electrodes (Potter, 1911). However, the subject remained relatively unexplored until the early 1990s due to the fact that at the time fossil fuel based energy was still cheap whereas MFCs were not efficient and did not have long-term stability. Although interest in MFCs recovered in the 1990s, it was not until the breakthrough in 1999 when it was recognized that mediators did not need to be added (Kim et al. 2002).

The way a microbial fuel cell works is that "microorganisms degrade organic matter thus producing electrons that go through respiratory enzymes in the cell and make energy for the cell in the form of ATP. The electrons are then released to a terminal electron acceptor (TEA), which accepts the electrons exogenously (outside the cell) to a TEA such as a metal oxide like iron oxide. It is these bacteria that can exogenously transfer electrons, called *exoelectrogens*, that can be used to produce power in an MFC" (Logan, 2008).

In an MFC it is important to maintain the pH of the anode feed solution in order to ensure the proper growth of the microbes that inhabit the anode chamber. Another reason why the pH must be monitored constantly is because of the reactions occurring between the anode and cathode chambers. If the pH values vary too much, it can lead to an abrupt halt of the growth and metabolism of the microorganisms. This can be explained in many ways, one of them being the change in shape of proteins because of the presence of more hydrogen ions. If the modified proteins stops performing a vital function, the normal functioning and even the survival of the microbes can be at risk.

It would only seem normal to believe that since the cathode reactions in MFCs consume protons in equal amount as electrons, that the protons are transferred through the ion exchange membrane. This way electro-neutrality can be observed without pH changes at the cathode. However, MFCs function near neutral pH in the anode and cathode chambers, thus causing the concentration of cations other than protons (Na^+, K^+, NH_4) to be 10^5 higher than H^+ ions in solution. This significantly affects MFC performance (Barron et al.).

When the substrate degrades, protons are produced by the bacteria in the anode chamber after which they are transported and eventually consumed at the cathode. Still, if because of the competition and concentration gradients, protons cannot migrate at a sufficient rate to the cathode, the pH will decrease at the anode and increase at the cathode. The pH decrease means damage for the bacterial respiration, and, therefore, current generation.

MATERIALS AND METHODS

In the experiment three two-chamber MFC were monitored (Fig.1).

- Two plastic recipients (biological cultures recipients) with a volume of 250 ml;
- Two cylindrical electrodes: graphite anode and cathode with Palladium as a catalyst, both electrodes having a length of 10.5 cm and 6 mm in diameter;
- One variable resistor MEGATRON POTENTIOMETER type 2510 (maximum resistance of 10 kΩ);
- Voltmeter type MAS830 MASTECH;

- Ammeter type PeakTech 3340DMM;
- The device we used to measure the pH values was a Consort NV Turnhout, model C 931.
- The material used for the proton exchange membrane was Nafion purchased from Alfa Aesar, 0.09 mm thick, 2 cm diameter.

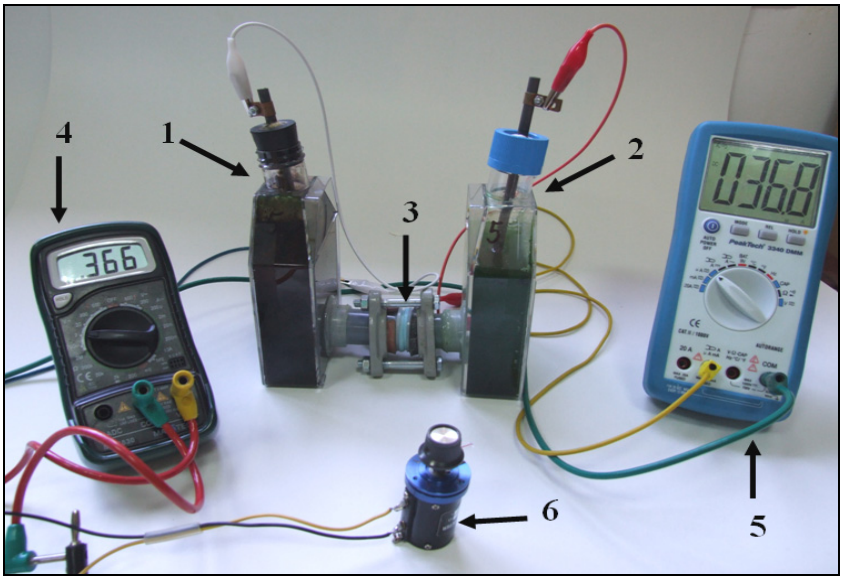

Fig. 1. *Experimental two-chamber MFC: (1) Anode chamber; (2) Cathode chamber; (3) Nafion membrane; (4) Voltmeter; (5) Ammeter; (6) External resistance.*

All three anode chambers of the studied MFCs had sludge from the wastewater treatment plant Someseni from Cluj Napoca. There were two types of sludge that were used as substrate for the bacteria in the anode chambers (Table 1).

Table 1. *Types of substances used in the experimental microbial fuel cells*

Microbial fuel cell	Type of sludge in the anode chamber	Type of catalyst in the cathode chamber
A1	Active sludge in excess	Distilled water + 1% NaCl
A2	Active sludge in excess	Synechocystis sp.
A3	Digested concentrated sludge	Distilled water + 1% NaCl

We used two types of solutions for the cathode chambers. Two of the MFCs, named A1 and A3, contained distilled water with a pH of approximately 7, in which we added 1% NaCl. The other MFC, A2 contained a type of algae *Synechocystis* that would be kept under artificial light for several hours every day. *Synechocistis* is a cyano bacteria, also known as blue-green algae (Fey, 1983). The pH of the algae solutions would vary between 9.6-9.8 in A2. We measured the pH of *Synechocystis* in its natural environment and it had a value of 10.48.

RESULTS AND DISCUSSION

We monitored in parallel the evolution of power and pH in the three MFCs. The A1 MFC was kept under observation for a period of approximately 40 days. During this period we fed periodically the bacteria with 10 ml 1 M of sodium acetate that kept the bacteria running. At the same time an equal amount of liquid was taken put from the anode chamber. We could observe that the time needed between two feeding cycles would be approximately 7 days (Fig. 2).

During the same period in which we measured the power generation, pH in A1 was also monitored.

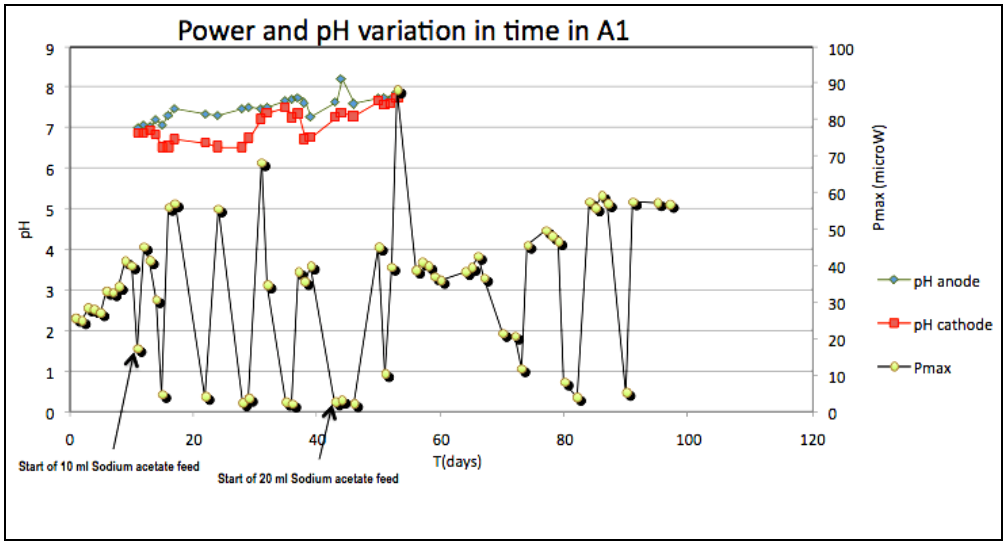

Fig. 2. *Graphics of the variation in time of pH and power in MFC A1.*

On the 36th day the sodium acetate quantity was increased in order to see if there would be any differences in the performance of the MFC. On this day the bacteria was fed 20 ml of sodium acetate instead of 10 ml.

The second MFC observed was A2 (Fig. 3). During the first 126 days the bacteria at the anode were fed with 10 ml of sodium acetate 1 M at approximately a week distance between feeding cycles. On the 127th days of observation we started giving them a larger dose of sodium acetate just like in A1 (20 ml 1M). This proved to react very well to this new way of life in that after the first day of nutrient it would take almost a month until another dose of nutrient would be required.

In terms of pH we could say that even without a pH buffer, the values remained relatively stable and did not present any disturbance in their progress.

The A3 MFC studied in this paper was different from the rest because it was the only one that used digested concentrated sludge (Fig. 4). Like A1 and A2 described earlier, it was fed 10 ml of sodium acetate once every 7 days for a period of 116 days. On the 117th day we changed the quantity of sodium acetate that was fed to the bacteria, from 10 ml to 20 ml.

The immediate response was the increase in time of the bacterial activity. At first the period between two feeding cycles grew from 7 days to 10 days and eventually to two weeks.

The pH suffered some alterations, in particular on the 13th day of pH observation that coincided with the 102nd day of power observation. Thus, the pH in the cathode chamber decreased abruptly and it took the addition of 1 g of salt to get it back on track. The water from the cathode chamber was changed once again, after 10 days from the previous modification.

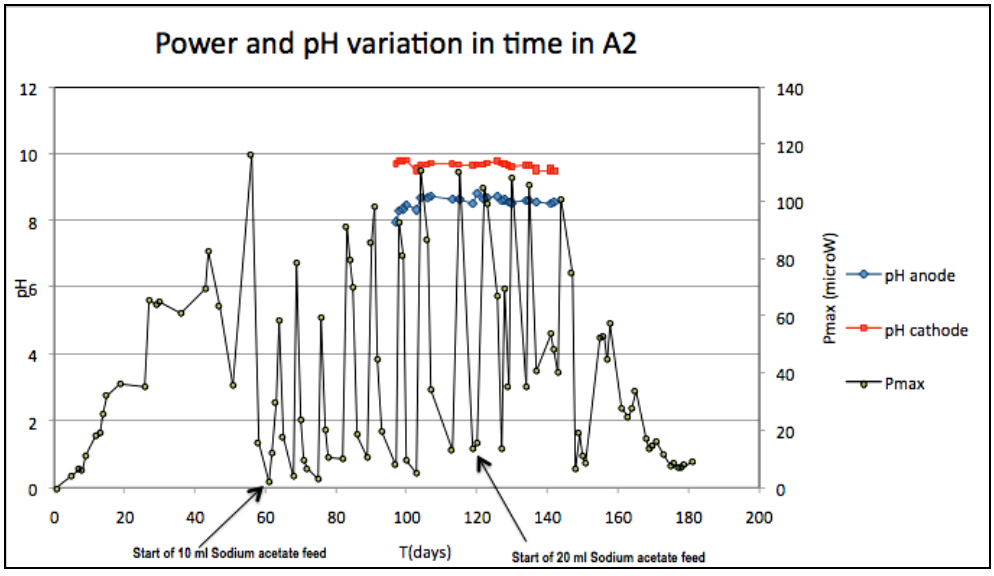

Fig. 3. *Graphics of the variation of pH and power in A2 in time.*

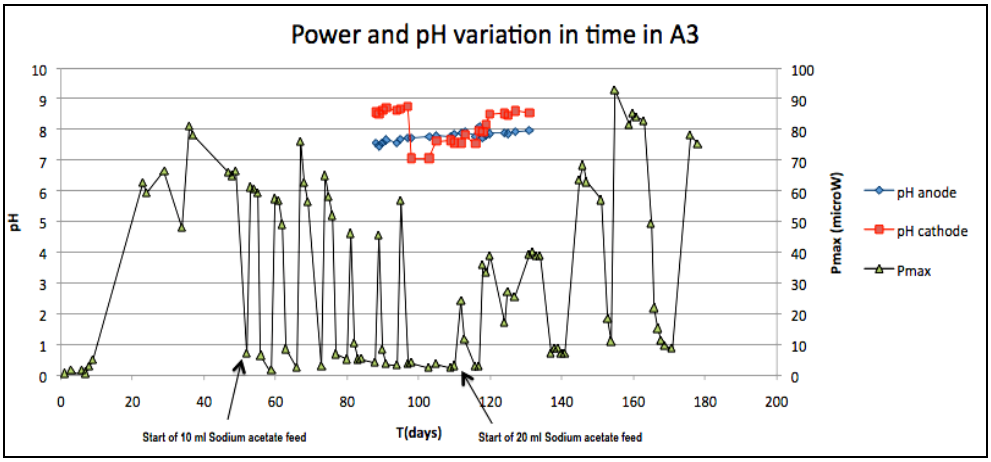

Fig. 4. *Graphics of the variation of pH and power in A3 in time.*

CONCLUSIONS

Although we did not use any buffer solutions to adjust the variations in pH, the modifications that appeared in pH values were capable of correlation with the external influences that were exerted on the MFCs.

We can conclude from the Figs.2, 3, 4 that although the amount of fuel in the anode chamber was doubled, this did not cause an increase in power generation, while the time needed for fuel consumption was doubled.

The maximum power in all three cells under observation was relatively the same; however digested sludge seems to be better than active sludge in excess for water purification, since it consumes the same portion of fuel in shorter time, Table 2.

Table 2. *Feeding cycles in MFCs based on the amount of nutrient.*

Cell	Feeding cycle for 10 ml	Feeding cycle for 20 ml
A1	7 days	14 days
A2	7 days	15 days
A3	7 days	13 days

Overall power density in the cells reached 200 mW/m^2 as opposed to other studies where power density reached 1030 mW/m^2 (Jong et al. 2006).

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STUDIA UBB AMBIENTUM, LVI, 1, 2011, pp. 23-29

RADON SYSTEM OF IRRADIATION IN VITRO (RADOSIV 2)

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ABSTRACT. The potential hazard of exposure of the general population at working places and in homes to radon (222Rn) and its decay products are based on quantification of induced aberrations at DNA level. So, the relationship between radiation and the induced effects to this kind of radiation is very important. In Radon exposure, the effects of low doses are usually much smaller than those for high doses, making it much more difficult to assess risks/effects due to inherent methodological/sensitivity of detection limits. *RADOSIV 2* give us the possibility to study different kind of biological sample, at different doses of alpha particle, respecting the time interval, starting from very low concentrations until higher Radon concentrations. In this way are facilitate the research in biology, radiation biology, and radiation physics by modeling and improving understanding of molecular, cellular mechanisms of both cancer and non-cancer diseases induced by radiation.

Key words: *Radon exposure, experimental setup, radiation*

INTRODUCTION

The presence of the most alpha emitters in the environment occurs naturally. For example, uranium-238, radium-226, and other members of the uranium decay series, give of alpha particles. These are present in varying amounts in nearly all rocks, soils, and water. However, the human activity can create or worsen the potential for exposure of people and contamination of various environmental media. For example, uranium-mining wastes, known as uranium mill tailings, have high concentrations of uranium and radium (Melody, 2011).

Exposure is present by the contact between a target organism and a pollutant at the outer boundary of the organism. Exposure can quantify as the amount of the pollutant available at the boundary of the receptor organism per specified period.

From an exposure-modeling standpoint, the principal goal is to estimate exposure as a function of both; the relevant human factors and the measured or estimated pollutant concentrations in the contact or exposure media (Baias, 2010).

During decay, radon emits high linear energy transfer (LET) alpha particles that cause DNA double strand breaks of high complexity and reduced reparability. Underground miners and people living in areas with elevated background radiation levels are exposed to significantly higher levels of radon (BEIR VI, 1999; Singh, 2002; Hofmann, 1986).

Most facilities from database, proposed for study of in vitro irradiation with Radon were designed to expose cells to doses above environmental and occupational exposures. In fact, the main priorities in area of low doses are here the step-wise elucidation of the mechanisms of radiation-induced stress responses and their impact on radiation induced cancers and non-cancer diseases. To achieve this Melody Program proposed starting research with radiation-specific effects, radiation-induced molecular, biological and pathological effects involving a systems biology approach as well as molecular epidemiology and mathematical modelling in order to come up with more solid low-dose health risk assessments.

In recent years, the development and application of microbeam facilities with heavy ions and Radon alpha particle has gained increasing interest among radiobiologists (Brenner, 2002; Prise, 2002; Folkard, 2009). These allow irradiation of the target cells with an exact number of particles where the linear energy transfer (LET) can be adjusted by the choice of the ion species and the ion energy, (Hauptner, 2004).

Many radon chambers, has been proposed until now, in order to provide a reference atmosphere for the calibration of radon concentration detectors (Vargas, 2004; Shweikani, 2005; Lee, 2004), but these chambers could not be used for expose the biological sample, e.g. cells.

Hamza et al. (2008) has done an irradiation in vitro of human blood and analyze the chromosomal aberrations induced to radon and descendents in further lymphocytes, using a portable irradiation assembly. The system has had a 4p geometry for uniform irradiation, and has provide a versatile and convenient facility for irradiation of whole blood cells in suspension or media. Has been possibly to irradiate the blood samples with radon concentrations ranging from 122 to 1 593 210 kBq/m^3.

We propose in this article an irradiation system with alpha particle, in vitro exposure to radon and its progenies, for study a number of phenomena that challenge the classical view of how ionising radiation interacts with biological sample. In our future studies, a standardized simple method will be need for quantify the exposure effect also, through cytogenetic analysis.

MATERIALS AND METHODS

Our in Vitro Exposure System has a cubic shape with sides of 50 cm. Made of metal, except one wall of glass; allow observation of samples during the experiment.

Each metal wall has a pocket on the outside which can contain (optional), a radioactive source. In this experiment, the irradiation was made keeping in the pocket, the pitchblende ore. Radon gas inside was generate by this source. At bottom of system can be seen a rotating disc, which can be turn around for introduce inside different cultures, according with the interest doses, Figure 1. The indoor doses were monitored by means of a Lucas Cell Radon Scout, Radim 2P, Radim 3A, Rad 7 and Sarad Radon detector.

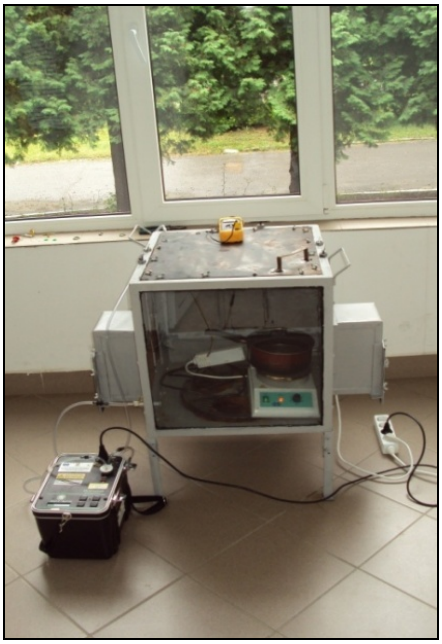

Fig. 1. *In Vitro Irradiation System, RADOSIV 2.*

RESULTS

RADOSIV 2 give us the possibility to exposure for different irradiation windows and for different Radon concentrations.

The continuous increasing of Radon concentration has been registered with Sarad Radon detector, figure 2. Also, in table 1 are presented comparative the concentrations, the relative humidity and the temperature, in each registered moment during the experiment.

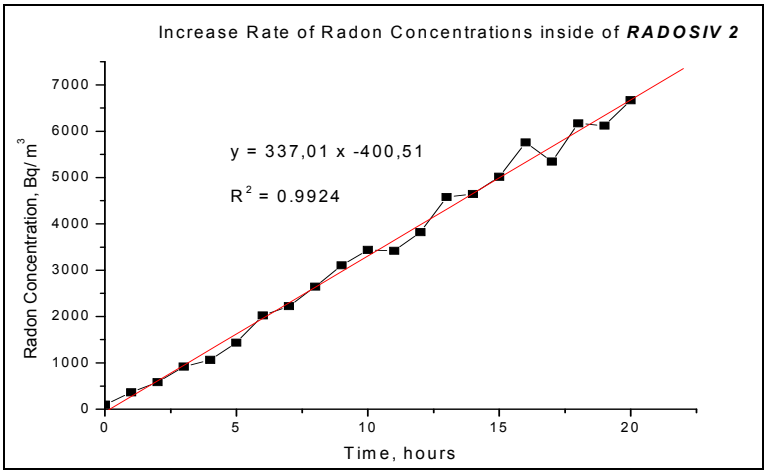

Fig. 2. *Linear increasing of Radon concentration, inside of our experimental setup.*

Table 1. *Radon-Scout SN: 453*

Time	Radon Bq/m^3	Error %	Temp. °C	Rel. Hum. %
19.07.2011 14:40	96	35	24.0	68
19.07.2011 15:40	364	16	24.5	65
19.07.201116:40	584	13	24.5	64
19.07.2011 17:40	920	10	24.5	63
19.07.2011 18:40	1063	9	24,5	63
19.07.2011 19:40	1437	8	24.5	62
19.07.2011 20:40	2021	7	24.5	62
19.07.2011 21:40	2222	7	24.5	62
19.07.2011 22:40	2644	6	24.5	62
19.07.2011 23:40	3103	6	24.5	62
20.07.2011 00:40	3439	5	24.5	62
20.07.2011 01:40	3420	5	24.5	62
20.07.2011 02:40	3822	5	24.5	62
20.07.2011 03:40	4579	5	24.5	62
20.07.2011 04:40	4646	5	24.5	62
20.07.2011 05:40	5019	4	24.0	62
20.07.2011 06:40	5757	4	24.0	62
20.07.2011 07:40	5345	4	24.0	62
20.07.2011 08:40	6169	4	24.0	62
20.07.2011 09:40	6121	4	24.0	62
20.07.2011 10:40	6667	4	24.5	62

The Radon'concetration inside of Radosiv 2, increase linear with an average per hour of 328.55 Bq/m^3.

DISCUSSION

RADOSIV 2 - Why is need?

It has been known that ionising radiation can damage living cells and tissues for over 100 years. Despite this, the effects of radiations at low doses remain poorly understood. At high doses, above a few gray, it is likely that exposed cells will be sterilised, or die. At lower doses, most cells survive, but with the possibility of mis-repair, leading to carcinogenesis. Elucidating the shapes of low-dose response relationships, resolving the question of thresholds and establishment of dosimetric tools in individuals (also as part of a cohort) is paramount to resolving questions of risk for both populations and individuals. Much is known about radiation-induced cancer in humans and animal models but this need to be pursued particularly at low doses.

Risk estimates cannot be reliably derived from epidemiological data and a linear extrapolation to zero-effect at zero-dose is applied (the so-called 'linear no-threshold' model). Folkard (2009) and Gunther et al. (2005), observed a good correlation between the physically calculated dose to bone marrow and the biologically estimated dose, when the levels of indoor radon concentrations was up to ≥ 5000 Bq/m^3.

In accordance with BEIR VI, domestic radon concentration of 20 Bq/m^3 results in an annual lung dose of 500 μGy, whereas blood receives an annual dose of only about 1 μGy. The annual radon and thoron derived dose to active marrow for an adult was calculated to be 90 and 30 μSv, respectively (Richardson, 1991).

Reports on the biological effects of alpha radiation at doses below 65 mGy remain controversial with some reporting increased chromosome aberrations at doses between 30 and 50 mGy. Hence there is a need to develop the irradiation methods to study the effects at these doses of concern (Pohl-Ruling, 2000).

In vitro irradiation with Radon gas – ancient studies

The lowest and highest activities computed in Hamza's study were 122 and 1 593 210 kBq/m^3, respectively, who made a portable, in vitro radon irradiation assembly by bubbling the gas through the blood. The delivering alpha radiation doses were between 0.01 and 127 mGy (Zareena, 2008). A few drawbacks has been notice, such is: technical aspect bounding to pumping of air to expel radon from the source chamber into the syringe causes dilution of radon, repetability due to difficulty in assess the doses when a pre-determined exposures was made, also although the Lucas cell is reusable, some limitations was observed with respect to its re-usage - Radon progeny tend to adhere to the ZnS coating and hence a new irradiation needs to be physically and thoroughly cleaned before. Also, was observed that while a new Lucas cell gave a background reading below 10 Bq, the counts in a cleaned cell could not be brought below 1000 Bq. A new ZnS sheet coating or a new cell culture was preferably while the planning of experiments was made for low-level activity.

CONCLUSIONS

Our vitro system ***RADOSIV 2*** offer the advantage to control various parameters such as exposure, temperature, relative humidity and Radon concentration inside, due to facility to opening that three outside pocket. The radiation-induced molecular, biological, and pathological effects in biological systems can be study starting with low environmental exposure, which means zero-effect or zero-dose until the higher doses of 6667 Bq/m^3, avoiding the confounding factors that mask epidemiological surveys. Also, the induced irradiation effect could be evaluate as consequence of Radon exposure, exposure windows smaller than equilibrium, (3 h time) or as a concequence of its progeny when exposure windows are higher.

The interaction of alpha particles with biological system is a consequence of its deposition. Due to these aspects in the future, research needs to clarify the dependence on track structure and microdosimetric features of the tracks' spatial distributions of energy deposition events. This needs to consider the interplay between the spectrums of damage induced and its repair ability and kinetics in modulating the shape of the dose response curve. This feeds into improving the scientific basis of ICRP's WR values. Biophysical models should be based on experimental evidence and lead to reliable prediction and interplay between experiments and models.

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RADON DIAGNOSTIC MEASUREMENTS IN A PILOT HOUSE FROM ŞTEI - BĂIŢA REGION, ROMANIA

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ABSTRACT. The exposure to radon and its decay products represents the most frequent cause for lung cancer, after smoking. The association between radon exposure in dwellings and lung cancer risk has been already known and confirmed by several surveys and pooled analysis of epidemiological studies world-wide. A follow-up study of radon levels has been carried out in 305 houses during 2010-2011, in four villages in Ştei-Băiţa region (Băiţa, Nucet, Fînaţe and Cîmpani) located near the old uranium mines in NW part of Romania. About 10% of investigated houses presents in at least one ground floor room values of indoor radon concentration higher than 600 $Bq \cdot m^{-3}$. Diagnosis of radon sources and higher indoor radon levels was carried out in 20 houses in Ştei-Băiţa region and a pilot house was selected to develops, tests and implements the most effective radon mitigation techniques.

Key words: *indoor radon, CR-39 nuclear track detector, radon-prone area, remedial techniques.*

INTRODUCTION

Radon gas represents worldwide the most important source of ionizing radiation of natural origin and the major contributor to the natural radiation dose received by the population (Cosma and Jurcut, 1996; Cosma et al., 2009).

A comprehensive radon survey has been carried out around Băița area, (Transylvania, Romania), in four localities (Băița, Nucet, Fînațe, Cîmpani) situated near of an old uranium mines in Roumania. Indoor radon concentrations were measured seasonally in 1200 ground floor rooms of 305 family houses, over the whole year, using CR-39 radon track detectors (Miles and Howarth, 2000). Measurements were carried out from December of 2010 until June of 2011.

An annual average indoor radon exposure of 287 $Bq \cdot m^{-3} \pm 20$ % was estimated, with maximum values of about 4000 $Bq \cdot m^{-3}$. About 10% of investigated houses present in at least one ground floor room indoor radon concentration values higher than 600 $Bq \cdot m^{-3}$ (Cucos et al., 2011).

The high values of indoor radon concentrations found in these villages make this region a *radon-prone area* (Cosma et al., 2009; Sainz et al., 2009). Statistical analysis of the measured data confirms that the levels of indoor radon concentrations depend primarily on the underlying soil and building characteristics (Sainz et al. 2009: Cosma et al. in press). In 20 houses in which indoor radon levels exceeded 600 $Bq \cdot m^{-3}$, radon was further investigated, in order to implement remedial methods (Cosma et al., 2011).

In order to developing, testing and implement the most effective radon mitigation techniques, a pilot house was selected. The location of it is in Fanate, no. 116A (Bihor county). The house was built between 1976-1978, and the used building material was gravel, stone, sand and ballast from Criş-river, passes closed to uranium mine. The area of the building site is 3198 m², and the part of the house for radon investigations and remediation consist from two bedrooms, one living, one bathroom and one cellar. Detailed radon diagnostic measurements were performed around this house during 2011 (Neznal and Neznal, report, 2011).

MATERIAL AND METHODS

Detailed radon diagnostic measurements of a familiar house consist from: inspection of the house; determination of radon index of the building site; detection of leakages in the contact between the subsoil and the building; continual and integral measurements of indoor radon concentration; determination of radon concentration of water sources; and measurements of external gamma radiation (gamma dose rate).

Inspection of the house represents the first step of radon diagnostics. The inspection is made with the goal to summarize relevant information on potential radon sources and of factors that influence indoor radon concentrations: age of the building; building materials and their origin; presence of filling (mainly in the sub-floor

region, and the origin of the filling); type and quality of the floors (mainly in the contact between the subsoil and the building); installations (tubes, pipes) going through the floors; disposition of the rooms in the house; type of the stairways (closed, or open), information on the way; how different rooms in the house are used; type of the heating system, type of the windows and their tightness; and source of drinking water used in the house.

Method of determination the *radon index of the building site* is based on direct in-situ measurements of two parameters: soil-gas radon concentration and permeability of soil, in the surroundings of the house, both in the depth of 0.8 m, below the ground surface. Detailed description of the method is given in (Neznal et al., 2004; Barnet et al., 2008).

For soil-gas sampling, small diameter hollow steel probes with a free sharpened lower end („lost tip“) are used. Samples are collected by a syringe that is connected to the upper end of the probe. Radon concentration of the collected soil-gas samples was measured using radon detectors based on scintillation techniques with Lucas cells (scintillometers LUK, SISIE). By this, the collected soil-gas samples are transferred into previously evacuated Lucas cells (volume of 125 mL) of the detectors, and measured the activity-concentration of radon gas.

For the soil permeability measurements, the same sampling probes were used, in connection with the RADON-JOK permeameter. Radon gas was extracted from the same depth, 0.8 m in soil. Both parameters, radon concentration from soil and soil permeability are measured in 15 measuring points, when radon index of the building site for a typical family house is evaluated. As for the soil-gas radon concentrations, values lower than 1.0 $kBq \cdot m^{-3}$ were excluded from statistical evaluation. As for permeabilities, values lower, or higher than the auxiliary limit, were replaced by the auxiliary limit.

The decisive values for assessing the radon index of the building site using a so-called radon potential model (RP), was the 3rd quartile (75th percentile) of the soil-gas radon concentration data set ($C_{\mathbf{Rn,75}}$) and the 3rd quartile of the permeability data set (k_{75}), where:

$$RP = (C_{Rn,75} - 1) / (- \log k_{75} - 10)$$

According to the model, the categories of radon index are the follow: if $RP < 10$, the radon index of the building site is low; if $10 \leq RP < 35$, the radon index of the building site is medium; and if $RP \geq 35$, the radon index of the building site is high (Neznal et al., 2004; Barnet et al., 2008).

Leakages in the contact between the subsoil and the building are detected by collecting air samples in places where leakages may appear (cracks, uptightness beside tubes going through the floors, etc.). Long needles and syringes are used

for sampling. Radon concentrations from samples are then measured using the same instrumentation as for the determination of radon concentrations from soil gas (for radon index of the building site). If radon concentration of the sample is substantially higher than the indoor radon concentration, the presence of a leakage is confirmed. Values greater than 1 $kBq \cdot m^{-3}$ confirms the presence of leakages. Such points have been found mainly in the bedroom 1, but also in the bedroom 2 and in the lobby. (Neznal and Neznal, report, 2011).

Continual and integral measurements of indoor radon concentration. Results of simultaneous continual and/or integral measurements of indoor radon concentrations in different parts (rooms) of the house enable to evaluate the most important radon sources and radon pathways in the building. RADON v.o.s. is equipped by continual monitors of radon concentration of different types (RADIM, based on semiconductor detection of the decays of radon and progenies), as well as by a system for integral measurement of radon concentration in air (RM-1, with electret detectors) (Neznal and Neznal, report, 2011).

Radon concentration in the source of drinking water used in the house is controlled by an emanometric method. Water is collected into a glass cell, then after radon gas from the sample is transferred into a previously evacuated Lucas cell (volume of 600 ml) and measured using a scintillation detector (device LUK) (Neznal and Neznal, report, 2011).

External gamma radiation. The main goal of gamma dose-rate measurement in the house is to identify any inhomogenities of gamma radiation field and the detection of any gamma anomalies, which indicate the presence of radioactive materials in the walls, in the floors or in the filling. For the measurement of gamma dose rate, RADON v.o.s. uses a portable radiometer (DC 3E-98).

All this devices (radon detectors) are regularly verified in the metrological centre by the National Institute for Radiological, Chemical and Biological Protection, Praha, and in the Czech Metrological Institute Praha, in accordance with the Czech Law on metrology. (Neznal and Neznal, report, 2011).

RESULTS AND DISCUSSIONS

Inspection of the house

The family house Fanate 116A was built between 1976 and 1978. Only a part of the house was used for radon diagnosis investigations (see Fig. 1). It is a ground floor house, with a cellar located below the bedroom no. 2. The dimensions of the cellar is 4 m x 2.5 m.

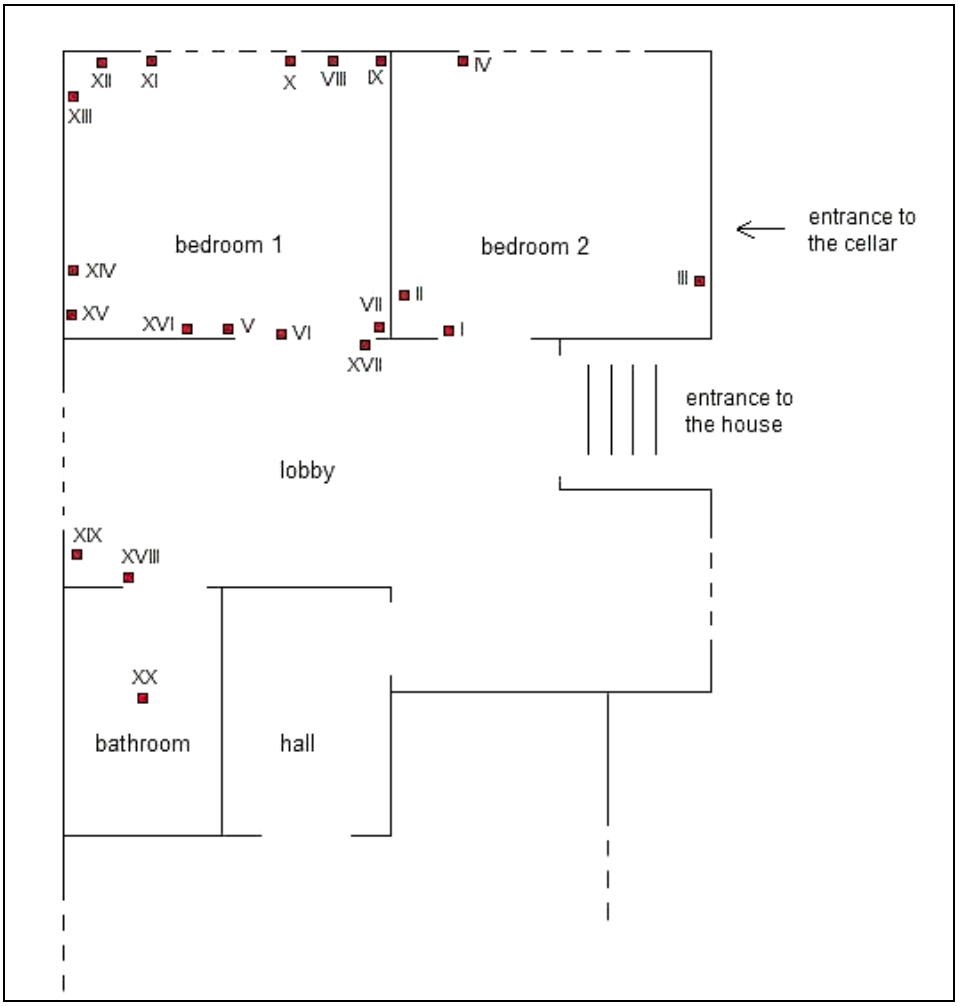

Fig. 1. *Fanate 116A, disposition of the rooms in the measured part of the house, and the distribution of the of leakages points, in the contact between the subsoil and the building - location of measuring points.*

Building materials used for the construction of the house was bricks, stones, sand and ballast from the river; basement - stones from former mining area (Baita-Plai); filling with stones from former mining area and local material (ballast from the river); walls with bricks. The whole house has been reconstructed during last years. The floors are new, made from concrete covered by parquet, or by paving. There are no installations going through the floors in the measured part of the house. Since 2009, the house is heated by a central heating (boiler). The windows are new and tight. Drinking water used in the house comes from a municipal water supply.

Nowdays (during radon investigations and remedial actions), the measured part of the house is not used for living. During diagnostic measurements, the rooms were tempered, uninhabited and mostly closed.

Radon index of the building site

Results of direct in situ measurements of soil-gas radon concentration (C_{Rn}) and of the permeability of soil (k) in the surroundings of the house are presented in Table 1.

Table 1. *Fanate 116A - Radon index of the building site*

Measuring point	**C_{Rn} (kBq·m^{-3})**	**k (*10^{-11}) (m^2)**
1	0,6	1,4
2	8,9	< 0,00052
3	2,1	1,2
4	0,3	1,6
5	2,2	0,78
6	2,5	0,37
7	10,7	< 0,00052
8	485,3	1,6
9	32,6	< 0,00052
10	12,2	0,68
11	40,9	< 0,00052
12	96,5	0,99
13	46,2	0,27
14	12,5	< 0,00052
15	16,5	0,42
Evaluation		
75th percentile	**40,9**	**9,9*10^{-12}**
RP	**39,7**	
Radon index	**high (RP ≥ 35)**	

Detection of leakages in the contact between the subsoil and the building

Results of measurements of radon concentration (***C$_{Rn}$***) in air samples collected in places, where contaminated soil-gas may enter into the house (cracks, etc.), are summarized in Table 2. Location of measuring points is presented in Fig. 1.

Table 2. *Fanate 116A - Detection of leakages in the contact between the subsoil and the building*

Measuring point	Description	C_{Rn} (kBq·m^{-3})
I	bedroom 2 - between parquets, 0,05 m from the wall, 0,4 m from the corner near the door	**1,1**
II	bedroom 2 - contact between the floor and the wall, 0,6 m from the corner	0,5
III	bedroom 2 - between parquets, 0,05 m from the wall, 1,5 m from the corner	1,0
IV	bedroom 2 - contact between the floor and the wall, below the window	0,4
V	bedroom 1 - contact between the floor and the wall, near the door	**2,6**
VI	bedroom 1 - in the door to the lobby, below the paving	0,7
VII	bedroom 1 - contact between the floor and the wall, near the corner	**2,5**
VIII	bedroom 1 - contact between the floor and the wall, 0,8 m from the corner	**1,7**
IX	bedroom 1 - contact between the floor and the wall, near the corner	**2,4**
X	bedroom 1 - contact between the floor and the wall, below the window	**1,8**
XI	bedroom 1 - contact between the floor and the wall, below the window	**2,5**
XII	bedroom 1 - contact between the floor and the wall, 0,6 m from the corner	**4,8**
XIII	bedroom 1 - contact between the floor and the wall, 0,5 m from the corner	**2,8**
XIV	bedroom 1 - contact between the floor and the wall, 1,3 m from the corner	**5,8**
XV	bedroom 1 - contact between the floor and the wall, 0,4 m from the corner	**6,7**
XVI	bedroom 1 - contact between the floor and the wall, 0,3 m from the corner	**4,1**
XVII	lobby - near the door	**1,7**
XVIII	lobby - between the paving and the wall, near the door	**4,7**
XIX	lobby - between the paving and the wall, 0,8 m from the corner	0,5
XX	bathroom - gulley	0,5

Continual and integral measurements of indoor radon concentration

Results of simultaneous continual and/or integral measurements of indoor radon concentrations in different parts (rooms) of the house are presented in Fig. 2. During continual measurements, minimas, maximas and averages values of indoor radon concentrations are given in Table 3. In the hall, was a performed only integral measurement, by an average value as result.

Table 3. *Fanate 116A – Minimas, maximas and average values of indoor radon concentrations (C_{Rn})*

Room	Measurement device	Minima C_{Rn} ($Bq \cdot m^{-3}$)	Maxima C_{Rn} ($Bq \cdot m^{-3}$)	Average C_{Rn} ($Bq \cdot m^{-3}$)
cellar	RADIM 5 No. 5	**25**	**2874**	**1131**
bedroom 1	RADIM 3 No. 63	**187**	**1425**	**889**
bedroom 2	RADIM 2P No. 77	**67**	**578**	**330**
lobby	RADIM 2P No. 86	**100**	**546**	**333**
bathroom	RADIM 5 No. 2	**56**	**731**	**395**
hall	RM-1 *	**-**	**-**	**300**

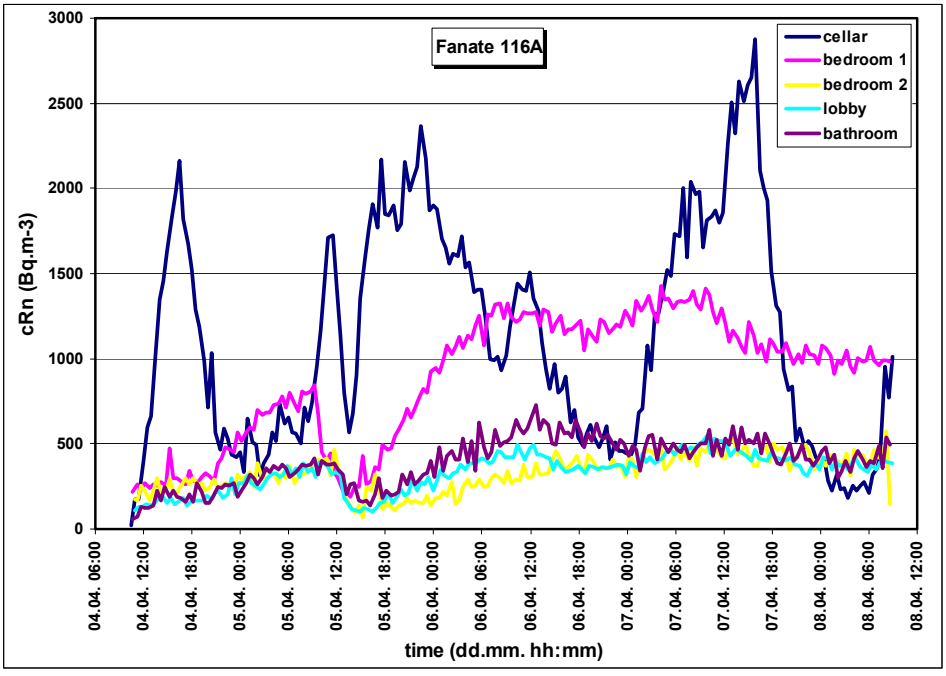

Fig. 2. *Continual measurements of indoor radon concentration*

The highest radon concentrations have been observed in the cellar, but the analysis of temporal changes indicates that there is no significant radon pathway for contaminated air from the cellar to the ground floor rooms. The temporal pattern of radon concentration is similar in all measured ground floor rooms and the indoor radon concentration in bedroom 1 is much higher than the indoor radon concentrations in other ground floor rooms. The main pathway for the penetration of contaminated soil-gas into the indoor environment is therefore probably located in bedroom 1.

Radon concentration in water (drinking water) is low (2,6 $\pm$ 0,1 kBq·m^{-3}).

External gamma radiation

Results of gamma dose rate (*D*) measurements (gamma anomalies) are summarized in Table 4.

Table 4. *Fanate 116A - Gamma anomalies, results of dose rate (**D**) contact measurements*

Description (room)	***D*** **(μGy·h^{-1})**
bedroom 1: hot spot near the window, 0,5 m : 0,5 m from the right corner (view from the door)	**0,74**
lobby: vase on the table near the door to the bathroom (not a fixed part of the construction)	**0,50**
outdoor wall near the entrance, basement	**0,28 - 0,40**

All observed anomalies are local. The background values in the surroundings of the house ranged from 0.14 to 0.17 μGy·h^{-1}. The gamma dose rate near the walls from bricks was comparable to the background, and a little higher values were observed in the cellar, near the basement and on the floors of ground floor rooms (0.17-0.30 μGy·h^{-1}).

CONCLUSIONS

Radon potential (RP = 39,7) indicates high radon index of the building site. Leakages in the contact between the subsoil and the building have been confirmed mainly in the bedroom 1 and in the lobby. The highest indoor radon concentrations have been found in the cellar, bur there is probably no significant radon pathways between the cellar and the ground floor rooms (bedroom 2).

Results of simultaneous indoor radon concentration measurements indicate that the most important radon pathways between the subsoil and the indoor environment are located in the bedroom 1.

Two local gamma anomalies have been found in the basement and in the filling between the floor and the ground - the negative influence of contaminated building materials in the lowest part of the construction thus cannot be neglected.

Radon concentration in drinking water is low.

Due to various sources of radon in soil, indoors, construction material and foundation, the house was chosen as the pilot house, in order to develop and test the most effective radon mitigation methods, during the project.

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STUDIA UBB AMBIENTUM, LVI, 1, 2011, pp. 43-55

RISKS LINKED TO THE HISTORICALLY CONTAMINATED SITES

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ABSTRACT. The PHARE 2006/018-147.03.03/04.07 project includes preparing applications to the European Regional Development Fund (ERDF) for financing three pilot projects to rehabilitate historically contaminated sites.

The main purpose of the pre-selection was to identify eligible projects for financing under the Sectoral Operational Programme Environment, Priority Axis 2, Major Intervention Domain 2 (SOP ENV PA2 MIF2), select three beneficiaries for the pilot projects, and prepare funding applications for them. The pre-selection was based on Romania's National Environmental Protection Agency's (NEPA) Contaminated Sites Inventory System (CoSIS). The three historically contaminated sites identified and selected are located in Cluj County, Dambovita Count and Prahova County.

The Feasibility Study for this the three pilot projecst to be implemented according to FIDIC Yellow Book, in compliance with HG 28/2008 and the 'Applicant's Guide' was prepared. Consortium experts conducted preliminary and detailed investigations (equivalent to Phase I and II Environmental Site Assessment (ESA) as per the American Society for Testing and Materials (ASTM) Standard Practice E 1527-05 respectively (ASTM E1903-97(2002), and internationally accepted procedures for ESA.

The three historically contaminated sites identified and selected were impacted by activities from the following industries: chemical, extractive and processing and pesticide.

Description of the current conditions, site history and historical activities developed on the site were based on the PHASE I and PHASE II Environmental Site Assessment by ASTM and a preliminary Conceptual Site Model (CSM,) prepared to illustrate the principal risk drivers at the contaminated sites.

There were identified and confirmed very clear pollutant linkages between the three contaminated sites (sources) via pathways to receptors as any member of the local community and environment.

Risks associated with all relevant pollutant linkages were to be appropriately reduced by the most expedient remedial option given the sites' constraints.

Key words: *lindane,rehabilitate historically contaminanted sites, risk assessment, HCH.*

INTRODUCTION

The Site used as dump site for hazardous waste known as lindane, is recorded in the Contaminated Sites Inventory data base managed by ANPM and was based on the Identification Questionnaire (Record no. APMCJ00022). Former UCT operated within administrative borders of Turda Municipality, industrial area. The factory operations' commenced in 1913-1914 known as Solvay Soda Factory. After nationalization in late 40's the UCT produced HCH (as a substitute to DDT) and more other 18 chemicals. The former UCT closed its operations in October 1998.

The uncontrolled disposal of HCH waste allowed contaminant's migration outside the site and its transfer in the food chain: the source of transmitting the HCH contaminated ground-water/airborne-pasture/milk/dairy products/human receivers (Lehr et al. 2001).

The lack of safety enclosure area measures has allowed residents to collect the waste with Lindane content and then to trade it in the neighboring localities or even at longer distances (Piatra Neamt – east of Romania) for purposes which have a high risk for human health (using it as insecticide for construction wood or as pesticide for agricultural lands).

Due to the high risk for the residential population in the vicinity of the Site and the environmental damage caused by the potential migration of the possible contaminants, a Detailed Investigation was recommended (Phase II ESA), through which this risk may be proved on the basis of quantitative evaluation of the contaminants in the soil, subsurface soil and groundwater on site.

PHASE I ESA

The Scope of Preliminary Investigation (www.astm.org/Standards/E 1527)

The each site investigation and assessment activities consisted of:

- Review of available historical information pertaining to the Site.
- Review of available records of environmental compliance.
- Visual inspection of the Site to determine past practices or circumstances that may present environmental concerns.
- Visual inspection of the properties within 1000 meters radius of the Site.
- Interviewing persons with significant knowledge of the Site.
- The preparation of conclusions which present an evaluation of the environmental conditions at the Site.

Specific environmental issues addressed in the Phase I ESA included inspection for the presence of the following on, in or under the Site:

- potential sources of soil and groundwater contamination;
- presence of groundwater wells;
- surface anomalies and stressed vegetation;
- chemical and/or liquid handling and storage practices;
- nuisance odours;
- exterior waste management practices;
- fill areas and dumped waste; and
- emissions to air and surface waters.

The Site was visited by experts to undertake the site reconnaissance, which included visual inspection of the sites and the surrounding lands and interviews with the "Site representatives".

Historical land use practices for the Site and the surrounding area were determined by interviewing local authorities, residents, former employees of the chemical plant and reviewing the following sources of information:

- Geiger's Group - Romania address from November 2001 to the Cluj Prefecture;
- Preliminary Study – Terranova SRL, Norr Ltd, Etalon Ba Co Consulting SRL.
- Parliamentary Debates - The Chamber of Deputies' Meeting May 20th, 2003.
- Article from the Local News in Cluj – January 18th, 2007
- Article from Faclia-Independent Newspaper in Cluj- September 2nd, 2009
- Aerial photos (2009)
- Interviews with the residents from the area of interest
- These documents are submitted in the Annexes no 8 through 13.

CONCLUSIONS ON PHASE I ESA

The PHASE I ESA has revealed the following evidence of *recognized environmental conditions* in connection with the Site:

- Most likely impact to the soil (on the surface and subsurface) and groundwater is generated by the potential for contamination with Lindane and heavy metal containing waste. The Site's potentially contaminated areas are shown graphically in Fig.1.
- Materials possibly containing asbestos lead and PCB have not been identified on the Site.

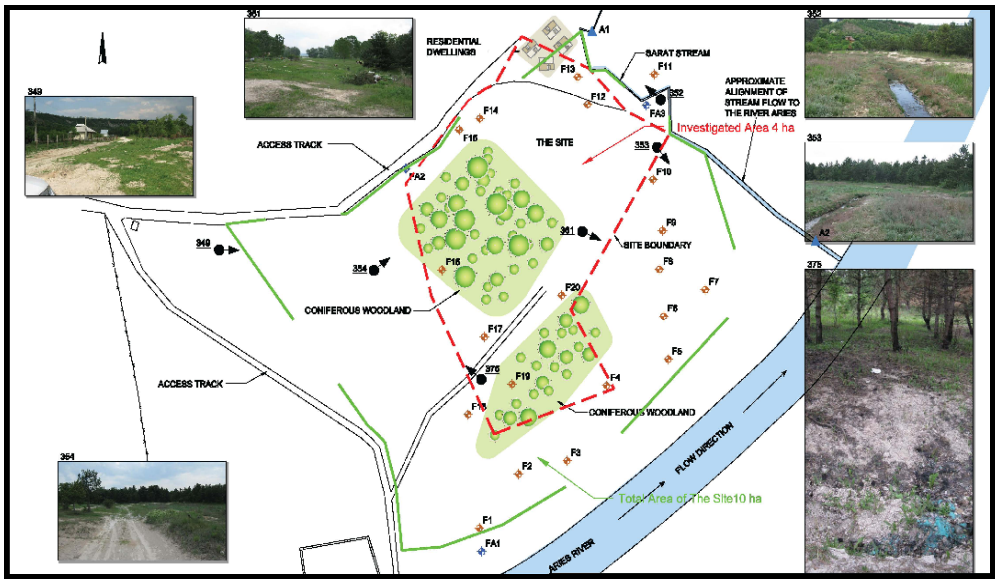

Fig. 1. *Site walk over.*

- The uncontrolled disposal of HCH waste allowed contaminant's migration outside the site and its transfer in the food chain: the source of transmitting the HCH contaminated ground-water/airborne- pasture/milk/dairy products/ human receivers.
- The lack of safety enclosure area measures has allowed residents to collect the waste with Lindane content and then to trade it in the neighboring localities or even at longer distances (Piatra Neamt – east of Romania) for purposes which have a high risk for human health (using it as insecticide for construction wood or as pesticide for agricultural lands).
- Considering the history of the Site's land use and the characteristics of the non-regulated disposal activities carried out at the former UCT, the possibility of contamination has not been caused by the current site owner's activity or the residents next to the site, but by the former UCT.
- Due to the high risk for the residential population in the vicinity of the Site and the environmental damage caused by the potential migration of the possible contaminants, a Detailed Investigation was recommended (Phase II ESA), through which this risk may be proved on the basis of quantitative evaluation of the contaminants in the soil, subsurface soil and groundwater on site.

PHASE II ESA

The purpose of this Phase II ESA was to determine if the subsurface soils and/or groundwater on the Site are environmentally impacted by historical/current uses and to address the *recognized environmental conditions* identified for the Site during the *Phase I ESA* (www.astm.org/Standards/E 1903).

However, due to size of the Site and limited budget the Turda Municipality the scope of works was limited to 4.0 hectars from the total of approximative 10 hectars.

The following scope of work was developed:

- Preparation and implementation of a detailed investigation plan through a site inspection in order to establish the locations for boreholes/wells and test pits (trial pits).
- Coordination and direction of the specialist Contractor provided by Turda Municipality for:
  - Drilling of 3 boreholes up to approximately 6 mbgl, 2 boreholes were completed as temporary groundwater monitoring wells. In addition, 20 test pits were excavated up to maximum 2.5 mbgl;
  - Collecting grab and composite soil samples starting from the ground surface;
  - Collecting groundwater samples from each of the monitoring wells on site;
  - Collecting 2 surface water samples from the Sarat Parau ("Salted Stream") from 200 meters upstream and downstream of the Site;
  - Selecting representative soil samples collected during investigation for laboratory testing based on visual and olfactory field observation.
- Analysis of the soil and groundwater samples, representative for heavy metals, pesticides, petroleum hydrocarbons, PAHs, VOC's and PCB's at an approved laboratory.
- Preparation of the conclusions and recommendation in the view of the geological and hydrogeological information and results of the soil and water analysis.

CONSIDERATIONS IN KNOWN AND UNCERTAIN SITE CHARACTERIZATION DATA

Known data

The study site is understood to be in Municipality of Turda ownership and is reputed to have received unknown quantities of waste materials associated with the herbicide industry since 1964 until mid 80's.

In addition, reports outlining programmes of scientific study were made available for review direct from municipality officials. These documents outline work undertaken in 2001 and more recently in 2008 to understand the concentration or loading of HCH (Lindane) in surface soils across suspected areas of uncontrolled tipping.

The physical site inspection confirmed the presence of mounds of material overgrown with patchy coniferous woodland and confirmed most significantly the presence of sensitive receptors such as residential housing directly over suspected waste deposits, a water course bisecting the site and animals grazing the scrubland overlying the imported materials. Although the lateral distribution and spatial extent of the tipping activity is yet to be confirmed through investigation, the soil chemistry data highlighted in the documents to date (referenced above), add support to the recommendation to undertake additional investigation and risk assessment across this site (www.frtr.gov).

The extent of soil and groundwater contamination was estimated, based on data from the field investigation, interviews with local authorities and residents, results of laboratory analysis were used for interpretation and preliminary risk assessment (www.clu-in.org).

A surface layer of material 0.5 – 1.2 m thick was described as powdery grey to grey/brown and in some areas carried an organic odour (*"…the smell of chloride pesticides."*). The general appearance of this horizon / layer was the only indication of waste material being present across the site.

Of the metal compounds data screen identified some exceedances of arsenic (>60% of samples), and some localised exceedances of lead (~20% of all samples). All other metals were generally below screening criteria.

Organic contamination within site soils across the low lying area at the Turda site is widespread. The focus of the analysis has been toward the *herbicide* group of contaminants (steered by knowledge of former site practices), and concentrations of these main contaminants of concern have been found to be elevated and quite commonly well above screening criteria. HCH compounds (α-, β-, γ-, δ-, and ε-) have been detected routinely, along with isolated trace concentrations of PCB (congeners 101, 153 & 180).

Soil conditions below the above ground waste materials and across the northern half of the site have been reasonably well documented, with conditions described in a series of geological logs F1 – F12. However, bedrock depth was not confirmed.

The waste materials deposited across the Turda site represent the obvious focus and priority for any remedial action.

Shallow organic contamination of soil mainly with total HCH and lead at a depth up to 2.5 mbgl for the area where the test pits and boreholes were completed.

Shallow metals contamination on soil mainly with arsenic at depths up 4.0 mbgl for the area where the test pits and boreholes were completed.

Groundwater strikes were encountered in 2 of the 3 groundwater wells during the investigation. Drilling difficulties in FA1 may account for the lack of a water strike with large boulders described in the factual report at this location. Rest water levels may now be within the response zone of this well; however it has to be acknowledged that with the installation also proving difficult, the depth of the pipe-work is very shallow relative to the likely elevation of the groundwater table. Response zone depths for the other 2 wells should be sufficient to enable intermediate to long term monitoring of the water table.

Groundwater quality at the Turda site shows low impact by mercury, BTEX and pesticides (as seen in FA2 and FA3). The impact seen in the groundwater data is corroborated by olfactory evidence during the soil investigations.

Surface water samples were taken at two locations, to the north and 200 m south of the site boundary. The laboratoty analysis shows a no impact of contaminants to the Salt Stream which passes the Site then flows to the Aries River, immediate south to the site.

Uncertainties

Soil conditions below the above ground waste materials and across the northern half of the site have been reasonably well documented, with conditions described in a series of geological logs F1 – F12. However, bedrock depth was not confirmed.

Limited field investigation was carried out covering only 4 hectars out of total 10 hectars of recorded as contaminated area in the ANPM questionnaire (APMCJ00022).

The *Arsenic* identified in soil can be explained as natural presence as well as from wastes of not identified or reported industrial sources from the region of Turda Municipality.

Total estimated volume of waste containing Lindane placed on the Site during former UCT operations was 10,000 m^3 (18,500 tons) as mentioned in previous studies. Moreover, there are no records available to quantify an accurate volume of waste or to identify spot on the piles on the 10 hectars area. Back in 70's the Site area was flooded and the waste piles were levelled to the terrain surface and then covered with grass and conifers.

Therefore, the volume of waste containing Lindane can only be estimated based on the findings within 4 hectars investigated area and then by assumption to evaluate for the entire 10 hectars site.

A variety of waste deposits reside across parts of the site at a range of thicknesses. The spatial distribution is shown on the site walkover plan (Figure 1), however the true thickness of above ground waste deposits have not been determined due to site conditions.

Groundwater and Surface Water Conditions

Very limited groundwater investigations did not offer enough data to estimate a groundwater flow direction and a plume of contamination. Furthermore, surface water and groundwater samples were not tested for *Arsenic*.

DETAILED INVESTIGATION CONCLUSION AND RECOMMENDATIONS

The information which was submitted in this study is based on investigations lead/supervised by experts, designed to supply the data necessary for the Environmental Assessment of current environmental conditions for the „Hazardous waste deposit – UCT Posta Rat (Municipality of Turda)". The data from this study reflects the existing conditions from the site at the time of the (preliminary and detailed) investigations. The results of the Detailed Investigation (Phase II ESA) are based on the analytical results of soil and water samples from specific locations and they represent the ground's condition at the time of sampling. The concentrations of chemical elements in the ground may vary in time from one location to another. These results shall not be used for the condition prediction from other areas or future conditions. More specific information on the ground conditions between sampling locations (which have already been carried out) or the contamination's lateral and vertical expansion may become apparent throughout the actual retrieval works.

RISK ASSESSMENT

The Site Risk Assessment described is based on the data obtained during the Preliminary (Phase I ESA) and Detailed Investigations (Phase II ESA).

The risk assessment and the remedial options have been outlined on the basis of the knowledge and understanding of the Conceptual Site Model and – where appropriate – the interactive risk evaluation and assessment. All the information has been used for the evaluation of relevant contamination source – pathway – receptor for the location and the most appropriate remedial action.

For the Risk Assessment, the values within the limits of Romanian standards/ orders/regulations have been used, and where no threshold values exist according to the Romanian regulations, alternative standards have been used from UK standards or the *Drinking Water Directive*.

THE CONCEPTUAL SITE MODEL

A preliminary Conceptual Site Model (CSM) has been prepared to illustrate the principal risk drivers at the Turda site. This is shown as Fig. 2. The following contaminant sources have been assumed in the preliminary CSM.

- Powdery residues (presumed to be pesticide wastes strewn across the site in a series of hummocky mounds);
- Raw sewage discharged to small stream bisecting the site (S2).
- The principal pathways considered applicable in the initial conceptual model are as follows:
- Dermal contact and/or ingestion of powdery materials (P1);
- Direct inhalation of powdery materials fraction (P2), and
- Ingestion of bio-accessible fraction of prevailing contaminants taken up by on-site vegetable / fruit produce (P3).
- Plant uptake (P4).
- Infiltration and migration into underlying groundwater via Leaching of site soils (P5).
- Receptors, considered in line with the most contemporary knowledge of the site and in accordance with best practice have been assessed to be as follows:
- Local residents, trespassers (R1), and
- The controlled water environment (ground and any surface water in the vicinity) (R2 and R3);
- Vegetation (R4).

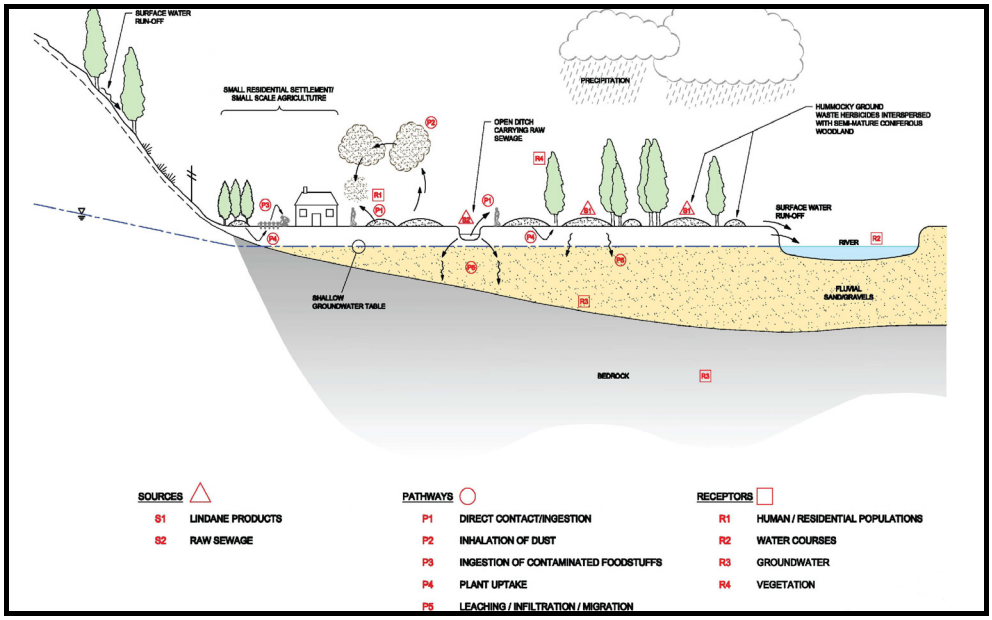

Fig. 2. *Conceptual Site Model.*

CONFIRMED POLLUTION RELATIONS (SOURCE-MEANS-RECEIVER)

With reference to the above analytical data and the CSM (Figure No. 4), there is a clear pollutant linkage between the waste materials across the Turda site (S1) and members of the local community (R1), via direct (dermal) contact (P1), ingestion of contaminants directly (P1) or via uptake on foodstuffs (P3). Similarly there is a confirmed pollutant linkage between wind-borne dusts (S1) and members of the local community (R1) via direct inhalation (P2).

There is not proven pollutant linkage between soil contamination (S1) and the groundwater and surface water (R2 and R3) via leaching and/or migration (P5) evidenced by the low impact on groundwater and surface water quality.

To break the pollutant linkages confirmed and to address the associated human health and environmental risks, some form of remedial action will be warranted. The options available, which will are dependant on proposed end use and the nature of the contamination are discussed below.

EXTENT OF CONTAMINATION

To estimate the extent of soil and groundwater contamination, data from the field investigation, interviews with local authorities and residents, results of laboratory analysis were used for interpretation and preliminary risk assessment.

The study site is understood to be in Municipality of Turda ownership and is reputed to have received unknown quantities of waste materials associated with the herbicide industry since 1964 until mid 80's.

In addition, reports outlining programmes of scientific study were made available for review direct from municipality officials. These documents outline work undertaken in 2001 and more recently in 2008 to understand the concentration or loading of HCH (Lindane) in surface soils across suspected areas of uncontrolled tipping.

The distribution of all elevated soil concentrations on the investigated area is summarised on Fig. 3.

The solid waste materials deposited across the Turda site represent the obvious focus and priority for any remedial action.

Very limited groundwater investigations did not offer enough data to estimate a groundwater flow direction and a plume of contamination.

GENERAL RECOGNISED METHODS OF REMEDIATION

Following identification of relevant pollutant linkages, feasible remediation options have been considered. 'Best Practice' considers three main ways to reduce or control unacceptable risks. These are to:

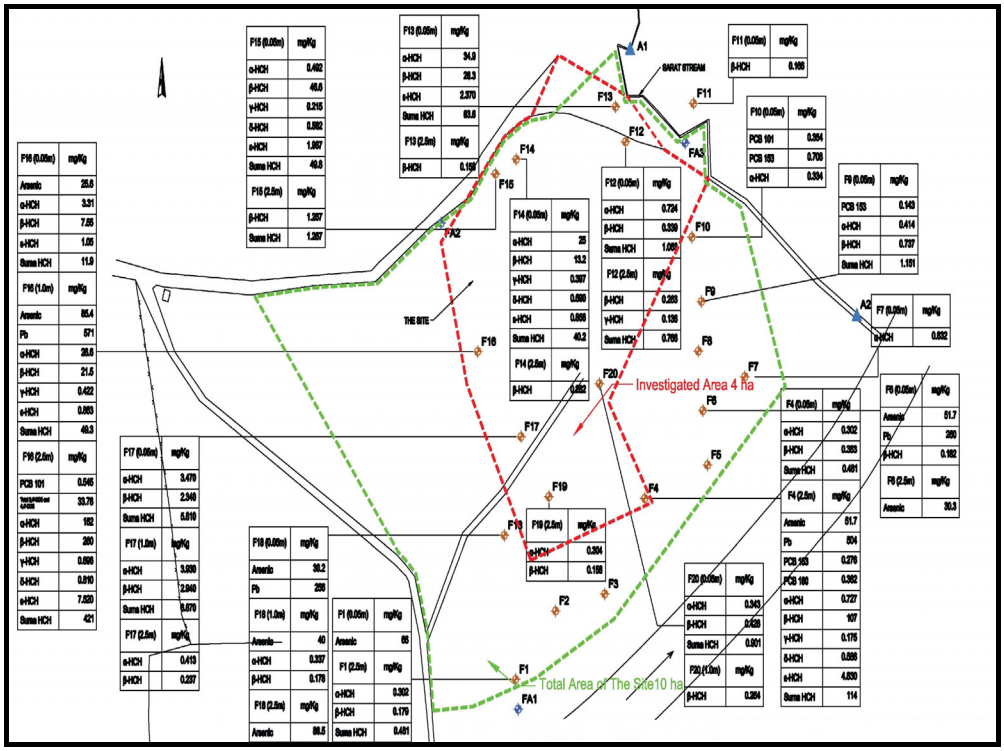

Fig. 3. *Elevated concentrations in soil*

- Remove or treat the source of pollutants;
- Remove or modify the pathway(s);
- Remove or modify the behaviour of the receptor(s).

REMEDIAL ACTION OBJECTIVES ("RAO")

The principal objective of the remedial work is to reduce the mobility of contaminants present on site to protect the land use to a standard suitable for use as a green area for the public, to include areas of landscaping (planting) and recreational access for the general public, as well addressing any impact to the local environment from previous site activity. Risks associated with all relevant pollutant linkages are to be appropriately reduced by the most expedient remedial option given the sites' constraints. Remediation objectives are then to be defined by site specific action criteria.

Based on site history, field investigations and laboratory results for soils and groundwater it is confirmed the presence of HCH contaminant on the 4.0 hectars investigated area. The main problem to remediate only 40% (investigated area) from the total area will occur when the site has to be divided in a remediated part opened to

the public and a contaminated part closed to the public which will be difficult to organise. Therefore, all the 10 hectars of the site is subject to remediation works.

The main source of soil contamination on the site is the total HCH from the waste piles spreaded on the area. Since the waste has been disposed of in piles not all the soil for the entire 10 ha area is contaminated. The estimated volume of contaminated soil with HCH contaminants of 70,000 m^3 is based on the 4.0 ha investigated area where only 16 soil samples were above 2 mg/kg total HCH (screening criteria for sensitive land use) and then extended to the total contaminated area of 10 hectars as reported by ANMP questionnaire. Therefore total HCH is higher than maximum accepted values in probably less than 50% of the potential contaminated area of 10 ha.

To accurate assess the volumes of contaminated soil the main remedial objective will be to carry a further investigation of total site area.

The surface water (Salted Stream) shows minimal impact from the contaminants present on site. In addition low concentrations of contaminants in groundwater indicate unlikely migration towards the Aries River.

However, considering the low concentrations of Hg, BTEX and HCH this project will not address any active action with regard to the surface and groundwater on the site (Fig 4).

Therefore the main RAOs for this pilot project application are the following:

1. Extensive surface investigation; and
2. Elimination of contact risk to the land users

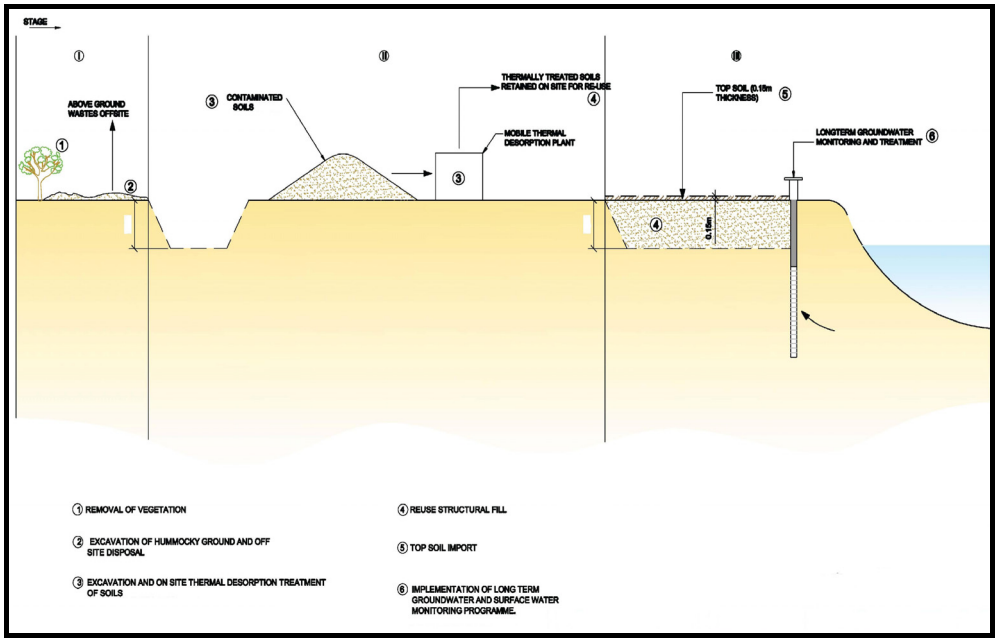

Fig. 4. Remedial Stages.

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www.astm.org/Standards/E 1903.htm Standard Practice for Environmental Site Assessments: Phase I Environmental Site Assessment Process II - ASTM E1903 -97(2002); Copyright © American Standards for Testing and Materials International

www.frtr.gov Federal Remediation Technologies Roundtable (US)

www.clu-in.org Contaminated Site Clean-Up Information (US)

STUDIA UBB AMBIENTUM, LVI, 1, 2011, pp. 57-65

METHOD FOR ASSESSING HUMAN EXPOSURE TO PHTHALATES

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ABSTRACT. The dialkyl - or alkyl/aryl esters of 1,2-benzenedicarboxylic acid, commonly known as phthalates, are high-production volume synthetic chemicals and ubiquitous environmental contaminants because of their use in plastics and other common consumer products. Globally there is significant concern for the ubiquitous presence of phthalates and their potential for causing adverse health effects in humans. Phthalates have possible teratogenic and carcinogenic effects, DEHP being included in Class B2 (probable human carcinogens). They are also suspected endocrine disruptors and an association between phthalate exposure and abnormal reproductive development has been suggested. In order to evaluate human exposure it is necessary to analyze the phthalates from environment, but also the phthalates metabolites from urine and serum. In this article it is presented a method for evaluate the concentration of phthalates metabolites in urine by enzymatic incubation and HPLC-MS/MS determination. Urine sample is conditioned with ammonium acetate solution. β –glucuronidase solution is added, the sample are sealed and incubated overnight at 37^{o}C. The SPE cartridges pretreated with phosphate buffer and acetonitrile and are sample is cleaned up over them with formic acid and water. Phthalate metabolites are eluting with acetonitrile and ethyl acetate. The sample is concentrate near dryness under nitrogen stream and analyzed on a C18 column by HPLC-MS/MS. Linearity was controlled in the range between 0,5 -250 µg/l and the detection limit between 0,2 µg/l for most of the compounds and 1 µg/l for mono-(2-ethylhexyl)phthalate. Hereinafter are presented and discussed the characteristics of the method.

Key words: *Phthalates metabolites, HPLC-MS/MS, Urine*

INTRODUCTION

Phthalates are a group of aromatic chemicals containing a phenyl ring with two attached and extended acetate groups. It is a used to keep plastics soft or more flexible. They are typically colorless liquids, man-made substance, used to make plastics

more flexible, soft and resilient. Because they are not a part of the chain of chemicals (polymers) that makes up plastics, they can be released fairly easily from these products. These plastics are found in products such as toothbrushes, automobile parts, tools, toys, and food packaging. Some are also used in cosmetics, insecticides, medical tubing, aspirin, blood storage bags and adhesives (ATSDR, 2008).

Phthalates have possible teratogenic and carcinogenic effects, DEHP being included in Class B2 (probable human carcinogens). They are also suspected endocrine disruptors and an association between phthalate exposure and abnormal reproductive development has been suggested. The main targets of di-(2-ethylhexyl) phthalate toxicity in oral animal studies are the liver and testes. Toxic effects include loss of spermatogenesis, decreased fertility and hepatocarcinoma (ATSDR, 2008).

Humans are exposed to phthalates through ingestion, inhalation and dermal contact (Latini, 2005). After entering the body, phthalates are rapidly metabolized to their respective monoesters, some of which can be further metabolized to oxidative metabolites (Hauser and Calafat, 2005). All these metabolites can be glucuronidated and excreted in the urine and feces. Measurements of metabolites in body fluids (mainly urine) are usually better biomarkers of exposure than those of the parent phthalates because the latter are easily affected by laboratory contamination (Barr et al., 2003). In most cases, the metabolite is more toxic than the parent phthalate (Peck and Albro, 1982).

The biological half-lives of parent compounds and identified metabolites are on the order of hours. For example, about 75% of the oral dose of di-(2-ethylhexyl) phthalate (DEHP) is excreted in urine within 48 h of exposure, as mono (2-ethylhexyl) phthalate (MEHP) and four other oxidative metabolites (Fig. 1.), mono(2-ethyl-5-carboxypentyl) phthalate (5cx-MEPP), mono-[(2-carboxymethyl)hexyl] phthalate (2cx-MMHP), mono(2-ethyl-5-oxohexyl) phthalate (5oxo-MEHP) and mono(2-ethyl-5-hydroxyhexyl) phthalate (5OH-MEHP) (Koch et al. 2004).

As non-persistent chemicals with short half-lives, urinary phthalate metabolites are used as biomarkers of recent human exposure to phthalates (Barr et al., 2003; Latini, 2005).

In this paper it is displayed a method for evaluate the concentration of six phthalates metabolites in urine by enzymatic incubation and determination by high performance liquid chromatography with tandem mass spectrometry (HPLC-MS/MS) equipped with APCI (Atmospheric Pressure Chemical Ionization).

Di-(2-ethylhexyl) phthalate, owing to its low cost, is the major plasticizer used in polyvinyl chloride (PVC) production. Benzyl butyl phthalate (BzBP) is used in the manufacture of foamed PVC, which is mostly used in floorings. Dibutyl phthalate (DBP) and diethyl phthalate (DEP) are used in consumer and personal care products, such as cosmetics, deodorants, and pharmaceutical coatings (Ying et al., 2011).

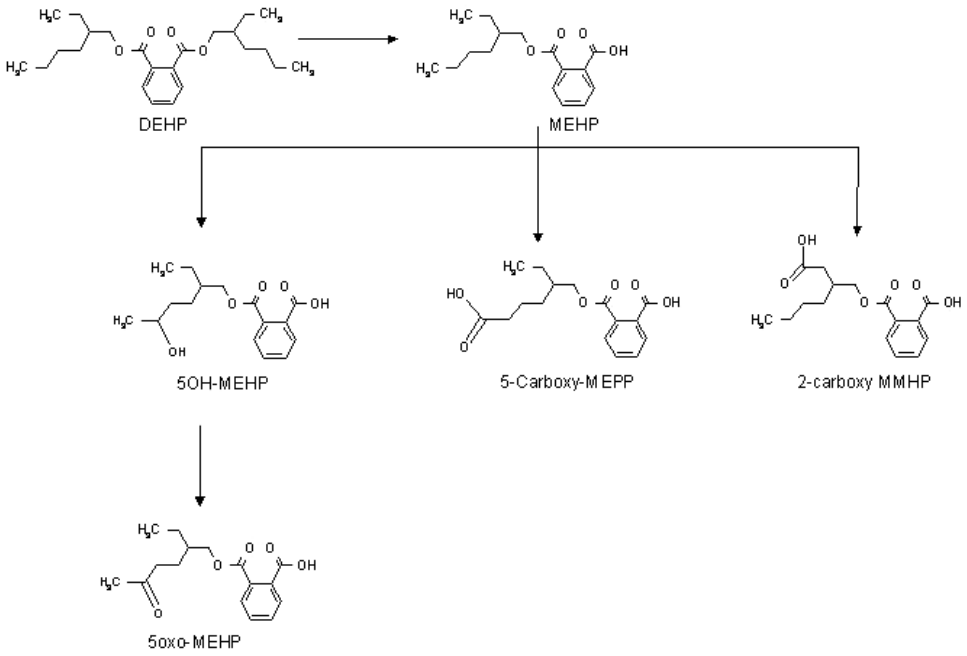

Fig.1. *DEHP metabolites.*

EXPERIMENTAL

The method developed here is adapted for our equipment after a laboratory standard procedure of Wadsworth Center, New York Department of Health after two week training in their laboratory in Albany. The HPLC approach was preferred due to low sensitivity and selectivity of gas chromatography method for oxidative metabolites.

Reagents

MEHP, monobenzyl phthalate (MBzP), monoethyl phthalate (MEP), mono-n-butyl phthalate (MnBP) were purchased from AccuStandard and others were purchased from Cambridge Isotope Laboratories. A mixture of isotopically-labeled phthalate metabolites (13C4-MEP, 13C4-MnBP, 13C4−mBzP, 13C4-MEHP) were purchased from Cambridge Isotope Laboratories. Acetonitrile (HPLC grade), ethyl acetate and orto-phosphoric acid were purchased from Merck, β-glucuronidase (113200 units/ml) (Escherichia coli), formic acid, sodium phosphate monobasic monohydrate and ammonium acetate were purchased from Sigma Aldrich. Reagents were prepared in acetonitrile and water. All standard solutions were prepared in glassware that was heated at 250^{o}C for two hours, acetone-rinsed and dried.

Sample preparation

Stock solutions of standards and internal standards were prepared in acetonitrile. The internal standard spiking solution consisted of 13C4-MnBP (20 ng) and 13C4-MEHP (12 ng). 13C4-MnBP was used as the internal standard for 5oxo-MEHP, 5OH-MEHP because of their similar retention on the HPLC column. 13C4-MEHP was used as the internal standard for MEHP.

1.0 ml of urine sample was transferred into a borosilicate glass tube and buffered with ammonium acetate (200µl, 1M, pH =6.5). 100 µl of the internal standard mixture was added to the sample. β-glucuronidase enzyme (50 µl, 200 units/ml) was added to each sample to deconjugate glucuronidated phthalate metabolites (Silva et al., 2004). The samples were sealed with aluminum foil (acetone-rinsed and dried), gently shaken and incubated overnight at 37^{o}C in a closed water bath.

Solid-phase extraction

The samples were processed through 60 mg polymeric SPE cartridges (Thermo Scientific) using solvents and buffered aqueous solutions. Vacuum manifold (Thermo Scientific) was used for extraction.

SPE cartridges were conditioned with acetonitrile (2 ml) and phosphate buffer (2 ml, pH=2). To prepare phosphate buffer 20 g of sodium phosphate monobasic monohydrate were diluted to 1000 ml with distilled water and 10 ml of orto-phosphoric acid were added.

After incubation phosphate buffer (1 ml, pH=2) is added to the sample and is loaded onto pretreated SPE cartridges. Formic acid (2 ml, 0.1 M) and distilled water (1 ml) are added to the cartridge and the eluate was discarded. The analytes were then eluted with acetonitrile (1.5 ml) followed by ethyl acetate (1 ml). The eluates were concentrated under gentle stream of dry nitrogen (Techne) at 55^{o}C. The residue is dissolved in 1.0 ml acetonitrile/water and transferred to autosampler vials. The samples were analyzed by HPLC-MS/MS equipped with APCI (Atmospheric Pressure Chemical Ionization).

Automated SPE method and equipment are available (Silva et al., 2004), but the volume of analyzed samples in our laboratory at the moment does not justify such expenses.

Instrumental analysis

An API 2000 electrospray triple quadrupole mass spectrometer (ESI-MS/MS) equipped with an Agilent 1100 Series HPLC system (Agilent) was used for the measurement of phthalate metabolites.

MS/MS parameters were optimized for each target compound, by infusion of 1 µg/mL-standard solution. 13C-MEP, 13C-MnBP and 13C-MBzP were used as surrogate standards for quantification of MEP, MnBP and MBzP, respectively.

Chromatographic separation was achieved using a Betasil C18 column (Thermo Electron; 100 mm×2.1 mm,5 µm). The mobile phase was 0.1% acetic acid in Milli-Q water (A) and 0.1% acetic acid in acetonitrile (B) at a flow rate of 300 µL/min. The mobile phase gradient was as follows: 0.0–2.0 min, 20% B; 6.0 min, 40% B; 7.0–9.0 min, 50% B; 12.0–17.0 min, 90% B; 19 min, 20% B; 26 min, 20% B. The injection volume was 10 µL. Nitrogen was used as both curtain and collision gas. The interface temperature is 400 °C and the capillary voltage is −4500 V. Target compounds were determined by multiple reaction monitoring (MRM) in the negative ionization mode (Table 1) (Ying et al., 2011).

Inline filters are used to remove particulate materials from the injected samples before reaching the column. A 5 mm phenyl guard column is used with the analytical column to extend the useful life span of the analytical column. The total run cycle time for the assay is 12.0 minutes.

Table 1. *Single Reaction Monitoring (SRM) Setup for Phthalate Monoesters Analysis Of Phthalate Monoesters.*

Analyte	Parent (Mass)	Daughter (Mass)	Coff(V) (Collision Offset)	RT Window (min)
MEP	193	77	21.5	1.0-5.5
13C4-MEP	197	79	21.5	1.0-5.5
MnBP	221	77	22.0	5.5-8.8
13C4-MnBP	225	79	22.0	5.5-8.8
5oxo-MEHP	293	121	22.0	5.5-8.8
5OH-MEHP	291	121	22.0	5.5-8.8
MBzP	255	183	14.2	5.5-8.8
13C4-MBzP	259	186	14.2	5.5-8.8
MEHP	277	134	22.0	8.8-11.5
13C4-MEHP	281	137	22.0	8.8-11.5

Calibration

Preliminary calibration curve of the method was performed in eleven points between 0.5-250 µg/l for each of the six compounds.

We obtained linear calibration curve for all analytes with correlation coefficient typically exceeding 0.99, for example for MEHP was 0.998 (Fig. 2).

Before mass spectral analysis of unknowns, a known standard is injected to confirm acceptable chromatographic resolution and mass spectral sensitivity. Once the instrument yields acceptable performance, a full set of standards followed by the unknowns, QC samples and the blank are analyzed. The analysis is completed by re-injecting the same eleven standards. The duplicate standards are used to draw a

daily calibration curve for each analyte (known concentration versus analyte/internal standard area ratio). (Each point in the calibration curve is weighted (1/x), with correlation coefficients typically > 0.99. The minimal contributions of the isotope to the native ion and native to the isotope ion are corrected by the software for all reported data. The calibration curve is used by the data analysis software for all unknowns, QC, samples and blanks analyzed on that day.)

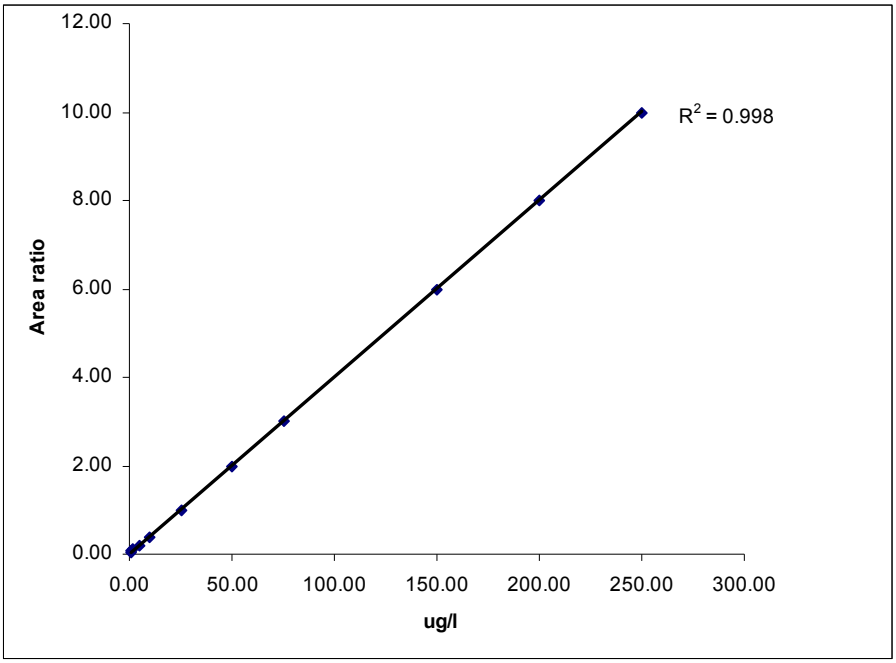

Fig. 2. *Calibration curve for MEHP. The calibration curve was linear across the range from 0 to 250 ppb with a correlation coefficient of 0.998.*

Method validation and interpretation of results

The detection limit of MEHP and other phthalate metabolites were 1 µg/l and 0.2 µg/l, respectively. The analytical limit of detection for each of the six analytes is calculated as 3 So where So is the value of the standard deviation as the concentration approaches zero. The So is determined by analyzing five duplicates of the lowest five standards and plotting the standard deviation versus the known standard concentration; *y* intercept of the best-fit line of this plot was used as So.

The SPE recoveries of the phthalate metabolites from urine were calculated as 100×[conc]a/[conc]b, where [conc]a and [conc]b are the concentrations obtained from spiking the urine sample with the isotopically labeled standards after and before the SPE separation, respectively (Table 2).

Table 2. *Mono phthalates recoveries for the method used.*

Phthalate metabolite	Recovery	Phthalate metabolite	Recovery
C13-MEP	86%	MEHP	89%
C13-MnBP	92%	MnBP	90%
C13-MBzP	96%	5OH-MEHP	87%
C13-MEHP	88%	5oxo-MEHP	93%
MEP	82%	MBzP	91%

The accuracy of the method was assessed by measuring the concentration of known standard solutions spiked in synthetic urine at two different levels (Table 3).

Table 3. *Concentration used for accuracy.*

Phthalate metabolite	Low concentration (µg/l)		High concentration (µg/l)	
	Actual	Theoretical	Actual	Theoretical
MEP	24.7	25	201	200
MnBP	24.1	25	199	200
5OH-MEHP	24.8	25	202	200
5oxo-MEHP	24.6	25	200.5	200
MBzP	24.5	25	203	200
MEHP	25.3	25	202	200

The method was tested in a European inter-laboratory comparison and the results were acceptable (Table 4). Urine samples from several people with know exposure to phthalates, low and high levels, were thoroughly mixed and sent to eight laboratories across Europe. Each laboratory had to report six analytical results for each concentration, the summary of the method used and other information (standard used, internal standard used, certified material used). Validation parameters for the method were also requested as repeatability, limit of detection and quantification and accuracy for each phthalate metabolite.

Table 4. *Mono-phthalates results in a inter-laboratory comparison. Conc A,B are our results and Mean conc. are the average concentration of the participant laboratories. RSD – standard deviation of the results in percents.*

Phthalate metabolite	Conc. A	Mean conc. A	Conc. B	Mean conc. B	RSD (%)
MEP	318.60	281.87	169.50	146.90	10.05
MnBP	27.10	27.50	27.10	33.00	6.84
5OH-MEHP	9.00	8.30	84.50	70.10	10.24
5oxo-MEHP	5.20	6.30	43.80	46.10	7.94
MBzP	9.70	7.80	3.70	3.60	9.59
MEHP	2.30	2.80	17.80	15.80	10.79

High (~200 µg/l) and low (~25 µg/l) quality control (QC) pools were prepared from split pooled human urine. The urine was spiked with the desired amounts of 5oxo-MEHP, 5OH-MEHP, MEHP, MnBP and MEP, mixed well and divided into aliquots. A reagent blank and one each of the concentrations of QC materials were analyzed during each analytical run to ensure proper operation of the method and the validity of the resulting data.

The concentration of the individual analytes in each sample is calculated using the calibration curve derived from known standard mixtures. Area ratio of analyte/internal standard = concentration ratio of analyte/Internal standard.

The range of concentrations reported for analytes in an unknown specimen are determined by the extent of exposure experienced by the donor, the time lapse since that exposure occurred, and the half-life of the analyte. The value can range from nondetectable to low parts per million. The test samples with values below the lowest standard are reported as non detectable. If a sample has levels higher than the calibration range, it is diluted so the level is in this range. The final result is then calculated by adjusting for the dilution.

CONCLUSIONS

The phthalate monoesters values obtained using this method of analysis are individual markers of phthalate exposure only. Future human exposure assessment studies should help reveal the potential role of phthalates in causing an increased risk of cancer and reproductive dysfunction.

The procedure is very labor intensive and requires very expensive instrumentation.

Sources of imprecision in the procedure may be intermittently imprecise pipetting and/or phthalate contamination in extraction materials and contaminated solvents.

Any contact with plastics during specimen acquisition, storage or sample analysis can result in interference.

Our method was proven to be suitable to analyze phthalate metabolites from human urine to analyze the exposure to parent phthalates.

Acknowledgments. This research (method development and inter-laboratory comparison) was supported by DEMOCOPHES program (LIFE09 ENV/BE/410) which aims to test the feasibility of a coherent approach to Human Biomonitoring (HBM) in Europe.

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THE EXPOSURE OF PRIMARY SCHOOL CHILDREN TO CARBON MONOXIDE, PARTICULATE MATTER AND MICROCLIMATE, FROM ALBA COUNTY

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ABSTRACT. The article presents the evaluation of schoolchildren from five primary schools (classes' I-IV), located in Alba County. The presented methodologies stand for thoracic and respirable particulate matter, carbon monoxide, -dioxide, temperature, relative humidity and ventilation rate.

The measurements were done in three classrooms, and one exterior point. The five locations were Unirea, Aiud, Alba Iulia, Sebeş and Vinţu de Jos.

This article is in consistent with the measurement protocol for indoor and outdoor of the SINPHONIE project (Schools Indoor Pollution and Health Observatory Network in Europe), for physical and chemical measurements.

Key words: *exposure of children, particulate matter, carbon dioxide, carbon monoxide, ventilation rate*

INTRODUCTION

In our schools the children are stimulated, and prepared in such a way that they can easily assimilate the information's given to them. This capacity to assimilate the given information's, in the classroom can diminish if some external conditions (like carbon dioxide, temperature, humidity, the concentrations of different particulate matter etc.) become higher than the maximum allowed value. These values can have different sources: missing ventilation systems, or the malfunctions of the ventilation systems, reduced ventilations, reduced cleaning of surfaces and the floor etc. A first step in maintaining a healthy "climate" in these classrooms is to evaluate the microclimate, and the potential pollutants. The evaluation strategy depends on the environmental

conditions, variations, the monitored "pollutants", and the available methods of evaluation (EN 482, 2010). In this stage, a list is created for the measured parameters, the methodology, the number of observations, and the duration of the measurements.

Site and measured parameters

In our study, we made measurements in five schools, from Alba County, Romania. The indoor evaluation of the exposure was measured simultaneously in three classrooms. To evaluate the outdoor exposure (like traffic) on the environment, a simultaneous monitoring was done outside in the school yard. The following parameters were measured indoor: particulate matter (PM_{10} and $PM_{2.5}$), carbon monoxide (CO), carbon dioxide (CO_2) for the calculation on the ventilation rate, temperature and relative humidity (ISO 16000-1, 2004). Outdoor all the above mentioned parameters were measured, except for PM_{10}. The measurements were done in a fixed point, at the respiratory height of the students. The duration of the measurements was 5 days for CO_2, CO, temperature and relative humidity. For PM_{10} 24 hours for each classroom, and for $PM_{2.5}$ five days, for each day the amount of time the children were in the classrooms (~8 hours).

METHODOLOGY AND EQUIPMENT

CO/CO_2/RH/T and ventilation rate

Carbon monoxide, -dioxide, temperature, and relative humidity were measured with passive sampling (EN 14626, 2005; ISO/DIS 16000-26) with an IAQ-Calc, model 7545 type multimeter (Fig. 1). The ventilation rate was calculated using the following equation (based on ASTM D6245 - 07):

$$\bar{A} = \frac{\left|\ln\left[C(t_2) - C\left(ext_{t_2}\right)\right] - \ln\left[C(t_1) - C\left(ext_{t_2}\right)\right]\right|}{(t_2 - t_1)}$$

were:

Ā= ventilation rate;
t = time in hours;
C(t) = CO_2 indoor concentration at time t, [ppm];
C(ext) = exterior (outdoor) concentration on CO_2, [ppm].

For the calculations, we take the CO_2 concentration and the end of the school day for the class (t_1), and the concentration of CO_2 the second day at 8:00 AM (t_2, beginning of the school day). When choosing the values for the calculation, we must consider the following: the interior concentrations of CO_2 are always bigger than the outside ones; t_1 is always a higher value than t_2. The value of the ventilation rate is always positive, and is always a value between zero and one.

Fig. 1. *IAQ-Calc, model 7545 type multimeter*

PM_{10}

For the measurement of PM_{10} is done with active sampling, with a Haz-Dust EPAM-5000 type particulate monitor (Fig. 2). The monitor works based on optical light scattering. The monitor contains a specific sampling inlet sleeve, holding a sampling inlet designed for 10 μm particulate matter. The concentration is instantaneously calculated and displayed by the monitor.

Fig. 2. *Haz-Dust EPAM-5000 type particulate matter monitor*

$PM_{2.5}$

For the determination of the 2.5 μm particulate matter, we used the gravimetric method (EN 14907, 2005). This method is and active sampling using an air pump (SKC Leland Legacy), pumping the air truth a filter (2 μm in pore size), placed in a personal monitor type PEM model 200, with a flow rate of ~10 l/min (Fig. 3). The flow can vary between 9.5 and 10.5 l/min. Before and after the sampling the filters must be conditioned, at the same temperature and humidity. The weighting was done using the same micro scale. The flow rate was measured with a digital flow meter (Bios Defender 510-H). For each location, indoor and outdoor a blank filter was also used. This filter at the beginning of the sampling point was put into the PEM, closed, then reopened and taken out of the PEM without pulling air trough it. The blank filters were conditioned the same way as the filters used for sampling.

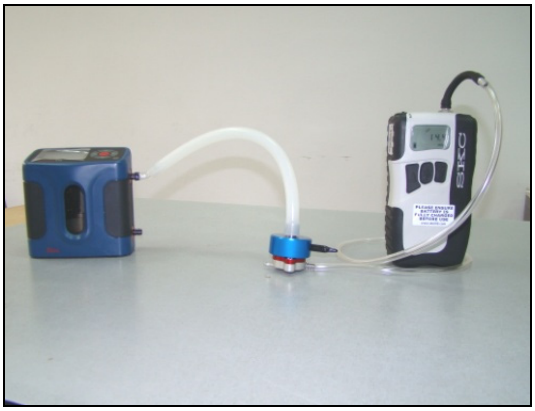

Fig. 3. *Pump connected with PEM and flow meter*

For calculating the amount of particle mass accumulated on the filters, we use the following equation:

$$M_S = (m_2 – m_1) – m_3$$

were:

M_S = mass of particles accumulated on the filter;
m_1 = the mass of the filter before the sampling, μg;
m_2 = mass of filter after sampling, μg;
m_3 = difference of mass of the blank before and after putting in the PEM, μg.

For the calculation of the amount of air sampled is done using the following equation:

$$V_S = \frac{Q \cdot t}{1000}$$

were:

V_S = air volume sampled, m^3;
Q = average flow rate of the air, L/min;
t = sampling time, min;
1000 = transformation factor from L to m^3.

From the above-mentioned equations, we can calculate de concentration of the $PM_{2.5}$:

$$C = \frac{M_S}{V_S}$$

were:

C = concentration of $PM_{2.5}$;
M_S = particle mass sampled on the filter, µg;
V_S = volume of the sampled air, m^3.

CONCLUSIONS

The data collected in the participant schools, in the project SINPHONIE, will be put in a data base. This data base will help create a European directive, which will help improving the schools indoor air quality. With this new directive, the European Union hopes to increase the quality of the indoor air, together with the health of the students.

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A COMPLEX APPROACH ON ENVIRONMENTAL MONITORING IN MINING AREAS

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ABSTRACT. Mining is generally considered among the most pollutant industrial activities currently running. However, the modern society needs ever increasing quantities of raw mineral materials that can be extracted from the Earth's sub- and near-surface. As the easily accessible deposits are depleting, new ore bodies are approached, very often in conditions that are more difficult and with lower grades. The environmental issues are more and more taken into account when opening a new mine, and in many cases, new operations are being rejected by the local communities, due to the failure of complying with the current environmental standards. We have to admit that any mine has a significant impact on the environment, and part of the economic benefit should be used for the environmental restoration/reconstruction of the area, but also creating new economic opportunities for the local community in the post-closure period. Under such circumstances, the environmental monitoring and management are very important. The conventional approach generally consists in periodically performing field measurements in discrete points, taking samples and doing laboratory analysis. This procedure is time-, money- and resources-consuming, although the obtained data are not always reliable and reproducible, and the interpretation lacks relevance in many cases. An accurate and cost-effective monitoring system is essential in the management of the environmental issues in mining areas. A new approach is proposed by the EU-funded project ImpactMin, consisting in combining the satellite remote sensing, and aerial lightweight measurements with the ground sampling for developing new models of environmental monitoring in mining areas. Four test-sites were selected for calibrating and demonstrating the new toolset. Among the benefits of the new approach should be mentioned: a more accurate description of the current state of the environment and changes overtime; future developments in the evolution of the environment can be predicted; reduction of the probability of loss by natural/technological disasters.

Key words: *remote sensing; hyperspectral / multispectral images; stress vegetation; fluorescence*

INTRODUCTION

Several studies of remote sensing for environmental quality assessment indicate that remote sensing applied methods are becoming increasingly important tools for studying different aspects in a wide variety of specific applications, at local, regional, and even global scales (Latifovic et al. 2005). Using remote sensing methodology, detailed information about land use conditions, land degradation, environmental conditions, ecosystem dynamics, and other aspects can be acquired and updated periodically. This offers the opportunity of monitoring the dynamics of the phenomena occurring at the ground surface. Remote sensing techniques have the ability to provide spatial and temporal views of the evolution of the environmental parameters that usually cannot be obtained from in situ measurements. By using satellite remote sensing, changes in environmental conditions can be monitored in larger areas at lower costs (Project 244166, FP7-ENV-2009-1).

The main objective of the EU-funded ImpactMin Project is to develop new methods and a toolset for environmental impact monitoring of mining operations by using Earth Observations and in-situ data. The proposed idea is to combine ground sampling (in situ data) like soil, water, vegetation, sediments samples with the use of satellite remote sensing, aerial lightweight measurements, and Unmanned Aerial Vehicles (UAVs). The aim of this study project is to develop a cost-effective, reliable, and repeatable approach for monitoring the impact of mining activities on the environment through time (Project 244166, FP7-ENV-2009-1).

Four test-sites (Fig. 1) were proposed for calibrating and demonstrating these new methods: Kristineberg / Malå (Sweden), Mostar (Bosnia Herzegovina), South Ural Mountains (Russia) and Roşia Montană (Romania).

Kristineberg is located in northern Sweden, and belongs to Skellefte mining district, one of the three Swedish important mining regions. Zinc, copper and lead are currently extracted in the area. The zone of interest comprises a large tailings area, five mines, a large central industrial area, and three open pits.

In the proximity of the city of Mostar (Bosnia and Herzegovina), the area related to the coal mine of Vihovici is under study in the frame of the ImpacMin project. It was operated underground between 1901 and 1963 and as an open pit from 1963 to 1991, when it was closed.

Three locations were considered as test-sites in the South Ural Mountains: Karabash, Gay, and Mednogorsk. Base metals, especially copper, were the materials that used to be extracted from the open pits and underground mines in the area. Most of the mines are currently closed, however the specific pollution processes as AMD are still active. In addition, important smelting capacities are in function, generating airborne pollution in the surrounding areas.

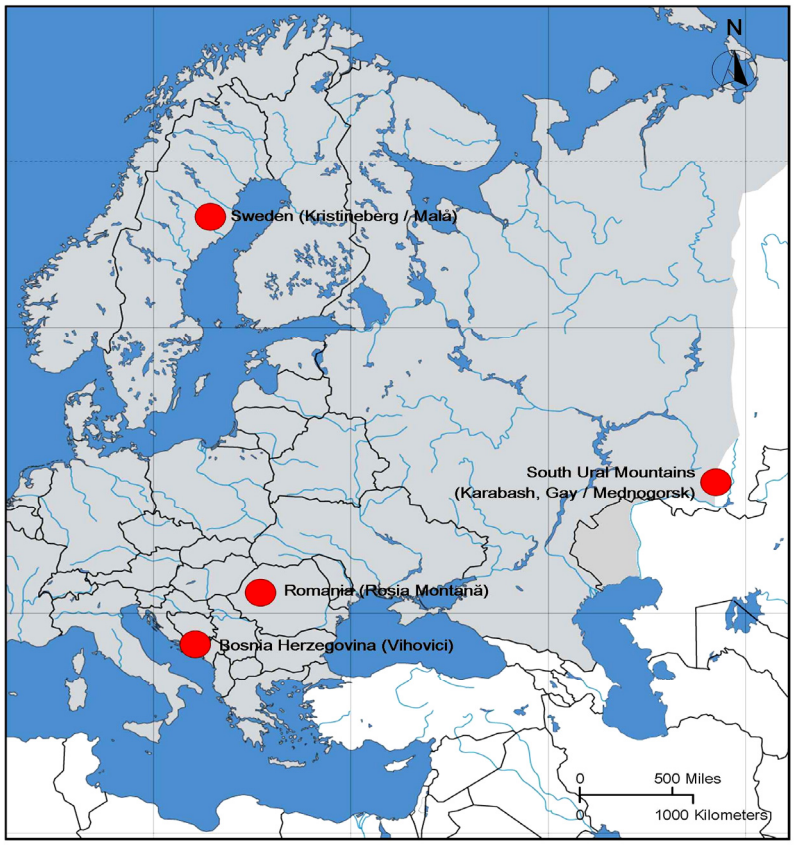

Fig. 1. *Location of the study sites.*

STUDY AREA

Roşia Montană test-site (Romania) (Fig. 2) has a particular position in this context, as the cumulated impact of almost 2000 years of gold mining may be observed. Here, mining operations were generally performed underground, with 140 km of known and mapped galleries mined in approximately 2000 years. Between 1970 and 2006, the ore was extracted in an open pit mine, and in 2006 the operations were stopped due to the low economic efficiency and the need for subsidies. Currently there are two inactive open pits, Cetate with an area of 19.75 ha, and Cârnic with an area of 5.2 ha, several waste dumps and two tailings deposits (Sălişte and Gura Roşiei).

A significant amount of precious metals was extracted from this site along the 2000 years, probably in the range of hundreds of tons, providing an important economic benefit to the local community, but especially to the rulers. A long mining tradition,

and the religious and cultural diversity are the main features of the communities that used to live in this region. However, the area is currently affected by the environmental impact of mining, including pollution of soils and streams, landscape scarring, and modifications in land use and biodiversity (Project 244166, FP7-ENV-2009-1).

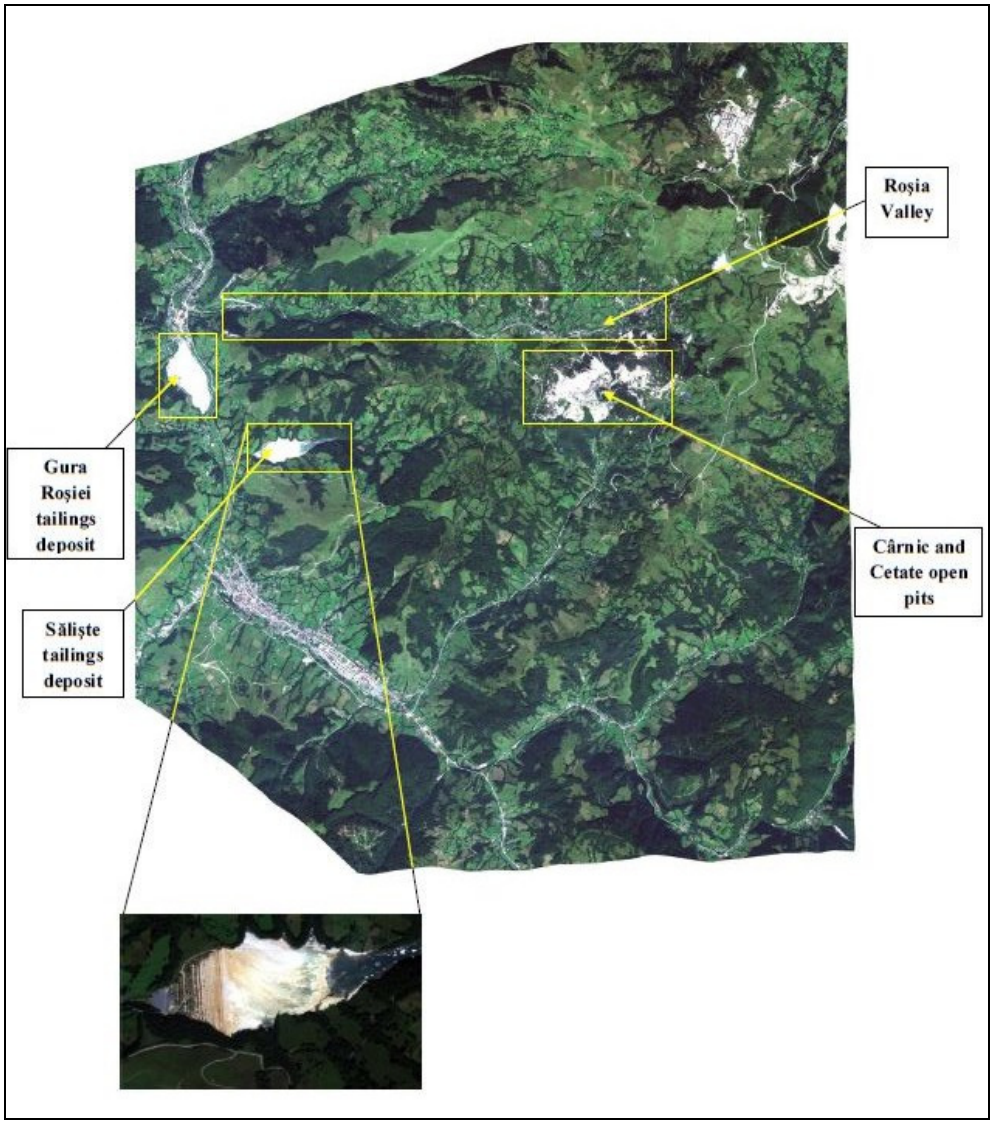

Fig. 2. *Quicklook of the WorldView-2 image of the Roşia Montană mining area, acquired on 15.08.2010 with areas of interest.*

One of the most important environmental issues is the acid mine drainage (AMD), that occurring both on the exposed surfaces and in the underground galleries. Mine waters flowing out from the open galleries or leaking from the tailings deposits have low pH and high contents of heavy metals, like Cd, Ni, Pb, Cr, As etc. The presence of the heavy metals affects especially the quality of the surface waters and to some extent the groundwater (Florea et al. 2005). Also the stream sediments have high contents of heavy metals (Bird et al, 2005). However, the soils show relatively low pollution levels at a short distance from the mining site (Lăcătuşu, 2007). In many cases, the presence of heavy metals in water and stream sediments is exceeding the maximum admissible concentrations (MAC).

The landscape and the land use were completely modified in the area mainly due to the open pit mining operations, the waste dumps and tailings deposits resulted from the ore extraction and processing.

Regarding the state of the vegetation, no in-situ measurements were previously performed in order to assess the vegetation stress along the AMD pathways (Project 244166, FP7-ENV-2009-1) and in the mining area.

The overall objective of the ImpactMin project in this test site is to assess the impact of mining activities by using satellite and airborne images combined with ground measurements (Project 244166, FP7-ENV-2009-1). The study is focusing on monitoring the relevant parameters for the environmental characterization, including the temporal change of vegetation and land cover, and the changes induced by the advancement of the mining/rehabilitation operations. Landsat MSS/TM/ETM+, ASTER, NOAA-AVHRR or SPOT-VGT imagery products and high spatial resolution satellite imagery like SPOT-5, WorldView-2 will be used to derive base maps, to identify polluted areas based on the mineralogical composition, to monitor the spatial extent of polluted areas and acid mine drainage, to monitor vegetation stress along the AMD pathways, and to monitor contamination of surface waters (Project 244166, FP7-ENV-2009-1).

In order to monitor stress vegetation along the AMD pathway and affected areas, it is necessary to compare it with the healthy vegetation existent in unaffected areas by using ground spectra, aerial images, and WorldView-2 images.

WorldView-2 is the first high-resolution multispectral satellite equipped with a red-edge detector (705-745 nm) that analyses vegetation in order to reveal plant type, age, health, and diversity (DigitalGlobe. Vegetative Analysis, 2010). Two WorldView-2 images of Roşia Montană area were acquired in July 2010 and July 2011 and these images are going to be used in analysing the status of vegetation in this area. The purpose of studying the applicability of the sensor is to analyse the extent and severity of AMD induced vegetation stress in the area, considering that currently there is no available information on this topic (Project 244166, FP7-ENV-2009-1).

All collected datasets (spaceborne, airborne, ground-based measurements) will be used to improve and complement the environmental appraisal of the area (Project 244166, FP7-ENV-2009-1).

MATERIALS AND METHODS

The first measurements started in the summer of 2011 with a field campaign when leaves samples were collected. As a first step, it was necessary to identify the plant species of interest for the proposed study, as the distribution of different plant species, especially the acid tolerant and acidophilic species is important for assessing the affected areas.

One of the task of our work was to determine whether the soil chemical composition (data not shown in the current work) and pH, correlate with the photosynthetic parameters, including chlorophyll *a* fluorescence and assimilation pigment composition.

At least five samples were collected and replicate measurements were performed per each canopy location for each species.

Leaves samples were prepared for laboratory analysis. Total chlorophyll was measured by using an Opti Sciences CCM 200 chlorophyll-meter indicating chlorophyll content per leaf area unit, related to the thickness of the leaf. Pigments were extracted by boiling the samples for 10 min at 80°C in 25 ml of ethanol. The extracts were cooled down in the absence of light. The absorbance of crude extracts was measured on a Metertek SP-850 spectrophotometer at the following wavelengths: 665 nm for chlorophyll *a*; 649 nm for chlorophyll *b*; 470 nm for carotenoids.

Photosynthetic pigment concentrations were calculated by using established equations that estimate concentration as a function of absorbance of foliar extracts at specific wavelengths (Lichtenthaler, 1987):

Chlorophyll *a* = $[(13.95 \times A_{665} - 6.88 \times A_{649}) / (d \times 1\,000 \times W)] \times V \times D$ mg / g FW

Chlorophyll *b* = $[(24.96 \times A_{649} - 7.32 \times A_{665}) / (d \times 1\,000 \times W)] \times V \times D$ mg / g FW

Carotenoids = $[(1\,000 \times A_{470} - 2.05 \text{ clf } a - 114.8 \text{ clf } b) / (245 \times d \times 1000 \times W)] \times V \times D$ mg / g FW

where: A - absorbance at a certain wavelength, V - volum of total extract, D – coefficient of dilution, W = fresh weight (g), d = lightpath (1cm) of cuvette, 1000 = conversion factor µg - mg. When expressed on the basis of sample fresh weight, the correction factor was the actual volume of the extraction divided by the sample fresh weight.

A HANSATECH – photosynthetic efficiency analyzer and an OPTI SCIENCES – OSI-FL fluorometer were used in order to measure parameters of the chlorophyll fluorescence. The following indices were determined: Fo – basal fluorescence, Fm – maximal fluorescence, Fv – variable fluorescence and Fv/Fm – maximum quantum efficiency.

PRELIMINARY RESULTS AND DISCUSSIONS

Correlated to the observed soil pH, the trends in concentrations of chlorophyll *a*, chlorophyll *b* and total carotenoids (Table 1.) were less consistent between species.

Table 1. *Content of the pigments and fluorescence parameters in leaves of different plant species collected in Roşia Montană, July 1st, 2011*

#	Species	CIm	clf.a (mg/g FW)	clf.b (mg/g FW)	car (mg/g FW)	Fo	Fm	Fv	Fv/Fm
1	Alder (*Alnus sp.*)	23.1±8.0	1.453	1.300	0.45	0940	4095	3198	0.783
2	Willow (*Salix sp.*)	31.7±5.0	0.35	0.13	0.03	0970	4095	3126	0.763
3	Birch (*Betula sp.*)	16.9±3.8	0.91	0.76	0.28	0905	4095	3193	0.778
4	Alder (*Alnus sp.*) (acidic soil)	24.7±19.7	1.429	1.247	0.44	0871	4095	3213	0.784
5	Willow (*Salix sp.*) (acidic soil)	26.4±19.1	0.26	0.08	0.01	0910	4093	3185	0.777
6	Birch (*Betula sp.*) (acidic soil)	21.5±10.6	1.777	1.48	0.55	0820	4095	3275	0.800

Generally. among all species. chlorophyll *a* levels were higher on the control soils. with the exception of *Betula sp.* which was highest on acidic sites. Similar trends were observed for chlorophyll b and for carotenoid levels among all three compared species. with significant ($p<0.05$) differences for *Betula sp*.

Chlorophyll fluorescence is an outstanding tool regarding the ability to separate regulation from stress compensation in primary reactions of photosynthesis. when combined with data from other homologous measurements. The parameters of chlorophyll fluorescence are influenced not only by the functional state of the photosynthetic system but also by the structure and composition of the sample and by the experimental arrangement. Photosynthetic efficiency was noted to be strongly dependent on leaf pH. Photosynthesis was diminished in plants when the leaf pH was low (Liu and Ding, 2008). However our work suggests that these findings are strictly related to the plant species. As can be shown in the table above, there are no significant differences between the total pigment content and the chlorophyll fluorescence at *Alnus sp* grown on control soil pH (6.8) and on acidic soil (2.9). In *Salix sp*. there is a significant decrease of the pigment content, but not significant differences concerning chlorophyll fluorescence parameters. In *Betula sp*. there is a significant increase of the pigment content but no significant differences concerning chlorophyll fluorescence parameters.

CONCLUSIONS

The present work suggests that the measurement of chlorophyll *a* fluorescence is a very fast and valuable technique for obtaining qualitative information about light dependent photosynthetic phase, even if only from chlorophyll fluorescence one should not conclude on the effect of environmental parameters such as soil pH on the photosynthetic activity.

Our results suggest that the soil pH has the capability to significantly modify chlorophyll content in relation to plant species but not the photosynthetic performance of leaves. However, in this case, we recommend that in such kind of experiments different techniques, combining multi-spectral and hyperspectral remote sensing data with the characteristics of the ground materials, should be used as complementary information sources to understand the adaptive and/or tolerance mechanisms of stress.

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PRELIMINARY DATA REGARDING THE STUDY ON PESTICIDES APPLICATION IN A RURAL COMMUNITY

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ABSTRACT. Extensive use of pesticides in agriculture is the most important exposure route for the rural population. Lately, specialists and public concern has increased considerably regarding the impact of pesticides on human health, as a number of studies highlighted the potential effects represented mainly by chronic diseases. Application of pesticides in agricultural practices represents a high risk that pollutants are carried away by the wind over long distances from the target areas and determine harmful effects upon populations outside the areas of application of chemicals.This study was performed in a rural area of Cluj County, in Sâncraiu locality, Romania, on the purpose to describe the circumstances regarding the application of pesticides. Population of Sâncraiu locality works mainly in agriculture and livestock, it is accessible in terms of culture and economics, it is stable without high rates of migration and industries present in the area are not important for the exposure to pesticides assessment. A sample of 100 inhabitants was randomly selected from the general population and invited to participate in a questionnaire-based survey. The questionnaire consists of a series of open and closed questions concerning: demographic data, lifestyle, personal pathological history, background information regarding activities within the household/farm. A percentage of 61 reported that they are the owners of the household they live and work in. It is worthy of note that, given the specific area and age of respondents, most of them (46%) declared that they worked in that farm for more than 30 years. At a rate of 75%, the respondents answered YES on the question whether they prepared or personally applied pesticides during their life. Despite progress registered in the environmental domain, research concerning the effects of environmental pollutants upon human health are insufficient at the moment, not only in Romania but throughout the world. In order to achieve these goals, a very well organized system is required. Emphasis should be set on the relationship between population exposure to environmental pollutants and human health. From the presented data it results that the investigated population has a prior as well as a present exposure to pesticides that if not controlled may be associated to some health effects. Next steps of the study will focus on highlighting the potential health effects, as well as the protection measures which should be implemented.

Key words*: pesticides, Romania, Sâncraiu*

INTRODUCTION

Pesticides are substances or mixtures of natural or synthetic substances, in order to control and remove any pests that compete with man for food, destroy the property and spread diseases (Tadeo, 2008). Pesticides occur often in small quantities, almost anywhere. The living environment and lifestyle largely determines the potential for exposure to pesticides. Exposure to pesticides as a result of their extensive use in agriculture is the most important exposure route for the rural population. Among the most serious diseases caused by pesticide poisoning, neurological disorders, internal organs disorders, skin disorders and cancer are to be distinguished. The majority of non-occupational exposures occur through food or by the use of pesticides in the home. In addition to the use in agriculture and forestry, pesticides are used in many public places, including office buildings, restaurants, schools, parks, etc. (US-EPA, 2002). The amount of pesticides applied and the area on which they are applied, are important for the exposure. Pesticides applied with a low frequency or in small amounts over a limited area in a remote location are unlikely to result in significant human exposure. In populated areas, notification regarding application of pesticides should reduce the probability of unexpected exposure for the population groups (US-EPA, 1999).

Pesticides are widely used in agriculture worldwide. During the last years, public concern has risen regarding their impact on human health. For this purpose, a series of studies have been developed in order to highlight the potential effects that cause chronic diseases, especially in children. Studies so far have related pesticides use with a variety of diseases including: cancer, nervous, mental and reproductive systems disorders. Children are more susceptible to the effects of pesticides due to increased exposure through food and breast milk, less developed immune system and longer life expectancy, time to develop diseases with long latency period (Gurzău et al. 2008). Some studies suggest organic food consumption in order to reduce exposure to pesticides, but there is a lack of precise evidence that this would certainly be a healthier option. In order to minimize exposure to pesticides it is recommended to reduce and even prevent their use in the household, to limit dermal exposure by using appropriate protective equipment and to consume organic food (Cohen, 2007).

Another study, performed in 2006 in the Philippines, attempts to demonstrate the effects of exposure to pesticides on human health, especially by the occurence of blood diseases. The study was performed on flower cultivators in La Trinidad, Benguet. 102 farmers were randomly selected and a series of questionnaires applied with respect to their work practices and everyone's state of health. Also, a series of tests for their hematological indicators were performed (Jinky, 2007). Most respondents were men in the age group 20-35 years old. The symptoms that they complained of were related to headaches, fatigue and cough. Laboratory analysis showed that the cholinesterase level (enzyme that destroys acetylcholine by hydrolysis) associated

with age, number of years of use of pesticides, use of contaminated clothing, incorrect mixture of pesticides, sex and diseases that respondents complained of was an abnormal one. Different from normal values were found also for hemoglobin, hematocrit, white blood cells and platelets count (Jinky, 2007).

Application of pesticides in agricultural practices represents a high risk that pollutants are carried away by the wind over long distances from the target areas and causes exposure to their harmful effects of populations located outside those areas. Using the GIS method (Geographical Information System, Geographic Information Systems), in Texas, USA, there have been identified a number of 1778 cases of cancer in children and 1802 control cases to identify cancer, between 1990 and 1998. These cases were associated with exposure to pesticides used in agriculture, based on proximity to the area of birth and to the cultivated fields. Multivariate models of analysis were used and the results obtained for most cases of cancer in children do not show any connection between the occurrence of the disease and the proximity to the area in which the children were born and the cultivated fields (Carozza et al. 2008a). In contrast, the assessments performed on the children living in areas with intense agricultural activity showed relatively high risks of cancer occurrence in children. The study was performed in the U.S.A on children aged 0-14 years old diagnosed with cancer, between 1995 and 2001. The results obtained, in terms of statistics indicated an estimated high risk for many types of cancer in children associated with the residence of the diagnosed ones in regions of moderate and intense agricultural activity. The risk for various types of cancer varies depending on the type of farming (Carozza et al. 2008b). Leukemia in children is another disease whose occurrence is associated with children's exposure to pesticides. There have been performed several studies in order to investigate the relationship between acute leukemia in children and their exposure to pesticides used in the household. In these studies, there have been taken into account data regarding the occupational exposure of parents, use of pesticides in homes and gardens and use of insecticide treatments against lice. The results showed that acute leukemia among children is associated with insecticide use by mothers during pregnancy and infancy and use of pesticides (especially insecticides and fungicides) in the household. Also, treatments with shampoos containing insecticides against lice present a high risk in the occurrence of leukemia.

A study was performed on the rural population (Saliste, Romania) regarding the use of pesticides. Specific data were gathered from a number of 49 people, data considering the following: demographic issues, medical history, indoor exposure, occupational exposure, habits (smoking, drinking alcoholic beverages, eating), etc. (Gurzău et al. 2008; Neamțiu et al. 2010). All survey respondents indicated that they use pesticides in their activities with one or more purposes: to control pests (weeds, diseases, insects) in crops, to control insects that affect animals and use of pesticides in their own home. Almost all respondents declared that they prepare and apply pesticides

themselves. Crops on which they apply pesticides are situated at relatively small distances from the households, but the application of pesticides in the household where children are present represents the highest risk (Gurzău et al. 2008; Neamțiu et al. 2010). In terms of qualification and training the population how to use pesticides, it lacks, those who apply pesticides do not have the necessary knowledge about safety and risk exposure. They do not use appropriate protective equipment, the face and hands being the most exposed parts of the body during preparation and application of pesticides. Quantities of pesticides applied and the conditions of application are not the recommended ones by the manufacturer (usually, much higher amounts than the recommended doses are applied). Respondents were not aware of the decontamination procedures in case of accidents.

Despite progress recorded in the environmental domain, research concerning the effects of environmental pollutants upon health are insufficient at present, not only in Romania but throughout the world. In order to achieve these goals a very well organized system is required. Emphasis should be posed on the relationship between population exposure to environmental pollutants and human health. Symptoms and diseases should be evaluated according to past and present exposure to pollutants concerned and the sources of exposure should be considered in terms of their effects on human health (Gurzău et al. 2008).

MATERIALS AND METHODS

In order to determine the magnitude of problems related to pesticides use, a study on population was performed during 2011 in the rural area of Sâncraiu locality, Romania. The following issues were considered in the selection of the geographical areas with a history of pesticides use:

- economic activity based mainly on agriculture and animal husbandry;
- accessible population in terms of: geographical, cultural, economical;
- absence of industrial activities to introduce confounders in data analysis.

Sâncraiu locality meets these criteria: the population in the area deals mainly with agriculture and livestock, it is accessible from geographically, culturally and economically points of view, it is stable without high rates of migration, the industries present in the area are not important for the assessment exposure to pesticides. Out of the general population a sample of 100 people was selected and invited to participate in the questionnaire-based survey. The questionnaire consists of a series of open and closed questions. Demographic data were collected, also data regarding the lifestyle, personal pathological history, background information about the activities performed within the farm. Databases and their processing were performed using Excel program.

Participants that were invited to participate in the study are residents of Sâncraiu, some who use pesticides in crops, orchards, livestock and others who have never used pesticides. Sâncraiu is a locality in Cluj County, Transylvania, Romania, and consists of five villages (Sâncraiu village - locality residence, Alunişu, Domoşu, Brăişoru, Horlacea). Sâncraiu locality, with a total area of 56.83 km is located at an average altitude of 600 m at a distance of 56 km from Cluj-Napoca (county center) and 5 km from the first city, Huedin.

Both in terms of scientific and economic/administrative and sustainable development strategy, the issue of pesticide exposure in rural areas represents a priority worldwide, at the European Union level, but mainly at national level. An issue that requires a careful and accurate approach is to identify and assess the risk areas to health and environment that exist in Romania, followed by the proposal for appropriate programs for risk reduction and control of the risk sources.

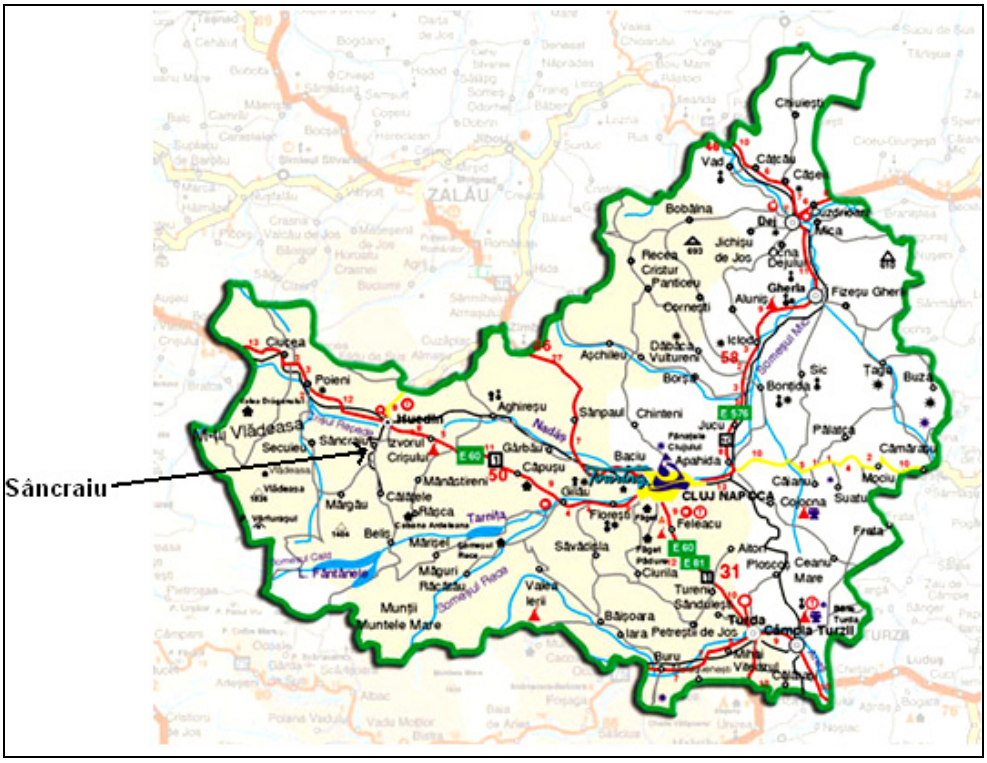

Fig. 1. *Location of Sâncraiu locality in the area.*

RESULTS

The sample of respondents consisted of 100 people, residents of Sâncraiu locality, out of which 50% were of feminine gender, the average age of the entire group being 50.71 years old.

Table 1. *Age of the population in study.*

Number of interviewed people	Average age	Standard deviation	Maximum age	Minimum age
100	50.71	15.23	89	22

Fig. 2 shows that the majority of respondents stated that they have completed 8 primary grades (33% respondents), in 30% of cases the answer was "high school", 6% graduated from college, 26% graduated from a vocational school and other 5% had completed less than four years of high school.

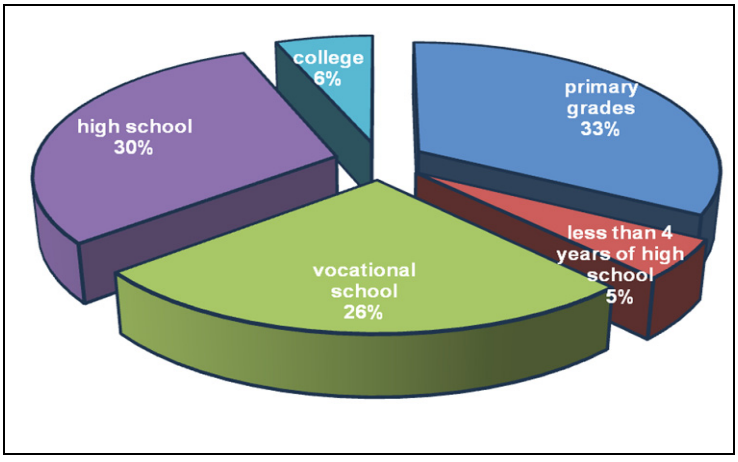

Fig. 2. *Distribution of the population in study by the level of education.*

The questionnaire included, besides the demographic and identification information, information about the lifestyle of the people concerned. Questions in this section target especially food, habits such as smoking and alcohol consumption (both the amount consumed and the frequency and consumption characteristics).

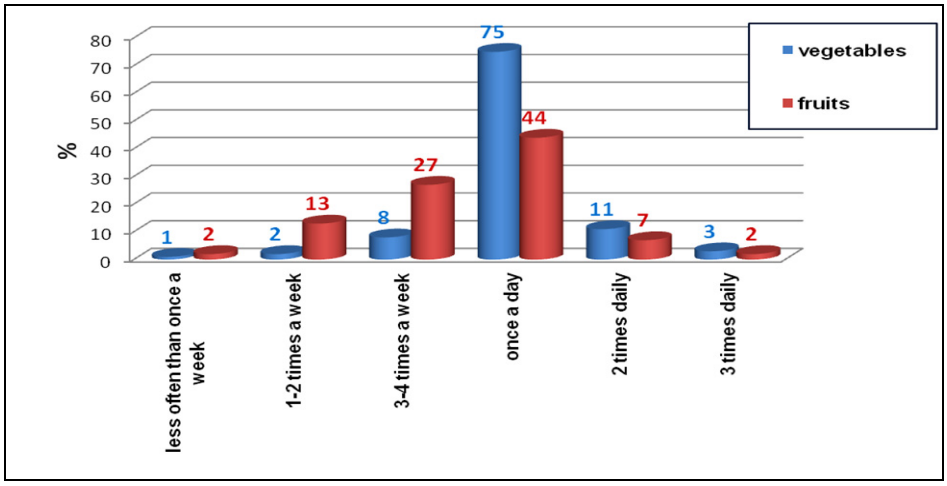

Fig. 3. *Consumption of vegetables and fruit of the population in study.*

Fig. 3 shows that 75% respondents stated that they consume vegetables at least once a day both from their own production and from other sources. Vegetable consumption varied generally from once a week to 3 times daily (three people of all respondents stated that they eat vegetables at every main meal of the day, i.e 3 times per day). With regard to fruit consumption, 44% respondents stated that they eat fruit at least once a day (consumption that is also the most frequently reported by the respondents).

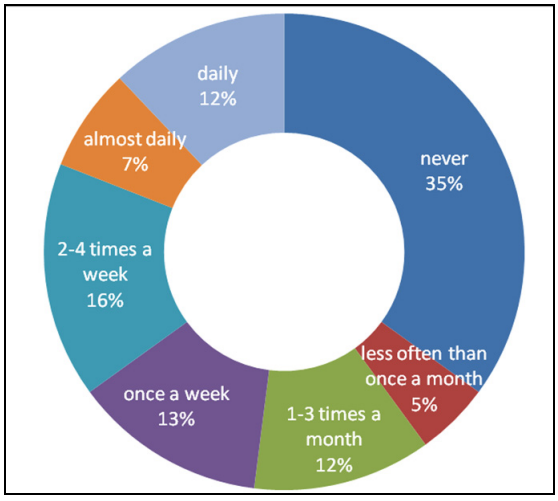

Fig. 4. *Alcohol consumption of the population in study.*

Regarding the personal history of alcohol consumption and also the alcohol consumption at the time of filling in the questionnaire, 16% declared that they consume alcohol 2-4 times per week, the history of alcohol consumption most frequently reported being 1 or 2 alcoholic beverages in the previous year prior to filling in the questionnaire.

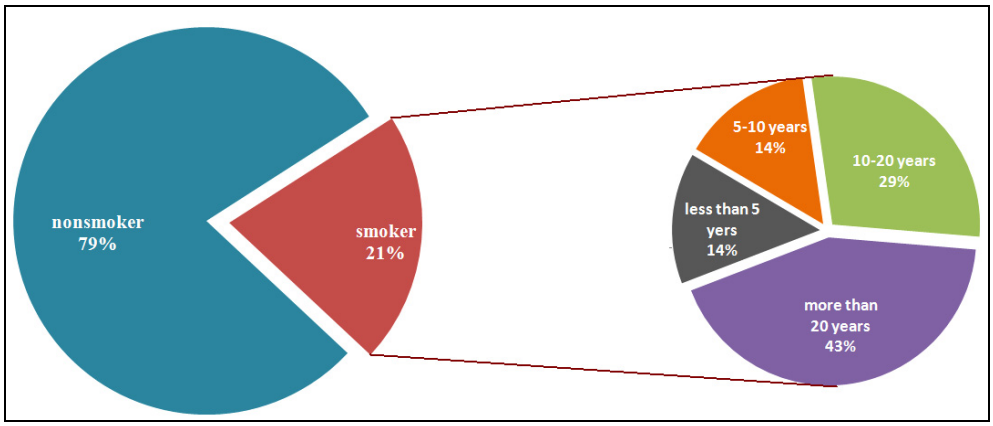

Fig. 5. *Cigarettes consumption of respondents.*

With regard to smoking, 28% declared that they had a history of smoking and 21% declared that they still smoke. Cigarette consumption in smokers was, on average, a pack a day. 14% of smokers stated that they have smoked less than 5 years, 14% between 5 and 10 years, 29% 10-20 years and 43% have smoked more than 20 years.

Pathological personal antecedents reported by the people enrolled in this phase of the study consisted of respiratory diseases, neoplastic pathology, cardiovascular pathology, renal diseases (excluding kidney stones), nervous system diseases and depression. The reported frequency of the investigated pathology was as follows: 2 respondents reported suffering from asthma, 1 respondent reported chronic bronchitis, 2 respondents reported COPD, 21 respondents reported a history of pneumonia, 1 respondent reported emphysema, 1 respondent reported Hodgkin lymphoma, 21 with cardiovascular diseases, 2 respondents reported suffering from diabetes, 4 with kidney diseases except urolithiasis, 5 with neurological disorders and 1 respondent declared suffering from depression in antecedents. A percentage of 61 reported that they are the owners of the farm where they live and work. It should be noted that, given the specific area and age of respondents, most of them (46%) declared that they have been working in the farm concerned for a period of more than 30 years. Regarding the farming activities within the farm, 26% respondents stated that they have performed such activities in the last agricultural season during one month (30 days), 27% between 31 and 100 days and 20% more than 100 days.

With respect to operating harvesters and other farm equipment most respondents stated that they never used the respective farm equipment (84%). 5 respondents reported an intense use of the farm equipment in the everyday work at the farm. Planting is another important activity in the economy of a farm and it is also important as a route of exposure. 25% respondents declared that they have never performed a planting operation, 63% declared that they planted 1-5 days and 11% between 6 and 25 days during the last agricultural season.

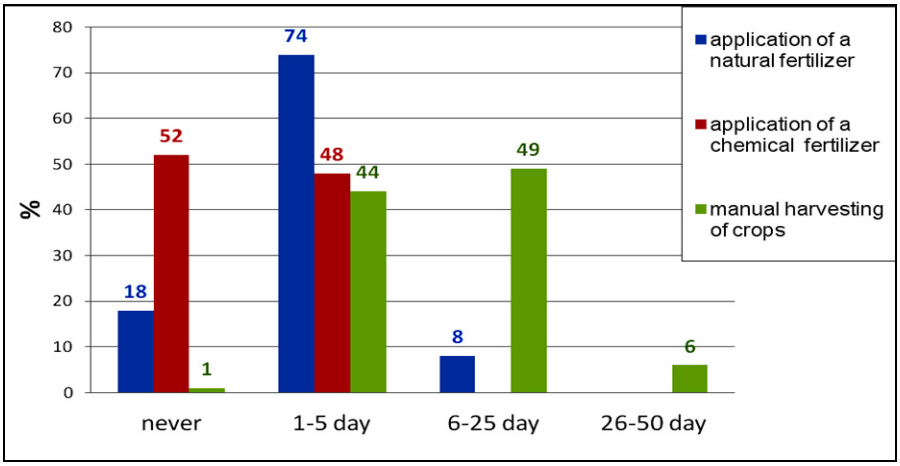

Fig. 6. *Application of natural and chemical fertilizers and manual harvesting of crops in the population in study.*

Application of a natural fertilizer was performed in the ratio of 74% in a period of 1-5 days. Respondents declared that application of chemical fertilizer was performed in the ratio of 48% in a period of 1-5 days during the last agricultural season while 52% never used chemical fertilizers.

In Sâncraiu area, the activity in farms is mainly non-mechanized, as stated in the questionnaires applied to the people from the group in study. Manual harvesting of crops was reported in a significant percentage (49%) as performed in a period of 6-25 days, 6% stated that they even exceeded this period, the activity being performed within 26-50 days.

It was observed that an important activity in a farm is animal husbandry. In most cases several species are raised of which the most important were: cattle (both for meat and milk) and swine. Potatoes and wheat were the most important crops, as resulting from the application and interpretation of the questionnaire for the population in study.

Farmland in question was mainly between 5 and 49 ares (37%) and in 22% cases, farmland was bigger than 200 ares.

In a percentage of 75% respondents answered YES to the question whether they have personally prepared and applied pesticides during lifetime. Most (49%) declared that they have applied the pesticides concerned for a period of time between 11 and 30 years, between 1 and 9 days on average per year.

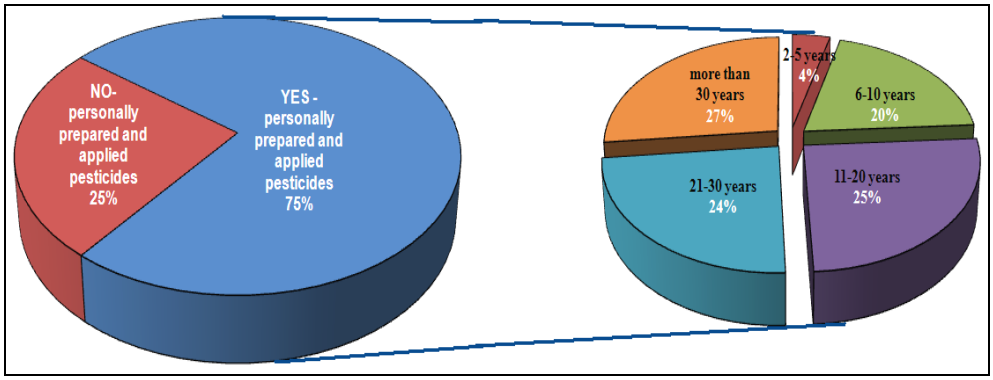

Fig. 7. *Application of pesticides in the population in study.*

Farming and animal husbandry in the area are important activities for the respondents. Preparation and application of pesticides are part of common activities. According to the statements of the respondents, the process of pesticides application is performed for a period of 5-9 days each year (90%). One respondent declared that he applies pesticides for a period longer than 40 days.

CONCLUSIONS

The rural population may be exposed to pesticides in several ways: by spraying into the air and ingestion of pesticide residues via food and drinking water. The actual incidence of pesticide poisoning is not known. Estimates suggest that the total number of acute poisoning cases with severe manifestations probably exceeds one million per year, with a death rate of patients of 0.4 ÷ 1.9%; it was estimated that the occupational exposure accounts for 70% of cases. The incidence of acute pesticide poisoning in Europe is not well known, and varies widely from one country to another.

The results from the data presented show that the population in study has previous and present exposure to pesticides due mainly to non-mechanized agricultural activities. The next steps of the study will focus on highlighting the potential health effects, as well as the protection measures that should be implemented.

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CONSTRUCTION AND CHARACTERISATION OF A MEMBRANE-FREE MICROBIAL FUEL CELL

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ABSTRACT. A functional membrane-less microbial fuel (ML-MFC) was constructed and evaluated in terms of optimizing performance. By increasing the concentration of free ions of the electrolyte by 1.3g/l NaCl the internal resistance (R_{in}) of the cell decreased from 1.56 to 1.19 kΩ. By decreasing the distance between the anode and cathode the R_{in} decreased by 0,01kΩ/cm and the electrical power increased by 4 μW/cm. By introducing air sparging at the cathode the electrical power increased by 278%. The cell reached a maximum power density of 8.6 mW/m^2. It has been observed that over time the power increases due to the fact that the microorganisms need a period of time to accommodate to the new ML-MFC's environment. The ML-MFC works well with sodium acetate as a carbon source and has the capacity of consumption of 20 ml sodium acetate 1M over a period of 30 days.

Key words*: renewable energy, microbial fuel cell, membrane-free*

INTRODUCTION

A microbial fuel cell (MFC) is a device that converts the energy stored in chemical bonds in organic compounds to electrical energy (Du et al. 2008) with the aid of the catalytic reaction of microorganisms (Jang et al. 2004). MFCs have great potential as a method of wastewater treatment and as power sources for autonomous sensors (Liu et al. 2008).

Traditionally, MFC consists of two chambers, anode and cathode, separated by proton exchange membrane (PEM). Microorganisms oxidize the substrate and produce electrons and protons in the anode chamber. Electrons, collected on the anode, are transported to cathode by external circuit and protons are transferred through the membrane internally. Thus, potential difference is produced between anode chamber and cathode chamber due to dissimilar liquid solutions. Electrons and protons are consumed in the cathode chamber by reducing oxygen, resulting water (Ghangrekar and Shinde, 2006).

Not using a PEM to separate the two compartments the construction of the MFC is simplified. But the main disadvantage of not using a PEM is the significant oxygen diffusion in the anode compartment (Shaoqiang et al. 2009), which can limit the development of the anaerobic microorganisms.

MATERIALS AND METHODS

Figure 1 shows a schematic of the membrane-less microbial fuel cell (ML-MFC) developed in this study. The ML-MFC was constructed from a PET bottle, with the height of 13.6 cm and diameter of 50 cm. The electrodes were made from two disks of graphite with active surface of 141.36 cm^2 and electrical resistance of 0.26 Ω/cm. The anode was placed at the bottom of the cell and the cathode was suspended in electrolyte in the top part. The distance between the electrodes could be varied from 2 to 9.5 cm. A disc of synthetic material (water filter for aquarium pumps) was used to separate the anode from the cathode areas.

As a microbial substrate it has been used concentrated fermented sludge, from the final step in the treatment of active sludge (from the fermentation sludge tank), collected from Water treatment Station, Cluj-Napoca.

During in time, a biofilm develops on the electrode surface. The nature of enriched microbial population is dependent on the enrichment conditions (Choo et al. 2006). When the population from sludge is feeded with acetate (our case), γ and δ Proteobacteria are the most present species (Lee et al. 2003).

The cell was operated in batch mode, supplying fuel through the top part of the cell. As fuel it was used sodium acetate, 1M. The electrodes were connected with a variable resistance of 5kΩ. The cathode was sparged with atmospheric air with the aid of an aquarium pump.

The current and potential difference was measured using with two multimeters, MAS Tech-MAS and UNI-T-M830BUZ.

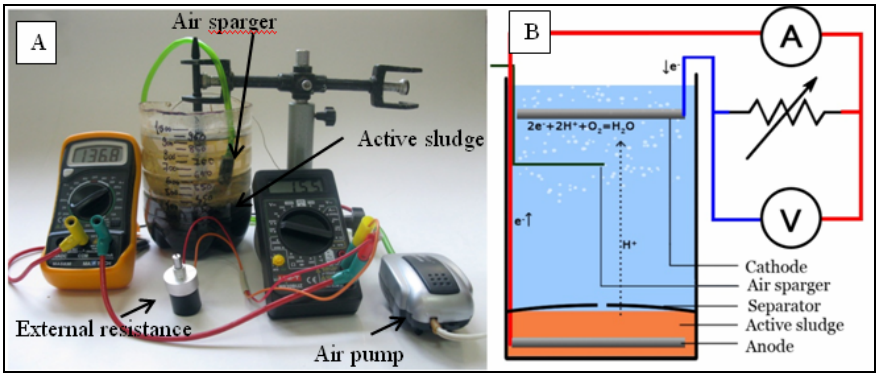

Fig.1. ***A.*** *Photograph of the ML-MFC;* ***B.*** *Schematic diagram of the ML-MFC.*

RESULTS AND DISCUSSION

Internal resistance

To evaluate the internal electrical resistance (R_{in}) has been used the polarization curve method, as described by Logan, 2008. The initial R_{in} was 1.56 kΩ. Internal resistance has a decisive influence on the power generated by the MFC. Thus we tried to minimise it by increasing the conductivity of the electrolyte by adding salt. Addition of salt can increase the power by decreasing the internal resistivity, but microorganisms can be affected at very high salt concentrations (Oh and Logan, 2006).

To determine the effect of adding salt on R_{in}, NaCl was added in portions until the concentration reached 1,3g/l, Fig. 2. After every portion of salt added it was waited 24 hours for the salt to dissolve completely, after which the R_{in} was evaluated.

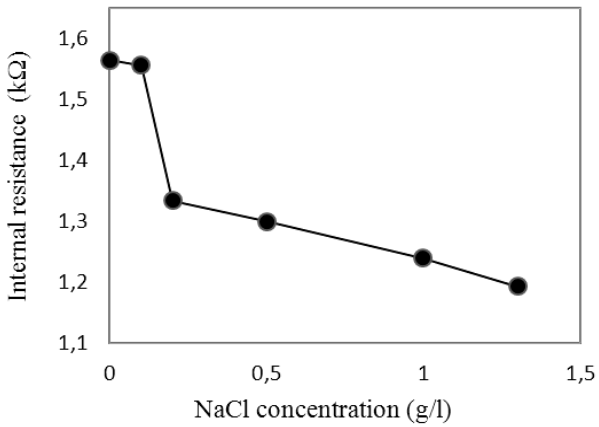

Fig. 2. *Effect of salt concentration on R_{in}.*

Effect of changing the distance between the electrodes

By changing the distance between the electrodes, the thickness of electrolyte that the electric current has to travel varies. The greater the distance that the current has to pass the bigger the ohmic resistance (Jiang and Li, 2009).

The distance was increased one centimeter at a time from 2.5 to 9cm. The distance directly influences the performance of the ML-MFC. The R_{in} increased from 1.14 to 1.22 kΩ, representing an increase of 0.011 kΩ/cm. The power decreased from 67.6 to 59.4 μW, representing a decrease of 1.25 μW/cm, Fig. 3.

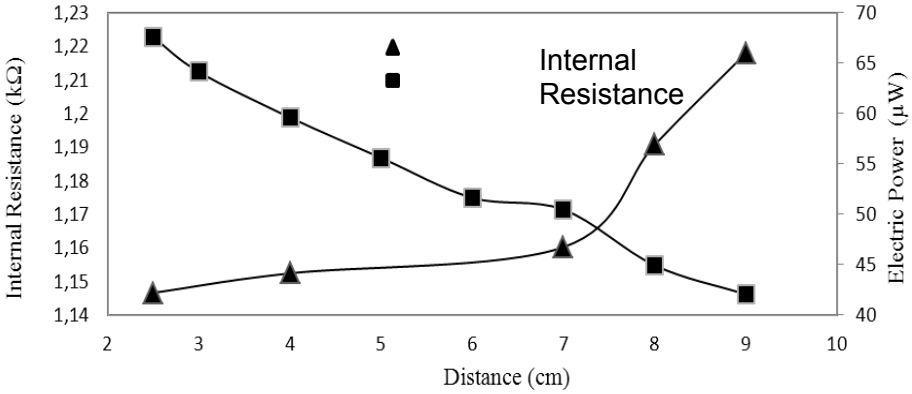

Fig. 3. *Effect of the distance between the electrodes upon the internal resistance and electrical power of the ML-MFC.*

Effect of air sparging at the cathode

To evaluate the effect of air sparging on the performance of the ML-MFC, we introduced aeration at the cathode with the aid of an aquarium pump. After we introduced the air sparging, we evaluated the electric power at specific time intervals. As shown in Fig. 4 after aeration is introduced, the power rapidly increases from 16.9 to 63.7μW in just 22 minutes, representing an increasing of 278%. Afterwards the power slowly stabilizes at the value of 67.2 μW after approximately one hour after the aeration was introduced.

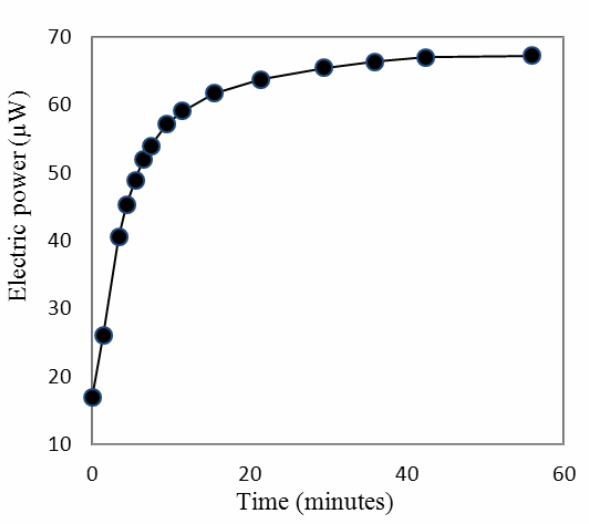

Fig. 4. *The evolution of electrical power from the moment of introduction of air sparging.*

Effect of sodium acetate

In the majority of MFC studies until know, sodium acetate was used as nutritive substance. Substances, like waste water, are more difficult to use in MFCs in comparison with acetate. Furthermore, acetate is a final product of microbial decomposition of more complex substances, like glucose (Pant et al. 2010).

The ML-MFC was fed with sodium acetate, 1M, in portions of 20 ml. The acetate was introduced through the top part of the cell. The cell was operated at an external resistance (R_{ex}) of 0.5 kΩ.

As shown in Fig. 5 after the introduction of sodium acetate the power increases significantly in the next days, afterwards decreases and arrives to a minimum comparable with the initial moment. By analysing the graph with approximation the cell consumes over a period of 30 days a portion of 20 ml of sodium acetate 1 M.

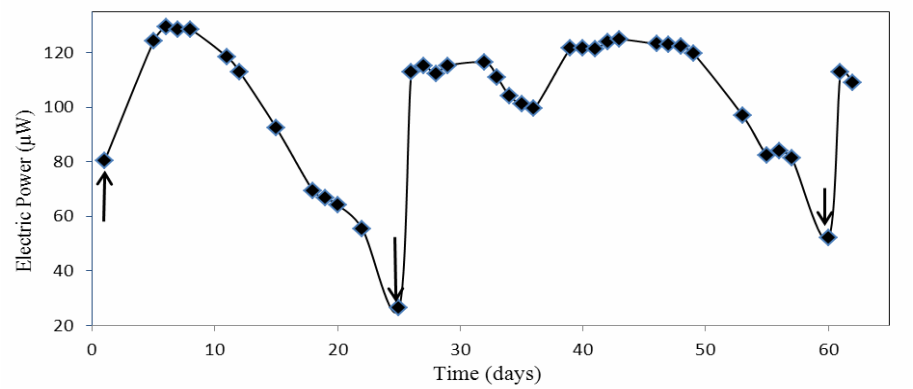

Fig. 5. *Electric power in time of ML-MFC. The arrows represent the moment of introduction of 20 ml sodium acetate 1M.*

CONCLUSIONS

In this research, we successfully constructed a functional ML-MFC using accessible materials. We have shown that by increasing the electrolyte electric conductivity the R_{in} decreases; that by decreasing the distance between the electrodes the R_{in} decreases and the electric power increases. Air sparging is essential for this ML-MFC, increasing significantly the power output. The cell works well with sodium acetate as a carbon source, reaching a maximum power density of 8.6 mW/m2 and has a capacity of consumption of 20 ml sodium acetate 1M over a period of 30 days.

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EXPOSURE ASSESSMENT AS A COMPONENT OF INDUSTRIAL HYGIENE

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ABSTRACT. The workplace today is becoming more complex. The variety of risks associated with workplace exposure to chemical, physical, and biological agents is increasing. Industrial hygiene is defined as "that science and art devoted to the anticipation, recognition, evaluation, and control of those environmental factors or stresses, arising in or from the workplace, which may cause sickness, impaired health and well-being, or significant discomfort and inefficiency among workers or among the citizens of the community." So, the first priority of the industrial hygienist is to protect the health of workers, but health risk is not the only risk he or she is asked to manage. Others would be regulatory risks, legal risks, and risks related to the anxiety inherently associated with many people's response to exposures. Exposure assessment is the heart of industrial hygiene programs as it supports all of the functional elements (hazardous materials management, engineering controls, administrative controls, personal protective equipment, medical surveillance, exposure monitoring, education and training). Occupational exposure assessments are performed in work-places employing a few, and up to, maybe, thousands of workers. The magnitude of these exposures varies from minute-to-minute, hour-to-hour, and day-to-day. For the industrial hygienist, the primary goal is to assess the exposures and occupational health risks for all workers to all environmental agents on all days. The challenge is to do this accurately and efficiently, regardless of the diversity of exposures across workers and across time. A thorough understanding of exposures allows the industrial hygiene program, including control efforts, to be prioritized to protect employees and manage exposure-related risks. It also puts the industrial hygienist in position to better manage the unpredictable changes that will occur both in knowledge of the health effects of environmental agents and in society's tolerance of workplace exposures. Coupled with good work history information, comprehensive exposure assessments will enable better epidemiology and refinement of our understanding of the relationship between occupational exposures and disease.

Key words: *exposure, industrial hygiene, occupational, monitoring*

INTRODUCTION

Industrial or occupational hygiene is the workplace health profession dedicated to the anticipation, recognition, evaluation and control of hazards in the ocupational environment. The focus is on chemical, physical and biological agents along with ergonomic and human factors, that cause or contribute to impaired function, disease, disability, injury and discomfort emerging from work (DiNardi, 1997).

The occupational environment is subject of major differences as compared its last decades evolution. Therefor, the large variety of risks related to workplace chemical, physical, and biological agents exposure is increasing, mostly from a mixture and/or combined perspective rather than high intensity of exposure.

Workplace risk assessment for employees and organization, will need to drive industrial hygienists to accountable indicators from day to day risks to future anticipation and prevention approach as state of the art and science translation into action. The industrial hygienist should never analyze exposure as a result of measurement against established exposure limits, it would rather explore whether exposures are characterized well enough, and controlled well enough to reach acceptable risks and to put the employeer in the position to manage future risks. Thus, the industrial hygienist have to address several major issues such as: whether the exposure affect employee health, if the exposure limit will protect worker health for its particular workplace situation, and what would be the associated risks for that specific exposure scenarious (Mulhausen and Damiano, 1998). Obviously, compliance with current or regulated limits is not sufficient for workplace health and safety as a state of the art approach. Very many chemicals have no occupational exposure limits, and the information used to set existing limits is often incomplete. Also, existing limits are not always designed to protect the most sensitive workers. Meanwhile there are so called “gratie” periods when during a certain period of time the employer must comply with new limits, while new toxicological, epidemiological and extrapolated experimental data are strong evidences for lower limits of hazardous substances and/or situations at the workplace (DiNardi, 1997). As a result most of the limits are subject of major changes in terms of new lower levels, and new substances will be taking into account and start to be regulated. Experience has shown that most exposure limits are lowered when they are changed, and there is no reason to believe that trend will not continue (Mulhausen and Damiano, 1998).

Exposure assessment is the heart of industrial hygiene programs as it supports all of the functional elements (Fig. 1).

The industrial hygiene evaluation has its major focus on exposure, exposure assessment and intervention. The industrial hygienist develop activities from workplace monitoring to training programs, better target medical surveillance programs, and define specific requirements for personal protective equipment (PPE).

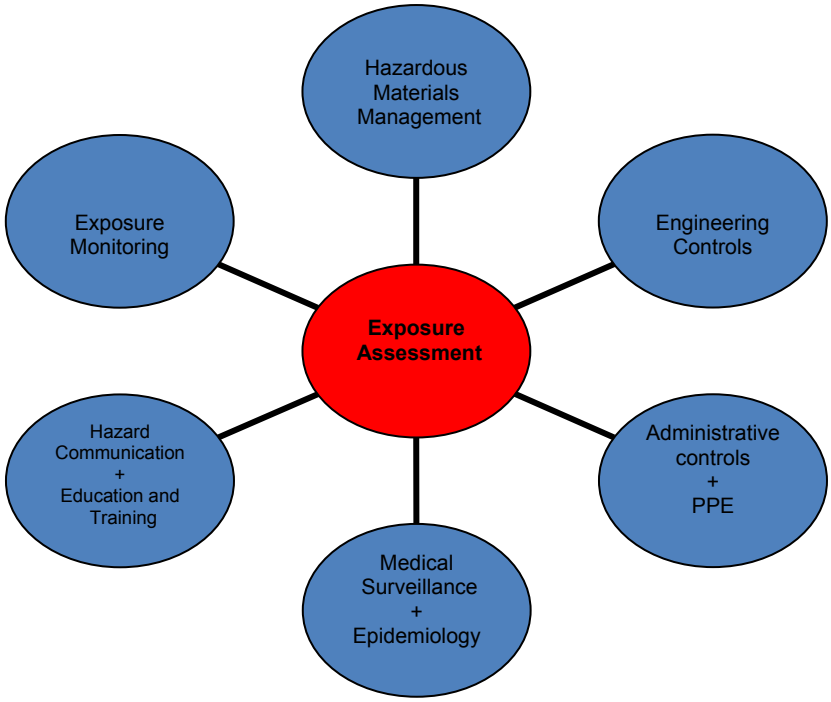

Fig. 1. *Exposure assessment's central role in industrial hygiene program management*

EXPOSURE ASSESSMENT STRATEGY

At every workplace the exposure assessment strategy has to be a process under a cyclic nature and a matter of continuous improvement and changes. This assessment need to take into account every new data on workplace related dose response relationship and the huge variety of working conditions currently or by chance observed at the level of workplace. The first step of exposure assessment will begin by collecting available information that is relatively easy to obtain. Then the data obtained by the initial exposure assessments based on that information will be used to prioritize follow-up control and information-gathering efforts. As a consequence, the allocated resources have to be focused on specific exposures with an emphasize on the highest priority associated to the potential health risk. This way the exposures are better understood and controlled, they will drop in priority and therefore the industrial hygienist will move over to the next cycles through the strategy and will therefore address the next tier priority exposures (DiNardi, 1997).

The major steps in the strategy are (Fig. 2):

START: ESTABLISH THE EXPOSURE ASSESSMENT STRATEGY. IN ESTABLISHING AN ORGANIZATION'S exposure assessment strategy, the following issues should be carefully addressed: role of the industrial hygienist; establish the exposure assessment goals; written exposure assessment program.

Basic Characterization: Gather information to characterize the workplace, work force, and environmental agents. The exposure assessment process should begin with collecting and organizing basic information needed to characterize the workplace, work force, and environmental agents. Gather information that will be used to understand the tasks being performed, materials being used, process being run, and controls in place so that picture of exposure conditions can be made.

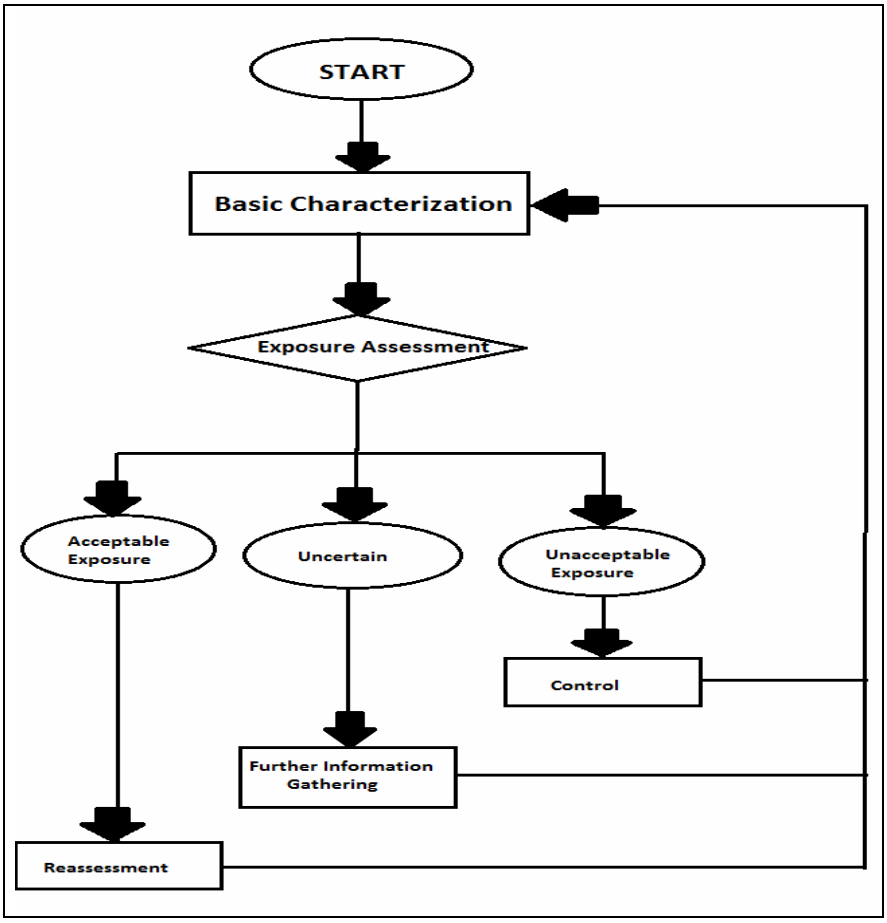

Fig. 2. *AIHA strategy for assessing and managing occupational exposure (Mulhausen and Damiano, 1998).*

Exposure Assessment: Assess exposures in the workplace in view of the information available on the workplace, work force, and environmental agents (Mulhausen and Damiano, 1998).

Define similar exposure groups – similar exposure groups (SEG) are groups of workers having the same general exposure profile for the agents being studied because of the similarity and frequency of the tasks they perform, the materials and processes with which they work, and the similarity of the way they perform the tasks. Data about jobs, processes, tasks, control equipment, and materials that have been gathered and organized in the basic characterization phase is used to divide workers into similar exposure groups.

Define exposure profiles. An exposure profile is an estimate of the exposure intensity and how it varies over time for an SEG. Information used for defining the exposure profile may include qualitative or quantitative data, or both. At the start of the exposure assessment process, few quantitative data may be available, so most early exposure profiles will be based on qualitative information. As the information gathering and assessing cycle progress, SEGs may be redefined and their exposure profiles modified based on new information.

Make judgments on acceptability of the exposure profiles foe each SEG. A judgment is made about the exposure, using the exposure profile and information collected on the agent's toxicity. This judgment is used to prioritize control efforts or the collection of more information based on the environmental agent's estimated level of exposure, severity of health effects, and the uncertainty associated with the exposure profile and health effects information. In this system:

- Exposures judged unacceptable are put on a prioritized list for control. The list should be prioritized such that higher exposures to higher toxicity will be corrected first.
- Exposures not certain enough for a decision are put on a prioritized list for further information gathering. The type of information needing to be collected may vary from one SEF to another. The exposure profile for one SEG may be well understood, but the toxicity data may be scarce. In that case it is important to collect, or in some cases to generate, toxicological or epidemiological data.
- Exposures judged acceptable are documented as such and may be put on a list for periodic routine reassessment to verify that exposures continue to be acceptable.

Further information gathering: Information gathering efforts should be prioritized. Higher priority should be given to information needs associated with higher exposure estimates, higher toxicity estimates, and higher uncertainty estimates. In some cases, if exposure and toxicity estimates are high enough, consideration should be given to the use of personal protective equipment or another interim control while the information is gathered or generated.

Information needs will vary for each exposure profile and judgment. The types of information that might be needed include: exposure monitoring, exposure modeling, biological monitoring, toxicological data generation and epidemiological data generation.

Health hazard controls. It is critical that industrial hygiene control programs be deployed and adjusted in view of exposure assessment findings. Exposure assessment findings can also be used to prioritize the implementation of health hazard controls. Diagnostic monitoring can be used to identify and measure the specific sources of unacceptable exposures, evaluate the effectiveness of existing controls, and determine whether new or modified controls are effective (Mulhausen and Damiano, 1998).

Reassessment. It is important for exposure profiles and SEGs to be kept up-date. This requires the entire exposure assessment process to be update on a timely basis or maintained through a comprehensive management-of-change process. This will ensure that exposures continue to well-understood and that the organization's industrial hygiene programs continue to respond to changing priorities.

Communication and documentation. Exposure assessment findings must be communicated in a timely and effective fashion to all affected workers and others who are involved in worker health protection. The entire exposure assessment process, including follow-up recommendations and closure on the recommendations, must be documented. Lists of SEGs, their exposure profiles, and judgment on their acceptability should be stored permanently so that individual exposure histories can be generated. Information on baseline and routine monitoring programs, as well as hazard control plans, must be kept – as should evidence that the recommendations were acted on appropriately.

INDUSTRIAL HYGIENE PROGRAMS (CASE STUDIES)

Foam Factory

The study focused on the exposure of workers to toluene diisocyanate in a Polyurethane Foam Factory located in Baia Mare, Romania. The technological process is simple, there is a foaming line, making continuous streams (all components meet in the foaming head).

Workplace air measurements were performed in different departments of the plant, after sampling either in fixed points or as personal monitoring. Fixed point (-ambient sampling) was carried out at breathing level (1.5 m) with a pump – silica cartridge device. Air sampling was correlated with duration of the pollutant emission. Personal monitoring is a sampling method very efficient for the exposure assessment of workers to occupational hazards, as it is a shift measurement timing. This method requires workers wearing the ensemble consisting of a personal pump device and the silica cartridge (Rusu et al. 2011).

Inside the factory, two measurements were performed at fixed points in the foaming department, at the ends of the plant: the first one next to the mixer in which take place the addition of the components and the second one at the end of the plant were foam block is already formed. The sampling time for this measurements was 100 minutes at a flow rate of 0.25 l/min.

In this department (foaming), a series of personal monitoring were also completed. Three workers with the workplace along the plant had worn the ensemble formed by personal pump and silica cartridge. These workplaces were situated at the beginning of the plant, next to the mixer, at the middle of the conveyor belt and at the end of the line. The sampling in this case was during one foaming process, with a flow rate of 0.25 l/min (Rusu et al. 2011).

More personal monitoring was made in the cutting area for two workplaces. The sampling time was 120 minutes with the flow rate of 0.25 l/min.

Laboratory analysis is gas chromatography (coupled with mass spectrometry) and begins with preparing the devices and the column according to instructions. After this, the calibration curve must be drawn; initially two series of standard solutions were prepared with the solvent. The extraction has been made in the following concentrations: 40 µg/l; 60 µg/l; 80 µg/; 100 µg/l. The standards were measured by recording the chromatogram for each standard solution. The device software plots the calibration curves, these being linear curves. Calibration curve should be checked no less than at 12 months, and always when using new reactors. Reagents utilized in this method are GC-purity methanol and E1 standard TDI (Merck supplier).

The purpose of this procedure is to determine TDI air concentration, after adsorption and desorption on activated silica gel cartridge. The method described is applicable to both industrial isomers (2,4 - and 2,6 - TDI). The principle of this method is quantitatively transfer of the sample from the silica gel cartridge in a vial followed by extraction of the toluene diisocyanate with methanol. The extract is afterwards measured using a mass spectrometry chromatograph (GC-MS Shimadzu QP2010). (Rusu et al, 2011)

As the monitoring process began right from the opening of the factory, a group of presumably unexposed new workers has been initially evaluated through out a health questionnaire, pulmonary function tests, serum TDI antibodies and individual polymorphisms, as well. At a 6 months follow up, lung function tests and blood sampling were repeated, while the questionnaire was reapplied to the subjects. TDI antibodies and individual polymorphisms are not discussed at this moment (Rusu et al. 2011).

Trained interviewers filled in the questionnaires independently. Questions were aimed to record respiratory health problems and allergic background in specific details. Smoking habits and close contact with pets or other animals, as well as home environment, were briefly asked in the questionnaire, while a special attention was

paid to the work practice – personal protective equipment, and exposure control measures such as ventilation and hygiene conditions, along with questions on workers' compliance to safety rules (Neagu et al, 2010). A matter of interest was the issue of previous contacts with polyurethanes, explicitly TDI and other diisocyanates; sections of the questionnaires covered information about pre-employments and exposure to insulating construction foams or sprayed paints.

The lung function tests were performed and their results interpreted by occupational healthcare professionals. Standard spirometry parameters were pursued and on their bases, the specific diagnostics were set (Neagu et al. 2010).

Tires Factory

The study case refers to a factory producing car tires. After the exposure assessment goals were established, the basic characterization begin. The technological process was complex with different exposure sources. The major workers exposure were the COVs. There were huge variations in terms of exposure, both temporal (during different stages of the technical process) and spatial (because of the workplace migration) (Harris et al. 1993).

The third step in the strategy for assessing and managing occupational exposure was the exposure assessment. The intensity of the exposure must be measured by personal monitoring of the workers because of the big variations of the exposure. COVs samples were taken by personal monitoring from different workplaces, along technological line. For sampling low flow pumps and activated charcoal cartridge were used. This sampling ensemble was carried on the workers during their shifts. After the sampling the cartridges were sealed to avoid contamination and kept in refrigerator until they were analyzed.

Laboratory analysis is gas chromatography (coupled with mass spectrometry) made with chromatograph-GS-MS Schimadzu QP 2010 Plus.

Based on the results a couple of health hazard controls were imposed: engineering controls (improve ventilation system, some raw material should be eliminated or substituted), administrative controls (reducing worker exposure time), work practice controls (worker education and training) and PPE (personal protective equipment).

Wooden products factory

The study addresses the assessment of formaldehyde exposure of the workers from a wooden products factory.

First two steps of the industrial hygiene program were anticipation and recognition of hazards in the occupational environment. The technological process is continuous and automated. The major workers exposures are on formaldehyde and noise. Formaldehyde is one of the most widely used organic compounds and is

indispensable chemical in many industries. Usually, the workers oversee the machines during the line process, so the exposure has different intensity in different workplaces.

The evaluation in industrial hygiene program suppose measuring formaldehyde and noise at the workplace. In order to measure formaldehyde, air samples were collected for 15 minutes on tubes (SKC 226118) containing 2-hidroxymethil piperidine, using an aspirating pump calibrated at 0.25 l/min, as sampling flow. The sampling points were located along the line process. After 15 minutes sampling time, the samples were stored at 4°C for transportation and were taken to the lab to be analysed. The formaldehyde collected on the SKC 226118 tubes was extracted on an ultrasound bath for 60 minutes using toluene. The extract was transferred into a chromatographic vial of 1.5 ml and the analysis was performed using a gas cromatograph coupled to a mass-spectometer (GS-MS Schimadzu QP 2010 Plus). The concentration of the compound is read on the calibration curve (Neamțiu et al. 2010).

For measuring the noise at the workplace the personal monitoring was preferred because of the spatial variations. Moreover, some area samples were taken in the control rooms in order to check the room tightness, because here the workers are not wearing their personal protective equipment.

The last step in the industrial hygiene program was the control. In this stage some health hazards controls were taken: administrative (for a couple of workers the schedule was change in order to reduce the exposure to formaldehyde), engineering (a better ventilation system was installed) and the workers have received a more efficient personal protective equipment.

CONCLUSIONS

Exposure assessment is the heart of industrial hygiene programs as it supports all of the functional elements. Different exposures may result in different health endpoints. Intervention strategies to control workplace exposure and associated health outcomes may vary to a large extent from one workplace to another even in the same plant or factory. A thorough understanding of exposures allows the industrial hygiene program, including control efforts, to be prioritized to protect employees and manage exposure-related risks. It also puts the industrial hygienist in position to better manage the unpredictable changes that will occur both in knowledge of the health effects of environmental agents and in society's tolerance of workplace exposures. Coupled with good work history information, comprehensive exposure assessments will enable better epidemiology and refinement of our understanding of the relationship between occupational exposures and disease.

Therefore industrial hygiene is a science, its specific approaches should focus on a "translating science into action" perspective.

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SAMPLING OF INDOOR DUST FOR ANALYSES OF BIOLOGICAL INDOOR CONTAMINANTS IN FIVE ROMANIAN SCHOOLS IN ALBA COUNTY

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ABSTRACT. The paper presents the sampling procedure of indoor dust for analyses of biological indoor contaminants in five schools in Alba county, Romania, included in the SINPHONIE (Schools Indoor Pollution and Health: Observatory Network in Europe) Project study. The SINPHONIE project is a complex research project covering the areas of health, environment, transport and climate change, aiming to improve air quality in schools and kindergartens. The sampling was performed during heating season, and consisted in three types of sampling procedures: sock sampling, EDC sampling and ALK sampling. The results of the sampling campaign and analyses will set the basis for a comprehensive risk assessment regarding the impact of indoor air quality in classrooms on children's health and performance.

Key words: *indoor air quality (IAQ), biological contaminants, children exposure, SINPHONIE project*

INTRODUCTION

Children's exposure to biological indoor contaminants during school hours may be the cause of many respiratory diseases. The indoor air quality depends, among others, on the building design, building materials, mainly synthetic, furniture, as well as on outdoor sources, which may be the main contributors to indoor concentrations of some contaminants (Jones, 1999).

Relevant studies have shown that IAQ also impacts work productivity (Wargocki et al. 1999). Moreover, ventilation rates lower than 25 L s−1 per person in buildings was correlated to an increase in the number sicknesses (Guyeisse et al. 2008).

The paper presents the sampling procedure of indoor dust for analyses of biological indoor contaminants in 5 schools in Alba county, Romania, included in the SINPHONIE (Schools Indoor Pollution and Health: Observatory Network in Europe) Project study. The schools included in the main study are located as follows: two in rural areas (one located on a European road with intense traffic and the other one is surrounded by gardens, orchards and a park), and three in urban areas (one located in a residential area of a large town, one in a small town but with a developed wood industry and one in another small town with former metallurgical industry).

The sampling was performed during heating season, and it lasted for 2 months, November 2011 and December 2011. The sampling campaign consisted in three visits to each school. During the first visit in the school, the Sock sampling was performed. This visit took place on Monday morning, before the children's arrival at school, regularly in the interval 06.00 – 07.30 hrs. The second visit was performed at the end of the same week, on Friday. During this visit, the EDC samplers were checked so that they have not been moved or closed. The third visit was on Monday, the fifth week, and it consisted in removal of EDC samplers and performance of ALK sampling.

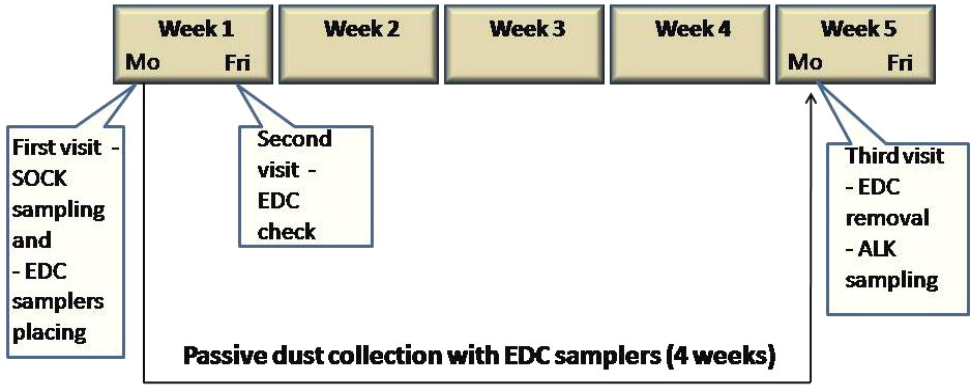

Fig. 1. *Sampling schedule of indoor biological contaminants within the SINPHONIE project*

MATERIAL AND METHODS

The sampling campaign consisted in three procedures. The first procedure was sampling of settled dust from surfaces above floor level - "Sock sampling". The second procedure was passive sampling of airborne dust with electrostatic dust fall collector or "EDC sampling". The last procedure was "ALK filter sampling", which involved the vacuum of dust on floors and other surfaces.

SOCK Sampling

The first procedure was sampling of settled dust from surfaces above floor level - “Sock sampling”. It consisted in collection of settled dust from surfaces above floor level using a dust sampling sock attached to a regular vacuum cleaner. The sampling time for this type of procedure was five minutes. The vacuumed surfaces were top of cupboards, top of shelves, doorframes, window frames. Areas with visible chuck deposition were avoided. As stated in the sampling protocol, the vacuum cleaner nozzle was cleaned with 70% ethanol and dried with a clean paper wipe between classrooms.

Figure 2 presents the socks with dust samples collected during the first visit during the first school.

Fig. 2. *Sock samples collected from the first study school (November 2011)*

Fig. 3. *Sock sampling performed in the first study school (November 2011)*

EDC sampling

The second procedure was passive sampling of airborne dust with electrostatic dust fall collector or “EDC sampling”. Airborne dust was collected using an electrostatic dust fall collector (EDC) developed at IRAS (Institute for Risk Assessment Sciences), Utrecht University (Noss et al., 2008; Noss et al, 2010). The EDC wipes were not touched and if touching these wipes was necessary, lab gloves were used. The optimum location of the EDC samplers was on top of cupboards, between 1.60 and 2.20 m height, with 50 cm air column above. The samplers were left at the location for 4 weeks (+/- 1 day).

After 4 weeks, the EDC samplers were closed and sealed with paper clips put in plastic bags and transported to the local study centre.

Fig. 4. *EDC samplers located on the top of a cupboard in one of the classrooms*

ALK filter sampling

The last procedure was “ALK filter sampling”, which involved the vacuum of dust on floors and surfaces above the floor level (desks, chairs, curtains, textile furniture, window shelves, and other horizontal surfaces above floor level). The classrooms were divided into two parts: the corridor part and the window part. Two ALK samples were collected, one from each part of the classroom as follows: 2 minutes on floor first, and then 2 minutes on parts above floor level. Between the classrooms, the “duck mouth” attached to the cassette filter was washed with tap water.

Fig. 5. *ALK filter cassettes*

Fig. 6. *ALK filter holder*

RESULTS

The samples resulting from the sampling campaign were stored at the local study centre at room temperature (the sock samples, EDCs and half of the ALK filter cassettes – those collected from the window part of the classrooms). The ALK filter cassettes collected from the corridor part of the classrooms were kept in the freezer, at -20º Celsius, according to the sampling protocol.

At the end of the sampling campaign in all study schools, the samples were shipped to analysis centers in Europe, partners in the project, as follows:

1) Sock samples were shipped to National Institute for Health and Welfare (THL) Department Environmental Health, Finland.

2) EDC samplers were sent to National Institute for Environmental Health (NIEH), Hungary.

3) ALK filter cassettes were sent to the Occupational and Environmental Medicine, University Hospital, Sweden.

The results of the sampling campaign and analyses are gathered in a large database, including all field data and measurements. These data are then interpreted and this will set the basis for a comprehensive risk assessment regarding the impact of indoor air quality (IAQ) in classrooms on children's health and performance.

CONCLUSIONS

Within the SINPHONIE project, a wide range of environment and health field studies will be undertaken and the results are analyzed while integrating existing available information on the topic.

On completion of the studies, recommendations will be developed for policy makers, architects, building managers, schoolchildren and staff on how to improve IAQ in European schools and make these paces a better environment for children.

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